

A Symposium
 Organized by the Getty
 Conservation Institute,
 Tate, and the National
 Gallery of Art

Modern Paints Uncovered

Tate Modern, London
 May 16-19, 2006



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Proceedings from the
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Symposium

Organized by the Getty Conservation Institute,
Tate, and the National Gallery of Art

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May 16–19, 2006

*Edited by Thomas J. S. Learner, Patricia Smithen,
Jay W. Krueger, and Michael R. Schilling*

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Foreword

On behalf of the organizing partners—the Getty Conservation Institute (GCI), the National Gallery of Art (NGA), and Tate—we are delighted to present the proceedings from *Modern Paints Uncovered*, a symposium that was held at Tate Modern, London, in May 2006. The four-day gathering brought together professionals from around the world who share an interest in the conservation issues of modern and contemporary painted surfaces. This volume comprises all the papers presented at the symposium, together with extended abstracts from the posters presented in an adjacent session.

Over the last seventy years, a staggering array of new pigments and binders has been developed and used in the production of paint. Because twentieth-century artists never limited themselves to using only paints that were specifically made for them, almost all of these new materials would have found their way into works of art—whether paintings, sculptures, or works on paper. Paints intended for houses, boats, cars, and other industrial applications now frequently turn up in modern art collections. However, conservators have almost no information on any of these new paints in terms of how they behave under various environmental conditions or during transportation, how they might become altered with age, or how they could be affected by conservation treatments.

Modern Paints Uncovered showcased the varied strands of research currently being conducted into the different types of paint that have been available to artists since 1930—the date at which synthetic materials began to make a significant impact on the paint industry. The wide-ranging and cutting-edge topics covered by the speakers included paint properties and surface characteristics, the development of methods for paint analysis and identification, the determination of their aging behavior, and assessments of safe and effective techniques for their conservation. There can be no doubting the high level of interest in this subject: over sixty-five abstracts were submitted by authors from fifteen countries; delegates at the symposium traveled from nearly thirty countries and included not only conservators and conservation scientists but

also artists, art historians, museum curators, and paint formulators and manufacturers; and tickets for the symposium sold out in just over a month. The positive and enthusiastic response from all the participants will help to ensure that this topic remains a priority for the conservation profession.

The symposium also marked an important milestone in the long-term and collaborative Modern Paints project, which primarily involves researchers at the GCI, the NGA, and Tate. Over the past three years, researchers from all three institutions have worked closely together in this area in an attempt to make as rapid progress as possible. Each of the project partners has taken the lead on one aspect of the study, often establishing additional partnerships with other museums, research institutions, universities, and paint companies. Many of the resulting findings from this rather broad network were presented during the symposium and are published in this volume. While there is still much to learn about the paints used by so many of the great masters of twentieth-century art, it is clear that significant advances have been made. The ongoing commitment to research in this area should ensure that this momentum is maintained in the future.

We would like to thank the volume editors for their energy and commitment in preparing the proceedings for publication; the Technical Committee, which crafted the program for the symposium; the Organizing Committee, which orchestrated the event and enabled its very smooth running; and all the other staff members at the GCI who worked so hard to produce this volume. We look forward to many more years of successful collaboration.

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Acknowledgments

Modern Paints Uncovered, both the symposium and this volume of proceedings, required extraordinary efforts by many individuals at the three organizing institutions—Tate, the Getty Conservation Institute (GCI), and the National Gallery of Art (NGA)—and we would like to acknowledge them here.

To our fellow members of the Technical Committee—Giacomo Chiari, René de la Rie, Jay Krueger, and Michael Schilling—our thanks, first, for their help in putting together a great program of presented papers and posters and, second, for so ably chairing their sessions, along with Jacqueline Ridge from Tate. We are indebted to all of the speakers for their excellent presentations, and to the poster authors for producing such fine-looking descriptions of their work.

We are extremely grateful to our colleagues on the symposium Organizing Committee: Kristin Kelly and Anna Zagorski from the GCI, and Caroline Brimmer, Harvinder Bahra, and Harriet Warden from Tate. Along with the audiovisual technicians at Tate Modern and the entire Tate Ticketing team, led by Emily Barnes, they all undertook an enormous amount of work to ensure that the event ran seamlessly. Our colleagues from Tate Conservation provided invaluable support and encouragement throughout the planning and execution of the symposium.

We appreciate the support of Nicholas Serota and Vicente Todoli in hosting the event at Tate Modern, and we thank them for welcoming our delegates to London. At the

GCI, the constant support we received from Timothy Whalen and Jeanne Marie Teutonico was essential to the realization of this project.

The final day of the symposium included a range of highly popular public events, and our warmest thanks go to all those who helped: Peter Blake and Jon Snow, for their detailed and good-humored discussion on Blake's art and materials; Rachel Barker, Dexter Dalwood, Emilie Gordenker, Sean Rainbird, Christian Scheidemann, and Piers Secunda, for their lively participation in "The Painted Surface" panel discussion; Hannah Andrassy, Mary Bustin, Rose Cardiff, Rosie Freemantle, Annette King, Fiona Rae, and Jemima Rellie, for their involvement in producing our Modern Paints podcast; Achim Borchardt-Hume, Alun Foster, Matthew Gale, Michael Harding, Emma Pearce, and the staffs at Cornelissen & Son and Russell & Chapple, for the wonderful tours they led or hosted.

Finally, we would like to thank all those who worked so hard on the publication of this volume, particularly Cynthia Godlewski at the GCI, Tobi Kaplan and Pamela Heath at Getty Publications, and Gary Hespenheide at Hespenheide Design. We are also indebted to our fellow volume editors for their help, and to Leslie Tilley for her excellent copy editing. The quality of this volume will speak far louder than any words in expressing how much work they have all put into producing it.

THOMAS J. S. LEARNER
PATRICIA SMITHEN

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PART ONE

Keynote Presentations

Modern Paints: Uncovering the Choices

Thomas J. S. Learner

Abstract: Numerous types of “modern” paints were developed in the twentieth century, and the vast majority, including those intended for the household or industrial market, are likely to have been used on works of art. Although an artist’s choice of paint—and the way it was applied—is the subject of much research and documentation, there is also a clear need to better understand how all these different paints behave and how their use will affect their future conservation. Each type of paint is likely to display different characteristics and properties, for example, with aging, with specific display conditions, and with any necessary conservation treatment. As an introduction to *Modern Paints Uncovered*, this paper will attempt to uncover the principal choices by outlining the salient features of the main types of paint available since 1930, discussing examples of their use, and summarizing the procedures that can be used to discover which paint type was used on a particular work. Although the subject is vast and complex, a reasonably good generalization can be achieved by classifying the principal types of paint into two main groups: artists’ paints, predominantly acrylic and oil; and house paints, usually alkyd and polyvinyl acetate. A number of methods are available for discovering which type of paint has been used, primarily analysis, interaction with the artist, documentation, and examination. Each of these will be discussed in terms of their particular advantages and disadvantages.

Introduction

It will not be news to most people reading this paper that there are numerous types of modern paints (fig. 1) available for artists to choose and utilize in their work (Crook and Learner 2000; Gottsegen 2006; Learner 2000; Mayer 1991). This is particularly true because a long time has passed since the choice was



FIGURE 1 A selection of modern paints. © Tate, London, 2004.
Photo: David Lambert.

limited to those paints intended purely for artistic use. When one considers the varied products that have been formulated for mass-market or industrial purposes, the choice really is mind-boggling. Along with this explosion of painting materials, artists throughout the twentieth century experimented with all means of applying the paint to the substrate, such as paint rollers, spray

guns, splashing, and pouring—and this is another factor that can significantly affect the characteristics of the final paint film and its subsequent reaction to aging and treatment.¹

So how does the conservation profession start to make sense of all the variables that accompany modern paints? I'm sure most of us would accept that different types of paints are going to display different characteristics and properties, and that these differences have important ramifications for the paints' conservation. Different paints will display different flexibilities, age differently, react differently to changing environmental conditions, react to and consequently require different conservation treatments, and so on. There is therefore an enormous amount of research needed to amass a level of understanding that is similar to our current knowledge of traditional oil paint—and many would argue that even that is in its infancy. As a means of introducing the topic of modern paints and *Modern Paints Uncovered*, this paper attempts to address three questions involved with uncovering the artist's choice of paint: What were the available choices? What considerations might the artist have had in his or her choice of which type of paint to use? And how do we now discover what those choices were?

As a broad overview, I first outline the types of paint that are most likely to be found on the painted surfaces of works of art. Doing so necessitates a major simplification of the various classes of paint that are available. Consequently, they are dealt with in two sections: artists' paints and house paints. Despite all the various paint types (e.g., acrylic, alkyd, epoxy, nitrocellulose, oil, polyester, polyurethane, polyvinyl acetate, silicone resin, water-miscible oil), and the sometimes misleading terms that are often used to describe them (e.g., *dispersion*, *emulsion*, *enamel*, *lacquer*, *latex*), this paper concentrates on three principal classes: acrylic, alkyd, and polyvinyl acetate, with only brief mention of other types. Examples are given of paintings in the Tate Collection on which each of these paint types was utilized, often with quotes from the artist about why that choice was made (Crook and Learner 2000).² This discussion leads into an overview of the sources of information that can be used for determining paint type on a work of art—namely, analysis, interaction with the artist, documentation, and examination of the work. For each of the sources, I also offer a few words of caution in their use.

Before discussing some of the materials used in modern paints, it is perhaps worth considering why it is so important to identify all the various paint types. First, this understanding enables accurate “materials and techniques” studies—which have played such a dominant role in conservation research

over the past decade—on modern and contemporary artists. For any such study, knowledge of the analytical techniques capable of identifying the various paint types is necessary, as is knowing the range of materials available to the artist. Second, familiarity with paint types can facilitate authentication studies, which, in addition to forgery detection, also include the far more common process of determining whether local areas of a painting are original or a later overpaint. The dates of introduction of all the various paint types can provide key evidence in determining originality and helping to date a work (see, e.g., table 1).

Third—and perhaps most important in the context of this volume—is an area that could be classified as “conservation implications”; this is the subject that is in greatest need of research for (and by) the profession. It involves understanding how different paints behave under all manner of conditions and phenomena, such as aging and response to various environmental conditions and conservation treatments. For example, some paints will be more brittle than others, making them less resistant to cracking should the painting be rolled, struck, or exposed to extreme fluctuations in relative humidity. Others will be more flexible but softer, making it vital not to have any packing material such as tissue in direct contact with their surfaces during transport. And of course each paint type is likely to change somewhat with age. We all know and accept that the brittleness of oil paint significantly increases with age through the oxidation processes that are required for proper drying. So will the other paint types exhibit similar dramatic changes in their physical properties that might affect their conservation strategies?

In terms of the ramifications for conservation treatments, the case of cleaning provides an excellent example. As we shall see in the next section, there are two types of acrylic paint: acrylic solution and acrylic emulsion. If similar-size fragments of these two paint types are immersed in water, the acrylic solu-

Table 1 Dates of introduction of principal binders in modern paints.

Paint Type	Date of Introduction
Oil artists' paint	Antiquity
Nitrocellulose house paint	Late 1920s
Alkyd house paint	Late 1930s
PVA emulsion house paint	Late 1940s
Acrylic solution artists' paint	Late 1940s
Acrylic emulsion artists' paint	Mid-1950s

tion paint will remain largely unaffected, whereas the acrylic emulsion paint might expand to between two and four times its area. If, however, the same two paints are immersed in a nonpolar organic solvent, such as mineral (white) spirits, this time the acrylic emulsion paint will remain largely unaffected, whereas the acrylic solution paint will dissolve. Although routine cleaning of a painted surface does not usually involve total immersion in a cleaning solution, this simple test illustrates how two paints that might—by many—be considered rather similar can respond entirely differently.

Types of Paint

Artists' Paints

Although a number of different types of paints currently are or were at one time produced by artists' paint makers, acrylic and oil have been by far the most widely used. Since oil has been the dominant paint medium for well over five hundred years, and there are plenty of sources of information on its chemistry and properties (Gottsegen 2006; Mayer 1991; Mills and White 1994), this paper does not devote much discussion to it. Some of the other types of paint encountered as artists' paints include polyvinyl acetate (PVA) emulsion (e.g., Flashe by Lefranc & Bourgeois), vinyl acrylic emulsion (e.g., New Masters, now discontinued), alkyd resin (e.g., Griffin by Winsor & Newton), water-miscible oil (e.g., MAX by Grumbacher),³ casein (e.g., by Shiva), gouache, and watercolor.

However, the success of acrylic emulsion paint has been unrivaled by that of other synthetic media in the artists' market, and for many years it has typically accounted for 50 percent of total paint sales at most manufacturers (Learner 2000). As mentioned above, however, the term *acrylic* encompasses two quite distinct types, acrylic solution (e.g., Magna) and acrylic emulsion (e.g., Liquitex, Aqua-tec, and Cryla). The principal difference between the two is that the solution paint is a straightforward system of polymer dissolved in an organic solvent, whereas the emulsion consists of an acrylic polymer dispersed in water (with the aid of surfactant and other additives).

Acrylic Solution Paints

When Magna was introduced in the late 1940s by Bocour Artist Colors, it was marketed as “the first new painting medium in 500 years” (Crook and Learner 2000). The acrylic polymer used for this acrylic solution paint was poly(*n*-butyl methacrylate), probably Paraloid F-10 (Rohm and Haas), which was dissolved in an organic solvent such as turpentine. This meant that it behaved

much like an acrylic varnish, in that it could be readily redissolved in the same solvent or by subsequent paint applications. Magna was the first artists' acrylic paint, but it was never a commercial success; its production was stopped in the mid-1970s (although a similar product, MSA paint, has been available from Golden Artist Colors since the 1980s). However, Magna's place in the history of twentieth-century painting has been secured by its use by a handful of extremely significant painters—Roy Lichtenstein, Morris Louis, and Kenneth Noland—all of whom used it extensively (Crook and Learner 2000; Upright 1985).

Morris Louis is a particularly fascinating artist to study in this context, as without the invention of Magna it is unlikely that he would ever have been able to produce much of his oeuvre, in particular, the Veil paintings, which involved numerous applications of heavily diluted and brightly colored paints poured down the canvas. See, for example, *VAV* (1960; Tate T01057), shown in figure 2. The individual colors can still be seen along the top edge of the painting, although for most of the painted surface they are mixed in together. The overall paint film is extremely thin, and is usually considered no more than a stain, even though it probably consists of more than five paint applications. When Kenneth Noland was asked to comment on his and Morris Louis's use of Magna for their stain paintings from this period, he said, “The advantage of Magna paint was that it could be thinned



FIGURE 2 Morris Louis (American, 1912–1962), *VAV*, 1960. Acrylic solution artists' paint on canvas, 260.3 × 359.4 cm (102½ × 141½ in.). London, Tate, T01057. © Tate, London, 2007. © 1959 Morris Louis.

with turpentine and (as it was thinned) it held an intensity of hues. It did this [better] than either the oil paint or the water soluble paint that was available at the time” (Noland 2004). The intensity of color was certainly crucial, but perhaps the most important property was that each paint layer could be redissolved and reworked with every subsequent pouring. Louis would only have been able to get the overall paint thickness so thin because he was able to redissolve the underlying paint layers (possibly with the use of rags soaked in solvent or pieces of card).

Roy Lichtenstein liked Magna’s fast-drying nature and its ability to produce areas of flat and uniform color: “To express [his images] in a painterly style would dilute [them]” (Swanson 1963). This summarizes two more of Magna’s properties very succinctly. It certainly dried much quicker than oil (often in a matter of hours, rather than days or weeks), and it was well suited to achieving large areas that were uniform in color, gloss, and texture and void of any obvious brushwork—a very different appearance to the brushy and gestural painting that had become associated with many of the Abstract Expressionists in the previous decade. That said, Lichtenstein continued to use oil paint throughout the 1960s for the areas of dots in his paintings, as seen, for example, in *Whaam!* (1963; Tate T00897). These were applied through a metal stencil, and the rapid-drying Magna paint would not permit Lichtenstein to apply many dots before the paint dried and adhered the stencil to the painting’s surface. He therefore continued to use oil for these areas to give him a longer working time, until he discovered the advantages of paper stencils, which could be peeled back during the application process (Crook and Learner 2000).

Acrylic Emulsion Paints

The first artists’ acrylic emulsion paint to appear was Liquitex (Permanent Pigments) in 1956, three years after Rohm and Haas produced the first pure acrylic emulsion, Rhoplex AC-33 (Hochheiser 1986). However, it was not until 1963, when Liquitex was reformulated as a thicker, tube paint (compared to the earlier, thinner paint sold in jars) that it became widely adopted by artists. By 1965 most artists’ paint makers were selling their own brands of acrylic emulsion paint. The use of this type of paint has been extremely widespread since the early 1960s and was used by artists such as Patrick Caulfield, Helen Frankenthaler, David Hockney, John Hoyland, Robert Motherwell, Bridget Riley, and Andy Warhol. It is the most commonly found synthetic paint in the Tate Collection.

Acrylic emulsion paint offered a range of advantages over traditional oils. In early advertisements, properties such as its rapid drying time and incredible flexibility were stressed, and in one ad for Liquitex, a whole list was given: “rapid drying, easy handling, versatility, exceptional durability, can paint on any material, completely permanent colors, thins with water and will not separate.” It is interesting that “thins with water” was included so far down the list, as the waterborne nature of these paints has probably accounted for much of their commercial success in the subsequent era of strict environmental concerns.

The binder used in acrylic emulsion paint is an acrylic copolymer, between methyl methacrylate (MMA) and either ethyl acrylate (EA) or *n*-butyl acrylate (*n*BA). The majority of early acrylic emulsions were of the p(EA/MMA) kind, for example, Primal AC-34 and AC-634 (Rohm and Haas). However, since the late 1980s most brands of artists’ acrylic emulsion paint have switched to a p(*n*BA/MMA) binder, such as Primal AC-235 and Primal AC-2235 (Rohm and Haas). These emulsions have increased toughness and hydrophobicity, both of which are beneficial properties for their primary intended application, namely, exterior house paint. Acrylic latexes, along with most constituents of modern paints, are almost never developed for use in artists’ paint, due to its minimal share of the overall paint market. Instead, artists’ paint makers rely on raw products intended for more commercial uses. However, when one considers the conditions that an exterior house paint is expected to survive (direct sunlight, rain, pollution, and extreme fluctuations in humidity and temperature), it is not unreasonable to think that its constituent materials will perform well in a paint that may ever experience only carefully controlled environmental conditions.

The usefulness of a particular acrylic resin as a paint binder is largely determined by its physical properties, especially glass transition temperature (T_g)—the point above which a polymer is flexible and rubbery. For acrylic emulsion paints, a copolymer is chosen with a T_g just below room temperature, around 10–15° C, which is sufficiently low for the film to remain flexible and therefore unlikely to crack in normal use, but high enough to prevent the dried film from becoming tacky and therefore absorbing dirt. For comparison, the T_g of acrylic solution paints is slightly higher, at around 20° C. However, the properties of the bulk resin are transformed by the multitude of additives incorporated into all acrylic emulsion paint formulations, as listed in table 2 (Learner 2000). Subsequent papers in this publication expand on the identity, function, and implications for use of many of these additives, in particular surfactants, which have been the focus of much recent study.

Table 2 Typical additives in an artists' acrylic emulsion paint.

Additive	Purpose
Surfactant	To disperse the hydrophobic acrylic polymer in water
Antifoam	To stop excessive foaming of paint if stirred or shaken
Thickeners	To improve the handling of the paint by providing a more “buttery” consistency
Freeze thaw agent	To prevent freezing of the formulation in cold environments
Coalescing solvent	To temporarily soften the polymer particles during film formation
pH buffer	To keep pH at an optimum level for all additives
Biocides	To prevent mold growth
Pigment dispersants	To disperse and reduce flocculation of finely ground pigments
Wetting agent	To reduce surface tension so that it more easily spreads around pigments (especially organic ones)

Acrylic emulsions cannot be redissolved in water once dry; they thereby lend themselves to wet-on-dry techniques. This is a direct result of the complex drying process, which involves coalescence of the polymer spheres into a continuous film after an initial stage of water evaporation (Nicholson 1989). David Hockney's *A Bigger Splash* (1967; Tate T03254), shown in figure 3, perfectly displays this technique. The blue of the sky and water was applied first with a paint roller, and the sharp edges at each border were achieved with the help of masking tape. This paint was applied directly to a piece of unprimed cotton canvas, highlighting one of the other great advantages of acrylic emulsion (compared to oil)—that there is no need for careful and time-consuming preparation layers on the substrate before paint is applied. The white paint used for the splash was then applied directly over the various shades of blue of the swimming pool, and there is absolutely no color bleed of the deep blue up into the white brushstrokes. Hockney has used many types of paint during his career, including acrylic, oil, and watercolor, and there seem to be several reasons that factor into his choice of which one to use, but as he has commented, “When you use simple and bold colors, acrylic is a fine medium” (Stangos 1988). It also clearly affected his working methods: “You can work on one picture all the time [with acrylic], because you never have to wait for it to dry, whereas you might work on two or three oil paintings at a time” (Stangos 1988).

John Hoyland was one of the earliest artists in Britain to turn to acrylic emulsion, almost as soon as it became available there, in 1963. He continued to explore the various effects that could be achieved with the paint throughout the ensuing decades, as seen in his paintings *28.5.66* (1966; Tate T00886), *25.4.69* (1969; Tate T01129), *Saracen* (1977; Tate T02402), and *Gadal 10.11.86* (1986; Tate T04924). As he said in 1996, “I remember reading articles in magazines. They talked about the radiance of [acrylic] and the fluidity of it and that it would never yellow. . . . As much as I like the smell of oil, to me the advantages of acrylic outweigh the disadvantages of oil. Acrylic was a more vivid color, a brighter, stronger color and of course it had the benefit of being quick drying, which when you painted pictures that [large] size was a factor” (Crook and Learner 2000).

The use of acrylic emulsion paint on a number of other Tate works is discussed in *The Impact of Modern Paints* (Crook and Learner 2000), including Patrick Caulfield's *Interior with a Picture* (1985–86; Tate T07112), David Hockney's *Mr and Mrs Clark and Percy* (1970–71; Tate T01269), Bridget Riley's *To a*



FIGURE 3 David Hockney (British, b. 1937), *A Bigger Splash*, 1967. Acrylic emulsion artists' paint on canvas, 243.8 × 243.8 cm (96 × 96 in.). London, Tate, T03254. © Tate, London, 2007. © David Hockney.

Summer's Day (1980; Tate T03375), and Andy Warhol's *Marilyn Diptych* (1962; Tate T03093).

Other Artists' Paints

Although the focus of this section thus far has been very much on acrylic, it should not be forgotten that oil is probably still the paint medium most widely used by artists today. Oil is an incredibly versatile medium, capable of producing areas of very high and sharp impasto, as seen typically in paintings by Frank Auerbach or Willem de Kooning, and applications of extreme thinness, as used by Francis Bacon or Mark Rothko. Modern oils have similarities with traditional oils, but there are some significant differences, in addition to the vast range of new synthetic pigments (both organic and inorganic) that are now used. Linseed oil is still found in many colors, although safflower and poppy oil would almost always be utilized as a less-yellowing oil in white and other light-colored paints. Winsor & Newton currently uses a blend of linseed and safflower in all their colors, the precise proportions dependent on the required balance of faster drying time (more linseed) and less yellowing (more safflower). The other big difference will be the incorporation of additives into most brands. Although the mixture is nowhere near as complex as an acrylic emulsion, driers, stabilizers and dispersing agents will probably be incorporated. The recent introduction of water-miscible oils—which are usually oil paints that have surfactant added so that they can be diluted (and brushes cleaned) with water—is an interesting development. These are beginning to attract interest in the field of research, although as yet they have not been seen in many museum collections.

House Paints

As already mentioned, acrylic emulsion binders are used extensively in the house paint market, especially for exterior paints, where toughness and resistance to weathering is required. However, their relatively high cost restricts their use in many other products, and in fact there are two other important types of synthetic binder that are far more widely utilized, at least in European markets: alkyd and polyvinyl acetate (PVA).

Plenty of other polymers have also been used in commercial house paint and industrial coatings, including vinyl-acrylic emulsion, styrene-acrylic emulsion, nitrocellulose, polyurethanes, epoxies, and silicone resins (e.g., Morgans 1982a, 1982b; Stoye 1993), but their occurrence in works of art is reasonably rare, so they are not dealt with here apart from a brief mention later. The only exception to this rarity is nitrocellulose, which

has secured its place in this story from its use by the extremely influential twentieth-century painter Jackson Pollock.

Alkyd Resins

Alkyd paints are oil-modified polyester paints. They were introduced in the late 1930s, although they did not make a significant impact on the paint industry until the late 1950s. Since then, the vast majority of oil-based house paints have incorporated alkyd resins as their principal binder. The term *alkyd* comes from the two main ingredients, a polyhydric *alcohol* (or polyol) and a polybasic *carboxylic acid*. The vast majority of alkyd house paints use just three compounds: glycerol (polyol), pentaerythritol (polyol), and phthalic anhydride (polybasic acid).

Typically, an alkyd house paint will be classified as a *long oil* type, meaning that it contains more than 60 percent oil by weight. The oil used in alkyd house paints has most commonly been linseed or soybean; soybean oil is currently far more widely used due to its lesser tendency to yellow. Safflower and sunflower oil are also less yellowing, but more expensive, so are used much less frequently. It is interesting to note that the oil component—and not the actual polyester—has the strongest influence on an alkyd's yellowing properties. The drying mechanism of alkyd is somewhat similar to oil—involving complex oxidative polymerization reactions—so a dried alkyd film is cross-linked and insoluble. However, since much of the polyester component is already cross-linked, far fewer reactions are needed for film formation, and alkyds therefore dry more rapidly than oils.

The development of alkyd resins completely revolutionized most other areas of paint production, especially house paint, and it is principally in this form that alkyd paint is found on works of art. Some of the more notable artists to have used alkyd house paints include Gillian Ayres, Peter Blake, Patrick Caulfield, Ben Nicholson, Francis Picabia, Pablo Picasso, Jackson Pollock, Pierre Soulages, and Frank Stella (Crook and Learner 2000; Lake, Ordonez, and Schilling 2004).

Figure 4A shows Patrick Caulfield's painting *Vases of Flowers* (1962; Tate T02031); figure 4B is a detail taken in raking light. This lighting highlights some of the "classic" characteristics of alkyd house paints: a high surface gloss, very low impasto, and wrinkling where the paint was applied more thickly. Although some slight brush marks are visible under this lighting, the paint has clearly continued to flow after its application—just as house paint is supposed to do. In this instance the paint was applied with the hardboard panel laid flat to avoid drip marks; this is presumably why so much dust and debris has become embedded in the paint film. In terms of why Caulfield

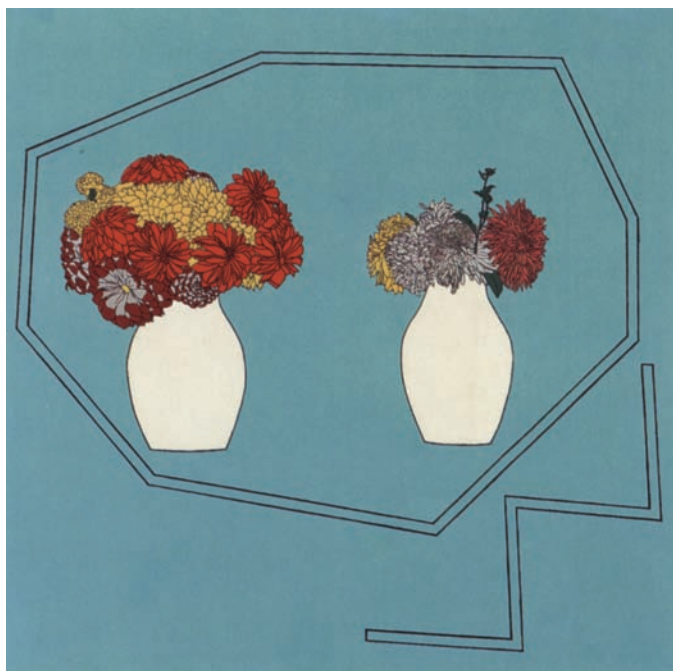


FIGURE 4A Patrick Caulfield (British, 1936–2005), *Vases of Flowers*, 1962. Alkyd house paint on hardboard, 121.9 × 121.9 cm (48 × 48 in.). London, Tate, To2031. © Tate, London, 2007. © The Estate of Patrick Caulfield/DACS 2006.

chose gloss house paint for almost every painting he executed in the 1960s, he recalled (in 1997), “The choice was an aesthetic decision. I wanted an impersonal surface, with . . . something that had a more decorative quality than art was supposed to have” (Crook and Learner 2000). Very similar surfaces are seen on areas of Gillian Ayres’s *Distillation* (1957; Tate To1714), Peter Blake’s *Tuesday* (1961; Tate To1934), and Pablo Picasso’s *Nude Woman with Necklace* (1968; Tate To3670).

PVA Emulsions

PVA made an impact on the paint market at about the same time as alkyds, after it had become available in emulsion form in the late 1940s. It has remained the principal type of binder used in interior emulsion house paint in many European countries (hence the term *vinyl emulsion*). It requires some slight modification to lower its glass transition temperature, either the addition of a plasticizer (common in early formulations) or copolymerization with a softer monomer. The latter has been the preferred option since the 1960s. It was often achieved with vinyl versatate or VeoVa monomers, which are mixtures of highly branched C₉ and C₁₀ vinyl esters. PVA emulsions con-



FIGURE 4B Detail of figure 4A taken in raking light from the left.

tain all the same kinds of additives as those listed for acrylic emulsions (see table 2).

The use by artists of PVA emulsion house paint does not appear to have been nearly as widespread as that of alkyd house paints. This is probably because artists’ acrylic emulsion paint was introduced soon after, and these offered all the same advantages, apart from cost. However, one of the more notable British artists to use PVA house paint was Bridget Riley, who used the emulsions made by Ripolin and Della Robbia for her black-and-white paintings in the early 1960s, of which *Fall* (1963; Tate To0616) is an excellent example (fig. 5). She described this choice in 1997 as being an aesthetic one: “I was trying to eliminate the suggestiveness of paint . . . I did not want to interfere with the experience of what could be seen. Personal handling, thick or thin paint applications: these are in themselves statements and irrelevant for my purpose. My painting had to be devoid of such incidentals” (Crook and Learner 2000).

PVA has also been detected in Sidney Nolan’s *Women and Billabong* (1957; Tate To0151) and in the background of Kenneth Noland’s *Gift* (1961–62; Tate To0898).

Other House Paints

Nitrocellulose is the term used to describe a range of paints and lacquers that contain blends of cellulose nitrate. Although these materials are not often found on artwork, the category is usually included in discussions of synthetic binding media due to its well-documented use by Jackson Pollock in his drip paintings. Although more recent work (Lake, Ordonez, and Schilling 2004) has shown that most of Pollock’s paints were actually alkyd or

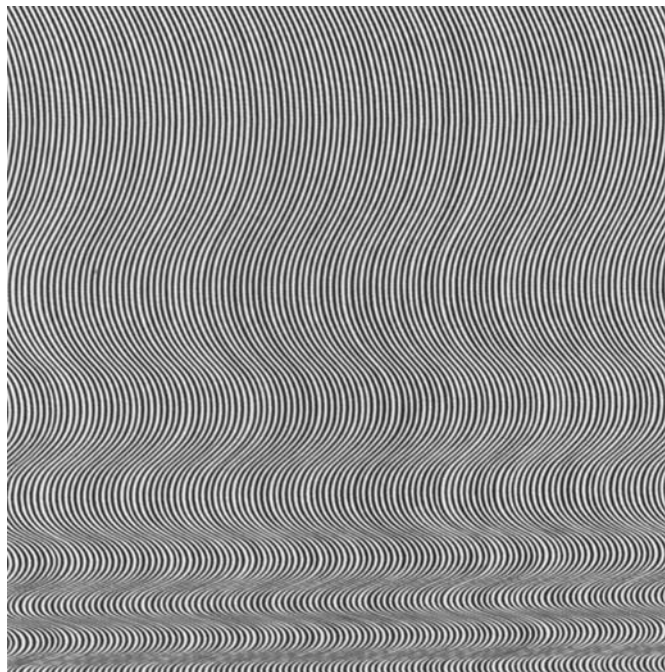


FIGURE 5 Bridget Riley (British, b. 1931), *Fall*, 1963. PVA emulsion house paint on hardboard, 141 × 140.3 cm (55½ × 55¼ in.). London, Tate, T00616. © Tate, London, 2007. © 2007 Bridget Riley, all rights reserved.

oil, there have been instances where analysis has detected nitrocellulose, for example, the orange paint in *Yellow Islands* (1952; Tate T00436). It was also used by David Alfaro Siqueiros on his painting *Cosmos and Disaster* (ca. 1936; Tate L02487), where the paint appears to have been both poured and sprayed onto the plywood support. Nitrocellulose paints are formulated as solution paints so that they can be readily redissolved, and are typically blended with a second resin (often an alkyd) and significant amounts of plasticizer (such as a phthalate).

The use of nitrocellulose in paint is no longer widespread and is mainly limited to low-cost spray paints, particularly those used for respraying cars. It was in this form that Richard Hamilton made frequent use of it in the late 1950s and throughout the 1960s for areas of paint that required an exceptionally smooth finish, for example, in his relief painting *The Solomon R. Guggenheim Museum (Neapolitan)* (1965–66; Tate T01195), as seen in figure 6. Hamilton admitted in 1988 that his use of nitrocellulose here was a purely aesthetic decision: “I do not think there’s anything peculiar about my

abilities as a spray man. . . . All I was concerned about was to get the best possible finish.” However, there have been other reasons. He recalled, “The first time I used [nitrocellulose] was on *Hers is a Lush Situation* [1958]. The reason was that the painting has a cut-out panel on it, which represents the side of a car. It’s all about cars and an elevational view of a car. . . . I wanted the work to have as close a connection with the source as possible: everything was directed not as representing the object but as symbolizing it. It’s meant to be a car, so I thought it was appropriate to use car color” (Crook and Learner 2000).

Just to illustrate that all kinds of paint types are used on works of art, analysis has revealed that epoxy paints were used on Frank Stella’s *Salta nel mio Sacco* (1984; Tate T07152), pigmented polyester resin on Chris Ofili’s *No Woman No Cry* (1998; Tate T07502), polyurethane-containing paint on Phillip King’s painted sculpture *Call* (1967; Tate T01360), and silicone resin on Nicholas May’s *Liminal 174* (1994; Tate T06990).



FIGURE 6 Richard Hamilton (British, b. 1922), *The Solomon R. Guggenheim Museum (Neapolitan)*, 1965–66. Nitrocellulose car paint on fiberglass, 121.9 × 121.9 cm (48 × 48 in.). London, Tate, T01195. © Tate, London, 2007. © Richard Hamilton. All rights reserved, DACS, 2006.

Determining Paint Type

Documentation

Much information is available in written and photographic sources, and this can clearly assist in informing us about the materials used by artists. For example, the knowledge that Pablo Picasso made use of Ripolin house paint in his artwork came originally from letters he wrote to his dealer Daniel Kahnweiler (Picasso 1912). Plenty of information can often also be gleaned from photographs of artists' studios, by identifying brands of tube color or commercial paint tins, or by viewing the technique with which paint was applied. Perhaps the best known example of this is Hans Namuth's film of Jackson Pollock in action, where his idiosyncratic method of paint application is famously documented.

However, documents can be misleading, and the presence of a can of paint in a photograph certainly doesn't prove the paint's use on a work of art. Consider the image shown in figure 7, of Patrick Caulfield in his studio in 1965. Caulfield has admitted in interviews to using gloss house paints almost exclusively during the 1960s, and this is supported by analysis of works from this period, which routinely show that alkyd paints were used (Crook and Learner 2000). Indeed, in this photograph the shelf is full of tins of house paint, with some of the individual brands visible. However, there is also a Nescafe tin. Coffee has never been identified in a Caulfield painting, nor has he ever divulged that he used it in his work, so we should assume that it was being used just as a tin, for storing brushes or mixing color. And in that case, a Dulux tin could also be used for this purpose, instead of containing paint that was about to be applied to an artwork.

Examination/Photography

Many paint types have surface characteristics, such as gloss and texture, that can assist in assigning their identity. Typically, for example, paint with high and sharp impasto is likely to be oil, paint that contains air bubbles in its surface is likely to have originated from an emulsion formulation, and a smooth, high-gloss finish is often indicative of alkyd house paint. Examination under raking light is particularly effective at revealing surface characteristics. Other visual clues include the way in which colors may have been blended together: oil paint is frequently worked wet-in-wet to take advantage of its longer working time, whereas such blending is less common in fast-drying media such as acrylic emulsion. In addition, the physical hardness of a paint film can help characterize it: alkyd house paint quickly dries to a hard film, whereas acrylic emul-



FIGURE 7 Patrick Caulfield in January 1965, photographed in his studio by Jorge Lewinski.

sion remains soft. Oil is more confusing, as young films can feel quite soft but become significantly harder with age. Some conservators also use solubility tests to differentiate between classes of media, with interpretation based largely on empirical observations.

Although often attempted, assigning paint type by purely visual means can be extremely unreliable, as each binder is capable of producing such a broad range of finishes. For example, many conservators would associate alkyd house paint with films of high gloss and a smooth finish. However, alkyd house paint that dries to a matte, textured surface can be produced simply by increasing the level of solids (particularly the extender) relative to the binder. This can be seen in Frank Stella's painting *Hyena Stomp* (1962; Tate T00730), for which he used one of Benjamin Moore's ranges of paint (Crook and Learner 2000). Figure 8A shows the painting. Figure 8B shows a detail taken in raking light, so that its surface can be compared to the more usual surface of an alkyd house paint (as seen in figure 4B). The visual characteristics of these alkyd paints could easily be mistaken for acrylic or PVA emulsion. And similarly, acrylic can be made to blend wet-in-wet, and air bubbles can appear in oil films.

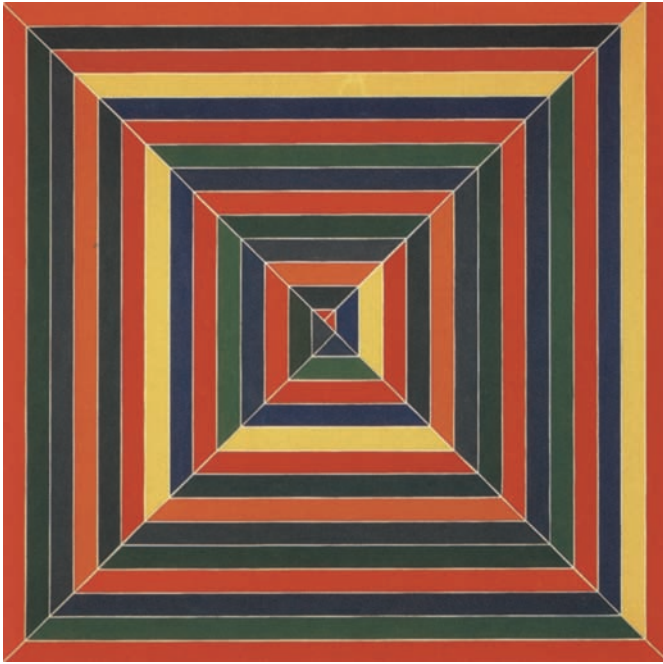


FIGURE 8A Frank Stella (American, b. 1936), *Hyena Stomp*, 1962. Alkyd paint on canvas, 195.6 × 195.6 cm (77 × 77 in.). London, Tate, T00730. © Tate, London, 2007. © Artists Rights Society (ARS), New York, and DACS, London, 2006.

Interaction with Artists

Valuable information can obviously be obtained directly from artists about the materials and techniques employed to make their artwork, and many museums attempt to do this systematically with their collections. Artists can have incredibly good memories about this type of information, especially if their materials haven't altered too much during their lives. Although often not possible, another valuable method of interacting with artists is to visit their studios, where paint types and brands can be identified and working practices can also become far more apparent.

The various reasons why a particular paint might be used by an artist are many, but perhaps fall into four categories, any one of which might be the deciding factor (Crook and Learner 2000):

- **Optical reasons.** An artist might desire a certain gloss, transparency, and/or surface texture, which might be achievable only with a specific paint type. In the examples above, this would apply to Caulfield's use of alkyd house paint.



FIGURE 8B Detail of figure 8A taken in raking light.

- **Practical reasons.** This would include considerations such as drying time, choice of diluent (e.g., a paint that dilutes with water might be an important factor), and also paint availability (in terms of what could be purchased locally as well as what might have been in the studio). Hockney's working practice, for example, was affected by the vastly different drying times of acrylic and oil paint.
- **Economic reasons.** Clearly, artist-quality paints are more expensive than house paints, and cost becomes a particular concern when painting in large formats.
- **Symbolic reasons.** Often an artist's materials play a role in the "meaning" of a work, and paint choice is no exception. An example of this would be Hamilton's use of nitrocellulose car paint to symbolize a car.

Many conservators will be aware of some of the problems with relying on artists' recollections for accurate information on the materials they used, especially if they made use of all sorts of different paint types and if the works discussed are decades old. Much, therefore, is dependent on the skills of the interviewer. One example, Bridget Riley's painting *Cantus Firmus*, was catalogued as casein on canvas for many years, based on information given by the artist. However, only acrylic emulsion was detected with analysis, and after further discussions with the artist, she accepted that this painting was indeed acrylic, unlike other similar paintings from that period for which casein was certainly used.

Analysis

A number of analytical techniques are now being used to identify the components in modern paints, and many papers in this publication will outline recent advances in this area. However, the focus here is on the two techniques routinely used to identify the various binders in modern paints: Fourier transform infrared (FTIR) spectroscopy and pyrolysis gas chromatography/mass spectrometry (PyGC/MS).

Some of the other techniques to have shown much potential include gas chromatography/mass spectrometry (GC/MS) for oil-based paints (Schilling, Keeney, and Learner 2004), direct temperature resolved mass spectrometry (DTMS) for all modern binders and organic pigments (Boon and Learner 2002; Learner 2004), Raman spectroscopy for organic pigments (Vandenabeele et al. 2000), and both liquid chromatography/mass spectrometry (LC/MS) and laser desorption/ionization mass spectrometry (LDI-MS) for the detailed characterization of surfactants (Digney-Peer et al. 2004; Smith 2005).

FTIR Spectroscopy

FTIR spectroscopy is an excellent way of obtaining information quickly about the basic chemical class of the majority of materials found in modern paint formulations. Indeed, for unpigmented media, FTIR spectra of the different synthetic binders are easily distinguishable (fig. 9). Major absorptions of each binder are described elsewhere (Learner 2004, 81–116), but in summary, the most diagnostic peaks for each type of binder are as follows:

- Acrylic paints: Carbonyl peak at around $1730\text{--}1735\text{ cm}^{-1}$. Acrylic solutions and emulsions (and different copolymers used) can often be differentiated at the C–H stretching region ($2800\text{--}3100\text{ cm}^{-1}$) and the fingerprint region $900\text{--}1500\text{ cm}^{-1}$.
- Oil paint: Carbonyl peak at around 1740 cm^{-1} .
- Alkyd paints: Broad C–O stretching peak at $1270\text{--}1280\text{ cm}^{-1}$.
- PVA emulsion paints: Broad C–O stretching peak at $1240\text{--}1250\text{ cm}^{-1}$.
- Nitrocellulose paints: N–O stretch at $1650\text{--}1655\text{ cm}^{-1}$.

However, FTIR spectra of paints are complicated by each additional component in the formulation, especially pigments and extenders, as these also absorb infrared radiation at different frequencies. Sometimes the various absorptions from each of the main components are so characteristic that it may be possible to “disentangle” them, and hence identify each

component from a single analysis. The technique is also semi-quantitative, so it can even be possible to assess an approximate relative proportion of each component—for example, to distinguish a leanly bound acrylic ground from a medium-rich paint.

However, it is more common for the absorptions from one component to dominate the spectrum and mask out the other ingredients. Perhaps the most common scenario is for the peaks from an organic pigment (which are often of such high tinting strength that they are added only in small concentrations to paints) to be masked by those of the binder and/or an extender. But there are ways of improving the sensitivity of

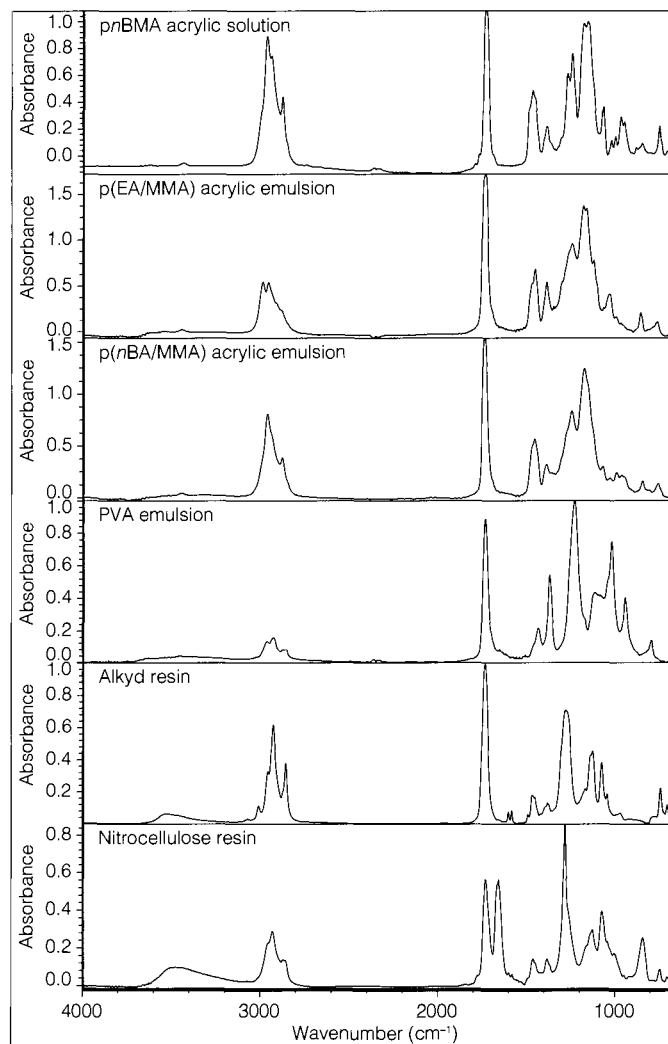


FIGURE 9 FTIR spectra of unpigmented films of acrylic solution, acrylic emulsion, PVA, alkyd, and NC resins.

FTIR to certain materials. One simple method that is particularly useful for the analysis of organic pigments is to carry out extractions with organic solvents or dilute acid. The extract and residue can then both be reanalyzed, and each will typically have become more or less rich in each component (Jönsson and Learner 2005). Another method is to use a different sampling mode. Recently, attenuated total reflectance (ATR), a reflective mode of FTIR that measures the surface of a material, has shown great potential in detecting the migration of polyethylene-type surfactants to the surface of acrylic emulsion paints (Whitmore, Colaluca, and Farrell 1996; Learner, Chiantore, and Scalarone 2002), and in monitoring their removal with various cleaning treatments (Ormsby et al. 2006). Many papers in this publication show such spectra.

PyGC/MS Analysis

The other principal method used for the analysis of modern paint types is PyGC/MS. Here, the pyrolysis stage breaks each of the polymeric binders down into smaller fragments that are sufficiently volatile to pass through a standard GC/MS instrument. As with GC/MS, the gas chromatography separates out the various components and the mass spectrometry is used to detect them; the resulting pyrogram plots the relative intensity of a material detected against time. The principal advantage of PyGC/MS over FTIR is that the technique can separate out complicated mixtures of different binders, and most pigments and extenders do not feature in the pyrogram (the exception being azo pigments), and hence diagnostic peaks are never masked.

Details of the technique are laid out in other publications (Learner 2001, 2004), but the main types of modern paint binders can all be readily distinguished (fig. 10). In summary, the principal features of each include:

- Acrylic solution paints, bound with a *n*BMA resin, produce extremely simple pyrograms consisting of a single peak of *n*BMA monomer via a “depolymerization” mechanism.
- Acrylic emulsion paints, bound in either a p(EA/MMA) or p(*n*BA/MMA) latex, produce strong peaks corresponding to both monomers, but also weaker groups of peaks from dimers and trimers later in the pyrogram (due to incomplete depolymerization when an acrylate component is present).
- Oil paints give featureless pyrograms, unless pyrolysis is performed with simultaneous methylation so that methyl esters of saturated fatty acids are produced. Ratios of methyl palmitate to stearate

can then be used to distinguish oil type through the method developed for GC/MS (Mills and White 1994).

- PVA emulsion paints produce strong peaks from acetic acid and benzene (which are often superimposed) from a “side group elimination” mechanism. In addition, the plasticizer is usually detected, including external plasticizers such as dimethylphthalate and internal plasticizers such as vinyl versate.
- Alkyd paints give a principal peak of phthalic anhydride in their pyrograms. Sometimes small fatty acid peaks from the oil component are detected.

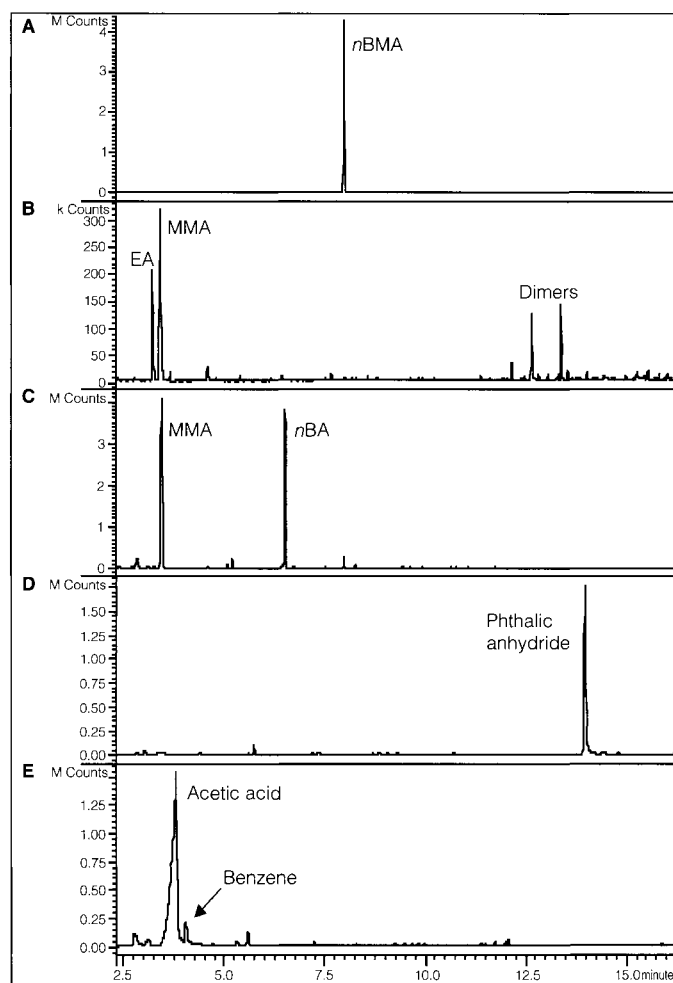


FIGURE 10 PyGC/MS pyrograms of films of (A) acrylic solution, (B) p(EA/MMA) acrylic emulsion, (C) p(*n*BA/MMA) acrylic emulsion, (D) alkyd, and (E) PVA emulsion.

- Nitrocellulose paints are detected “by suspicion.” The cellulose nitrate component gives a featureless pyrogram, but if the paint contains an alkyd resin and phthalate plasticizer as its other main components, these will be detected. Given that regular alkyd paints do not require a plasticizer, the presence of a plasticizer with the phthalic anhydride suggests a nitrocellulose formulation. Confirmation of nitrocellulose would be carried out with FTIR.

Nonetheless, we also need to be careful about the information obtained from analysis. The general inference given to anything that has been “scientifically” proved is that this confers a high level of certainty. However, most of the analytical instruments that conservation scientists use produce spectra that require careful interpretation. One recent example where this became apparent was in the analysis of the paints used by Chris Ofili for his painting *No Woman No Cry* (1998; Tate T07502). The dots of paint that characterize much of the surface were analyzed using PyGC/MS, which yielded a spectrum dominated by a strong phthalic anhydride peak, giving a close match to alkyd paint. Yet on further investigation (aided by communicating with the artist) it became clear that the dots were oil paint, and the strong phthalic anhydride peak was a contamination from the underlying polyester resin coating.

Conclusion

Although many kinds of synthetic binding media are used in paint, it is possible to uncover the likely binders present in the paint types commonly used by artists. These are oil, acrylic solution, and acrylic emulsion from artist-quality paints. The principal binding media used in house paint are alkyd resins in “oil-based” paint and PVA emulsions in interior emulsions. Several other paint types are possible in both artists’ paints and house paints, although none of these have been encountered very frequently on works of art in the Tate Collection. Several methods of uncovering information about an artist’s choice of paint may be used, including analysis, documentation, examination, and interaction with artists, but all are open to error and misinterpretation. Therefore the chances of misinterpretation are dramatically reduced if more than one source of information can be used.

Notes

- 1 As an overview, a podcast on modern paint is available at www.tate.org.uk/learning/learnonline/modernpaints.
- 2 Many of the works mentioned from the Tate Collection can be viewed at www.tate.org.uk/collection. All Tate works are cited with their accession number.
- 3 The recently introduced water-miscible oils might prove to be the next commercially successful development in artists’ paints.
- 4 E-mail from Kenneth Noland to author, October 29, 2004.

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Overview of Developments in the Paint Industry since 1930

Stuart Croll

Abstract: *The history of commercial paint is a large and complex subject, so the focus in this paper is restricted to commercial latex paint, which is very similar to acrylic artists' paint but is usually designed using slightly different criteria. Initially, paint technology developed slowly, but the need in the Second World War for synthetic rubber prompted the development of latex. This was aided by important scientific discoveries about polymers earlier in the twentieth century. Later external factors, including the rise of a consumer middle class, maintained the rate of development in many industries, including paint. Paint is a composite of polymer, pigments, and additives, most of which have changed significantly since 1930. Although the polymer component is usually viewed as the linchpin of coatings, the introduction of titanium dioxide white pigment was central to the success of all coatings. Advances in materials occurred, scientific understanding improved, and better characterization techniques were developed. A brief discussion of these advances is included along with the history of latex paint ingredients. Originally, latex coatings were attractive because they dried much faster than oil-based paint and they could be cleaned up easily with soap and water. In the present day, latex paint technology continues to advance and gain market share because it places much less stress on the environment and our health than solvent-based paint.*

Introduction and Background

The main focus of this article is on the technologies used in modern, commercial acrylic latex (emulsion) paint. In this article, the term *commercial paint* is used to designate types of paint other than artists' paints, and the term *latex* to mean polymer binders made using emulsion polymerization.

Building on the Industrial Revolution and further developments in the late nineteenth century (Bullett 1984), paint technology developed slowly during the first two decades of the twentieth century. It was catalyzed probably by the First World War (1914–18), and certainly by the Second World War (1939–45). Coatings technology has been enabled by many discoveries of a scientific and technological nature, but it has been, itself, an important enabling technology for many aspects and facilities of modern life. Current worldwide sales of paint, of all descriptions, are over \$80 billion, and the paint manufacturing industry employs approximately two hundred thousand people. The primary use for commercial paint is to change or enhance the appearance of its substrate. The other use for many types of commercial paint is protection, for example, against corrosion of metals, or from moisture and solar radiation in the case of house paint.

Until the end of the nineteenth century craftsman painters created their own recipes from pigments, oils, and other resins, when and where they were needed, since the sedimentation of dense mineral pigments in low-viscosity (“unbodied”) oils meant that the shelf life of paints was very short. Materials were developed that overcame such problems, and the rise of commercial coatings correlates to the rise of premixed paints. Figures 1A and 1B attempt to show graphically, as sigmoidal “technological maturity” graphs (Roussel 1984), how the pace of paint technology progressed during the twentieth century.

Prior to the 1930s, oil and other traditional paints were still primarily used. Cellulose nitrate lacquers arrived in the 1920s, particularly for use on cars, and useful alkyds started to appear in the 1930s. Many products for the increasingly consumer-oriented Western societies were made of metal that needed to be protected from corrosion. Technology development started

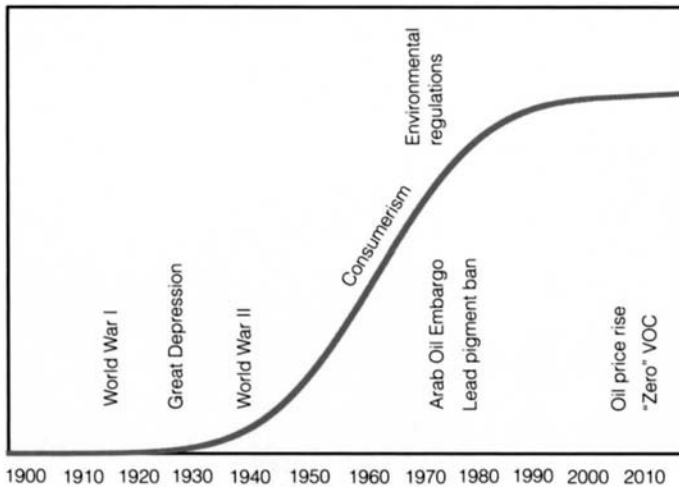


FIGURE 1A The rise of paint technology from the start of the twentieth century, showing dates of external events.

to accelerate in the 1930s, after the Great Depression, and was fueled by scientific discoveries and by the availability of low-cost petrochemical feedstock, an increasing energy supply, and the buildup to World War II.

Prior to about 1930, many held to the belief that “polymers” were actually agglomerations of small molecules held together in colloidal bodies by then-unknown forces. A crucial development in the science and technology of polymers occurred when Staudinger realized them to be very long, covalently bonded molecules, or “macromolecules” (Staudinger 1920; Morawetz 1987). The greatest number of technological changes probably occurred in the 1950s and 1960s, and their effect was felt primarily in the industrial application of coatings intended to provide increasing levels of performance—epoxies, urethanes, automotive coatings, and so forth. The number of major changes applicable to the house paint and artists’ paint markets was fewer, and most of these occurred early on.

Generally, the performance of the polymer binder determines the performance of the paint. Until the early 1970s, both paint and polymer technology were driven by performance, material choices, and costs. Later, the environmental and health effects of volatile organic compounds (VOCs) became much clearer. Starting in the 1970s, tightening of petrochemical supplies and increasing governmental regulation on solvent emissions and discharge levels led to the development of more benign technologies. Much of the current research and development in the paint industry and its supplier industries

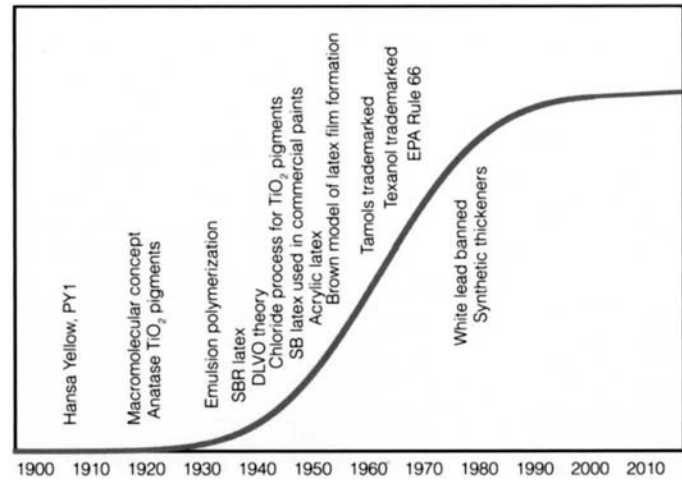


FIGURE 1B Important developments in paint technology from the start of the twentieth century.

is aimed at producing environmentally friendly and less toxic alternatives to current coatings without sacrificing performance. The principal approaches are to introduce waterborne systems, make high-solids paints, and use powder coatings.

Paint Formulations

Commercial coatings, like artists’ paints, are complicated composites. In many cases they contain special ingredients that meet specific end-use needs, such as corrosion inhibition, solvent resistance, and so on. However, they all share common features, as shown in the simplified, model house paint formulation in table 1. In this case, the pigment volume concentration in the dried film is approximately 45 percent, giving a competent, probably matte finish. The liquid paint has an overall solids concentration of around 38 percent by volume (54 percent by weight). In waterborne house paints, this can vary from 25 to 40 percent (by volume), depending on the quality, which roughly equates to price.

A waterborne latex paint designed for artists would be very similar, except that the color would be more intense, with less extender, and application viscosity would be higher, with more thickener. Ingredient price is a major factor: artists’ paint costs more than ten times what a medium-quality house paint does in North America.

Modern, practical commercial and artists’ paints may contain a mixture of latexes, more than one surfactant, more than one dispersant, and (commonly) two or more thicken-

Table 1 Simplified model acrylic latex formulation for a hundred gallons of a competent exterior house paint (white); given in approximate order of addition for manufacture.

Ingredients	Weight (pounds)	Volume (gallons)	Function
Water	340	41	Carrier fluid
Polyacrylate dispersant	6.8	0.69	Pigment suspension stabilization aid
Biocides	10	1	Fungicide, mildewcide
Nonionic surfactant	1	0.11	Wetting agent
Titanium dioxide	225	6.5	White pigment
Silicate mineral	160	7.3	Extender/filler; reduces cost
Calcined clay	50	2.2	Extender pigment
Acrylic latex (~60% solids)	283	32	Polymer binder
Coalescent	9.3	1.16	Film formation aid
Hydroxyethylcellulose	5	0.56	Thickener (viscosifier)
Glycols	60	6.72	Antifreeze, coalescent, evaporation control
Defoamer	2	0.26	Inhibits air entrainment
Ammonium hydroxide solution	2.2	0.29	Maintains alkaline pH
Total	1154.3	100	

ers. However, the first latex paints were more like the simple formulation in table 1.

Developments in Latex Paint Components

The formulation in the table contains thirteen ingredients; choosing each and its concentration on a purely scientific basis is so complex that it often is impractical. Much of the formulation is done by experts who have many years of experience, along with intuition that employs as much art as science. However, the properties of paint are not emergent phenomena and can be understood if basic science is applied.

Carrier Fluid: Water

The water in a paint formulation usually comes from the local water supply wherever the factory is sited. Water hardness (salts, etc.) may remain even after the water is treated. In addition, some water originates with the latex and from the titanium dioxide slurry commonly used in the United States to supply pigments for high-volume paint manufacturers. Some of the other, lower-concentration ingredients, such as surfactants, thickeners, and dispersants, are also supplied as aqueous solutions. Associative thickeners (discussed later) may have other solvents included as part of their carrier fluid.

An analysis of the inorganic content of the water in a commercial paint from the United States circa 1991 was shown to correspond approximately to an ionic strength of 0.07 M if it was considered to be entirely derived from a 1:1 electrolyte (Croll 2002). One may calculate the consequences of this ionic strength on the colloidal stability of the latex and pigment particles of waterborne paint using the theory that Derjaguin, Landau, Verwey, and Overbeek developed between 1939 and 1944 (Derjaguin and Landau 1941; Verwey and Overbeek 1948), which has been used to design the charge density on latex particles ever since. The polarity of water is advantageous, as it supports electrostatic stabilization of pigment and latex particles, as well as allowing steric stabilization (Rehbinder, Lazutkina, and Wenström 1930; van der Waarden 1950).

The unusually polar and hydrogen-bonded solvent restricts the polymer technology that can be used in aqueous systems. Technology was developed over the past decades (Padget 1994) to overcome this, often by creating aqueous dispersions of the various polymer binder technologies.

Other formulation problems arise because of inorganic material in the aqueous phase; also, many other ingredients partition substantially there. The aqueous phase will contain surfactants, dispersants, thickeners, coalescents (often in an emulsion), and so on. Resolving the compatibility issues is

very complicated. Early understanding of miscibility and solution behavior came through Joel Hildebrand, who had initially started work on the solubility of simple nonelectrolytes in 1916, and somewhat later (1950) coined the term *solubility parameter*. However, long-chain, high-molecular-weight polymers do not follow this solution theory well, and Flory's and Huggins's 1941 theory formed the basis for much of modern understanding of polymer solutions and polymer-polymer compatibility (Flory 1941; Huggins 1941).

Dispersant

Common dispersants are oligomeric polyacrylate salts. Their function is to adsorb on the surface of pigments, where they add more charge and thus electrostatic stability to particles. They may contribute a little steric stability to a pigment suspension as well. Their molecular weight is only a few thousand; otherwise, the viscosity of the paint would become too high due to the fraction that remains in the water.

Phosphates, such as potassium triphosphate (KTPP), tetra-potassium pyrophosphate (TKPP), and others, are still quite common, although they were more often seen in the early 1960s. Phosphate ions may become hydrated at high pH and not highly charged, thus not so effective, and they may participate in complex interactions with other paint ingredients. Phosphates remain water soluble in the dried coating and render it permeable to moisture. Other types of dispersant used before the polyacrylate salts became dominant were sodium salts of lignin sulfonates and aryl alkyl sulfonates (Patton 1964, 258).

The best-known dispersants are the Orotan (Tamol in the United States) polyacrylate salts made by Rohm and Haas (Hochheiser 1986). Tamol/Orotan 731, a sodium polyacrylate-olefin polymer, was patented in 1960 in the United States and is still very widely used. Similar materials were, and are, made by other companies as well. A hydrophobic modification allows the dispersant to wet the surfaces of organic pigment types, provides compatibility with glycols and modern associative thickeners, and has reduced tendency to stabilize foam.

In the United States, TiO₂ slurries from pigment manufacturers contain a dispersant to help maintain their suspension stability, and one can find commercial paints containing two different dispersants.

Biocides

Biocides are toxic materials that are sometimes called preservatives, particularly when used to inhibit biological growth while paint remains in its container. Mercury compounds are very effective biocides and were commonly used in the

1970s and earlier. In the United States, mercury compounds have been banned in interior latex paints since 1990 and in exterior paints since 1991. However, it seems that artists' paints are exempt from this. Phenyl mercuric acetate was the most common form of biocide, but oleate and di-phenyl mercury dodeceny succinate were also available. Dioxin was also tried as a biocide for paint, but it has likewise been banned. Copper compounds are very effective and much less toxic to humans, but their color means that they found limited use. Tin compounds were an option, but they are less effective. Skane M-8 mildewcide, introduced in 1971, gave the paint companies an effective alternative to mercury compounds.

More modern use includes a wide range of toxic halogenated and other compounds, which are thought to be less persistent in the environment. Unfortunately, some of the current materials may produce measurable yellowing when exposed to ultraviolet light. Zinc oxide is used, since it appears to inhibit the growth of mildew as well as providing some pigmentary value. It has been used for many years, although it can cause some problems in the stabilization of the colloids in aqueous paint.

Wetting Agents

A wetting agent is included by the paint formulator, but another source of surfactant is the latex. From the time latexes were first introduced up until the late 1980s, it was possible for approximately half of the surfactant in a latex paint to come from the emulsion polymerization process. Naturally, those surfactants were not identified to the paint company by the manufacturers of latex.

Surfactants play multiple roles. They allow water to spread upon the surface of pigments and displace the air, and so incorporate the pigment. There may be a small steric contribution to pigment stabilization from the surfactant and the more closely held water molecules that are associated with the hydrophilic part. Ionic surfactants also contribute to electrostatic stabilization. In the United States, most latex house paint and light industrial paint is made from base paints that are more or less white; color dispersions are added at the consumer or wholesale store. So the same base paint must incorporate a variety of pigments. Applying a priori scientific principles to surfactant choice is very difficult because there are so many competing products. Often more than one surfactant in commercial paint is competing for the various interfaces, and many complications are possible. In addition, most grades of TiO₂ have organic treatments with some sur-

factant character, and many cosolvents are surface active and form micelles.

After the paint has dried to form a film, the surfactants may not be evenly distributed within the film, depending on concentration, phase separation behavior, and compatibility with the other ingredients. They may dissolve in the latex, separate to the air interface (producing a hazy, low-gloss appearance and increasing adherence of dirt), or gather among the latex particles (limiting film integrity) or at the substrate (reducing adhesion, particularly in humid environments). Another problem is that many typical surfactants are intrinsically yellow and may affect color when concentrated after drying.

One of the most important and practical technical developments was the introduction of the hydrophilic-lipophilic balance (HLB) concept by William C. Griffin in about 1949 at the Atlas Powder Company (Griffin 1956).¹ Each surfactant has an HLB number; this number characterizes the structural balance between its hydrophilicity and lipophilicity (hydrophobicity). This provides the user with a guide to choosing from among the many hundreds of surfactants available. The HLB system has been used extensively since its introduction.

The fundamental nature of surfactants in paint probably has not changed significantly; however, variations and designations have proliferated. Alkyl benzene sulfonates and short-chain alkyl naphthalene sulfonates were originally invented in Germany during the First World War because Germany lacked a supply of animal fats, which at the time had competing technological uses. These are still useful wetting agents. During the 1920s and 1930s, sodium sulfonates of long-chain alcohols were produced, and long-chain sodium alkyl aryl sulfonates were made from petrochemicals in the United States. Clearly, a considerable diversity of surfactants was already available by the end of the 1930s. Nonionic octylphenol ethoxylates (Triton from Dow² and Igepal from Rhodia) were invented in the 1930s.

There are many variations on structures that have different wetting characteristics, tolerance of electrolyte concentrations, or foaming characteristics. The octylphenol ethoxylates were probably more common in emulsion polymerization than other types in the early days of latex manufacture, but many function well, and the choice has as much to do with price and availability. Anionic aerosols (e.g., Aerosol OT from Cytec, now) and Sisonate (alkyl aryl sulfonates and alpha olefin sulfonates from Alcolac, now) are all names that one associates with latex paint formulations going back to the 1950s.

White Pigments

Until the advent of latex paint, white lead and lithopone were the most common white pigments, but their use diminished sharply in the 1950s. White lead in oil paints made a durable and waterproof system for exterior use, although the paints lost gloss fairly quickly and atmospheric pollution could react to form black lead sulfide. Not only was white lead an opacifier, but it catalyzed the oxidative curing of oil and alkyd binders and provided some corrosion inhibition. However, the toxicity of lead pigments was widely recognized, and lithopone and zinc oxide had replaced white lead for interior wall and trim house paints by the 1930s. Calcium carbonate (chalk) was common in ceiling paint. White lead and zinc oxide are also slightly soluble at the pH of aqueous paints and have other interactions that lead to colloidal instability; thus, white lead never found its way into commercial latex paint. Titanium dioxide has very significant advantages due to its high refractive index and nontoxic nature. One can argue that titanium dioxide pigments were crucial to the rise of latex paint and may be the most important single material innovation in the whole of coatings technology.

White pigments operate by scattering light, rather than by absorbing light. Thus, ideally, no light is absorbed to give color, but all light is scattered away from the specular direction to produce a diffused, white opacity. The choice and design of white pigments can be made from very basic physical principles, that is, Fresnel's equations, dating from 1818 to 1823 (Born and Wolf 1964). More reflection takes place when there is a greater difference in refractive index between the medium and the included particle. Most polymer binders have a refractive index of approximately 1.5 (1.4–1.6). Fresnel's equations demonstrate why rutile titanium dioxide has become the white pigment of choice (table 2).

Extenders, or fillers, are inorganic minerals (silica, clay, calcium carbonate, etc.) that have refractive indices approximately equal to that of the binder and so have very little scattering power. Air voids in a polymer medium also scatter light due to the difference in the refractive indices. If paint is formulated with less binder than is necessary to completely encapsulate the other particulates (with more than a critical value of pigment) it will include air voids when dry. Since the early 1960s this approach has been used in cheap house paint, latex and alkyd, to provide inexpensive opacity.

In a similar vein, there are varieties of calcined clays that have an expanded structure that includes air. These contribute to opacification, cost substantially less than the principal white pigments, and do not leave the coating so weak or prone

Table 2 Reflected light intensity at a material-polymer interface.

Material	Material Refractive Index	Reflected Relative Intensity ^a
Titanium dioxide	2.76	0.08
White lead	2.0	0.02
Zinc oxide	2.0	0.02
Lithopone	1.84	0.01
Mineral extender	1.56	0.0004
Air	1.0	0.04
Polymer	1.5	0.0

Note: Reflected intensity at an air-TiO₂ interface is 0.2—i.e., very effective (diamond has a refractive index of 2.42).

^a Values were calculated from Fresnel's equations.

to dirt “pickup.” Since 1982, a hard latex, “opaque polymer,” that provides opacity from an interior void has been available commercially, but its use tends to fluctuate with the price of raw materials. Other attempts have been made to design polymer particles with internal air voids, but none has competed successfully.

Mie theory (Mie 1908; Bohren and Huffman 1983) describes the interaction of electromagnetic radiation with spherical particles, giving a result for the optimum diameter of particles for scattering light of a specified wavelength. The theory demonstrates that light is scattered by a pigment particle even if its path is only very close to the particle; it does not have to impinge directly upon it. Thus, one can have a situation where the scattering power of each pigment particle ceases to be independent and is diminished due the proximity of neighboring particles. Consequently, most commercial paints are formulated so that the (relatively) expensive titanium dioxide pigment is below this concentration and does not waste raw material value in this so-called dependent scattering. Another formulating problem is that, depending on the relative concentration of titanium dioxide pigment and extender particles, the smaller pigment particles are crowded into the interstices between the larger extender particles, bringing about dependent scattering and loss of efficiency.

The very first TiO₂ pigment was synthesized in 1916 and produced in small amounts of the anatase form mixed with barium sulfate in 1919 (Napier and Balfour 1998). Anatase has a slightly lower refractive index (2.52) than the rutile form, and a much greater propensity to form free radicals under the influence of ultraviolet light, which degrade the immedi-

ately surrounding polymer binder. All forms of TiO₂ strongly absorb UV light and behave like a sunscreen. This protects the polymers that degrade easily, such as alkyds, but the free radicals damage binders that would be otherwise more stable.

Anatase pigments were introduced in France in 1923 (Napier and Balfour 1998); rutile pigments did not appear until the early 1940s. White lead was finally banned in commercial paint in 1978 in the United States, but titanium dioxide had already become more economical to use, more even than lithopone, and lacked toxicity problems. The high opacity of titanium dioxide pigment enables very thin coatings to effectively hide the substrate.

Little titanium dioxide pigment is still produced by the earlier sulfate process, whereby the ore is purified by digestion in sulfuric acid and reprecipitation by hydrolysis. Most pigment is produced by the chloride process, introduced by DuPont in 1948, which makes a purer product and produces rutile in the oxidizing part of the process.

The 1950s saw the introduction of pigments with surface treatments (fig. 2). Usually, titanium dioxide pigments have two layers of surface treatment that surround each particle to a depth of a few nanometers. The inner layer is usually silica, which forms a barrier to the processes that form the free radical production. The outer layer is hydrated alumina, Al(OH)₃, which was originally deposited so that the pigment particles

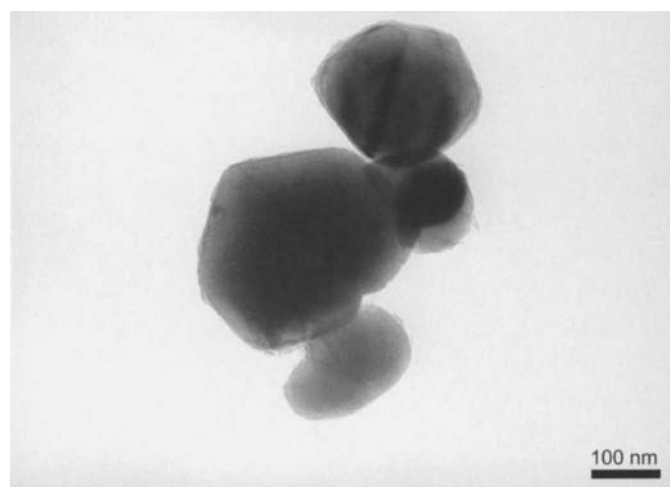


FIGURE 2 Transmission electron microscope image showing particles of a general-purpose type of titanium dioxide pigment. Less-dense surface treatment layers of silica and hydrated alumina can be seen around the darker core of titanium dioxide.

could be more easily separated in the production process. Many other surface treatments were also tried, and pigment grades proliferated in the 1960s to meet the needs of various types of paint, but by the 1980s “universal” grades had been developed so that fewer products were necessary. It is still possible to find titania and zirconia as surface treatments, but grades with tin or zinc oxide treatments have disappeared. Inclusion of compounds like zinc also helped the conversion to rutile from anatase in the sulfate process. It is common to find an organic compound on the pigment that is an aid in the manufacture of the pigment; it is sometimes also claimed to help pigment dispersion and stability in the aqueous paint.

In 1972, DuPont, closely followed by NL Industries, was the first to supply the U.S. coatings industry with slurry (although DuPont had supplied the paper industry with slurry since the 1960s). These slurries comprise approximately 50 percent pigment by volume in water, with a dispersant, biocide, and defoamer.

Colored Pigments

Apart from the modern iridescent types (Zorll 1998), pigments impart color because they absorb particular wavelengths of light dictated by their chemical structure. Most pigments are made with particle sizes that are small and do not scatter light much; thus the color is not diluted. As an illustration, figure 3 shows a transmission electron microscope view of copper phthalocyanine pigment particles.

Carbon black pigments that are formed from the burning of a variety of carbonaceous feedstocks have been known and used for centuries (for example, bone black). Many highly colored pigments were developed during the twentieth century (Lewis 1988; Herbst and Hunger 1997; Buxbaum 1998) and have changed the way the world looks. These pigments are essentially organic compounds, many of which will be degraded by exposure to ultraviolet light, heat, or acid pollution. The rate of bleaching diminishes approximately exponentially with exposure time, as the number of labile chromophores diminishes.

Traditional colored pigments, based on minerals (e.g., iron oxide, cobalt blue, etc.), are very lightfast but do not give intense monochromatic colors. However, they are very cost effective, and iron oxides remain the highest volume production pigment for yellow, brown, and red paints.

The first Hansa yellow arylide pigments were developed in Germany before the First World War; they are fairly light stable. Diarylide yellow pigments were produced in 1935 at the same time as the most useful blue pigment, copper phthalocyanine, which is very lightfast. A green halogenated version

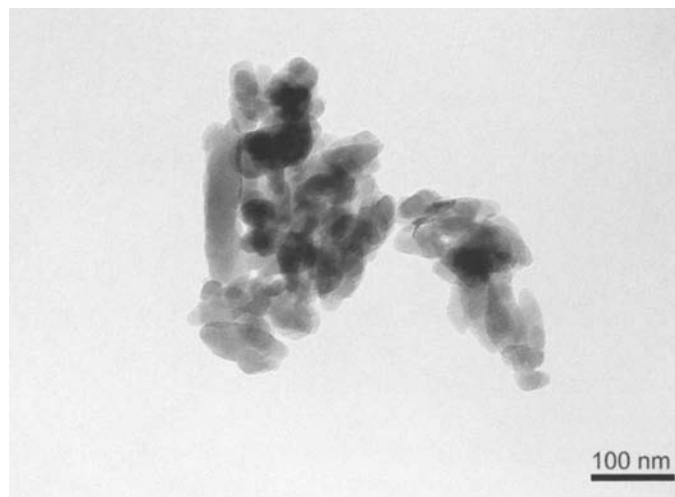


FIGURE 3 Transmission electron microscope image of some particles of green halogenated copper phthalocyanine pigment, PG7. Note that the primary particles are smaller than the wavelength of visible light.

of this chemistry (“phthalo green”) appeared fairly soon after that, in 1938. Among many others developed from 1930 until the present, the quinacridone reds are very lightfast. They first appeared in 1955, shortly followed by the perylene reds in 1956.

It has proved to be comparatively easy to modify molecular structure to change color, and too many organic pigments have been developed for me to deal with them here individually. Unfortunately, intensity of color and lightfastness are not inexpensively attained properties, so much commercial paint has been made with colors that fade, particularly in the yellow, red, and orange ranges.

Extenders

As mentioned earlier, extenders are usually inorganic minerals. The objective is to replace polymer or pigment volume and reduce the raw material cost. Typical mineral extenders are silica, calcium carbonate, and several others. The particle size of these materials is often in the micrometer range, since smaller sizes are impractically expensive to produce. Mineral extenders are not supplied as completely pure compounds and may include colored impurities. Pre-1960s commercial exterior house paint could use calcium carbonate as an extender; however, it was made obsolete by the advent of acid rain, which dissolves carbonate and may leave an unsightly efflorescence of sulfate.

Shipping costs are often a significant fraction of the cost of extenders to paint manufacturers, so it was not unknown, particularly in the 1960s to 1980s, for the same paint product made in different parts of the country to include different extenders. Industry consolidation within the extender suppliers and the advent of very tight specifications (e.g., ISO 9000) has led to a considerable reduction in this practice.

Extenders must be encapsulated by the polymer binder, just like pigments. Thus, they are often used to determine whether the coating film dries to include air voids by being above the critical pigment volume concentration (CPVC). This has been an important formulating option in the paint industry since at least the 1920s (Asbeck, Laiderman, and van Loo 1952). The air voids scatter light themselves, and increase the ability of TiO_2 particles to scatter light (by reducing the refractive index outside parts of the pigment surface). Thus, increased opacity results very cheaply, but the mechanical and chemical integrity of the coating may be greatly diminished.

Mineral particles may have other uses. Colloidal silica particles form structured flocculates that can be used to control paint rheology in both aqueous and nonaqueous media. Colloidal silica has been known since the 1930s (Kistler 1932) and is used elsewhere: as a polishing medium for silicon wafers since the 1960s, and as an abrasive and rheology control agent for toothpaste. “Fumed” silicas became economical in the 1960s and have supplanted some of the precipitated grades.

Latex

Latex polymers are very different from earlier paint binder technologies. In lacquers, such as nitrocellulose, the solvent evaporates and the polymer is precipitated as a coherent mass of entangled long-chain molecules. More complicated polymer binders are formed from chemical reactions between smaller molecules that proceed as the paint dries and an insoluble, cross-linked polymer network is formed; for example, oil paints react with oxygen in the air, epoxies, urethanes, and so forth. Latex polymers are made with a very high molecular weight (500,000 to millions of daltons), and are thus not appreciably soluble but formed in droplets or particles of 50–500 nm diameter in the emulsion polymerization process. The particles are stabilized by electrostatic repulsion (Derjaguin and Landau 1941; Verwey and Overbeek 1948), as well as by steric hindrance. As the water evaporates from the paint, the particles migrate to the surface, where evaporation is taking place (Croll 1986; Sutanto et al. 1999), pack together with each other and the other ingredients, and ultimately settle into place on the substrate. The latex particles then coalesce

under the action of surface tension and van der Waals forces. Finally, these very large polymer molecules must interdiffuse across the particle boundaries and eventually entangle to form a continuous film (Kim and Winnik 1995; Eckersley and Rudin 1990). Latex particles must initially be soft under ambient conditions so that this deformation and interdiffusion can take place, but the coatings must not be soft under normal use or they will not be durable and will pick up dirt. This transformation is achieved by including a slow-evaporating plasticizer that reduces the effective glass transition temperature of the polymer to well below ambient; this allows the deformation and interdiffusion to take place in the hours to weeks after initial film placement. Ultimately, this “coalescing aid” evaporates, and the film is left harder and tougher.

The simplest and most useful description of latex particle deformation in film formation was provided by Brown (1956), whose equation showed how important softness and smaller particle size are in responding to capillary forces. More advanced research came later (Routh and Russel 1999; Keddie 1997) but the value of Brown’s work remains. Although a little cross-linking eventually occurs in latexes, it is not usually a fundamental part of the film formation process. It may occur slowly as ultraviolet radiation produces free radicals in the polymer or other built-in chemistry takes place. Cross-linking latexes do find some niches, for example, in factory-applied (and baked) wood primers and in waterborne automotive base coats, but there is competition from other waterborne polymers, such as polyurethane, epoxy, and alkyd dispersions. Modern waterborne coating technology continues to change, with increasing use of mixtures of latex with these more specialized (and expensive) types.

The first water dispersion polymerization seems to have been done in Germany on isoprene, with more recognizable emulsion polymerization patented by I. G. Farbenindustrie, again in Germany, in the 1930s. In the United Kingdom, PVA homopolymer was used in paints before the Second World War, in 1939. The first commercial waterborne emulsion paint widely sold in the United States was probably Kemtone, manufactured by Sherwin-Williams beginning in 1941. It used a binder system of casein, corn protein, rosin, and some linseed oil in an emulsion. It was pigmented with TiO_2 , chalk, clay, and mica.

The need for artificial latex emerged during World War II: the Allies had to find a substitute for rubber in tires and other uses because the rubber plantations were under the control of the Axis powers. Thus, styrene-butadiene (SB) rubber was developed. The U.S. government formed a consortium of

chemical companies and universities, which made the “Mutual Recipe” for SB rubber starting in 1942. It contained 75 parts of butadiene to 25 parts of styrene and a little mercaptan. After the war, it was found that a mixture that was 40 percent styrene (hard component) and 60 percent butadiene (soft) made a polymer that was useful as a binder for waterborne paint. Latex paints dried to the touch in a matter of minutes, were easy to clean up, and did not have much odor, all of which accounts for their early and continuing success with consumers.

In 1946, styrene-butadiene latex was commercialized in paper coatings; then in 1948 Glidden’s Spred Satin became the first latex house paint to be made with this binder. This paint competed very well against oil paint for interior use—helped by the introduction of the roller applicator, where cleanup is greatly facilitated by water-based paint. Soon thereafter, polyvinyl acetate (PVA)—alone or modified with acrylate, maleate, fumarate, or ethylene esters—was investigated as a latex paint binder. These PVAs were cheaper than SB rubbers and did not have their characteristic smell.

Neither of these varieties performed very well, nor were they less expensive than oil-based paints, but they were fast drying and easy to clean up. Even polystyrene emulsions with suitable plasticizers were considered in the early days, but it is doubtful whether they gained much popularity. Styrene-butadiene latex continued to be used in commercial paints for some time because it had better mechanical toughness and overall exterior durability than early PVA-type binders, although it had chalking and yellowing problems.

Styrene-butadiene latexes remain in use in paper coatings today, but their use in architectural paints was waning by the end of the 1960s. Styrene-acrylic latexes were introduced in 1953 to overcome the problems with SB latexes. Sometimes called *modified acrylics*, styrene-acrylic latexes were actively considered more widely for house paint in the United States in the 1970s and 1980s than today. These materials were attractive for cost reasons and continue to be used in Europe, because the craftsman tradition there is for people to repaint their houses more frequently than do consumers in the United States, where fears about weatherability held styrene back. In addition, since most of Europe is farther north than the United States, it receives much less ultraviolet radiation and heat from the sun. Moreover, there may be a level at which the weatherability problems of styrene are insignificant, because it does find use in industrial latex coatings where its hydrophobicity (water resistance) is useful.

An all-acrylic emulsion polymer based on a mixture of ethyl acrylate (soft) and methyl methacrylate (hard) was com-

mercialized as Rhoplex (Primal in Europe) AC-33 in 1953. It was also used in artists’ paint. This all-acrylic chemistry, from Rohm and Haas, provided a binder that was quite durable and was not saponified by alkaline substrates. Although it did not have the gloss or the ability to adhere to wood or old layers of oil or alkyd paints that oil-based paints had, it succeeded on interior walls and on masonry. In 1961, Rohm and Haas introduced AC-34, which was similar to AC-33 but had some additional ureido functionality (Harren 1990) to improve its adhesion to a variety of surfaces. This functionality allowed a little cross-linking to take place once the coating was exposed. This cross-linking, together with the entanglements in the already very-high-molecular-weight polymer, provides much better adhesion, mechanical properties, and water resistance than the original material.

Subsequent improvements to acrylic latex chemistry resulted in very durable binders that resist solar ultraviolet and moisture, contain less superfluous surfactant, and provide improved gloss while requiring less coalescing aid. Until comparatively recently (about 1990), acrylic latexes had some problems in adhering to old oil-based paint surfaces that had become chalky. The typical remedy, in the United States, was to include a water-dispersible alkyd resin. These resins enhanced adhesion to degraded surfaces but caused some problems themselves; because they decreased the overall durability of the coating, they were only marginally compatible with the aqueous medium, and thus reduced gloss and hindered pigment dispersion. The best current practice in the United States and Europe is to use all-acrylic emulsions for exterior house paints because they are very durable to ultraviolet light, moisture, and pollution.

Starting in about 1983, other latexes specifically designed for use in field-applied industrial coatings came into use. These paints are usually harder, and thus require more and different coalescing aids. They may be cross-linkable, have greater chemical resistance, and possess a smaller particle size in order to aid film formation and yield a good gloss. Additionally, some industrial latexes are not electrostatically stabilized, because stabilization can inhibit film formation when the carboxylate functionality reacts with other resins (although this may also be a useful cross-linking reaction), and the counterions, like sodium, promote corrosion. Latexes may be used in combination with epoxy or polyurethane dispersions in coatings, exploiting the acrylic nature of the latexes to provide good color, hardness, and durability. The latexes also improve the cost of the overall system.

The last fifteen years has seen increasing interest in avoiding coalescing aids and their contribution to VOC. Judicious

mixtures of soft and hard latexes with different particle sizes provide a paint that forms a usefully hard coating. Latexes that, at ambient conditions, have a low degree of oxidative cross-linking (similar in spirit to alkyds) help form a film. By tailoring solubility characteristics (e.g., by using styrene), one can make latex that is more sensitive to plasticization by coalescents, such as glycols, and thus the paint does not release so much volatile organic content on drying.

Coalescents and Cosolvents

Most latex compositions that make useful dried coatings are too hard to coalesce by themselves at normal ambient temperatures. In early paint formulations, diethylene glycol performed as an antifreeze and plasticizing solvent; that is, as a coalescing aid. Other early coalescents were materials such as dialkyl succinates, methyl cellosolve, carbitol, butyl cellosolve (Hoy 1973) and the like, depending on the hardness of the polymer. In the 1960s, PVA emulsions also used dibutyl phthalate or even tricresyl phosphate as coalescing aids.

The most significant technological development in coalescing aids was the introduction of Texanol (2,2,4-trimethyl-1,3-pentandiol-monoisobutyrate; Eastman Chemical). It was introduced commercially in 1964. This material helped the market penetration of latex paints tremendously. It remains very widely used but, with the other cosolvents, does give off a characteristic odor in freshly painted areas. The drawback to coalescing aids remaining in the paint for a long time is not only odor but dirt pickup due to prolonged softness.

Cosolvents are sometimes required so that other paint ingredients will be compatible in the aqueous environment. Butyl carbitol is a cosolvent that controls the solubility of “associative” thickeners—and thus their viscosity and ease of mixing into the paint.

Thickeners

Originally, formulations exploited the tremendous effect that soluble polymers have on solution viscosity (Sperling 2006). Other options would be to use the flocculating nature of colloidal-size materials, such as silica, or to use swellable acicular clays, as many alkyd paints do. Soluble polymers like hydroxyethylcellulose (HEC) have been, for many years, a very cost-effective and straightforward method for viscosifying aqueous paint. Cellulose ethers were introduced after World War II as more efficient alternatives to casein and derivatives of other natural polysaccharides (e.g., alginates and xanthan gum), whose use in commercial paint did not really die out until almost 1980. Alkali-soluble cellulose ethers, such as HEC,

carboxymethylcellulose, and others, proved to be both compatible with a wide range of ingredients and very economical, being derived most often from wood pulp.

Cellulosic thickeners are sold in different grades of molecular weight, from less than 100,000 Da to well over a million Da. High-molecular-weight polymers are very economical, because they provide high viscosity at low shear rates while present in fairly low concentrations (Croll and Kleinlein 1986). In contrast, at high shear rates solution viscosity is controlled more by the molar concentration of material dissolved than by the molecular interactions. It is very difficult to get good performance with just one cellulosic thickener, and paint formulations often use two cellulosic thickeners of different molecular weight.

Cellulosic materials can be attacked in the can by microbes, with attendant loss of viscosity, and are invaded by mildew in the dried coating. They are slow to dissolve and equilibrate in solution. Alternatively, grades of the dry powder are available with different particle size and surface treatment that help the dissolution process. Cellulosic thickeners do not permit the highest possible gloss in latex paints. Nevertheless, they (especially HEC) continue to be an important and common ingredient in aqueous paint.

Other technologies have appeared that provide improved performance over HEC. The first was acrylic polyelectrolytes of roughly the same molecular weight and chain stiffness as HEC. These are made and supplied to the paint manufacturer as liquid emulsions at acid pH. Then, upon neutralization in the alkaline pH of aqueous paint, the polyelectrolyte chain extends due to the charge repulsion and becomes a large soluble polymer that viscosifies the paint. These emulsions are not attacked readily by microbes and are comparatively easy to incorporate into liquid paint due to their liquid emulsion form, as opposed to dry powder. These materials were introduced in 1971 but only seriously commercialized in about 1981 on both sides of the Atlantic. They challenge the economics of cellulosic thickeners, and they usually offer some improvement in application properties and coating appearance.

“Associative” thickeners (Schaller and Sperry 1992) were introduced in 1981 after being patented in 1978 (Emmons 1978). These are often known as hydrophobically modified ethoxylate urethane (HEUR) block copolymers. Again, these are based on petrochemicals and are not broken down easily by microbe infestations in manufacture or storage. The simplest form comprises water-soluble polyethylene oxide polymer blocks joined by urethane linkages; the overall molecule has a hydrophobe at each end. The hydrophobes associate to form small, loosely bound micelles (Vorobyova, Lau, and Winnik

2001); thus, in the aqueous phase, the polymer forms a three-dimensional viscosifying network.

These thickeners are more complicated to use. It is not unusual to find cosolvents in an aqueous paint for controlling the solubility and viscosity imparted by these HEUR thickeners. Other difficulties lie in their interactions with other paint ingredients. Choice of surfactant may be crucial (Mahli et al. 2003), as is choice of dispersant. Depending on their compatibility, aqueous solutions of dispersants and associative thickeners may phase separate (fig. 4).

In this figure, a coexistence curve, the region above the curve denotes the concentration regime where phase separation occurs. Normally, in undried liquid paint, both dispersant and thickener concentrations lie below the line, but the situation will change when the water evaporates during drying. In particular, the more ionic types of dispersant may provoke phase separation more easily in a mixture with an associative thickener. This may then provoke partitioning of the latex or pigments into one of the phases that they find most compatible, essentially flocculating the system (Baxter, Sperry, and Fu 1997). Any polymer system that suffers phase separation is likely to cure into a film that has microscopic droplets of one phase dispersed in a matrix of the other. These films have poor mechanical integrity, poor pigment dispersion, and reduced gloss.

Associative thickeners are more expensive than other thickeners and more difficult to incorporate, so HEC is still widely used, often in conjunction with these other thickener types. In fact, hybrid materials are available that combine

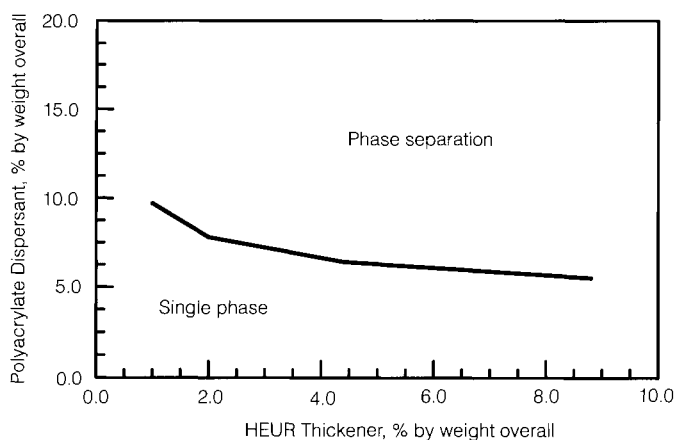


FIGURE 4 Coexistence curve for HEUR thickener and sodium polyacrylate dispersant, measured at pH 9.0.

the functions of soluble polymer and associating polymer (hydrophobe-containing), even to the extent that an associative version of HEC is now a well-known alternative.

Summary

The history of commercial paint technology is a large and complex subject. In the 1930s, oil paint was widely used, with practical alkyds being introduced in industrial applications in competition with nitrocellulose lacquers. It is very striking how the technology developed from small beginnings and important scientific discoveries in the first thirty years of the twentieth century and then accelerated as the discoveries fed upon each other, in the 1940s, '50s, and thereafter, to meet the needs of external events and an increasing and wealthier population. Paint technology has also benefited tremendously from concurrent advances in instrument analysis.

Although the paint industry has been dominated by polymer binder developments, the advent of titanium dioxide white pigment has been central in modern paint technology because it is not toxic, is almost inert, and permits high, controlled opacity. The oil embargo of the early 1970s and the increasing awareness of atmospheric and environmental pollution changed the reasons for progress in the use of waterborne paints from ease of use to environmental health. As the technology has improved, waterborne paints have been increasingly able to compete in areas where solvent-borne technology previously dominated, and thus they continue to claim an increasing share of the market.

At the introduction of latex paint, in the 1940s, with water as the carrier fluid, other necessary ingredients, such as surfactants, thickeners, cosolvents, and the like, were already available, and these materials would still be recognizable now. It is difficult to know where the technology will develop further, but new methods of synthesizing polymers and other molecules are still being investigated. There will always be a need to change or improve something's appearance or protect it from its environment, so it is difficult to imagine a future without paint and coatings.

Acknowledgments

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Notes

- 1 Atlas Powder later became ICI Surfactants.
- 2 By way of Union Carbide and, originally, Rohm and Haas.

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Modern Paints, Conservation of

James Coddington

Abstract: *This paper reviews a twenty-year-old survey of paintings from the Museum of Modern Art (MoMA) in New York. This survey of almost 150 paintings using synthetic paint media revealed that the condition of these paintings is in general quite good. The survey also provided direct responses from the artists regarding their selection of materials and thoughts on longevity of the specific works. The paper goes on to review in depth a treatment of a complex painted object, VI:XXXII by David Novros (1966), as well as noting examples of restorations of several others: an architectural model of Alvar Aalto's Church of the Three Crosses made in 1998 for the architect's retrospective at MoMA, and the painted sculptures Two Cheeseburgers, With Everything, a work from 1962 by Claes Oldenburg, and Donald Judd's 5 Green Rectangles from 1968. The paper concludes with some reflections on the future of the study and treatment of works that incorporate synthetic paints.*

Introduction

The title of this paper, “Modern Paints, Conservation of,” is fashioned like a single entry in an index. That sense of an indexed entry affords an approach to the topic in several discrete sections. The first section is motivated by the observation that we are becoming what may well be called the “survey generation” of conservators. We are collecting information at a rapid clip. I do occasionally wonder how much of this data will ultimately be used by future conservators, but only occasionally, and never often enough to interfere with the collection of survey data on the Museum of Modern Art's collections. That said, I think it opportune to revisit a survey, now almost twenty years on, of acrylic paintings in MoMA's collection. I do so mostly as a means to address the topic of the conference,

but also as a means to assess the ultimate usefulness of a survey some reasonable amount of time down the road. In addition, some of the key information in the survey came directly from the artist, and this is a critical contribution to the ultimate goal of *Modern Paints Uncovered's* proceedings—the proper care of modern art. I find many of these entries to be useful combinations of common sense and thoughtful reflection, and so I resort to them rather frequently.

After first reviewing the survey and using it to provide examples, I discuss in some detail the treatment of a single painting, David Novros's VI:XXXII (1966). I do this for two reasons: first, because it deals with a painting with a synthetic paint medium; and second, because the treatment also involved close collaboration with the artist in essentially refabricating the work. The latter allows a deeper discussion of the role an artist can, or should, play in actual restorations—not just in surveys. While this is not a new topic by any means, I thought it worth adding one more example to this ongoing discussion within our profession. In this case, the treatment was driven by the nature of the paints the artist used.

The final section will discuss a few instances of works in MoMA's collection that I suspect, along with new surveys and other restorations, will be fodder for *MPU: The Sequel*.

The Survey

The somewhat misleadingly named Acrylics Survey at MoMA was initiated nineteen years ago (MoMA 1989); the principal conservator in charge of the project was Carol Stringari. Almost 150 paintings were surveyed, including a detailed examination of materials and condition as well as sampling of a select number of works. A questionnaire was sent to the artists, with

a reasonable return rate of about 20 percent. Before getting into the details of the survey, some general observations are in order. First, it was not just acrylics that were surveyed; synthetic media more generally were the topic. In addition, these works were not just paint on canvas; they included a variety of substrates. Those that were painted on canvas involved a range of different initial preparations of the canvas. Some were sized; others were unsized. Some had ground; others did not. Some used commercial grounds; some grounds applied by the artist. And so on. Most grounds were acrylic gesso, and there was a definite understanding that it was bad practice to use acrylic paints on some other preparation, such as an oil ground.

Similarly, some artists noted that diluting the acrylic gesso could lead to problems. As Richard Artschwager observed, “Where gesso was cut with water there can be flaking. This is well known I think.” The artists also showed a definite sense of understanding of the general material properties of paint; quite a number of them noted that bad things happen when paintings, acrylic paintings in particular, get cold. For example, one artist noted, “At cold temperatures acrylic films will shatter.” Indeed they do.¹

This clear attention to craft and materials was, of course, the starting point for a great deal of experimentation. The following materials were observed by the conservators and/or attested to by the artists: oil paint mixed with Lucite 44, polyurethane lacquer and oil paint, collage, India ink, Rhoplex, chalk, powdered glass, sand, pebbles, wood shavings, Styrofoam pellets, cotton, string, seeds, fish scales, and eggshells. Thus the paint, albeit modern, may be in some cases more a convenience for the artist, a means to an end, or more accurately, a vehicle for getting other materials onto a surface.

A few other general observations/statistics gleaned from this review were as follows:

- Of the approximately one hundred and fifty works surveyed, eleven were clearly varnished, although local varnish was suspected in additional instances.
- Twenty works were sampled for more extensive technical analysis, and each work was tested for solubility. In very general terms, solubility in water was found to be minimal. The same was true for benzine. However, the paints were almost universally and unsurprisingly susceptible to solvents such as xylene and acetone.
- A bare handful had either known or suspected prior treatments. Of the known treatments, most involved surface cleaning. Almost none of these treatment records indicated structural treatment of any sort.
- The survey form closed with an opportunity for the artists to offer general observations on their materials and techniques. It is no surprise that no artist feared for the long-term prospects of their paintings. If the notion of longevity was noted at all, it generally took the form of, If you take care of the painting it will last. Perhaps the most memorable formulation of this was from Susan Rothenberg, who wrote, “Try not to let roof leak on the pntgs. Once a pntg got a terrible fungus + ripped from mildew on the back of the canvas. If your roof is ok, so is my picture.”

With these general trends and observations in hand, I pulled out at random eight survey sheets and went to MoMA storage to examine each of the works.²

Edda Renouf's *This I*

The first painting examined was Edda Renouf's *This I* (fig. 1). Painted in 1973 and acquired in 1983, it is in excellent condition. The most notable feature of the painting is that in several long runs the artist has pulled threads out of the canvas to create



FIGURE 1 Edda Renouf (American, b. 1943), *This I*, 1973. Synthetic polymer paint on canvas, 40 × 40 cm (15¾ × 15¾ in.). New York, The Museum of Modern Art, The Riklis Collection of McCrory Corporation. Digital images © 2006 The Museum of Modern Art. Published with permission of the artist.

trenches for the ground to fill. It is these lines, where there is no fill thread and where the regular texture of the canvas has been disturbed, that create the geometric composition. Short threads were added on the surface to mimic the base threads of the fabric, which are in fact intact and visible on the reverse. The artist on her questionnaire indicated that the ground is straight acrylic gesso, on top of which she applied glazes in oil. As noted, despite the weakening of the canvas structure, the painting is in fine condition, with no planar distortion or other problems arising.

Malcolm Bailey's *Hold, Separate but Equal*

The second work examined was a Malcolm Bailey: *Hold, Separate but Equal*. This work, painted in 1969 and acquired by the museum in 1970, is on untempered Masonite and, according to collection records, is painted in synthetic polymer paint, presstype, watercolor, and enamel. Examination of the work in 1987 also revealed a varnish on the painting that was applied somewhat unevenly over the surface. Some of the figures, painted in white, show incipient cleavage, but the varnish would seem to be preventing flaking in these areas. Close examination revealed the varnish had trapped some dirt and frass beneath it, further evidence that the artist had applied it. The unevenness of application of the varnish also suggested application by the artist, yet the actual nature of the varnish remains unclear. The report indicates, without citing the source of the information, that the varnish may be Krylon. While no sample of the varnish was taken for further

testing, solubility tests indicate it is slightly soluble in benzene and readily soluble in xylene.

This is one of the few pictures in the survey with any prior treatment. An attempt to clean the painting was made in 1984, when some test cleanings were done. But in the end the attempt was abandoned without recording the reason. Although some structural problems with this work were observed (the already-noted incipient cleavage), it looks to be restricted to areas estimated to be watercolor/gouache, and does not affect the synthetic paint areas.

Robert Goodnough's *Struggle*

Robert Goodnough's *Struggle* (fig. 2A), painted in 1967 and acquired by the museum in 1969, is also a mix of media. Collection records indicate oil, synthetic polymer paint, charcoal, and pencil. The shapes on this canvas are made by painting within masked-out forms, the crisp edges of tape being evident on close examination of the forms. Here too there is use of local varnishing. In this case the artist manipulated the gloss throughout the picture as a fundamental aesthetic, a means of further distinguishing the forms and shapes of the composition (fig. 2B).

Overall, the painting is in sound condition; just one small area of cracking is visible along one edge, very likely the result of some careless handling in the past. Notes from the 1988 examination indicated some yellowing of the ground then, thought to possibly be due to a reaction with the canvas. The



FIGURE 2A Robert Goodnough (American, b. 1917), *Struggle*, 1967. Synthetic polymer paint, oil, and charcoal on canvas, 149.8 × 294.8 cm (59 × 116½ in.). New York, The Museum of Modern Art. Given anonymously. Digital images © 2006 The Museum of Modern Art.

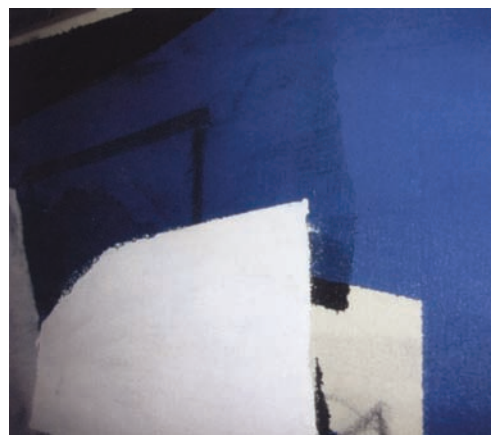


FIGURE 2B Detail of figure 2A.

local varnish was also noted to be somewhat yellowed at that time, but it is difficult to say whether the yellowing in either case has advanced significantly since then. In any case, however, this picture is in sound condition.

Alan Cote's *Distant Warmth*

Alan Cote's *Distant Warmth*, painted in 1978 and acquired in 1979, is acrylic painted in multiple layers on cotton duck. The artist stated in his questionnaire that he sometimes adds gel medium to his paints, and this probably accounts for the varied gloss throughout the painted surface. Cote's questionnaire contained extensive responses, a number of which reflect the practice of other artists. In 1988 he was using Golden Acrylics, having switched from Bocour Aquatec, a transition also made by several other artists. He also notes, tellingly, "I think acrylic conservation should deal with use of the best matte or gloss varnish to protect the surface." This concern with varnish is, in my experience, rather common. Artists, when discussing their paintings, will frequently regard the varnish as a protective layer; yet they are also aware that the varnish (and ultimately devarnishing) can have profound effects on the appearance of their painting. Cote addressed this by going on, rather enigmatically, "considering that the pigment is safe underneath."

Jules Olitski's *Thalass, Mystery #10*

Jules Olitski's *Thalass, Mystery #10*, painted in 1978 and acquired in 1982, was the next painting examined. The painting is executed on a heavyweight cotton duck mounted on an expansion bolt stretcher, but it is somewhat different from the other works in this random selection from the survey. A considerable buildup of impasto—probably due to direct application of medium to create a sculpted surface—characterizes this painting. Olitski wrote, "I use gel medium when it serves such purpose as having to do with luminosity or surface quality or both." This material remains slightly soft, and thus the painting shows no signs of cracking or lifting paint. The softness of the impasto and paint does not appear to be the result of plasticizers or other material that is migrating to the surface, or if it is, it is not attracting an inordinate amount of dust.

The edges are infused with an unknown adhesive, while the ground, which can only be seen along the edges, appears to have been applied by the artist. The paint Olitski used was, according to his written response, Bocour Aquatec. The gel medium has discolored somewhat, perhaps depriving the painting of the luminosity the artist initially sought from the gel medium. However, it is impossible to know if this discol-

oration has changed significantly in the nineteen years since the survey.

The solubility of this work is also somewhat different from that of others in the random selection, showing only slight solubility in ethanol, whereas others are very soluble in both ethanol and aromatic hydrocarbons such as xylene. Test cleaning of this surface in 1988 indicated that with repeated application of moisture a "foaming effect" was observed.

Billy Al Bengston's *Gregory*

Billy Al Bengston's *Gregory* (1961), acquired by the museum in 1962, is oil and metallic paint on composition board. This is the only work in the survey selection that relies extensively on airbrushing. The base color is oil paint, and then Bengston sprayed, according to his response, a polyurethane lacquer mixed with pigment. The result is a fairly glossy surface that remains in sound condition.

Agnes Martin's *Red Bird*

A very different paint surface from that of the Bengston can be seen in Agnes Martin's *Red Bird* (1964), which came into the museum's collection in 1970. Her typical matte white is subtly marked by lines drawn across the width of the canvas. The paint layer is composed of a thin acrylic gesso layer, and then acrylic paint. The lines were drawn with a red wax pencil. This is one of the few works in the survey that had prior treatment. In this case there were two campaigns. One was the removal, or more accurately diminishing, of handling marks by retouching the disfiguring marks with Hyplar (Grumbacher) acrylic paint. The other treatment was the removal with xylene of a blue ballpoint pen mark.

On her questionnaire, the artist suggested the work could be sprayed with "Blair" acrylic spray if needed, but a somewhat uneven spray can be seen on the surface, suggesting the artist had already applied one. A test cleaning of the varnish in 1988 showed it was slightly discolored at that time. Otherwise this too is a work in very good condition.

Donald Judd's *Untitled* (1961)

Finally, Donald Judd's *Untitled* from 1961 (fig. 3A), is oil and acrylic painted on a Masonite panel. A subtle combination of paints and colors characterizes the surface, a very matte blue that also shows a thin layer of red over much of it. The white horseshoe shape is also very matte and thick, but has less texture than the blue base color. Both the white and the blue show many air bubbles throughout, indicating these are probably aqueous media. The construction of this painting is,



FIGURE 3A Donald Judd (American, 1928–1994), *Untitled*, 1961. Synthetic polymer paint, oil, charcoal grit, and sand on composition board, 183 × 121.7 cm (72 × 47% in.). New York, The Museum of Modern Art. Gift of Leo Castelli. Digital images © 2006 The Museum of Modern Art. Art © Judd Foundation. Licensed by VAGA, New York.

like so many of the others cited here, complex. The texture on this panel is the result of Judd having put clots of paint and a considerable amount of sand and charcoal grit on the surface, after which he painted over them. These materials can be seen in a few areas where the upper layer is lost, thus revealing the structure. It is difficult to see how Judd isolated these materials, particularly the charcoal, from the final layer of blue paint, but it appears that there was an overall layer of white on these coarse materials. Of even more interest is that he was also



FIGURE 3B Detail of figure 3A.

manipulating the gloss of the overall surface, locally varnishing quite noticeably (fig. 3B). Despite the loss of the tips of impasto in a few areas, this painting, too, is in basically sound condition.

Restoration of David Novros's *VI:XXXII*

So what does this survey of a survey reveal? That, typically enough, when artists turned to modern paints, experimentation of all sorts continued. We can also conclude that, to the extent the eight randomly selected works represent the entire survey, the works are in good condition. Nevertheless, there are times when good structural condition may be almost beside the point. For this reason, it is fruitful to examine in some detail the conservation of a single work, David Novros's *VI:XXXII*, from 1966, acquired by MoMA in 1971 (fig. 4).

The restoration was undertaken because of the discoloration of the synthetic paint medium Novros used.³ However, the path the treatment took and the role the artist played, ultimately leading to his repainting of the work, led to useful discussions regarding how the overall aging of synthetic paints may affect treatment options and, more generally, how we confront works that are fundamentally altered from the artist's original intention.⁴

Condition and Materials

The collection management information on this work is as follows:

VI:XXXII / David Novros / 1966 / vinyl lacquer paint on shaped canvases in 6 panels / overall 14'7¼" × 6'9¾"

The canvases, after stretching, had been prepared with several layers of white vinyl house paint, the kind, according to the artist, "they use on the rubber walls in insane asylums" (MoMA Object Files). Novros then mixed pearlescent pigments (brand name Murano) into the vinyl lacquer and sprayed multiple layers onto the canvas. The result was a multichromatic surface, as the pearlescent pigments changed color with angle of viewing.

The work was exhibited relatively rarely, and the issue of its condition was raised by the artist on a visit to the museum's storage in the mid-1980s. He noted that the medium, while still quite flexible, had yellowed, significantly diminishing the effect of the Murano pigment. The wooden stretchers, made by the artist in order to achieve the precise shape and depth he wanted, were staining through the canvas, resulting in a kind of foxing effect on many edges. All in all, the surface of these panels—meant to glow and refract light—had lost that essential luminescence. The stains had also cost the work its ability to float off the wall, since they obdurately declared the plane of the canvas.

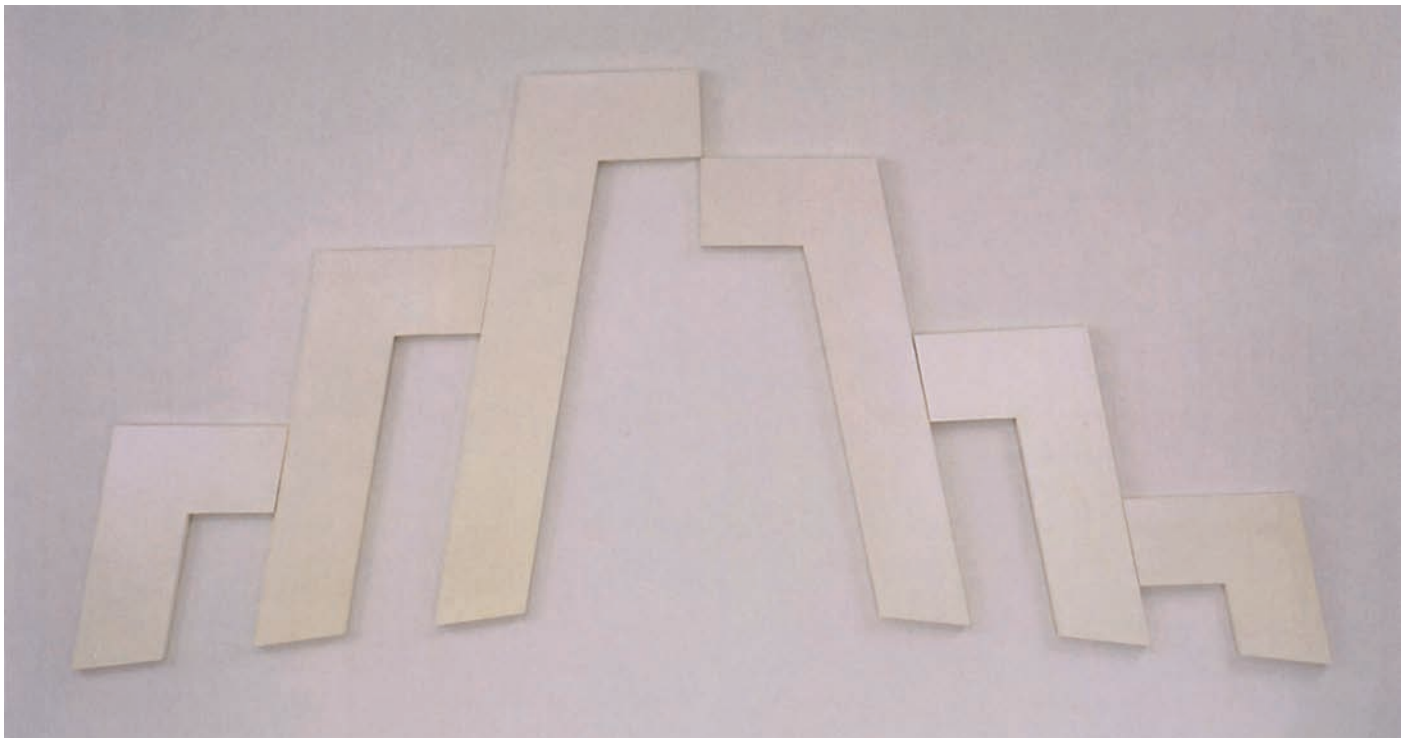
Treatment Discussion

MoMA conservators undertook research into Novros's materials to try to understand what had happened. The artist had recently restored a similar work, so he was able to provide guidance on where to find these materials. Considerable discussion ensued with Novros about the restoration, concerning both materials and procedures.

The first treatment step, which was easy to determine, was the removal of the canvases from the stretchers in order to address the cause of the staining at the edges. The stretchers were then isolated with Marvelseal (Ludlow Corp.) and the canvases reattached to the stretchers.

Various options for treating the painted surface were considered, and all were discussed at length with the artist. Complete refabrication, suggested by the artist, was rejected. It was also decided that painting over the existing paint layer would not be satisfactory, as Novros thought the underlayers

FIGURE 4 David Novros (American, b. 1941), *VI:XXXII*, 1966. Vinyl lacquer paint on shaped canvases in six parts, overall 207.6 × 445.1 cm (81¾ × 175¼ in.). New York, The Museum of Modern Art. Gift of Charles Cowles. Digital images © 2006 The Museum of Modern Art. Published with permission of the artist.



would be likely to bleed into the new layers, creating new discolorations and disturbances on the surface. It was also thought that the additional paint would soften the edges too much, diminishing the crisp, sculptural quality.

Removal of the discolored layer became the only solution, but this, of course, would entail removing original material, and in this case *pigmented* original material, not merely an original varnish, raising significant ethical issues. However, it was decided that the discolored surface was irredeemable and that repainting would be a more authentic presentation of the artist's original vision. This possible treatment was further complicated by the fact that the exact original paint materials were no longer available. The pearlescent paint, Murano, was no longer available, and the medium it was mixed into had changed as well. It was decided that test panels would be made with the available paints to determine the best formulation for the projected repainting. It was also decided to see whether the original panels could be cleaned of dirt and grime, and then the discolored coating removed to reveal the base white layer.

Cleaning

Dirt and grime were removed with a simple saliva cleaning. Various cleaning solutions were tested for removing the coatings. These included emulsions of xylene, Triton X-100, and either ethanolamine or benzyl alcohol, in the hope that an emulsion would give more control than solvents. The increased control was desired to keep the cleaning restricted to the clear coating layer, although it and the base white had very similar solubility. In the end it was decided to remove this top layer with a toluene-acetone mixture, thinning the layer successively (fig. 5). Novros saw the cleaning in progress and offered the additional suggestion that when the cleaning was done, another layer of white be put down to even out the surface before he sprayed the opalescent paint on.

It would be nice to say that this cleaning went smoothly, but in fact an unusual series of problems arose. More accurately, they were unusual in the context of cleaning a traditional oil painting, but were perhaps not unusual for cleaning a complex layering of polyurethane spray paint.

- After the last panel was cleaned, a review of the previously cleaned panels, which had been stored in the dark for some time, showed that they had acquired a mottled appearance. The darker, yellow areas showed clearly under UV examination as residual lacquer, but they were much more yellow than any of the origi-



FIGURE 5 David Novros, VI:XXXII (fig. 4), during cleaning.

nal had been, suggesting some sort of reaction with the solvents and/or that underlying paint layers had contributed to the discoloration. These residues were then removed with additional cleaning, this time with a benzene-acetone mix.

- In addition, during the cleaning a swelling of the white layer was readily seen—the canvas texture all but disappeared for a few hours. Ultimately this layer shrank back and revealed the canvas texture quite fully. The long-term effect this swelling might have on the work is not known but is of clear concern.
- During this final cleaning another unusual phenomenon cropped up: the appearance of a few small red dots with a slight pink halo around them. Presumably the result of migrating materials, the spots tended to spread slightly when solvents were applied in an attempt to remove them. It was decided to cover and isolate them with white acrylic paint before the artist returned to begin repainting the canvases.

Repainting

Before repainting could begin, additional research was necessary to find a viable substitute for the vinyl paint. The vinyl lacquer was extremely flexible when applied and had retained that elastic quality. As a possible substitute Novros suggested Cel-Vinyl (Cartoon Colour Company), a paint used in the animation industry. However, in the end an acrylic lacquer,

Duracryl White Mixing Acrylic Lacquer DMA 311, was used. Added to this were DX 316 Flexative and DCA 468 Acrylic Lacquer, all thinned with DTL 16 Duracryl Acrylic Lacquer Thinner (all PPG Industries). Test panels were sprayed to arrive at the proper proportions of the ingredients, and then the bottom edge of one panel was sprayed to make sure there would be good adhesion between this new white layer and the original.

Several weeks were allowed for drying and to determine that the new paint was performing as expected. Novros then returned to spray all the panels with a thin coat of white. This was decided upon in order to achieve the most consistent white layer possible, for, as noted before, Novros was clear that the tinted lacquer layer would only be as good as the initial white layer.

After again allowing several weeks' drying time, during which the panels were also evened out by rubbing with cheesecloth, the artist returned for the final spray coats of tinted lacquer. This mix was thinner than the white pigment layer and contained surprisingly little opalescent pigment. Each panel was sprayed with an initial thin coat of this paint mix, and then, after drying for a minute or so, was sprayed again with a thicker layer. Although some differences in the density of the lacquer layer were evident from panel to panel, Novros was not concerned, saying, "This is part of the deal, they don't have to be exactly alike."

After he was done spraying each panel, it was closely examined. A few spots where lacquer had accumulated were shaved back down into plane, and one was sprayed just with thinner, to re-form the surface to be smoother, glossy, and thus more consistent with the other panels. In the end, the artist declared himself satisfied with the restoration. The work was shown several years later in an exhibition in a New York gallery.

Discussion

The artist's satisfaction with the results, while gratifying, does not, of course, answer all the questions that the restoration poses to conservation practice. It was clear at the outset that the polyptych was a pale representation of the artist's intention. The inherent vice of the vinyl lacquer, its discoloration, was global. This necessitated an irreversible treatment much the same as a varnish removal, with the critical difference that it was a pigmented coating being removed. Yet it was precisely the compromising of the pigments by the discolored lacquer that had necessitated the treatment in the first place. That there were, and remain, unanswered questions surrounding this treatment is reflected well in the

closing at the end of the treatment report: "To be continued." Perhaps this too can be revisited whenever a second MPU conference occurs.

Conservation of Painted Surfaces

This would be a cramped presentation of the conservation of modern paints if it were restricted to paintings. There is a great deal of paint to be found on three-dimensional surfaces as well. The following sections describe just a few examples of complex paint problems we have found in the MoMA collections.

Claes Oldenburg's *Two Cheeseburgers, With Everything*

The first example is a Claes Oldenburg sculpture, *Two Cheeseburgers, With Everything*, a work from 1962. The "everything" seems to include a persistent efflorescence of the paint film. The work is recorded as plaster-soaked burlap with enamel paint, and it would seem that the plaster moves through the paint film, breaking through in small areas, suggesting a slightly moldy hamburger. It is not so much the paint that is the problem here but the substrate, and yet there is little we can do to rectify the problem, as the paint film and substrate are so intimately bound up together.

Model of Alvar Aalto's Church of the Three Crosses

A second example is an architectural model of the Church of the Three Crosses. Made in 1998 for the Alvar Aalto retrospective at MoMA, it quickly showed a very disfiguring eruption on the roof of the church (figs. 6A and 6B). The defect shown here suggests a fault that may lie more with application technique than with the materials used. According to the model maker for the museum's Aalto exhibition, he used exactly the same materials for all of the models constructed: a phenolic foam, calcium carbonate-rich filler, and acrylic emulsion paint. However, this model was the only one to have suffered any changes. The fault could be related to the fact that the builder made this model last, completing it the night before the opening and painting directly on wet filler.

X-ray diffraction and Fourier transform infrared (FTIR) spectroscopy confirmed that calcium formate was produced at the filler-paint interface and caused the efflorescence and paint bubbling. This was caused by formate ions originating from the foam matrix and reacting with the filler, which was underbound calcium carbonate (McGlinchey and Griffith 2001). The calcium formate then pushed its way through the acrylic film. But the most disturbing aspect of this alteration was the blister that formed beneath the paint. Aside from the high likelihood



FIGURE 6A Model (1998) of Alvar Aalto's (Finnish, 1898–1976) Church of the Three Crosses (1955–58) in Vuoksenniska, Imatra, Finland. Plastic, cardboard, and synthetic polymer paint, 38.1 × 76.2 × 137.1 cm (15 × 30 × 54 in.). New York, The Museum of Modern Art. Purchase. Digital images © 2006 The Museum of Modern Art.



FIGURE 6B Detail of figure 6A.

that artists will mix materials that are incompatible in this way, the fact that museum collecting is expanding to include such objects as architectural models, where the work itself was originally intended to have a limited lifespan (one-time use), other examples of incompatible materials are bound to arise with increasing frequency.

Donald Judd's *Untitled*

My final example is a Donald Judd sculpture.³ Here again there are some profound aesthetic decisions that must be made when undertaking global restorations like this one, especially when we must substitute different materials from the original.

Judd's untitled piece also known as *5 Green Rectangles*, from 1968 (fig. 7A), had been restored at least once before, in 1979, at which time it had been completely repainted. It was repainted again in 2004, in preparation for MoMA's reopening. In the intervening years, corrosion of the steel and damage to the surface (fig. 7B) had accumulated to such a degree that a complete repainting was deemed necessary. Repainting of Judd works, while not routine, has been done—in some instances with his approval (Temkin 2004). However, because the artist died in 1994 these critical restoration decisions must now be made without his approval.

In this most recent case, the first issue after it was decided the work needed restoration concerned the color to paint the sculpture. Records do not indicate what the original color was, and the 1979 restoration had removed all apparent traces of the original paint. That repainting was a collaboration with one of

the artist's assistants and was done with a color called Sumatra Green, one of the colors used by Volkswagen at that time (Ditzler 2480 Sumatra Green). Sumatra Green is no longer manufactured, but a color chip of the original color was found. The current color and the color chip were each measured, and paints were mixed that matched these spectrophotometrically. The colors were blended into an acrylic-urethane medium (MPC Single-Stage Satin Acrylic Urethane base, Matthews Paint Company), and each was sprayed onto a metal tab and then compared to the original. (Acrylic-urethane was chosen for both its durability and its ability to achieve a sheen and surface similar to other Judd-painted sculptures.)

Curators, in consultation with conservators, decided on the color that matched the current color rather than the one that matched the Sumatra Green as the most appropriate to use to repaint the sculpture. The work was then shipped to a foundry (Carlson and Co.), where each section was sand-blasted and then solvent-cleaned to a near-white condition. Primer (MPC E-Prime 908 White Epoxy, Matthews Paint Company) was applied, followed by a sealer (PCL Polyprimer 901 Gray, Pacific Coast Lacquer). Then the custom-tinted acrylic-urethane was applied.

What was essential to achieve in the restoration was Judd's desire for the sculpture to look like green metal, not *painted* green metal. Thus the paint had to be applied very thinly, yet it also needed to be rich and deep in color. Obviously the choice of vehicle and pigment was critical, and this is just one more example of how we all need to be keenly aware of



FIGURE 7A Donald Judd (American, 1928–1994), *Untitled*, 1968. Painted steel, 122.8 × 305 × 307.6 cm (48% × 120 × 121 in.). New York, The Museum of Modern Art. Mr. and Mrs. Simon Askin Fund. Digital images © 2006 The Museum of Modern Art. Art © Judd Foundation. Licensed by VAGA, New York.

new materials and their properties, often with an eye toward, when necessary, closely replicating obsolete materials.

In an effort to extend the life of the current restoration it was decided to add adjustable bolts as feet for the sculpture. This would both raise the sculpture slightly off the ground to slow down moisture-related corrosion and allow for bringing the piece into apparent plane on uneven surfaces.

Conclusion

Having surveyed a survey, surveyed a complex restoration, and at least alluded to the conservation difficulties we are finding on a range of painted surfaces, what might we conclude about “Modern Paints, Conservation of”? In answer to that question, it seems appropriate to return to the artists’ comments from the 1987 questionnaire. The last question on the form was whether they had any recommendations for the care of their work. David Novros succinctly summed up why conservators do what we do when he wrote, “My work will be preserved by being seen.” Finally, Jules Olitski offered the following: “I have no specific suggestions. I can only hope, in this context, for an abundance of common sense (+ prudence) in our present + future conservators + curators.” So let us add these useful reminders, as well as the wealth of knowledge



FIGURE 7B Detail of figure 7A showing corrosion.

we are accumulating, to the entries under “Modern Paints, Conservation of.”

Notes

- 1 More than thirty detailed responses from artists and artists’ studios were received. The direct quotes used in this paper were garnered from those responses.
- 2 All information relating to the eight paintings discussed in this section is taken directly from the survey (MoMA 1989).
- 3 The project was initiated by Al Albano while he was head of Paintings Conservation at MoMA. The treatment was done by several interns at MoMA: Felicity Campbell, Elizabeth Estabrook, and Hannah Streicher.
- 4 Information relating to works cited in this section and the Conservation of Painted Surfaces section, such as treatment records and artist statements, are found in conservation files and curatorial files for the specific work at MoMA (MoMA n.d.).
- 5 See “The Re-restoration of Donald Judd’s *Untitled*, 1965” (Khandekar et al. 2007), pp. 157–64 in this volume, for a more detailed description of another Judd restoration.

Manufacturers

Cartoon Colour Company, Inc., 9024 Lindblade Street, Culver City, California 90232, USA; www.cartooncolour.com

Grumbacher, Sanford Corp., 2707 Butterfield Road, Oak Brook, IL 60523, USA; www.sanfordcorp.com/sanford/consumer/grumbacher

Ludlow Corporation, Laminating and Coating Division, 1 Minden Road, Homer, LA 71040, USA

Matthews Paint Company, PPG Industries, One PPG Place, Pittsburgh, PA 15272, USA; www.ppg.com

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PART TWO

Paint Formulations and History

“Eternity Is in Love with the Productions of Time”: Joaquim Rodrigo’s Classical Palette in a Vinyl Synthetic Medium

Joana Lia Ferreira, Maria João Melo, Ana Maria Ramos, and María Jesús Ávila

Abstract: *Aqueous emulsion paints were developed in the 1950s and have been used in works of art in Europe and in the United States ever since. During this period, the Portuguese artists’ material company A Favrel Lisbonense developed several series of vinyl aqueous paints: Sabu colors, Geo fluorescent colors, and Vulcano V7 binding medium. Until 1974 in Portugal, all imported materials were extremely expensive, and this was one of the reasons Favrel products were so popular among Portuguese artists. Favrel was initially founded in Porto, and was transferred to Lisbon in 1891 by José Netto Varella. His grandson, António Varella Gomes, introduced large improvements in the company and was responsible for the development of the vinyl aqueous paints. Joaquim Rodrigo (1912–1997) was one of the first Portuguese artists to use this new synthetic medium. From 1961 on, Joaquim Rodrigo always made his own paint using the V7 vinyl emulsion. An outstanding artist, Rodrigo was a key figure contributing to Portuguese modernism. A detailed characterization of the original colors found in a handmade catalogue of the Sabu line, owned by the Varella family, is presented in this paper. Twenty-one colors are displayed in it, and are characterized at the molecular level by in situ X-ray fluorescence (a nondestructive technique) or by Fourier transform infrared microspectroscopy (requiring microsampling). Finally, the results obtained are compared to samples from works of Joaquim Rodrigo.*

Introduction—The History of Favrel

A Favrel Lisbonense¹ is the oldest Portuguese fine arts materials company still in business and it has a long tradition; it was the first to introduce vinyl paints for artistic use in Portugal. The first reference to this company, “Favrel Portuense,”² was in the eighteenth century³ and, according to the family, it pre-

pared paints for the naval industry. Information from written records, such as catalogues, begins with José Netto Varella, who was Favrel’s manager from 1869 to 1891 in Porto. He was also responsible for the company’s branch in Lisbon, to where, in 1891, the business was transferred. Favrel also ran a shop known as Casa Varella.⁴

José Netto went to Paris to learn about the art of gilding and, when he returned, introduced some new techniques to Portugal, such as working with aluminum-based products. After this trip, Favrel advertised the production of gold, silver, platinum, and aluminum leaf and powder (fig. 1). This information can be found in Favrel’s first catalogues, from the early twentieth century, which list a diversity of materials, such as gold and other metal leaves, powders, and liquid paints; metal powders for pyrotechnics; crystal tears and blood for religious sculpture; glass and crystal eyes; brushes and all kinds of artists’ tools; oil paints, watercolors, pastels, pigments, varnishes, and essences; and enamel paints (as early as 1904). Favrel produced its own metal leaves and varnishes and was also the representative in Portugal for many international companies: Reeves & Sons, Lefranc, Winsor & Newton, Paillard, Talens, Pelikan, Nelis, Shemink, Whatman, Nipon, Molin, Colorin, and Pearlin.

From 1925 to 1949, the family business was owned by José Netto Varella’s daughter Arminda Pereira Varella and, after her death, her sister Maria Pereira Varella Gomes. They maintained the company but did not introduce significant changes. After about 1935 the business was managed by António Varella Gomes, Maria P. Varella Gomes’s son.

In a 1939 catalogue, a few new materials produced by Favrel were introduced—paint, fixative, and white glue, as well as some kind of powder glue named Vulcano—but no reference was made to the materials used in their formulation.



FIGURE 1 Favrel catalogue cover from the early twentieth century; main advertisements include “Gold, Silver, Platinum and Aluminum leaf and powder factory. Materials and Tools for Painters, Gilders, *Santeiros* [saint-image makers], Bookbinders, and Pyrotechnists.”

Over a decade later things began to change. In the 1950s Favrel was already advertising a selection of new modern products, such as the “New, Plastic, Modern—Opaque tempera colors” Sabu (fig. 2), described as a “waterproof product,”⁵ Omar synthetic enamels, synthetic dyes, and Radex “atomic age paints,” which were fluorescent colors. António Varela Gomes, who became the owner in 1952, was responsible during the fifties for the company’s development and for the production of modern plastic paints. In particular, he developed a series of vinyl aqueous paints with trade names such as Vulcano V7 white glue, Sabu tempera colors, and Geo fluorescent paints. Varela

Gomes was a cultured person with an eclectic upbringing and a inquisitive mind. He owned an art gallery and was close friends with many Portuguese artists. He was also a persistent man, an “entrepreneur,” who was able to run a successful business in a time when this was very difficult in Portugal (Callapez 2000), as António Oliveira Salazar (Portugal’s dictator from 1932 to 1968 and president of the Minister’s Council) did not approve of industry. Varela Gomes died in 1970, but the business continues to be managed by his family today.⁶ Sabu paints and Vulcano V7 glue became Favrel’s most popular materials.⁷ The development of these modern artists’ paints was especially important during the 1960s and the 1970s, when imports were restricted in Portugal. The development of local products meant that new materials were made accessible to Portuguese artists at acceptable prices.⁸ Their availability and price were the key reasons Portuguese artists⁹ used Favrel vinyl paints or the Vulcano V7 glue to prepare their own paint during this period.

Favrel Emulsions

To our knowledge, Favrel usually used two different polymer brands for the Vulcano V7 glue and the Sabu line (see fig. 2). After 1954, Synres Portugal,¹⁰ a chemical company in Portugal, produced a polyvinyl acetate (PVA) emulsion, Synresil LM15, which was composed of PVA, 2,2-ethylhexyl phthalate as plasticizer, and a cellulose ether as emulsifier.¹¹ This company was



FIGURE 2 Inside of a Sabu catalogue from the 1960s, where the twenty-one Sabu colors are hand painted in cardboard triangles.

one of Favrel’s suppliers;¹² therefore, it is possible that António Varela Gomes prepared the first emulsions in the fifties using a Synres vinyl emulsion to make V7 white glue. Furthermore, according to the company’s formulation notebooks,¹³ it appears that between 1954 and 1987 the polymer used in the Vulcano V7 (white glue) formulation was Synresil LM15.¹⁴

On the other hand, in the Sabu line (PVA-based aqueous paint), the binding medium was Vinamul.¹⁵ There is a reference in a 1978 notebook to Vinamul as the binder used, and a 1985 notebook refers to Vinamul 6975, vinyl acetate–vinyl versatate copolymer. Nowadays, the polymer used is a vinyl acetate–vinyl chloride–ethylene terpolymer. The films formed with this terpolymer are considered to be more resistant to hydrolysis than PVA homopolymer and copolymer dispersions, and they also have a higher mechanical strength (Stoye and Freitag 1991). Furthermore, at least since 1978, the pigments have been first encapsulated in a cellulose ether and only afterward mixed with the vinyl emulsion.

Geo is another aqueous paint formulation by Favrel, for fluorescent colors, and it was first made as a casein tempera. However, its formulation changed and the binding medium became the same as that used for Sabu.

Finally, since the early 1990s Favrel has also produced an acrylic series. In these paints the binder is a copolymer p(EA-MMA) produced by Marl Polymer Latex and distributed in Portugal by Sarcol. According to the literature, p(EA-MMA) is also the acrylic polymer used in Grumbacher (Learner 2004) and Liquitex (Langley and Burnstock 1999) paints from the early 1990s. An acrylic varnish is also available, in which a blend of p(nBMA) and p(MMA) is used.¹⁶

Joaquim Rodrigo and V7

One of the most important Portuguese modern artists to use Vulcano V7 to produce his own paints was Joaquim Rodrigo (1912–1997). Rodrigo was an agronomist who worked at the city hall in Lisbon and was one of those responsible for the construction of Monsanto Park, an important park still known as the city’s “lungs.” In 1950, when he was 38 years old, Rodrigo started to paint after a journey to Italy and Paris. There he had had the opportunity to view the work of Renaissance masters, impressionists, and modernists, particularly Picasso and Mondrian (Rodrigo 1982; Lapa 2000).

Following a foray into geometric abstraction, Rodrigo entered the Portuguese art scene in 1961 with a collection of new figurative works—a new paradigm that turned him into a central figure in Portuguese visual art. His strong bent toward



FIGURE 3 Joaquim Rodrigo (Portuguese, 1912–1997), *M.L.*, 1961. Vinyl on plywood, 73 × 100 cm (28¾ × 39¾ in.). Private collection, deposited at the National Museum of Contemporary Art (MNAC—Museu do Chiado). Photo: José Pessoa, Divisão de Documentação Fotográfica—Instituto Português de Museus. Reproduced by permission of Maria Henriqueta Miranda Rodrigo.

storytelling led Rodrigo to use the paintings as a “diary” in which he recounted episodes of the Portuguese political scene and the colonial war that troubled him, under titles encoded in enigmatic initials in order to escape censorship. Formally, this work establishes a unique synthesis of the primitive paintings from Lunda (a region of Angola),¹⁷ the orthogonal matrix that structures the paintings of Joaquim Torres-García,¹⁸ and the austere colors shared by both of these influences (Lapa and Ávila 1999; Ávila 2003). The first work chosen as a case study belongs to this period: *M.L.* (*Morte de Lumumba/Death of Lumumba*), shown in figure 3.

Later, from 1969 onward, Rodrigo theorized and put into practice a “scientific and universal” pictorial system that he called “*pintura certa*” (correct painting).¹⁹ The system involves formal, chromatic, and compositional construction of works. Minute perceptions of banal events in his travels led to a narrative based on the distribution of graphically synthetic signs, isolated and mapped within the space of the image. Subject to the rigor of the orthogonal system and to a precise chromatic configuration, the signs function as an index to the movement (intensifying the movement suggested by the title) and inscribe a temporal value (França 1984; Lapa and Ávila 1999). The painting *Port-Ligat—Granada* (1980) is an example from this period (fig. 4).



FIGURE 4 Joaquim Rodrigo (Portuguese, 1912–1997), *Port-Ligat—Granada*, 1980. Vinyl on plywood, 89 × 130 cm (35 × 51 in.). Private collection, deposited at the National Museum of Contemporary Art (MNAC—Museu do Chiado). Photo: José Pessoa, Divisão de Documentação Fotográfica—Instituto Português de Museu. Reproduced by permission of Maria Henriqueta Miranda Rodrigo.

For his correct painting Rodrigo would use only the four colors that he considered to be used in the “eternal paintings”: “prehistoric painting, some Egyptian painting, Chinese and Japanese, most of the Greek painting, Etruscan, pre-Columbian, Romanic Catalan, aboriginal African, Australian, and Amazonian” (Rodrigo 1982). He used two colors, red and yellow ochres, and two limits, titanium white and a suitable black. As he stated, “I prefer to use as white—the titanium dioxide (as there isn’t a more convenient natural white), as yellow—the yellow ochre or earth (the most hydrated iron oxide), as red—the red ochre or earth (the least hydrated iron oxide), and as black—the iron oxide (dehydrated) or the vine black (as there is not a more convenient natural black)” (Rodrigo 1982). Other reasons given by Rodrigo for his pigment choices were that these were the most natural and ubiquitous ones, with better hiding power and durability, and also that they were economical. Moreover, he considered the earth ochre colors to be “fertile” colors.

The four colors (red ochre, yellow ochre, black, and white) used by Rodrigo were prepared with white glue (Vulcano V7, Favrel’s PVA emulsion glue). The PVA emulsion was first diluted in water; then the water was thoroughly mixed with the emulsion, using both hands, until a certain viscosity—“measured” by feel—was obtained (fig. 5A). The emulsion thus prepared was conserved in a bottle and used to prepare the paints by mixing in the pigment with the aid of a brush (fig. 5B). The paints

FIGURE 5 (A) Vulcano V7 PVA emulsion mixed with water; (B) paint prepared with V7 and red ochre (both prepared by Sofia Agrela).



A



B

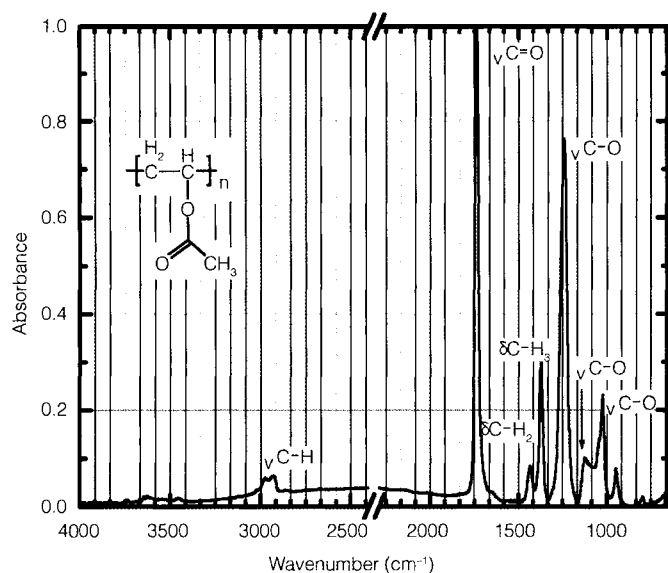


FIGURE 6 FTIR spectra of polyvinyl acetate homopolymer from Sigma Aldrich (MW 83000), obtained with a diamond compression cell, in a Continuum-Nexus from Nicolet microFTIR.

obtained were allowed to rest overnight. This allowed some of the water to be removed before the paint was used, if necessary, since it would separate out. Rodrigo usually made his colors with a rather high concentration of PVA, which accounts for their final appearance, that of shining velvet.²⁰

Case Studies

Sabu Hand-Painted Catalogue

Until the 1970s, Favrel produced hand-painted catalogues for its colors, like the one shown in figure 2. It is a 16.3 × 20.1 cm piece of cellulose cardboard, with twenty-one colors applied on 2.7 cm equilateral cardboard triangles. We were able to study one of these catalogues made with the original paints from the Sabu line, which used a PVA emulsion as the binding medium.

Sabu colors were analyzed by means of Fourier transform infrared microspectroscopy (microFTIR) and X-ray microfluorescence (microXRF). From the infrared spectra, it was possible to obtain information concerning the pigments used, as well as about the binder and filler. As a reference material, a PVA homopolymer from Sigma-Aldrich (MW 83000) was also analyzed (fig. 6). With FTIR it was possible to conclude that, in all the samples, PVA was used as binder and calcium carbonate as extender (fig. 7). The PVA polymer is clearly identified by the

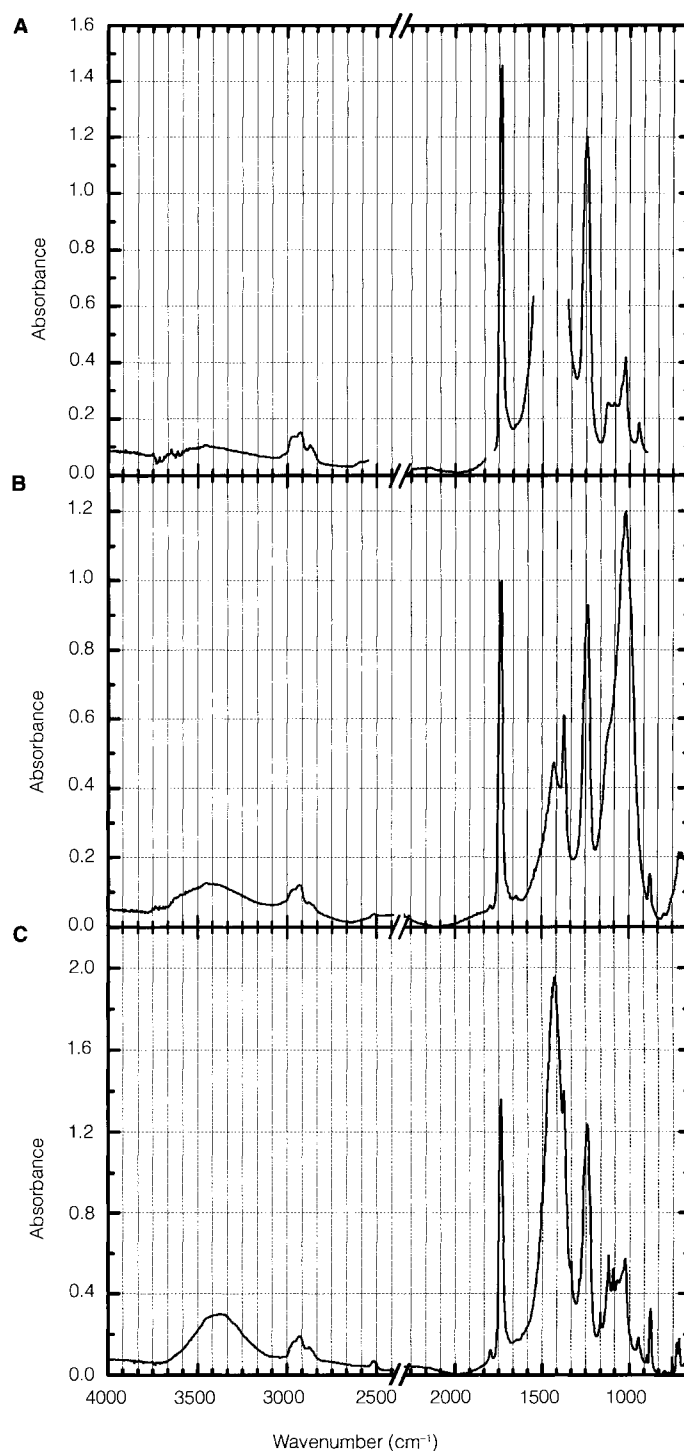


FIGURE 7 FTIR spectra of Sabu microsamples, obtained with a diamond compression cell: (A) Burnt Sienna, where the PVA fingerprint is clearly displayed (the intense absorption peak due to the calcium carbonate was blanked, as it was out of scale); (B) French Ultramarine, absorptions due to the binder (PVA), extender (calcium carbonate), and pigment (ultramarine blue); (C) Prussian Blue, absorptions due to the binder (PVA), extender (calcium carbonate), and pigment (phthalocyanine).

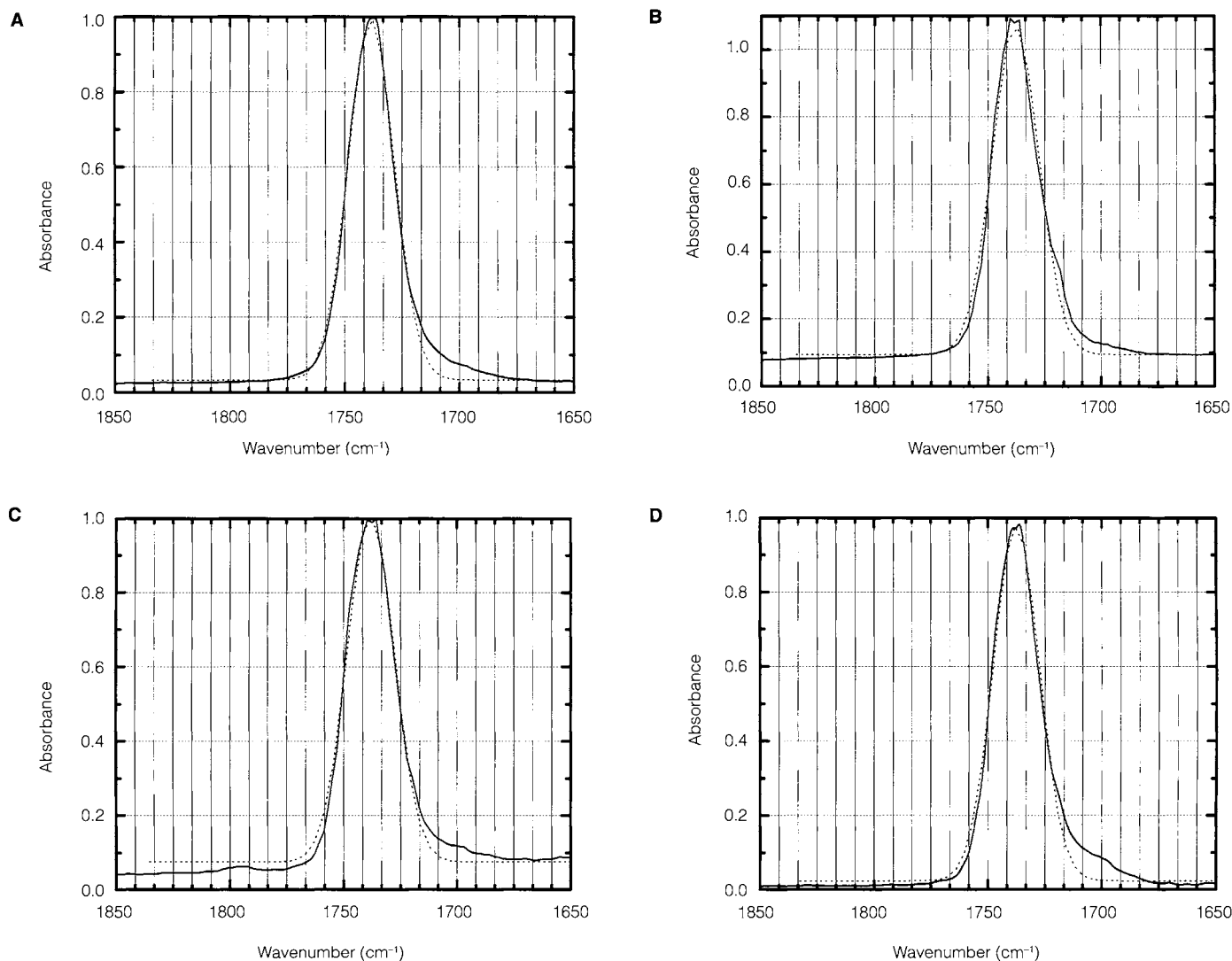


FIGURE 8 Fitting with a Gaussian function of the C=O stretching absorption for (A) polyvinyl acetate from Sigma-Aldrich with values of peak center $\mu = 1738.44$, full width at half maximum $\sigma = 19.98$, and correlation coefficient $\rho = 0.992$; (B) Vulcano V7 PVA emulsion with values of $\mu = 1737.80$, $\sigma = 20.57$, and $\rho = 0.991$; (C) Sabu Ultramarine Blue with values of $\mu = 1738.08$, $\sigma = 20.68$, and $\rho = 0.990$; (D) polymer extracted from Joaquim Rodrigo's last white paint with values of $\mu = 1737.53$, $\sigma = 20.23$, and $\rho = 0.987$.

two strong absorption peaks assigned to the carbonyl stretching at about 1740 cm^{-1} and the C–O stretching at circa 1240 cm^{-1} , with an intensity ratio $\text{C=O}^{1740}/\text{C-O}^{1243}$ of 0.72 (Melo et al.

2006; Chicago Society for Paint Technology 1969). This ratio, together with the CH stretching absorption, is important for distinguishing among homo-, co-, and ter-PVA polymers (see the Appendix section of this paper). The presence of calcium carbonate can be easily ascribed to the broad CO_3^{2-} stretching absorption centered at about 1430 cm^{-1} , together with the 877 cm^{-1} absorption due to O–C–O bending.

No broadening of the carbonyl band was observed in any of the samples (fig. 8), which can be seen as an indication of the molecular degradation of the vinyl polymer (see Appendix). Moreover, in the samples that allowed a clean window for the O–H stretching, no relevant absorptions were present that could be assigned to the formation of polyvinyl

alcohol (PVAL) or hydroperoxide groups. On the other hand, it was not possible to measure the ratio $C=O^{1740}/C-O^{1243}$, due to the strong overlap of the carbonate absorption.

It was also observed from the FTIR and micro XRF data that the color names of the paint often corresponded not to the pigments used but to their shades. All of the blue colors, with the exception of Ultramarine, were found to be made with pigments that differed from their names: Cobalt Blue was a mixture of ultramarine and white, Prussian Blue was a phthalocyanine, and Turquoise was probably a manganese blue.

The molecular characterization obtained for the colors in the Sabu catalogue was further compared with recipes from a 1978 notebook in the Favrel archives belonging to the family. This confirmed that the name of the paint was not always related to the name of the pigment(s) used. Nonetheless, all pigments used in the paint formulations are among the best colors available, with regard to stability and chroma.

Joaquim Rodrigo’s Vinyl Paintings

Microsamples from *M.L.* (1961) and *Port-Ligat—Granada* (1980), which are held at the National Museum of Modern Art,²¹ and from a white paint, the last made by the artist in the 1990s, were studied.

In all samples, the binding medium was proven to be PVA by means of micro-FTIR analysis (fig. 9). Moreover, it was also possible to calculate the ratio $C=O^{1743}/C-O^{1240}$, $C=O^{1740}/CH_3^{1374}$, and $C=O^{1743}/C-H^{2968, 2935}$; therefore, a first characterization of the molecular-level evolution of the PVA polymer was achieved (see the Appendix to this paper).

The white colors were the first to be analyzed, because of the expected higher degree of photo-oxidation in the presence of TiO_2 pigment, a well-known effective photocatalyst (Wu, Li, and Chu 2003). The PVA from the final white was carefully extracted with acetone, to avoid the interference of the TiO_2 pigment, specifically in the quality of the FTIR spectra baseline. The spectra of the extract is represented in figure 9A, and it is constituted by pure PVA homopolymer (Melo et al. 2006), with $C=O^{1740}/C-O^{1243} = 0.74$, $C=O^{1743}/CH_3^{1374} = 0.31$, and $C=O^{1743}/C-H^{2968, 2935} = 0.10$ and 0.11 . This compares well, within the limits of experimental error, with an Aldrich PVA homopolymer, $C=O^{1743}/C-O^{1240} = 0.76$, $C=O^{1740}/CH_3^{1374} = 0.30$, and $C=O^{1743}/C-H^{2968, 2935} = 0.06$, as shown in table 1. It is possible to reach the same conclusions from the spectra obtained for the microsamples analyzed from *Port-Ligat—Granada* (1980) and *M.L.* (1961) (also shown in table 1), even though they do not display the same spectral quality and purity.

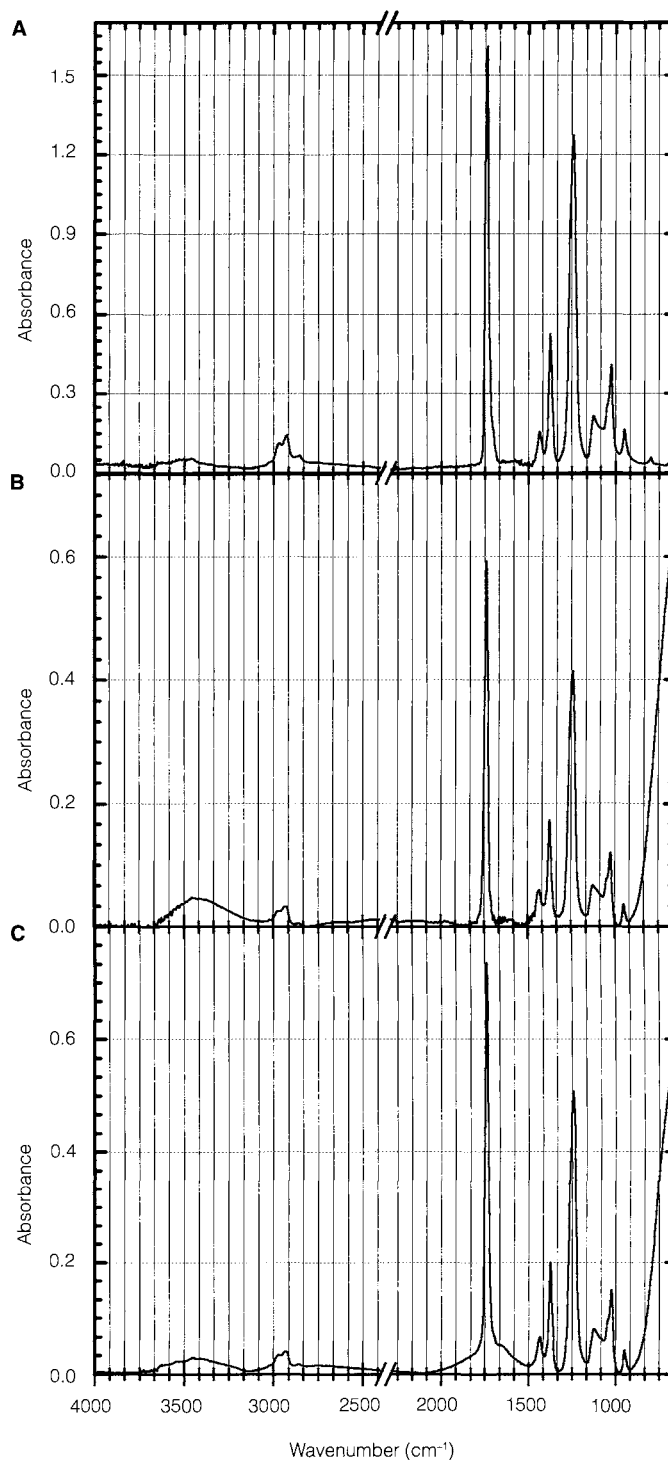


FIGURE 9 FTIR spectra of Joaquim Rodrigo’s white micro-samples, obtained with a diamond compression cell for (A) extract of the last white paint left by the artist in his studio; (B) *Port-Ligat—Granada*, 1980; (C) *M.L.*, 1961.

Table 1 Relative intensities of selected FTIR spectra bands of Joaquim Rodrigo's paints from 1961, 1980, and the 1990s and of a PVA homopolymer from Sigma-Aldrich.

	$\nu(\text{C-H}) \text{ CH}_3$ 2968 cm^{-1}	$\nu(\text{C-H}) \text{ CH}_2$ 2935 cm^{-1}	$\delta(\text{C-H}) \text{ CH}_3$ 1374 cm^{-1}	$\nu(\text{C=O})$ 1740 cm^{-1}	$\nu(\text{C-O})$ 1243 cm^{-1}
Final white (ca. 1990)	0.10	0.11	0.31	1.00	0.74
Port-Ligat—Granada (1980)	0.07	0.09	0.30	1.00	0.73
M.L. (1961)	0.07	0.07	0.41	1.00	0.71
Sigma-Aldrich PVA	0.06	0.06	0.30	1.00	0.76

The results indicate that no relevant hydrolytic degradation is taking place in the PVA from Rodrigo's works, and consequently there is no PVAL formation or acetic acid release, even in the presence of the efficient photocatalyst TiO_2 .

Conclusions

It was possible to conclude that a PVA binder was used both in the Sabu handmade catalogue and in Joaquim Rodrigo's paintings. Furthermore, it could be concluded that in Rodrigo's paints, the PVA was a homopolymer, based on the intensity ratios between $\text{C=O}^{1740}/\text{C-O}^{1243}$ and $\text{C=O}^{1740}/\text{C-H}^{2968, 2935}$.

After analysis of samples of Favrel vinyl emulsions taken from a catalogue from the sixties, it was also concluded that only the more stable colorants were chosen for the Sabu line, and that in the PVA used as binder, no relevant changes at the molecular level were observed. Moreover, the analyses of three samples of vinyl paints prepared by Rodrigo by mixing a white glue, probably Vulcano V7, with titanium dioxide, indicated that no relevant molecular changes occurred in the PVA polymer. In addition, all works by Rodrigo are in excellent condition with regard to paint cohesion and its adhesion to the support.

Therefore, in considering that no hydrolytic degradation is observed in naturally aged samples from Rodrigo's paintings and the Sabu catalogue, it is possible to conclude that these vinyl paints are well preserved.

At this point, further studies are required to confirm the good stability displayed by these vinyl paints, particularly to obtain the molecular-weight distribution of the PVA polymer and to compare the results with accelerated aging studies.

Acknowledgments

J. L. Ferreira gratefully thanks the Portuguese Science and Technology Foundation (FCT-MCTES) for her PhD grant (SFRH/BD/18109/2004). M. J. Melo and J. L. Ferreira would like to thank Sofia Agrela for her kindness and vital assistance in the study of the materials and techniques used by Joaquim Rodrigo. We would also like to thank Ricardo Caiado, Favrel's manager from 2002 to January 2006, for his collaboration and kind assistance. Finally, we wish to acknowledge João and Mário Varela Gomes for their generosity in giving access to all the information and materials used in this work. A. M. Ramos and J. L. Ferreira additionally thank Raúl Morgado Costa for his extensive knowledge and the information he provided on the Portuguese polymer industry.

Appendix

In PVA degradation, besides the photo-oxidative degradation mechanisms present in polyolefin matrix (de la Rie 1992; McNeill 1992; Lemaire et al. 1996), acetate hydrolysis can also be present. The photo-oxidative mechanism evolves through a series of reactive intermediates and radicals, which is responsible for the chain scission and cross-linking reactions that affect polymer performance. Some of the most frequent intermediates include a wide variety of carbonyl-based functional groups, such as carboxylic acids, peracids, ketones, and lactones (Kopecký 1992; Lemaire et al. 1996; Rabeck 1995; Turro 1991). As a result, their presence can be inferred in a PVA infrared spectrum from the broadening of the carbonyl band, resulting from the appearance of several carbonyl functions besides the original ester one, as well as from the appearance of hydroxide and hydroperoxide absorptions from the O-H stretchings. Moreover, the degree of acetate hydrolysis can be followed through the ratios $\text{C=O}^{1743}/\text{C-O}^{1240}$, $\text{C=O}^{1740}/\text{CH}_3^{1374}$, and $\text{C=O}^{1743}/\text{C-H}^{2968, 2935}$.

A similar procedure is routinely used to assert the cellulose acetate degree of substitution (Heinze and Liebert 2004; Samios, Dart, and Dawkins 1997) or hydrolysis/degradation (Ballany et al. 1998). On the other hand, the broadening of the carbonyl band can be quantified with spectra deconvolution by nonlinear least-square method in a sum of Gaussians, or by simple fitting with a Gaussian equation. The full width at half maximum, together with the statistical fitting parameters, χ^2 , and the correlation coefficient, allows an assessment of whether the carbonyl absorption band has broadened or not.

The possible degradation pathways for PVA, described in literature (Down et al. 1996; McNeill 1992; Rabek 1995), involve the formation of acetic acid and PVAL. This degradation may proceed through a homolytic (bond homolysis with the generation of radicals) or heterolytic (bond heterolysis) mechanism (Bracci and Melo 2003). In both cases, if PVAL is formed at the expense of PVA, it will be possible to follow the evolution of the reaction by FTIR, in particular, the degree of hydrolysis through the growth of the O–H stretching band and the ratios $C=O^{1743}/C-O^{1240}$, $C=O^{1743}/CH_3^{1374}$, and $C=O^{1743}/C-H^{2968, 2935}$ (Melo et al. 2006). In a previous study, carried out to calculate the minimum amount of PVAL formed from PVA degradation, it was concluded that it would be possible to quantify PVAL above 5 to 10 percent conversion (Ferreira, Melo, and Ramos 2006).

Notes

- 1 Although the name of the company is A Favrel Lisbonense, Favrel from Lisbon, throughout the text it will be referred to simply as Favrel. According to official documents, it was registered as a trademark in 1906.
- 2 Favrel from Porto.
- 3 A 1952 catalogue reads, “Favrel Lisbonense was founded in 1891 in Lisbon, and its founder, José Netto Varella, had already worked at his grandparents’ company (Favrel Portuense), dated from 1752.”
- 4 House of Varela. Although José Netto Varella’s name was written with two *ll*s, the spelling of the family name was changed to Varela in the twentieth century, when modern Portuguese came into use. The simplified spelling that was generally introduced eliminated most double consonants, and many families altered their names accordingly.
- 5 “Water mixable, unmixable after drying.”
- 6 After 1970, the family business was owned and managed by Varela Gomes’s daughter and two sons: Maria Helena dos Santos Varela Gomes F. Caiado, Mário Augusto dos Santos Varela Gomes, and João António dos Santos Varela Gomes. In 1985, it was decided to separate the factory and the materials shop, which was then registered under the name of Varela Gomes—Artes Plásticas. From that year until 2002, the factory was managed by Maria Helena’s husband, António Micael Franco Caiado. More recently, from 2002 to January 2006, it was managed by their son, Ricardo Varela F. Caiado, and since then by their daughter, Maria Varela F. Caiado. The shop is still managed by António Varela Gomes’s sons and daughter.
- 7 Information supplied by R. V. F. Caiado, Favrel’s manager from 2002 to January 2006, in an interview in November 2004.
- 8 Under Salazar’s dictatorship (1932–68) and up until 1974, imports were extremely restricted and imported products were very expensive. Imported products became more readily available and affordable in the 1980s.
- 9 These artists include Joaquim Rodrigo (1912–1997), Julião Sarmiento (b. 1948), Eduardo Batarda (b. 1943), and Eduardo Nery (b. 1938).
- 10 Indústria Química Synres Portugal, Lda, a joint venture between Synres (Netherlands) and Sociedade Nacional de Sabões (Portugal). In 1971, Synres was bought by DSM Chemicals (according to the DSM Web site), and Synres Portugal became DSM Portugal. It stopped production in 1989, and in 1991 the company became 100 percent Dutch owned.
- 11 Conversation with Raúl Morgado Costa (a chemical engineer who worked for Synres Portugal from its establishment in 1954) in May 2005.
- 12 Confirmed by Favrel’s written records and R. M. Costa.
- 13 Examined in February 2005 with the manager’s permission.
- 14 Presently, it is a PVA emulsion that was first distributed in Portugal by Sarcol under the name of Imofan, and afterward by Globalcor as Albucol 25 P.
- 15 According to R. M. Costa, there was an industry in Porto named E. Brunner producing aqueous emulsions that used technology from Vinyl Products in the UK (i.e., Vinamul).
- 16 This varnish is also distributed in Portugal by Sarcol.
- 17 In 1961, Rodrigo read José Redinha’s book *Paredes pintadas da lunda* (Lunda’s Painted Walls), which had a decisive influence on the artist’s work (Lapa and Ávila 1999).
- 18 Among Rodrigo’s belongings can be found several references to this Uruguayan artist, namely, newspaper articles. Rodrigo and Torres-García used the same colors (black, white, and red and yellow ochres) and the same orthogonal matrix, which organizes the painted forms. Both artists used abstraction as a way of reducing forms to basic schemes.
- 19 In 1982, Joaquim Rodrigo published his theories in a book called *O complementarismo em pintura: Contribuição para a ciência da arte* (The Complementarism in Painting: Contribution for the Science of Art), and in 1995, *Pintar certo* (Painting Right).

- 20 Information supplied by Sofia Agrela, who helped Joaquim Rodrigo in his studio, in an interview and workshop in April 2005.
- 21 Museu do Chiado—Museu Nacional de Arte Contemporânea (MNAC), Lisbon.

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The Performance and Properties of Artisan Water Mixable Oil Colour Compared with Other Oil-Based Paints by Winsor & Newton

Alun Foster

Abstract: *Technically, water-in-oil or oil-in-water emulsions are nothing new, but applying the concept to a short, buttery oil color is a recent innovation. Artisan Water Mixable Oil (WMO) Colour was developed in the 1990s to provide a traditional oil color that could be diluted with water rather than traditional hydrocarbon solvents. An international increase in allergies and stiffer studio and college health and safety regulations contributed to a change in artists' outlooks, and the need for such a color emerged. There were two main concerns in the development of the paint: first, to ensure a behavior as near as possible to that of a conventional oil color and provide a range of compatible media with similar chemistry; and second, to ensure the paints work well during application (like all other Winsor & Newton colors) and that the finished painting is structurally sound and permanent (notwithstanding the influence of the artist's technique). The collective knowledge and experience of manufacturing and developing oil color for more than 165 years largely contributed to our ability to fulfill both those concerns. However, as always where new materials are being used, we continue to test and study them. During the past three years we have compared Artists' Oil Colour, Winton Oil Colour (student grade), and Griffin Alkyd in the following areas: drying times, gloss levels, hardness of films, water and solvent resistance, adhesion and flexibility, and the release of water from the oil film. The results, along with conclusions and further studies, are discussed.*

Introduction

The modern-day artist thinks in the general terms of oil color, watercolor, and acrylics. From the questions we are asked at Winsor & Newton, the use of water has led artists to relate

Artisan Water Mixable Oil (WMO) paints to watercolor or acrylics, which they are not. They are oil colors that have been modified so that water can be added to them—this has often led to the comment “But oil and water do not mix.”

Many different descriptions are applied to “water paints.” Some may be familiar to the artist; others may not. These terms include *aqueous coatings*, *water-based*, *water-thinned*, *water-reducible*, *water-dispersible*, *water-soluble*, *emulsion*, *latex*, and *powder color*. *Aqueous coatings* and *water-based paints* are clearly terms used for products that contain water. The others may have water added only at the time of application. The use of these terms has caused confusion, especially as some are often used incorrectly. Winsor & Newton decided to describe its Artisan range as water-mixable oil colors because that is what they are: oil colors that do not contain water, but can be mixed with water.

Paints containing oil and water are not new; they have existed since prehistoric times. Egg tempera is an oil-in-water emulsion. Egg tempera mixed with oil color has been in use by artists for well over five hundred years. More recently, drying oils were added to casein paints to improve water resistance. The first U.S. paint patent was issued in 1865 and covered a paint containing milk, resin, and linseed oil. Oils gradually became the major component, and the paints became oil emulsions rather than casein paints. The oils were later replaced by alkyds for more rapid drying. Such paints were used in 1939–40 at both the New York World's Fair and the San Francisco Golden Gate Exposition. Emulsified linseed oil house paints have been marketed since the late 1950s, and only declined with the introduction of synthetic polymer emulsions such as vinyls and acrylics.

Why Develop Artisan?

So-called water-soluble oil colors were first marketed for artists about twenty years ago, and Winsor & Newton evaluated the available modified oils at that time. Since then, the socio-political climate has changed, and artists are more aware of the hazards to themselves and the environment posed by the solvents associated with traditional oil painting. Some artists are allergic to the solvents and are not happy with acrylics. The use of solvents in colleges and universities is tightly controlled by legislation, and in some instances it is banned altogether. When Winsor & Newton began to develop Artisan, it took note of the clear problems with some of the existing products on the market, and these had to be overcome by extensive research into available materials to ensure the optimum performance. Interestingly, the final choice of oil for the range was very similar to one we had tested twenty years ago, but it has now been specially refined for our use.

How Does Artisan WMO Differ from Other “Water Paints”?

There is a misconception that Artisan WMO is soluble in water—it is not. Linseed oil is not soluble in water and never will be. In a water-soluble system, the binder is dissolved in water and the paint remains water sensitive. Once the water evaporates, a continuous film of resin binds the pigment to the substrate. Of the paint offered by Winsor & Newton, Artists’ Water Colours would be the closest match to this category.

Artisan WMO is also not a water-dispersed coating, as there is no water present. Such systems contain water-soluble components to stabilize the suspended binder. An example would be acrylic emulsions, where the water-soluble components remain in the dried film, which is not continuous and remains to a certain extent permeable.

Artisan WMO Colours are, strictly speaking, water-reducible. The color in the tube contains no water—it is added by the artist. Water-reducible paints contain conventional solvent-reducible components, such as linseed oil, but the presence of components that are compatible with both water and oil enable these paints to be thinned with water. Their properties are therefore somewhat intermediate; they behave somewhere between solvent- and water-based paints.

Since Artisan WMO is not a watercolor or an emulsion, it does not tolerate large quantities of water, such as those used in a wash, and it must be thinned carefully and cautiously,

mixing thoroughly after each addition. Excessive amounts of water will cause the color to break up on the palette.

Artisan WMO, like any conventional oil paint, dries by oxidation. This is a slow process, which gives time for volatile components, including water, to evaporate. By controlling the evaporation it is possible to prevent film formation from occurring before the water has evaporated, so that it does not become trapped in the film. It is important to note that the components that aid the water mixability are also volatile, so they do not remain in the film either.

All Artisan WMO Colours have been tested from the tube, with and without adding each of the Artisan WMO media, with and without water, and at different thicknesses. Samples have been painted out on canvas and examined over several years, and no indication has been found that water was trapped in the film. Samples with and without water show no differences in film behavior.

During the development process, colors were tested for adhesion, flexibility, drying, film hardness, and water resistance, as well as application properties such as mixability with water, flow, texture retention, and wetting of the substrate. Water does have a higher surface tension than conventional solvents, and this can make wetting some surfaces more difficult. Acrylic-primed canvases are probably therefore more suitable for Artisan WMO paints than are oil or alkyd primings.

Testing the Colors

Questions have been asked about the durability of Artisan WMO relative to conventional oil colors. Artisan WMO does not have any long-term history, but we have been examining samples up to ten years old, as well as accelerated-age samples, and have compared them to conventional oil colors. In our minds, the pigmentation is not in question, since all have a good record of stability and lightfastness in other oil-based media.

The drying mechanisms of Artisan WMO and conventional oils are theoretically the same. Drying times for both paint types (with a similar pigment) are certainly equivalent, although one potential concern was whether certain chemicals in the WMO formulation remain in the film after drying.

A number of samples applied ten, three, and one year ago on canvas, in impasto, at various brushed-out thicknesses, alone and with water and/or media, have been exposed in a weatherometer for four hundred hours to artificially age the samples (using an Atlas 25WT weatherometer, in accordance

with ASTM D4303). For some tests, oil and alkyd colors were included for comparison.

Fourier Transform Infrared (FTIR) Spectroscopy Analysis

FTIR spectra on dry samples of Artisan WMO paint of various ages were collected on a PerkinElmer FTIR with an attenuated total reflectance (ATR) accessory (64 scans at 4 cm⁻¹ resolution). While interpretation is difficult, no obvious differences were detected between the spectra of Artisan WMO and Winton Oil Colours, when measured at the same times after application. These results appear to suggest that the mechanism by which Artisan WMO dries is indeed similar to that of Winton Oil Colour, and this would indicate that those additives that are present in Artisan WMO but absent in Winton Oil do not appear to alter the drying process.

The absorption in the 3000–3500 cm⁻¹ region (which indicates O–H stretching, and can therefore be used to follow the presence of water) was not any higher than levels seen in regular oil colors, even in samples that had 10 percent water added before application. Although the limits of detection of FTIR in this instance are not fully known, this analysis would suggest that, at the levels tested, there is minimal water trapped in the “dried” paint film and the bulk of the water probably evaporates from the film at an early stage in the curing process (i.e., after a few months). This observation was backed up by Karl Fischer analysis (using a Mettler-Toledo Karl Fischer volumetric titrator).

Drying Times

Drying times for a selection of colors were obtained from Winsor & Newton quality control records (table 1). Paint films of 0.015-inch thickness were applied by palette knife to oil sketching paper and checked for their tack-free state by finger touch. Drying times for each color can vary widely, depend-

ing on temperature, humidity, film application, and method of manufacture. However, it was possible to determine that Artisan WMO, Artists’ Oil, and Winton Oil all have similar drying times, color for color. The similarity of drying times was not unexpected, as the basic chemistry for drying is similar for the three ranges. In contrast, Griffin Alkyd was designed to dry faster.

Gloss

In the short term, the gloss of Artisan WMO colors is comparable to that of conventional oil color. Readings were taken using a Sheen Instruments Microgloss 60 glossmeter. Gloss readings were taken on samples after seven days and fifteen and thirty months (fig. 1).

What is noticeable from the data is that all ranges, with the exception of that of Griffin Alkyd, show an increase in gloss over time. Artisan WMO is initially visibly glossier than any of the other oil color ranges, but in the longer term this difference seems to lessen. Also, it was observed that a significant proportion of the Artisan WMO swatches examined were tacky to the touch, when compared to Winton Oil, Artists’ Oil, and Griffin Alkyd. This property is observed in both freshly applied films and also in two-year-old films. It has been suggested that this could be attributed to surfactants in the film migrating to the surface. We are looking at investigating this issue further.

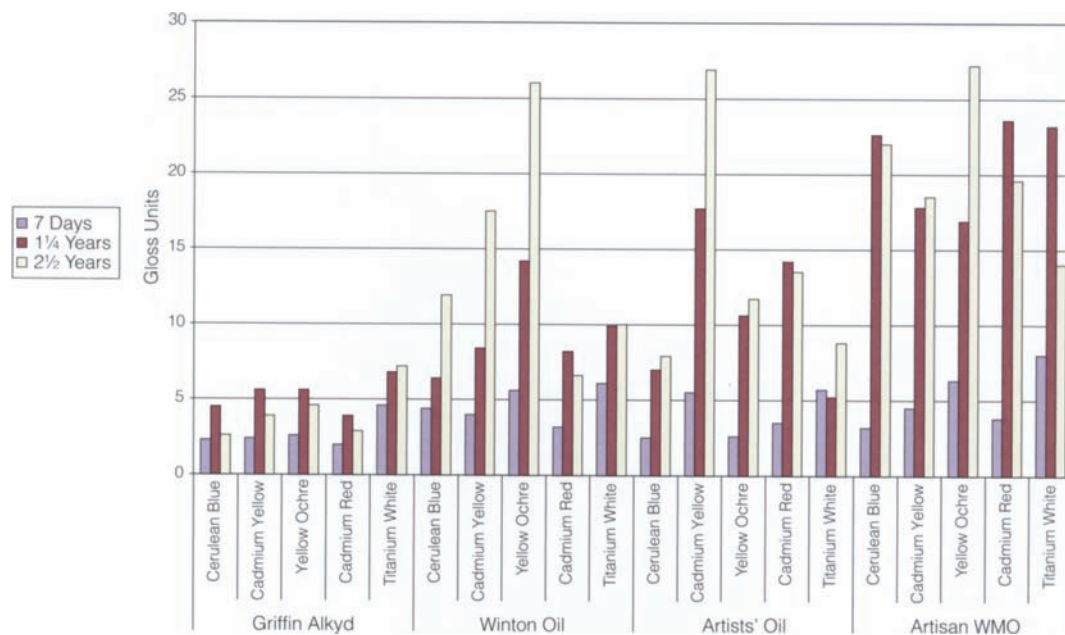
Film Hardness

Titanium white samples of each range were drawn down by hand using a Sheen applicator #S202247 (thickness ≈ 100 μm) onto glass plates. The applications were then left to dry for a month, after which the hardness was measured using a Sheen 703/704 hardness rocker. After testing over several months, no variation in hardness was found, so it was decided that the rocker test was not the most appropriate method to gauge the

Table 1 Drying times of Winsor & Newton oil colors (in days).

Color	Artisan WMO	Artists’ Oil	Winton Oil	Griffin Alkyd
Burnt umber	1–6	1–4	1–6	0.5–1
Cadmium orange hue	2–12	3–11	5–14	0.5–1
Cadmium red dark	4–12	3–11	3–10	0.5–1
Cadmium yellow hue	2–8	3–12	2–8	0.5–1
Cerulean blue	2–8	3–13	2–7	0.5–1
Titanium white	2–12	2–12	2–12	0.5–1

FIGURE 1 Changes in gloss of oil colors with age.



hardness of this material, as the respective films are too soft for it to be effective and accurate. Therefore, a Film Pencil Hardness Test was subsequently carried out, conforming to ASTM D3363.

The coated glass plates were placed on a firm horizontal surface. A pencil was held firmly against the film at a 45-degree angle (pointing away from the operator) and pushed away in a continuous stroke. The process started with the hardest pencil (4H) and continued down the scale of hardness until the pencil no longer cut into or gouged the film. The results are shown in figure 2.

From the results we can see that Artists' Oil produces the hardest film initially, impenetrable with an H-grade pencil. Griffin Alkyd is the next hardest; after four months it is not penetrable with a B-grade pencil. Artisan WMO and Winton Oil have the softest films; Artisan WMO holds up at 3B and the Winton oil film at 2B. Although the Pencil Hardness test is rather more subjective than the Rocker test, it is far better suited to gauging the film hardness of artists' paints.

After two years of curing, we can see a distinct difference between Winton Oil and Artisan WMO with regard to the hardness of each film. The results indicate that between the first and second year of curing, Winton Oil and Griffin Alkyd have reached the maximum film hardness on the test. The films are impenetrable with a 4H pencil. Artists' Oil had reached this level of hardness after one year. Artisan WMO, however, remains at the same level of hardness between the first and

second year. More succinctly, this indicates that Artisan WMO does not continue to harden after the first year of curing.

This finding is supported when observing the color swatch records held by quality control. Some of the Artisan WMO films are physically softer and tackier to the touch than Winton Oil swatches of the same age. This differentiation has been observed in quality control records from as far back as 2003. Of the Artisan WMO Colours observed, it can be noted that Titanium White (PW6)—and indeed colors containing PW6 in the formulation—dried with the least amount of tack and formed harder films. The fact that the differences

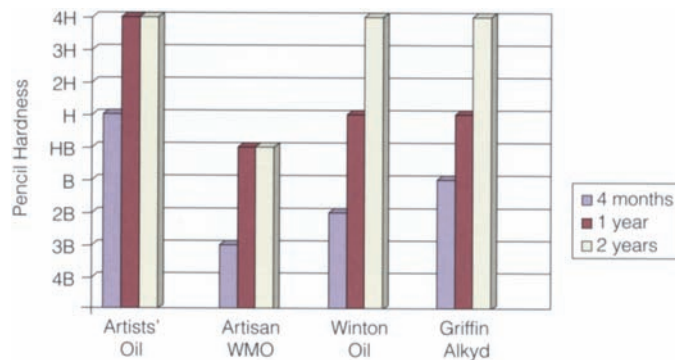


FIGURE 2 Pencil penetration resistance after four months, one year, and two years.

in film hardness revealed by the pencil test were illustrated for samples of titanium white shows that for other colors in the Artisan WMO range the film may actually be even softer.

Water/Solvent Resistance

Double-rub testing (one hundred double rubs, across and back, with lint-free cloth moistened with solvent, and assessed by eye for any color transfer onto the cloth) was carried out on both new and aged titanium white samples of Artisan WMO, Artists' Oil, Griffin Alkyd, and Winton Oil. All ranges show a good level of resistance to water and mineral (white) spirits after two months (fig. 3). When tested with xylene, Artists' Oil and Griffin Alkyd display a good resistance. Artisan WMO and Winton Oil both share a lower (yet comparable) resistance to xylene. However, this should not be too much of an issue, as neither application is considered fully cured after eight weeks. All samples appear to be fully resistant to water, mineral spirits, and xylene after two years. The tests were repeated after eight years, and on films that had been exposed to the ultraviolet equivalent of thirty years, and all samples remained fully resistant to all three solvents.

Adhesion and Flexibility

Adhesion and flexibility are probably two of the most important properties that give an indication of the durability of a film. Poor adhesion is obviously detrimental to a painting, as is flexibility—a rigid paint on a flexible substrate will tend to crack. Unfortunately, both properties are difficult to measure without very expensive equipment, and so only opinions can be given at this stage. Artisan WMO, Winton Oil, Artists' Oil, and Griffin Alkyd all show excellent adhesion to a wide variety of substrates, including primed canvas, glass, steel, and paper.

Samples of Titanium White of each range were painted onto a canvas substrate and treated for four hundred hours in a weatherometer (Atlas 25WT, in accordance with ASTM D4303). The samples were then folded lengthwise and then again along the width. The point where the folds met at the center of the samples was then analyzed under a microscope at $\times 10$ magnification, and images were taken to record and

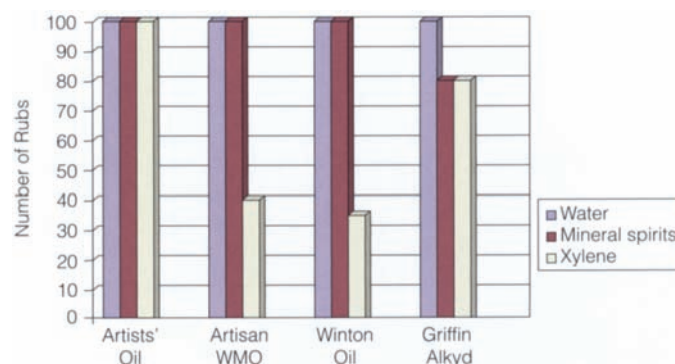


FIGURE 3 Resistance to water/solvents: double-rub testing of samples painted on glass after curing for two months. Tests stopped at 100 rubs.

compare the extent of surface cracking between the samples. Using this method, the film flexibility was found to be similar between the Artisan WMO and Winton Oil ranges.

More recently, a cross-hatch adhesion test (using a Sheen Cross Hatch Cutter, eight blades with 1 mm spacing, BS 3900) was carried out on samples that had been painted out onto primed canvas in early 2004. The test results showed that after two years, the adhesion of the paint to the canvas is very similar between Artisan WMO and Winton Oil Colours.

Conclusion—Future Developments

Various samples of Artisan WMO paint films painted onto Winsor & Newton artist-grade primed canvas are being analyzed by a chemist in the United States to determine what changes occur during the drying process and whether any volatile components, including water, become trapped in the film. Samples range from two weeks to ten years old; some have 10 percent added water and others are their equivalents without any water. This analysis, in combination with our own continued work, will provide us with further evidence to reassure the artist regarding the long-term durability of Winsor & Newton's Artisan WMO range.

From Formulation to Finished Product: Causes and Potential Cures for Conservation Concerns in Acrylic Emulsion Paints

James Hayes, Mark Golden, and Gregory D. Smith

Abstract: *The physical and chemical properties of acrylic emulsion paints are largely determined by choices made at the point of product formulation. The selection of binder material and additives imparts the many celebrated characteristics of this medium: a waterborne coating that dries quickly and remains tough, yet flexible. However, most of these choices bring with them concomitant properties that often are not desirable. Many of these characteristics are a source of concern for artists and conservators alike. Primary among these are the tendency of acrylic emulsion paints to collect surface dirt, their propensity to adhere to adjacent surfaces, and the sensitivity of the medium to water and solvents typically used in art conservation. This paper explores the relationship between formulation choices and the major longevity concerns regarding artwork executed in acrylic emulsion media. New directions in coatings formulations, primarily arising from the industrial coatings sector, are discussed in relation to their potential for improving properties of artists' paints. Finally, intervention at the level of the artist, especially regarding aqueous cleaning, isolation coatings, and picture varnishing, are discussed as a means of mitigating conservation concerns in the future.*

Introduction

Paint formulation is a balancing act (see table 1). While the formulator targets desirable properties like film flexibility and toughness, adjustable drying times, and a variety of sheens and textures in order to deliver a high-value, safe, waterborne paint, there are often concomitant paint properties that are not intended, but arise from the same ingredients, and must be tolerated or perhaps mitigated by the addition of yet further additives. The physical and chemical properties of acrylic

emulsion paints are largely determined by choices made at the point of product formulation. The selection of binder material and additives imparts the many celebrated characteristics of this medium: a waterborne coating that dries quickly and remains tough, yet flexible. However, most of these choices bring with them associated properties that often are undesirable. Many of these characteristics are a source of concern for artists and conservators alike (Jablonski et al. 2003). Primary among these are the tendency of acrylic emulsion paints to collect surface dirt, their propensity to adhere to adjacent surfaces, and the sensitivity of the medium to water and solvents typically used in art conservation.

This paper explores the relationship between formulation choices and the major longevity concerns regarding artwork executed in acrylic emulsion media. New directions in coatings formulation, primarily arising from the industrial coatings sector, are discussed in relation to their potential for improving properties of artists' paints. Finally, intervention at the level of the artist, especially regarding aqueous cleaning, isolation coatings, and picture varnishing, is discussed as a means of mitigating conservation concerns in the future.

Background

Acrylic dispersion paints are a complicated cocktail of additives that, in simplest terms, attempts to place a hydrophobic polymer into a water dispersion (table 2). This necessitates at least a binder and an emulsifier, although one can count as well on the presence of numerous residual polymerization reactants. However, making a paint that can withstand temperature fluctuations, meet market demands for shelf life and safety, and fulfill artists' demands for versatility and perfor-

Table 1 General considerations for formulating a commercially acceptable fine art paint.

Category	Consideration
Shelf life	Viscosity stability
	Freezing and thawing
	Syneresis/separation
	Flocculation
	Spoilage
Environmental, health, and safety	CPSC federal regulation
	Foreign regulation
	Environmental impact
	Studio practices
	Commercial and professional use
	Use by children
	Employee safety
Dry film properties	UV resistance
	Flexibility/hardness
	Adhesion
	Block resistance
	Chemical sensitivity
	Surface clarity
	Color development
	Nonbleeding
	Film formation
	Durability
	Cleaning
Changes over time	
Application properties	Consistent feel
	Ease of mixing
	Control of foam
	Drying rate
	Compatibility with other acrylic artists' paints
Commercial issues	Traditional expectations
	Material costs
	Market size
	Color space
	Single-pigment systems
	Ease of use

Table 2 Components of acrylic paints.

• Acrylic binder:
—Water
—Hydrophobic acrylic polymer
—Emulsifier/surfactant
—Adhesion promoter
—Initiator
—Buffer
• Pigment (possibly surface treated)
• Wetting agent
• Dispersing agent
• Thickener/rheology modifier
• Freeze-thaw stabilizer
• Coalescent
• Biocide
• pH buffer
• Defoamer

mance, both now and in the future, requires numerous other ingredients. The paint formulator can utilize a host of additives to affect drying time, surface finish, rheology, viscosity, texture, and pigment load. Within each class, a multitude of commercial products are available to perform each task.

Acrylic dispersions are commercially available to cover a range of glass transition temperatures (T_g)—the temperature above which the polymer acts as a rubbery and flexible solid and below which the polymer behaves as a glassy solid. For an artist-quality paint, the ideal flexibility arises from the choice of binder with a T_g slightly below room temperature, such that at room temperature the polymer film is just in its rubbery and flexible phase. However, with such a low T_g a slightly warm room will give a soft, tacky surface to these thermoplastic polymer films. When acrylic dispersion paints become overly soft, dust and dirt can readily adhere. Additionally, the paint surface can easily stick to adjacent surfaces (termed blocking in industry literature), and finger pressure, for example, can cause permanent deformation of the paint.

One significant consequence that results from the need for and inclusion of the emulsifier is that these surfactants remain in the film after drying. The tendency of such surfactant emulsifiers to migrate to surfaces and crystallize has been well documented (Digney-Peer et al. 2004; Niu and Urban 1998; Tzitzinou et al. 1999). In the process, the crystallized surfactant reduces the clarity of the film (Whitmore, Colaluca,



FIGURE 1 Surfactant exudates on pours of acrylic dispersion polymer (both pours are two weeks old): (A) soaked in water for 10 minutes, (B) untreated.

and Farrell 1996), imparting cloudiness (fig. 1B, unwashed pour). As these surfactants are hydrophilic, water is a very effective solvent for removing the surfactant exudates (see fig. 1A, washed pour).

The effect of washing away the surfactant exudates is evidenced not only by the improvement in dry film clarity but also by the increased firmness of acrylic paintings. This latter phenomenon is a result of the plasticizing nature of surfactants in acrylic media. The effect of washing away the plasticizing surfactants is shown clearly in figure 2 by the increasing T_g of an acrylic paint, as measured by differential scanning calorimetry (DSC), with increasing immersion time in water (see Appendix A of this paper for the experimental method). An overall change of approximately 5°C is shown within the first hour of immersion.

Improving Key Physical Properties

Acrylic Dispersion Binders

Artists' paint manufacturers are aware of how current formulation options restrict the ability to deliver quality paints with few or no adverse material properties. Research and devel-

opment efforts at Golden Artists Colors (GAC) have been directed toward investigating new additives and binders from the industrial coatings sector that may address such shortcomings. In the sections that follow, we share some of our attempts to address these negative consequences of current choices in acrylic dispersion paint formulations.

The first attempt at GAC to reduce the blocking of acrylic artists' paints was to adjust the hardness of the resulting paint. In 1994, acrylic polymer manufacturers phased out the use of ethyl acrylate-co-methyl methacrylate, replacing it with a more durable butyl acrylate-co-methyl methacrylate polymer. During the reformulation stage, additional changes were made to increase the T_g values of the entire product line, by blending in a higher T_g polymer (also a butyl acrylate-co-methyl methacrylate polymer). As evidenced from measurements utilizing DSC, the T_g of the Hansa Yellow Medium paint before 1994 was 13°C , whereas after the reformulation, the measured T_g was found to be over 15°C (fig. 3). The reformulation also resulted in less surface tack, and thus an improvement in block resistance (see Appendix A for experimental methods).

Over the years GAC has experimented with a range of different acrylic polymers. The most significant attempt at this was a joint project with Dr. Frank Jones and colleagues at Eastern Michigan University (Jones et al. 2005). The proj-

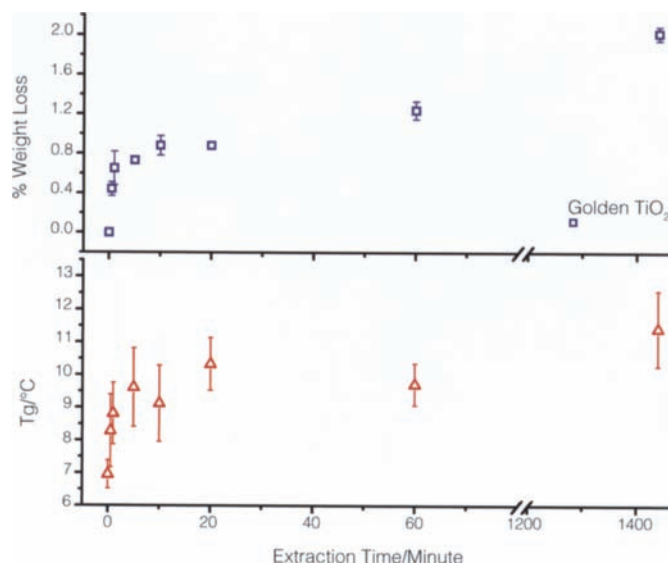


FIGURE 2 Surfactant extraction: Films of Golden Titanium White were soaked for various periods of time in water. Lower portion shows resulting changes in glass transition temperature (T_g). Top portion shows resulting weight loss from the films.

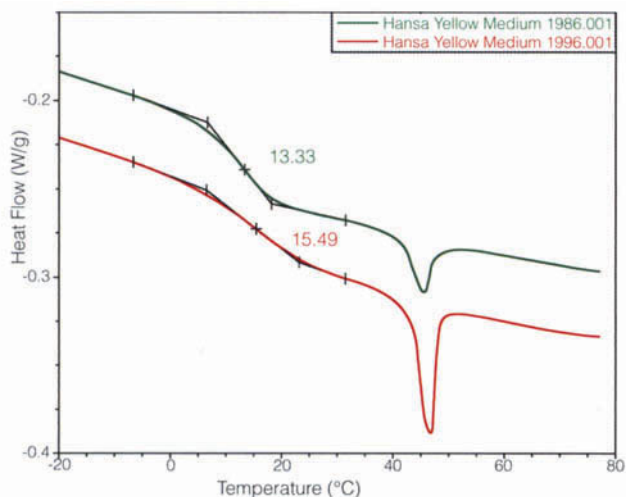


FIGURE 3 Glass transition temperatures, as measured by modulated differential scanning calorimetry, for Golden Hansa Yellow Medium. Upper curve represents a paint made in 1986; lower curve represents a paint made in 1996.

ect, sponsored by the National Science Foundation, investigated a wide range of newly formulated acrylics. The goal was to develop an acrylic dispersion specifically made for artists' materials, as opposed to using acrylic polymers intended for other industries, where ingredients may be chosen more for economy, or unique requirements, than for optimum durability. The main focus of the research was to work with monomers that would minimize the concentration of tertiary hydrogen atoms as well as maximize the steric hindrance of the ester groups, thus theoretically maximizing the resistance to photodegradation and hydrolysis. As a result, *n*-butyl methacrylate and *n*-dodecyl methacrylate, along with variations of surfactant types and loads, redox chasers, and adhesion promoters, were investigated. Polymers in the target T_g range of 5–25°C were synthesized, formulated into paints, and exposed for accelerated aging studies (exterior South Florida and Q-Panel Weatherometer with UV-A lamps). Tests proved that the water resistance was improved, but it was at the significant loss of color acceptance and clarity, and thus was unsuccessful (see Appendix A for experimental methods).

Alternative Binders

Another approach was to evaluate alternative polymer chemistries. While 100 percent acrylic dispersions are widely recognized in the coatings industry as having excellent weathering and ultraviolet resistance, they are not necessarily the best

choice for film toughness and water resistance. GAC evaluated various other polymer chemistries, including polyurethane and silicone dispersions, which are both known for their high degrees of film toughness and water resistance. Furthermore, polymers capable of self-cross-linking are also commonly used in industry to reduce blocking and increase water resistance. Unfortunately, experimental paints formulated with polyurethane and silicone dispersions and with cross-linking polymers saw either minimal improvements in key properties or excessive loss of color acceptance, or they showed an unacceptable yellow appearance in the dry films.

Functional Additives

The use of functional pigments and additives (those that impart paint features aside from lower cost) is yet another mechanism for improving blocking and water resistance in the coatings industry. The use of waxes in the past, both synthetic (polyethylene, polypropylene, polyamide, etc.) and naturally occurring (carnauba), generally resulted in significant yellowness of the film. Polytetrafluoroethylene solids are well known for their low surface energy and high level of slip. While these additives generally increased the slip of the surface, they did not offer substantial improvements in the reduction of blocking and water sensitivity, as expected.

As acrylic paint surfaces seem to readily attract and collect dust and dirt, we investigated whether a static attraction was involved. Paints were formulated with a mica-based pigment having a surface layer of tin oxide doped with antimony, thus making the particles semiconducting. The results indicated that the acrylic paints do not carry any significant static charge, as there were no differences in dust buildup with and without the conductive pigment (see Appendix A for the experimental method).

Because a matte or rougher surface should suffer less from blocking and tack, experiments with matting solids to reduce the films' softness were conducted. The results showed a dramatic reduction in the surface tack and improvement in the block resistance, both desirable traits in an artists' paint. The significant problems with these materials were loss of clarity and yellowing in the most successful matte materials (especially noticeable in gels and mediums). Matte lines of paint also have a reduced level of color brilliance, and suffer from problems of marring and permeability.

Reducing Surfactant Migration

Residual surfactants from the acrylic dispersion do not stay homogeneously dispersed throughout the film after drying.

Instead, they develop areas of higher concentration near each interface—the film-substrate interface as well as the film-air interface. This surfactant migration to the film surface contributes to the water sensitivity of the paint film by increasing the hydrophilic nature of the surface; it also has the effect of lowering the T_g and thus softening the paint surface via hydroplasticization. The industrial coatings industry has developed several means of mitigating surfactant mobility in acrylic paints, and these tactics have also been investigated at GAC for their potential use in artists' paints.

While reducing the level of surfactant may seem like the most straightforward approach, one must remember the balance that must be maintained in paint formulation. One of the prime areas of concern is dispersion stability prior to use. Shelf life stability and freeze-thaw stability are related to the surfactant structure, its effectiveness, and—most importantly—the amount added to the dispersion. From the point of view of the paint manufacturer, a paint that does not last well in the studio, or that congeals after a freeze-thaw cycle, would not be commercially acceptable.

In actuality, the majority of the surfactant present in a system is already in the neat-polymer dispersion that is received from the polymer manufacturer and used as a raw ingredient by the artists' colormen. Without these surfactants, the polymer solids would not remain dispersed and homogeneous. One research focus was to investigate surfactant-free polymers, in which different approaches were taken to stabilize the polymer solids (Buckmann, Overbeek, and Nabuurs 2001). Unfortunately, our attempts to work with such polymers were unsuccessful and resulted in an unexpected increase in water sensitivity, as well as color-acceptance issues. Another potential avenue of investigation is the use of surfactants that can evaporate from a paint film along with the other volatile ingredients. Although such an ingredient would contribute to the volatile organic components (VOCs) for the coating system, thus reducing one of the significant advantages of dispersion paints, the potential payoff in reducing film haze and surface tack could be worthwhile. Only one surfactant on the market claims to be volatile and would thus leave the paint film. Unfortunately, this one was not suitable for an artist-quality paint as it had poor pigment-wetting properties and a very disagreeable odor.

A final strategy that was investigated as a potential means of reducing surfactant migration was the use of cross-linking surfactants (Aramendia et al. 2003; Hellgren, Weissenborn, and Holmberg 1999).¹ Although many research papers discuss the benefits of having a surfactant that reacts with the polymer

to form a permanent bond, and thus becomes immobilized in the dry film, the reality is that few are available at a competitive price. As a result, polymer manufacturers are reluctant to use them, thereby limiting the paint manufacturer's ability even to experiment.

Tools for the Artist

Research into viable formulation options for improving surface tack and reducing surfactant migration in artist-quality acrylic paints to this point has proven disappointing. Without the ability to eliminate the source of these conservation concerns, one can perhaps deal with the problem in a preventive way: by removing the surfactant from the surface of the dried acrylic paint film. The surfactant is responsible for much of the paint's water sensitivity, and its manifestation at the surface, as a tacky film, increases the likelihood of dirt adhering to the paint. Although conservators are still debating the appropriate methods for treating acrylic paintings in the conservation lab, paint manufacturers can provide recommendations to working artists who are seeking a remedial intervention for performance issues—such as varnish adhesion and issues relating to surfactant exudates.

In order to provide “best practice” advice, GAC has explored and tested (Jablonski, Hayes, and Golden 2001) some of the ways that artists can intervene to remove excess surfactant from dried films of acrylic paint. This work has led to a recommendation to artists to lightly wipe the paint surface with a damp, lint-free cloth. This recommendation may not be applicable in all cases, as it can and will lead to removal of original material from the work, including water-miscible components, as well as some degree of color. To mitigate the potential loss of color, the recommendation is to apply an isolation coating of composition similar to that of the acrylic-dispersion colors, without pigment solids. This recommendation has recently been endorsed by other manufacturers of artist acrylics (Liquitex 2003, 22).

Artists will be able to make a valid choice, as long as they are properly informed of the value and risks of their decisions. Conservators will have to come up with their own recommendations for proper cleaning, but it is important for them to be aware that many paintings that they may see in the future will have been constructed according to these recommendations (see Appendix B).

Conclusion

Although discrete instances of failures in acrylic paintings have been reported, overall, these materials have fared extremely well over their fifty-year history and have not, as a group,

suffered from major deterioration or structural problems. However, the conservation of acrylic dispersion paints does present new challenges to conservators. Solvent and water sensitivities are key factors that greatly affect how an acrylic painting can be treated in the future.

For those artists concerned about the longevity of their art, GAC proposes that there are tools and techniques available to preserve their work. Light water washing of the surface of paintings should prove a significant step toward reducing the negative consequences of surfactant migration, and the application of an isolation coat and removable varnish will provide additional protection against physical damage to the paint film, providing that the accompanying change in surface gloss is compatible with the artist's aesthetic.

Paint manufacturers will continue to improve their product line, while working with artists as well as the conservation community to better define the underlying factors that influence the longevity and appearance of this medium. However, based on current knowledge, paint formulation is still a matter of balance: one cannot modify a formulation without understanding the effect on the entire system.

Acknowledgments

The authors would like to warmly thank Dr. Frank Jones, Eastern Michigan University, for providing both his profound collaboration and research to make this presentation possible. We are also grateful for the ongoing encouragement of Dr. Alison Murray, Queen's University, who has continued to provide an endless source of questions that we are only somewhat successful in answering. We would also like to acknowledge the work of our colleague Elizabeth Jablonski for giving us incredible insights into the field of conservation. Finally, we thank Ross Merrill, chief conservator, National Gallery, Washington, D.C., for bringing together, in his own quiet way, an incredible consortium of talent for us to be able to work with and contribute to.

Appendix A: Experimental Methods

Differential Scanning Calorimetry

Glass transition temperatures for two archived dry paint films of Golden Heavy Body Hansa Yellow Medium from 1986 and 1996 were measured using a Q1000 calorimeter (TA Instruments). Sample fragments were scraped from their card support, weighed on a 0.1 μg sensitive balance (Mettler

Toledo UMX2), and sealed in crimped aluminum pans. Films of Golden Heavy Body Titanium White (manufactured in 2002) were used for the immersion tests. These films were soaked in deionized water for various times, removed, and dried for three days prior to measuring weight loss. The dried films were prepared for DSC using a method similar to that described above. All samples were heated at a rate of 10° C/minute from -60° to 80° C under a nitrogen purge. The T_g was calculated using Universal Analysis software (TA Instruments) as the inflection point along the step transition. Both Hansa Yellow samples and the Titanium White paint that was not immersed showed an endothermic peak at approximately 46° C, corresponding to the melting of exuded crystalline surfactant.

Block Resistance

Block resistance was tested following the ASTM D-4946 Standard Method for Blocking Resistance of Architectural Paints, which measures the potential of a paint film to stick to itself under some level of pressure (typically 1000 grams). We have also used the ASTM D-2091 Standard Method for Print Resistance of Lacquers, which includes pressing cheesecloth onto a paint film using a weight and rating the degree of impression that remains after weight and cheesecloth are removed.

Color Acceptance

Color acceptance is a subjective test in which trials are visually compared side by side with standards, as 10-mil drawdowns that had air dried, and rated for key color attributes. These attributes are typically hue, value, chroma, gloss, and opacity, rated in both masstone (10 mil) and undertone (thin scrape of color). Typical substrate is Leneta form 18A, with white and black areas, as well as lacquered and unlacquered areas.

Water Resistance

The water resistance test was carried out on 10-mil drawdowns that had air dried for twenty-four hours. Using filter paper soaked in water, an operator performed ten double rubs with moderate finger pressure and made a visual assessment of any color transfer onto the filter paper.

Dust Accumulation

The dust accumulation test method involved a 10-mil drawdown that was allowed to cure and remain stored in an area of relatively high dust content. Drawdowns were inspected monthly for dust buildup (visual inspection noting degree of dust on surface) for twelve months.

Appendix B: Golden Artists Colors' Guidelines for Increasing Longevity of Acrylic Emulsion Paintings

Washing to Remove Water-Extractable Materials

The following are the guidelines developed by Golden Artists Colors for cleaning acrylic emulsion paintings:

- **Tools and materials.** A relatively soft, low-lint cloth works well (e.g., 50-50 cotton-polyester low-lint T-shirt fabric). It is best to use deionized water to avoid contaminants in the water that could be deposited on the paint film. Tap water is not recommended, as it contains various levels of minerals that can lead to a deposit on the paint film, as well as bacteria that may introduce new concerns of contamination and growth.
- **Drying times.** Although very dependent on the painting support and environmental conditions, the surfactant typically begins moving to the surface immediately, and can take two weeks or more to concentrate at the surface. While the surface can be cleaned at any time and result in a reduction of surfactant, ideally a two to four weeks' drying time is best and allows for more complete removal. It is best to rinse the cloth in fresh water after each area is wiped clean. Repeating the washing process two or three times is also advisable.
- **Paint film thickness and texture.** The degree of washing should be dependent on the stability of the paint surface. A stain painting should *not* be washed, as the film integrity is not sufficient. Moreover, there should be very little surfactant present in such a diluted medium, and thus such an aggressive preventive treatment is not necessary. A painting with very matte colors would also not necessarily need cleaning, as they do not seem to collect surfactant at the surface, perhaps due to an anchoring effect of the matting agents on the mobile surfactants. It is best to avoid washing paintings that have some fragile areas, or at least to take care when washing to avoid these delicate areas. Thick, impasto areas of acrylic should be the most resistant to the cleaning process. Mixed media present challenges; the composition must be factored in to determine if an aqueous washing treatment would be safe.

- **Color rub-up.** Inevitably, some color will be removed by even light washing. Ideally, no color would be extracted with the wet cloth, but the reality is that some colors bleed more than others. However, this should be fairly minimal with all colors. As the surface is "washed" with the damp rag, care must be taken to use minimal pressure. Small amounts of color that soak into the cloth are normally not a concern for artists (such amounts would have no impact on overall appearance of paint film). If there are concerns about one color streaking into another, such as where there is a hard edge between very contrasting colors, constraining the wiping motions to each color passage is recommended.

Applying a Removable Varnish

While lightly washing an acrylic painting increases its surface hardness, the application of an appropriate varnish is an additional step that GAC recommends for better protection against physical damage. A varnish will typically create a surface that is harder than that of the paint, and thus less receptive to the retention of dust and dirt. However, it is recognized that this will also affect the gloss and gloss variation of a paint surface, especially in matte areas.

Our preferred system of varnishing is to apply a chemically reversible varnish over an isolation coat of acrylic dispersion medium. This isolation coat, a permanent, nonremovable film, acts as a physical barrier between the paint surface and the varnish, and thus reduces the potential for solvent to damage the paint layers if there is ever a need to clean the painting by removing the top varnish at a later date. While the processes involved will not be discussed here, extensive information is available on manufacturers' Web sites concerning isolation coatings and removable varnishes suitable for acrylic dispersion paints.²

Notes

- 1 The latter paper is also a good reference concerning the how and why of surfactants in dispersions, their migration, competition with associative thickeners, and so forth.
- 2 Information regarding the removal process for Golden MSA Varnish can be found at www.goldenpaints.com/technicaldata/msavar.php#rem. Information on removing Golden Polymer Varnish can be found at: www.goldenpaints.com/technicaldata/polvar.php#rem.

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Adapting Military Camouflage Paint for Matte Outdoor Sculpture

Abigail Mack, Shelley Sturman, and John A. Escarsega

Abstract: *The National Gallery of Art (NGA) has embarked on a collaborative research project with the U.S. Army Research Laboratory (ARL) to find a more durable matte paint for outdoor sculpture. One matte black paint patented by the U.S. military and nine commercially available matte black paints were compared. Paints chosen for this study were selected from those used for outdoor sculptures by Tony Smith and Alexander Calder; a few promising commercial alternatives; and the military patent camouflage paint. General types consisted of acrylics, acrylic polyurethanes, polyester polyurethanes, alkyds, silicone alkyds, fluoropolymers, and water-dispersible acrylic polyurethanes. These studies compared samples through artificial and real-time weathering in terms of color change, gloss change, and mar resistance. Two decades of the NGA's experience with various matte paints on outdoor sculpture, coupled with test results, revealed the poor durability of the commercial matte paints. In contrast, the military patent paint contains a novel flattening agent that provides a more durable and weather-resistant paint film compared to the typical silica-type flattening agent found in most commercial paints. As a result, the NGA and ARL have adapted the military patent camouflage paint for outdoor sculpture in a range of glosses. One monumental outdoor sculpture at the NGA has been repainted recently with a new formulation of military paint, and a second sculpture is scheduled. This paper will include test results of the matte-black paint comparative study and the latest results of military paints adapted for outdoor sculpture.*

Introduction

The National Gallery of Art (NGA) and the U.S. Army Research Laboratory (ARL) have established a collaborative effort to develop and formulate water-dispersible-type coat-

ings for painted outdoor sculptures that are more durable than ones currently available (Mack, Chang, and Sturman 2002; Escarsega, Mack, and Sturman 2003). This effort focuses on matte black coatings because they have proven to be the most fragile and difficult to maintain. The first part of this paper will identify acceptable parameters for the appearance of painted outdoor sculpture under the NGA's care. The second will elaborate on a comparative study set of commercially available matte paints. Data from real-time and accelerated-aging tests of the study set reinforce the NGA's experience with the durability of matte outdoor coatings. The third part reports on the performance of ARL's patented water-dispersible polyurethane coating, which is widely used in the military (Escarsega and Chesonis 1997). And finally, this paper introduces the development of a series of modified coatings, referred to herein as "matte suite," specially designed for outdoor sculpture. The suite consists of a series of five coatings adapted from the military paint, each with a different matte level; four range from totally flat matte to semigloss and one is glossy. These paints are patterned after those of existing painted outdoor sculptures, including pieces by Alexander Calder, Tony Smith, Louise Nevelson, and Albert Paley. At this time, the NGA has completed the test application of one sculpture with the most matte paint in the series. Work on this project is ongoing and consists of further test paintings of sculptures using the other paints in the series and creating a mechanism to bring the matte suite to the commercial market.

Appearance of Painted Outdoor Sculpture

The conservator's obligation to preserve the artist's surface aesthetic is complicated by the eventual change in the paint in an



FIGURE 1 The painted coating on *Wandering Rocks* by Tony Smith abides by the artist's choice of a dull, semigloss surface. Photo: Abigail Mack, May 2006.

Tony Smith (American, 1912–1980), *Wandering Rocks*, 1967. Painted steel. Washington, D.C., National Gallery of Art. Gift of the Collectors Committee, 1981.53. Image © 2006 Board of Trustees, National Gallery of Art, Washington, D.C. © Tony Smith Estate/Artists Rights Society (ARS), New York.

outdoor setting. For outdoor sculptures that were created by fabricators, painted by professionals, and put in an environment with full understanding of change due to weathering, the original surface is, by design, expendable. However, even while accepting certain loss as inevitable, it is critical that we preserve the artist's intent, that is, the *choice* the artist made about surface appearance regarding gloss, color, and texture (fig. 1).

When weathered coatings fail to convey the appearance the artist intended, repainting becomes necessary; this is an accepted practice within objects conservation. According to the American Institute for Conservation of Historic & Artistic Works (AIC), "The aesthetic requirements of the maker/artist may necessitate compensation practices that sacrifice original material and surface to obtain a specified result" (AIC 1997). Once a treatment involving repainting is deemed necessary and has been approved by the NGA's board of trustees, NGA conservators prepare mock-up coupons (samples) for gloss and color, and then work closely with the artist (or his or her estate) and NGA curators to make the appropriate selection. However, this approach does not necessarily apply to

all painted outdoor sculpture. It is essential that each sculpture be evaluated on its own criteria, according to the artist's wishes and within the AIC's Code of Ethics and Guidelines for Practice (AIC 1994).¹

As noted above, this project developed while trying to solve problems associated with matte coatings on existing outdoor sculptures. By extension, painted outdoor sculptures by Alexander Calder and Tony Smith have become a subfocus of our research. NGA conservators have worked closely with the Calder and Smith estates and have learned that the artist's original choice is the key factor in making any decision. The estates indicated that preserving the artist's intent is more important than preserving the extant, compromised (and often previously repainted) coating. For example, the surface appearance of black-painted Smith sculptures is described by his estate as "dull semi-gloss," a finish that is elusive and difficult to achieve. Conservators and artists sometimes chose a glossier paint than desired in the hope that it would weather to an acceptable surface. This meant that for some time a sculpture would be exhibited with an incorrect surface appearance.

For situations such as this one, our immediate goal became to provide the correct coating initially. We felt that there had to be a better way to conserve painted outdoor sculpture than to accept the wrong coating on a newly treated surface, only to have it look "right" upon degradation. In addition, while a glossy coating may have weathered to an acceptable degree after a few years, it is likely that the paint would have suffered during that time from scratches and other losses. A more durable paint with the correct gloss and color has great

advantages. It provides an accurate surface from the beginning, does not need to be altered over the accepted lifetime of the coating, and reduces the frequency with which the sculpture requires repainting.

NGA Experience

The NGA has more than two decades of experience with a variety of outdoor painted coatings on sculptures. Since the early 1980s, NGA conservators have been challenged to maintain the painted surfaces on outdoor sculpture—with uneven success. With the opening of the Sculpture Garden in 1999, the number of outdoor sculptures at the NGA increased from nine to twenty-four. This includes nine painted outdoor sculptures, four of which have matte black surfaces.

Annual overall cleaning and regular condition examinations provide object conservators the opportunity to monitor changes in condition and deterioration of various paints. Careful light cleaning to remove bird droppings, pollen, insect debris, dirt, and handprints has shown that most matte paint surfaces abrade easily. Because of the low binder content in traditional matte paints, their surfaces readily absorb oils and retain stains from human contact and bird droppings. Mild

detergents are ineffective, and the paints have shown sensitivity to stronger detergents and solvents. Outdoor exposure has resulted in streaks, blanching, chalking, and fading, as degraded coatings slough off unevenly (fig. 2). As a result, sculptures under the NGA's care can appear faded or have disfiguring stains and streaks, even on some paint surfaces less than a year old. In addition, localized compensation for damages is rarely successful, because fresh paint does not match weathered paint and deteriorates at a different rate from the original paint.

Once the condition of the paint dominates the visual impact of the sculpture and interferes with the artist's conception of planes and forms, it is no longer representative of

FIGURE 2 Example of a deteriorated coating on *Moondog* by Tony Smith: (A) after installation in April 1999, (B) in May 2006. Photos: Abigail Mack.

Tony Smith (American, 1912–1980), *Moondog*, 1964/1998–99. Painted aluminum, 521.34 × 468 × 467.36 cm (205¼ × 184¼ × 184 in.). Washington, D.C., National Gallery of Art. Gift of the Morris and Gwendolyn Cafritz Foundation, 1997.137.1. Image © 2006 Board of Trustees, National Gallery of Art, Washington. © Tony Smith Estate/Artists Rights Society (ARS), New York.



A



B

the artist's vision. In the NGA's experience, conservators have observed that the longevity of acceptable surfaces ranges from less than one year to almost six years. In all cases, money and time constraints have necessitated tolerating weathered or damaged coatings until repainting could be arranged. Repainting these monumental or multipart outdoor sculptures is an enormous and expensive undertaking for museum staff, and requires the coordinated efforts of many departments. Deinstallation, transportation expenses and reinstallation for works treated off site, and/or construction of enclosures for in situ treatments can easily cost tens of thousands of dollars (fig. 3).

It is understandable that artists were partial to certain coatings that had a consistent low gloss, an imperceptible texture, and a beautiful surface without a plastic appearance, even though there were concerns about the paints' permanence. Therefore, the NGA continued to use the artist- or estate-approved paints, even though their overall durability did not meet our desired criteria. Following years of discussions with artists and artists' estates, we learned that they were willing to consider alternatives, provided the paint had the same overall appearance and remained faithful to the artist's choice of color and gloss. With their endorsement and the encouragement of our colleagues, we began our testing and experimental phases and pursued the goal of finding a better coating for outdoor painted sculpture.

Evaluation of Different Paint Types

The first step of this project was to evaluate the paint coatings on NGA outdoor sculpture and assess their condition. However, it became clear that many questions could not be answered in this manner. Therefore, in order to gather better, comparative data for evaluation, a study set consisting of nine different coatings was designed for testing. One sample set was for outdoor exposure, another was for accelerated aging, and the third was kept as a control. The paints chosen for this study were related to NGA sculptures and included those recommended by artists' estates as well as other promising alternatives, some of which had been suggested by conservation colleagues. The study was not intended to be comprehensive but was rather a qualitative test to compare the durability of typical matte paints used on outdoor sculpture. Paints evaluated included the general categories of acrylic, acrylic polyurethane, alkyd, silicone alkyds, fluoropolymers, and polyester polyurethanes² (table 1). Various paints were sprayed onto steel and aluminum coupons according to manufacturer guidelines, fixed to a slant board, and placed on the roof of the NGA



FIGURE 3 Installation in November 2004 of *Tom's* by Alexander Calder. The adapted paint's superior resistance to weathering should make this type of major disruption and expense far less frequent. Photo: Abigail Mack. © Calder Foundation.

for four years. The samples were evaluated at regular intervals for gloss retention, color retention, and mar resistance using accepted measuring techniques and instrumentation, as detailed below. Accelerated aging was performed at ARL using a CI65 Xenon Atlas weather chamber.³

The data from the real-time exposure of the prepared coupons mimicked the NGA's experience with actual outdoor painted sculptures in terms of the changes observed during natural weathering. Visible changes in gloss, color, and mar resistance occurred on all samples within three months. After one year, the coatings were completely transformed and bore no resemblance to the original paint surfaces of the controls. Most striking was the combined effect of the changes in gloss and color, resulting in a large visual difference. None of the paints performed to our desired specifications: longevity of

Table 1 Paints selected for study set.

Manufacturer	Product	Product Type
Akzo Nobel Coatings	Grip-Gard Acrylic Urethane Enamel 4ALU 43311 Anodic Black	Acrylic polyurethane (sign finishes)
	Grip-Gard Clear (top coat) Low Gloss Clear VPS-2	Acrylic polyurethane
Benjamin Moore & Co.	IronClad Alkyd Low Lustre Metal & Wood Enamel (163-80 Black)	Alkyd (architectural)
DuPont	Imron 333 40M Flat Black	Acrylic polyurethane (automotive)
	Imron 613P Flat Clear (top coat)	Acrylic polyurethane
Keeler & Long	Megaflon MS UMS2301015 Black 15% gloss	Fluoropolymer (industrial)
Keeler & Long	Poly-Silicone Enamel 0177 Black	Silicone-alkyd (moderate industrial)
Rust-Oleum	Rust-O-Crylic Industrial Enamel Flat Black	Acrylic (exterior grade)
Sherwin-Williams	Sunfire Acrylic Urethane 336-1738 Black + TIF271 Matte Agent	Acrylic polyurethane (automotive)
Tnemec	Endura-Shield Series 75 35GR Black	Acrylic polyurethane (industrial exterior grade)
	Endura-Clear Series 76-763 Satin Finish (top coat)	Acrylic polyurethane
U.S. Paint	Awlgrip G2002 Flat Black	Polyester polyurethane (marine coating system)

gloss, color fidelity, and resistance to abrasion and loss. Owing to their relatively small size, the test coupons aged evenly and did not exhibit streaks from uneven weathering or staining from biological debris and human contact that occurs on outdoor sculpture.

Gloss units (GU) were measured using a handheld BYK Gardner micro-TRI-gloss meter at 60- and 85-degree angles. All of the samples lost gloss after four years' exposure (fig. 4; only the 60-degree measurement is reported here). However, the relative change in gloss number is a better indicator of the observed change in gloss on the coupons.⁴ Those coupons with the highest relative number, in particular the more matte samples, had the greatest visual change in gloss.

Changes in color were measured on a HunterLab XE spectrophotometer using CIELab color space (fig. 5). The graph shows the change in chroma and value represented by delta E 94 over time.⁵ Due to the angle of detection in the spectrophotometer, the samples represent a reading of color only—without the interference of gloss.

Abrasion resistance was measured using a balanced beam scrape abrasion tester with an adapted version of ASTM D5178-98, the standard mar resistance test for organic coatings (ASTM 1998). For this test, a stylus is drawn across the sample, with successive weights applied until the coating is marred.⁶ After three months of exposure, no sample performed to our desired specifications of durability. That is, all of the samples marred during the second testing period without the use of weights—the stylus alone marred the surface.

Formulation Efforts

The development and formulation of new coatings is often motivated by the necessity to improve the coating system's durability and environmental compliance. Our current efforts with water-dispersible hydroxyl functional coatings are aimed toward achieving enhanced performance, complying with environmental regulations, and meeting the aesthetic criteria for the surface appearance of individual outdoor sculptures in

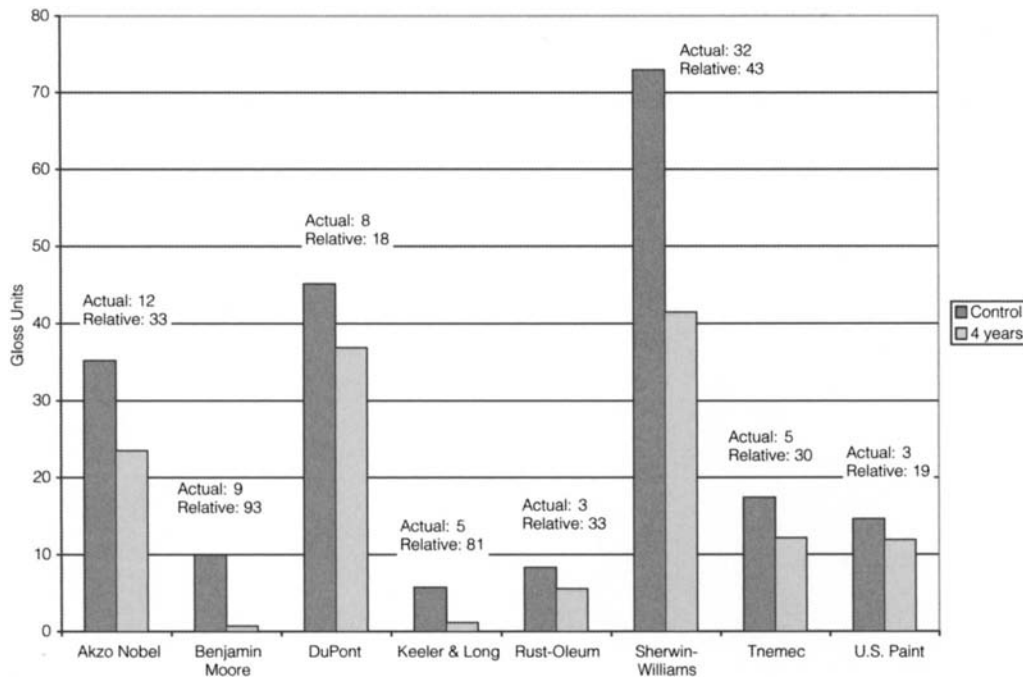


FIGURE 4 Gloss change over four years. Both actual and relative reductions in gloss units are shown.

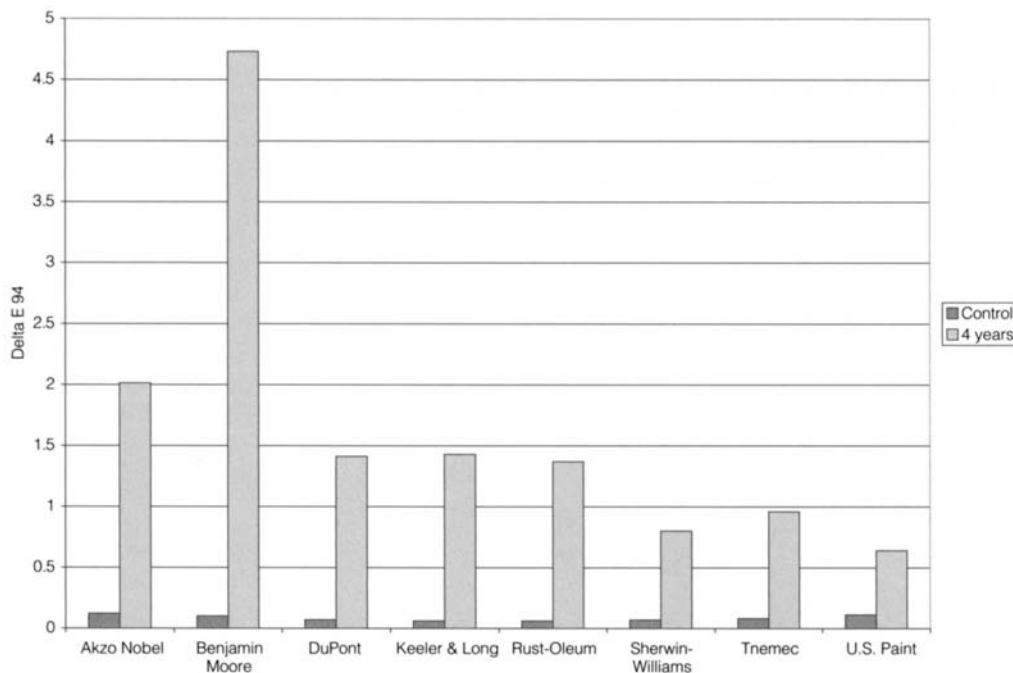


FIGURE 5 Color change over four years.

a very low-gloss composition. Historically, the most expedient approach to getting a lower gloss in a coating is to fill or load the formulation with conventional extenders, such as talc, diatomaceous silica, or other inert fillers. This is a very reasonable path for manipulating gloss in emulsion- and alkyd-type chemistries. Owing to their cost and performance, these

paints are generally not expected to have enhanced durability, yet they may be environmentally benign.

In applications where durability and low life cycle maintenance cost is paramount, alternative pathways to achieve low gloss (0.3 to 15 GU at a 60-degree angle) must be implemented. ARL has eliminated the use of silica-based flattening agents

and is using multifunctional flattening materials in its military coatings to enhance durability and minimize maintenance associated with repainting and cosmetic touch-up (U.S. Department of Defense 2002). The coatings are also implementing multifunctional flattening materials. Our criteria were to select materials similar in composition to our base binder in order to maximize homogeneity, to minimize pigment-to-binder ratios, and to enhance physical parameters. Additionally, in the low-gloss formulations, we also stayed below our critical pigment-to-volume concentration, which also ensured higher performance (Patton 1979, 189; Gray 1987, 359).

Formulations based on these criteria, including selection of easily dispersed pigmentation, were created and manufactured. By varying the formulae, we have been able to use a quantitative approach for making a suite or palette of varying gloss, color (including differences in saturation and hue), and minimal texture. This allows ARL and NGA to evaluate pigments, additives, and binder ratios for future-generation coatings in a more efficient manner. Finally, in an effort to rapidly evaluate materials for UV resistance and associated outdoor elements, formulations are being subjected to an accelerated outdoor exposure protocol implementing Q-Lab's Q-Trac, which uses natural sunlight with mirrors that direct the light to the test specimens for maximum megajoules (MJ) of irradiance (fig. 6). The protocol also employs a periodic water spray to further degrade the coatings. This approach has demonstrated a reliable

methodology to replicate the degradation mechanism seen in long-term outdoor exposure with these particular chemistries (Escarsega and Chesonis 1997), yet without the lengthy delay often required when evaluating high-performance coatings outdoors.⁷ The system also provides confidence in evaluating and selecting new materials that conventional accelerated xenon or QUV chambers may not reliably reproduce or manifest with regard to degradation.

Several black-tinted formulations with varying degrees of multifunctional flattening agents were generated. Highlights of the delta E values for the given formulae are seen in figure 6. Our weather data in megajoules per square meter will assist in quantifying results with future formulations and eventually permit transiting to accelerated-exposure chambers for convenient quality control and validation. Relative to our designated original formula, several of the black formulations show promise.

Matte Suite

As described above, the NGA and ARL, together with Spectrum Coatings, Inc., are developing five coatings specially designed for outdoor sculpture (fig. 7). The first four paints are within the matte range and measure less than 15 GU at 60 degrees; the fifth paint is glossy. (Hereafter, all gloss measurements reported were taken at a 60-degree angle.) The range for the gloss suite reflects to some extent the painted outdoor sculpture for which the NGA is responsible and for which no suitable paints were

FIGURE 6 Delta E average for black formulations after total ultraviolet radiometer (TUVR): 280 MJ/m² Arizona exposure.

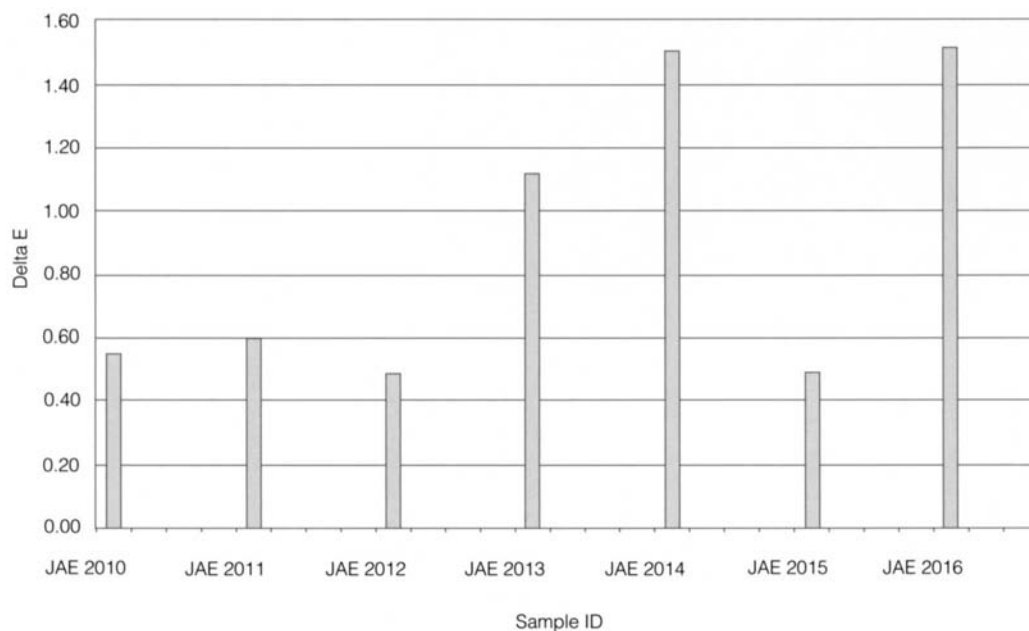




FIGURE 7 Selecting coupons to be included in matte suite.

Photo: Judy Ozone.

available. Our aim was to produce a variety of gloss levels—or more specifically, matte levels.

The first paint in the series is the most matte and measures between 1.5 and 2.5 GU. It was matched to a matte black sample provided by the Calder Foundation for the repainting of *Tom's* (on long-term loan from the foundation). We introduced a minimal increase in gloss for the second paint in the series in order to provide an alternative to the completely flat matte option of the first. It measures between 3 and 4 GU. The third paint in the series was made to duplicate the dull semigloss required by the Tony Smith Estate; it measures between 7 and 8 GU. The fourth paint measures between 15 and 16 GU. It was chosen to provide a paint with the slightest hint of gloss and a viable alternative to standard semigloss paints. The last paint in the series is a glossy paint; it measures 87–88 GU.

Visual appearance was the key selection factor for each paint in the matte suite. A gloss meter was used as a tool to record choices and provide a means to assure quality control. As mentioned previously, conservators, curators, and artists' estates were critical to the development of the matte suite. Of particular interest is the route to creating the dull semigloss paint (number three in the series) stipulated by the Smith Estate. In preparation for repainting *The Snake Is Out* (fig. 8), four different samples with varying formulae for gloss were prepared and circulated to the Smith Estate, the fabricators, the NGA curator, and two NGA conservators. All of the parties involved independently chose the same sample from the four possible choices.

Conclusion

This project has created a forum not only among chemists, paint manufacturers, and conservators but also with artists, curators, and those who represent artists' estates. It has been enlightening to learn how the special properties of an adapted military paint are tied to the subtleties in surface aesthetics that the NGA is obligated to maintain on outdoor sculpture. The NGA experience coupled with test results from the recent study set give a realistic view of the durability of some commercially available matte paints. Our current focus is to complete a matte suite for black-painted outdoor sculpture by adapting the chemistry of the military camouflage paint. At this time, a usable product set is close to completion. Future work includes seeking patent protection for the product and initiating a similar testing protocol on a matte series of colored paints, including red, orange, yellow, and blue. Additionally and most importantly, we intend to identify a path to bring the matte suite to the commercial market.



FIGURE 8 East building of National Gallery of Art with *The Snake Is Out* by Tony Smith in the foreground. Photo: Abigail Mack.

Tony Smith (American, 1912–1980), *The Snake Is Out*, model 1962, fabricated 1992. Painted steel, 457.2 × 706.1 × 574 cm (180 × 278 × 226 in.). Washington, D.C., National Gallery of Art. Gift of the Tony Smith Estate and Patrons' Permanent Fund, 1992.21.1. © 2006 Board of Trustees, National Gallery of Art, Washington, D.C. © Tony Smith Estate/Artists Rights Society (ARS), New York.

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Throughout this paper certain commercial materials are cited in order to specify accurately the particular experimental procedures that have been employed. Such identification does not imply recommendation or endorsement by the authors, nor does it imply that the products identified are necessarily the best available. Any opinions, findings, and conclusions or recommendations expressed in this research are those of the authors and do not necessarily reflect the views of the United States Department of Interior.

Notes

- 1 This statement should not be construed as an endorsement by the NGA for repainting all outdoor sculpture. Each case must be evaluated on its own merits and approval sought from the appropriate authorities only after careful consideration of all options.
- 2 As mentioned, this study was not a survey of all paint types or brands within types. In compliance with rulings on volatile organic compounds (VOCs), the use and availability of polyester polyurethanes is much decreased, especially in California, and therefore only one polyester polyurethane was tested. Replicate coupons were tested in each study set.
- 3 The weather chamber had borosilicate inner and outer filters with 102-minute light cycles and 18-minute front deionized water spray cycles (Escarsega, Mack, and Sturman 2003).
- 4 The equation for calculating the relative number of change in gloss is as follows:

(actual value GU-final value GU/original value gloss unit \times 100 = relative value
- 5 Calculating CIE delta E 94 includes weighted functions that account for a visual uniformity found in the CIE delta E with respect to measured differences between colors (Berns 2000, 120-21; de la Rie et al. 2000, 53).
- 6 This test incorporates the use of a BYK Gardner balanced beam scrape abrasion and mar tester. This test was modified to include two repeats rather than seven for each different weight load.

- 7 Degradation mechanisms in conventional accelerated weathering chambers may differ from natural outdoor exposure, or weathering may not be initiated, thus providing misleading data for formulation changes.

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“Cover the Earth”: A History of the Manufacture of Household Gloss Paints in Britain and the United States from the 1920s to the 1950s

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Abstract: *Ever since household gloss paints became widely available in the first decades of the twentieth century, artists worldwide have used them in place of those intended for artistic purposes. Such paints have been found in the work of Pablo Picasso, Willem de Kooning, Gillian Ayres, Jackson Pollock, Ben Nicholson, and Alfred Wallis—to name but a few. Gloss paints have a number of physical characteristics that appeal to artists: they can be poured, a smooth glossy surface can be achieved, and they are inexpensive. Furthermore, their status as industrial or commercial materials, rather than artists’, has prompted artists to make sociopolitical commentary through their use. Although museums and galleries have been performing technical analyses of the commercial paint present in works of art for a number of years, the lack of a coherent history of the developments made in gloss paint manufacture can make these results difficult to interpret meaningfully. This paper provides such a history, through a discussion of the synthetic and semi-synthetic binding media that were used in gloss paint manufacture in Britain and the United States from the 1930s to the late 1950s. These include nitrocellulose, phenol-formaldehyde, and oil-modified alkyds, alongside the traditional range of naturally occurring oils, gums, and resins that continued to be used until well into the 1960s. The extent of the availability of these different types is discussed, and examples of when each has been found in works of art are given.*

Introduction

The research and development of the formulation of coatings based on synthetic and semisynthetic resins in the early part of the twentieth century was carried out by large chemical companies, rather than traditional paint manufacturers, and this

discussion thus centers on two of the most prominent: Nobel Industries Limited (one of the companies merged to form Imperial Chemical Industries Ltd. [ICI] in 1926) in Britain, and E. I. du Pont de Nemours (DuPont) in the United States. These companies both began life as explosives manufacturers and both entered the coatings business via this route.

ICI and DuPont are important not only for being the first to make decorative coatings from synthetic resins but also for a unique agreement they had to share patents and processes. This certainly played a vital role in the development of gloss paints in Britain (Standeven 2004). The agreement dated back as far as 1897 and pertained not only to explosives but, significantly, to their associated products as well (Crane 1923)—hence the inclusion of coatings based on nitrocellulose. The “associated products” clause was to prove vital in the 1920s and 1930s, when both companies entered the paint and varnish industry, as it was expanded to include new decorative coatings such as those based on oil-modified alkyds, the resin that revolutionized the coatings industry.

Oleoresinous Paints

Prior to the mid-twentieth century, protective and decorative coatings were made exclusively from a range of naturally occurring oils, gums, and resins (Standeven 2004). Linseed oil was undoubtedly the most widely used oil, closely followed by quick-drying tung (otherwise known as China wood oil). In the United States, semidrying oils such as soybean, perilla, and safflower were also used, usually in admixture with drying oils such as linseed and tung. Congo copal was the predominant resin, although alternatives such as amber, dammar, rosin, and colophony were also used.

Oils used in commercial paint manufacture are first treated to moderate their properties. They are heated or blown until partial polymerization occurs. This increases the drying rate and gives the paint good leveling properties, desirable characteristics in gloss paint. The resin component increases the gloss and hardness of the film, although it also contributes to its yellowing, embrittlement, and eventual breakdown. In Britain and the United States, the highest quality paints and varnishes were made from linseed oil and Congo copal, which remained the primary binding medium for commercial gloss paints until well into the 1950s.

Rosin and its derivatives have also been used in commercial paint manufacture, despite the resin's questionable durability. The reasons for this were twofold: rosin was inexpensive, and rationing and shortages of vegetable oils during both world wars forced companies to look for alternatives. Lime-neutralized rosin, glycerol-esterified rosin (ester gum), and maleic anhydride-reacted rosin neutralized with glycerol were widely used rosin derivatives (Brewer 1984, 58). Limed rosin was the primary component of gloss oils, which were cheap, very fast-drying interior enamels. Ester gum also found an important use in paint and varnish manufacture, where its superior color stability and alkali resistance compared to unmodified rosin compensated for its poor durability. Due to their lack of durability, paints containing rosin derivatives were intended for interior use.

Paints based on naturally occurring oils, gums, and resins were widely available until well into the 1950s, and continued to be manufactured until the 1960s—long after paints based on synthetic resins were well established.

Nitrocellulose Brushing Lacquers

Nitrocellulose was the first semisynthetic resin to be formulated into a coating. These coatings contained nitrated cellulose mixed with solvents and plasticizers. As nitrocellulose is used in explosives production (in a more highly nitrated form), turning it to other uses made good business sense. Thus, most explosives manufacturers also produced a line of nitrocellulose dipping lacquers, and both ICI and DuPont entered the coatings business via this route. DuPont had begun making nitrocellulose dipping lacquers in 1904, when it had acquired the International Smokeless Powder and Chemical Company (DuPont n.d.), and Nobel had been manufacturing them from a similar time. By 1912, Nobel (known at that time as the New Explosives Company) was manufacturing its Necol coatings for a diverse range of industrial applica-

tions, including protective films, paper varnishes, dipping varnishes, and pigmented lacquers for metals. These lacquers were too thin and volatile to allow brushing or spraying, so they remained firmly in the realm of industrial applications.

The first decorative enamel based on nitrocellulose was reportedly introduced in Britain by Nobel in about 1919. It comprised airplane dope pigmented with antimony oxide and was known as Glossy White S.2567 (ICI n.d., 5). By 1920, the New Explosives Company was manufacturing its range of nitrocellulose-based Cranko enamels, which it described as high-grade finishes for metal and wood.

In 1923, DuPont devised a method of producing a low-viscosity spraying lacquer of high nitrocellulose content, and Duco automobile enamel was launched. As Duco was based on nitrocellulose, it fell under the "associated product" clause, and Nobel imposed the longstanding agreement. The formulas were duly handed over, reportedly with some reluctance (ICI n.d., 6). The formula was changed to suit the different climate and available raw materials, and Belco automobile enamel was launched on the British market in 1926.

That year also marked the formation of ICI, from a merger of Brunner Mond and Company, United Alkali Company, British Dyestuffs, and Nobel Industries Limited. ICI took on the patents and processes agreement with DuPont, so the exchange of technical information continued. Within a few years, this agreement, which had been restricted to explosives and associated products, was extended to include many other processes, decorative coatings included (*U.S. vs. ICI* 1951).

Following the success of Duco, American companies such as Glidden and Sherwin-Williams introduced a range of nitrocellulose brushing lacquers. Brushability was achieved via the addition of an alkyd resin. Thus, Glidden introduced its Lack brushing lacquer in September 1925, and Sherwin-Williams introduced its Rogers Brushing Lacquer in the mid-1920s (McDermott and Dyer 1991, 45). In response to these, and to other competitors' quick-drying products, DuPont developed its own brushing lacquer, Brush Duco, which was launched on March 6, 1926 (DuPont 2006a). By 1930, about 250 companies in the United States were manufacturing Duco-like lacquers intended for both industrial and domestic applications (Zintl 1947, 52).

However, the success of these brushing lacquers was somewhat short-lived, due to a number of undesirable characteristics: their high solvent content made them unpleasant to use, and the speed with which the solvents evaporated made the paint difficult to brush out. W. M. Zintl, director of sales in DuPont's Paint Department in the 1920s, was perhaps

being a little unfair when he lamented the company's inability to “change the habits of women who believed that they were painters . . . [and had a] habit of brushing out lacquer like they were accustomed to doing with an oil paint, which they could brush and brush and brush” (Zintl 1947, 85), as the fault was clearly with the paint rather than the practitioner.

Brushing lacquers would appear to have been more popular in the United States than in Britain. However, neither the consumers nor the manufacturers were happy with these lacquers. Indeed, DuPont was so dissatisfied with Brush Duco that, shortly after its launch, the formulation of the paint was changed to an alternative quick-drying product without the consumer being informed (Zintl 1947, 85).

Although numerous British companies manufactured nitrocellulose lacquers, it is not clear how many of these were intended for decorative purposes. In Britain, Nobel's nitrocellulose-based Glossy White predated DuPont's Duco patent, although the formulation of Glossy White is unclear (ICI n.d., 5). However, in an interview in 2002, former Berger Paints employee Ken Arbuckle said that nitrocellulose finishes were rarely used as decorative coatings since they were very difficult to brush out, and they were certainly not manufactured by Berger.¹ But in 1939, Walter Carson & Sons was advertising these coatings alongside its range of Ultralux synthetic enamels, and in the mid-1930s, Nobel's range of nitrocellulose-based Necol products were available as bronze mediums, cements, and plastic wood (Nobel n.d.). It would seem that it was primarily explosives manufacturers, rather than paint companies, that were involved in their production in Britain, as the participation by the latter was extremely limited. The extent of their use by artists is unclear, although of the eighteen cans of commercial paints found from Jackson Pollock's studio that underwent scientific analysis, four were found to be alkyd-modified nitrocellulose coatings.²

Phenol-Formaldehyde Resins

Phenol-formaldehyde resins were developed by the plastics industry in the early 1900s, and were designed to replace the naturally occurring gums and resins that were used as electrical insulators. They were made via an addition reaction between phenol and formaldehyde. Solubility in oil—usually tung or an admixture of tung and linseed—was achieved through the addition of rosin.

Although their use in decorative coatings was brief and by no means widespread, phenolics' excellent electrical, corrosion, alkali, and water resistance meant they found numerous

industrial applications, especially for marine paint. However, the presence of rosin and tung meant that these resins discolored significantly, and in response to this, 100 percent, or “straight,” phenols were introduced in 1929. Direct solubility in drying oils was achieved by using highly selected or substituted phenols, which eliminated the need for the rosin component completely. Although very durable, 100 percent phenols still discolored due to the presence of tung oil.

The extent of the use of such resins in the decorative coatings industry is unclear, but by the 1930s numerous British companies were manufacturing quick-drying “four hour enamels,” which were probably formulated from phenol-formaldehyde (Boxall 1978, 18; Lilley 1951, 307; Elliot 1981, 13). For example, in the late 1930s, the British company Walter Carson & Sons advertised a noncellulose “Four Hour Synthetic Lacquer Paint” that dried in four hours, became hard in eight, and was recommended for use in kitchens and bathrooms (Walter Carson n.d.). In 1939, Williams and Howard advertised Quadlac gloss paint that dried in four hours. Walpamur's early Rockfast enamel paints were reportedly based on phenol-formaldehyde resins, and the Goodlass Wall Company's Valspar was a similar product in the 1930s.³ The manufacture of decorative paints based on phenolic resins seems to have been confined to traditional paint and varnish manufacturers, and there is little evidence to suggest that either ICI or DuPont manufactured them for this purpose.

Oil-Modified Alkyds

The most important binding media of the twentieth century, arguably, are oil-modified alkyds, and they have remained the dominant binder for industrial and domestic applications to the present day. Alkyds contain a polybasic carboxylic acid and a polyhydric alcohol, which can be oil modified via co-esterification with fatty acids or their glycerides. Although a huge array of acids and alcohols can be used in alkyd manufacture, decorative paints are commonly made from phthalic anhydride (the acid) and glycerol or pentaerythritol (the alcohol). Oil-modified alkyds can be divided into three main categories, distinguished by their *oil length* (proportion of oil to resin). The oil length is expressed as a percentage and denotes the number of grams of oil required to make 100 grams of resin. Decorative alkyds typically have an oil length of 60–80 percent and are formulated with drying or semidrying oils. They are soluble in aliphatic hydrocarbon solvents.

Alkyds, or glyptals, as they were known until the 1920s, were first patented in 1901 by General Electric. Hard and brittle,

they were used as electrical insulators, and it would appear that their potential as surface coatings was not recognized at this stage. Following the discovery that part of the phthalic anhydride could be replaced by a fatty acid, further work with unsaturated oils, such as vegetable oils, was carried out, primarily by M. Callahan, J. van Bemmelen, and the Ellis-Foster Company in the United States (Bevan and Robertson 1951, 340). Once modified with a fatty acid, glyptal resins could be formulated that were sufficiently flexible to be used as a coating. DuPont's archive reveals that the company began to research oil-modified glyptals in 1924, reportedly upon the appointment of Callahan, who had worked on their development at his previous employment with General Electric (Zintl 1947, 75).⁴ In 1926, DuPont introduced its first alkyd-based primers. These "Dux" primers were formulated from glycerol, phthalic anhydride, and linseed oil acids.

The name Dulux was also born in 1926, when DuPont launched its first oil-modified alkyd top coat onto the U.S. trade market. This paint also contained phthalic anhydride, glycerol, and linseed oil acids, and was intended for industrial applications such as signs, freight cars, and gas pumps. Although the durability of Dulux was not in question, the paint was not popular with the trade, as it had poor brushing qualities and coverage. More successful was Dulux Refinishing Enamel, which was introduced to the car trade in 1930. This immediately became popular with automobile dealers, as, although slower drying than Duco, it was considerably cheaper, and therefore popular for repainting lower priced cars that did not warrant a Duco finish (DuPont 1949, 2).

In May 1931, the first exterior Dulux house paint, Dulux GA-11, was released. It comprised a 62 percent linseed-modified glyptal resin pigmented with titanium white. In 1934, DuPont began to advertise Dulux Super White, a new finish for home interiors. One of the first advertisements appeared in *The American Painter and Decorator* in March 1934; it extolled the paint's nonyellowing properties, quick drying, and easy application. Once Dulux house paints had been successfully formulated and marketed, DuPont's Brush Duco, which had been unsuccessful on a nitrocellulose base and currently contained an alternative, quick-drying medium, was replaced in the can with the new Dulux alkyd resin. In 1937, after several years of field testing, improved Outside White, for exterior use, was released. At the same time, Dulux Super White was improved for interior use (there is no indication as to how the interior and exterior Dulux differed).

Throughout the 1920s and 1930s, while DuPont was developing Dulux resins, its continuing agreement with ICI

ensured that new processes and patents were introduced swiftly to the British market via its Nobel Chemical Finishes Limited division. Through Nobel, Dulux industrial undercoats had been launched in Britain in 1929, and Dulux Glossy decorative paint in 1932. Papers from ICI's archive reveal that the company played no role in the development of post-Second World War Dulux, so these paints were based entirely upon DuPont technology (ICI n.d., 11). Therefore, Dulux Glossy comprised phthalic anhydride, glycerol, and linseed acids; it had an oil length of 60 percent. ICI made no effort to enter the retail market at this stage, and the paint was sold to the trade via twenty-eight merchants, served by twenty representatives.

During the 1930s, several other British companies began to conduct research into alkyd resins, and Jenson and Nicholson reportedly put their Robbialac range of paints onto alkyds at that time.⁵ However, most British and American companies did not produce alkyd resins until after the Second World War, and these paints have not, to date, been found on works of art from that period.

The Impact of the Second World War: 1939–45

The Second World War significantly affected the development of both Britain's and the United States' paint industries. In their capacities as explosives manufacturers, both ICI and DuPont had been working around the clock to meet demand. In addition, they were called upon to produce large quantities of camouflage and gas-resistant paint for the war effort. The production of synthetic resins for the British decorative market all but ceased shortly after the outbreak of war in 1939. The story was the same when the United States entered the war, in 1941. Although some U.S. paint companies continued to make synthetic resins, including phenol-formaldehydes and alkyds, they were restricted to military use during the war years (Price 1943, 81). The production of interior paints suffered more than that of exterior as a result of war shortages, and decorative paints' status as cosmetic rather than essential finishes led to many American companies ceasing their production altogether (*Modern Plastics* 1945). For those that did continue manufacture, shortages of raw materials forced them to look for alternative ingredients. The 1940s and 1950s thus mark the period in which the most diverse range of oils and resins were used in paint manufacture. Linseed, oiticica, tung, and soybean oils were in short supply, so companies used the unrationed rosin, which had previously been used only for cheap paints because of its doubtful durability. The use of limed rosin and ester gum (rosin esterified with glycerol) thus reached its

peak during this period. Rosin-based paints certainly formed the bulk of the production of the British company Cray Valley Products at the end of the war.⁶ Indeed, when British artist Jon Catleugh's poured painting *Untitled* (1951) was analyzed, it was found to contain rosin, glycerol, and a drying oil, suggesting the presence of ester gum.⁷

Post-Second World War Alkyds

The research and development of postwar alkyd resins was also driven by the availability of raw materials. When the war ended, in 1945, both ICI and DuPont found themselves left with plants capable of producing large quantities of coatings and explosives, but no large-scale market to speak of. However, in their capacities as explosives manufacturers, both had been producing considerable quantities of pentaerythritol, and experimentation began with using this alcohol in the place of glycerol. Pentaerythritol has three main advantages over glycerol: First, it has a functionality of four as opposed to glycerol's three, which allows greater amounts of oil to be incorporated into the resin. This not only imparts greater flexibility to the film and improves the resin's rheological properties but also makes its manufacture more economical, as oil is less expensive than either glycerol or pentaerythritol. Second, it lends a water resistance that is far superior to that of glycerol alkyds. And third, it offers better gloss and gloss retention. The use of pentaerythritol in place of glycerol was a significant development in the manufacture of postwar alkyds.

ICI resumed its research into alkyds in 1945 and, after several years of testing, reintroduced decorative Dulux in 1949, based on a phthalic anhydride, pentaerythritol, and linseed oil (Lilley 1959).

It is probable that DuPont and ICI continued to share technical information with regard to the development of these postwar alkyds, although it is worth noting that the agreement was severed by the enforcement of the Sherman Antitrust Act, in 1948, and the exchange of information ceased on June 30th of that year (*U.S. vs. ICI* 1951). By the late 1940s, many other companies were also producing alkyd resins, and those without the necessary expertise and plant could simply buy a license to manufacture or buy the premixed resin from a manufacturer and blend it with the necessary pigments and additives. By the late 1960s, in Britain, only ICI and Berger, Jenson, and Nicholson continued to manufacture their own resins (Armitage 1967, 23). Also in Britain, Berger and Walpamur (which later became Crown Decorative Products) began to manufacture alkyds in the late 1940s, while in America, both Benjamin Moore and Sherwin-Williams introduced their

alkyd-based Impervio and Kem-Glo enamels, respectively, in 1949 (McDermott and Dyer 1991, 63).⁸

Oil-modified alkyds have been found on works of art only after 1947. Susan Lake, at the Hirshhorn Museum, used gas chromatography/mass spectrometry (GC/MS) to analyze the commercial paint on eight paintings by Jackson Pollock dating from 1943 to 1951. She found extensive use of alkyd paint only after 1947; before that the paints were invariably oleoresinous.⁹ Lake obtained similar results from Willem de Kooning's paintings dating from that period. Scientists at Tate also found alkyd only after 1947, and its Pollock painting *Summertime: Number 9A* (1948) was found to contain an oleoresinous house paint.¹⁰

As discussed above, by the early 1950s, many of the oil-modified alkyds intended for decorative purposes incorporated pentaerythritol as the alcohol. But despite the obvious advantages of such formulations, the tendency of pentaerythritol alkyds to bloom meant that many companies preferred to use glycerol until the late 1950s.¹¹ Glycerol also continued to be used for applications such as undercoats, where its superior hardness allowed the finish to be sanded. A glycerol alkyd was detected on Pollock's *Number 14*, which dates from 1951.¹²

Semidrying Oils

A second important development in post-Second World War alkyds—especially for the British market—was the use of semidrying oils in the place of the drying oil linseed. Although linseed has excellent drying properties, it does have a tendency to yellow, making it unsuitable for pale-color paints. Semidrying oils such as soybean, tobacco seed, and safflower are paler in color, and although they are incapable of producing a hard film when used alone, they will dry when co-esterified with an alkyd. Soybean oil was introduced to the British paint market in the late 1950s, and its use became widespread in the early 1960s (the oil's expense had prohibited its use prior to this time). Soy had, however, been used in U.S. paint formulations at a much earlier date, as it grew well in the Midwest. Along with similar indigenous oils such as cottonseed, it had been used as a cheap adulterant for the more expensive linseed since the early part of the twentieth century (Heckel 1928, 461). It was also used in alkyd production at an earlier date in the United States, and has indeed been detected on Pollock's *Yellow Islands* (1952), which contains a pentaerythritol alkyd formulated with a semidrying oil.¹³

It is important to remember that throughout the period when these synthetic resins were being introduced, the market for traditional oleoresinous binders remained buoyant.

Many companies produced both alkyd and oleoresinous paints within the same range—perhaps using alkyd for exterior paints, where durability was essential, and oleoresinous paints for interior use, where durability was not such an issue.

These oleoresinous binders were available in the 1960s, and they have been detected on Ben Nicholson's *White Relief*, which although it originally dates from 1935, was repaired and repainted with Ripolin house paint in 1955 (Nicholson 1955).

The Popularity of Synthetic Paints

It would appear that upon their introduction, decorative paints based on synthetic resins were more popular in the United States than in Britain. This can probably be accounted for by the considerably larger retail market in the United States. U.S.

companies had been exploiting the do-it-yourself (DIY) market since the early 1920s, and advertisements suggest the products were geared very much toward female DIY users, as exemplified by DuPont's 1927 ad for Brush Duco (fig. 1). These consumers not only valued quick drying over the paints' other qualities, but they tended to be one-time users, and were thus more likely to be swayed by the massive advertising campaigns launched. This might help to explain the popularity of synthetic resins in America, as well as the initial success of the wholly unsatisfactory nitrocellulose brushing lacquers in the 1920s.

Indeed, the popularity of synthetic paints caused an unlikely problem in America in the 1940s. When the production of decorative paints all but ceased during World War II, the popularity of prewar synthetic resins led some unscrupulous dealers to fraudulently label their exterior paints as plastic, and attempt to sell them to an unwitting public at an inflated price. In 1945, the American National Paint, Varnish and Lacquer Association tested a number of these paints and found that none contained any type of synthetic resin (*Modern Plastics* 1945).

By contrast, the notoriously conservative British decorating industry was mistrustful and suspicious of new materials, and preferred to stick to the tried and trusted traditional materials.

Articles have appeared in the daily press and even in some technical journals, hailing various substitutes as the only possible media for post-war use. It is probable that many of the authors of these articles are enthusiastic rather than experienced; possibly even thinly disguised journalists searching for something new, rather than practical men with a knowledge of building materials. (Jay 1942, 171)

Paints based on synthetic resins were evidently not embraced to the same degree in Britain, nor was the DIY market exploited fully until a considerably later date. ICI did not even attempt to enter the retail market until the early 1950s, and until that time, paint advertisements were very much geared toward tradesmen in white coats and flat caps (figs. 2 and 3) and found predominantly in professional journals such as *The Decorator*.

But what was behind this fundamental difference in attitude? The manner in which science and technology were promoted and perceived in America—exemplified by DuPont's promotion of its activities—must certainly have played a role. DuPont's slogan until the 1980s, "Better Things for Better Living . . . Through Chemistry" was first introduced in about 1939 (DuPont 2006b).



FIGURE 1 Advertisement for DuPont Duco house paint from *The Saturday Evening Post*, February 19, 1927. Courtesy Hagley Museum and Library.



FIGURE 2 Advertisement from *The Decorator*, February 1936.

The slogan epitomized the company's marketing campaign, in that it extolled the benefits that developments made in science and technology would have on day-to-day living. This notion acquired particular resonance in the post-World War II years, when a truly astonishing array of synthetic plastics and fibers, which did indeed revolutionize many aspects of everyday life, were manufactured and marketed. To this day, DuPont claims that materials developed before and during the war, including neoprene, nylon, and rayon, not only helped to win the war but “remained vital to the national defense effort in the Cold War years” (DuPont 2006c). This almost blind faith in the benefits of science and technology continued until the 1960s, when

America's post-war economic expansion and consumer optimism yielded to concerns about environmental pollution and social justice . . . [and] the tide of public opinion [began to turn] against the chemical industry.



FIGURE 3 Advertisement from *The Decorator*, July 1934.

A nation once enamored of chemicals and their benefits now grew uneasy and suspicious. (DuPont 2006c)

Until they soured, the positive associations evoked by developments in science and technology, coupled with the aggressive marketing campaigns of companies such as DuPont, must have played a role in the wider acceptance of new synthetic materials in the United States.

These very different markets certainly had an effect on the British and American artists who used these commercial paints, and is indeed reflected in their attitudes toward and use of these materials (Standeven 2004, 2006). Commercial gloss paints have been popular among artists since the 1920s, and they remain popular to the present day. Our understanding of when and why artists have used particular materials not only helps to ensure that artworks are cared for appropriately but also greatly enriches our appreciation of artistic practice.

Notes

- 1 Personal interview with Ken Arbuckle, 2002.
- 2 E-mail from Susan Lake, Hirshhorn Museum, 2001.
- 3 Letter from Tom Graham, May 16, 2002.
- 4 The history of these early glyptals by DuPont is comprehensively outlined in DuPont's Experimental Station project files, held in its archive (Patterson 1927–37).
- 5 K. Arbuckle, interview.
- 6 Personal interview with Graham North, Cray Valley Products Ltd., June 12, 2002.
- 7 Personal communication with Michael Schilling, Getty Conservation Institute, Feb. 2003. Analysis by gas chromatography/mass spectrometry (GC/MS).
- 8 E-mail from Barbara Meyer, Feb. 12, 2001.
- 9 E-mail from Susan Lake, Hirshhorn Museum, 2001.
- 10 Personal communication with Tom Learner, Tate, Feb. 2003. Analysis by pyrolysis GC/MS (PyGC/MS) and Fourier transform infrared (FTIR) spectroscopy.
- 11 G. North, interview.
- 12 Personal communication with T. Learner, Tate, Feb. 2003. Analysis by PyGC/MS and FTIR.
- 13 Ibid.

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PART THREE

Analysis and Characterization

Mass Spectrometry of Modern Paints

Jaap J. Boon, Frank G. Hoogland, and Jerre van der Horst

Abstract: Mass spectrometry provides molecular-level information about a broad range of paint constituents present in modern paint systems used by artists. A wide choice of instruments and ionization methods is available to identify all the main classes of modern binding media, to analyze molecular weight distribution of polymers, to characterize synthetic pigments and coloring substances, to characterize some classes of additives, and to determine oxidized compounds developing in oil paints. Relevant examples of direct temperature resolved mass spectrometry (DTMS), laser desorption/ionization mass spectrometry (LDI-MS), matrix assisted laser desorption/ionization mass spectrometry (MALDI-MS), electrospray ionization mass spectrometry (ESI-MS), and imaging SIMS (secondary ion mass spectrometry) applied to research questions on paint composition are presented.

Introduction

The organic constituents in modern paints are a challenge for the analytical chemist but equally challenging for the conservator, who is facing ever-changing paint compositions in modern and contemporary works of art with unpredictable aging behavior. Few techniques provide the necessary details for informed decision making about how to protect and conserve these works. Although slightly invasive, mass spectrometry has the potential for molecular-level information on modern paints, perhaps even more than it has so far achieved with traditional paints. When minute samples can be taken, mass spectrometry can address the molecular-level composition and compositional changes, while chemical microscopy and spectroscopy can address the more overall features and spatial distribution of the constituents. This paper reviews some

aspects of the application of mass spectrometry to modern paint samples and presents some examples where mass spectrometry provides the necessary details for decision making by conservators.

Polymers like the acrylates, as well as polymer networks that develop from oil and alkyd paint, require that molecular-level techniques be used for their characterization. Synthetic pigments and dyes are an especially challenging group of compounds to identify, but at least many are thought to be chemically stable and don't change in composition as aging proceeds. Many modern paints also contain a variety of additives—metal soaps for oil paints, and amphiphilic oligomers in the case of the acrylates—to enable compatibility of materials, for emulsification, and to improve the workability of the paints (Learner 1996, 2004).

The composition of these materials is likely to have changed appreciably over the last fifty years, although such changes take place when dictated by the demands of the bulk chemical industry and are never announced. Since many of the raw materials or intermediate industrial products are poorly specified on the molecular level and such information often remains proprietary, the paints made from these products as produced by the colormen are only understood in fairly general terms. In fact, paint makers often have to add substances from a vast repertoire of additives to maintain the workability of the paints according to their own specifications.¹

Organic Mass Spectrometry

Organic mass spectrometry is frequently the method of choice for the analysis of the organic (and sometimes inorganic) constituents in modern paints, but the method of introduction of

the sample or sample components requires careful consideration. Fillers and inorganic pigment components of the paint can be readily characterized by X-ray-based techniques—for example, X-ray diffraction (XRD), X-ray fluorescence (XRF), and scanning electron microscopy/energy dispersive X-ray (SEM/EDX) analysis—and to some extent by Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy.

Mass spectrometry has undergone a revolutionary development in the last decade, with advancements in ionization, mass separation, detection, and data processing. Many instruments are now turnkey systems that require little expert knowledge of either vacuum systems or mass spectrometry. A wide choice of ionization methods is available, and data processing programs are much more user oriented. Gas chromatography/mass spectrometry (GC/MS), electron ionization (EI) and chemical ionization (CI) are the standard techniques for fragment ion pattern formation (structural information) and molecular ion detection (molecular weight of the compound). Pyrolysis GC/MS (PyGC/MS) has been applied to characterize oil and acrylate binding media, as well as fragments from modern synthetic pigments (Learner 1996, 2004; van den Berg, Boon, and van den Berg 1998; Sonoda 1999).

Electrospray ionization (ESI) is the preferred ionization technique for high-performance liquid chromatography/mass spectrometry (HPLC/MS). The analysis of some additives by HPLC/ESI-MS in a modern paint provided by Golden Artist Colors has shown the great potential of this approach (Smith 2005). Field desorption (FD) and field ionization (FI), laser desorption/ionization (LDI), and matrix assisted laser desorption ionization (MALDI) are mostly or solely suitable for direct probe analysis of mixtures or pure compounds with a high polarity or high molecular weight. Combined with suitable mass separation systems, these methods have enabled the elucidation of the composition of oligomers, polymers, synthetic colorants, and oxidized varnishes (van Breemen 1995; Montaudo and Lattimer 2002, 584; Wyplosz 2003; Scalerone et al. 2005).

When compounds can't be desorbed and ionized directly, some form of prefragmentation is required. This approach has been explored at AMOLF² for several decades (Boon 1992), first in the form of Curie-point pyrolysis mass spectrometry (PyMS) with a home-built system, and later as direct temperature resolved mass spectrometry (DTMS) using commercial instruments. The advantage of both methods is the very minimal sample pretreatment that is necessary. Submicrogram amounts of complete paints can be analyzed with DTMS by desorption from a resistively heatable platinum/rhodium

(Pt/Rh) filament. The methodology was explored for modern acrylic paints and selected synthetic pigments in collaboration with Tate (Learner 2004; Boon and Learner 2002), and van den Berg explored the applicability of DTMS to oil paints (van den Berg 2002, 291; van den Berg et al. 2004).

Spot Analysis with LDI-MS

Laser desorption/ionization mass spectrometry (LDI-MS) can be used as a spot-analysis technique; the analytical spot is selected by light microscopy. Although the light microscopic setup in most commercial MS systems is rather elementary and the beam diameter of the laser rather large (>20 micrometers), it can still yield information from cross sections, provided that the sample absorbs the light and forms ions from the analytes of interest. Wyplosz (2003) tried this out on a cross section from a painting by Patrick Caulfield, *Interior with a Picture* (Tate T07112), and showed the presence of PR170 (naphthol red), PY3 (azo yellow), and some potassium that was later shown to be a trace compound in cadmium yellow pigment (PY37).

Further studies with imaging SIMS (secondary ion mass spectrometry) and SEM/EDX confirmed the chlorine from the PY3 azo yellow in the respective layer, and the cadmium, zinc, sulfur, and potassium from the PY37 in the cadmium yellow paint layer (Boon, Keune, and Learner 2002). Although the presence of PR170 could not be demonstrated at first, it was later detected by SIMS after improvement of the surface preparation (unpublished data). Wyplosz (2003) reports the detection by LDI-MS of PV19 (quinacridone) in a sample from a sculpture of Phillip King (*Dunstable Reel*; Tate T01361), but studies on paint cross sections from Mark Rothko paintings remained inconclusive. Recent explorative studies at AMOLF have shown that this may be caused by penetration of the embedding medium into the embedded paint sample.

Many synthetic pigments give good LDI-MS spectra when analyzed as pure compounds or in dried paints. The acrylic binding medium is fully transparent for UV-LDI at 337 nm. Wyplosz identified by LDI-MS paints containing the following organic pigments: PR207, PR209, PR206, PR188, PR178, PR122, PY83, PV23, PV19, PB15, PG7, and PG36 (Wyplosz 2003). Only molecular ions are observed as negative ions, while some diagnostic fragment ions can appear as positive ions. The dioxazine (PV23) with the chemical formula $C_{34}H_{22}N_4O_2Cl_2$ displays a protonated molecular ion in positive mode (m/z 589) and a molecular ion at m/z 588 in negative mode in standards and in Liquitex Brilliant Purple.

Remarkable differences were observed in the LDI-MS spectra of phthalocyanine PG7 and PG36 from different suppliers. Figure 1 shows the positive ion spectra from the copper chloro-phthalocyanines (PG7) obtained from Cornelissen & Son (fig. 1A) and from Winsor & Newton (fig. 1B). The inset in figure 1A shows the theoretical isotope distribution for the $\text{Cu-C}_{32}\text{N}_8\text{Cl}_{16}$ isomer. The PG7 from Cornelissen is indeed a hexadecachloro-phthalocyanine, although isomers with fewer chlorine substitutions (Cl_{15} to Cl_{10}) are also observed. A very small amount of a bromoquindecachloro isomer is also detected. The "PG7" from Winsor & Newton is clearly a mixed bromo-chloro phthalocyanine (isomers with up to five bromine substituents detected). The degree of halogen substitution is also limited (see the Cl_7 to Cl_{15} series).

PB15 and PG7 could be demonstrated by LDI-MS in the Winsor & Newton Finity series Permanent Green Light acrylic paint, which is a mixture of various pigments in polybutyl acrylate/methyl methacrylate p[BA/MMA] medium (Boon and Learner 2002). Here the PG7 is indeed only the fully chlorine-substituted compound. A series of ions from polyethylene glycols (up to mass m/z 2250) was also detected, which demonstrates that LDI-MS has the potential for selective ionization of additives as sodium adducts.

Microscopy Mass Spectrometry

Micron-level spatial resolution has been obtained with imaging static SIMS on cross sections from traditional oil paintings (Keune 2005) and from a painting with acrylic medium (Boon, Keune, and Learner 2002). In traditional paintings, the analytical focus is frequently on the distribution of fatty acids and diacids obtainable in negative mode and the fatty acid soaps and acylglycerides obtainable in positive mode (Keune and Boon 2004a; Keune, Ferreira, and Boon 2005). The yields of these ions can be improved by sputtering a few nanometers of gold on the surface of the polished cross section (Keune and Boon 2004b). Evidence for differences in the composition of acrylic paint layers was observed in the cross section from the Caulfield painting (Boon, Keune, and Learner 2002), but an influence of the other paint components on the ion patterns of the acrylic polymers cannot be excluded. Further work on acrylic paints and relevant standards is required.

Synthetic pigments can also be detected with static SIMS, as demonstrated in figure 2 on a test cross section composed of nine acrylic paint layers. A $[\text{M}-\text{H}]^-$ ion at m/z 385 is detected for paint layer 4 with the azo yellow PY74. Paint layer 5 shows a strong signal for the chlorine distribution and an absence

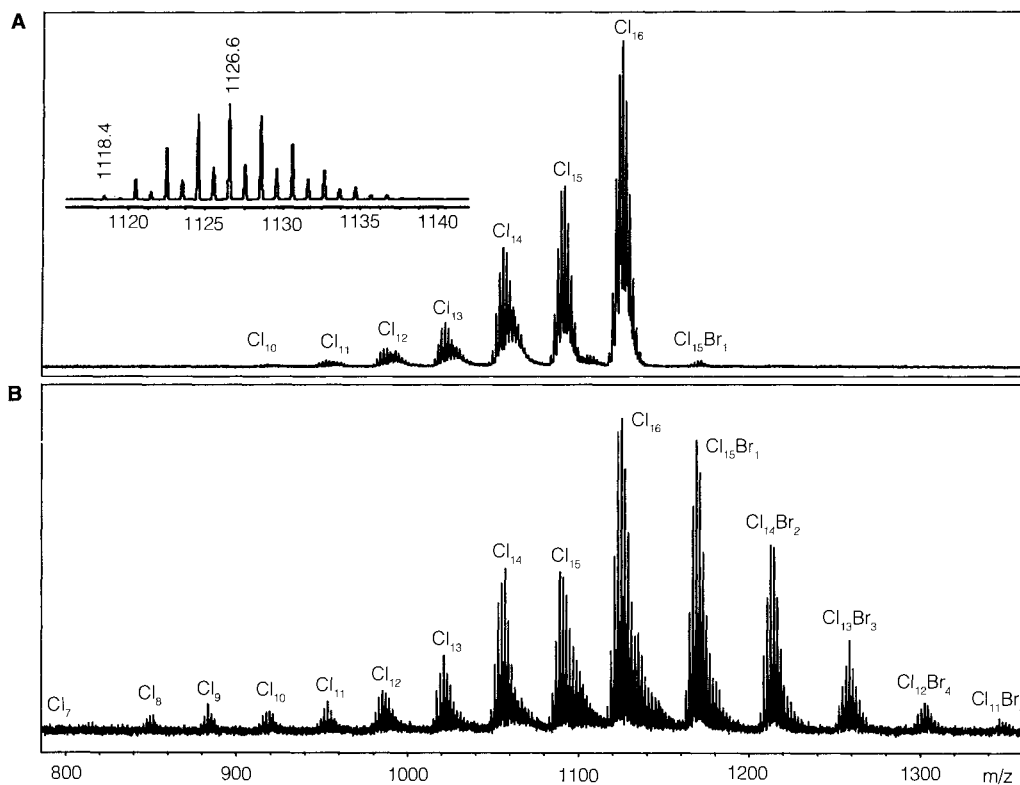


FIGURE 1 LDI-MS spectra of phthalocyanine green PG7 from (A) Cornelissen & Son, (B) Winsor & Newton. Inset in A: theoretical isotopic distribution of $\text{Cu-C}_{32}\text{N}_8\text{Cl}_{16}$, with the monoisotopic (MW_n 1118 Da) and dominant isotopic (MW_d 1126 Da) peaks.

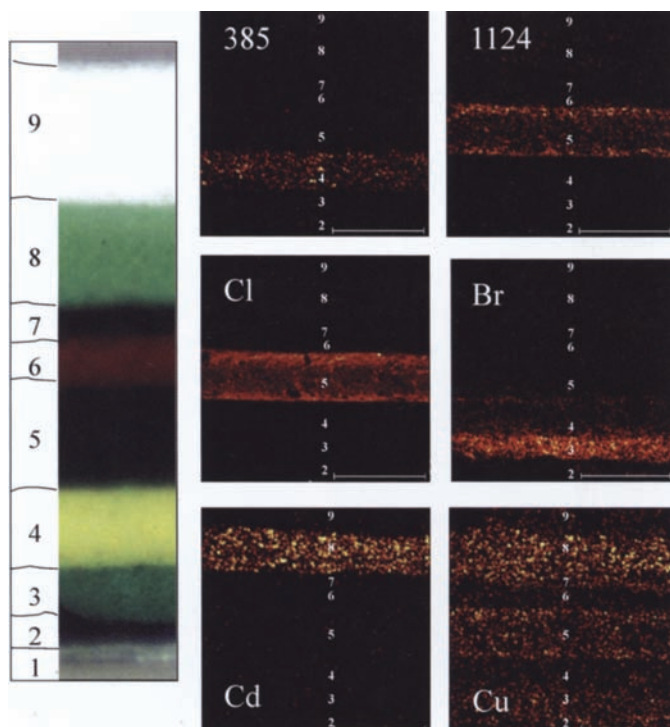


FIGURE 2 Imaging static SIMS maps of an embedded cross section of a paint made by superimposing nine different acrylate paints: (1) Talens White (PW6), (2) Liquitex Phthalocyanine Blue (PB15), (3) Winsor & Newton Finity Emerald Green (PG36, PW16), (4) Winsor & Newton Finity Brilliant Yellow (PY74, PO62), (5) Liquitex Phthalocyanine Green (PG36), (6) Winsor & Newton Finity Naphthol Red Medium (PR 170), (7) Liquitex Phthalocyanine Blue (PB15), (8) Winsor & Newton Permanent Green Light (PY37, PG7), (9) Talens White (PW6). Layer 1 is just outside the field of view of the SIMS. The maps shown are from the positive ions of Cd and Cu, and the negative ions from Br, Cl, the m/z 385 from PY74, and the m/z 1124 from PG7. Note that paint layer 5 does not contain PG36 (no Br), although it is listed on the paint's label.

of bromine, while the m/z 1124 maps an isotope peak in the ion peak pattern of a PG7. These results are remarkable, considering that the label on the Liquitex paint tube lists a PG36 (the fully brominated phthalocyanine green) as the coloring component. DTMS indeed confirms the absence of PG36 and the presence of PG7. Bromine is found in layer 3, the Winsor & Newton Finity Emerald Green paint, which, according to the label, contains PG36 and PW6. Copper from various phthalocyanines is detected in layers 2, 3, 5, 7, and 8.

In summary, static imaging SIMS as a microscopic technique is useful for investigation of the spatial distribution and

detection of modern pigments, as well as for gaining information on oil paint components and fragments from polymers. We expect that further research on modern paints using dynamic and static SIMS will greatly expand the potential of this molecular chemical microscopic approach for paint studies.

DTMS of Acrylate Paints

Acrylic polymers and acrylic emulsion paints can be analyzed with relative ease using DTMS (Learner 2004; Boon and Learner 2002). Learner has published a number of DTMS analyses of acrylic homopolymers, and the compounds evolved by pyrolysis were identified separately by PyGC/MS (Learner 2004). Ethyl acrylate/methyl methacrylate (EA/MMA) and butyl acrylate/methyl methacrylate (BA/MMA) copolymers used in emulsion paints produce monomeric and oligomeric subunits by pyrolysis. Oligomers up to hexamers were observed by pyrolysis high-temperature GC/MS (Boon unpublished; Hoogland 2002, 27). Such oligomers (up to the octamer) are also observed by DTMS of EA/MMA as pseudomolecular ions $[M+NH_4]^+$ under chemical ionization using ammonia as the ionization reaction gas (Boon and Learner 2002). The electron ionization spectrum of EA/MMA shows high-intensity peaks for ions, with a strong loss of an ethoxy radical leading to a homologous series of m/z 255 (trimer), 355, 455, 555, and so on, in the mass spectrum. The DTMS analysis of the BA/MMA does not show high-molecular-weight oligomers. Only the trimers of BA and MMA are dominant features in the CI and EI spectra. These differences are thought to be caused by the relative weakness of multiblocks of MMA units in the polymer.

Emulsion paints often show multiple desorption events that relate to the presence of coloring agents, additives, acrylic polymers, and inorganic fillers. The azo- and naphthol-based pigments desorb very well and give interpretable spectra when analyzed at low-energy EI (16 eV). Analysis at high EI energy (e.g., 70 eV) leads to increased molecular fragmentation and hence to less informative fragments for these pigments (Lomax, Schilling, and Learner 2007). The problem of identification in complex mixtures can be solved by DTMS/MS, where the preselected molecular ion is fragmented by collision-induced dissociation and the fragment ions are further analyzed in a second mass spectrometer. Applications of this approach are described by Marino et al. (2005) and Boon and Learner (2002).

Some commonly used pigments do not perform well under DTMS conditions because they are too large or too

polar. For example, it has not been possible in our hands to obtain DTMS data from dioxazines, whereas they can be detected with LDI-MS (Wyplosz 2003, 165–66). However, it has been possible to detect polyethylene glycol additives using ammonia chemical ionization conditions in paints (Boon and Learner 2002) and in water extracts (Hoogland 2004), but these compounds are much more easily analyzed with MALDI or ESI-MS (see below).

The phthalocyanines, although of high molecular weight (especially PG36), are readily detected with DTMS, although they appear after the thermal dissociation event of the polymers (i.e., at high temperature). The potential danger of such a high desorption temperature is the pyrolysis of the phthalocyanine ring into its subunits $C_8N_2X_4$, evidenced by isotopic multiplet ions around m/z 266 (tetrachloro) and m/z 444 (tetrabromo). Another complication is the potential elimination of the chlorine and bromine substituents, leading to more complicated ion patterns at high mass.

Mass resolution is an issue as well (depending on the mass spectrometry system), and it is generally not easy to obtain the correct isotopic distribution patterns (software-implemented corrections over the full mass range are often erroneous). Negative ionization under ammonia chemical ionization conditions creates milder analytical conditions, but the appearance of the phthalocyanine subunits at m/z 264 or 444 that result from partial pyrolysis of the phthalocyanine ring system is still unavoidable. We have often also observed the appearance of ions at m/z 35 and 37 from Cl and m/z 79 and 81 from Br, which points to elimination reactions due to pyrolysis. Both types of ions may assist in the identification of phthalocyanine-containing paints when the relative amounts of the target compounds are small and disappear in the chemical noise.

Two PG36 preparations obtained from AVECIA and Winsor & Newton, respectively, were investigated by DTMS negative CI to determine their composition (fig. 3). Remarkably,

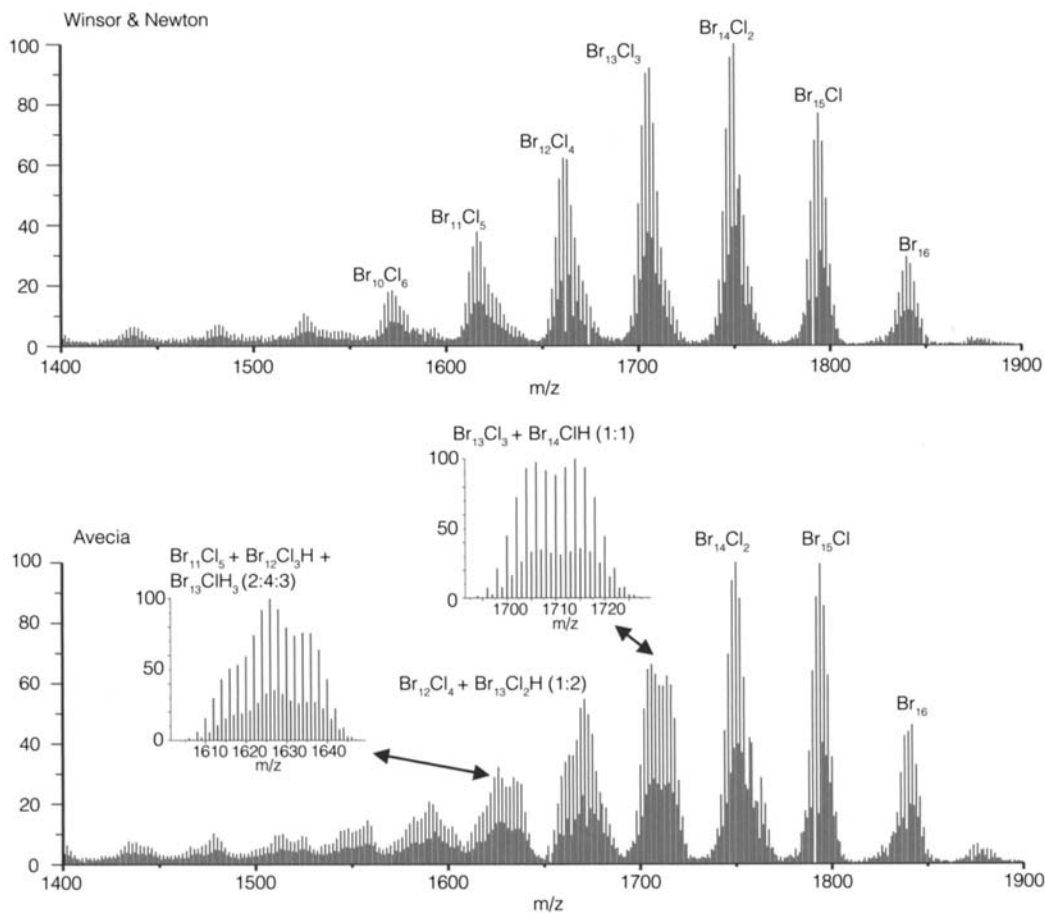


FIGURE 3 DTMS spectra of two PG36 preparations from Winsor & Newton and AVECIA. Insets: Theoretical isotopic distributions of some phthalocyanine isomers.

both preparations contain more than one type of bromophthalocyanine. The Winsor & Newton preparation is the purest, showing a set of ions from the phthalocyanines with the sixteen bromine substituents (hexadecabromophthalocyanine: Br₁₆ isomer [m/z 1820–1850]) and the isomers Br₁₅Cl, Br₁₄Cl₂, Br₁₃Cl₃, Br₁₂Cl₄, Br₁₁Cl₅, Br₁₀Cl₆. At lower mass, some Cl₁₆, Cl₁₅Br, and Cl₁₄Br₂ are also observed (spectral range not shown). The Avecia preparation, however, shows differing isotopic peak patterns that could be related to less halogenated phthalocyanines.

The insets in figure 3 show the calculated patterns for mixtures of Br₁₃Cl₃ and Br₁₄ClH (1:1), which match the isotopic pattern in the m/z 1680–1760 range, and a mixture of Br₁₁Cl₅ + Br₁₂Cl₃H + Br₁₃ClH₂ (2:4:3) in the m/z 1600–1650 range. The peak pattern between those multiplets matches a mixture of Br₁₂Cl₄ and Br₁₃Cl₂H. We assume that these differences in composition relate to the synthetic conditions in the factory and perhaps that small differences in color resulting from these different substitution patterns are intended.

MALDI and Nanospray ESI-MS of Polyethylene Glycol Additives

Surfactants like the polyethylene glycols (PEGs), with polar and nonpolar end groups, are used to keep acrylic polymer droplets dispersed in water (Keddie et al. 1995). As the paint film dries, these compounds become incompatible with the polymer mass and may appear at the surface or the reverse, as was shown by MALDI-MS (Digney-Peer et al. 2004). Hoogland (2004) describes comparative studies with MALDI-MS and ESI-MS on base and modified acrylic emulsions, liquid paints, dry paints, palettes, and samples from paintings. Extracts for mass spectrometry analysis were made by extracting dry and dried acrylic films with water. For MALDI analysis, the extract was mixed with a matrix solution, spotted on a target, and dried at room temperature. Ions were generated by a pulsed UV laser (337 nm). MALDI-MS on a time of flight (TOF) mass spectrometer shows the distribution of polyethylene glycol pseudomolecular ions that can be used to calculate the average molecular weight and to estimate the end-group mass. In this way it could be shown that the different investigated samples show a wide range of different end groups. Further studies to identify these end groups required a different analytical approach involving MS/MS. Good results were obtained with ESI in combination with nozzle-skimmer dissociation and analysis of the ions on a Quadrupole-TOFMS system. Since ESI could be performed with nanospray needles, the typical amount of solution could be limited to 10 microliters with a

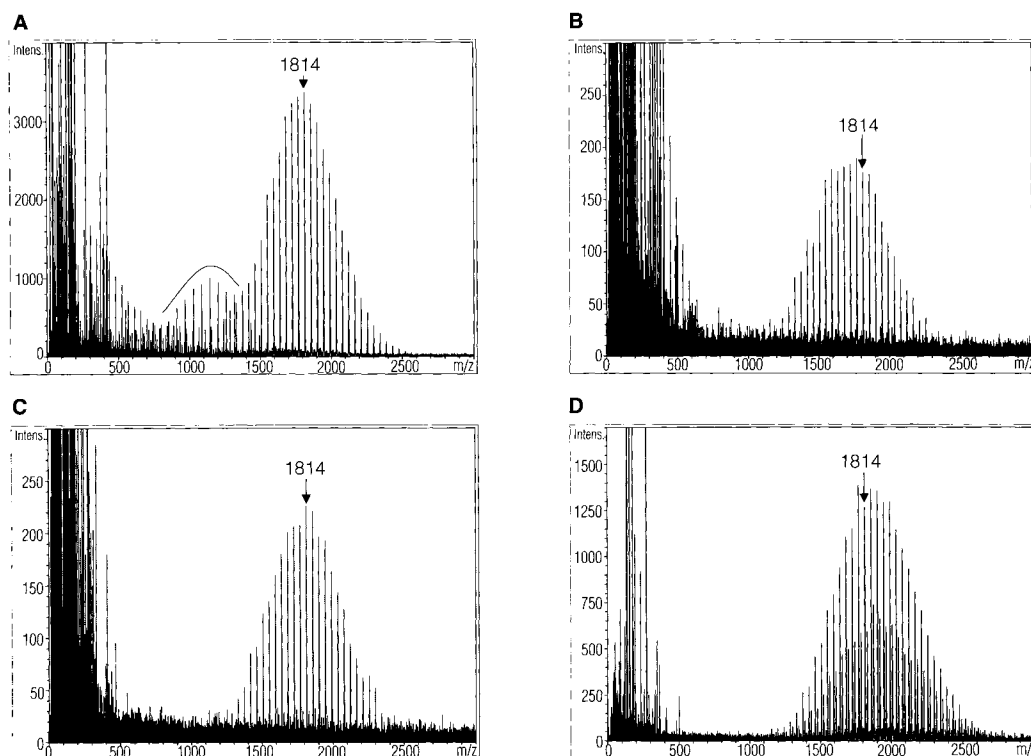
flow of 10–80 nl/minute. Under these conditions, it was even possible to analyze water extracts of minute paint chips from paintings.

Figure 4 shows a collage of MALDI-MS spectra from water extracts of a cream-colored paint from *Interior with a Picture* (1985–86) by Patrick Caulfield (fig. 4A) and several standard reference materials, namely Liquitex Gloss Medium (fig. 4B), Primal AC-634 (fig. 4C), and Triton X-405 (fig. 4D). It is immediately clear that the paint used by Caulfield contains a polyethylene glycol with a molecular-weight distribution very similar to those of all three reference materials, including Triton X-405. This is a PEG with an octylphenyl and a hydroxyl end group. Also visible in figure 4A (the water extract of the cream-colored paint) is a polypropylene glycol (PPG) with a maximum at m/z 1150 daltons (Da), and a series of peaks from a second PEG is also just visible, with a weight-average molar mass (M_w) at m/z 573 Da (hydroxyl end groups).

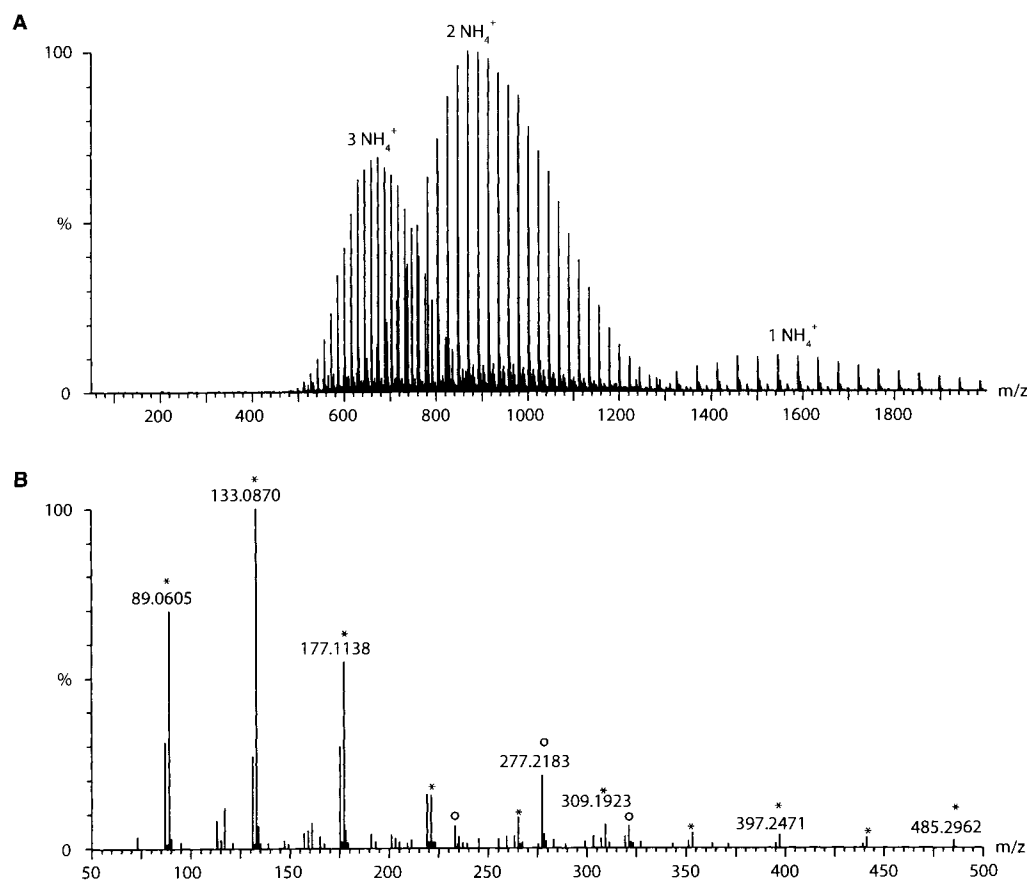
A white paint sample from another painting by Caulfield (*Grill*, 1988; Tate To7150) shows a different MALDI-MS profile of lower M_w PEGs, with end groups containing an octyl- and nonylphenyl end group (M_w 1262 and 1147 Da, respectively) and a doubly hydroxylated PEG with M_w at 798 Da (Hoogland and Boon, forthcoming). Another paint sample (dark green) from a third Caulfield (*Second Glass of Whiskey*, 1992; Tate To6727) contains yet another profile, which demonstrates that we have to expect different additive profiles on paintings reflecting different paints, aging conditions, and production periods of the paint materials (Hoogland and Boon, forthcoming).

Figure 5 shows the nanospray ESI-MS of Triton X-405. The spectrum shows the mass peak distribution of ammoniated singly, doubly, and triply charged ionic species typical of electrospray spectra of these types of compounds. The ion at m/z 1897 was chosen for MS/MS analysis; its lower mass fragment ion spectrum is shown in figure 5B. A series of peaks with the formula H-[OC₂H₄]_n is observed at m/z 89, and ions with a mass increment of m/z 44, which form one end of the PEG molecules. The other nonpolar end group representing the octylphenyl group is evidenced by m/z 277 (C₈H₁₇-C₆H₄-[OC₂H₄]₂) and some related ions that are 44 Da lower (m/z 233) or higher (m/z 321) than this mass. With this methodology, a large number of end groups could be identified in the samples investigated, including several types of sulfated end groups (Hoogland and Boon, forthcoming).

Both the MALDI and the ESI-MS approaches have great potential for direct analysis of microliter extracts from samples of paintings. Since nanospray ESI-MS is more sensitive and it is


FIGURE 4 MALDI-MS spectra:

(A) cream-colored paint from *Interior with a Picture* by Patrick Caulfield, (B) Liquitex modified base emulsion, (C) Primal AC-634 base emulsion, (D) Triton X-405. All samples show a polyethylene glycol distribution with approximately the same weight-average molar mass. The cream-colored paint sample also contains polypropylene glycol with a maximum at m/z 1150.


FIGURE 5 Nanospray ESI-MS spectrum of Triton X-405: (A) singly, doubly, and triply charged ammoniated ion species, (B) nanospray ESI-MS/MS spectrum of m/z 1897 (m/z 50–500 only is shown). Fragments are observed for both end groups: $\text{H}-[\text{OC}_2\text{H}_4]_n$ (*) and $\text{C}_8\text{H}_{17}-\text{C}_6\text{H}_4-[\text{OC}_2\text{H}_4]_n$ (o).

possible to calculate the molecular-weight data from the ion pattern, it has become our preferred method for unknown samples.

Nanospray ESI-MS of a Modern “Weeping” Oil Paint

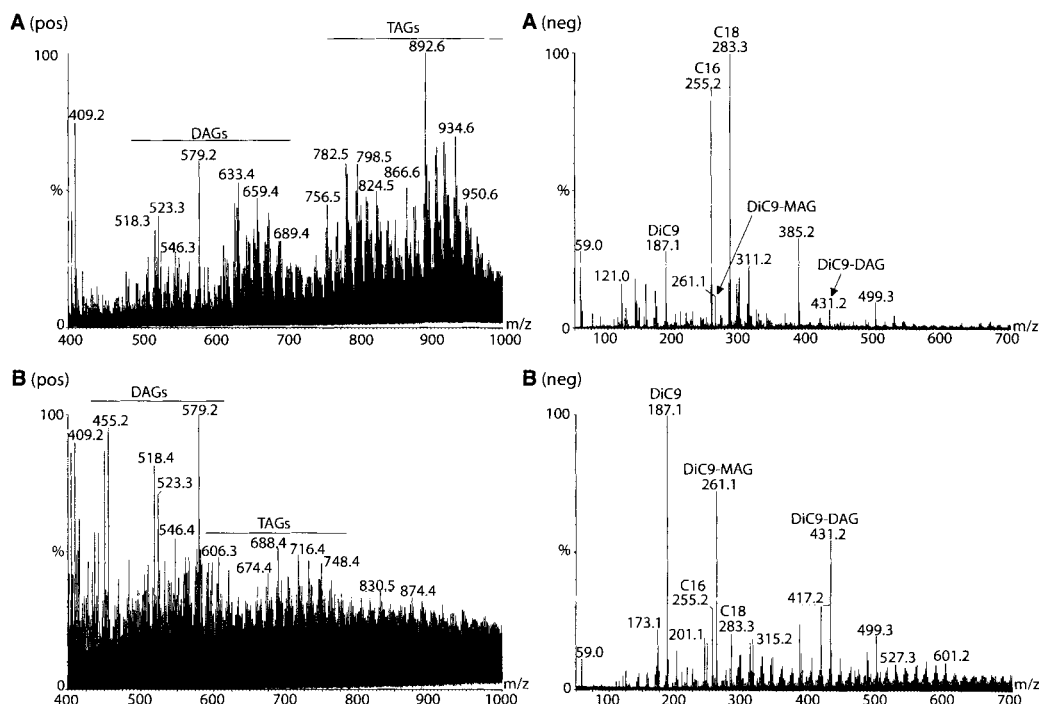
The potential of electrospray mass spectrometry with sub-microliter sample consumption was also explored for the identification of modern oil paints, as well as their extracts and hydrolysates. Earlier studies at AMOLF using ESI high-resolution mass spectrometry at higher flow rates or using Fourier transform ion cyclotron resonance mass spectrometry had shown the potential of ESI for identification of egg lipids (triglycerides and phospholipids) and their light-aging products in egg tempera paint dosimeters (van den Brink 2002), linseed oil (van den Berg 2002), and light-aged oil-asphalt model systems (Languri 2004). The methods for nanospray ESI-MS were developed on a Q-TOFMS system, which allows MS/MS studies and high-resolution measurements of the ions.

The case study presented involves a disturbing oil paint defect where a flesh-colored commercial paint, which although drying initially, about six years after completion of the works started to have a molten appearance and developed a very viscous, sticky layer on the paint surface (Hoogland, van der Horst, and Boon 2007). DTMS demonstrated that the strongest

differences between the bulk paint layer and this sticky top layer are the extractable (“volatile”) fractions. Therefore, nanospray ESI-MS of ethanol extracts was performed to investigate the nature of the materials accumulating in that top layer.³

Figure 6 depicts the ESI-MS data in the positive and negative modes of the extracts of the bulk of the paint layer (fig. 6A) and the sticky top layer (fig. 6B). The main categories in the paint extract are the triacylglycerols (TAGs) and the diacylglycerols (DAGs), with maximums at m/z 523 and 633 for the DAGs and 782 and 892 for the TAGs. These ions were matched with nanospray ESI-MS of hydrolysis data of the extracts. The higher m/z TAG and DAG distributions have two or three midchain-functionalized fatty acids, whereas the lower distributions contain one diacid moiety and one or two midchain-functionalized fatty acids. For example, m/z 866 represents the TAG of two palmitate moieties and one unsaturated midchain-functionalized C18 fatty acid moiety, and m/z 756 represents the TAG of two palmitate moieties and one azelate moiety. ESI-MS analysis of the paint in the negative mode shows that palmitic acid (m/z 255) and stearic acid (m/z 283) dominate the spectrum. Components originating from the oil due to oxidation and hydrolysis are significantly less pronounced; note the low-intensity azelaic acid (diC9, m/z 187), the monoacylglyceride

FIGURE 6 Nanospray ESI-MS analysis of (A) main paint layer and (B) its top layer in the positive and negative ion modes. The components observed in the positive mode are diacylglycerols (DAGs) and triacylglycerols (TAGs). In the negative mode, palmitate (C16), stearate (C18), and various derivatives of azelaic acid (diC9) are observed (diC9, diC9-MAG, and diC9-DAG).



of azelaic acid (diC9-MAG, m/z 261), and the diacylglyceride of azelaic acid (diC9-DAG, m/z 431).

The TAGs and DAGs of the top-layer extract in figure 6B are lower in mass and have significantly different relative intensities compared to those observed in the paint layer. For the TAGs, the main distributions can be assigned to two diacids and one midchain-oxygen-functionalized fatty acid moiety and three diacids. The DAGs observed contain one diacid and one midchain-oxygen-functionalized fatty acid moiety or two diacids. These compounds suggest that more polar fractions are accumulating in the top layer. This explanation is supported by the major components in the negative mode. Most prominent in the top layer (fig. 6B) are azelaic acid (diC9) and its acyl glycerides (diC9-MAG and diC9-DAG), whereas the saturated fatty acids are significantly lower in intensity there, compared to the bulk of the paint layer.

There is clearly a much larger amount of loosely bound polar oxidation products in the top layer of the paint. We have proposed elsewhere (Hoogland, van der Horst, and Boon 2007) that these compounds are expelled from the main paint mass by a physical mechanism pointing to incompatibility of polar substances in a much less polar main mass of paint. The loose consistency of the top layer and its stickiness point to an absence of stabilizing substances or processes, for example, the absence of metal coordination of the various acid groups. As a consequence, the top layer is weeping and developing distortions in the impasto and ugly drips on the painting.

Chemical drying of contemporary oil and alkyd paints and the innovative water-based oil paints still poses many questions, especially when defects are appearing so soon after the paints dry. Nanospray ESI-MS analysis of microliter extracts not only is useful for additive determination in emulsion acrylate paints but is demonstrated here as a new tool in oil-paint analysis.

Conclusion

Mass spectrometry is in its infancy as far as applications to paint studies are concerned. The technique is still developing, thus further expanding the potential for analytical studies in art and archaeology. Microscopy mass spectrometry is a valuable addition to the field in that it allows the investigation of the microscopic distribution of organic and inorganic constituents in the paint layers. This is even more important in the investigation of the aging phenomena that often take place on

interfaces. Mass spectrometry will be vital in studies of modern paints and painting because of nontraditional materials used in making these art objects and the rapid changes in paint composition. The group at AMOLF has been pioneering applications of mass spectrometry in the characterization of paint constituents. Since this research effort at AMOLF recently ended (in 2006), it is hoped that these efforts will stimulate the field to apply and use mass spectrometry to solve the many molecular-level problems in conservation.

Acknowledgments

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Appendix: Experimental Method

- The instrumentation and procedures used for DTMS and LDI-MS analysis are described in Boon and Learner (2002).
- Instrumentation and procedures used for MALDI-MS and nanospray ESI-MS analysis are described in Hoogland and Boon (forthcoming).
- Nanospray ESI-MS was performed on a Micromass Q-TOFMS.
- For ESI-MS analysis of polyethylene glycol additives, samples were extracted with water. Three parts of the water extract was mixed with seven parts of methanol; 10 mM ammonium acetate was used to aid ionization. The mixture was sprayed at a flow of about 10–80 nL/minute⁻¹.
- For ESI-MS analysis of the weeping oil, paint samples were extracted with ethanol. Three parts of the ethanol extract was mixed with seven parts of dichloromethane; 10 mM ammonium acetate was used to aid ionization. The mixture was sprayed at a flow of about 200 nL/minute⁻¹.

Notes

- 1 Personal communication with Mark Golden, 2001.
- 2 Institute for Atomic and Molecular Physics, one of the five research institutes of the Dutch Foundation for Fundamental Research on Matter (FOM).
- 3 For a fuller description, see the poster “Liquefying Oil Paint in Some Late-Twentieth-Century Paintings” (Hoogland, van der Horst, and Boon 2007), pp. 282–83 in this volume.

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The Macro- and Microassessment of Physical and Aging Properties in Modern Paints

Oscar Chiantore and Dominique Scalarone

Abstract: *The aging of modern artists' paints occurs through a combination of physical processes and chemical reactions that ultimately affect the appearance of the surface, the morphology of the upper film layer, and the reactivity of the polymeric binder. These chemical and physical changes can be assessed with techniques used for the characterization of surfaces. After coalescence of the water-dispersed polymer particles, the films obtained from acrylic paints, for instance, develop surface heterogeneities deriving from migration of additives and from the photo-oxidation reactions that induce, at the same time, loss of low-molecular-weight by-products together with formation of a cross-linked polymeric network. The overall changes in the polymer films are quantified by macroscopic chemical and surface techniques. However, greater understanding is obtained when chemical and morphological mapping is carried out on the micrometric and submicrometric level. Fourier transform infrared (FTIR) microspectroscopy in attenuated total reflectance (ATR) mode allows the measurement of chemical heterogeneity with approximately 50 μm lateral resolution, whereas the surface appearance may be easily monitored by atomic force microscopy (AFM) in the micron and submicron range. Chemical information on the inner parts of paint layers is also important, as the effects of aging and of conservation treatments develop from the paint surfaces toward the interior. Depth-resolved analyses of paint layers are possible with confocal Raman microspectroscopy. The physical characterization of paints with micron and submicron resolution allows us to assess the influence of different aging conditions, and the results from local film properties can be correlated with the chemical and structural changes of paints.*

Introduction

The binder for modern paints can contain a natural, synthetic, or semisynthetic polymer (i.e., a natural compound that has been chemically modified). A number of different polymers are mixed with pigments to create paint and are then applied in the form of thin films onto appropriate supports chosen by the artist. The chemical structures of paints are grouped into families such as oils, cellulose, vinyls, acrylics, alkyds, polyurethanes, and acrylic-urethanes, to mention only the most important ones. The paints applied in modern or contemporary works of art may be specifically produced as artists' colors, but they may also be commercial household paints that were adopted by artists for reasons such as practicality and availability (Crook and Learner 2000).

Aging of such modern paints occurs through a combination of physical processes and chemical reactions that will, ultimately, affect the appearance of the surface, since both the morphology of the upper film layer and the structure of the polymeric binder change over time. More precisely, the aging of a polymer-based paint is a degradation process that depends on intrinsic factors such as the paint formulation and the chemical nature of components, and also on external factors produced by interactions with the environment and with other materials. Paint formulations can be extremely complex, involving a number of components, each with its own characteristics. Variables include the chemical composition of the polymeric binder in terms of its structural units; the relative amount of each structural unit when the binder is a copolymer; the molecular weight and molecular weight distribution of the polymeric components; the type, function, and amount of additive in the paint; and the liquid medium (e.g., organic solvent or water) used for dilution and application.

The most important external cause of degradation is usually the environment. Under natural or artificial conditions, light, oxygen from the air, temperature, and relative humidity are continuously interacting with works of art and with any painted surface. The paint's sensitivity to natural external factors may be further affected by the presence of gaseous pollutants and particulate matter in the atmosphere, which enhance natural degradation processes or induce new chemical reactions through the introduction of new reactive chemical species and the deposition of dirt and soil on the surfaces. Contemporary works of art, and therefore all their painted surfaces, are by their nature quite often exposed to uncontrolled environmental conditions, from private collections to public spaces, in indoor or outdoor exhibitions.

Aging Properties of Paints

The chemical aging of polymer paints can occur through a series of oxidation and elimination reactions, covalent bond scissions, and intermolecular cross-linking reactions producing structural and molecular changes (Grassie and Scott 1985). Side elimination reactions typically occur in cellulosic and vinyl binders, with production of acidic gaseous compounds, such as nitric acid from cellulose nitrates, acetic acid from cellulose acetates and polyvinyl acetate, and hydrochloric acid from polyvinyl chloride. Oxidation reactions develop to some degree in all organic materials. In polymer paints they give rise to increased polarity of the structure, which becomes more reactive and more sensitive to water and other polar solvents. Paint discoloration due to the formation of chromophore groups is also a consequence of the overall degradation process.

The oxidation of polymeric compounds is a chain reaction process occurring via a radical mechanism, and among the various reactions a very important one is the rupture of the main-chain covalent bonds from the carbon-carbon "backbone." If this occurs, the molecular weight of the polymer decreases, and this can have severe effects on adhesion and on all mechanical properties. Scission reactions can also bring about the formation of short fragments (i.e., liquids and even gases) that can accumulate on the paint's surface, which can then become sticky and further attract dust. Other oxidative reactions are intermolecular couplings of polymeric radicals, giving rise to a cross-linked material. If this occurs, solubility then decreases, until eventually all the polymer phase becomes insoluble. The physical behavior of a paint changes accordingly, with increasing hardness, stress resistance, and embrittlement.

Physical aging also develops in paint, affecting mainly its optical characteristics and mechanical properties, but it also influences the reactivity of the surfaces. Physical aging obviously depends on the chemical and molecular structure of the formulations and the environmental conditions; it is mainly correlated to the molecular mobility of paint components (Struik 1978). Therefore, additives in general and plasticizers in particular, which are typically present in acrylic emulsions and in vinyl polymers, tend to migrate to surfaces and interfaces. The result is staining, loss of flexibility, and an increase of dirt pickup. Chain-segment relaxations in polymer molecules may induce crystallization, with volume shrinkage, hardening of the material, and change of optical properties like transparency and gloss (McGlinchey 1993). In cases where the paint surfaces are in contact with other materials, extraction of paint components may take place due to molecular mobility and preferential solubility. Macroscopic results of such physical processes can include cracking and delamination of paint films.

The overall structural and molecular changes occurring during the degradation of polymer paints are normally revealed and quantified by spectroscopic techniques, such as infrared spectroscopy, thermal analysis, and molecular-weight measurements (Chiantore, Scalarone, and Learner 2003). Moreover, even small amounts of oxidative aging can induce enough molecular transformations to severely affect physical properties. The loss of mechanical properties is revealed by tensile measurements, as demonstrated by results (shown in fig. 1) obtained on films from an aqueous dispersion of an ethyl acrylate-methyl methacrylate copolymer exposed to artificial sunlight. The elastic modulus increases after this light

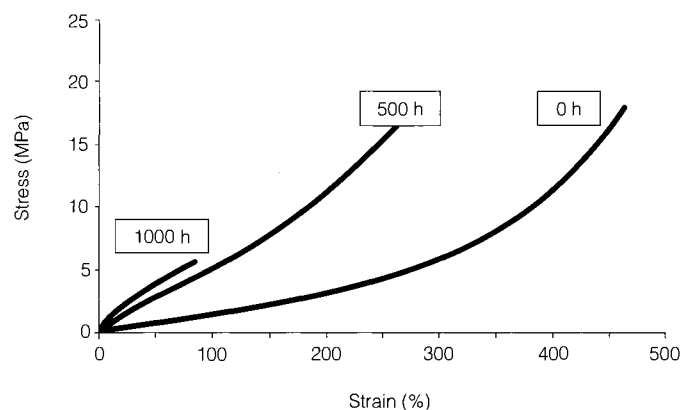


FIGURE 1 Effects of accelerated light aging (xenon lamp, $\lambda > 295$ nm) on the stress-strain curves of a Primal (Rohm and Haas) ethyl acrylate-methyl methacrylate copolymer latex acrylic film.

exposure, while elongation and tensile strength decrease, indicating that the film becomes weak and brittle. Infrared spectroscopic measurements on the same polymer films showed limited chemical alteration.

The aging process of paints typically develops on the surfaces that are exposed to light, oxygen, and dust and other particulate matter, and from there eventually proceeds to the interior of the paint film. On weathering, the paint surface changes over time in chemical composition as well as in micro-morphology and optical appearance. Surface polarity and reactivity increase, while at the same time molecular modifications generate stresses, cracks, and failure of adhesion to the lower layers. Low-molecular-weight compounds formed in scission reactions can accumulate on the surfaces, causing the surface to become tacky and further contributing to the incorporation of dust and soil. The development of such modifications across the surfaces is often inhomogeneous, depending on the film structure, the distribution of additives, and the effects of pigments. As a consequence, chemical and/or physical surface heterogeneity appears, and its characterization requires advanced levels of details on the lateral scale. At the same time, aging and degradation reactions proceed from the surface to the inner layers of the paint, forming gradients of chemical compositions, structures, and molecular rearrangements, which must be investigated with depth-profiling analytical techniques.

Surface Characterization

There are several ways of obtaining surface characterization at the microscale level, each of which involves specific and often quite expensive instrumentation. Point information is perhaps most easily obtained with a spectrophotometer, where the radiation is focused and detected through an optical microscope. Larger sample areas may be investigated when scanning devices are available for mapping along selected lines. Finally, more advanced techniques make use of detector arrays for fast acquisition of the required information from significant and representative surface areas, in a real imaging mode. Depending on the modes available for probing the surface, it may be possible to map chemical, morphological, or physical features. Such types of surface characterization are most useful for monitoring the aging processes and the effects of conservation treatments in works of art.

The Film Formation Process

Modern emulsion paints are water-based formulations that produce a dry paint film after application on the substrate and evaporation of water. Film formation in such systems is

a complex process that proceeds through several steps. In the wet state, spherical polymer particles of micron size dispersed in water are stabilized by a homogeneous distribution of surfactant molecules on their surfaces. As water evaporates, the polymer particles come into contact to form close-packed layered arrays where water is still present in the interparticle spaces. As the polymer particles come into contact, surfactant desorption begins. Film formation follows, with progressive particle deformation (from spherical to hexagonal), in order to maximize the interparticle contact. Surfactant molecules continue to be extruded from the particle packing to the interfaces, in particular at the paint-air interface. Full coalescence is finally reached when interdiffusion of polymer molecules occurs between the particles that are in contact: individual particles merge and disappear, and a theoretically homogeneous isotropic film is formed (Tzitzinou et al. 1999).

Film formation in such systems is dependent on a complex interaction of several factors, such as the nature of the polymer particles and the chemical structure of the surfactant molecules. Considering the influence of surfactants, one type commonly used in latex paints is polyethoxylated, nonionic surfactants; members of the homologous series differ in the molecular weights of the hydrophilic portion of the molecules. In this case, the lower the molecular weight of the surfactant, the more hydrophobic it tends to be, which leads to increased solubility in the polymeric film. Any dissolved surfactant acts as a polymer plasticizer and facilitates the film formation process, as well as increasing film hydrophilicity and water interaction with the polymer film.

The size and distribution of particles influence the particle packing and quality of the resulting film. Smaller particles with a narrow size distribution favor faster coalescence and give more homogeneous films than do the larger particles. Voids and defects in the film structure, resulting from imperfect particle packing, can cause blistering and film discoloration and facilitate the diffusion of small molecules (Eckersley and Rudin 1990). Packing efficiency and particle coalescence are also favored by polymers with a lower glass transition temperature (T_g).

The migration of surfactants from water-based polymer films is an important process affecting the quality of a paint film. The distribution of the surfactants depends on the interfacial tensions involved. For example, if the film-substrate surface tension is too high, the surfactant molecules will tend to order themselves at this interface in order to reduce the energy. Accumulation of surfactant molecules at the paint surface will change its optical properties, water repellency,

and photostability, whereas accumulation at the film-substrate interface will cause loss of adhesion between the paint layer and the substrate. For the above reasons, film formation of latex-based polymer paints and coatings has been the subject of many studies, focusing particularly on the migration and distribution of surfactant molecules.

Fourier Transform Infrared Spectroscopy

Investigation of paint film surfaces, either their changes with time or for conservation treatment, can be successfully performed with Fourier transform infrared (FTIR) spectroscopy in attenuated total reflection (ATR) mode. This technique suffers from the limits intrinsic to infrared analysis of materials; that is, often it is possible to identify only the class of organic compounds (e.g., oils, acrylics, vinyls, etc.), not their precise chemical structure, and inorganic components may exhibit interfering absorptions. However, ATR-FTIR has many advantages: there is no sample preparation and it is a nondestructive technique; it gives molecular information on inorganic and organic components; and, when it is used in conjunction with a microscope, the lateral resolution can be less than 50 μm . The appearance of acrylic films, when cast on glass, changes because of surfactant accumulation on the surface. And infrared ATR spectra taken on selected spots show the typical absorption bands of the acrylic binder together with the components coming from the surfactant (Learner, Chiantore, and Scalarone 2002; Scalarone and Chiantore 2005).

The chemical species on the surfaces can be monitored with time, as shown in figure 2 by the ATR spectra of a commercial acrylic artists' color (a complete paint formulation including pigment), submitted to different types and periods of aging. In the dry, unaged film, only the absorption bands of the acrylic polymer are visible, whereas on the paint surfaces with more than five years of natural aging under laboratory exposure, and after 32 weeks of artificial-light exposure, the bands of surfactants are easily detected. The latter condition corresponds to a large number of years of exposure in museum conditions, and the surfactant absorption intensities here indicate a lower surface concentration than in the other case; that is, the aging time is long enough to have reached the stage when the surfactant molecules on the surface are being slowly degraded. In practice, there is an initial slow increase of surfactant concentration on the paint surface, because the molecules migrate to the film-air interface, followed by a progressive decrease, leading to total disappearance because of photo-oxidative degradation. The rates of the two opposing processes will depend on factors such as the paint film thick-

ness and composition and the type of light and atmospheric conditions.

In order to monitor processes in less time than is required with light-aging treatments, aging and diffusion dynamics of surfactants in latex-based paint films have also been investigated with thermal aging. In these experiments, performed on a laboratory-made poly(methyl methacrylate-co-butylacrylate) latex, ATR spectra were collected through the infrared microscope and paint areas of $700 \times 700 \mu\text{m}$ have been scanned with the instrument's motorized stage. The relative concentration of surfactant at each point measured on the surface has been calculated from the height ratio of the peak at 1108 cm^{-1} , which is diagnostic of a polyethoxylated-type surfactant, divided by the 1238 cm^{-1} acrylic peak. Chemical mapping of the surface can be obtained by correlating the concentration data to a color scale. Figure 3 shows a comparison of chemical maps between the same acrylic film after drying, after two hours of thermal treatment at 120°C , and after subsequent rinsing with water. It is clear that the unaged film has a quite homogeneous color, which corresponds to low surfactant concentration, whereas thermal aging has produced high concentrations of surfactant molecules unevenly distributed after just two hours. After the water rinse, the surfactant has been removed from the surface, and the concentration map is more similar to the initial situation. The difference between

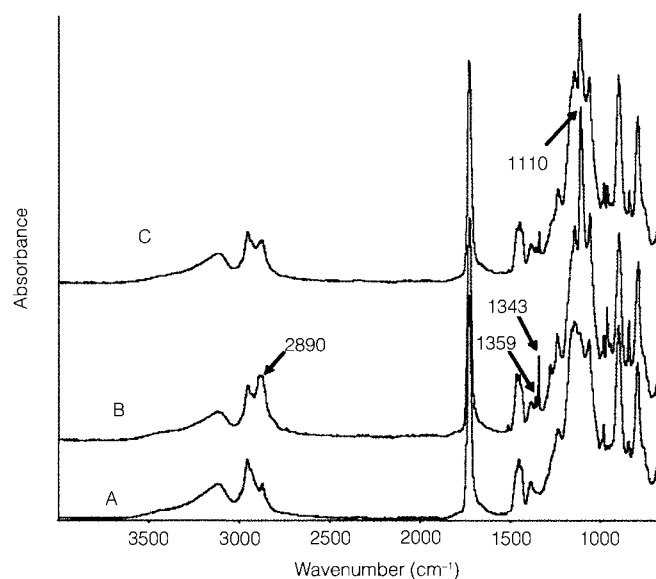


FIGURE 2 ATR-FTIR spectra of Cryla (Daler Rowney) yellow ochre acrylic color: (A) unaged, (B) naturally aged >5 years, (C) light aged ($\lambda > 400 \text{ nm}$) 32 weeks.

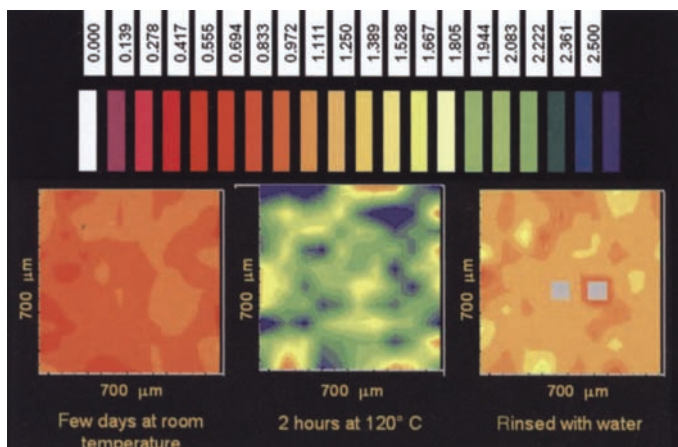


FIGURE 3 Chemical mapping by micro-ATR of surfactant concentration on acrylic films made from poly(methyl methacrylate-co-butylacrylate) latex prepared with SDS and polyethoxylated-type surfactant.

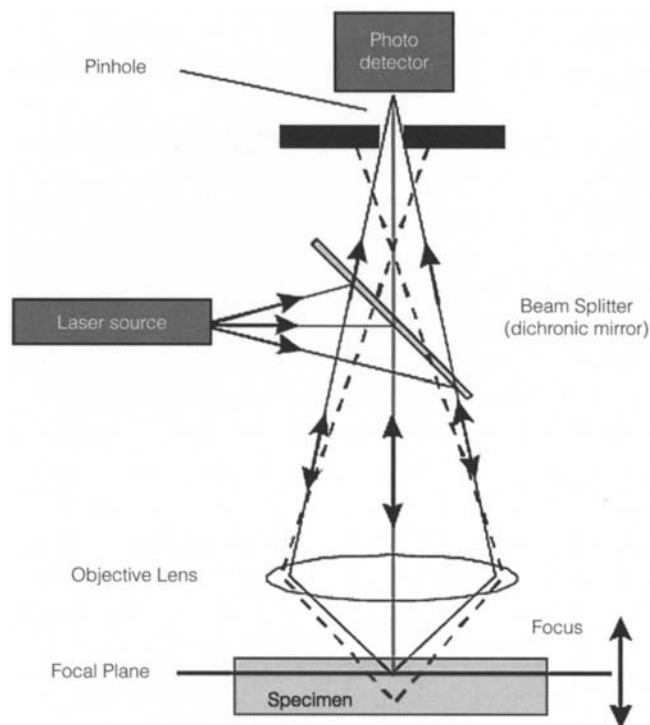


FIGURE 4 Scheme of confocal Raman microspectroscopy. The broken line indicates the out-of-focus laser light beam, which cannot reach the detector. (Marton et al. 2005; reprinted with permission.)

the fresh, dry film and the film after the water rinse is attributed to the surfactant concentration on the layers immediately below the surface (those not reached by the washing), being higher than before the aging. This is detected by ATR, which has a penetration depth of a few microns.

Confocal Raman Microspectroscopy

A complete picture of the chemical distribution of species within a paint film may be obtained with measurements on cross sections; however, these require a significant amount of sampling and film manipulation. A better solution for clear polymer films is confocal Raman microspectroscopy, which is a powerful characterization tool. This technique allows one to acquire Raman spectra of different layers below the film surface just by tuning the plane of focus of the microscopy system, as shown schematically in figure 4. Penetration depths of up to hundreds of microns are possible, which permits chemical information on the inner paint layers to be obtained. In one study of acrylic films (Belaroui et al. 2003), the concentration distribution of surfactant was determined by application of confocal Raman microspectroscopy, showing that the higher concentrations at the interfaces gradually decrease toward the central layers (fig. 5). Mapping of the Raman intensities at constant depth has also been used to image the presence of aggregates in the bulk of the films (Belaroui et al. 2003).

Depth profiling of chemical processes taking place in paint films may be followed by confocal Raman microspectroscopy in the same way. In one study of the drying of alkyd paints, the time dependence of the gradual consumption of carbon-carbon double bonds was monitored at different depths from the surface (Marton et al. 2005). Using a similar approach, chemical degradation processes can be mapped, if suitable diagnostic bands are available in the sample.

Atomic Force Microscopy

Chemical and/or physical aging, as well as cleaning/conservation treatments, produces morphological changes on the paint surfaces. These can be conveniently investigated with atomic force microscopy (AFM). This technique works by tip-probing surface points at the nanoscale level, and by scanning a selected surface area. Depending on the way the experiment is set up and on the type of signal recorded, different types of images are obtained. Each one bears different information: topography, frictional forces, and phases. AFM is, therefore, capable of detecting, at the submicron level, surface changes occurring during film formation of latex-based paints, the migration of additives, cleaning treatments, and degradation reactions, all

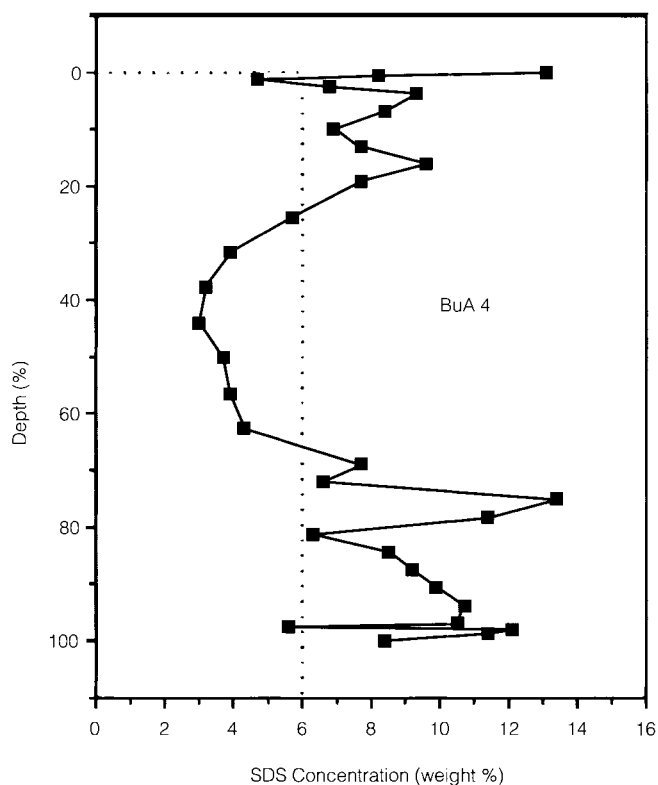
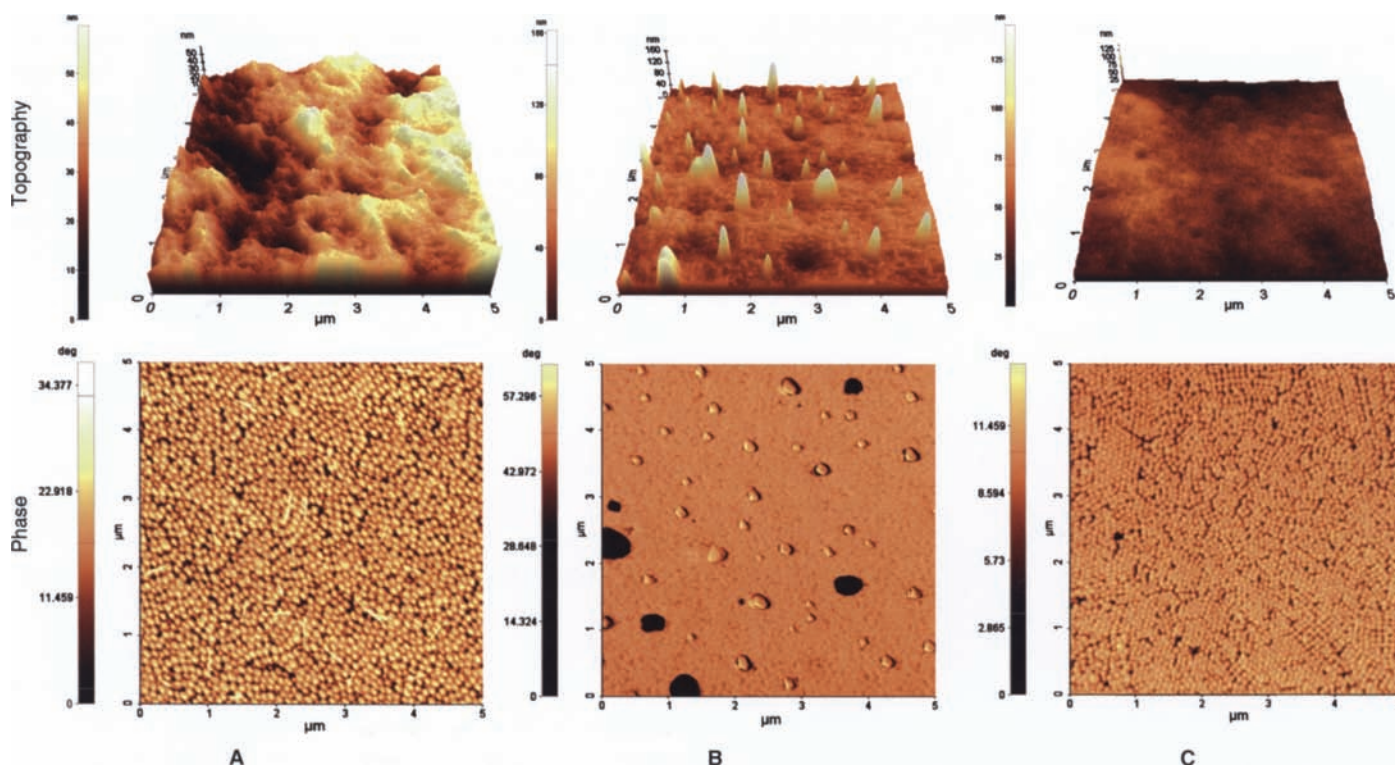


FIGURE 5 Concentration profiles of sodium dodecyl sulfate (SDS) surfactant molecules (an anionic surfactant) in an acrylic film (butyl acrylate/acrylic acid [96:4] copolymer) determined by confocal Raman microspectrometry. Average surfactant concentration was 6% by weight; air at 0% depth; substrate (polyethylene) at 100%. (Belaroui et al. 2003, reprinted with permission.)

of which may affect the roughness or hardness of the upper film layers. The interpretation of morphologies is simplified by the comparison between topography and phase images, as shown by the AFM images in figure 6. There, great differences appear after twenty-four hours of thermal aging, and after subsequent washing with water, in a film obtained from an experimental laboratory-made acrylo-styrenic latex. The topography images (top row) highlight the surface roughness, whereas the images acquired in phase mode (bottom row) are better suited, in this case, to visualizing the polymer particles.

FIGURE 6 Topography (top) and phase (bottom) AFM images of a laboratory-made acrylo-styrenic latex film. The same film is shown after (A) one week of drying, (B) 24 hours at 120° C, (C) rinsing the copolymer in water.



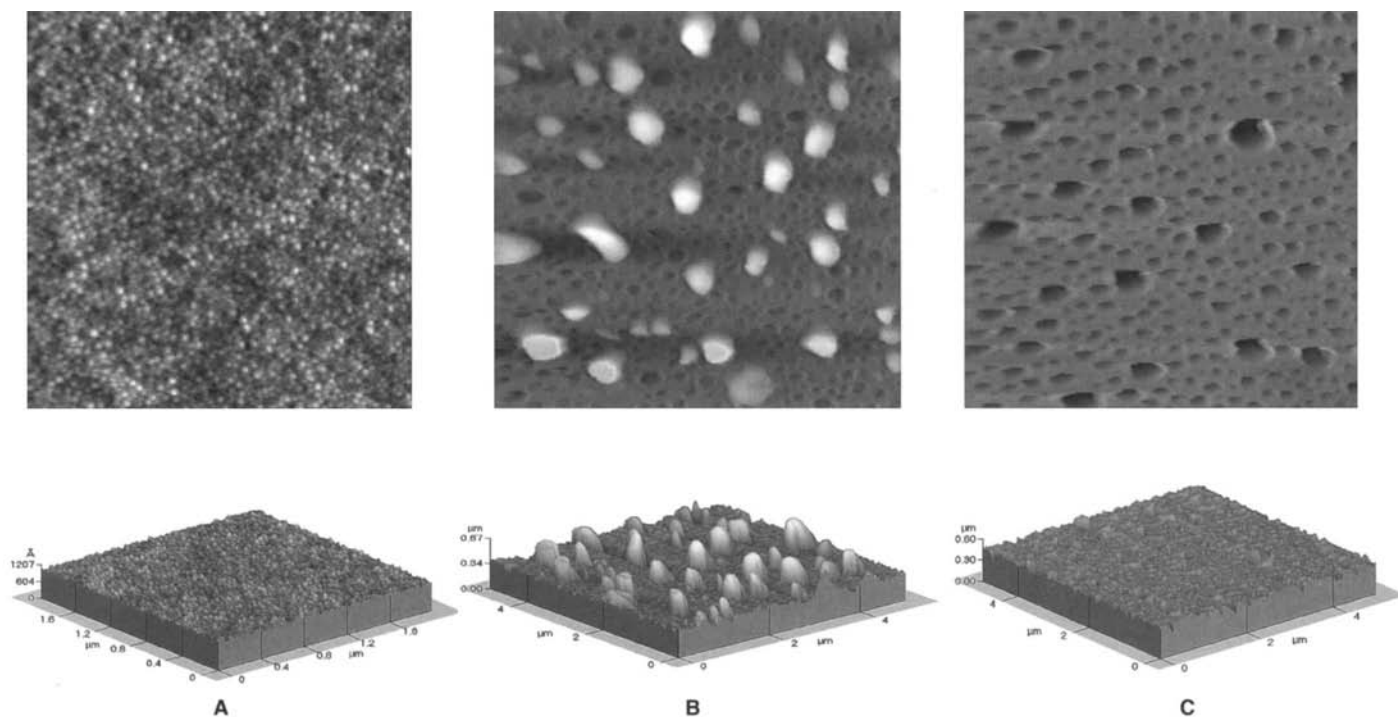


FIGURE 7 AFM images of an experimental methyl methacrylate-butyl acrylate copolymer film, formulated with 4.6% (by weight) sodium dodecyl sulfate surfactant; T_g of copolymer = 10°C : (A) dry film, (B) after thermal treatment, 2 hours at 120°C , (C) after thermal treatment and rinsed in water for 5 minutes.

phy images clearly demonstrate the effects of the treatments: the surfactants that have migrated to the surface form isolated blobs, or protrusions, due to the high local concentrations. When the surfactants are removed by the water, a smoother surface is recovered. An interesting finding is that, due to the particular microstructure of the polymer particles in this latex, which is formed by a styrenic shell, the high glass transition temperature of the external shell has prevented particle coalescence and the polymer particles are still visible after heating.

With more traditional types of latex particles, and typical T_g values of paints around room temperature or lower, coalescence takes place completely, and this is visible in the AFM images. Figure 7 shows an example of an acrylic emulsion copolymer composition made with methyl methacrylate, butyl acrylate, and a combination of SDS with a polyethoxylated surfactant. Complete coalescence is obtained rapidly as a result of the thermal treatment, while at the same time the

surfactant molecules appear to be abruptly extruded from the film, forming blobs and leaving craters on the surface. This type of measurement can therefore be used to monitor how aging, diffusion of small molecules, and solvent treatments will affect the morphology of paint surfaces. This is relevant because roughness influences gloss, and it can affect the interaction of the paint substrates with subsequently deposited or applied solid and liquid particles.

In addition to morphological characterization, mechanical mapping of surfaces can also be done using specifically calibrated AFM systems. Hardness, elastic moduli, scratch resistance, fracture toughness, and frictional and visco-elastic properties of film surfaces can therefore be calculated. For typical paint films, measurements with micron depth resolution are sufficient and can be obtained with microindentation instruments. These are computer-controlled diamond indenters where the tip penetration from an applied load is measured continuously in a full loading and unloading cycle. The total deformation is the sum of the plastic, permanent component, and elastic component, which is recovered in the unloading part of the cycle. The microhardness data and other mechanical parameters may be correlated with the chemical transformations during aging and treatments of the materials, in particular with degradation or curing of polymer molecules

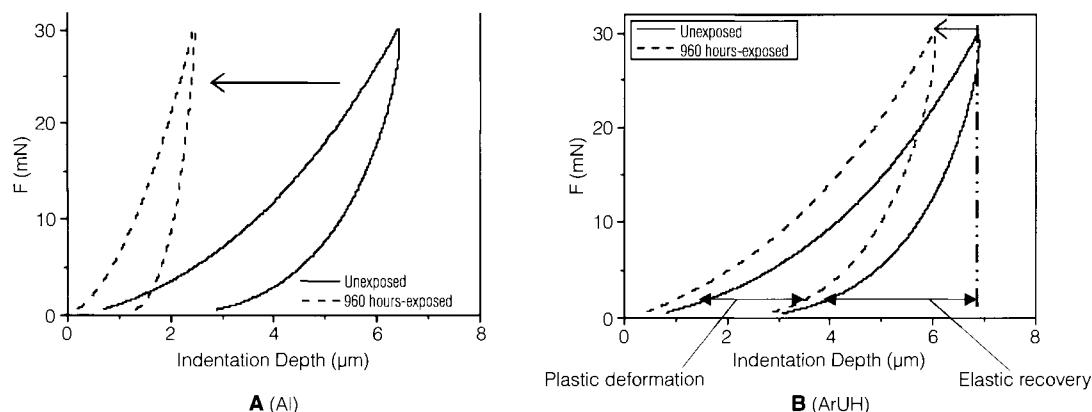


FIGURE 8 Microindentation curves of acrylic-urethane paint films. Change in the loading-unloading curves for the effect of accelerated UV aging: (A) aliphatic urethane, no light stabilizers; (B) aromatic urethane, light stabilizers added. (Adapted from Lee and Kim 2006, with permission.)

and with the related morphological changes. The migration of plasticizing molecules, or the different cross-linking densities across the film surface and depth, is revealed through the localized mechanical properties on the film.

An example of the results obtained from these measurements on modern paints is seen in figure 8. In different acrylic-urethane films exposed to artificial weathering, the extent of cross-linking induced by the light exposure depends on the paint formulations. The resulting increased hardness gives lower plastic and elastic deformations of the surface layers. The progressive photo-oxidation increases the cross-linking density of the surface layer. Films become brittle, while tensile strength and adhesion to the substrate both decrease. With parallel AFM measurements, it is shown that on the same films the exposure to light produces increased surface roughness, resulting in a reduction in the gloss of the paint.

Other Techniques

Other surface characterization techniques introduced in recent years are potentially useful for paint characterization and investigating conservation treatments (Slough et al. 2005). Promising results in studies of polymer paints and weathering processes have been reported with microthermal analyses performed with a modified AFM apparatus where a controlled heat source and a detector are added as a second tip for simultaneous observation of morphology and thermal properties of the materials surface (Hässler and Mühlen 2000). In addition to the topography image from the atomic microscope, a second image is obtained based on the material thermal conductivity at different points. Hard and soft regions, which have different thermal properties, may be distinguished and associated with heterogeneous processes during curing or degradation or with

sample components' immiscibility. Currently, however, testing opportunities are restricted due to the limited availability of commercial instrumentation.

Conclusion

It has been demonstrated that surface and depth characterization of modern artists' paints can be performed at micron- and submicron-level resolutions, allowing one to obtain a detailed description of the chemical and physical properties of the material and how it varies across the surface and through the underlying layers. Thus, correlations and parallels between chemical structures, compositions, and reactivity and the physical behavior of paints can be immediately highlighted. The different techniques have straightforward applications to the investigation of film-formation processes, quality of paint surfaces, mechanisms of degradation, chemical and physical aging, and interactions with gas and liquids, as well as to conservation treatments.

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The Identification of Synthetic Organic Pigments by FTIR and DTMS

Suzanne Quillen Lomax, Michael R. Schilling, and Thomas J. S. Learner

Abstract: A group of more than 160 synthetic organic pigments was acquired from pigment manufacturers. These pigments span the range of azo and non-azo colorants used in architectural, automotive, and artists' paints; printing inks; and for the coloration of plastics and textiles. The pigments were examined by Fourier transform infrared (FTIR) spectroscopy and direct temperature-resolved mass spectrometry (DTMS). These techniques proved useful in combination in identifying pigments. Infrared spectroscopy provided information about the pigment class and could, in most cases, be used to identify the individual dry pigment. DTMS at moderate energy (70 eV) gave a good combination of molecular ion and fragmentation, useful in interpreting the spectrum. The DTMS technique worked well for pigments that were not lakes (e.g., salts), including neutral organics and organometallics. DTMS was also useful for pigments that, because of inherent stability due to conjugation, do not easily pyrolyze, such as quinacridones.

Introduction

Synthetic organic pigments are carbocyclic, ring-containing manufactured pigments. They can prove difficult to analyze through techniques commonly used to identify mineral pigments, and their high tinting strength means that they are frequently present in low quantities in paint. X-ray diffraction (XRD) often gives a pattern characteristic of the fillers and extenders in the paint, but not of the colorants. The small particle size of these pigments makes examination by polarized light microscopy virtually impossible. X-ray fluorescence spectrometry (XRF) and scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) also do not give useful characteristic elemental profiles for synthetic organic

pigments. Pyrolysis gas chromatography (PyGC) and pyrolysis gas chromatography/mass spectrometry (PyGC/MS) have also been used in the examination of these pigments. The most successful identifications of these pigments have used a combination of these techniques. (For a more detailed discussion of techniques used to examine synthetic organic pigments see Lomax and Learner 2006.)

Fourier transform infrared (FTIR) spectroscopy has been used in the analysis of paints. This technique allows for determination of the functional groups present in a molecule, and the spectrum of an unknown can then be compared to a spectrum in a reference library. Spectra of paints are often complicated, since contributions from the binder, pigment, and in particular extenders often have overlapping absorbances. Usually the pure pigments give sharp, strong absorbances. Learner has used infrared analysis to examine the binders and pigments in commercial paints, as well as in samples removed from paintings in the Tate collection (Learner 2004). Infrared spectroscopy has also been used to identify synthetic organic pigments in works by Alfred Pellán, including PY1, PY3, PO15, PR1, PR3, and PR4 (Corbeil, Moffatt, and Miller 1994). A recent study by Jönsson and Learner (2004) showed some simple methods of sample pretreatment to enhance the detection of diagnostic peaks from organic pigments in paints, such as extracting organic azo pigments in organic solvents or removing the strong absorbance of chalk with dilute hydrochloric acid.

Some synthetic organic pigments have been examined by pyrolysis and PyGC/MS. Sonoda used this technique—as well as XRF, XRD, and FTIR spectroscopy—to look at a series of paints containing monoazo and disazo pigments, phthalocyanines, and quinacridones, and found that there were limitations in the detection of chemically and thermally stable pigments

(Sonoda 1999). Learner used PyGC/MS to look at acrylic paints as well as other modern binders (Learner 2004).

Direct temperature resolved mass spectrometry (DTMS) is an in-source pyrolysis mass spectrometry (PyMS) technique employing a temperature-programmable sample probe. The principal advantage to this modification over more standard PyMS systems is that the temperature ramp on the probe can often be used to separate out various components in heterogeneous samples, such as organic pigment and binding medium in paint.

The DTMS technique has been applied to the examination of varnishes and components of paint (Boon 1992; Scalarone et al. 2003). Typically, low-molecular-weight materials volatilize at lower temperatures, whereas polymeric materials pyrolyze at higher temperatures. Regarding the analysis of paints, DTMS can provide mass spectra of synthetic organic pigments as well as characteristic fragments from the binding medium, as the temperature ramp provides a degree of separation of the spectra for the medium, additives, and pigments (Boon, Keune, and Learner 2002; Boon and Learner 2002).

Most classes of synthetic organic pigments appear well suited to analysis by DTMS (Learner 2004). DTMS was used to examine a range of organic pigments, including red, orange, and yellow azo pigments; red and violet quinacridones; and blue and green phthalocyanines. This technique, in combination with FTIR spectroscopy, was used to identify PR9, PR170, PY3, and PR3 from paint samples removed from works of art. An earlier study (Boon and Learner 2002) examined paints containing arylide yellow pigments PY3, PY73, and PY74, as well as the much-higher-molecular-weight phthalocyanine green PG7. These analyses were performed at 16 eV in order to decrease the amount of fragmentation, thereby increasing the molecular ion abundance to facilitate the identification of pigments in the paints. The main advantage of DTMS over PyGC occurs with phthalocyanines and other pigments with very stable ring structures that either require high pyrolysis temperatures for cleavage or produce thermally labile products (Sonoda 1999).

This paper examines the techniques of FTIR spectroscopy and DTMS in the examination of a broad range of dry synthetic organic pigments collected from various pigment manufacturers. The Colour Index system of nomenclature is used in this paper; pigments have been assigned a name and a five- or six-digit number according to the Colour Index (www.colour-index.org). The chemical class provides some information about the basic structure of the pigment. The pigments examined in this study included members of the following classes: monoarylide, diarylide, pyrazolone, disazo condensation, benzimidazolone,

β -naphthol, Naphthol AS, BONA, perinone, perylene, DPP, quinacridone, phthalocyanine, and triarylcarbonium pigments.

Experimental Method

A group of 162 dry pigments to be used as reference materials was collected from pigment manufacturers, including Albion, Avecia, Bayer, Ciba, Clariant, Daler-Rowney, EC Pigments, Golden, Heubach, Kremer, Lansco, Magruder, and Sun Chemical.

Infrared spectra were recorded on a Nicolet Avatar 360 spectrometer, using a diamond cell and Spectra Tech IR Plan microscope. One hundred twenty-eight scans were collected at 4 cm^{-1} resolution. The wavelength range was from 4000 to 650 cm^{-1} . The spectra were processed, including baseline correction, and analyzed using OMNIC software.

DTMS experiments were done at the Getty Conservation Institute on a JEOL M Station JMS-700 double-focusing mass spectrometer equipped with an in-source platinum filament (100-micron diameter) insertion probe. The current on the filament was ramped at 0.5 A/minute over 2 minutes, giving an approximate final temperature of 800–1000° C. The mass spectrometer was scanned from either m/z 10–800 with a 1-second cycle time or m/z 50–2000 with a 5-second cycle time, depending on the pigment examined. The ions were generated by electron impact at 70 eV in an ionization source kept at 220° C and accelerated to 10 kV. A droplet of methanol was suspended on the tip of the DTMS filament, and a few flakes of the pigment were applied to the droplet with a tungsten needle. The methanol was then evaporated by gentle heating over a hot plate to adhere the sample particles to the filament.

FTIR Spectroscopy of Dry Pigments

Infrared spectroscopy provides information about functional groups present in molecules based on the energy of vibrational transitions. Most of the infrared spectra of the synthetic organic pigments contain discrete, sharp absorbances. The $-\text{N}=\text{N}-$ stretching vibration of trans azo compounds, however, is a forbidden absorbance in the infrared and either does not appear or appears as a very weak band (Bassler, Silverstein, and Morrill 1981). Synthetic organic pigments usually have extensive aromatic conjugation, and these aromatic vibrations occur in the region of 3100–3000, 1600–1585, and 1520–1400 cm^{-1} as well as from 900–675 cm^{-1} . Primary or secondary amide-containing pigments have absorbances in the region of 1665–1550 cm^{-1} . The position of the carbonyl bands in synthetic organic pigments usually occurs between 1705 and 1730 cm^{-1} . Many of these

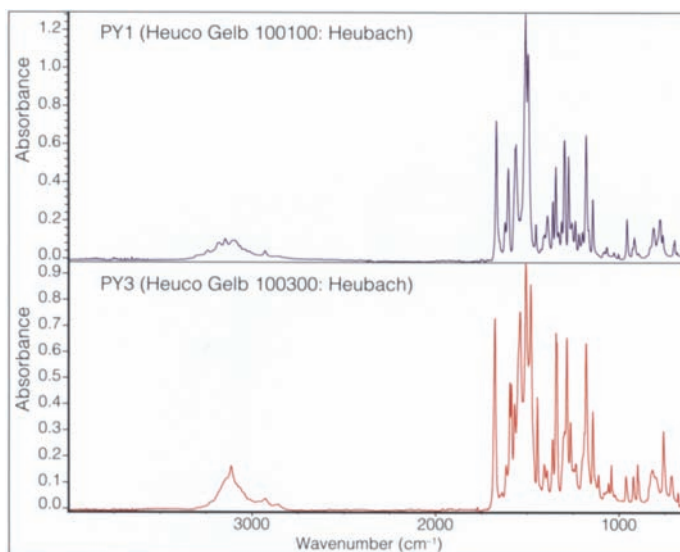


FIGURE 1A Infrared spectra of PY1 and PY3.

pigments are halogenated, and these absorbances are usually found in the region of 850–650 cm^{-1} for aliphatic halogens and between 1100 and 1020 cm^{-1} for aromatic halogens.

Figure 1A shows infrared spectra of the monoarylide yellow pigments PY1 and PY3; figure 1B shows the structure of PY3. Monoarylide pigments are known to exist in the ketohydrazone tautomer (Christie 1993), and there is a pronounced carbonyl absorbance at 1672 cm^{-1} consistent with the ketohydrazone structure with strong intramolecular hydrogen bonding. The $-\text{C}=\text{N}-$ absorbance appears at 1590 cm^{-1} . There are also amide stretches, and the peaks at 1479 and 1337 cm^{-1} are due to the aromatic nitro group. An absorbance due to the aromatic chloro group of PY3 is found at 1036 cm^{-1} .

The major difference in structure between PY3 and PY1 is the chloro groups found on the two aromatic rings of PY3, which are not present on PY1. A methyl substituent is present on one of the aromatic rings on PY1, but its absorbance at 1388 cm^{-1} is not of great diagnostic value. This subtle difference in spectra highlights the danger of making absolute pigment identifications with infrared spectroscopy alone.

Diarylide yellow pigments have structural features in common with monoarylides, consisting of two monoarylide functionalities connected to two conjugated aromatic rings. The major absorbance of these pigments is at 1506 cm^{-1} and is attributable to the vibrations of these aromatic rings. The absence of the carbonyl absorbance suggests that these pigments exist in an enol form (Nicolaou and Da Rocha 1995).

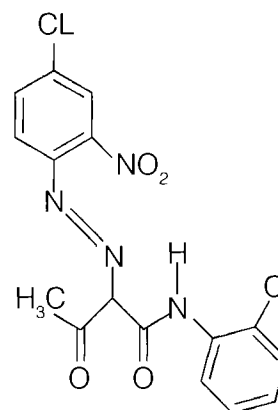


FIGURE 1B Structure of PY3.

Diarylide pigments also have five or six characteristic bands between 1180 and 1310 cm^{-1} . Amide stretches are also apparent at 1660 and 1540 cm^{-1} .

Benzimidazolone pigments, developed in the 1960s, also have structural similarities to the monoarylides, but additionally contain a benzimidazolone ring ($\text{C}_7\text{H}_5\text{N}_2\text{O}$). The infrared spectrum of a representative of this class, PO36 (fig. 2), is

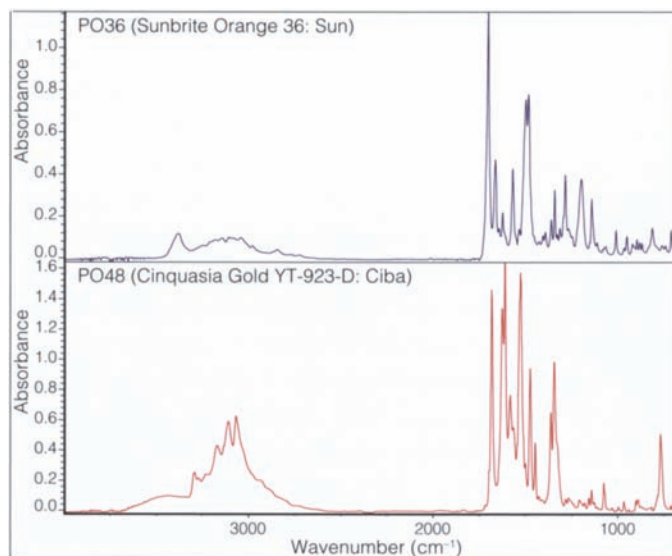


FIGURE 2 Infrared spectra of PO36 and PO48.

characterized by a ketone carbonyl absorbance at 1698 cm^{-1} and amide I and II stretches at 1659 and 1566 cm^{-1} . The nitro group, as well as the aromatic rings, shares the absorbances between 1494 and 1479 cm^{-1} , while the aromatic chloro absorbance is found at 1005 cm^{-1} .

Naphthol AS pigments represent an important class of red azo colorants. They are characterized structurally by a β -naphthol ring substituted with both an aromatic azo and an aromatic amide. The amide I and amide II stretches occur around 1665 and 1540 cm^{-1} , while the aromatic ring stretches are in the region of 1500 – 1470 cm^{-1} . The aromatic C–Cl stretches in representatives of this class that are substituted with halogens are from 1036 to 1014 cm^{-1} , and the asymmetric and symmetric C–O stretches are found from 1260 to 1200 cm^{-1} and around 1100 cm^{-1} . The aromatic in-plane hydroxyl absorbance of the naphthol is found at 1324 cm^{-1} .

Quinacridones are a class of extremely lightfast violet, red, and orange pigments. They can be either pure linear transquinacridone or a mixture of linear transquinacridone and quinacridone quinone (an oxidized quinacridone). As is discussed in the section on DTMS, there are several pigments (PO48, PO49, and PR206) that differ only in the amount of these two components. The spectrum of PO48 (fig. 2) is characterized by the conjugated carbonyl absorbance of the quinone at 1681 cm^{-1} , the secondary vinylogous amide stretches at 1622 and 1525 cm^{-1} , and absorbances from the aromatic rings from 1607 to 1570 cm^{-1} . The spectrum of the chemically related PO49 is virtually identical.

Phthalocyanines are the most important blue and green synthetic organic pigments. The infrared spectrum of PB15:2 (the flocculation-resistant stabilized α form of copper phthalocyanine) is characterized by strong absorbances due to aromatic rings of the metallo-porphyrin ring structure between 1075 and 1490 cm^{-1} . These multiple bands are attributed to the stretching deformations of the aromatic rings (C–C bonds) and the bends of the C–H bonds in the porphyrin ring system. Although McClure and coworkers report that the two crystal phases of phthalocyanine blue are distinguishable by infrared spectroscopy (McClure, Thomson, and Tannahill 1968), the infrared spectrum of PB15:4 (the stabilized β form of copper phthalocyanine) is essentially identical to PB15:2. Bromination/chlorination of the porphyrin rings shifts bands to higher wavenumber, while chlorination shifts to even higher wavenumber.

Infrared spectra of pure pigments provide information about the pigment class and the identity of the individual pigment. However, if the pigment is not pure or is part of a paint system, obscuring absorbances due to the binder and fillers may be present. Figure 3A shows the infrared spectrum of a

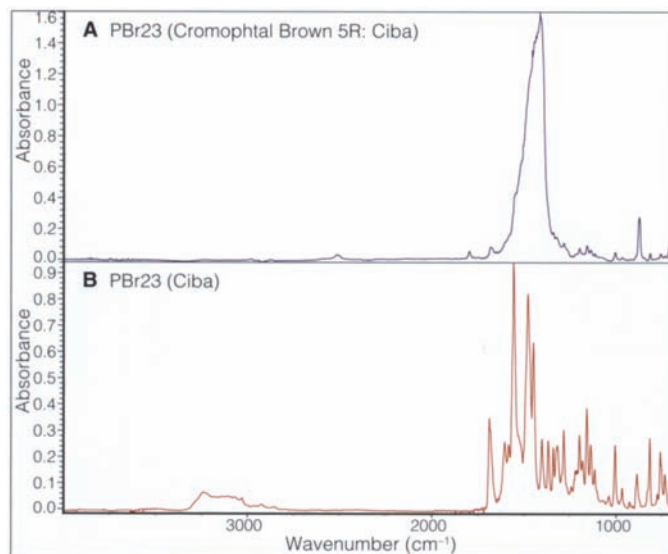


FIGURE 3 Infrared spectrum of PBr23: (A) sample with CaCO_3 filler, (B) sample of pure pigment.

brown pigment that was labeled by its manufacturer as PBr23, a disazo condensation pigment. However, the major absorbance at 1427 cm^{-1} is due to a carbonate absorbance, and other diagnostic peaks at 713 , 877 , 1795 , and 2515 cm^{-1} confirm the presence of calcium carbonate (Learner 2004). Although this

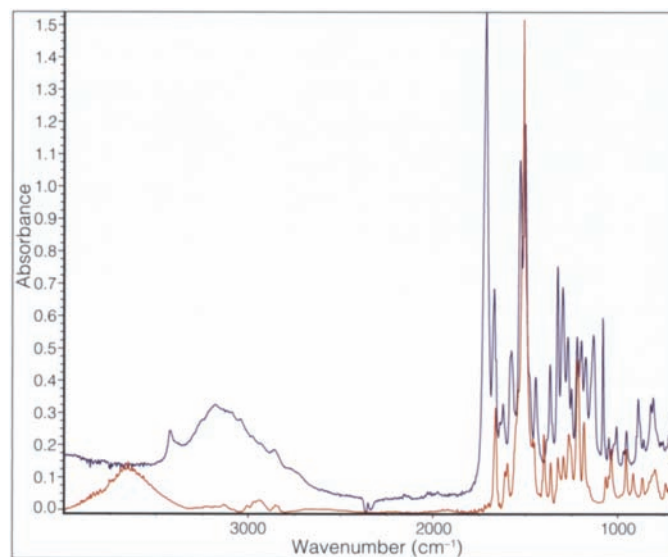


FIGURE 4 Overlay of infrared spectrum of PY83 (red) with acrylic paint containing PY83 (blue).

is the spectrum of a dry pigment, it is clear that absorbances from the inorganic filler obscure any information from the organic pigment, making identification impossible. The infrared spectrum of the pure pigment obtained from the same manufacturer is shown in figure 3B.

Figure 4 shows an overlay of the infrared spectra of (diarylide) pigment PY83 (red line) with an acrylic paint containing PY83 (blue line). Although many of the pigment absorbances can be discerned in the spectrum (especially the prominent aromatic ring vibration at 1506 cm^{-1}), the contributions of the carbonyl and the C–O stretches of the acrylic binder make the interpretation difficult. A library search on the spectrum of the paint did not come up with either PY83 or another diarylide pigment as a possible match.

In summary, infrared spectroscopy is most commonly used as a comparative technique, in which the spectrum of an unknown is compared with that of a reference material. It is a useful technique for gaining information about the class of synthetic organic pigment, and frequently the individual pigment as well. However, the presence of binders and extenders frequently complicates spectra of paints. Care should be taken, therefore, in making an absolute pigment identification based on infrared spectroscopy alone.

DTMS of Dry Pigments

All the pigments were examined using DTMS. Tables 1–7 summarize the pigments examined, their class, and prominent ions in the mass spectrum, including whether the molecular ion is present.

DTMS provides excellent structural information on monoarylide and diarylide pigments. The mass spectrum of PY3 (Hansa yellow 10G) shows an isotopic pattern suggesting incorporation of two chlorine atoms. The peak at m/z 359 is due to the loss of one chlorine. The base peak at m/z 127 is due to the cleavage of the amide bond and transfer of hydrogen to the N–H group. The m/z 129 peak is the isotope peak for the m/z 127 peak. The mass spectrum of PY83, a diarylide yellow pigment, shows a molecular ion peak at m/z 816 (isotope 818). The peak at m/z 533 is due to cleavage of the azo linkage with retention of the positive charge on the multiply chlorinated fragment. The base peak at m/z 187/189 is due to cleavage of the amide functionality with H atom transfer, while the peak at m/z 172 is due to loss of the aromatic side group by cleavage of the N–aromatic bond.

The DTMS technique was also very successful in the examination of naphthol-containing pigments. For example,

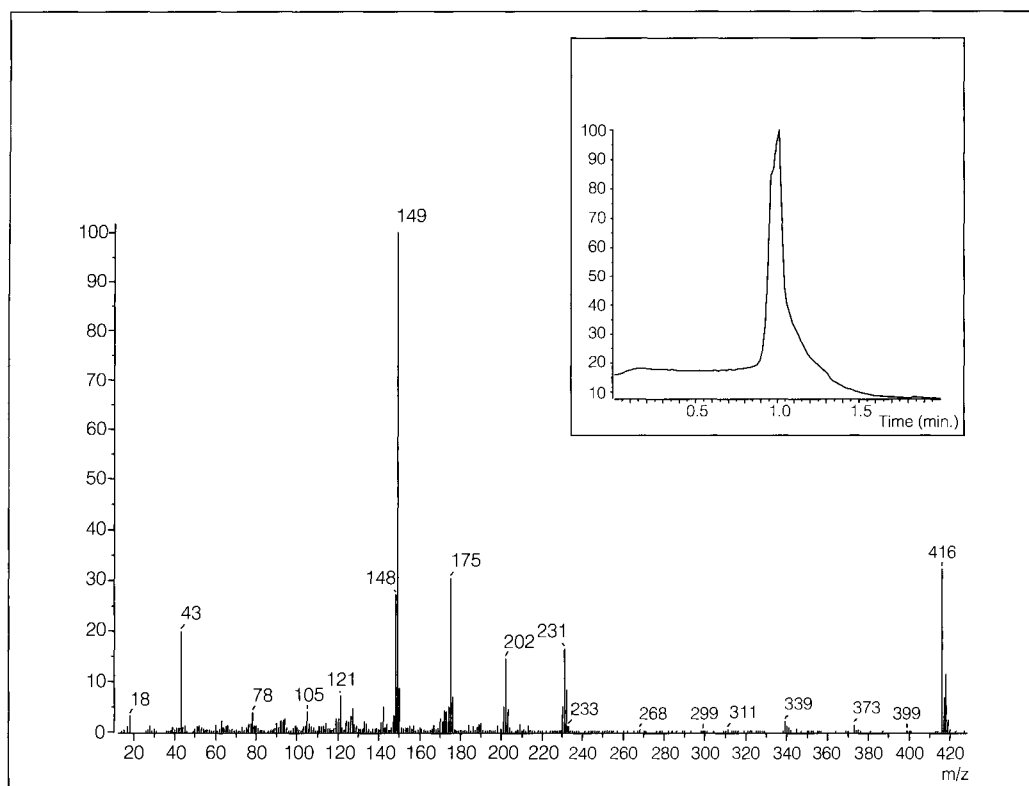


FIGURE 5 DTMS of PO36.

the β -naphthol pigment PR3, toluidine red, has a mass spectrum with a molecular ion present at m/z 307. The preferred cleavage is between the nitrogen of the azo linkage and the naphthol ring, and is the typical mode of cleavage for these pigments. The spectrum of the naphthol AS pigment PR9 contains a molecular ion at m/z 465. The base peak at m/z 161 is due to cleavage of the azo linkage, while the peak at m/z 343 is due to cleavage of the amide bond. Cleavage at the amide bond is a common fragmentation pattern for these pigments.

The DTMS of the benzimidazolone PO36 is shown in figure 5. The molecular ion is prominent at m/z 416. The base peak occurs from a McLafferty rearrangement followed by a decarbonylation reaction. This is a preferred method of fragmentation of benzimidazolones.

The DTMS technique works well even for pigments with extremely conjugated ring structures. In general, these pigments show a prominent molecular ion. For example, PR179, a perylene pigment, has a mass spectrum consisting almost exclusively of the molecular ion (m/z 418). This predominance of the molecular ion is also the case for the phthalocyanine pigments. Figure 6 shows the DTMS spectrum of phthalocyanine blue (PB15:1; stabilized α form). The molecular ion appears at m/z 575. The peaks of increasingly smaller intensity

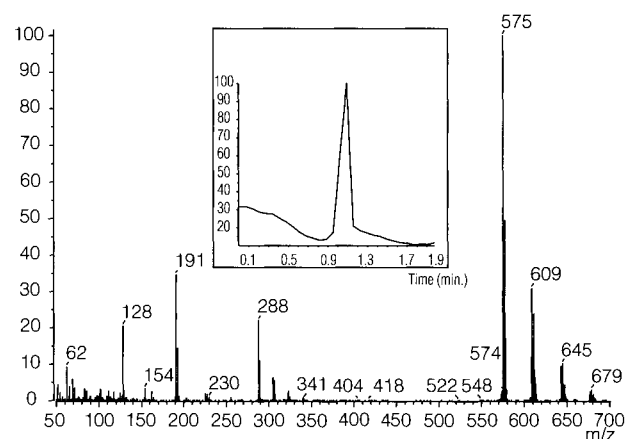
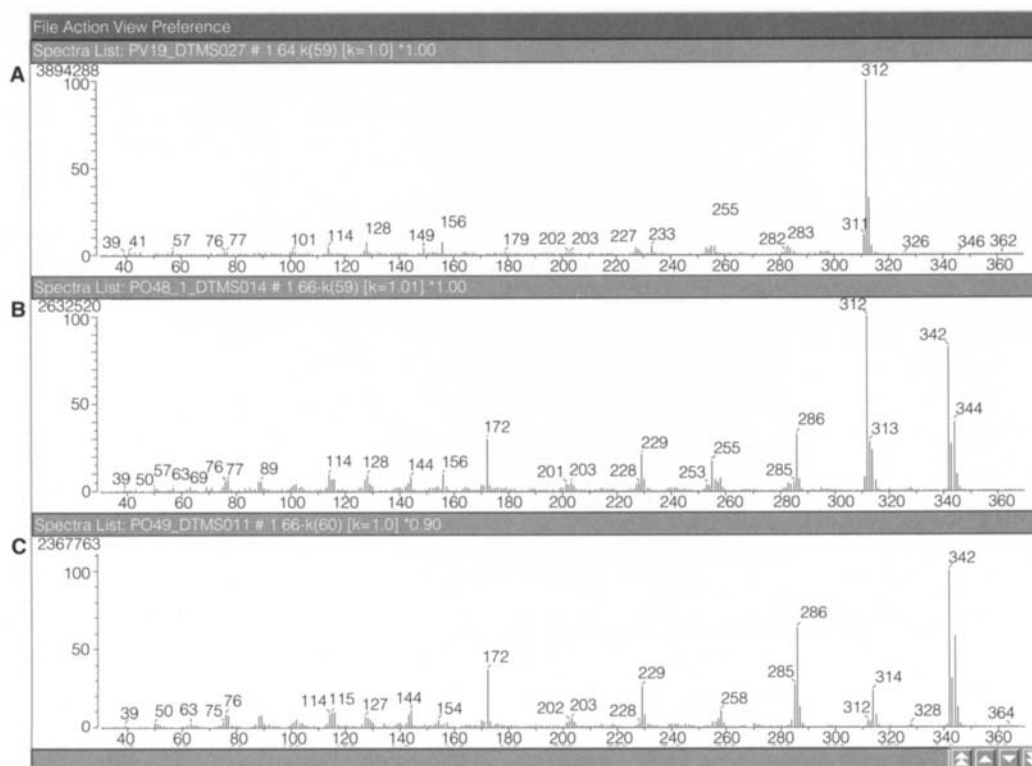


FIGURE 6 DTMS of PB15:1.

at m/z 609, 645, and 679 are due to partial chlorination of the molecule. Partial chlorination is frequently used to increase the stability of the pigment to flocculation (Herbst and Hunger 2004). DTMS spectra were also obtained for the much-higher-molecular-weight phthalocyanine greens PG7 and PG36.

FIGURE 7 Overlay of mass spectra: (A) PV19, (B) PO48, (C) PO49.



Other organometallic pigments gave good mass spectra as well. In addition to the phthalocyanines described above, PG8, PG10, PY150, and PR257 gave well-defined pyrograms with mass spectra that, in general, did not include a peak for the molecular ion.

DTMS was also able to provide some information about the relative amounts of quinacridone and quinacridone quinone in pigments consisting of solid solutions of these components. The parent linear transquinacridone has a molecular weight of 312, while the corresponding quinacridone quinone has a molecular weight of 342. Figure 7 shows an overlay of mass spectra of PV19, PO48, and PO49. PV19 consists exclusively of the parent quinacridone, and has a base peak with the molecular weight of 312. PR206 consists of both components, with a major amount of the quinacridone, and shows a larger ion at m/z 312 than at 342. The orange pigment PO48 is seen to consist of almost equal amounts of the two species, while the pigment PO49 contains more of the quinacridone quinone. These results are consistent with the differences in the color of the components, since the quinacridone quinone has a more yellow shade. Greater amounts of this component lead to a difference in the shades of the pigments. The pure quinacridone PV19 is a red-violet to bluish red pigment (depending on crystalline phase). PR206, consisting of the mixture with the major amount being the quinacridone, is

a violet-maroon color. The more maroon pigment PO48 has more of the quinacridone component, while the more orange-brown pigment PO49 has more of the quinacridone quinone component.

DTMS spectra, collected in positive ion mode, enabled the examination of pigments that are "lakes," or "salts," for which the organic component is cationic. An example of this is the pigment PR81:1, a phosphotungstomolybdic acid salt of a triphenylcarbonium ion. The molecular weight of the cationic portion is 443, and it is possible to pick out the molecular ion in the spectrum, although none of the other ions were attributable to any structural fragments. However, the results for anionic lake, or salt, pigments were poor using the technique. Initial attempts to examine the anionic organic components using negative ion mode were not successful. In negative ion mode, peaks were generally observed at 44 and 64, representing carbon dioxide and sulfur dioxide from carboxylate and sulfonate groupings on the pigments. These pigments are not used as frequently now, but historically several have had widespread use, including PY100, PR48, PR49, PR52, PR53, PR57, and PR63. Future studies will continue efforts to examine these pigments in negative ion mode.

Moderate success was seen in adapting the DTMS method to the analysis of paints. As shown in figure 8, the DTMS chromatogram of Golden Artist Colors acrylic paint containing PY3 shows two humps. The first, smaller hump is due to the desorption of the pigment, which can be picked out at m/z 394 in the mass spectrum. The larger hump at longer retention time is due to the pyrolysis of the acrylic binder. This technique was also used to examine several oil paints, and although the pigment and binder were not as well resolved, they could, in general, be separated.

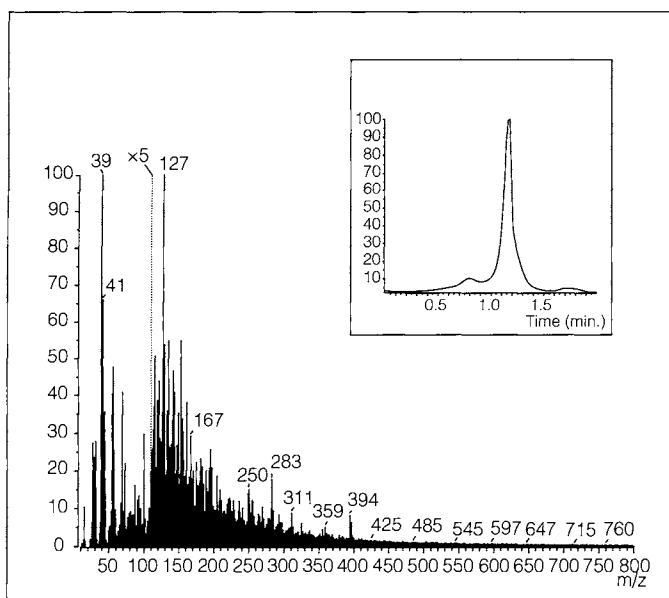


FIGURE 8 DTMS of Golden acrylic paint containing PY3.

Conclusions

In an attempt to develop a protocol for their identification, infrared spectra and DTMS summation spectra were acquired for 162 synthetic organic pigments. Many of these pigments are frequently used in artists' paints. Others are used in the coloration of plastics, printing inks, or architectural paints.

Infrared spectroscopy was shown to be useful for the identification of organic pigments, providing they were present in sufficient quantity. Sometimes the technique was able to detect only the chemical class of a pigment, due to the minor differences of substituents on aromatic rings between individual pigments within that class. Absolute identification of a specific pigment can sometimes be difficult using this technique.

Table 1 Mass spectral data for yellow synthetic organic pigments.

Pigment	Class	Characteristic Ions ^a	Other Ions ^b	T _{max}
PY129	Metal complex	324	261 , 325, 647	0.8
PY150	Metal complex	[337]	43, 85 , 126	1.2
PY1	Monoarylide	340	93 , 121, 189, 310	0.7
PY139	Isoindoline	139, 367	139, 367	1.1
PY194	Benzimidazolone	108, 149, 367	108, 123, 149 , 231	0.9
PY151	Benzimidazolone	381	119 , 231, 328	1.1
PY65	Monoarylide	386	108 , 279, 356, 387	0.7
PY74	Monoarylide	386	108, 123 , 167	0.8
PY2	Monoarylide	388	43, 121 , 345	0.5
PY73	Monoarylide	390	108, 123 , 149, 360	0.7
PY3	Monoarylide	394	43, 127 , 153, 359	0.7
PY75	Monoarylide	404	108, 137 , 161	0.7
PY154	Benzimidazolone	405	149 , 175, 231	0.9
PY24	Anthraquinone	408	176, 352, 408	0.7
PY116	Monoarylide	415	108, 150	0.7
PY111	Monoarylide	420	142, 157 , 159	0.7
PY173	Isoindolinone	434	130, 365, 400	0.9
PY120	Benzimidazolone	122, 453	178 , 209, 231	0.9
PY175	Benzimidazolone	230, 453	149, 177, 209	0.9
PY153	Dioxime, metal complex	498	77, 93 , 467	0.7
PY181	Benzimidazolone	499	120, 175 , 364	0.8
PY97	Monoarylide	590	172, 187 , 404	0.9
PY12	Diarylide	628	252, 465, 628	1
PY110	Isoindolinone	638	268, 640, 642	1.1
PY109	Isoindolinone	652	268 , 386, 619, 654	1
PY14	Diarylide	656	107 , 276, 479	0.9
PY55	Diarylide	121, 656	107 , 452, 479	1
PY126	Diarylide	659	93 , 628	0.7
PY174	Diarylide	670	121 , 285	0.7
PY13	Diarylide	684	147, 252 , 468	1
PY188	Diarylide	628, 629, 684	121 , 252, 467	1
PY127	Diarylide	[687]	93 , 440, 628	0.9
PY17	Diarylide	688	108, 123 , 252	1
PY170	Diarylide	122, 688	123 , 251, 470	0.7
PY138	Quinophthalone	[689]	692, 694	0.8
PY63	Diarylide	696	127 , 474, 501	0.8
PY152	Diarylide	137, 716	108, 137	0.7
PY155	Bisacetoacetarylide	209, 412, 716	177, 209 , 412	1
PY16	Bisacetoacetarylide	724	212 , 468, 726	0.9
PY180	Disazo benzimidazolone	732	149, 175	0.8
PY176	Diarylide	750	121 , 239, 285, 684	0.7
PY81	Diarylide	752	121 , 322, 754, 537	1
PY172	Diarylide	756	142, 157 , 758	0.8
PY83	Diarylide	816	189 , 252, 534, 818	1
PY128	Disazo condensation	1229	154 , 440	1
PY61	Monoarylide, Ca salt	[anion 405]	66, 93 , 119	1
PY183	Monoarylide, Ca salt	[anion 504]	28 , 64, 161	1.2

^a Molecular ions shown in *italics*, molecular weights in brackets.^b Base peak in the mass spectrum shown in **bold**.

Table 2 Mass spectral data for orange synthetic organic pigments.

Pigment	Class	Characteristic Ions ^a	Other Ions ^b	T _{max}
PO64	Azoheterocycle	<i>302</i>	148, 162	1.1
PO49	Quinacridone	342	172, 286, 342	1.1
PO48	Quinacridone	<i>312, 342</i>	172, 286, 312	1.1
PO5	β -naphthol	338	115, 143 , 321	0.7
PO1	Monoarylide	370	107 , 167, 327	0.6
PO62	Benzimidazolone	382	108, 149	0.9
PO67	Pyrazoloquinazolone	384	170, 226, 382	0.8
PO24	Naphthol AS	401	169, 309, 401	1
PO43	Perinone	412	206, 412	1
PO36	Benzimidazolone	416	149 , 175, 231	1
PO51	Pyranthrone	474	346, 348, 474 , 476	0.9
PO38	Naphthol AS	501	150, 352	0.7
PO69	Isoindoline	525	149, 397 , 523	0.9
PO68	Methine metal complex	528	115, 169, 527	0.9
PO16	Diarylide	620	43, 93 , 119, 431	0.9
PO13	Disazopyrazolone	622	252 , 436	1
PO34	Disazopyrazolone	650	91 , 252, 450, 452	1
PO61	Isoindoline	760	371, 373 , 758, 760	1.1
PO72	Benzimidazolone	[Unknown]	149 , 304, 627	0.8

^a Molecular ions shown in *italics*, molecular weights in brackets.

^b Base peak in the mass spectrum shown in **bold**.

This work demonstrates the utility of DTMS in the absolute characterization of synthetic organic pigments. A database has been compiled of the mass spectra. The spectra collected at 70 eV show a combination of fragmentation and molecular ion, which should prove useful in the characterization of unknown pigments.

This work will be expanded to study “lake” pigments with anionic organic substituents. Methods to convert the anionic portion to a neutral moiety will be explored, as well as optimization for analysis in negative ion mode. More examples of commercial paints will be examined. These techniques will be used to examine samples from works of art.

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(www.avescia.com); Bayer, Coatings and Colorants Division (www.bayercoatings.com); Ciba Specialty Chemicals PLC (www.cibasc.com/index/ind-index/ind-paints_and_coatings.htm); Clariant UK Ltd (paclariant.com); Daler-Rowney (www.daler-rowney.com); EC Pigments (www.ecpigments.com); Golden Artist Colors Inc. (www.goldenpaints.com); Heubach GmbH (www.heubachcolor.de); Kremer Pigmente GmbH & Co KG (www.kremer-pigmente.de/englisch/homee.htm); Lansco Colors (www.pigments.com); Magruder Color, LLC (www.magruder.com); and Sun Chemical Corporation (www.sunchemical.com).

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Table 3 Mass spectral data for red synthetic organic pigments.

Pigment	Class	Characteristic Ions ^a	Other Ions ^b	T _{max}
PR83:1	Anthraquinone	[278]	41, 55	1.1
PR1	β -naphthol	293	115, 143, 293	0.5
PR3	β -naphthol	307	115, 143	0.7
PR207	Quinacridone	312, 380	312 , 380	0.8
PR206	Quinacridone	312, 342	255, 312 , 342, 344	1.1
PR4	β -naphthol	142, 159, 297, 327	115, 143 , 171	0.7
PR6	β -naphthol	156, 327	115, 143, 327	0.5
PR122	Quinacridone	340	170, 340	1
PR254	DPP pigment	356	138, 191, 358	1
PR202	Quinacridone	312, 380	312, 380	1.1
PR209	Quinacridone	380	289, 380	1.1
PR181	Thioindigoid	240, 363, 392	363, 392	0.5
PR224	Perylene	248, 320, 392	248, 348, 392	0.8
PR21	Naphthol AS	[401]	77, 275, 367	0.5
PR179	Perylene	418	390, 418	1
PR268	Naphthol AS	424	234, 303	0.7
PR22	Naphthol AS	426	121, 122 , 305, 334	0.9
PR88	Thioindigo	432	434 , 436	1
PR2	Naphthol AS	435	161 , 343	0.8
PR12	Naphthol AS	440	122 , 305, 334	0.8
PR17	Naphthol AS	440	121 , 334	0.8
PR150	Naphthol AS	440	150, 214, 440	0.7
PR213	Naphthol AS	158, 242, 440	150, 214, 328, 440	0.7
PR245	Naphthol AS	234, 348, 440	348, 440	0.7
PR266	Naphthol AS	318, 440	169, 317, 318	0.7
PR210	Naphthol AS	440, 454	169, 318	0.8
PR177	Anthraquinone	444	387 , 415	0.9
PR170	Naphthol AS	454	137, 169, 318	0.7
PR8	Naphthol AS	334, 460	305, 334	0.6
PR14	Naphthol AS	197, 460	289, 354	0.8
PR168	Anthanthrone	462	248, 464	1.2
PR7	Naphthol AS	463	294, 323	0.6
PR9	Naphthol AS	465	161 , 343	0.8
PR18	Naphthol AS	471	113 , 139, 334	0.7
PR175	Benzimidazolone	481	149, 217, 333	0.8
PR112	Naphthol AS	483	195, 197 , 485	0.8
PR23	Naphthol AS	487	169, 350	0.9
PR32	Naphthol AS	516	424, 516	0.7

Table 3 Mass spectral data for red synthetic organic pigments (continued).

Pigment	Class	Characteristic Ions ^a	Other Ions ^b	T _{max}
PR208	Benzimidazolone	523	217, 375, 523	0.8
PR253	Naphthol AS	542	169, 289 , 436	0.9
PR258	Naphthol AS	551	459, 551	0.7
PR185	Benzimidazolone	560	149 , 230, 412	0.8
PR31	Naphthol AS	561	424, 561	0.7
PR147	Naphthol AS	564	150, 242, 424	0.8
PR184	Naphthol AS	564, 610	150 , 242, 424	0.9
PR176	Benzimidazolone	572	150 , 242, 424	0.8
PR269	Naphthol AS	580	139, 303, 424	0.7
PR149	Perylene	598	477, 698	0.8
PR190	Perylene	602	328, 479, 602	0.8
PR146	Naphthol AS	610	150, 242, 424	0.9
PR41	Disazopyrazolone	614	77, 428, 614	0.7
PR5	Naphthol AS	626	122 , 440	0.9
PR123	Perylene	630	328, 493, 630	0.8
PR188	Naphthol AS	642	169 , 520, 522	0.9
PR257	Metal complex	[649]	264, 266	1.1
PR38	Disazopyrazolone	738	77, 252, 710	1
PR178	Perylene	750	77, 540	0.9
PR166	Disazo condensation	792	161 , 450	1.1
PR144	Disazo condensation	794	161, 343 , 484	1.1
PR214	Disazo condensation	860	161 , 234, 520, 862	1.1
PR220	Disazo condensation	213, 395, 924	134, 395 , 530, 896	1
PR221	Disazo condensation	193, 375, 924	151, 193, 375	1
PR242	Disazo condensation	928	195 , 377, 930	1
PR53:1	β -naphthol lake	[anion 375]	144, 231, 266	1.1
PR49:1	β -naphthol lake	[anion 377]	143, 239, 268	1.1
PR49:2	β -naphthol lake	[anion 377]	144, 239, 268	1.1
PR52:2	BONA lake	[anion 402]	91, 239 , 302	1
PR52:1	BONA lake	[anion 402]	44, 48, 64 , 266	1.2
PR48:2	BONA lake	[anion 418]	44 , 64, 266	1.1
PR169	Triarylcarbonium	493 (<i>cation</i>)	427 , 441	0.7
PR238	Naphthol AS	[unknown]	169, 424 , 580	0.8
PR239	Naphthol AS lake	[unknown]	142 , 293, 449	0.9
PR256	Naphthol AS	[unknown]	169 , 268, 450, 572	0.9
PR262	Disazo condensation	[unknown]	323 , 780	0.8

^a Molecular ions shown in *italics*, molecular weights in brackets.^b Base peak in the mass spectrum shown in **bold**.

Table 4 Mass spectral data for blue synthetic organic pigments.

Pigment	Class	Characteristic Ions ^a	Other Ions ^b	T _{max}
PB60	Indanthrone	<i>442</i>	442	0.9
PB16	Phthalocyanine	[512]	129 , 257, 514	0.8
PB15:4	Phthalocyanine	<i>575</i>	128 , 191, 288	1.1
PB15:6	Phthalocyanine	<i>575</i>	128, 191, 288, 575	1
PB15:1	Phthalocyanine	<i>575</i>	191, 288, 575 , 609	1.1
PB15:2	Phthalocyanine	<i>575</i>	191, 288, 575 , 609	1
PB15:3	Phthalocyanine	<i>575</i>	191, 288, 575	1.1
PB62	Triarylcarbonium	[cation 478]	462 , 477	1
PB1	Triarylcarbonium	[cation 478]	106, 156 , 171	1

^a Molecular ions shown in *italics*, molecular weights in brackets.^b Base peak in the mass spectrum shown in **bold**.**Table 5** Mass spectral data for green synthetic organic pigments.

Pigment	Class	Characteristic Ions ^a	Other Ions ^b	T _{max}
PG8	Metal complex	[558]	129 , 159, 280	1
PG10	Metal complex	[655]	43, 85, 126	0.8
PG7	Phthalocyanine	<i>1118</i>	1023, 1057, 1127	1.2
PG4	Triarylcarbonium	[cation 329]	165 , 208	0.9
PG1	Triarylcarbonium	[cation 385]	341, 371, 385	1.1
PG36	Phthalocyanine	[variable]	1715, 1753, 1795	1.2

^a Molecular ions shown in *italics*, molecular weights in brackets.^b Base peak in the mass spectrum shown in **bold**.**Table 6** Mass spectral data for brown synthetic organic pigments.

Pigment	Class	Characteristic Ions ^a	Other Ions ^b	T _{max}
PBr25	Benzimidazolone	<i>491</i>	161 , 343, 345	1
PBr23	Disazo condensation	<i>848</i>	53 , 354	1.1

^a Molecular ions shown in *italics*, molecular weights in brackets.^b Base peak in the mass spectrum shown in **bold**.

Table 7 Mass spectral data for violet synthetic organic pigments.

Pigment	Class	Characteristic Ions ^a	Other Ions ^b	T _{max}
PV19	Quinacridone	312	255, 312	1.1
PV29	Perylene	390	390	0.8
PV44	Naphthol AS	530	105 , 530	0.7
PV32	Benzimidazolone	576		0.8
PV23	Dioxazine	588	559, 590	1
PV37	Dioxazine	726	105	1.1
PV3	Triarylcarbonium	[cation 358]	253, 372	0.7
PV3:1	Triarylcarbonium	[cation 358]	237, 253 , 373	0.7
PV1	Rhodamine	[cation 443]	158 , 326, 397, 441	0.8

^a Molecular ions shown in *italics*, molecular weights in brackets.

^b Base peak in the mass spectrum shown in **bold**.

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Modern White Pigments: Their Identification by Means of Noninvasive Ultraviolet, Visible, and Infrared Fiber Optic Reflectance Spectroscopy

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Abstract: *In the first half of the twentieth century, the chemical industry provided artists with a new white pigment, titanium white, in its two crystalline forms, anatase and rutile. These were utilized along with other common whites such as lead white, zinc white, and lithopone. The identification of these white pigments is of particular interest in regard to the evolution of their use in art. Ultraviolet (UV), visible (Vis), and infrared (IR) fiber optic reflectance spectroscopy (FORS) is a noninvasive analytical technique that is appropriate for in situ pigment identification. It can also be a complementary method to other noninvasive techniques.*

In the present work, FORS results on modern white pigments (including kaolin from the canvas preparation) will be presented. These pigments can be positively identified by their reflectance spectra in the 270–1700 nm range. Indeed, zinc sulfide (specifically one of the lithopone compounds), zinc white, and titanium white (in both the anatase and rutile crystalline forms) are clearly identified in the 330–420 nm region, where their spectral slopes make it possible to unambiguously distinguish them. In addition to the UV and visible regions, the 1300–1600 nm range is considered. There, kaolin, together with lead white and gypsum, reveals characteristic absorption features due to the hydroxyl groups (from the first overtone of stretching-mode vibrations).

Finally, several examples of FORS application on twentieth-century artworks are reported. The cases selected for investigation belong to three different collections, all located in Florence: the Self-Portrait Collection of the Galleria degli Uffizi; the Fondo Pasolini, Archivio Contemporaneo Alessandro Bonsanti of the Gabinetto G. P. Vieusseux; and the Iconographic Collection of the publishing house Giunti Editori S.p.A.

Introduction

The historical evolution of the production and use of white pigments in the twentieth century provides interesting parameters regarding the chronology of their use, which may be related through comparative analysis with other data to the artworks in which they have been detected. These white pigments include titanium dioxide (titanium whites), in either the rutile or anatase form, zinc oxide (zinc white), a mixed pigment produced from zinc sulfide and barium sulfate (lithopone), and the white pigment that is historically most well known, lead white (basic lead carbonate).

Reflectance spectroscopy in the visible region (Vis) was applied to characterize paints and pigments for the first time during the 1930s (Barnes 1939), at the Department of Conservation and Technical Research of the Fogg Art Museum, in Cambridge, Massachusetts. In the following years, when fiber optical devices became available, this methodology was further developed at the Conservation Laboratories of the National Gallery in London (Bullock 1978; Saunders 1986). Since the early 1980s, the noninvasive technique of fiber optic reflectance spectroscopy (FORS) has been applied in this field using portable instruments, and the operating range has been extended from the ultraviolet (UV) to the near infrared (NIR) region (Bacci et al. 1992; Bacci and Picollo 1996; Leona and Winter 2001; Dupuis, Elias, and Simonot 2002; Leona et al. 2004; Dupuis and Menu 2006).

Due to its completely noninvasive nature and to the fact that it can be used for in situ measurements, conservators and curators can use the FORS technique to glean data useful for the identification of pigments, dyes, and alteration products by correlating the sample spectrum to a suitable spectral database. Moreover, FORS can be used to complement other non-

invasive techniques, most notably X-ray fluorescence (XRF) spectroscopy, X-ray diffraction (XRD), particle induced X-ray emission (PIXE), and Raman spectroscopy (Bacci 2000; Bacci et al. 2003). FORS has also proved to be very useful for locating areas of specific interest for subsequent microsampling and in extending the relevance of local data obtained through microanalyses to a broader scale across a work of art.

Experimentation with FORS carried out for the present research, aimed at the identification of white pigments, was undertaken on paintings deriving from three different collections, chosen specifically for this purpose:

- Approximately thirty works painted by various artists from the Self-Portrait Collection in the Galleria degli Uffizi, dating from 1900 to the present day.
- Three mixed-media (oil and tempera) paintings, each painted on both sides of a single canvas, by Pier Paolo Pasolini (1922–1975), held by the Gabinetto G. P. Vieusseux, Archivio Contemporaneo Alessandro Bonsanti, Fondo Pasolini (undergoing treatment at Opificio delle Pietre Dure [OPD] Painting Conservation Laboratory).
- Five tempera drawings on paper by Attilio Mussino (1878–1954), made to illustrate a 1911 edition of *Pinocchio*. These are held in the Iconographic Collection of the publisher Giunti Editori S.p.A. and are undergoing treatment at OPD Prints and Drawings Conservation Laboratory.

The strictly noninvasive method described here appeared particularly suitable for aiding in the analysis of these works (Bacci 2000).

White Pigments in the Twentieth Century: A Brief History of Change

The principal white pigments used for artistic purposes in the twentieth century were lead white [$2\text{PbCO}_3\text{Pb(OH)}_2$], lithopone ($\text{ZnS}+\text{BaSO}_4$), zinc white (ZnO), and titanium dioxide (TiO_2), the latter occurring in the rutile and anatase forms. Kaolin (also called china clay or hydrated aluminum silicate), calcite (calcium carbonate), gypsum (calcium sulfate dihydrate), and several materials based on barium sulfate (e.g., barites, lithopone) have also been used for artistic purposes, but mainly as fillers, which are commonly used in pigmented grounds and primers.

Lead white, known since antiquity, was the primary white pigment used until modern times, in particular for

easel painting. Prepared artificially, it was perfectly suitable in both tempera and oil media (Gettens and Stout 1966, 174–76; Gettens, Kühn, and Chase 1993). It was produced on an industrial scale from the nineteenth century on, even though it was known to be a poisonous compound when inhaled as a dust or ingested. Lead white was especially dangerous during the manufacturing process (Franklin 1987), as reported in Charles Dickens's firsthand account of its effects on the workers of a London lead mill (Dickens 1868).

Mainly in response to increasing awareness of its health hazards, attempts were made to find viable substitutes for lead white in white paint (Gettens, Kühn, and Chase 1993). Thus, such alternative whites as zinc oxide (ZnO), derived from zinc metals and ore, were developed and refined, in particular by B. Courtois and G. de Morveau (Kühn 1986; Clausen 1988). Although known since antiquity, these minerals had apparently never been used to make pigments. Zinc white was initially marketed as an artists' color in a watercolor medium, first commercialized in 1834 by Winsor & Newton in England as Chinese White. It was subsequently improved for use in an oil medium by Leclair (France), which improved its previously unsatisfactory drying and covering properties by grinding it with poppy seed oil whose siccative properties had been improved by boiling it with pyrolusite (MnO_2). By 1850, zinc oxide whites were being produced on an industrial scale in Europe and the United States. Manufactured worldwide, they have remained widely used for artistic purposes up to the present (Kühn 1986).

Another white material developed in this period was the composite pigment lithopone, a mixture of white zinc sulfide and barium sulfate (Rigg 1956; Clausen 1988). In 1874, J. B. Orr (Glasgow) patented a process for producing a new white pigment, Orr's Zinc White, by first co-precipitating zinc sulfate and barium sulfide and then calcining the mixture. Further patents for making purer, higher strength varieties of this nonpoisonous white were granted elsewhere in the following decades. An important improvement was achieved in the 1920s, when it was made lightfast through the addition of small quantities of cobalt salts prior to calcination (Rigg 1956; Clausen 1988; van Alphen 1998, 41–43).

However, for several decades the most important modern white pigment has been titanium dioxide (TiO_2), which occurs in nature in three forms: rutile, anatase, and brookite (Blakey and Hall 1988; Woditsch and Westerhaus 1993; Laver 1997). Rutile and anatase are today produced industrially in large quantities, and are used in the production of ceramics and electronic materials in addition to their main use as pigments and catalysts.

The elementary metal titanium was first discovered in ilmenite (FeTiO_3) by William Gregor in 1791, and later in rutile ores by M. H. Klaproth, who isolated and named the element titanium in 1795. But it was only in the early twentieth century that titanium dioxide white, in its anatase crystal form, was first produced—almost simultaneously by Titanium Pigment Co., in New York, and Titan Co. AS, in Norway, using sulfation and calcination methods, respectively (Laver 1997). Not until 1937, however, did manufacturers first successfully obtain synthetic rutile. During the second half of the twentieth century, TiO_2 whites (mainly rutile, pure and composite) became increasingly available on the market at competitive prices and as artists' colors. The diffusion of white TiO_2 pigments, produced worldwide, has continued up to the present day, where they predominate because of their scattering properties, chemical stability, and nontoxicity.

Experimental Method

Equipment

FORS measurements were performed using two Zeiss spectroanalyzers on white laboratory standard (mock painting) samples and on the analyzed artworks (fig. 1). The spectral resolution of the two spectroanalyzers—an MCS501 model operating in the 200–1000 nm range, and an MCS511 NIR 1.7 model operating in the 900–1700 nm range—was of 0.8 and

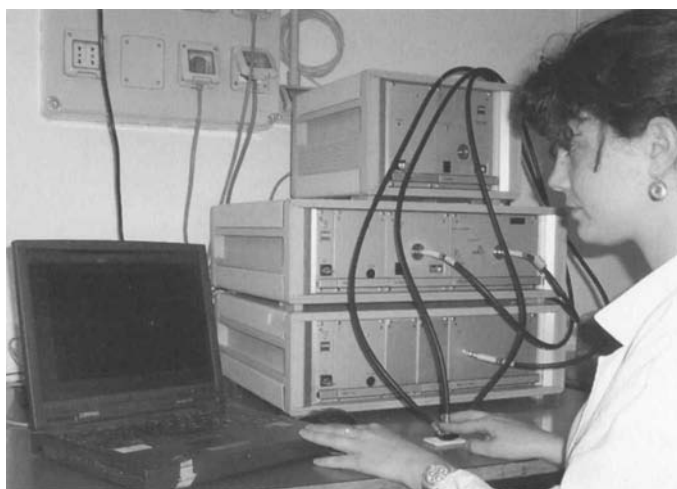


FIGURE 1 Apparatus used for noninvasive, in situ measurements. From top to bottom: xenon light source module, UV-Vis-NIR spectroanalyzer with a tungsten-halogen lamp module, NIR spectroanalyzer module.

6.0 nm/pixel, respectively. A 99% Spectralon diffuse reflectance standard was used to calibrate the spectroanalyzers. Two light sources were used: for the 270–800 nm range, xenon lamp model CLX 500; and for the 320–1700 nm range, tungsten-halogen lamp model CLH 500. Two reflectance configurations were adopted to avoid specular reflected light in the measurements: $2 \times 45^\circ/0^\circ$ with the MCS501 for the 270–800 nm range, and $45^\circ/0^\circ$ with both spectroanalyzers for the 320–1700 nm range. Both configurations covered an area of about 2 mm in diameter at a working distance of approximately 4.5 mm. For the 270–800 nm range, a bifurcated bundle of pure fused quartz fibers was used to send the incident light illuminating the sample from two different symmetrical directions, $2 \times 45^\circ$, and a linear bundle for receiving the back-scattered light. For the 320–1700 nm range, instead, three linear bundles of anhydrous quartz fibers were used: one to convey the light to the surface under investigation, and the other two to reconvey the back-scattered light to the two detectors.

Reference Materials

Laboratory mock paintings were prepared starting from rectangular samples of canvas on a 3×5 cm cardboard support. A kaolin–titanium dioxide (rutile) ground was used, and then a final layer of pigment mixed with a linseed oil binder was added. The white pigments investigated were

- Basic lead carbonate: lead white (Σ -Aldrich chemical reagent code 243582)
- Zinc oxide: zinc white (Σ -Aldrich chemical reagent code 251607)
- Titanium dioxide: titanium white in the two crystalline forms—anatase (Carlo Erba chemical reagent code 488257) and rutile (Σ -Aldrich chemical reagent code 224227)
- Lithopone (Zecchi Co., Florence)

Their chemical compositions were checked with XRD, XRF, and Fourier transform infrared (FTIR) spectroscopy techniques.

Works Examined

The choice of artworks for examination was guided not only by the presence of relatively uniform fields of color (including those obtained with the white pigments to be investigated in particular) but also by the certainty of provenance and date, by their characteristics (dimensions, physical nature, etc.), and because

they appeared to constitute suitable examples of changes in modern painting materials during the twentieth century.

Uffizi Self-Portraits

To date, around thirty works painted by various artists from 1900 to the present day, mostly on canvas or wood, from the

Self-Portrait Collection of the Galleria degli Uffizi have been examined with FORS (table 1). These paintings are part of the modern component of the collection, which numbered 1044 works when the museum's *General Catalogue* was compiled (Uffizi 1980; Berti 1981, 1983).

Table 1 Paintings in the Self-Portrait Collection of the Galleria degli Uffizi analyzed using FORS.

Date of Work	Artist	Material	Size (cm)
ca. 1900	Francesco Franchetti (1878–1931, born Livorno, Italy)	Oil on panel	26.5 × 23.5
ca. 1918	Elisabeth Chaplin (1890–1982, born Fontainebleau, France)	Oil on canvas	94.55 × 65
1926–29	Baccio Maria Bacci (1888–1974, born Florence)	Oil on canvas	224.5 × 180
ca. 1930	Sergio Tomberli (1913–1964, born Empoli, Italy)	Oil on canvas	95 × 71
1934	Adriana Pincherle (1905–1996, born Rome)	Oil on canvas	165 × 69
1936	Leonardo Savioli (1917–1982, born Florence)	Oil on plywood	102 × 76.5
1936	Giovanni Barbisan (1914–1988, born Treviso, Italy)	Oil on canvas	95 × 73
1938	Enzo Fanfani (born 1911, Florence)	Oil on paperboard	77 × 59
1949	Lidia Innocenti (born 1920, Florence)	Oil on canvas	100 × 65
1951	Carlo Carrà (1881–1966, born Quargenento, Italy)	Oil on canvas	85 × 70
1960	Raúl Soldi (1905–1994, born Buenos Aires)	Oil on cardboard	40 × 30
1961	David Alfaro Siqueiros (1896–1974, born Chihuahua, Mexico)	Acrylic on masonite	80 × 60
1963–64	Fernando Farulli (1923–1997, born Florence)	Oil on canvas	150 × 100
1966	Carlo Cañas (born 1928, Buenos Aires)	Oil on canvas	60 × 50
1971	Mario Fallani (born 1934, Florence)	Oil on canvas	195 × 100
1971	Raymond Pitré (born 1940, Balzan, Malta)	Oil on canvas	50 × 40
1974–75	Reinier Lucassen (born 1939, Amsterdam)	Acrylic on canvas	80 × 100
1975	Afewerk Tekle (born 1932, Ankober, Ethiopia)	Oil on canvas	51.5 × 66.5
1976	Jerome Witkin (born 1939, New York)	Oil on canvas	61 × 46
1980	Zarin Indulis (born 1929, Latvia)	Oil on canvas	92.5 × 70
1981	Camille Hirtz (1917–1987, born Strasbourg, France)	Oil on canvas	65.3 × 54.1
1981	Corneliu Baba (1906–1997, born Craiova, Romania)	Oil on canvas	105 × 80
1981	Maria Lassnig (born 1919, Kappel am Krappfeld, Austria)	Oil on cardboard with canvas	45.5 × 35.5
1981(?)	James Nolan (born 1929, Dublin)	Oil on canvas	91 × 71
1981	Newton Mesquita (born 1949, São Paulo)	Acrylic on canvas	50 × 50
1981	Juan Carlos Liberti (born 1930, Buenos Aires)	Oil on canvas	80 × 45
1981	Ary Brizzi (born 1930, Avellaneda, Argentina)	Acrylic on canvas	80 × 80
1981	Camille Claus (1920–2005, born Strasbourg, France)	Oil on canvas	81.5 × 100
1990	Juliusz Joniak (born 1925, L'viv, Poland)	Oil on canvas	92 × 73
Unknown	Arikha Avigdor (born 1929, Romania)	Oil on canvas	81 × 65
Unknown	Oswaldo Viteri (born 1931, Ambato, Ecuador)	Oil on canvas	160 × 110

Works by Pasolini

The three paintings examined, each painted on both sides of a single canvas using a mix of tempera and oil media, are the work of the young Pier Paolo Pasolini. They probably date from 1943–46, before Pasolini's departure for Rome in 1950, after which he became internationally known as a writer and film director. Presently undergoing treatment at the OPD Department of Easel Painting Conservation, these artworks are part of a vast collection of material relative to Pasolini's multiform artistic production, conserved in the Archivio Contemporaneo of the Gabinetto G. P. Vieusseux in Florence. The application of FORS to these works was especially suitable, given the possibility of selectively investigating the various painted surfaces present, and to thereby gather information about the succession of materials used in the complicated layering of the works.

Pinocchio Drawings

Four plates from the complete series of illustrations for an early-twentieth-century edition of *Pinocchio* were chosen for examination. The drawings were made by Attilio Mussino between 1908 and 1911, and were painted in a tempera rather than an oil medium—unlike the majority of other objects examined for this study.

Results and Discussion

The visible-region reflectance spectra of the white pigments studied in the present work are all characterized by high overall reflectance. All of them could be easily identified on the basis of their absorption bands in the 330–420 nm or 1350–1600 nm ranges. In figure 2, the 1350–1600 nm spectral range for lead white, kaolin, and gypsum revealed characteristic absorption features. These are due, for lead white and kaolin, to their hydroxyl groups' first overtone ($2\nu_{\text{OH}}$) of the stretching mode vibrations. The gypsum, in addition to the first overtone ($2\nu_3$) of the asymmetric stretching mode vibrations from its water molecules, also presents absorption features from the first overtone ($2\nu_1$) of the symmetric stretching mode vibration of water, and from the combinations of stretching and bending mode vibrations, $(\nu_1 + \nu_3)$ and $(\nu_1 + 2\nu_2)$, of the water groups (Hunt and Salisbury 1970, 1971). The presence of gypsum, however, frequently used in ground layers (and sometimes left uncovered as a white color field, as, for example, in one of the paintings by Pasolini, or in the paint composition as a filler), may somewhat hinder the identification of lead white. This occurs because the absorption bands of the gypsum's

water molecules can interfere with the lead white absorption bands in the 1450–1550 nm region (fig. 2) (Hunt, Salisbury, and Lenhoff 1971; Bacci 2000).

The reflectance spectra in the 330–420 nm range could be successfully used to identify zinc white (ZnO), lithopone (specifically zinc sulfide, ZnS, one of the lithopone compounds), and the two most important titanium dioxide (TiO_2) crystallographic forms (fig. 2). Indeed, ZnS, ZnO, and TiO_2 (both crystalline forms) are semiconductors, and the typical S-type band shape of their reflectance spectra corresponds to the electromagnetic energy necessary to make electrons overcome their characteristic band gaps (Hunt, Salisbury, and Lenhoff 1971; Kühn 1986). The positions of the inflection points of the reflectance spectra, can be identified by calculating the first derivative of the spectra, where, for ZnS (in the lithopone), ZnO, and TiO_2 (rutile and anatase), the maximum peaks of the derivative curves are positioned at around 341, 384, 404, and 372 nm, respectively (fig. 3). Although these positions may differ by a few nanometers when works of art are examined (caused by, for example, yellowing of the binder/vehicle or eventual varnish layers, or by materials' dif-

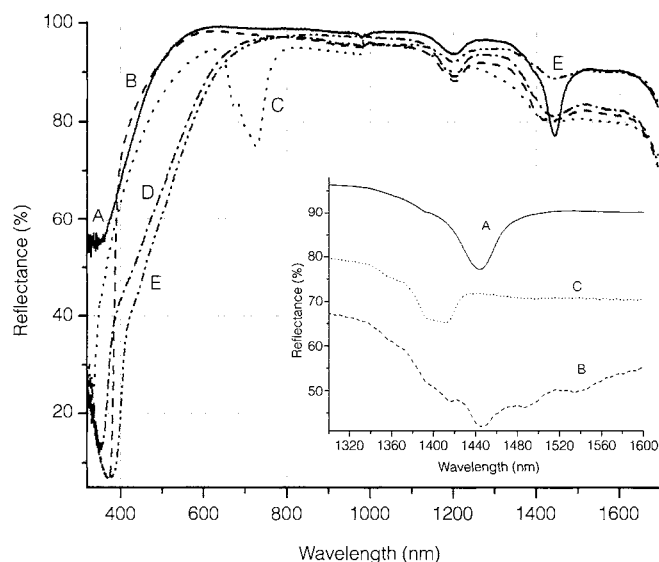


FIGURE 2 Reflectance spectra of the reference white mock paintings in the 320–1700 nm range: (A) lead white (solid line), (B) zinc white (dashed line), (C) lithopone (dotted line), (D) anatase (dash-dot line), (E) rutile (dash-dot-dot line). **Inset:** Reflectance spectra in the 1310–1600 nm range of (A) lead white (solid line), (B) gypsum (dashed line), and (C) the kaolin of the ground (dotted line).

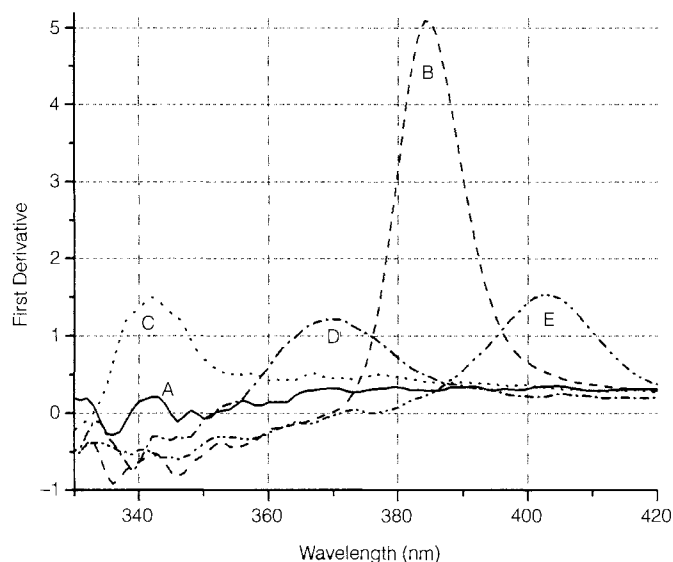


FIGURE 3 First derivative of the reference white mock paintings' reflectance spectra in the 330–420 nm range: (A) lead white (solid line), (B) zinc oxide (dashed line), (C) lithopone (dotted line), (D) anatase (dash-dot line), (E) rutile (dash-dot-dot line).

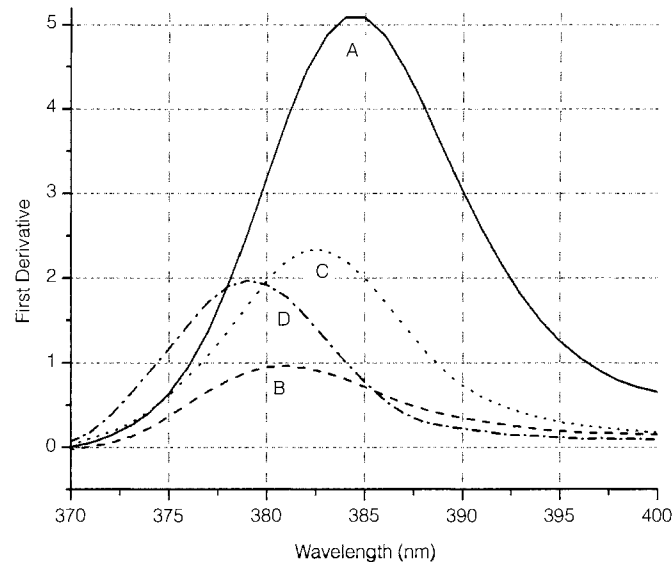


FIGURE 4 First derivative of the reflectance spectra in the 370–400 nm range: (A) reference zinc white (solid line), (B) white spot from Franchetti self-portrait (dashed line), (C) white spot from Carrà self-portrait (dotted line), (D) white spot from Indulis self-portrait (dash-dot line).

ferent provenances), the positive identification of these white pigments remains valid.

Uffizi Self-Portraits

This section discusses a selection of reflectance spectra of white spots from several paintings chosen from the self-portraits held by the Uffizi Gallery and investigated to date. These paintings are by Francesco Franchetti (1900), Enzo Fanfani (1938), Carlo Carrà (1951), Raymond Pitré (1971), and Zarin Indulis (1980).

All the spectra reported present the typical band shape of semiconductors, although some of these appear partially modified by the occurrence of absorption bands related to the presence of other, different-colored pigments (either in mixture, present in the immediate vicinity, or in other layers). The identification of these white pigments still remains possible, however, by observing their first derivative reflectance spectra. Figure 4 shows the correspondence of the first derivative peak of a zinc white reference with the peaks of the spectra taken from the paintings by Franchetti, Carrà, and Indulis. In the paintings by Franchetti and Indulis, lead white is also detected by its typical absorption band in the NIR region at around 1450 nm.

The white pigment lithopone was found in Fanfani's self-portrait, as disclosed by the typical S-type band shape of the reflectance spectrum caused by the presence of ZnS in its composition. When the first derivative of the spectra are calculated, the inflection points are seen to be positioned around 340 nm (ZnS) in correspondence with the lithopone laboratory mock paintings (fig. 5). Moreover, this reflectance curve shows a very weak composite absorption band in the 650–750 nm range (fig. 5 inset), as would be expected for a cobalt (II) ion in a pseudotetrahedral sulfur coordination in ZnS (Weakliem 1962). In fact, this is characteristic of lithopone pigments produced after the mid-1920s (van Alphen 1998, 41–43).

The anatase form of TiO_2 white pigment was found in only one case among the entire group examined, in the Pitré self-portrait. The reflectance spectrum shows several weak-medium absorption bands in the visible region due to the presence of other colored pigments; however, it clearly presents the S-type band shape in the UV-Vis range (350–380 nm). The position of the first derivative maximum of the reflectance spectrum, around 370 nm, confirms that in this case the artist used the anatase white pigment (fig. 6). In contrast, the other TiO_2 white, rutile, was found in several paintings, as confirmed by their first derivative reflectance spectra; this makes

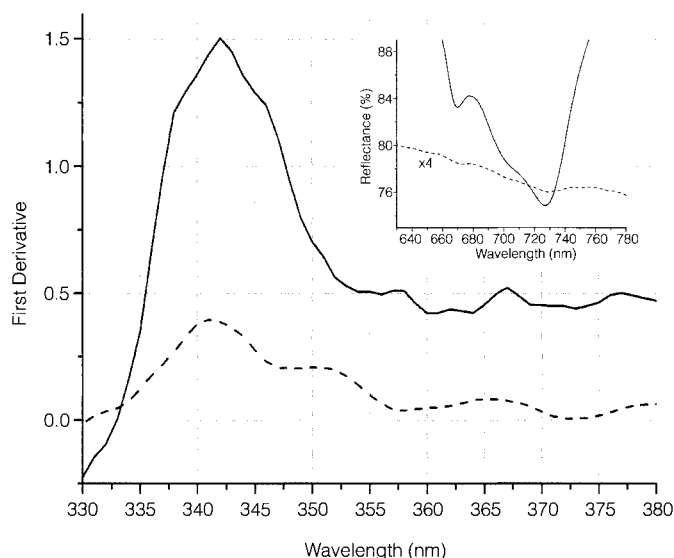


FIGURE 5 First derivative of the reflectance spectra in the 330–380 nm range acquired from Fanfani self-portrait (dashed line) and from reference lithopone (solid line). **Inset:** Reflectance spectra in the 630–780 nm range of the white spot acquired from Fanfani painting (dashed line) and from reference lithopone (solid line). Also shown are composite absorption bands in the 650–750 nm range, caused by the Co(II) ion in a pseudo-tetrahedral sulfur coordination.

it possible to assign these curves to rutile. Moreover, in a few paintings kaolin, used for the ground of the canvas, was also identified due to its characteristic double absorption bands at 1390–1415 nm when compared to the laboratory mock paintings' spectra.

Works by Pasolini

In analyzing the three unusual artworks by Pier Paolo Pasolini, only two white pigments were found. Basically, the entire set of reflectance spectra shows the presence of gypsum (fig. 7) as ground and ZnO and lithopone as white pigments, without any traces of lead white or TiO₂ whites.

Pinocchio Drawings

The spectra acquired from these drawings on paper (dated 1908–11) revealed the presence of lead white, as might be expected in this period, for all the white areas investigated, as well as ZnO in several mixed-color spots (fig. 8). Although the spectra collected on the colored areas were less clear than the reference spectra (due to the presence of mixtures of pig-

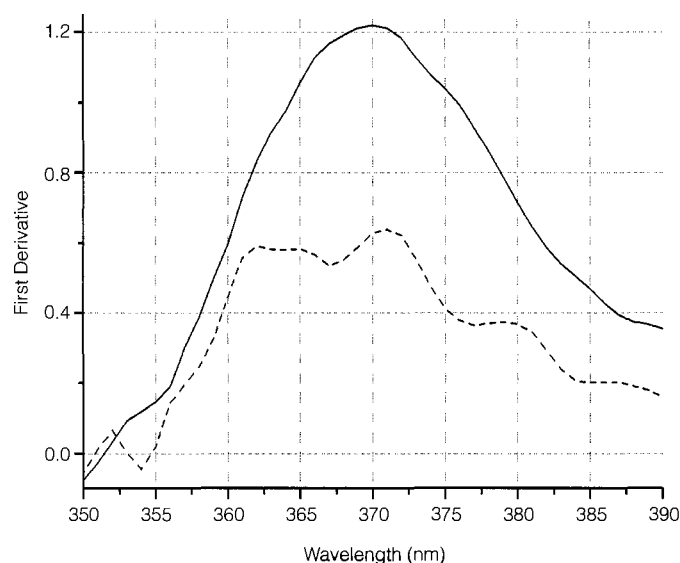


FIGURE 6 First derivative of the reflectance spectra in the 350–390 nm range of the reference anatase (solid line) and the white spot from the Pitre self-portrait (dashed line).

ments), the slope and position of the reflectance bands typical of the semiconductor compounds are visible. The first derivative of the spectrum collected from the skin of *Il Pescatore Verde* (The Green Fisherman) shows a peak around 382 nm, which can be confidently attributed to the presence of zinc white as a result of comparing it with the laboratory standard spectra and spectra reported in literature (Kühn 1986).

Conclusions

In this project, the FORS technique in the 270–1700 nm range was used to characterize and identify white pigments such as lead white, zinc white, titanium white (rutile and anatase forms), and lithopone, on twentieth-century artworks (dating from 1900 to the present day). FORS offers the important advantage of in situ, noninvasive identification of the pigments, providing a simple, safe method of investigating objects of cultural significance.

The data acquired on these three sets of objects are summarized in table 2. From these data it can be said that at

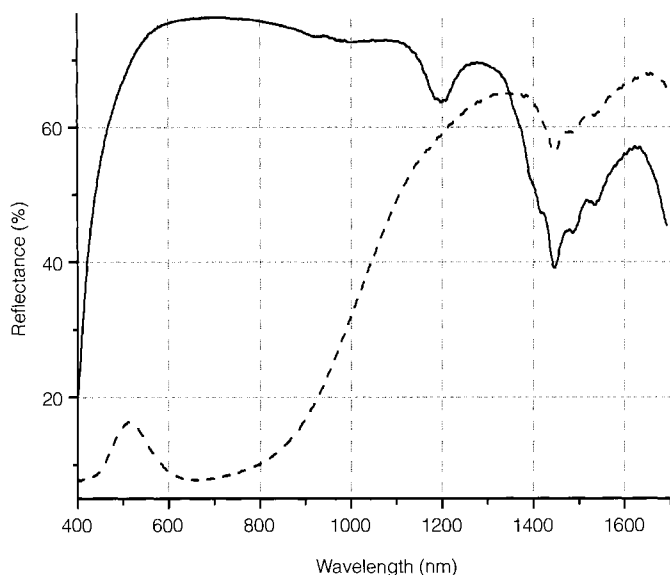


FIGURE 7 Reflectance spectra in the 400–1700 nm range of the reference gypsum mock painting (solid line) and of a blue-green spot in the recto of one of the Pasolini paintings (dashed line).

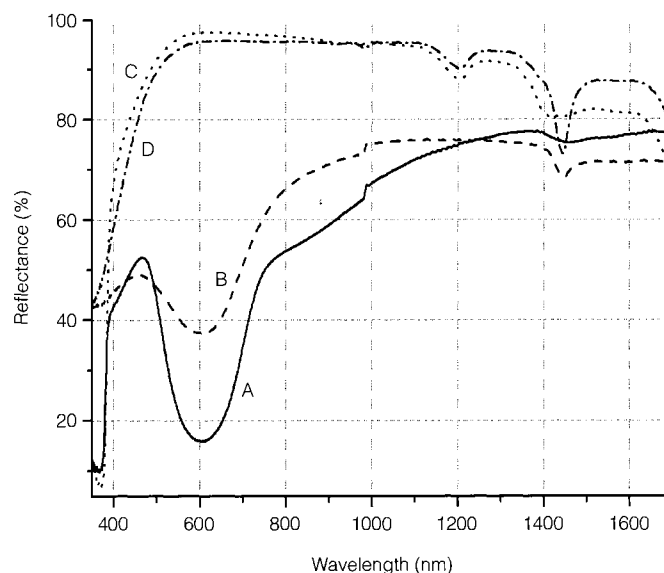


FIGURE 8 Reflectance spectra in the 350–1700 nm range of two light blue spots from *Il Pescatore Verde* (one of Mussino's original drawings for *Pinocchio*) and two white laboratory references: (A) solid line; (B) dashed line; (C) zinc white (dotted line); (D) lead white (dash-dot line).

Table 2 Occurrence, timeline, and maximum peak position range of the first derivative of the reflectance spectra of the white pigments studied in this data set.

Pigment	Occurrence	Timeline	First Derivative Position
Lead white	Uffizi: 4/31 Pinocchio: 4/4 Pasolini: 0/6	1900–1980	
Zinc white	Uffizi: 21/31 Pinocchio: 1/4 Pasolini: 4/6	1900–1990	378–384 nm
Lithopone	Uffizi: 3/31 Pinocchio: 0/4 Pasolini: 4/6	1938–1949	338–342 nm
Anatase	Uffizi: 1/31 Pinocchio: 0/4 Pasolini: 0/6	1971	370–373 nm
Rutile	Uffizi: 11/31 Pinocchio: 0/4 Pasolini: 0/6	1961–1990	397–404 nm

Note: Uffizi = Self-Portrait Collection of the Galleria degli Uffizi. Pinocchio = Paper drawings for *Pinocchio*, Giunti Editori S.p.A., Iconographic Collection. Pasolini = Pier Paolo Pasolini paintings from the Gabinetto G. P. Vieusseux, Archivio Contemporaneo Alessandro Bonsanti, Fondo Pasolini.

present the most important and widely used artists' white pigment is rutile. Its use has steadily increased since World War II, although zinc white is also still widely used for artistic purposes. Lithopone and anatase were more popular between the 1920s and 1950s, with the latter pigment being more common than rutile before and during the First World War. Nowadays their use as an artists' pigment has practically disappeared. Lead white also practically disappeared after 1950; it appears in only a single case: a self-portrait by Zarin Indulis painted in 1980. Finally, as expected, the *Pinocchio* drawings made in 1911 do not show the presence of any titanium dioxide whites or lithopone doped with cobalt salts, but only lead white found in the pure white color fields, and zinc white when mixed with different color pigments.

Acknowledgments

The authors would like to thank Antonio Paolucci (soprintendente per il Polo Museale Fiorentino), Director Antonio Natali and staff of the Uffizi Gallery, Giunti Editori, and Gabinetto Vieusseux, all in Florence, who kindly gave permission for investigation of the artworks from their collections. Special thanks for their active collaboration go to Soprintendente Cristina Acidini of the Opificio delle Pietre Dure in Florence; to the director of the OPD Easel Painting Conservation Department, Marco Ciatti; and to Director Cecilia Frosinini and Conservator Letizia Montalbano of the OPD Prints and Drawings Conservation Department. Masahiko Tsukada thanks the Italian National Research Council and the Japan Society for the Promotion of Science for financially supporting his stay in Florence in conjunction with the project Investigation of Modern Paintings by Using Noninvasive Spectroscopic Techniques, a joint effort of the Institute for Applied Physics Nello Carrara of the Italian National Research Council (IFAC-CNR) and the National Museum of Western Art in Tokyo.

Appendix: A Brief History of the Collections

Self-Portrait Collection of the Galleria degli Uffizi

The acquisition of artists' self-portraits at the Uffizi (Uffizi 1980) began in 1664, when Cardinal Leopoldo de' Medici (1617–1675) started gathering examples of this particular type of artwork. The collection, which initially numbered about 80 paintings, had increased to more than 180 by the beginning of the eighteenth century, in particular under the guidance of Filippo

Baldinucci (1625–1696), who catalogued the collection in 1681. Tuscan artists were those most represented, together with others from Bologna, Venice, Rome, and Naples. Later, works by foreign artists were added, including Rembrandt, Van Dyck, Vouet, and Ribera. In 1682, Cosimo III de' Medici (1642–1723) organized the collection assembled by his uncle Leopoldo in a room in the west wing of the Galleria.

A further increment dates from 1768, when Pietro Leopoldo di Lorena purchased 112 self-portraits composing the Pazzi collection, including various doubtful ones. Acquisitions proposed by princes, diplomats, collectors, descendants of the artists, and living artists themselves continued until the mid-nineteenth century, eventually resulting in the necessity to limit the addition of works, which in fact halted temporarily in 1858, with a self-portrait by Ingres. The appeal for self-portraits from Italy and abroad was renewed in 1864 by the central government and was extended after 1912 to include sculptors' portraits. These efforts brought works by such artists as Corot, David, Delacroix, Böcklin, and Ensor. Italian artists of the nineteenth and early twentieth centuries were well represented, together with numerous artists from Russia, Poland, Scandinavia, Hungary, Switzerland, Germany, Spain, Portugal, France, Belgium, Holland, Great Britain, and the United States, forming a collection that numbered about seven hundred pieces in 1937.

The modern period began in 1973, with the reopening of the Corridoio Vasariano, where part of the historic collection of self-portraits was displayed. Works by Chagall, Siqueiros, Rosai, and other significant artists were added in the years to follow. The fourth centennial celebration of the founding of the Uffizi, held in 1981, was the occasion for numerous artists or their heirs to answer the request for donations proposed by the director, resulting in the addition of another 230 works to the collection by 1983. Most recently (2002), 295 self-portraits by contemporary artists (paintings, drawings, prints, and photographs) were acquired from the heirs of the Swiss collector Raimondo Rezzonico.

Fondo Pasolini, Archivio Contemporaneo Alessandro Bonsanti, Gabinetto Vieusseux, Florence

The Gabinetto Vieusseux institution was founded in 1819, originally as a literary club and circulating library open to the public (Desideri 2001). The Fondo Pasolini is part of the vast collection of over 500,000 documents and 50,000 volumes conserved in the Archivio Contemporaneo Alessandro Bonsanti, which was founded in 1975 and named after the former director of the Vieusseux. This special section of the

scientific-literary institution contains manuscripts, documents, and the libraries of significant representatives of contemporary culture, covering activities ranging from literature (prose and poetry) to music, theatre, architecture, painting, photography, and literary and art criticism. The archives also make this important patrimony available to the public according to precise rules of conservation, and promote conferences, exhibitions, studies, and publications. The Pasolini collection consists of some 340 objects, including manuscripts and typed originals of Pasolini's literary works, scripts, and correspondence; numerous drawings and paintings; photographs (of people and of his film sets); bibliographical materials, including magazine and newspaper clippings; and his library (mainly poetry in dialect).

The three double-sided paintings examined in this study date from Pasolini's initial period of experimentation in the visual and poetic arts, which began in 1941 when he was studying at the University of Bologna and concluded with his departure for Rome in the early 1950s. They are the only paintings on a canvas support among the many art objects in the Vieusseux Pasolini Collection (those of known date range from 1941 to 1975). These works are mainly drawings and paintings on paper but also include some on cardboard, fiberboard, and even cellophane.

Pasolini seems to have had little or no formal training as a painter, relying for the basics of technique and materials on contact and close friendship with artists such as Federico De Rocco (1918–1962), a pupil of Bruno Saetti at the Venice Accademia, and Giuseppe Zigaina (Pasolini 1993). Of the three works examined, the closest to a traditional painting is the landscape of a Tagliamento river scene in the vicinity of Versuta, near Casarsa in Friuli, where Pier Paolo taught school during a period of refuge from the dangers of the war. The subject matter of the paintings and drawings made at this time appears closely anchored to the persons and scenery with which the artist was most familiar.

Iconographic Collection of the Giunti Editori S.p.A.

The rich patrimony conserved in the archives of Giunti Editori S.p.A. in Florence includes more than a thousand sets of original plates and drawings that the historic Florentine publishers Paggi, Bemporad, and Marzocco used to illustrate their books for over a century (Giunti Editori S.p.A. 2007). A special section of the archives is dedicated to the iconographic collection of *Pinocchio*, containing the original drawings for various historic editions of Carlo Collodi's masterpiece: from the first, published by Paggi in 1883, illustrated by Enrico Mazzanti

(1852–1893), to those by Carlo Chiostrì (1863–1939), Attilio Mussino (1878–1954), and Piero Bernardini (1891–1974). The series of drawings in question was made at the request of the editor Enrico Bemporad by Attilio Mussino in 1908, to illustrate a new edition of *Pinocchio*. They were presented with success by the artist at the Esposizione Internazionale (world's fair) in Turin in 1911. The long-nosed wooden figure of Pinocchio created by Mussino is still among the most famous and familiar in the history of this classic of Italian literature, and may be admired in various editions of *Pinocchio* still present today in the Giunti catalogue.

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Studies of Modern Oil-Based Artists' Paint Media by Gas Chromatography/Mass Spectrometry

Michael R. Schilling, Joy Mazurek, and Thomas J. S. Learner

Abstract: *The range of modern, oil-based paint media used by artists has expanded far beyond the traditional drying oils. This category of media now includes three diverse product classes with vastly different chemical formulations and physical properties. Processed drying and semi-drying oils such as linseed, safflower, sunflower, and castor form the first class. From a compositional perspective, these modern oils are nearly identical to the traditional triglyceride oil paint media, but are often modified by treatment with heat and air to produce desirable working properties. Alkyds, the second major class of oil-based paint media, were introduced in the 1940s and may be broadly considered as oil-modified polyesters. Alkyd resins are manufactured from polyols (typically glycerol or pentaerythritol), polybasic acids (phthalic anhydride is the most common), and a source of fatty acids (usually a vegetable oil); styrene, acrylics, and isocyanates may be added as modifiers. The polyester component greatly enhances drying rate, weatherability, and gloss, making alkyds highly suited for house paint and industrial applications. Water-mixable oil (WMO) paints, introduced in the 1990s, make up the final class of artist-quality modern oil paints. These paints are typically formulated with nonionic surfactants, amine soaps, and other additives that eliminate the need for organic solvents for thinning and cleanup. There is an obvious need for a comprehensive analytical technique for differentiating among the three classes of modern oil-based paint media. Fourier transform infrared (FTIR) spectroscopy works well for differentiating modern oils from alkyd resins due to the abundance of phthalate esters in alkyds, but is incapable of detecting the reduced amounts of additives present in water-mixable oils. Pyrolysis gas chromatography/mass spectrometry (PyGC/MS) using tetramethylammonium hydroxide shows great promise in differentiating all three classes qualitatively, but is less effective*

in resolving mixtures of oil media. Recently, a gas chromatography/mass spectrometry procedure for quantitative analysis of alkyd resin components was introduced that utilized aminolysis with n-butylamine followed by trimethylsilylation. Application of this procedure on numerous oil paint samples from the three classes was tested to build up a reference database. Next, the procedure was used to study samples from a number of drip paintings by Jackson Pollock. Lastly, tests on water-mixable oil paints revealed that the nonionic surfactants could be detected in the form of silylated ethers, although not quantitatively.

Introduction

Prior to the twentieth century, artists were limited in their choice of oil paint media to the three common drying oils: linseed oil, walnut oil, and poppy oil. By comparison, today's artists have access to three diverse oil-based paint classes: drying and semi-drying oils, alkyds, and water-mixable oils (WMOs). All three classes have different chemical compositions and physical properties, and although they are all produced as artist-quality paints, the alkyds are far more commonly formulated for commercial applications, in particular for house paint. To properly care for paintings made with these paints, it will be important to understand how each of these classes differs physically and chemically from traditional oil paints, and how it will change with age. As a first stage in achieving this understanding, there is a need to identify and test a comprehensive analytical technique capable of differentiating among the three classes of modern oil-based paint media. Proper identification of modern oil paints in works of art first requires an understanding of their formulations, especially their organic components. The intent of this

paper is to (1) provide a general survey of the three classes of modern commercial oil paints, (2) describe a gas chromatography/mass spectrometry (GC/MS) procedure for analysis of key constituents in the binding media, (3) discuss application of the procedure to studying numerous reference materials, including alkyd, oil, and WMO paints, and (4) characterize several important drip paintings by Jackson Pollock.

Modern Oil-Based Paint Types

Modern Oils

Processed drying and semi-drying oils such as linseed, safflower, sunflower, tung, and castor form the first class of modern oils. From a compositional perspective, these oils are nearly identical to the traditional triglyceride oil paint media, but they are often modified by treatment with heat, air, and chemicals to produce desirable working properties such as viscosity, drying rate, and color (Wicks, Jones, and Pappas 1999, 264–66). In addition to the seed oils, purified fractions of unsaturated fatty acids are an inexpensive source of fatty acids used in modern oil paints. Many companies, including Akzo-Nobel, BASF, Cognis, Croda, and Ecogreen, manufacture and distribute these so-called oleochemicals under a variety of names. Table 1 gives a compilation of the compositions of most of the modern oils that have been used as paint media (Crombie, Comber, and Boatman 1955; Wicks, Jones, and Pappas 1999, 259; APAG 2006).

Table 1 Fatty acid compositions of common modern oil media.

Oil	Fatty Acid Weight Percentages					
	Palmitic	Stearic	Oleic	Linoleic	Linolenic	Other
Castor	1	1	7	3		Ricinoleic 87
Coconut	48	15	29	9		
Cotton	23	3	25	45	1	
Linseed	6	4	19	24	47	
Oiticica	6	10	14	21		Licanic 48
Peanut			54	26		
Rapeseed	1	1	15	15	8	Erucic 60
Safflower	7	3	18	69	4	
Soybean	11	4	23	54	8	
Sunflower	7	5	23	65		
Tall oil			46	41	3	Rosin 8
Tung	2	2	5	3		Eleostearic 87

From the perspective of an analytical chemist, it is important to note that the oil medium in a modern paint formulation may not originate from a single product. Suppliers of oils to paint manufacturers are at liberty to combine oils and/or fatty acid products to take advantage of seasonal market availabilities and to control costs, as long as they remain consistent with the specifications of the paint formulation.

Alkyds

Since the 1940s, alkyds have been the cornerstone of the paint and coatings industry. Alkyds are synthetic resins made through the condensation of polyhydric alcohols with polybasic acids in the presence of fatty oils or fatty acids. Some formulations are modified with other types of resins (Wicks, Jones, and Pappas 1999, 268–85; Jones 1985, 409–23; Lin 1992). Figure 1 shows an idealized structure of an alkyd. From the standpoint of their chemistry, alkyds can be considered as oil-modified polyesters. Although recently supplanted in the house paint market by acrylic dispersions, alkyds continue to find wide application as binders in paints and inks, pavement striping, rubberized coatings, plasticizers, caulks, and adhesives. Alkyds remain a favorite of paint manufacturers because they are relatively inexpensive to manufacture and their properties can be customized by varying the key ingredients.

There are three major classes of alkyd resins (Learner 2004, 17–22). Drying alkyds have a high content of multiply unsaturated fatty acids that, like drying oils, cause them to dry primarily by autoxidation. Drying alkyds are common in house and artists' paint formulations. Nondrying alkyds are formulated from oils that contain low levels of unsaturated fatty acids (such as coconut oil). They dry mainly by solvent evaporation and are used in baking enamels or as polymeric plasticizers. Modified alkyds contain additional monomers, such as styrene, vinyl toluene, rubber, isocyanate, and acrylic, that alter their physical properties and resistance to weathering; they are used in specialty paint applications.

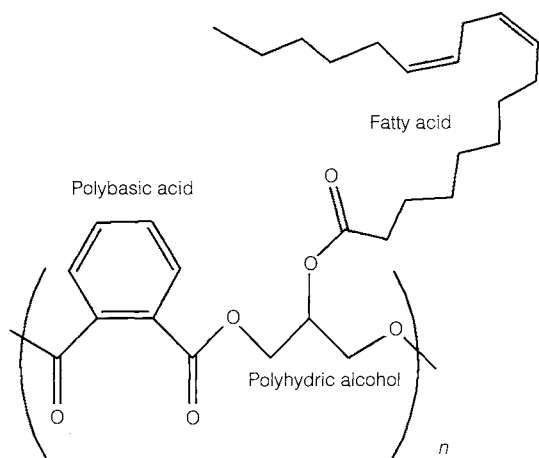


FIGURE 1 Idealized structure of an alkyd resin.

Although a wide range of key ingredients have been used by alkyd formulators in various commercial paints (Schilling, Keeney, and Learner 2004), in actuality only a few ingredients are common to most artists' alkyd tube colors and alkyd house

paints. The most commonly used polybasic acid is phthalic anhydride (fig. 2). Although it is an acid anhydride, it reacts like the difunctional *orthophthalic acid*. Glycerol and pentaerythritol (fig. 3) are the most frequently used polyhydric alcohols; they possess three and four alcohol functional groups, respectively. Regarding the oils that are compatible with alkyd formulations, the selection is quite broad and is not limited solely to conventional drying oils, because the increased functionality of the polyols enhances the development of highly branched polymer chains regardless of the susceptibility of the fatty acids contributed by the oil to autoxidation. Thus, depending on the desirable working properties, alkyd formulations routinely incorporate drying, semi-drying, and nondrying oils. Typical oils in drying alkyds include castor, linseed, soy, safflower, and tung.

Oil length is a term used by alkyd formulators to specify the weight percentage of oil, triglyceride equivalent, or fatty acids in a finished alkyd resin. Short-oil alkyds have 35–45 percent oil or fatty acids; medium-oil alkyds have 46–55 percent; long-oil alkyds have 56–70 percent; and very-long-oil alkyds have more than 70 percent oil or fatty acids. Most artists' and house paints are in the long-oil alkyd category.

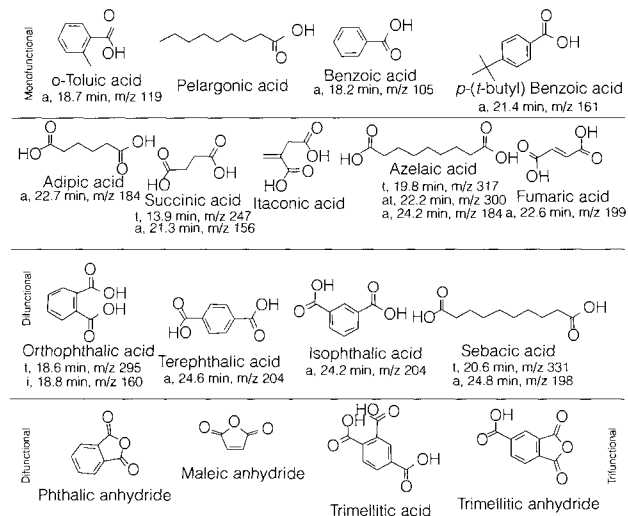


FIGURE 2 Structures and relevant chromatographic information for polybasic acids commonly formulated into alkyd resins. Listed below the molecular structures are the types of derivative formed (t = trimethylsilyl ester, a = amide, i = imide), retention time, and the ion used for GC/MS quantification. Acids with no data listed cannot be detected by the modified ASTM GC/MS procedure.

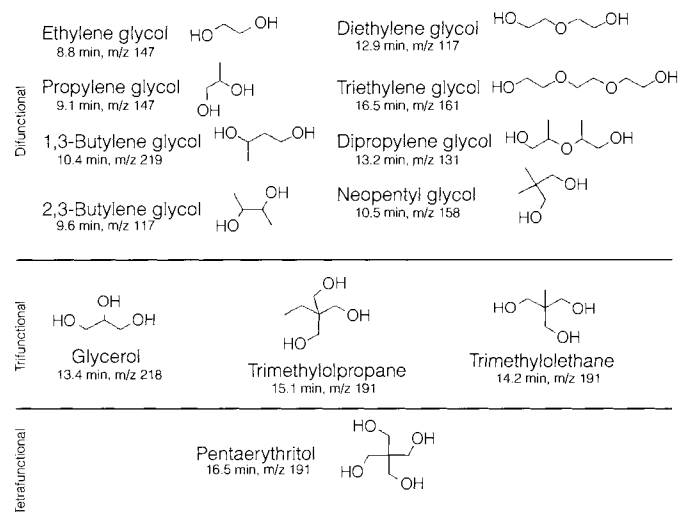


FIGURE 3 Structures and relevant chromatographic information for polyols commonly formulated into alkyd resins. Listed below the molecular structures are the retention time of the trimethylsilyl ether derivative and the ion used for GC/MS quantification.

Water-Mixable Artists' Oil Paints

Due to stringent environmental regulations, health and safety concerns, and economic incentives to control raw material costs, water has come to replace volatile organic solvents in many industrial, commercial, and retail trade paint formulations. In keeping with this trend, extensive experimentation by artists' paint manufacturers led to the development, in the mid-1990s, of specially formulated brands of oil tube colors that could be diluted with ordinary tap water instead of the usual turpentine or paint thinner. Moreover, brushes, palettes, and other implements used with these "water-mixable" oil paints could be quickly and easily cleaned with warm, soapy water. However, the paints lose their water solubility when fully dry.

Known in trade circles by a variety of names, including *water-soluble oil* and *water-reducible oil*, these products were manufactured to match, as closely as possible, the buttery consistency, drying rate, transparency, and appearance of traditional oil tube colors as described in ASTM D4302-90. Today, four manufacturers produce a full line of water-mixable oil paints: Winsor & Newton (Artisan), Holbein (Aqua Duo), Grumbacher (Max), and Royal Talens (Van Gogh H2Oil). As evidenced by increased product sales, WMO paints are becoming more popular with artists and especially university art programs, where health and safety issues are paramount.

Relatively little is known in the conservation field about the composition of water-mixable oil paints because only a few publications describe these comparatively new commercial products (Dye 2001, 12–26; Creevy 1994, 168–69). The patent literature states that polyoxyethylene-based nonionic surfactants (or POE, for short), which have the general structure $R_1O-(CH_2CH_2O)_n-R_2$, are a versatile option for enhancing the water mixability of oil paint media (Chambers, Hoyte, and Stegmeir 1994, 1995; Katsuya 1995). POE emulsifiers that impart the best overall performance to WMO paints have hydrophilic-to-lipophilic balances between 8 and 18 and incorporate unsaturated fatty chains into their structures. Unsaturated fatty acids on the POEs are capable of cross-linking with the fatty acids from the oil component, which vastly improves their long-term stability. The patents list several POE products that perform well in WMO paint formulations. Atlas G1086 (from Uniqema, a division of Imperial Chemical Industries) is classified as a polyoxyethylene sorbitol hexaoleate compound (fig. 4). Tergitol 15-S (Dow Chemical Company) is composed of ethoxylated secondary fatty alcohols, whereas Neodol (Shell Chemicals Limited) contains ethoxylated primary fatty alcohols. Other additives used in WMO paints are reported to be amine soaps of fatty

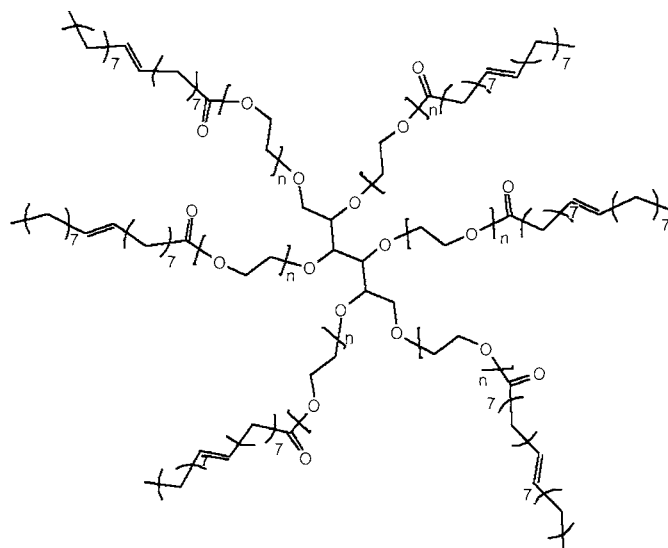


FIGURE 4 Structure of Atlas G1086, a polyoxyethylene sorbitol hexaoleate surfactant.

acids and thixotropic stabilizers based on castor oil derivatives (Chambers, Hoyte, and Stegmeir 1994, 1995).

Analysis of Modern Oil Paints

Although characterization of modern oil paint media may be problematic due to the complexity of the formulations and variety of components, there have been some notable successes with qualitative analytical techniques. For example, phthalate esters and modifiers in alkyds are readily detectable using FTIR spectroscopy and PyGC/MS (Learner 1996; 2001; 2004, 37). As a class of compounds, POE additives present analytical challenges due to their large molar masses, their low concentrations in paint formulations, and the vast number of commercially available products (Hummel 2002, 213–26). POE additives in water-mixable oils cannot be detected by FTIR due to their low concentration, whereas they may be detected in the form of methyl ether derivatives using PyGC/MS with online tetramethylammonium hydroxide derivatization (Greet 2006). Limitations of PyGC/MS procedures include the inability to resolve mixtures of modern oil media (such as oil and alkyd) on the basis of simple qualitative ratios, and the inherent variability of the pyrolysis process that restricts the possibility of performing quantitative analysis (Learner 2004, 80).

In 1996, the American Society for Testing and Materials (ASTM) published a procedure for quantitative analysis of

polyols in bulk samples of alkyd resins (ASTM 2002). In a two-step reaction utilizing aminolysis with *n*-butylamine followed by trimethylsilylation (fig. 5), the amine reacts with alkyd ester groups to liberate polyols, which subsequently are silylated on a quantitative basis to form trimethylsilyl (TMS) ether derivatives. Depending on their functionality within the alkyd resin, fatty acids and polybasic acids may form several types of derivatives, giving rise to additional peaks in the chromatograms that the ASTM did not quantify. Unfortunately, alkyd modifiers, which do not produce volatile products from this two-step reaction, cannot be detected.

Adapting this procedure to accommodate small paint samples made it possible to measure quantitatively the polyols present in numerous alkyd resins and in Griffin alkyd paints. The acidic components were quantified using Meth Prep reagent (Alltech Associates) on a replicate set of samples (Schilling, Keeney, and Learner 2004). Obviously, the modified ASTM procedure would have even greater utility if it could quantify polyols, polybasic acids, and fatty acids in alkyd and modern oil paints in a single sample. Accomplishing this first requires an appreciation of how the acidic components might react with the derivatization reagents.

Each polyol forms a single TMS ether derivative, but the situation is more complex for saturated fatty acids, dicarboxylic fatty acids, and phthalates, because each may bond to the oil or alkyd resin in several ways. Carboxylic acid esters in the oil or alkyd form amide derivatives, whereas free acids form TMS esters. Dicarboxylic acids (such as azelaic acid, sebacic acid, and all phthalates except the ortho isomer) form at least three derivatives: free dicarboxylic acids form di-TMS derivatives, diesters form diamides, and compounds with an ester on one end and an acid group on the other form mixed TMS-amide derivatives. Orthophthalates form imides in addition to the aforementioned dicarboxylic acid derivatives. However, one distinct advantage of this procedure is the capability of estimating the degree of hydrolysis from the relative contents of free and esterified acids.

Experimental Method

Sample Preparation

1. Weigh paint sample (<100 μg) into a crimp-top vial, add 40 μl of *n*-butylamine, crimp the seal, and heat for five hours at 95° C. Remove from heat, allow to cool, and centrifuge.
2. Remove crimp top, add 1 μl of 2000 ppm 1,4-butanediol (internal standard) and 1 μl of water. Recap with a new crimp-top lid, seal the vial, and heat for five

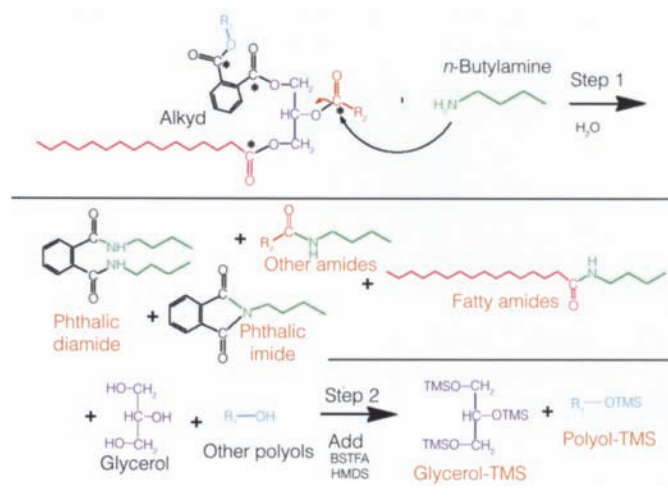


FIGURE 5 Chemical reactions showing aminolysis and silylation of an idealized alkyd resin.

hours at 95° C. Remove from heat, allow to cool, and centrifuge.

3. Remove crimp top and transfer contents to a 2 mL autosampler vial using a long pipette tip. Add 58 μl of derivatization mixture [one part *N,O*-bis(trimethylsilyl)trifluoroacetamide to four parts hexamethyldisilazane], recap with a new crimp-top seal, and heat for thirty minutes at 70° C. Remove from heat, allow to cool, and centrifuge.
4. Transfer contents to a 100 μl conical glass insert and inject into GC/MS.

GC/MS Conditions

- 30 M \times 0.25 mm \times 1 μm DB-5MS column with helium carrier gas flow rate of 1.6 mL/minute.
- Splitless inlet set to 280° C with a total flow rate of 51 mL/minute.
- Temperature program: 50° C for one minute. Ramp at 10° C/minute to 230° C. Ramp at 25° C/minute to 325° C. Isothermal for 25 minutes.
- Secondary ion chromatograms facilitate the resolution of any partially overlapping peaks.
- Pyridine is used as wash solvent for the autosampler.
- Information pertaining to the analyte peaks—such as derivative type, retention time, and quantitation ion—is listed in table 2 and figures 2 and 3 to aid in setting up the GC/MS method.

Table 2 Fatty acids that may be quantified using the modified ASTM GC/MS procedure, following the same convention as in figure 2.

Fatty Acid	Amide		TMS-Ester	
	Time (minutes)	Ion for Quantitation	Time (minutes)	Ion for Quantitation
Lauric acid	21.5	115	18.3	257
Myristic acid	22.6	115	20.2	285
Palmitic acid	23.4	115	21.5	313
Oleic acid	24.3	337	22.4	339
Stearic acid	24.4	115	22.5	341
Ricinoleic acid	25.4	311	N/A	N/A
Arachidic acid	25.7	115	23.3	369

- All calibration curves gave quadratic or linear responses forced through zero with correlation coefficients 0.95 or better, with the vast majority exceeding 0.99.

The components of modern oils and alkyds are numerous and chemically diverse and possess a wide range of solubilities; these factors affect the selection, preparation, and handling of the GC/MS calibration standards. Methyl esters, selected to represent the corresponding acid esters in the oil or alkyd matrix, are easy to obtain from chemical suppliers, as are polyols, free fatty acids, and free phthalic acid isomers. Of the monomethyl esters of dicarboxylic acids, only monomethyl azelate could be located from the typical vendors.

Recommendations and Caveats

- It is best to prepare separate 3000 ppm mixed-stock solutions of polyols in water, methyl esters of fatty acids and phthalates in toluene, and free fatty acids and phthalic acid isomers in a 1:1 mixture of chloroform and ethanol.
- It is important to handle the calibration standards carefully during derivatization, as some of the individual components may be slightly volatile. Accordingly, the polyol standard should not be evaporated in the crimp-top vials prior to derivatization, but instead introduced with the internal standard to the *n*-butylamine into their respective vials at the step in the procedure when the internal standard and water are added to the samples.
- Concerning the methyl ester and free acid stock solutions, the corresponding organic solvents are quite

volatile and can be evaporated safely with a gentle stream of nitrogen.

- Although 25 ml hypovials of the silylating reagents are less expensive, contamination by phthalates and other plasticizers can be minimized through the use of 1 mL ampoules of the reagents.
- Because *n*-butylamine may partially degrade the crimp-top seals, they must be replaced at each stage.
- To ensure proper injection, it is also important that, once the autosampler vials are loaded into the tray, the caps be opened in order to release pressure from within the vials.

Expression of Data

One distinct advantage of quantitative GC/MS testing is that the data can be expressed in different ways, such as molar ratios and weight percentages, to aid in characterizing pure and mixed oil-based media (Schilling and Khanjian 1996; Schilling, Keeney, and Learner 2004). In this study, the analytes were quantified as underivatized compounds (and phthalic acid was quantified as phthalic anhydride) to facilitate the calculation of component molar ratios and the percentage compositions of the oil media.

Results for Alkyd Resins and Griffin Alkyd Paints

The modified ASTM procedure was found to work extremely well for quantitative GC/MS analysis of the polyols, polybasic acids, and fatty acids in both their ester and free acid forms. Reproducible compositional results were obtained in tests of selected Griffin alkyd paints (table 3); moreover, these results were consistent for sample weights ranging from 15 µg to 220 µg. In tests of five-year-old films of commercial alkyd resins with

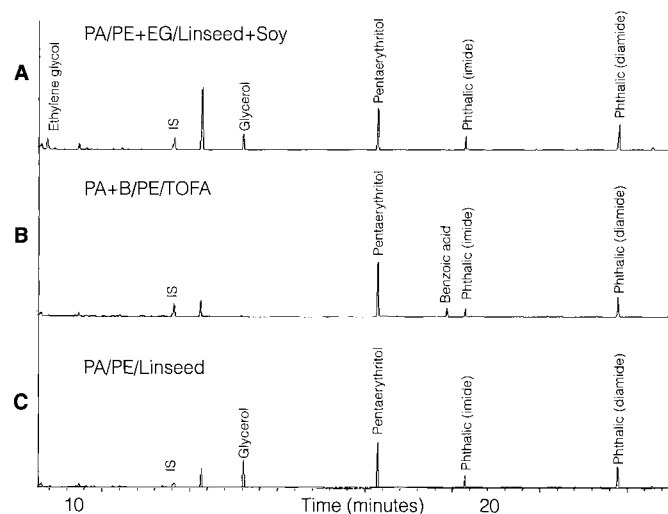
Table 3 Compositional results for Griffin alkyd paints from GC/MS analysis.

Griffin Alkyd Paints (20–50 µg replicates)	Concentration, Weight %			Molar Ratios				
	<i>o</i> -Phthalic Acid	Glycerol	Pentaerythritol	A/P	P/S	P/G	A/G	<i>o</i> -P/A
London Red								
mean	6.3	2.9	3.9	0.84	2.3	0.37	0.30	4.0
standard deviation	0.5	0.2	0.4	0.15	0.3	0.12	0.04	0.3
% RSD	8	5	10	17	15	33	13	7
Phthalocyanine Blue								
mean	7.2	3.6	4.5	0.84	2.2	0.39	0.32	3.3
standard deviation	0.3	0.0	0.1	0.09	0.2	0.07	0.02	0.2
% RSD	4	1	1	11	10	18	7	5
Lamp Black								
mean	10	5.3	6.1	1.34	1.7	0.28	0.4	2.8
standard deviation	0.3	0.1	0.2	0.15	0.1	0.06	0.0	0.2
% RSD	2	3	4	11	6	21	10	7
Titanium White								
mean	5.2	2.6	3.2	1.3	1.9	0.23	0.3	3.5
standard deviation	0.5	0.3	0.3	0.04	0.02	0.01	0.01	0.1
% RSD	9	12	11	3	1	6	5	4
Cadmium Red								
mean	4.7	2.5	2.9	1.2	2.0	0.26	0.30	3.4
standard deviation	0.4	0.1	0.3	0.07	0.1	0.06	0.05	0.3
% RSD	9	5	9	6	3	22	16	10

known compositions (fig. 6), the relative error for all the components (with the exception of benzoic acid) was ± 15 percent. No free fatty acids were detected in any of the resins, indicating that hydrolysis has not yet occurred.

Drawbacks of the procedure include (1) the calibration graph for the chain-stopping agent benzoic acid did not give a good curve fit, which means the analysis is only qualitative; (2) maleic anhydride and some of the acids in figure 2 could not be detected; (3) multiple derivatives for the dicarboxylic acids make it difficult to estimate their total concentration.

FIGURE 6 GC/MS results for alkyd resins composed of (A) phthalic anhydride, pentaerythritol, ethylene glycol, linseed oil, and soy oil; (B) phthalic anhydride, benzoic acid, pentaerythritol, and tall oil fatty acids; and (C) phthalic anhydride, pentaerythritol, and linseed oil. IS=internal standard.



In summary, if the sample quantity is limited, the ASTM procedure alone is quite good for general identification of alkyd and oil media. If, however, sample quantities are adequate, one sample should be tested with the modified ASTM procedure and a second with Meth Prep for optimum quantitative results (White and Pilc 1996; Schilling et al. 2000).

“Drip” and “Poured” Paintings by Jackson Pollock

A technical study of five “drip” and “poured” paintings by Jackson Pollock was undertaken in order to investigate the relationship between the development of his painting style and his adoption of commercial paints (Lake, Ordoñez, and Schilling 2004). As a later follow-up to this detailed study, selected samples were tested using the modified ASTM procedure to assess its suitability, to obtain further compositional details about Pollock’s paint media, and to compare the data to the earlier results from Meth Prep. All of the paintings are from the collections of the Museum of Modern Art, New York: *There Were Seven in Eight* (1945), *Full Fathom Five* (1947), *Number 1A* (1948), *Number 12* (1949), *One: Number 31* (1950).

Figure 7 shows a typical result for a sample of blue paint from *Number 1A* (1948). The absence of phthalates and the characteristic peak pattern of fatty acids and glycerol indicate that this is an oil paint medium, possibly linseed oil. It is also apparent that there are significant levels of free fatty acids in the paint, indicating that hydrolysis has occurred. Table 4 lists the quantitative data for the full set of Pollock paints. High levels of phthalic acid were detected in five of the samples, mainly from the more recent paintings, and traces in five others. Pentaerythritol was present in only two samples. Most of the samples have hydrolyzed to a fairly large extent.

The molar ratio data for the Pollock samples are listed in table 5. Drying oils were identified on the basis of azelaic acid/palmitic acid (A/P) ratio, and oil type by palmitic acid/stearic acid (P/S) ratio. The palmitic acid/glycerol (P/G) ratio for most drying oils is between 0.2 and 0.5, but very low values may indicate the presence of tall oil fatty acids (TOFA) instead of oil. The phthalic anhydride/azelaic acid (PA/A) ratio permits the estimation of oil length (Schilling, Keeney, and Learner 2004). Overall, there was good agreement between the results from the modified ASTM procedure and Meth Prep, although the recovery of azelaic acid was more variable

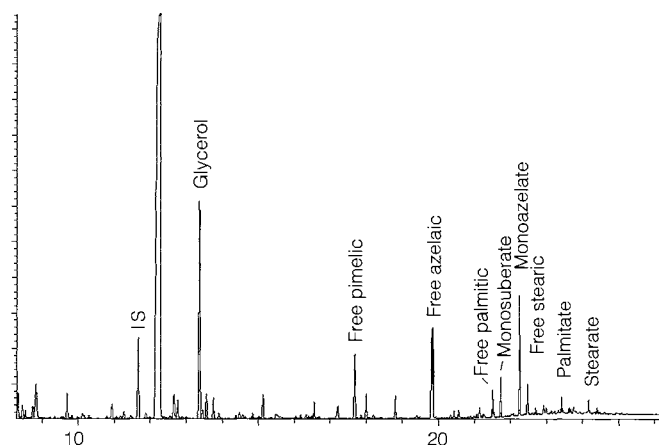


FIGURE 7 GC/MS result for blue paint from *Number 1A* (1948) by Jackson Pollock. IS=internal standard.

than expected. This may be explained by a variation in proximity of each sample to the painted surface, because azelaic acid is a product of oxidation. To summarize the GC/MS results: Jackson Pollock used artists’ oil colors and commercial alkyd house paints to make his drip paintings. In the five paintings examined, it was evident that alkyds appeared more frequently in the later paintings.

Analysis of Artists’ Water-Mixable Oil Paints

The final topic is determining whether or not WMOs can be differentiated from traditional oil and alkyd paint media using the modified ASTM procedure. It was clear from the outset of this research that large molecules such as POE additives could not possibly be recovered intact from a dried WMO paint on a quantitative basis, but it was hoped that characteristic marker compounds could be identified. Figure 8 shows the results of GC/MS analysis of three water-mixable oil media and Cirrasol. Small peaks from the POEs detected in the total ion current (TIC) mode have mass spectra with a significant ion at m/z 161, which correlates to a series of di-TMS derivatives. With the use of selected ion chromatograms, the POE additives are plainly visible in the WMOs, even after light aging, whereas they were absent in artists’ oil tube colors (Greet 2006). This is the first documented case in which WMOs have been successfully identified by instrumental methods. Future studies will explore the effects of pigments on aging of these marker compounds.

Table 4 Weight percentages obtained by GC/MS analysis of Jackson Pollock paint samples.

Painting	Color	Concentration Weight %				% Hydrolysis
		Glycerol	<i>o</i> -Phthalic acid	Pentaerythritol	Oil	
<i>There Were Seven in Eight</i> (1945)	White	0.9	0	0	14	40
	Yellow	1.9	0	0	34	70
<i>Full Fathom Five</i> (1947)	Lighter blue	2.2	1.4	0	24	30
	Darker blue	3.3	12	0	38	70
	Green	6.5	1.3	0	43	60
<i>Number 1A</i> (1948)	Silver-colored	0.9	0	0	13	80
	Blue	1.3	0.1	0	68	60
	Dark purple	1.7	0.2	0	71	70
	Cream-white	4.7	15	0	43	80
	White	0.8	0	0	42	30
<i>Number 12</i> (1949)	Blue	1.4	21	3.8	39	30
	Brown	0.7	0.2	0	16	70
<i>One: Number 31</i> (1950)	Gray-green	2.8	20	0	15	90
	Beige	1.6	4.3	0.5	18	60

Notes: Data of interest are shown in bold. The oil content is estimated from the concentration of azelaic acid using the calculations described in Schilling, Keeney, and Learner 2004. Percent hydrolysis is based on the amount of free palmitic acid relative to the total recovered by the ASTM procedure.

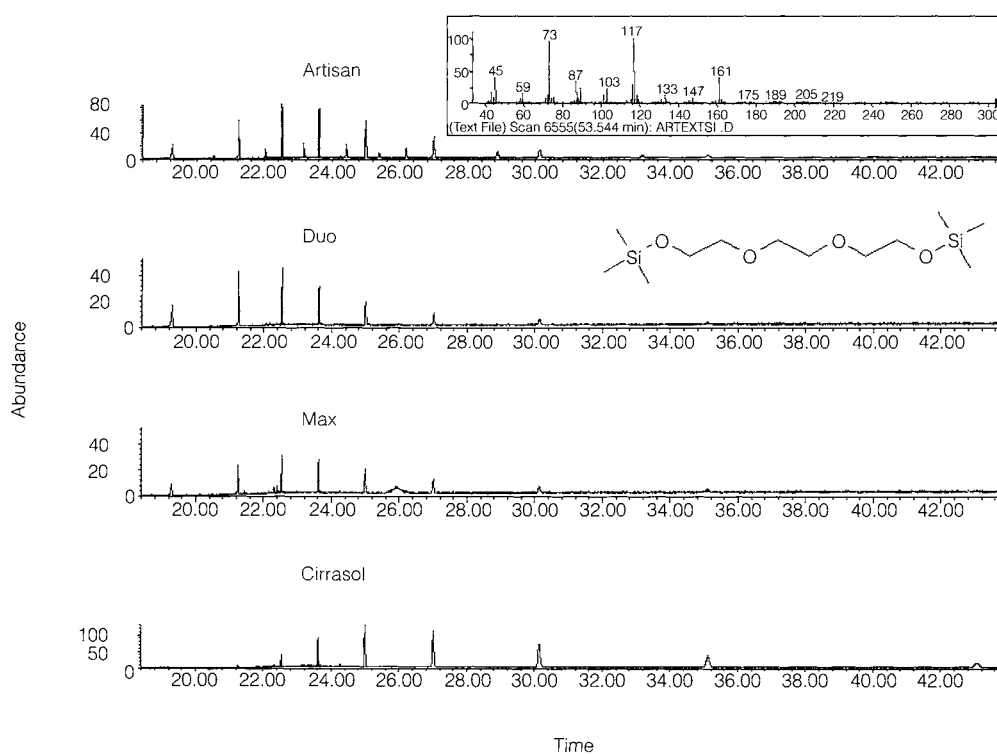


FIGURE 8 Selected ion chromatograms of *m/z* 161 for three water-mixable oil media and Cirrasol (a POE-based additive). Inset shows the mass spectrum and molecular structure for one of the POE additive peaks.

Table 5 Molar ratios for Jackson Pollock paint samples obtained by GC/MS analysis.

Painting	Color	Molar Ratios					Medium
		A/P	P/S	P/G	A/G	PA/A	
<i>There Were Seven in Eight</i> (1945)	White	1.6 (0.1)	3.5 (3.5)	0.39 (0.17)	0.62 (0.02)		Walnut
	Yellow	1.7 (0.9)	2.0 (2.0)	0.41 (0.52)	0.72 (0.48)		Linseed
<i>Full Fathom Five</i> (1947)	Lighter blue	1.8 (0.4)	1.7 (2.0)	0.25 (0.21)	0.45 (0.09)	0.8	Linseed/alkyd mixture?
	Darker blue	22	0.6	0.02	0.47	4.3	Long-oil alkyd
	Green	1.4	1.8	0.19	0.27	0.4	Oil/alkyd mixture?
<i>Number 1A</i> (1948)	Silver-colored	2.4 (9.6)	1.8 (1.4)	0.25 (0.33)	0.59 (3.1)		Linseed
	Blue	6.5 (8.9)	2.0 (1.7)	0.33 (0.20)	2.2 (1.8)		Linseed
	Dark purple	11 (6.6)	1.0 (0.9)	0.16 (0.25)	1.7 (1.6)		Castor
	Cream-white	3.8 (3.2)	1.5 (1.4)	0.10 (0.15)	0.38 (0.47)	4.7	Long-oil alkyd
	White	1.7 (0)	4.4 (6.1)	1.3 (0.18)	2.2 (0)		Poppy
<i>Number 12</i> (1949)	Blue	3.0 (4.0)	2.9 (1.5)	0.38 (0.26)	1.1 (1.1)	7.2	Medium oil alkyd
	Brown	0.7 (1.0)	4.8 (4.6)	1.2 (1.3)	0.91 (1.3)	0.2	Poppy oil/alkyd mixture?
<i>One: Number 31</i> (1950)	Gray-green	12 (8.4)	1.0 (1.3)	0.02 (0.05)	0.22 (0.42)	19.0	Short-oil alkyd
	Beige	3.4 (4.5)	2.1 (1.6)	0.14 (0.18)	0.46 (0.83)	3.3	Long-oil alkyd

Notes: Meth Prep data for the acid components are accompanied by the ASTM results (in parentheses). Oils are tentatively identified on the basis of P/S. PA/A, the ratio of phthalic acid to azelaic acid, permits oil length to be estimated using the graphical procedure described in Schilling, Keeney, and Learner 2004. Data in bold indicate samples for which the results from the ASTM and Meth Prep methods agree.

Conclusions

Using a modified ASTM procedure, it is possible to differentiate among the three classes of modern oil paint media. Quantitative analysis of fatty acid, polybasic acid, and polyol components in alkyds provides a means of dealing with mixtures of alkyds and oils in paintings, as demonstrated by the Pollock study. For those acid compounds that cannot be detected by the procedure, Meth Prep provides an acceptable alternative. The Pollock study showed the potential for estimating the extent of hydrolysis of oil and alkyd paints, which could be useful information in assessing their susceptibility to cleaning. Polyoxyethylene-based surfactants in water-mixable oil formulations could be detected qualitatively, which differentiates them from oils. One significant drawback in the procedure is that alkyd modifiers cannot be detected, although PyGC/MS and FTIR spectroscopy are good complementary methods.

Acknowledgments

The authors wish to thank the many colleagues who contributed to this study. Our collaborators in the Pollock research were Susan Lake, Hirshhorn Museum and Sculpture Garden; Chris McGlinchey, Museum of Modern Art; and Narayan Khandekar, Straus Center for Conservation. Casey Greet, a graduate student in chemistry from California State Polytechnic University, Pomona, and her thesis advisers Chuck Millner and V. C. (Bud) Jenkins, were our partners in the WMO research. Philip L. Shuffett from Akzo Nobel Resins graciously provided the alkyd resin samples.

Materials and Suppliers

Paints

Grumbacher (c/o Sanford), 2707 Butterfield Road, Oak Brook, IL 60523, USA; www.sanfordcorp.com/sanford/consumer/grumbacher

HK Holbein, Box 555, 175 Commerce St, Williston, VT 05495, USA;
 www.holbeinhk.com

Royal Talens, P.O. Box 4, 7300 AA APELDOORN, The Netherlands;
 www.talens.com

Winsor & Newton, Whitefriars Avenue, Wealdstone, Harrow,
 Middlesex HA3 5RH, UK; www.winsornewton.com

Laboratory Supplies

2 mL autosampler vials (#5182-0866), 100 µl glass inserts for 2 mL
 vials (#5181-1270), and 2 mL glass screw vials (#5183-4432):
 Agilent Technologies, Inc., 5301 Stevens Creek Blvd., Santa Clara,
 CA 95051, USA; www.agilent.com

100 µl conical crimp-top glass vials (#9480), 11 mm crimp-
 top aluminum seals with TFE-faced liner (#98742),
 hexamethyldisilazane (HMDS) (#18003): Alltech Associates,
 Inc., 2051 Waukegan Road, Deerfield, IL 60015, USA;
 www.discoverysciences.com

N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) (#38830);
 pyridine-sequal grade (wash solvent for autosampler)
 (#25104); screw caps (#13208); Tuf-Bond discs (#12708): Pierce
 Biotechnology, Inc., P.O. Box 117, Rockford, IL, 61105, USA;
 www.piercenet.com

Butylamine (#471305-250ML); calibration standards (various part
 numbers): Sigma-Aldrich, 3050 Spruce St., St. Louis, MO, 63103,
 USA; www.sigmaaldrich.com

Long pipette tips (#37001-150); GC/MS-grade water (#BJ365-4):
 VWR International, Goshen Corporate Park West, 1310 Goshen
 Parkway, West Chester, PA 19380, USA; www.vwr.com

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PART FOUR

Treatments

Unforgiving Surfaces: Treatment of Cracks in Contemporary Paintings

Mary H. Gridley and Dana Cranmer

Abstract: *This paper describes a method for closing up and flattening cracks in paint films. Whether caused by handling, stress, impact, or contact with the stretcher, small cracks can seriously compromise the aesthetic interpretation of an artwork. A method was developed that used water, alcohol, warm gelatin, and mild heat applied to the face of the painting, followed by drying under weight. The technique is described and illustrated using various case histories, and its successes and failures are discussed.*

Introduction

At Cranmer Art Conservation, Inc., a private conservation studio in New York, we specialize in modern and contemporary paintings and works on paper. In many contemporary paintings featuring very smooth, flat, monochromatic surfaces, the presence of small stress cracks creates a visual disruption out of proportion to the size of the damage. The reflection of light along the edges of the cracks distracts the eye and compromises the viewing experience. As paintings from the 1960s and 1970s enter the museum world in ever greater numbers, there is an increasing tolerance for damages of this type. However, in the marketplace they impinge not only on the aesthetic experience and the artist's intent but also on the commercial viability of the work. With austere formats, nearly perfect is not good enough.

The genesis of this treatment came from one of our clients. We do a lot of work for collectors and institutions, but we also work with artists and their dealers. We had been in a lengthy collaboration with one artist and his dealer over some of the older paintings in his studio—getting them ready for exhibition or sale and generally addressing conservation and restoration issues. One of the overall goals was to establish a

protocol for treatment and an acceptable threshold of visual integrity that honored both the artist's vision and the reality of the paintings as physical objects with lives of their own.

However, our traditional approach to flattening the raised cracks was not always entirely successful, and often filling and retouching were required, which on such pristine surfaces poses challenges of quality and reversibility. Finally, at the heartfelt request of the artist and dealer, we started experimenting with modifications of our standard treatments to see if we couldn't come up with something that worked better, looked better, and lasted longer.

While the method described in this paper can work astonishingly well, not every artwork is a suitable candidate. Because of the materials used, the paint surface must be able to tolerate water, alcohol, and mild heat and not be overly susceptible to burnishing. Further, the paint surface must be clean and varnish-free. Acrylic and/or matte paint films are generally too sensitive for this technique to be applicable. The best results were realized on paintings with an oil layer over an acrylic or traditional gesso ground.

As the treatment is performed on the face of the painting, several benefits are attached to the method. Handling requirements are reduced, as there is no need to unstretch the painting or to find or construct a flat surface that will accommodate the entire painting face down.

When successful, the treatment closes and flattens the cracks entirely, obviating the need for filling and retouching, which for several reasons—minimal intervention, maintenance of the original surface, time constraints, reversibility issues—is a significant bonus.

Some of the difficulties we have run into have included discoloration of underbound paint, loss of sensitive paint

by abrasion, and adhesive residue. While issues of longevity remain unknowable, it should be pointed out that the minimalist nature of the treatment does not preclude repetition or the application of any other, more extensive treatment.

Materials and Procedure

This treatment is a twist on an old classic, and involves the use of water, alcohol, and a vegetable or hide glue, all applied to the face of the painting.

Materials Required

- Water
- Ethanol or isopropanol
- Warm, fairly watery gelatin
- Premoistened swabs (saliva)
- Tacking iron set to lowest temperature (120° F/56° C)
- Silicon paper
- Stiff board or metal plate of smallest possible dimensions
- Weights (1–3 pounds per square inch, or 500–1500 grams per 5 square centimeters pressure, depending on the sensitivity of the surface)

This is a low-tech procedure that uses the wetting properties of alcohol to introduce moisture into a local area. The moisture and alcohol wick into the paint, ground, and canvas layers, and the gelatin follows this path. The heat is used to drive off any remaining moisture, while the heavy weights provide drying in plane.

Procedure

Place the painting face up on a table. Construct a stiff platform topped with silicon paper to be placed under the area being worked on. Squares of Gatorfoam, Fome-Cor, or museum board, topped with a metal plate, can be taped together to reach the desired height. For areas under the stretcher rails and bars, thin metal plates can be inserted. The surface area of the underlying support should exceed that of the board that will be placed on top of the area being treated. The idea is to create a very stiff, smooth “sandwich” so that the paint, ground, and canvas layers can dry in plane.

Using a small brush, apply a stroke of water into the crack. Follow with alcohol (both ethanol and isopropanol work well), and another pass with water. When these have evaporated from the surface, carefully brush again with water and alcohol, followed by a pass with the gelatin and

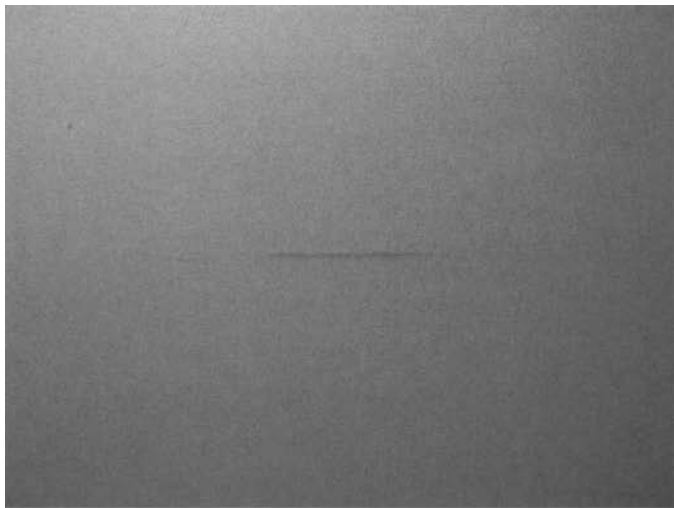
another stroke of alcohol. You will see that the alcohol and gelatin are antipathetic, and the former drives the latter both into and away from the crack. Quickly clean the area with the premoistened swabs, and apply gentle heat and pressure through a piece of silicon paper. Place a stiff board or metal plate on top, and place weights upon it. A drying time of one to two hours seems adequate. The whole procedure can be adapted to a portable vacuum or suction system if desired.

Results

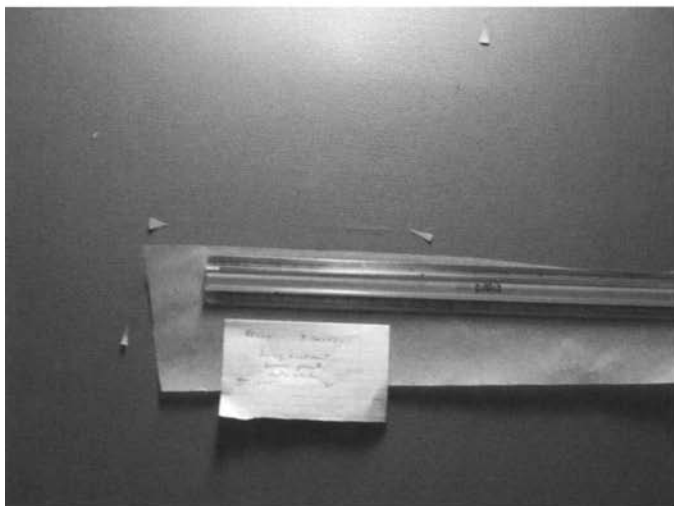
Examples of how well this procedure works are now discussed. A large triptych of 1975 by an artist known for his shaped, monochromatic paintings was riddled with small handling cracks. Particularly irksome was a 6-inch horizontal crack in the lower panel caused by contact with the stretcher bar (fig. 1A). The crack was treated in sections until the area appeared as shown in figure 1B. Similarly, in a painting by Guillermo Kuitca, the unpainted background had sustained numerous impacts, resulting in concentric circles of cracks (fig. 2A). Figure 2B shows the final appearance of the area around one impact crack located in the upper right quadrant of the painting.

Although this treatment was developed to tackle smoothly painted surfaces, we found it successful on more impastoed paintings as well. The treatment of a 1979 Willem de Kooning painting was hampered by a previous treatment that incorporated a loose lining, complicating access to the reverse. Because of the thick and brittle paint film, which had multiple layers, we were skeptical about the efficacy of treating the raised cracks in this way. However, we were pleasantly surprised by the results (figs. 3A and B). We achieved a considerable improvement without having to unstretch or even unframe the painting to get at areas behind the stretcher rails.

A Mary Heilmann work from 1998 exhibited cracks caused by the collision of technique and relative humidity fluctuations. The artist’s technique involves a heavy sizing of rabbit-skin glue, followed by acrylic gesso priming and relatively thin layers of oil paint, making for a very brittle substrate. Many of the cracks in this painting were found at the extreme edges, where they were caused by contact with the thin lip of the stretcher rail. Figure 4 shows a crack at 50× magnification before treatment (fig. 4A) and after (fig. 4B), which resulted in the successful sealing of the crack and the return to plane of the surrounding paint.

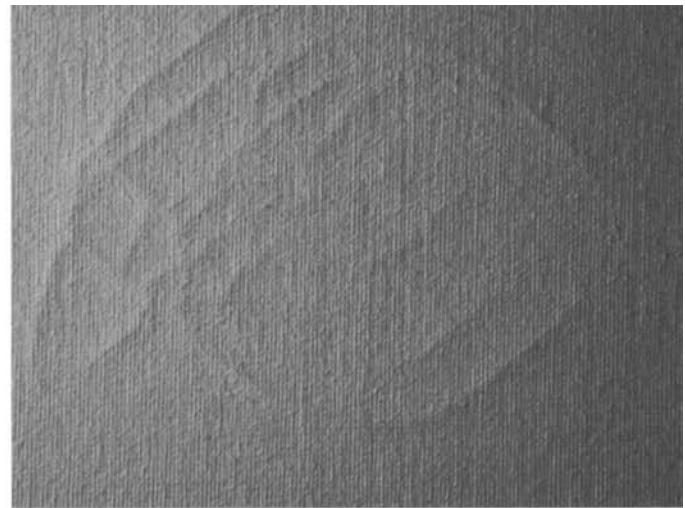


A

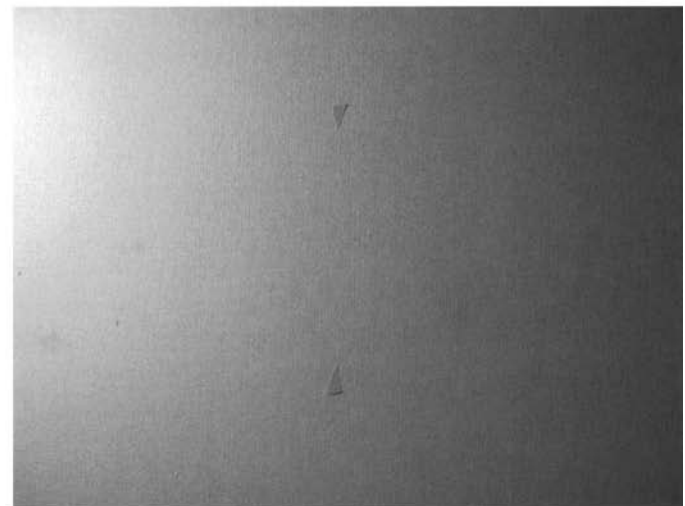


B

FIGURE 1 An oil painting on preprimed linen, 1975. Raking light details of lower panel showing 6-inch crack caused by contact with the stretcher bar: (A) before treatment, (B) progression of treatment. Published with permission of Matthew Marks Gallery and the artist.



A



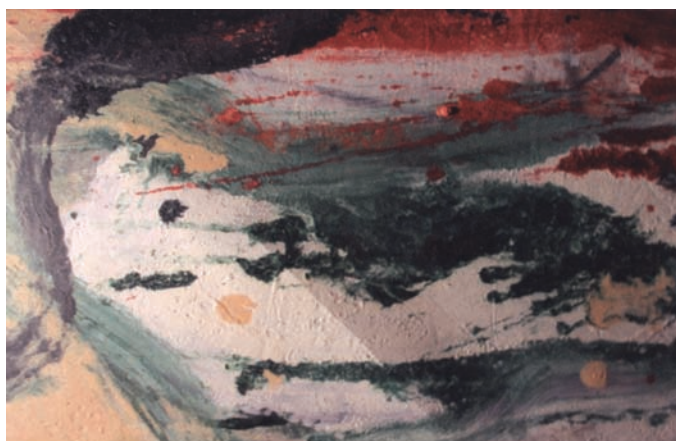
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FIGURE 2 Guillermo Kuitca (Argentine, b. 1961), oil on pre-primed canvas. Raking light details showing damage in upper right quadrant: (A) before treatment, (B) after treatment. Published with permission of Galeria Ramis Barquet and the artist.

Potential Problems

As stated earlier, not every application of this procedure resulted in complete success. The first and most common failing is partial closure, where the crack is significantly but not entirely reduced. This occurred in a Roy Lichtenstein work of 1964, a detail of which is shown at 50× magnification in figure 5, before (fig. 5A) and after (fig. 5B) treatment. Although no

analysis was carried out on this painting, Lichtenstein's technique from this period is well documented (Crook and Learner 2000) and known to consist primarily of Magna acrylic paint layers (the yellow in the detail), although oil paint was being used for the Benday dots (the red in the detail). However, the incomplete closure of a crack may be deemed a sufficient improvement on the work, depending upon the tolerance of the viewer and the visual complexity of the image.



A



B

FIGURE 3 Willem de Kooning (American, 1904–1997), oil on preprimed canvas, 1979. Raking light details showing diagonal crack in lower right corner: (A) before treatment, (B) progression of treatment from near to far. © The Willem de Kooning Foundation/Artists Rights Society (ARS), New York.

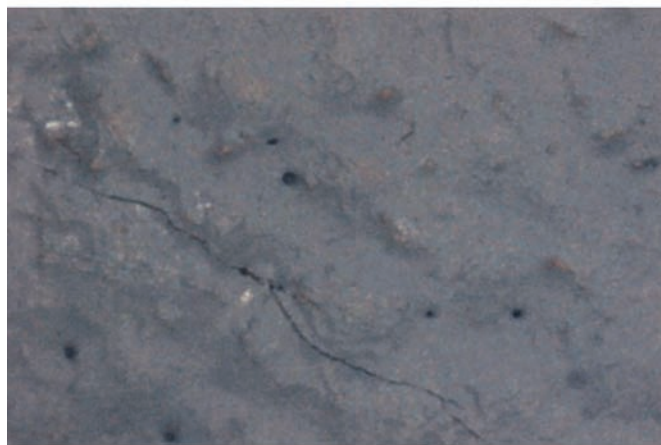
A less common occurrence is paint loss resulting from the abrasive action of rolling the swab during removal of residual adhesive.

Permanent color change in more matte paint films is also a risk, and was observed in an Andy Warhol work dating from 1981. In that painting, a treated area consisted of concentric circles of cracks in which the glossier yellow paint responded well, but the more matte gray paint was slightly stained by the alcohol and/or gelatin, causing a darkening of the film.

The final impediment encountered was that of adhesive residue. Although invisible to the naked eye, residue was



A



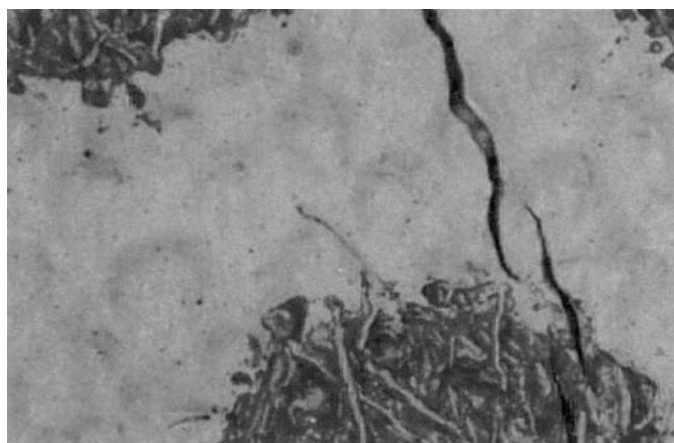
B

FIGURE 4 Mary Heilmann (American, b. 1940), oil on acrylic gesso on cotton duck, 1988. Details at 50× magnification: (A) before treatment, (B) after treatment, (the shiny spots are adhesive residue). Published with permission of the artist.

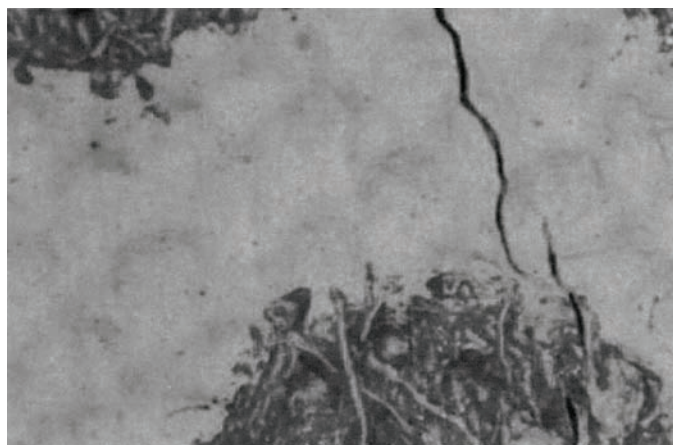
detected at 50× magnification (discernable in figure 4B as shiny spots). The use of a high-grade or perhaps bleached vegetable or animal adhesive may mitigate the inevitable darkening, but in any case it remains unclear how such residues will affect visual appreciation in the future.

Discussion

Many questions about what is occurring on a microscopic level during this process remain without firm answers at this point. The water, alcohol, and adhesive may be combining to



A



B

FIGURE 5 Roy Lichtenstein (American, 1923–1997), oil and Magna on preprimed linen, 1964. Details at 50× magnification: (A) before treatment, (B) after treatment (note some paint loss in the thin red layer caused by swab abrasion when adhesive was being removed). Published with permission of the Estate of Roy Lichtenstein.

cause a chemical and/or physical reorientation of the materials, or they may be acting separately to address different parts of the problem. It also seems that the application of mild heat may aid the process by temporarily raising the temperature above the glass transition temperature of the acrylic substrate, allowing the molecules to move more easily into a new configuration.

The gelatin, which shrinks and stiffens on drying, is absorbed by the canvas layer, where it acts to pull the fab-

ric back in plane during the drying process. The gelatin may also be migrating into microfissures or voids in the paint and ground layers left by aging or leaching, and acting as an adhesive along the walls of the crack.

The role of the alcohol is less well understood. At the very least it is acting as a wetting agent, enabling the water and gelatin to travel more easily to the canvas and ground layers, thereby coating most of the walls of the cracks. The alcohol may also be acting as a swelling agent on the acrylic ground, allowing it to coalesce and re-form in plane while drying under weights. This could account for the excellent results obtained on paintings composed of an oil film on top of acrylic priming. Numerous studies of the action of water and alcohols on acrylic (Jablonski, Golden, and Hayes 2001; Zumbühl et al. 2007) and oil (Phenix 2002) paint films demonstrate that various degrees of penetration (Colaluca, Morris, and Whitmore 2007), swelling (Digney-Peer et al. 2004; Zumbühl et al. 2007), and leaching (Hagen et al. 2007; Ormsby et al. 2007; Ploeger et al. 2007) occur during immersion. In our own tests on acrylic and alkyd paint samples, exposure to alcohol vapors alone caused dramatic softening and swelling. Given that the research unanimously agrees that alcohol, and to a lesser degree water, swells acrylic films, the question now becomes whether or not the swelling and subsequent compression is resulting in the re-formation of a continuous film during this treatment.

Conclusion

Among the various established treatment options for reducing or eliminating cracks in contemporary paint films, the method described here has many practical and aesthetic advantages: it requires only basic studio tools and materials, it reduces handling, it can eliminate the need for filling and retouching, and its minimal nature doesn't preclude other treatments.

While the exact forces at work remain unquantified, the known stiffening power of gelatin and the swelling properties of water and alcohol are here exploited to return the paint film to plane in a simple and localized manner.

Acknowledgments

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Restoring the Immaterial: Study and Treatment of Yves Klein's *Blue Monochrome* (IKB 42)

Christa Haiml

Abstract: A comprehensive technical study and restoration treatment of *Blue Monochrome* (IKB 42) (1960), by Yves Klein, was carried out at the Menil Collection. The findings from the technical investigation were complemented by information gathered in interviews with Yves Klein's widow, Rotraut Klein-Moquay, and his paint materials supplier, Edouard Adam, who was instrumental in formulating a novel paint medium that would satisfy the artist's needs. The damages consisted of numerous finger marks in the extremely underbound paint surface, as well as two deep gouges in the paint film. The strongly textured paint surface had been created by the application of the artist's trademark International Klein Blue (IKB) paint with a lambskin roller. A final spray coat of IKB paint contributes a slight grittiness to the surface. The specific texture and unforgiving nature of the paint surface required an unconventional treatment solution. Fabrication of a series of mock-ups helped in gaining an understanding of how Klein achieved a variety of surface textures and ultimately functioned as an aid in the restoration treatment. When a mock-up with a texture similar to the original had been achieved, a mold was taken of its surface and used in the creation of a "paint insert," which was adhered directly to the compressed and deformed area of paint. The finger marks, which were confined to the surface of the paint film, could be visually reintegrated with a thin spray coat of IKB paint through individually cut templates.

Introduction

Yves Klein's *Blue Monochrome* (IKB 42) (1960), owned by the Menil Collection in Houston (fig. 1), had suffered two different kinds of damage. While on loan to an exhibition in Paris in 1984, the bottom half of the fragile paint surface was marred



FIGURE 1 Yves Klein (French, 1928–1962), *Blue Monochrome* (IKB 42), 1960. Pigment, resin on fabric on board: 199 × 153 × 2.5 cm (78 $\frac{3}{8}$ × 60 $\frac{1}{4}$ × 1 in.). Houston, The Menil Collection. Photograph taken after treatment. Photo: Hester + Hardaway Photographers. © 2007 Artists Rights Society (ARS), New York/ADAGP, Paris. © The Menil Collection, Houston.

by finger marks. As a result, the painting was deemed unexhibitable and confined to museum storage. A second damage occurred in 2003, when shelving in storage was being dismantled and the edge of a metal support hit the painting in the bottom left quadrant, leaving two deep gouges in the paint layer. This second incident prompted a comprehensive technical study of the work and subsequently restoration treatment.

The Artist (1928–1962)

Yves Klein's name is typically associated with ultramarine blue. From about 1956 until his death in 1962, he dedicated himself almost solely to this color, in which he executed not only monochromes but also sculptures, sponge sculptures, sponge reliefs, relief portraits, shrouds, and anthropometries.

A central aspect of Klein's blue monochrome paintings is his pursuit of the "indefinable." He derived this notion from Delacroix, whose writings he read avidly and who claims that the true merit of painting lies in the "*indéfinissable*" (Klein 2003, 234), beyond the material aspect of the painting. Klein sees this quality in blue, a color that suggests the infinite (Klein 2003, 82, 138).

Klein did not see his monochrome paintings as his final works; to him "my monochrome paintings are . . . the preparation for my work, they are what is left of the creative process, the ashes" (Klein 2003, 379). More important than producing paintings was to create atmospheres, "pure energy," that would impregnate the viewer who is open and receptive to it.

Even though Klein's greatest concern with his monochrome paintings lay beyond the visible, the immaterial aspect of his work, the choice of material, the technique of its application, and the pristine condition of the paintings proved to be crucial for his ability to convey his vision.

International Klein Blue (IKB)

When Klein first started to paint monochromes, in the mid-1950s, he experimented with different colors and different traditional binding media available at the time, such as oil, hide glue, gum arabic, and casein, none of which allowed him to achieve what he was aiming for: pure color and a paint surface in which the luminosity of pure dry pigment would be preserved. He said, "I did not like colors ground with oil. They seemed to be dead. What pleased me above all were pure pigments in powder like the ones I often saw at the wholesale color dealers. They had a burst of natural and extraordinarily autonomous life. . . . What upset me was to see this incandes-

cent powder lose all its value and become dulled and lowered in tone once it was mixed with a glue or whatever medium was intended to fix it to the support. . . . Obviously, I was quite charmed by the possibility of leaving the grains of pigment in total freedom, as they exist in powder" (Klein 2003, 244–45; translated in Stich 1994, 59–60).

On several occasions, Klein exhibited pure, unbound pigment, either in trays or spread out on the floor like a carpet. At the Galerie Colette Allendy in Paris in 1957, Klein showed, among other objects, a low trough containing ultramarine blue pigment in powder form installed on the floor. With a small rake, visitors could create texture on the surface (Rosenthal 1976, 186).

It was not until the fortunate encounter with Edouard Adam, *droguiste*, or "color merchant" (as he liked to call himself), in Paris, that Klein found a medium that satisfied his needs—a medium that allowed him to work quickly and at the same time preserved the radiance and luminosity of the dry pigment. Once introduced to Klein's endeavors, Adam consulted with a chemist at the French chemical company Rhône-Poulenc who suggested different materials, among them a stable, colorless polyvinyl acetate resin named Rhodopas M. It was also available in a 60 percent solution in 190-proof (95 percent) alcohol and distributed under the name Rhodopas M60A (Mancusi-Ungaro 1982, 258). Adam experimented with it and formulated a binding medium for Yves Klein, in 1956, by adding specific amounts of ethyl alcohol and ethyl acetate to the resin in solution. To make the paint, "pure ultramarine blue, reference 1311" was stirred in by hand (Adam 1974). On May 19, 1960, Yves Klein registered his paint formulation under the name International Klein Blue (IKB) at the Institut national de la propriété industrielle (fig 2). It received the Soleau envelope number 63 471.

The properties of Rhodopas M make it particularly well suited for realizing what Klein wanted to achieve. The high adhesive strength of polyvinyl acetate allows a low resin-solvent concentration. In addition, its relatively low refractive index minimizes the change of appearance inflicted upon the pigment (Sonoda, Rioux, and Duval 1993, 116).¹

Blue Monochrome (IKB 42)

The structure of *IKB 42* is typical of Klein's blue monochromes: it is executed on medium-weight linen canvas that is stretched around a single piece of plywood with rounded corners. The plywood acts as a solid support behind the canvas for the application of the paint with a roller (Allain 1980).² It is reinforced with a six-member butt-joined wooden strainer with

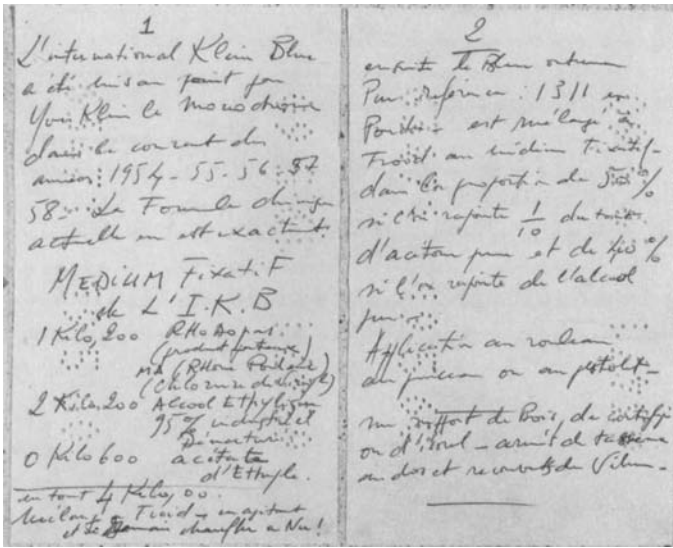


FIGURE 2 Yves Klein, *IKB formula*, Soleau envelope number 63 471. Red ballpoint pen on paper, 21 × 13 cm (8¼ × 5¼ in.). Courtesy of the Yves Klein Archives, Paris.

two horizontal cross members. The battens of the strainer are attached to the plywood with nails through the front of the panel. In this case, two nails had worked their way out, and the protruding heads caused roundish deformations in the canvas. Klein used thumbtacks to attach the canvas to the strainer; some of them had been replaced with staples, presumably during a previous restoration treatment. The thumbtacks are inscribed “Baionnette,” a brand he frequently used. The work is signed “Yves Klein Le Monochrome 1960” in blue paint on the reverse of the plywood panel.

The paint layer was applied directly onto the unprimed canvas with a lambskin roller.³ Roller marks are apparent across the width of the canvas when viewed in raking light; they are approximately 17 cm wide. According to Adam, Klein’s favorite lambskin rollers were 17 cm (6¾ inches) long (Adam 1974). Figure 3 shows Klein with a paint roller of this type attached to a long pole.

There appear to be at least two paint layers: on the reverse and the tacking margins a clear distinction can be made between a darker blue on the bottom and a lighter blue on top (fig. 4).

The surface texture is pronounced and fairly uniform overall. Although distinct up close, it almost disappears at a distance. In Yves Klein’s words “the blue kills the relief!” (Klein 2003, 78). Due to the fast drying time of the paint for-

mulation, the sharp peaks that were created by the long hair of the lambskin roller were retained. The crispness of the peaks is somewhat subdued by a spray coat of IKB paint, which gives a certain grittiness to the surface. The spray coat is not immediately apparent to the naked eye or under magnification, since it does not clearly show up as a separate layer. With careful examination, however, small blobs of paint become apparent, as do dry pigment particles on the surface. In fact, the larger blobs of paint appear to have melted into the paint surface to some degree, suggesting that the spray coat partly redissolved the underlying paint layer. Finally, there is a subtle color difference between the two layers: the sprayed paint is somewhat darker and more purplish in tone than the paint applied with a roller. Although no records of a previous restoration treatment exist, there are indications that the spray coat is not original,

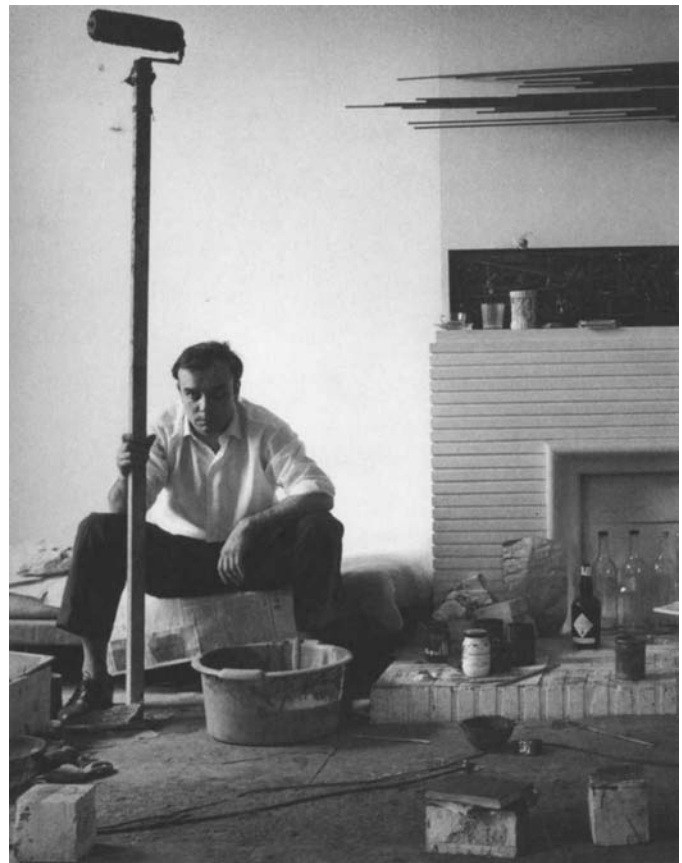


FIGURE 3 Yves Klein in his home studio, 14 rue Campagne Première, October 21, 1961. Photo: Harry Shunk. Courtesy of the Yves Klein Archives, Paris.

FIGURE 4 Detail from the tacking margins of *IKB 42* in raking light. A lighter blue layer is visible on top of a darker blue layer. Photo: Christa Haiml. © 2007 Artists Rights Society (ARS), New York / ADAGP, Paris © The Menil Collection, Houston.



or at the very least that it had been applied some time after completion of the painting.⁴

Restoration Treatment

Given the complex surface texture of the painting and its unforgiving nature, which makes experimentation impracticable, an alternative was sought to a more conventional treatment, such as filling and retouching.

Mock-ups

Fabrication of a series of mock-ups helped in gaining an understanding of how Klein achieved a variety of surface textures and hues, and ultimately functioned as a tool in the restoration treatment. The original paint formulation was used as a starting point, and the proportions of pigment and medium were modified to replicate the original surface texture as closely as possible.

Linen canvas was stretched around plywood panels as a support. The original binding medium Rhodopas is no longer available, so AYAA (Union Carbide), a polyvinyl acetate resin of similar molecular weight was used as a substitute.⁵ Different

concentrations of AYAA were prepared in 4:1 mixtures of ethyl alcohol and ethyl acetate (5%, 10%, 24%, and 30% w/w). In the original paint formulation, the binding medium concentration is 24%. Acetone, optional in Klein's formula, was added to some of the paint formulations.

Varying amounts of pigment were added to create a range of pigment/volume concentrations (40%, 60%, and 80% w/w). In the original paint formulation, the addition of pigment at 40% of the total weight (if no acetone is added) or 50% (if acetone is added) is indicated. Three different hues of ultramarine blue were tested: Kremer Ultramarine Blue Dark (K45010), a reddish tone (K45020), and an unspecified ultramarine blue pigment that the Conservation Department at the Menil Collection had ordered directly from Edouard Adam in 1982.⁶ The pigment was stirred into the medium by hand and strained through cheesecloth to obtain a homogeneous mixture.

Two different kinds of paint rollers, foam and lambskin, were used to apply the paint. Figure 5 shows used foam and lambskin rollers that Klein turned into a sculpture by attaching them to a perforated metal plate. Each band of paint was painted out in three passes, as suggested by the artist's widow, Rotraut Klein-Moquay (2004).⁷ It became apparent that a whole range of textures, hues, and saturations could be achieved depending on the kind of roller, the number of paint layers, the evaporation rate of the paint mixture, the concentration of the binding medium, the pigment/volume concentration, and the type of ultramarine blue pigment. There is no one true IKB pigment. The "pure ultramarine blue, reference 1311," which sounds so precise in Klein's formula, refers to a blue that Adam purchased from his pigment supplier at the time, but his suppliers changed over the course of the years and he cannot trace back exactly where 1311 came from.⁸

In general, foam rollers create a smoother texture and the long hair of the lambskin rollers creates a rougher texture. Because of the different absorbency of the two materials, the same paint mixture will result in a darker and more saturated paint when applied with the foam roller and a lighter and more underbound paint when applied with the lambskin roller. Experimentation with the paint application confirmed that the fast drying time of the paint allows only three or four passes before the underlying paint that is already beginning to dry begins to be picked up. However, once the first layer has completely dried, a second paint layer can be applied without disrupting the first one. It was found that painting out a second layer of the same paint formulation on top of the first layer



FIGURE 5 Yves Klein (French, 1928–1962), *Assembly of Used Paint Rollers (S 8)*, 1956–62. Paint rollers on metal plate, 26.5 × 28 × 25 cm (10½ × 11 × 9⅞ in.). © 2007 Artists Rights Society (ARS), New York / ADAGP, Paris. © Yves Klein.

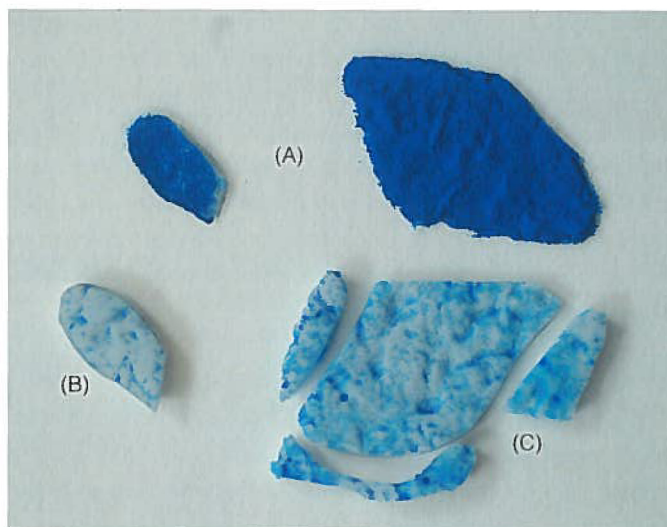


FIGURE 6 (A) Two test inserts created from silicone molds cut to the shapes of the gouges. The small insert on the left is face down in order to show the Japanese paper on the reverse (visible in the small portion of the paper that extends beyond the bottom right edge). (B) Mold for the smaller gouge. (C) Molds for the larger gouge. Photo: Christa Haiml. © The Menil Collection, Houston.

resulted in a much lighter, more matte, and less saturated paint surface. Speeding up the evaporation by adding acetone also made the paint surface appear more matte.

The closest replication of the paint surface of *IKB 42* was achieved by lowering the binding medium concentration to 10%, increasing the pigment medium concentration to 60%, and applying the paint with a lambskin roller.

Preparation of the Inserts

Once a close replication of the original surface texture had been achieved in a mock-up, a mold was taken from it to create an insert to be attached to the gouges (fig. 6).

Dow Corning 3110 RTV rubber with catalyst no. 1 (10% w/w) was used to create the mold. The paint surface of the mock-up was first sprayed with silicone spray to facilitate subsequent removal of the mold. The exact shapes of the gouges were then transferred and cut from the mold. Because the larger gouge was deeper in the center and shallower around the edges, the mold was cut in several pieces: one for the center part and three to fit around the edges (fig. 6C). For the smaller gouge, a single mold was sufficient (fig. 6B).

In preparation for the cast, a number of different binders (a polyvinyl acetate dispersion and various water-based binders) were tested for visual appearance and handling properties. However, the original paint formulation—modified in terms of pigment and medium concentration as described above—was the only one of the tested materials to imitate the original paint surface in a satisfactory way. The pigment mixture was established empirically by painting out different hues of ultramarine blue (the same hues that were used for the mock-ups), both pure and in mixtures. A 1:1 mixture of ultramarine blue dark and reddish pigment provided the best match. Again, the mold was coated with silicone release spray to facilitate the subsequent removal of the paint layer. The paint was applied onto the mold as thinly and evenly as possible with a small bristle brush. In order to improve the handling properties of the fragile insert, a small piece of Japanese paper, previously cut to the shape of the mold, was attached to the paint layer (reverse of the insert) while the paint was still wet. Once dry, the paint could easily be separated from the mold (see fig. 6).

Once the inserts were removed from the mold, a thin spray coat (of the same *IKB* paint formulation) was applied

to the front to replicate the distinctly gritty texture of the painting. Different spray guns were tested for this purpose: a Badger Model 400 and an airbrush produced a spray coat that was too homogeneous, whereas an aerosol sprayer provided the desired unevenness, creating larger droplets of paint and smaller dry particles. In order to achieve a darker and more purplish tone than in the base coat, the pigment mixture in the paint formulation was replaced with Edouard Adam's blue from 1982.

Attachment of the Inserts onto the Painting

A number of adhesives were tested to attach the insert onto the damaged area. Mowilith DM 427 (polyvinyl acetate emulsion) was chosen for its ease of application and the good adhesion it provided without the application of heat or weights. The adhesive was thinly brushed onto the reverse of the insert. Then the inserts were positioned using a pair of tweezers and gently pressed into place using a tool with a pointed silicone tip.

Final Retouching and Local Spraying

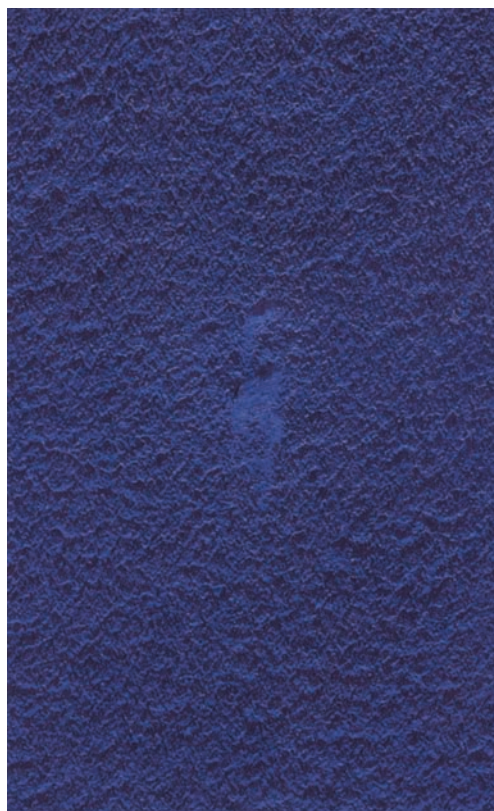
Inserts

The small insert blended well into the surrounding paint and required hardly any additional retouching around the edges. The contours around the larger insert, as well as the generally abraded area around the damages, required minor blending in with a fine brush. Kremer Ultramarine Blue Dark and Adam's pigment were used, depending on whether a lighter or darker, more purplish tone of blue was required. Figure 7 shows the area of the gouges before treatment (fig. 7A) and after (fig. 7B).

Finger Marks

Generally, the finger marks were confined to the very surface of the painting, compressing the top spray coat and making the paint appear lighter. To visually reintegrate these areas by darkening and restoring the grittiness of the surrounding paint, a light spray coat was applied with the aerosol sprayer through mylar templates cut to match the configuration of

FIGURE 7 Details from *Blue Monochrome (IKB 42)* (see fig. 1) in raking light, showing the area of the gouges: (A) before treatment, (B) after treatment. Photo: Christa Haiml. © 2007 Artists Rights Society (ARS), New York / ADAGP, Paris. © The Menil Collection, Houston.



A



B



FIGURE 8 Aerosol spray can and template for local spraying of the finger marks, photographed in front of *Blue Monochrome (IKB 42)* (see fig. 1). Photo: Christa Haiml. © The Menil Collection, Houston.

of the finger marks (fig. 8). In some areas where the marks were deeper, a small brush was used to build up some texture. All spraying and retouching of finger marks was carried out with Adam's pigment.

Conclusion

This comprehensive technical study of a monochrome painting by Yves Klein allowed me to gain a deeper insight into his choice of materials and his working methods, which proved crucial in devising a restoration treatment. In order to reintegrate the missing and damaged areas in the most unobtrusive manner possible, it was found essential to use materials that had the same properties as the originals, or very similar ones, and to employ the same application techniques as the artist. Due to the unforgiving nature of *IKB 42*, it was extremely helpful to devise a treatment in which the two main visual components of the painting—color and texture—could be developed in separate steps before working on the painting itself.

Acknowledgments

My special thanks go to Elizabeth Lunning and Bradford Epley in the Conservation Department of the Menil Collection; Rotraut Klein-Moquay, Daniel Moquay, and Philippe Siauve at the Yves Klein Archives; as well as Monsieur Edouard Adam.

I am grateful to Tom Learner and Kate Duffy for pigment and medium analysis, and to Carol Mancusi-Ungaro for sharing her insights into Klein's painting techniques. I am also indebted to Geri Armanda, Julie Barten, Debby Breckeen, Jim Coddington, Benoît Dagon, Judith Hastings, Laramie Hickey-Friedman, Jacques Hourrière, Otto Hubacek, Bear Parham, Carol Stringari, and Tom Walsh.

Notes

- 1 A Soleau envelope is a free registration system that is less complicated than a patent. It provides only temporary protection (Semin 2001, 66). Klein refers to Rhodopas M60A as "Rhodopas MA" in his IKB formula, and describes it as *chlorure de vinyl* (vinyl chloride). As previously determined, the Designation of Rhodopas M60A as vinyl chloride is incorrect (Mancusi-Ungaro 1982, 258).
- 2 Bernadette Allain worked closely with Klein when he first began to experiment with different materials for his monochrome paintings.
- 3 Not all IKB paintings are unprimed. Both Bernadette Allain and Arman have stated in interviews that Klein used a casein-based primer for his IKBs (Allain 1980; Arman 1981). Pierre Restany and Nan Rosenthal also mention Klein's use of casein primer (Restany 1982, 14; Rosenthal 1976, 100). The only analysis carried out on a ground layer sample of a blue monochrome painting by Yves Klein that the author is aware of suggests an oil binder (Sonoda, Rioux, and Duval 1993, 116).
- 4 The original thumbtacks on the reverse were at some point removed from the right edge and replaced with staples. Small pieces of mylar, plastic, and glassine are attached to some of the staples and are covered in blue spray paint. It appears that they are remnants of material that had been attached to protect the bare edges of the canvas on the reverse from the spray paint.
- 5 Other polyvinyl acetate resins that have properties comparable to those of Rhodopas M are Mowilith 30 and 40 (Hoechst) and Vinnapas B 17 and B 60 (Wacker) (Harscher 1994, 25).
- 6 The pigment had been ordered for display in a tray as part of the 1982 Yves Klein retrospective at Rice University in Houston.
- 7 With regard to Klein's application technique, Klein-Moquay further pointed out that Klein tried to make roller marks less apparent by lightly going over the buildup of paint (where the roller bands overlap) with a fairly dry roller before the paint had completely dried.
- 8 Conversation with Edouard Adam, Paris, September 20, 2004.

Materials and Suppliers

Mowilith DM 427 (Hoechst): Distributed by Conservation Resources International, 5532 Port Royal Road, Springfield, VA 22151, USA; www.conservationresources.com

PVA-AYAA: Union Carbide Corporation; www.unioncarbide.com

Ultramarine Blue Dark (K 45010), Ultramarine Blue Reddish (K45020): Kremer, 228 Elizabeth Street, New York, NY 10012; www.kremer-pigmente.de/englisch/homee.htm

Ultramarine blue (not specified): Maison Adam, 11 boulevard Edgar Quinet, F-75014 Paris

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The Re-restoration of Donald Judd's *Untitled*, 1965

Narayan Khandekar, Eleonora Nagy, Julian Miller, Pia Gottschaller, and Carol Mancusi-Ungaro

Abstract: In 1976, a seminal work by Donald Judd at the Whitney Museum of American Art consisting of an anodized aluminum tube with ten colored aluminum boxes was “stripped, primed and repainted” in a car repair shop. Research revealed that the boxes had originally been sprayed with a Harley-Davidson motorcycle color called Hi-Fi Purple, a cellulose nitrate paint manufactured by DuPont. When the work was repainted in 1976, the original color was out of production. A mismatched “purple” acrylic paint, Candy Apple Maroon, was used instead. When the artist saw the work in 1990, he complained that the treatment had been unauthorized by him, disapproved of the color, and declared it “ruined.” An investigation was launched to ascertain the current condition of the work and how it had been altered. Cross-section and paint samples were taken from this work and from another comparable Judd sculpture at the Phoenix Art Museum. Comparison of analytical results from the two objects, a sample of original Harley-Davidson paint, and a replicated Hi-Fi Purple paint sample allowed an informed re-restoration of the Whitney work. This paper provides insights into why the artist preferred a certain type of paint in terms of both its aesthetic and working properties.

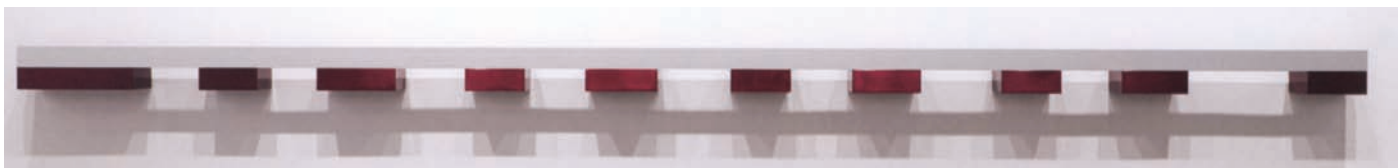
Introduction

The Whitney Museum of American Art acquired Donald Judd's sculpture *Untitled*, 1965 (fig. 1), from the Leo Castelli Gallery in March 1966 (Whitney n.d.).¹ It comprises ten painted alu-

minum boxes positioned at progressive intervals along a bare, square-profile aluminum beam measuring approximately 21 feet in length (8¼ in. × 21 ft. × 8¼ in.). The dimensions of the boxes relate to gaps between their positions on the bar, resulting in a mathematical progression of positive and negative spaces. According to records, the Treitel-Gratz Company, one of several fabricators that Judd used during his career, fabricated the work on February 5, 1966, in New York City (Gratz and Gratz 2006; Smith 1975, 139).²

The Whitney Museum regularly exhibited the sculpture until May 1975, when it traveled to Canada for inclusion in a Judd retrospective at the National Gallery of Canada. A year later, in May 1976, for reasons presumably related to poor condition, the boxes were removed from the work of art and sent to Ralph's Motor Repairs in New York for restoration. According to the sales receipt, the boxes were “stripped, primed and repainted” (Whitney n.d.). The Whitney continued

FIGURE 1 Donald Judd (American, 1928–1994), *Untitled*, 1965. Aluminum: 21 × 642.6 × 21 cm (8¼ × 253 × 8¼ in.). New York, Whitney Museum of American Art. Purchase, with funds from the Howard and Jean Lipman Foundation, Inc. 66.53. Shown after the most recent restoration, as it is now displayed. Photo: Sheldon C. Collins. Art © Judd Foundation. Licensed by VAGA, New York.



to display the work after this intervention, but in 1988 the museum contacted Judd because a number of deep gouges and scratches had appeared in the aluminum beam. No treatment resulted from this consultation, and ultimately the sculpture was returned to display.

In 1990, Judd wrote to the Whitney to express his serious dissatisfaction with the restoration of the boxes (Whitney n.d.). However, the matter was not resolved before he died in 1994. The sculpture was included in the 1994–95 exhibition *From the Collection*, and subsequently was relegated to storage, where it has remained ever since.

Judd's correspondence from 1990 and a desire by the Whitney to return the sculpture to an exhibitable condition were the impetus for this project. In addition, the recent treatment of an earlier Judd piece (*Untitled*, 1964) provided a new approach to cellulose nitrate-painted Judd sculptures, which included the identification of paint and pigments, confirming the color of the object and the original material (Nagy and Adamsons, 2007). This work became an invaluable guide in the treatment of the sculpture described in this paper.

Researching the Original Color

Although photographic documentation exists, early images of the sculpture either are in black and white or the color of the archived transparency has shifted considerably. Therefore, the photos were of diminished value in determining the original color of the piece. The Treitel-Gratz Company did subcontract the painting of the boxes, but there is no record that details the procedure (Gratz and Gratz 2006).

Eventually, a reproduction of a preliminary drawing for the sculpture was discovered (fig. 2), on which the intended color of the boxes was annotated as “H-D H-F Purple” (Agee 1968, 34). As Judd used Harley-Davidson colors, including Hi-Fi Red (Nagy and Adamsons 2007), the meaning was immediately apparent: Harley-Davidson Hi-Fi Purple. The drawing also specified that the aluminum used for the boxes should be 0.05 inch thick and that the square “tube” or beam be “bare” (unpainted aluminum). In the sculpture the tube is actually “clear” anodized, so that it appears to be the color of freshly prepared aluminum metal. In addition to providing crucial information, the drawing also confirmed Judd's preoccupation with accuracy; indeed, some of the measurements are to the thousandths of an inch.

Records from the Harley-Davidson Company indicate that the color Hi-Fi Purple was available from the 1963 model year through 1966. The paint was a Baking Enamel alkyd

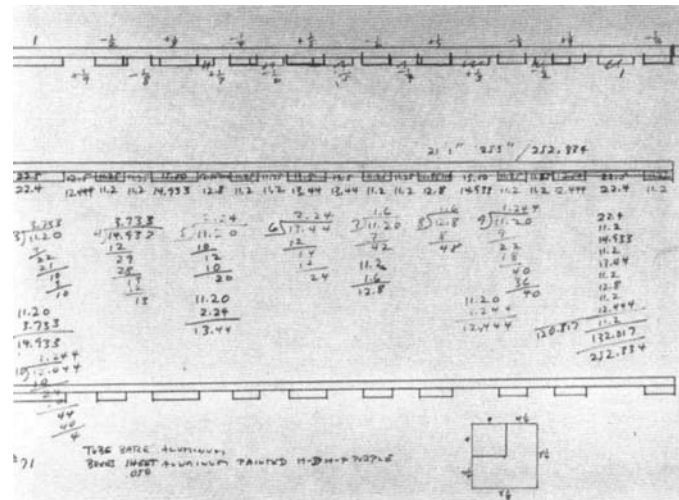


FIGURE 2 Donald Judd (American, 1928–1994), preliminary drawing for *Untitled*, 1965. Ink on paper, 42.6 × 55.3 cm (16¾ × 21¾ in.). Current location unknown. Art © Judd Foundation. Licensed by VAGA, New York.

(DuPont paint code Y797-77894) applied over an undercoat of “Ready Mix Aluminum” (DuPont paint code 166-65084).³ In contrast, the Whitney's receipt from Ralph's Motor Repairs lists the 1976 restoration color as “Manuf # C-6 Candy Apple Maroon. Base silver.” This paint clearly diverges from the original color on two counts. First, a silver base that prevents reflection from the underlying aluminum is noted on the sales receipt, but none is mentioned in the drawing or seen in comparable works. And second, the Candy Apple Maroon color is distinctly different from Hi-Fi Purple in hue (fig. 3).

The need to locate other examples of original Hi-Fi Purple paint on contemporaneous Judd sculptures became apparent. The Phoenix Art Museum in Arizona had such a work: *Untitled* (DSS 68), from 1965 (fig. 4). This piece was produced a few months earlier than the Whitney work, by the same fabricators, and fortunately the museum agreed to lend it to the Whitney for the duration of the project. Described in the 1975 catalogue of Judd's work as “purple lacquer on aluminum and light cadmium red enamel on aluminum,” the sculpture was an ideal match (Smith 1975, 139). Untreated and unexhibited for years (Phoenix Art Museum n.d.), the Phoenix sculpture became a prime candidate for our research, and the museum agreed to our sampling the paint for the purpose of analytical review. From Antique Cycle Supply, vintage Harley-Davidson specialists, the authors obtained a sample of Hi-Fi Purple retouching (Touch-up) paint that was sold in

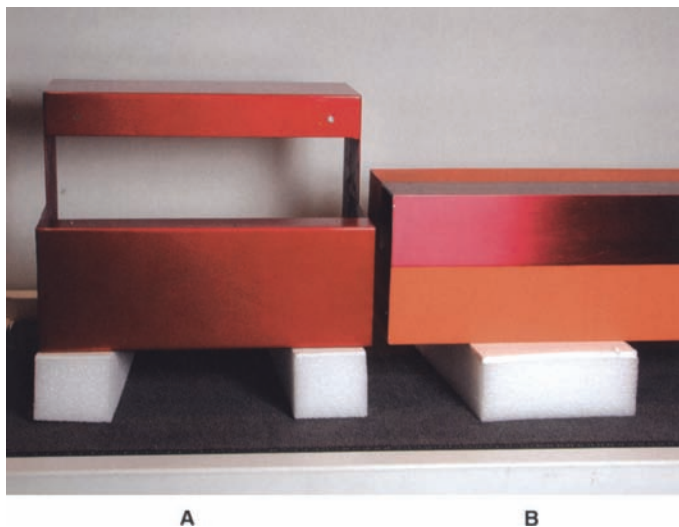


FIGURE 3 A side-by-side comparison showing differences in color and texture: (A) the 1976 restoration of the Whitney piece (fig. 1), (B) the Phoenix piece (fig. 4). Photo: Narayan Khandekar.

a spray can by Harley-Davidson in the mid-1960s. This paint was also used for comparative purposes. In addition, a post-1974, double-size version of the Phoenix piece from a private collection was visually examined in May 2006 by Nagy. The application of the purple paint appeared to match that of the Phoenix sculpture, although no scientific analyses were conducted.

Close examination indicated that the restored color of the Whitney boxes was significantly different from that of the Phoenix piece (fig. 3). It was also apparent that the silver base applied to the Whitney piece in the 1976 restoration was absent in the Phoenix sculpture, where the purple paint was

applied directly to the aluminum, allowing light to enhance the interaction of the brushed metal finish and the smooth paint. In effect, the 1976 restoration had obscured the aluminum, and the applied silver base coat provided a velvety appearance to the metal that varied considerably from the look of the Phoenix piece.

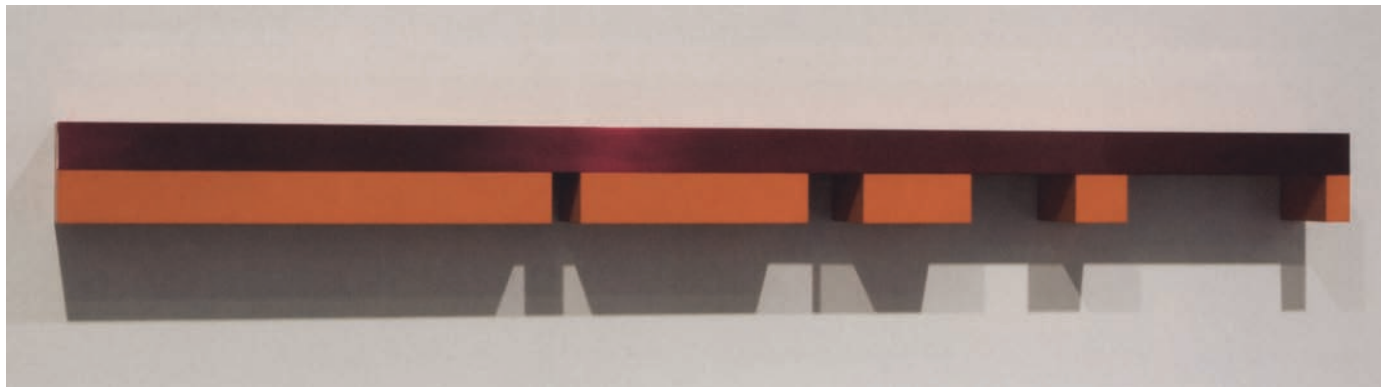
Media Analysis

The media of the various paints were analyzed by Fourier transform infrared (FTIR) spectroscopy. Comparing the FTIR spectra to the Infrared and Raman Users Group (IRUG) database revealed that samples from both the Phoenix sculpture and the 1960s Harley-Davidson Touch-up spray can were a nitrocellulose medium. In contrast, paint from the 1976 restoration was an acrylic medium. Miller confirmed that by the mid-1960s, nitrocellulose was used to repair paint on automobiles rather than applied as an overall color (Learner 2004, 22). Therefore, the implication is that the original paint on the Judd sculptures in this study came from a secondary source, such as a body shop or a supplier of automotive paint to body shops, and was not the Baking Enamel alkyd that Harley-Davidson applied to motorcycles at the factory.

Cross-Sectional Analysis

Figure 5 shows cross sections from the Whitney sculpture (1976 restoration), the Phoenix sculpture (original Hi-Fi Purple), and the 1960s Hi-Fi Purple from the spray can.

FIGURE 4 Donald Judd (American, 1928–1994), *Untitled* (wall sculpture) orange and purple, 1965. Purple lacquer on aluminum tube, cadmium red enamel on aluminum boxes, L 189.9 cm (74¾ in.). Phoenix Art Museum. Gift of Howard and Jean Lipman, 1983.109. Art © Judd Foundation. Licensed by VAGA, New York.



The sample of original purple from the Phoenix piece rested directly on the metal. The paint fluoresces under ultraviolet (UV) illumination. Cross-sectional analysis detected eight to twelve thin, transparent layers of paint. However, there could easily be more, since nitrocellulose dries with very little change in refractive index between layers. This attribute allows the paint to be built up into a deep and transparent coating that “bites” into the underlying layer as it is applied. Such melding makes the detection of layering difficult. Since nitrocellulose paints are partially redissolved with the application of each subsequent layer, the layers blend together well, with a barely detectable interface, which is precisely what made them such suitable paints for car finishing and repair work. As expected, the paint on the Phoenix sculpture dried to a smooth surface.

Antique Cycle Supply provided a sprayed-out sample of Hi-Fi Purple from a can of 1960s Harley-Davidson retouching paint. The purple was applied over an aluminum flake pigmented paint (as specified by Harley-Davidson). This sample was used for comparison with samples taken from the sculptures. Like the sample from the Phoenix piece, it fluoresces under UV light and includes orange and blue particles. There are also extraneous purple particles (determined by

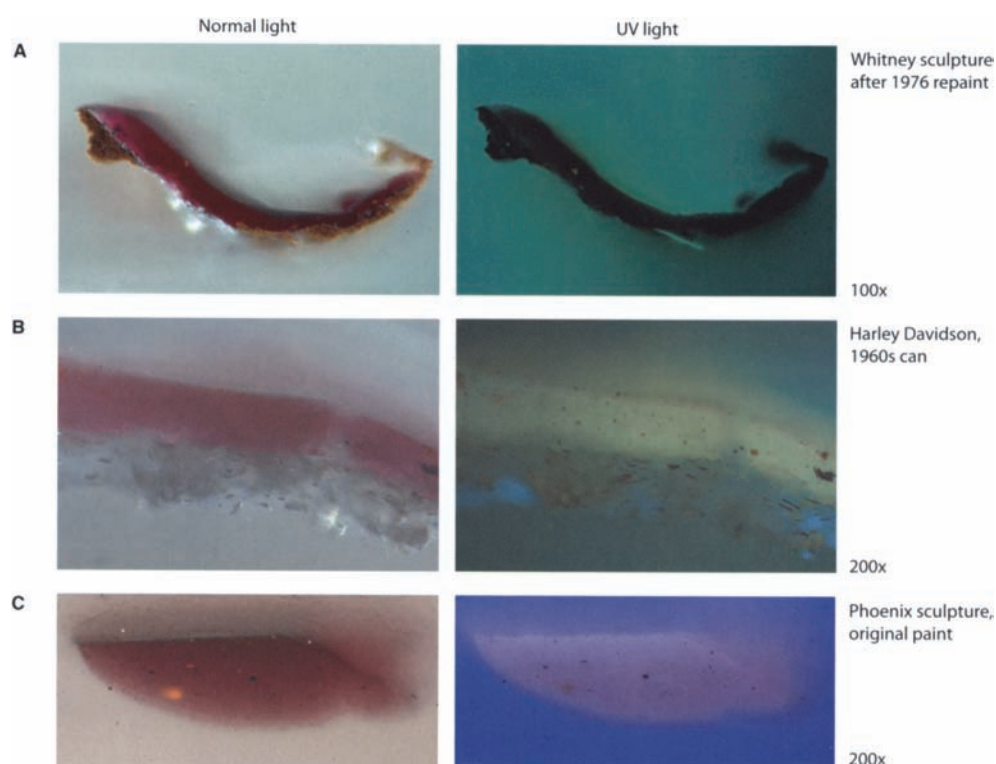
MALDI-TOF-MS analysis to be PV19; see below) that probably precipitated from the mixture in the can after 40 years of storage.

In contrast, the paint from the 1976 restoration on the Whitney piece consisted of three main layers: a thick layer of opaque red primer, an overlayer of metallic aluminum flake paint, and a final colored transparent layer, which is also UV absorbing. The UV absorbance gives the paint a decidedly different appearance from one that fluoresces, such as the paint from the Phoenix work. In effect, a UV-fluorescing paint will look brighter in the same way that optical brighteners in modern paper or laundry detergents change the ultimate appearance of a material. Cross sections that were taken down to the metal substrate on the Whitney work confirmed that the boxes had indeed been stripped prior to repainting.

Identifying the Pigment

It was decided to use matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) as a technique to identify the pigments. MALDI-TOF-MS gives interpretable data from a microscopic sample. In certain cases, solvents were used to dissolve and concentrate the pigment

FIGURE 5 Paint cross sections in visible light and ultraviolet light from (A) Whitney Judd sculpture, (B) Harley-Davidson 1960s Hi-Fi Purple spray retouching paint, (C) Phoenix Museum Judd sculpture. (A) The Whitney sculpture shows all the paint layers from the 1976 restoration. A red primer was applied to the stripped metal, over which was applied an aluminum flake paint, and finally the transparent Candy Apple Maroon paint. No original paint from the sculpture was observed in cross-section analyses. (B) An aluminum flake base paint was applied according to Harley-Davidson instructions, followed by the transparent Hi-Fi Purple. The paint is made up of a transparent purple, square or rectangular particles and blue particles. The paint fluoresces under UV light, unlike the paint in the Whitney cross section. (C) The optical properties of the Phoenix sculpture’s paint are identical to those of the 1960s spray can. Photo: Narayan Khandekar.



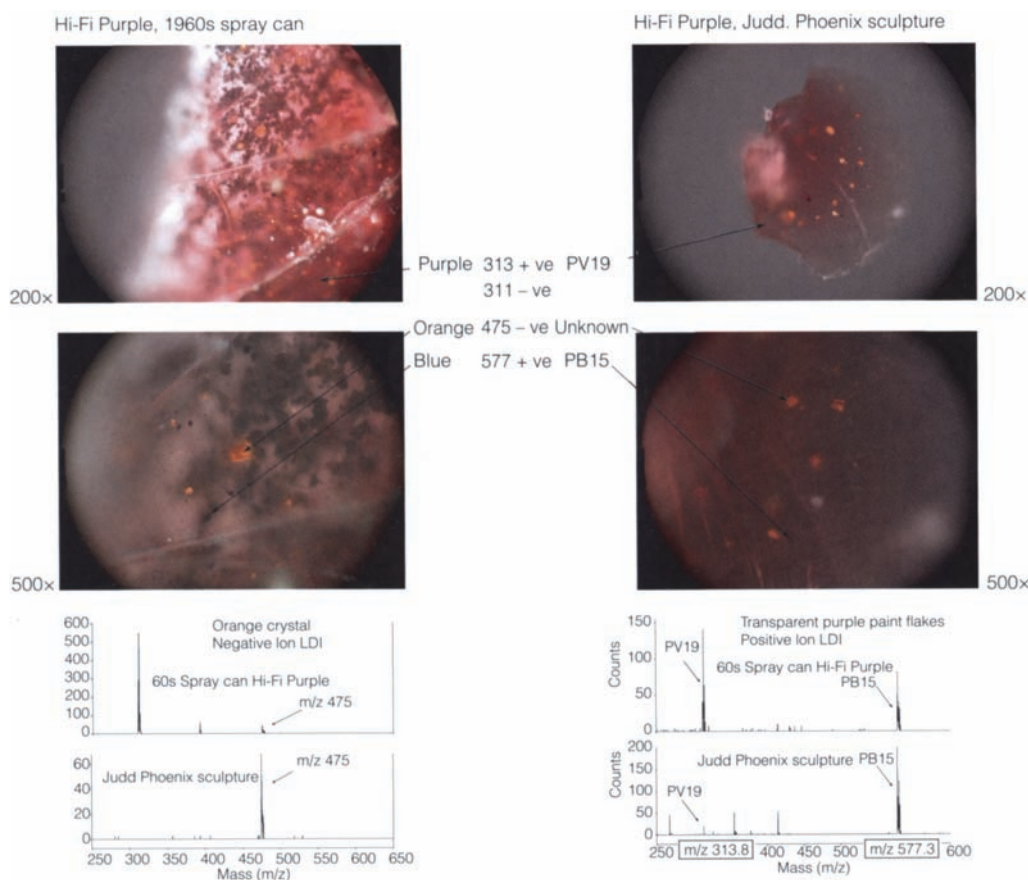


FIGURE 6 MALDI results for the Phoenix piece and spray can samples. Photo: Narayan Khandekar.

sample. A matrix was not needed, as some of the pigments acted as a matrix and ionized themselves. They also imparted energy to the surrounding material, so that the technique was neither entirely MALDI nor entirely LDI but somewhere between the two.

The same combination of pigments was identified in samples from the touch-up spray can and from the Phoenix sculpture (fig. 6). The parent ion for the blue pigment was 577 (positive ion), while the parent ions for the purple pigment were 311 (negative ion) and 313 (positive ion), which corresponded respectively to phthalocyanine blue (PB15) and quinacridone PV19. The orange pigment had a parent ion of 475 (negative ion), but the fragmentation pattern did not correspond to any of the standards; thus it remains unidentified at this time.

By comparison, the paint from the 1976 restoration also contained PV19, the unidentified orange pigment, and other unidentified pigments, but it lacked the blue colorant noted above. As this paint was not original and would ultimately be removed during the re-treatment, further identification of its components was deemed unnecessary.

The Restoration

Formulating the Restoration Paint

Having ascertained that the original paint was nitrocellulose and that Judd carefully exploited the subtle properties of the medium for visual effect, we decided to use the same medium for the impending treatment. The aim was to duplicate the inherent optical qualities of the material and to utilize its ability to build up thin layers in an attempt to achieve the right color density. Unfortunately, nitrocellulose is no longer commercially manufactured in the United States because of federal health and safety regulations. Even though importation is difficult and requires special licenses, antique car restoration is one industry that retains a very limited access to nitrocellulose paints.

Identifying an Appropriate Collaborator

Finding a collaborator who could legally handle nitrocellulose paint, mix a proper color match, skillfully apply the paint, and share a conservator's regard for the physical nature of an

object undergoing treatment was essential for the execution of this project. Fortunately, around this time (spring 2005), an important group of historic vehicles was exhibited at the Museum of Fine Arts, Boston, in the exhibition *Speed, Style and Beauty: Cars from the Ralph Lauren Collection* (Kimes, Goodfellow, and Furman 2005). The cars were restored in Essex, Massachusetts, by Paul Russell and Company. We contacted Alex Finnegan at the company, who immediately referred us to Julian Miller, owner of Sublime Restorations in Rowley, Massachusetts.⁴ Miller's experience with events such as the Pebble Beach Concours d'Elegance proved invaluable throughout our project.

The high quality of the manufacturing required for Judd sculptures has been recorded (Coplans 1971). The precision working of the aluminum sheet metal by helium TIG (tungsten inert gas) welding was carried out by highly skilled workers of mostly European origin (Whitney n.d.). Although alternative metals were available for fabrication, Judd chose the more difficult aluminum for its visual characteristics, and relied on the fabricators to resolve the technical difficulties.

Repainting the Boxes

The Phoenix sculpture was used as a point of reference at every step in the process. A number of aluminum test panels that matched the graining and brushing on the original aluminum tube of the Phoenix sculpture were prepared.

A color-matched formulation for Hi-Fi Purple in polyurethane was found in automotive restoration databases. Pigment mixtures for automotive paint vary according to the medium. For example, polyurethane car paints consist of a pigmented coating followed by a gloss clear coat. Although the polyurethane formula was not appropriate for a nitrocellulose medium, it provided a starting point.

After fifty hours of color mixing, Miller produced a close visual match to the Phoenix piece in nitrocellulose paint. Further tests and refinement were conducted in the conservation laboratory of the Whitney Museum. Several test panels were sprayed out and compared side by side to the Phoenix piece for color, translucency, sheen, and surface texture (fig. 7). Once we concurred on the closest match, we checked the medium by FTIR (fig. 8) and found a very good correlation between the Phoenix paint and the newly mixed paint. The boxes were then shipped from the Whitney Museum to Miller's shop in a specially designed crate that offered support to the boxes but did not touch any of the external painted surfaces.

The boxes were stripped of the 1976 color using a dichloromethane-based product, Tal-strip II aircraft coat-



FIGURE 7 Side-by-side comparison of paint applied to a test panel and the Phoenix sculpture, showing a very good color match. Photo: Eleonora Nagy.

ing remover (Bondo Corporation), and a soft plastic spatula to ensure that the underlying metal was not damaged in any way. During the stripping process, some small remnants of the original paint were revealed but could not be salvaged for analysis or incorporation in the repainting. Careful observation during the stripping of these remnants indicated that the original paint had been applied directly to the metal, as had been suspected. Fortunately no filler had been applied to the boxes prior to the 1976 repainting, nor had any abrasion taken place. Much of the surface texture of the boxes was still intact, along with evidence of their manufacture that had been hidden. Such evidence as the impression of a piece of grit caught on the jaws of the folding machine or a sagging corner caused by a moment of hesitation during the aluminum welding became visible.

Areas of damage in the aluminum were regained and blended into the surrounding area using scouring pads of various grits. The boxes were then spray painted and the high gloss of the new paint was reduced to that of the Phoenix piece.

In order to determine a level of treatment for the beam, all parts of the sculpture were examined together, but unassembled. The aluminum beam that originally supported the ten boxes was cleaned of dirt, dust, and grease, and the gouges were appropriately toned in. After its return to the Whitney Museum, the sculpture was reassembled and exhibited by the museum for the first time in over a decade.

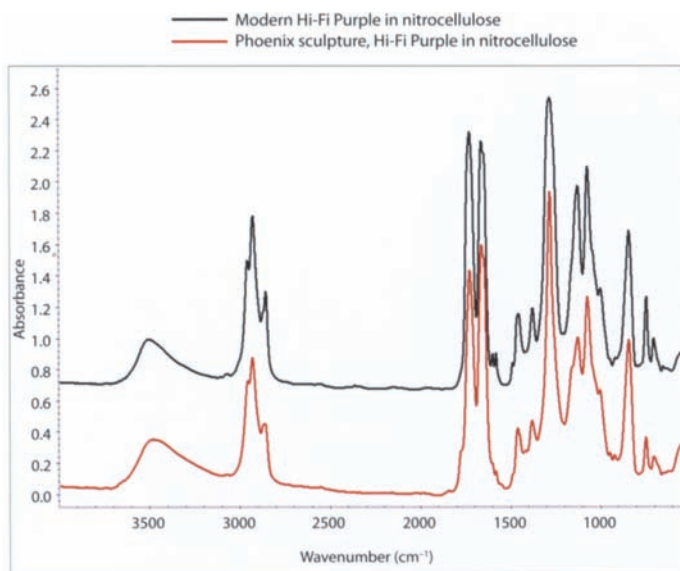


FIGURE 8 FTIR spectra of the newly formulated purple and Hi-Fi Purple from the Phoenix sculpture, showing a very good correlation.

Conclusion

Analysis of the Hi-Fi Purple paint confirmed that the fabricators used paint from a secondary market for automotive repair rather than the alkyd enamel that Harley-Davidson had been using to manufacture motorcycles. The formulation of the paint from the Phoenix sculpture and that from the secondary market were identical. Careful examination also confirmed that the Whitney sculpture embodied a high quality of construction that belies the deceptively simple shapes and apparent expediency of industrial methods.

The sculpture was stripped and repainted using a reproduced color match for the original purple found on the Phoenix work. The reformulated nitrocellulose medium's properties matched those of the original paint. The new medium also ensured easy reversibility should such an undertaking be necessary in the future.

The reassembled sculpture was included in the Whitney's celebratory exhibition of its seventy-fifth anniversary, entitled *Full House*, which opened in June 2006. It commanded the wall on which it was installed and today remains a testament to the collaborative efforts of a conservation scientist, conservators, and an automotive expert in re-restoring a seminal work by Donald Judd.

Acknowledgments

The authors would like to thank the following: Brady Roberts, curator of the Phoenix Art Museum, for his enthusiastic support of this project—without his cooperation, this study would not have been possible; Heather Cox, conservation coordinator, Whitney Museum, for details too numerous to mention; Dan Kirby for developing and executing the MALDI-TOF-MS analyses; Antique Cycle Supply for their knowledge and assistance on all things Harley-Davidson related; the staff at Harvard University's art museums and the Whitney Museum of American Art, and Tom Learner (Tate Gallery), who supplied organic pigment standards for analysis.

Appendix: Experimental Details

FTIR Spectrometry

FTIR spectrometric analyses were carried out using a Nicolet 510 instrument coupled to a Spectra-tech IR-plan infrared microscope with a 32× objective. The sample was compressed onto a diamond cell (2 × 2 mm) with a stainless steel roller, and the sample area defined by double shutters contained in the microscope. An absorbance spectrum was measured and subtracted against a blank background. The spectrum was compared with the IRUG database of artists' materials (<http://www.irug.org>). Care was taken to examine visually homogeneous areas.

MALDI-TOF-MS

A PerSeptive Biosystems⁵ Voyager-DE Biospectrometry Workstation time of flight mass spectrometer was used to obtain laser desorption ionization mass spectra. The instrument was equipped with a pulsed nitrogen laser (337 nm) and operated in linear mode. Typical operating conditions in positive (negative) ion mode were accelerating voltage, 23000 (−23000); grid voltage, 60.0%; guide wire voltage, 0.05%. Typically, 100 spectra were co-added to obtain spectra with adequate signal-to-noise. Resolution was such that monoisotopic molecular weights could be measured in the mass range of interest. Mass was calibrated with CsI in both positive and negative modes. Samples were prepared by placing small paint particles on a stainless steel sample plate with a needle point, and then using a drop of acetone to self-adhere the sample in place. Neither sample dimensions nor weight was measured, but typical samples were on the order of 10–20 μm along an edge, and, generally, the smallest sample that could be handled with a sharp needle point was sufficient to produce spectra.

Notes

- 1 The Whitney work was acquired through the generosity of the Howard and Jean Lipman Foundation, New York.
- 2 Eleonora Nagy, Carol Mancusi-Ungaro, and Dudley del Balso, (who had been an office assistant for Donald Judd) interviewed Roberta Brandes Gratz (the widow of Donald Gratz, who managed the art fabrication) and Bill Gratz (who managed the industrial fabrication), on April 5, 2006, at the Whitney Museum of American Art. The interview transcript resides with the Judd Foundation, New York.
- 3 E-mail from Peter Simet, market compliance and VIN research specialist, Harley-Davidson Motor Company, Nov. 10, 2004.
- 4 Miller had worked with Russell on two of Ralph Lauren's cars, which had won best in show at the Pebble Beach Concours.
- 5 Now Applied Biosystems, Framingham, Massachusetts.

Suppliers

- Antique Cycle Supply, Sand Lake, MI 49343, USA; www. antiquecyclesupply.com; e-mail: getparts@antiquecyclesupply.com; (616) 636-4028; fax: (616) 636-8669
- Bondo Corporation, 3700 Atlanta Industrial Parkway, NW, Atlanta GA 30331, USA; www.bondo-online.com; (800) 622-8754, (404) 696-2730
- Sublime Restorations Inc., 295 Newburyport Turnpike, Route 1 North, Rowley, MA 01969, USA; www.sublimerestorations.com; e-mail: SUBLIMERESTO@aol.com; (978) 948-8510

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A History of the Treatment of Acrylic Painting

Patricia Smithen

Abstract: *In Tate's permanent collection, 171 paintings were identified as having acrylic paint in the design layer. The conservation record for each work was examined to determine trends in condition and treatment of these works from the past fifty years. Acrylic paintings in the Tate Collection tend to crack less and be larger in size than post-1959 oil paintings. They also tend not to be varnished or coated. This paper describes surface cleaning, consolidation, and inpainting treatments with short case studies, with all the materials used at Tate for these procedures included in tables. Accumulation of dirt, grime, and transferred marks from handling are noted as pervasive problems for most of the works. Current methods of surface cleaning are not always satisfactory. Consolidation and inpainting treatments are not often performed, as the acrylic paintings at Tate have not exhibited frequent or extensive cracking and loss. Treatments at Tate have tended to be minimal and conservative, which has been a successful approach for this collection.*

Introduction

This paper is a review of the condition and treatment of acrylic paintings at Tate over the past fifty-odd years, set against a background of the published conservation literature. Tate, fortunately, had excellent record keeping from early on, and files from the 1950s and '60s carry a valuable amount of information. Data on condition and treatment were collected in this study by surveying all the object files and digital files for each identified acrylic painting.

Acquisition of Acrylic Paintings at Tate

Contemporary work was being exhibited at Tate in the 1950s, but it was not being purchased in great numbers. Successful

exhibitions of modern and contemporary painting influenced British artists but failed to convince those with buying power at Tate. According to *Tate, A History*, the director at the time, Sir John Rothenstein, disliked abstract art and spoke out on this topic after leaving Tate in 1964 (Spalding 1998, 138).

The first works with acrylic paint were acquired as gifts in the early 1960s, but none executed entirely in acrylic paint were purchased until 1964, when Sir Norman Reid became director. Contemporary works in general were purchased in greater numbers than before, due to a rise in acquisition funding and because Reid supported the purchase of contemporary and conceptual works, even when he didn't personally like them (Spalding 1998, 178). The number of acrylic paintings now hovers just above 20 percent of the total number of paintings in the collection with a post-1959 date. There was a peak in the 1970s, when 40 percent of acquired contemporary paintings had acrylic paint, but acquisitions in all other decades lie within a few points of 20 percent.

By May of 2006, out of the 790 post-1959 paintings in Tate's permanent collection, 181 works by 122 artists were identified as having acrylic paint in the design layer. About a third of these are mixed-media works. Two-thirds of these paintings were acquired within five years of their creation, and more than half were acquired either directly from the artist's studio or after their first exhibition.

Characteristics of Acrylic Paintings at Tate

Information about paint media is gathered from labels, dealers, and artists when the painting enters the collection. After acquisition, artists or their representatives may be asked for further details about the construction of the works and about

issues regarding display and future treatment. Approximately one-third of the artists in this study have completed questionnaires or participated in interviews.

Further information is gathered through examination and analysis of the paint. Scientific analysis of acrylic media wasn't available in the museum sector in the United Kingdom prior to 1990.¹ In the mid-1990s, Stephen Hackney obtained funding for a project to analyze modern paint at Tate and brought Tom Learner in to begin his research in that area. Since then, twenty-seven paintings have had acrylic media confirmed in their paint layers by pyrolysis gas chromatography/mass spectrometry (PyGC/MS).

The preanalytical accuracy of information at Tate was fairly good; however, a few works that were listed as acrylic in the Tate database were subsequently analyzed and found to contain polyvinyl acetate (PVA) paint rather than acrylic. Terminology also can be vague and easily misinterpreted, with some early works labeled as having “plastic” or “polymer” paint—which could refer to acrylic, vinyl, or other synthetic media. Finally, references in early modern paint manuals and articles recommend mixing media, for example, Magna acrylic into oil paint, and acrylic emulsion with vinyl (Taylor 1964; Gutierrez and Roukes 1965; Pomerantz, Goist, and Feller 1977). Unless artists were specific about the media they used, this type of mixture may not have been identified.

Visual recognition of acrylic media often relies on the perception that this paint has distinctive features. Generally speaking, acrylic paint is thought to contain bubbles, have a plastic appearance, and not crack. While it is true that acrylic paint may often be aerated or contain small bubbles when it is vigorously mixed or handled, bubbles have been recorded as features in only about 10 percent of the Tate's acrylic works, evenly distributed across decades. Furthermore, aeration can be a feature in other fast-drying paint media, and has occasionally been noted in oil paint. Thus the presence of bubbles cannot be used to confirm media on its own. Similarly, acrylics can resemble oil paint, and modern acrylic emulsions can be modified to result in a wide range of finishes and effects. It is not possible to rely on a plastic appearance to identify acrylics.

In contrast, the absence of cracking is a feature of acrylic paint borne out in our collection. The extent of cracking in any painting will be influenced by factors such as the number of times it has been transported for loan and/or displayed, as well as the condition it was in when it was acquired by Tate. However, in terms of the current state of the Tate Collection, statistically, post-1959 paintings with oil paint in the design

layer at Tate are over three times more likely to be cracked than paintings with acrylic paint.² Fewer than 10 percent of our acrylic paintings have inherent cracking, although there are some drying cracks, which tend to occur in thick or multilayered applications or on fold-over edges. An additional 10 percent show mechanical cracks—either edge cracks due to restretching or tensioning or isolated fractures, generally referred to as “fine” or “minor,” and often directly attributable to an external incident. With both types of cracking, approximately half of the works have mixed media, which may contribute to material weakness or poor adhesion.

Another characteristic of acrylic paintings at Tate is their size. These works are significantly larger than the post-1959 oil paintings. Three-quarters of acrylic paintings are larger than two meters in one direction and a third of all acrylic paintings are greater than three meters. For oil paintings of the same period, only one-third are greater than two meters and fewer than 10 percent are larger than three meters in one direction.

Size does influence treatment. Large works, particularly color field paintings, must be treated holistically to reduce the risk of creating patches of variable surface gloss or color. When Margaret Watherston was cleaning large color field paintings in the 1970s, she mentioned that to ensure an even finish they needed to be retreated several times, and that the process became very boring. She recommended the use of art students and other untrained labor (Watherston 1974).

The Problem with Surface Coatings

Since the introduction of acrylic paint, the advisability of applying protective surface coatings has been discussed. Most early sources were in agreement that you could not use natural resin varnish as you would for oils, but many did recommend the use of unpigmented acrylic media as the ideal protective layer. This advice is given widely today throughout artists' manuals and by paint manufacturers.

The same sources noted that, very differently from a soluble varnish, acrylic medium applied over acrylic paint becomes an intrinsically bound layer that cannot be removed without harming the underlying paint. Varnishes can only be considered protective if they form a sacrificial layer that can be removed and replaced periodically. If not formulated specifically as varnishes, some unpigmented media—without the pigments to toughen the film—may produce softer films than the underlying paint, and consequently collect more dirt. Some currently available commercial varnishes are formulated to be removable, but there are no reports in the conservation

literature discussing successful removal of these coatings from acrylic paintings.

Only 12 works of the 181 acrylic paintings at Tate are known to be varnished or coated. Spray varnish layers may be thin and the same medium as the paint film, making them difficult to identify. It is possible that varnishes or unpigmented layers are present that have not been identified in the collection, but most of the artists collected by Tate do not use varnish on acrylic paint.

Treatment of Acrylic Paintings

The same properties that provide acrylic paints with such advantages in terms of their longevity can also make them difficult to conserve. The relatively soft, thermoplastic nature of acrylic emulsion paints results in great adhesion and flexibility, but these paints also are susceptible to abrasions, are sensitive to solvents, and retain dirt. This paper reviews three types of treatment on acrylic paintings at Tate: cleaning, consolidation, and retouching.

Cleaning

Surface cleaning methods for acrylic paintings appear in the artists' and conservation literature in the 1960s (Gutierrez and Roukes 1965; Pomerantz 1962), and specialized treatments, often techniques adapted from paper and textile conservation, appear in the 1970s (Watherston 1974; Brenner 1974).

The problem of dirt retention in acrylic emulsion films is reiterated throughout the 1980s (Lamb 1982; Lodge 1984), as more conservators realized the extent of the problem. Most treatments relied on swabbing aqueous solvents or detergent solutions over a paint surface, or they used mechanical methods such as erasers or rolling putty. From the 1990s onward, however, some entirely new approaches were considered, as conservators and scientists tested lasers (Real et al. 1996) and atomic oxygen (Rutledge et al. 2000) to clean acrylic paint. Ongoing studies into the nature of acrylic paint will lead to better understanding of solvent-dirt-paint interactions and assist conservators with cleaning treatments in the future. And they will be needed. A recent soiling study (Druzik and Cass 2000) noted that the average time for perceptible soiling on a white surface is fifty years. Given that the earliest acrylic paintings at Tate are from the 1960s, the coming decades will show increasingly apparent dirt on surfaces.

Approximately two-thirds of the 181 acrylic paintings at Tate have some level of dirt noted on the surface; the most common condition is a moderate accumulation of grime, fingerprints, and transferred marks caused by handling.

Jeremy Moon's Untitled 2/72

A good illustration of the problems encountered during cleaning can be seen in the attempted treatment of a work at Tate, *Untitled 2/72* by Jeremy Moon (fig. 1A) (Fife 1996). This large



FIGURE 1A Jeremy Moon (British, 1934–1973), *Untitled 2/72*, 1972. Acrylic emulsion paint on primed cotton canvas, 203 × 290 cm (80 × 114 in.). London, Tate, T02052. © Tate, London, 2007. © The Estate of Jeremy Moon, Courtesy Rocket Gallery, London.

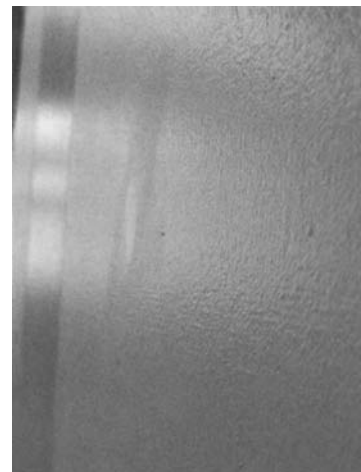


FIGURE 1B Detail of a cleaning test of Moon's *Untitled 2/72* taken in raking light at an oblique angle to show gloss differences.

painting has a consistent, evenly applied acrylic emulsion paint layer with a slight surface gloss. As well as the usual black finger marks and scuffed corners, it also has chalky white drips and black accretions across its surface. In 1996, a Tate conservator attempted to clean the painting, and when the paint on the edges seemed secure with a saliva swab, a test was carried out on one of the marks in the center of the painting. The white drips and black spots seemed to be embedded into the paint, and only the surface white material was removed. When the test was viewed at an oblique angle, it appeared as a polished mark with a surrounding matte halo (fig. 1B). Unsure as to whether this surface change was an improvement or damage, and given the amount of material that could not be removed with saliva, the cleaning was put on hold until better techniques and evaluation methods could be developed. The painting remains in this state today.

Tables 1 and 2 list all the materials that Tate conservators have used to clean acrylic paintings since the early 1960s. Treatments were not particularly experimental. All solvents and solutions were applied with swabs, treatments were conservative, and several were deemed “partial” dirt removals or “unsuccessful.” A little more experimentation with dry cleaning materials was made, but this usually consisted of variations on a theme: lots of erasers, lots of putty. Most of these treatments were used specifically on edge scuffs and black marks, again with varying degrees of success.

David Hockney’s A Bigger Splash

The one exception to conventional treatments was the attempt to test and use commercial dry-cleaning solutions to deal with

Table 1 Wet cleaning treatments on acrylic paintings at Tate.

Wet Cleaning	Year of Cleaning
Water	1969, 1971, 1972, 1973, 1976, 1977, 1980 (two works), 1986, 1992, 1993 (two works), 1994, 2000, 2004, 2005
Saliva	1973, 1975, 1979, 1984, 1989, 1991, 1992 (two works), 1997 (two works), 2000, 2002, 2004
Mineral (white) spirits	1969, 1988, 2004
Lissapol 1% in water	1973
Dry-cleaning solutions	1983 (two types tested)
Rowney’s art cleanser (unidentified)	1973
1% triammonium citrate in water	1991

a specific problem on the exposed canvas of David Hockney’s *A Bigger Splash* (1967) (Holden 1983). A greasy stain on the raw canvas appeared (fig. 2), apparently after the painting had hung behind a chair for many years (prior to acquisition; the suspected culprit was hair grease). In 1981, a Tate conservator found two commercial dry-cleaning solutions (K2r Stain Remover Spray by Dylon International Ltd. and Dry Clean Grease Spot Remover by J. Goddard & Sons Ltd.) that were sprayed onto a surface as a powder.³ This was essentially a solvent poultice: when the solvent evaporated, the grease was drawn into the powder, which was simply brushed off when dry. The treatment improved the appearance of the stain and reduced some particularly greasy fingerprints, but the last traces of white powder were difficult to remove. Note that this treatment was undertaken on the *unpainted* canvas portions of the painting, not on the acrylic paint itself. The paint was cleaned by brushing with a stiff stencil brush.

Watherston’s Methods

In 1974, Margaret Watherston was the first person to publish treatment methods specifically designed to clean modern paintings. “The Cleaning of Color Field Paintings” (Watherston 1974) is a seminal article in which she describes treatments, borrowed and adapted from methods used by textile conserva-

Table 2 Dry cleaning treatments on acrylic paintings at Tate.

Dry Cleaning	Year of Cleaning
Soft brush	Continuously
Mars plastic eraser	1970, 1980, 1983, 1986, 1987, 1988, 1991, 1992, 1995, 2004
Putty eraser	1969 (two works), 1970 (two works), 1972, 1973, 1976
Tapered pencil eraser	1984
Colonel Green tracing eraser	1979
PVA eraser	1979
Pencil eraser	1975
Art eraser	1977
Stencil brushes	1983
Dry cotton swabs	2003
Tweezers	2000
Groomstick	1986, 1995, 1999, 2002 (four works)
Smoke sponges	2000 (two works), 2002, 2003, 2005 (two works)
Bread crumbs	1995

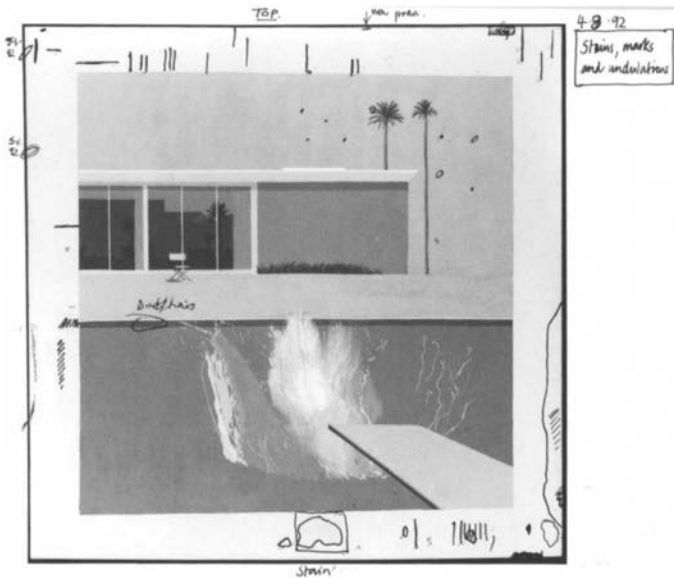


FIGURE 2 Annotated image of David Hockney's *A Bigger Splash* (1967). © Tate, London, 2007. © David Hockney.

tors, to clean vast areas of raw, stained, and painted canvas. She used the same methods on different works done in solvent-based acrylic, acrylic emulsion, oil, and other media.

To clean these works, Watherston removed the canvases from their stretchers, loomed them up (in the process she used paint stripper to remove “interfering” paint from the tacking edges on the reverse and trimmed the excess material on the edges to a uniform length), removed loose dirt from the front and back with erasers or putty, and proceeded to wash the works by flushing water through the raw and stained canvas and by scrubbing the canvas with a variety of tools. The areas with paint films were washed by sponging on water (containing a wetting agent) and then blotting. All processes were repeated several times, and huge amounts of water were used. It was a radical treatment then, and while it is rather more extreme than current recommended practice, Watherston correctly identified many of the issues we grapple with today. She knew that the behavior of the painted and unpainted sections needed to be considered separately but treated in tandem. She knew she was removing materials other than dirt, and tried to compensate by reapplying size layers, although she also applied them to the painted areas as well as the exposed canvas. She attempted to treat the works holistically, in a new manner specifically adapted for modern paint and techniques. However, the works she treated look visibly different today when compared to similar works that have not undergone the

intensive washing and resizing. There have been reports that they look slightly scrubbed and have a bluish cast.

Conservators at Tate were aware of Watherston’s methods. In a lecture Anna Southall gave in 1988 she stated, “We have experimented rather nervously with washing canvases, following Margaret Watherston’s methods, but tests show that while light washing can be effective, the heavy washing needed to remove heavy soiling visibly affects the acrylic paint” (Southall 1988).

Watherston’s understanding of the integrity of the artwork was of her time. In her attempts to preserve the color contrasts and tonal balance of freshly painted works, she had no qualms about removing unseen original material, such as canvas and paint on the reverse tacking edges or visible discolored media. She described the process for removing discolored original sizing media from the front face of canvases from Morris Louis’s *Veil* and *Floral* works, when she felt the stains detracted from the original appearance (Watherston 1974). The first artist-versus-conservator ethical papers were published in the 1980s and marked the beginning of a change in attitude regarding the interpretation of the artist’s intent. A shift has occurred away from prioritizing the resuscitation of the original appearance toward the conservation of the original material. Consequently, conservators today would tend not to draw large amounts of water and solvent through acrylic paint and canvas, for fear of removing original material, even if the loss or change was not immediately visible.

Morris Louis’s Alpha-Phi

In contrast to the Watherston method, the four treatments of color field works undertaken by Will Shank in the mid-1990s at Tate were conservative and much more successful by today’s criteria. One example is *Alpha-Phi* (1961) by Morris Louis (fig. 3), a *Magna* acrylic on cotton canvas painting from the *Unfurled* series (Shank 1995). The paint and canvas were stained and grimy, despite two earlier dry cleaning treatments, and the stretcher appeared as a visible ghost image on the front. The work was removed from its stretcher, revealing staining that was caused by the stretcher off-gassing components into the cotton duck.

The painted surface was brushed and vacuumed. The canvas surface was cleaned by rolling conservation-grade soft, white bread crumbs over the surface (from bread made by the conservator without oil, salt, or sugar). The stretcher was cleaned and coated with polyurethane incorporating calcium carbonate as an acid buffer. The work was then restretched over a loose lining of cotton fabric coated with Spectrum acrylic primer on the reverse.



FIGURE 3 Morris Louis (American, 1912–1962), *Alpha-Phi*, 1961. Magna acrylic (poly methacrylate resin) paint on unprimed cotton canvas, 259.1 × 459.7 cm (102 × 181 in.). Tate, London, T01058. © Tate, London, 2007. © Morris Louis, 1961.

While some stains remained, the overall appearance was very even and the grimy appearance was lifted. The loose lining blocked the reflected shadow caused by the stretcher and provided even support for a sagging canvas. The painting was improved considerably in appearance and avoided all the excesses of a moisture-based cleaning.

Michael Kidner's Column in Front of Its Own Image II

This change in emphasis is illustrated by a treatment done at Tate in 2001 on *Column in Front of Its Own Image II* (1971), a work by Michael Kidner (fig. 4A) (King and Green 2002). This work has two components: a stretched painting on cotton duck and a multimedia column. The painting component has an overall layer of white acrylic emulsion paint with strips of colored acrylic emulsion paint layered over it. Over the white paint and around the colored strips was another, discrete layer of thin, water-soluble white paint.

Prior to its acquisition, the work had been damaged by water. The white, water-soluble paint layer had partially dissolved and the medium had pooled around drip marks, yellowing significantly. Brown water stains and accumulated dirt further marred the surface. Before arriving at Tate, the work had had a semicircular area cleaned, removing the water-soluble white layer, and losses were retouched. A detail in ultraviolet light (fig. 4B) shows the area from the top of the painting. In normal light, this cleaned area looked too white in comparison to the surrounding paint.

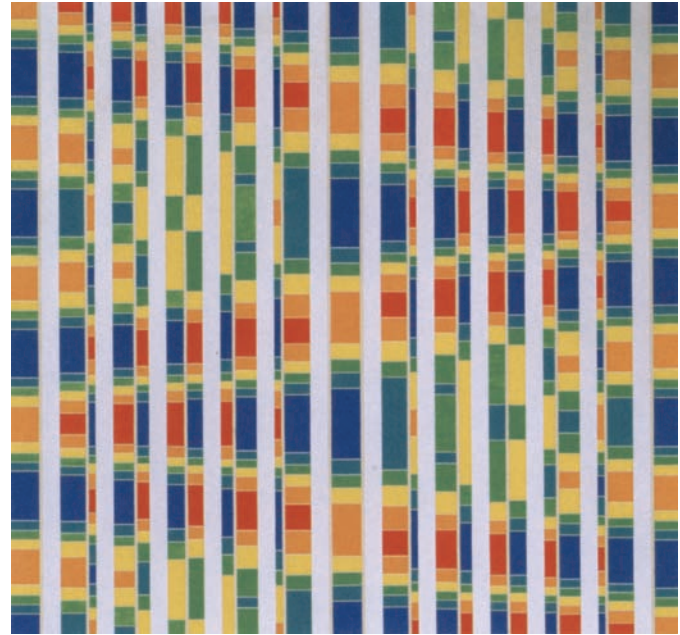


FIGURE 4A Michael Kidner (British, b. 1917), detail of the painting component of *Column in Front of Its Own Image II*, 1971. Acrylic emulsion paint and graphite on primed canvas. London, Tate, T07791. The painting is part of a larger work that also comprises a sculptural element. © Tate, London, 2007. © Michael Kidner.

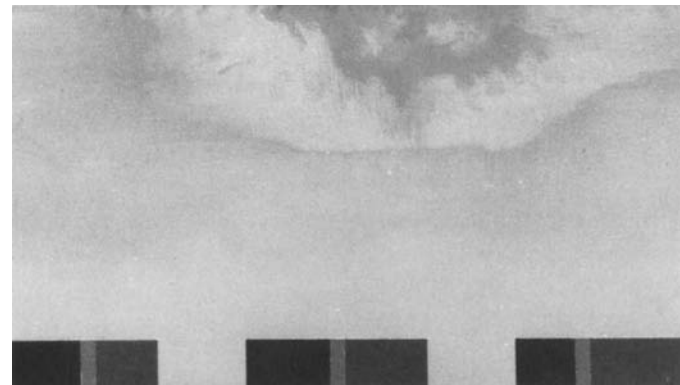


FIGURE 4B Detail of the top right corner of the painting component of *Column in Front of Its Own Image II* taken in ultraviolet light.

The conservators had two options: to clean the painting by removing the dirt and stains, and the water-soluble layer along with them, or to leave the work intact and accept the compromised surface. The conservators chose to retain the original, artist-applied layer and accept the damage. The solution

to integrating the too-white surface around the previous restoration was to “dirty up the area by running a graphite pencil lightly across the surface” (King and Green 2002). Rather than a cleaning treatment, this became a retouching/reintegration treatment.

Consolidation

Most consolidation of acrylic paint at Tate was done only when there was imminent danger of losing the paint. Thus, lifting paint and loose flakes were treated, but there has been very little preventive consolidation, as is often done on oil paintings, whereby adhesive might be infused into an otherwise secure crack or abraded area, for example.

While reversibility of consolidation treatments is not always practical, the application of the consolidants must be considered carefully. Most adhesives are applied in a liquid form, which requires clearance from adjacent surfaces. The ease with which acrylic emulsion paint can be damaged by pressure, abrasion, and aqueous/solvent exposure increases the risk of damage to surrounding paint during clearance. In addition, any application of heat to set the adhesive or for use with hot-melt materials, such as wax or BEVA film, risks deforming the paint and changing the local appearance of gloss. The combination of acrylic paint’s susceptibility to visual changes under these circumstances and its flexible

nature means that doing nothing is often preferable to preventive intervention.

Table 3 lists all the consolidants used by Tate conservators on acrylic paintings by decade. These are essentially a subset of the consolidants used on oil paintings. Wax resin, BEVA, and BEVA film were all used on paintings that incorporated oil paint, where local areas were tested for reversibility of the consolidant. The one innovation for acrylic paint was when a conservator reattached an area of delaminated paint by softening the lower layer with a drop of xylene, allowing the top layer to be gently replaced and secured (Learner 1997).

With so few occurrences it is difficult to draw conclusions. However, most of the works were of mixed media and the treated paint was described as lifting, delaminating, or having isolated flaking. About half of all acrylic paintings with reported cracking were treated. One example is from *The Firemen of Alijo* (1966), a work by Paula Rego (fig. 5A), on which acrylic emulsion paint had cracked and delaminated from acrylic emulsion gesso along the edge of a paper collage element (fig. 5B). The cracks and lifting paint were consolidated with Jade 403, a PVA adhesive (Smithen 2001). The glue was fed in using a small brush, cleared from the surrounding area with a damp swab, and allowed to dry under weights.

Data allowing direct comparisons for consolidation treatments on all paintings at Tate exist for seven years. Out of

Table 3 Consolidating materials used on acrylic paints at Tate.

Decade	Material	Number of Uses	Paint Media Consolidated
1960s	Wax resin	2	Acrylic, enamel, and oil paint Acrylic emulsion paint, silkscreen ink, and oil paint
1970s	Plextol B500 (ethyl acrylate/methyl methacrylate copolymer)	1	Plastic paint
1980s	None		
1990s	Sturgeon glue	2	Acrylic emulsion paint, enamel, and oil paint Acrylic emulsion paint
	Gelatin	1	Acrylic emulsion paint, silkscreen oil, and oil paint
	PVA dispersion	3	Acrylic emulsion paint, silkscreen oil, and oil paint Acrylic emulsion paint, wax crayon, and wax varnish Acrylic emulsion paint and oil paint
	BEVA (ethylene-vinyl acetate copolymer)	1	Acrylic emulsion paint, oil paint, and paper collage
	Xylene to soften paint	1	Acrylic emulsion
Since 2000	PVA dispersion	2	Acrylic emulsion paint, oil pastel, resin, charcoal, and paper collage Acrylic emulsion paint and house paint
	BEVA Film	4	Acrylic emulsion paint, oil paint, oil paint stick, graphite, and house paint



FIGURE 5A Paula Rego (British and Portuguese, b. 1935), *The Firemen of Alijo*, 1966. Acrylic emulsion paint, oil pastel, natural resin, PVA glue, paper, and metal foil on primed canvas, 153.9 × 184.3 × 4.5 cm (60½ × 72¼ × 1¾ in.). London, Tate, T07778. © Tate, London, 2007. © Paula Rego.



FIGURE 5B Detail of figure 5A showing losses and raised cracks. The acrylic emulsion paint has separated from the acrylic emulsion gesso along the side of a collage element, which contributed to the local weakness.

208 treatments, only one was carried out on an acrylic painting.⁴ The very nature of acrylic paint that makes consolidation such a risky operation also means that it should seldom be necessary.

Inpainting and Retouching

Just as fewer acrylic paintings need consolidation treatments, less retouching is done on acrylic paint. The fact that acrylic paintings tend not to have large areas of loss is a tribute to their stability and flexibility; however, it also means that developing media specifically for inpainting acrylic paints has not been a priority for the profession. Even when promising new materials (e.g., Regalrez 1094 resin and Gamblin colors) have been introduced, publications testing their usage on acrylics have not been forthcoming. At Tate, minor losses and disfiguring abrasions on acrylic surfaces tend not to be retouched, unless they interfere with the visual continuity. A colleague noted that when working privately, she was told that it is best to attend to the edges and corners when inpainting difficult surfaces because this would make the biggest visual difference.⁵ This commonsense practice is well known and, likely, widespread.

Table 4 lists all the media ever used by Tate conservators when inpainting and retouching acrylic paintings. In the 1960s

through the early 1980s some variety and experimentation occurred. There were problems matching surface gloss, which is why conservators were using some strange, occasionally irreversible combinations like emulsion over emulsion.

For example, retouches in solvent-based, acrylic media over acrylic emulsion paint occurred when a set of Magna paints and media was sent over from the United States. According to one report, “Magna was chosen because it appears to remain soluble in white spirit for a considerable period of time, although n-butyl methacrylate eventually tends to cross link” (Southall 1980). The conservator knew it might be a problem in the future, but options were few.

In these three cases, however, the risks were contained. All of the paintings were very dark or black paintings with only isolated or minor retouching required on scratches and edge abrasions. In practice, even if the Magna media discolored, it was unlikely to become a problem on these dark works with minimal inpainting. One conservator did note that the Magna retouchings appeared matte (Perry 1979), highlighting the problem of matching gloss.

The mid-1980s to 2000 was a conservative period at Tate, with no experimentation—mainly watercolor and gouache were

Table 4 Retouching media used on paintings with acrylic paint media at Tate.

Decade/Years	Material	Number of Uses	Paint Media
1960s	B72 (acrylic resin) + pigment	1	Acrylic, enamel, and oil
	MS2A (reduced ketone resin) + pigment	1	Acrylic, enamel, and oil
	Unidentified	1	Acrylic, tempera, and silkscreen ink
1970s	Acrylic emulsion paint	1	Acrylic, tempera, and silkscreen ink
	B72 (acrylic resin) + pigment	1	Acrylic emulsion and PVA
1979–80	Magna (acrylic resin) + pigment	3	Acrylic emulsion
1980s	Acrylic emulsion paint	1	Acrylic emulsion
	Watercolor/gouache	1	Magna acrylic and oil
1990s	Watercolor	5	Magna acrylic
			Silkscreen oil and acrylic emulsion
			Acrylic emulsion and PVA
			Acrylic emulsion and charcoal
			Acrylic emulsion
	Unknown	2	Acrylic emulsion, silkscreen oil, and alkyd paint Acrylic emulsion
Since 2000	B72 (acrylic resin) + pigment	1	Acrylic emulsion
	Acrylic emulsion	1	Acrylic emulsion
	Graphite	1	Acrylic emulsion
	Watercolor/gouache	2	Acrylic emulsion, oil pastel, charcoal, resin, and paper collage Acrylic emulsion, graphite, and ink

used. These retouchings would be reversible and, for the most part, minimal or isolated. However, they also tended to be matte and visible at oblique viewing angles. Some conservators rubbed microcrystalline wax over retouches or over local areas affected by cleaning to improve the gloss.

At the turn of this century, different media were revisited again, as conservators tried to match the complex surfaces. While some media were used only on fills or over isolating layers, the border of the retouch with acrylic paint could be vulnerable when these materials are removed in the future. Navigating the balance between acceptable finish and reversibility can be very difficult with acrylic paint.

Conclusion

Currently, treatments on acrylic paintings tend to be minimal. Recent studies devoted to the surface cleaning of acrylic paints should result in a better understanding of the effects of treatments and, hopefully, give conservators the confidence

to remove dirt, stains, and accretions with minimal impact on the paint. However, other areas—such as consolidation and inpainting methods and media—also require attention. The lack of materials and methods for reversible treatments hampers the ability of modern conservators to maintain the appearance of acrylic paintings.

Even so, recent survey information confirms that most of the acrylic paintings at Tate are stable and acceptable for display and loan, albeit with a few grubby surfaces. This suggests that the past forty-five years of conservative and minimal treatment has been appropriate for this collection to date. There has been no need for treatment reversals, and retreatments have been few. The “less is more” approach, when applied to acrylic paintings at Tate, has been successful.

Acknowledgments

This paper could not have been completed without the contributions from my colleagues at Tate, past and present. Special

mentions must go to Rachel Barker, Tom Learner, Tim Green, Annette King, Roy Perry, and Jacqueline Ridge. I would also like to thank Will Shank and Sandra Amann for their valuable assistance.

Notes

- 1 Stephen Hackney, personal communication, 2006.
- 2 According to digital records, there are six hundred paintings in the permanent collection at Tate with oil paint in the design layer and with a date later than 1959. One hundred twenty-one records for these works were randomly examined and, of these, 82 works exhibited some form of cracking, while 39 exhibited no cracking. This is compared to post-1959 paintings with acrylic paint in the design layer: out of 181 records examined, 36 showed cracking, and 144 were not cracked. Thus, post-1959 oils at Tate exhibit cracking 3.4 times more than acrylics. This number is significant to well below the level of 1 percent predicted using Pearson's chi-square test. (Statistical analysis was provided by Jon Clarke.)
- 3 According to literature for the Johnson Wax product, "Six powerful solvents go to work" (Johnson Wax Ltd. pamphlet, "How to Use Dry Clean," ca. 1982).
- 4 Unpublished research by Jacqueline Ridge, 2006.
- 5 Rebecca Hellen, personal communication, 2006.

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PART FIVE

Cleaning Issues

An Investigation of Water-Sensitive Oil Paints in Twentieth-Century Paintings

Aviva Burnstock, Klaas Jan van den Berg, Suzan de Groot, and Louise Wijnberg

Abstract: The study examined the cause of sensitivity of well-bound oil paint to aqueous and polar solvents used for surface cleaning. The composition of oil paints from selected unvarnished twentieth-century paintings and tube paints was examined using light microscopy (LM), scanning electron microscopy/energy dispersive X-ray analysis (SEM/EDX), Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), gas chromatography/mass spectrometry (GC/MS), and direct temperature resolved mass spectrometry (DTMS). Crystal-like structures were found on all the paint samples that contain elemental aluminum, suggesting that aluminum stearate was added in manufacture as a dispersant, although positive identification of the stearate was possible in only one sample. A possible alternative, hydrated alumina, was identified in two samples containing ultramarine, while zinc stearate was identified in two water-sensitive paint samples. A hypothesis is proposed that links hydrolysis of metal stearates with the formation of surfactant-like functionalities in the paint related to aluminum,

zinc, and/or other fatty acid soaps, and this could explain water sensitivity during treatment. It is postulated that the presence of hydrated alumina may increase the sensitivity of the paint to water and act as a swelling agent.

Introduction

This investigation of the water sensitivity of oil paint was motivated by issues that arose from the treatment and technical study of the large Jasper Johns triptych *Untitled* (1964–65) in the Stedelijk Museum in Amsterdam (fig. 1). In the conservation treatment, it was noted that the surface of the unvarnished paint of every color is highly sensitive to the aqueous solvents normally used for surface dirt removal.

The problems with water sensitivity of unvarnished twentieth-century paintings are well known to conservators. Selected passages of paint may be sensitive to swab rolling with water or saliva, and it may be difficult to predict which



FIGURE 1 Jasper Johns (American, b. 1930), *Untitled*, 1964–65. Oil on canvas, 182.9 × 478 cm (72 × 188 in.). Amsterdam, Stedelijk Museum. © Jasper Johns c/o Beeldrecht, Amsterdam 2007.

paints are sensitive. While the issues of cleaning underbound paint have been the subject of some research, the sensitivity of relatively well-bound oil paint has not been investigated before; this is the focus of the present study. The effect of a wet swab on these medium-rich surfaces is distinctly different from the problems of cleaning underbound paint, where the mechanical action of a swab can readily remove pigment, irrespective of solvent. Here, pigment and binder both come off instantly, as soon as the wet swab touches the paint surface. In contrast, no such effect is seen with nonpolar solvents.

The present investigation summarizes the findings of an analytical study that included paint samples from the Johns painting; a fuller description of this work, including its provenance and context, is given elsewhere (Wijnberg et al., forthcoming). The study also included samples from Karel Appel's *L'homme* (1953) (fig. 2) and *Grande fleur de la nuit* (1954), *Painting 6* (1961) and *October 1958* by Robyn Denny, and *Seascape at Clodgy* (1935) by Borlase Smart.¹ All of these paintings are unvarnished, are painted in oil medium, and exhibit sensitivity of some or all of the paint when water is used for surface cleaning.

Analysis of some artists' oil tube paints, combined with a literature search on oil paint manufacture in the twentieth century, presented a range of possible causes for this phenomenon. These include certain pigments and extenders, as well as some of the organic additives that are used. The aim of this study is to increase the profession's understanding of the behavior of such sensitive oil paints, which will contribute to the risk assessment and predictive knowledge of surface cleaning of modern oil paints.

Composition of Oil Paint in the Twentieth Century

The introduction of new pigments and media in the twentieth century significantly extended the range of available materials for both industrial and artists' paints. Although the use of acrylics and alkyd paints is widespread in works of art, oil paint remained the most popular paint type throughout the twentieth century. Linseed and safflower oils seem to have been used most in artists' paints. The extent to which safflower oil, which replaced nut and poppy oil in the twentieth century, was used in the formulation of artists' paints is not clear, although recipes for artists' paints closely follow manufactured paint technologies in the twentieth century.²

The preparation of linseed oil also changed when large-scale processing was required. It involved heating the oil to



FIGURE 2 Karel Appel (Dutch, 1921–2006), *L'homme*, 1953. Oil on canvas, 210 × 130 cm (82½ × 51½ in.). Amsterdam, Stedelijk Museum. © Karel Appel Foundation.

about 260° C to separate out albuminous material, followed by refining with alkali or acid and then water washing. Sometimes oils were bleached with activated earth. Faster-drying boiled oils were made using hot steam with lead and manganese driers. More viscous stand oils were made by heating linseed oil to 260–300° C for six to eight hours, with no driers being used (Heaton 1947). The condition and preparation of the oil binder and its pH influence the relationship between pigment and binder, as well as the extent of hydrolysis of the oil and other components of the formulation. The use of alkali-refined oil or oil with significant mucilage content may influence the pH and affect the sensitivity of the dry paint to polar solvents.

New formulations also introduced new additives to facilitate the dispersion of pigments into the medium. Dispersing agents were added to paints during the nineteenth century

(Carlyle 2001), and aluminum and zinc stearates were patented as dispersion agents and widely used after 1920 (Tumosa 2001). Figure 3 illustrates pigment dispersed with a metal stearate. Technical grades of metal stearates are traditionally made by reacting metal oxides/hydroxides with tallow or related hard fats. Consequently, the materials also contain varying amounts of fatty acids, mostly palmitates and stearates, and aluminum stearates may also contain mono- and distearates.³

Twentieth-century artists' paint manufacturers acknowledge the incorporation of metal soaps (usually between 1 and 5 percent by weight), such as aluminum and zinc stearates, in oil paints (Heaton 1947). Aluminum stearates improve a paint's working properties by increasing the oil's viscosity and reducing the amount of pigment needed. Other dispersing agents include other metal stearates, ethanolamine oleate, blown castor oil, magnesium silicate, magnesium or aluminum octoate, and modern rubber (Heaton 1947; Wendt 1953; Dintenfass 1958). However, dispersion of basic pigments, such as lead white and zinc oxide, in oil is achievable without additives via metal soap formation (lead or zinc "oleate"; see fig. 3B), although wetting these particles can be enhanced with small quantities of free fatty acids (Dintenfass 1958; Davidson 1960). Other methods used include "flushing" pigments with water prior to dispersion (Crowl 1963), the addition of aluminum oxide (Al_2O_3) as a dispersant, and coating pigment particles with silica to limit pigment-binder reactions (Clarke and Arnold 1955; Elbrechter and Muller-Fokker 1970).

A number of other possible additives are mentioned in the literature that might affect the sensitivity of the dry oil paint films to water. Multiple references appear from the 1920s onward regarding problems associated with making oil paint using hygroscopic and poorly wetting pigments, notably ultramarine and chrome and cadmium yellows. In 1950, Browne found that oil paint absorbs the most water, either

ambiently or via immersion, when applied in medium-rich films to which zinc and titanium pigments and magnesium silicates are added (Browne 1955, 1956).

Also discussed frequently throughout the twentieth century is the problem of preventing drying defects in relation to maintaining the dispersion of pigments in oil media (Holley 1920; Heaton 1947; Bennett et al. 1949; Patton 1964; Hess 1979). Antiskinning agents include volatile antioxidant materials such as butylaloxime and tetrabutyl-dimethylphenol; excessive amounts may cause problems with drying and separation of the pigment and media (Clarke and Arnold 1955). The addition of stearates of aluminum, zinc, magnesium, and other metals to disperse pigments in oil medium is mentioned in almost all the studies for this purpose, and the necessity for limiting the percentage of this additive is discussed with regard to the handling and drying of the paint (Gardner 1928; Clarke and Arnold 1955; Weiss 1957; Turner, Kemp, and Harson 1958).

Analysis and Results

Results of analysis of pigments and other inorganic materials, as well as the organic materials, in the examined paintings are summarized in table 1.

Surface Characterization and Analysis of Well-Bound Oil Paints

All the paintings investigated are unvarnished. Superficial observation of the paintings by light microscopy (LM) suggests that all colors are well bound and in some passages medium-rich at the surface. Scanning electron microscopy (SEM) examination showed that paint samples from all the works show common surface features of crystal-like structures ranging from 200 nm to 2 μm in size on the paint surface. A typical image of the structures on a sample of blue paint from

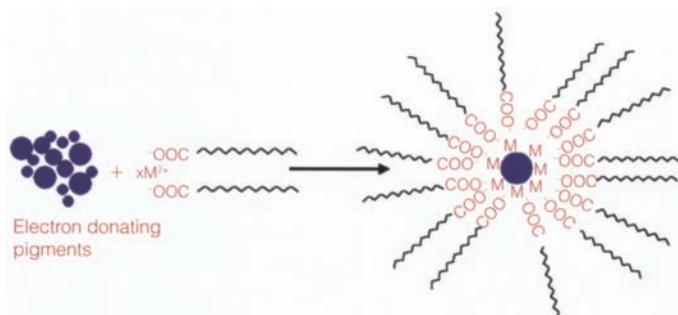


FIGURE 3A Pigment dispersion with a metal stearate (zinc stearate).

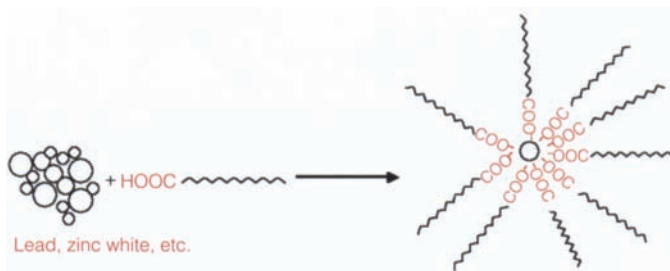


FIGURE 3B Wetting and dispersion of alkaline pigments with fatty acids.

Table 1. Results of sample analysis.

Origin	Sample	EDX	XRD	FTIR	GC/MS ^a , DTMS	Conclusions
Jasper Johns, <i>Untitled</i> (1964–65)	White priming	Pb, Ca, Ba, S		Oil, chalk, lead white		Lead white, chalk, and barium sulfate in oil
	Yellow	Cd, S, Al, Ba, Zn (Mg, Cl)	Cadmium zinc sulfide, zinc oxide	Oil, barium sulfate, magnesium carbonate	Drying oil: P/S 2.5, P/S 1.5, Cd, S	Cadmium (zinc) yellow, zinc white and barium sulfate (and/or lithopone), magnesium carbonate, and aluminum compound(s) in oil
	Blue	Al, Na, Si, Ba, Pb, S, Ti, Co (Fe, P, Ca, K, Mg, Cl)	Quartz, hydrocerussite, cobalt oxide (CoCo ₂ O ₄), titanium dioxide (anatase), sodalite, calcite	Oil, magnesium carbonate	Drying oil: P/S 2.0, P/S 1.6	Cobalt blue, sodalite and/or French ultramarine, lead white, titanium dioxide (anatase), barium sulfate, magnesium carbonate, quartz, calcite in oil
	Red	Cd, Se, Al, Fe, Ba (Zn, As, Pb, Mg)	Cadmium selenium sulfide, barium sulfate, magnesium carbonate	Oil, barium sulfate, magnesium carbonate	Drying oil P/S 1.8, P/S 2.0, Cd, S	Cadmium red, red iron oxide, barium sulfate, magnesium carbonate, and unidentified aluminum compound(s) in oil
	Transparent yellow ^b				Heat-bodied oil. P/S 1.6	Unpigmented (strongly heat-bodied) stand oil
	Orange	Cd, S, Si, Ba (Al, Mg)	Barium sulfate, cadmium sulfide, quartz, magnesium carbonate			Cadmium sulfide orange, quartz, barium sulfate, and unidentified aluminum and magnesium compound(s)
	Green	Cr, Si, Cl (Al, Ba, S, Zn)				Viridian, quartz, barium sulfate, and unidentified zinc and aluminum compound(s)
	Purple	S, Zn, Br, Co, P Ba (Al, Mg)	Barium sulfate, cobalt arsenate		Heat-bodied oil	Cobalt violet, red lake containing bromine, barium sulfate, unidentified aluminum and magnesium compound(s)
	Surface entities	Al, Mg				Unidentified aluminum and magnesium compound(s) ^c
Winsor & Newton deep yellow paint, dry (dated 1971) ^d	Dark yellow	Cd, S, Al, Ba (Mg)		Oil, barium sulfate, magnesium carbonate	Strongly heat bodied oil, P/S 2, P/S 1.8.	Cadmium yellow, unidentified aluminum compound, magnesium carbonate, and heat-bodied oil ^e
Winsor & Newton vermilion paint, dry (dated 1970) ^d	Red	Hg, S, Al; medium separated out: Al		Oil, magnesium carbonate, oxalate? (1322 cm ⁻¹)	Strongly heat-bodied oil, P/S 1.8. Hg.	Vermillion, unidentified aluminum compound, and magnesium carbonate in strongly heat-bodied oil ^e
Karel Appel, <i>L'homme</i> (1953)	Brown	Si, Mn, Fe (Mg, Al, K, Ca) ^f	Iron oxide (goethite) ^g	Oil, ochre (Zn), oxalate?	Heat bodied drying oil. P/S 1.1, P/S 1.3	Brown earth/umber in heat-bodied oil
	Dark green	Fe, K, Si, Mn (Ca, Al) ^f		Oil, Prussian blue (+1456, 1414 cm ⁻¹)	Drying oil, P/S 1.0, P/S 1.7	Umbre with Prussian blue in oil

Table 1. Results of sample analysis. (continued)

Origin	Sample	EDX	XRD	FTIR	GC/MS ^a , DTMS	Conclusions
Karel Appel, <i>L'homme</i> (1953)	Green	Cr, Al, (P, Ca) ^f		Oil, chrome oxide, ^h bone black?, aluminum stearate	Strongly heat-bodied drying oil, P/S 1.4, P/S 1.0	Chrome oxide green, some chalk, and aluminum stearate in strongly heat-bodied oil
	Yellow/brown	Si, Mn, Fe (Al, Ca, Zn) ^f		oil, ochre, (zinc) stearate and oxalate	Drying oil, P/S 1.9, P/S 1.2, Zn	Yellow/brown earth/umber, zinc white in oil, and zinc stearate and oxalate
	Dark blue	Na, Al, Si, S, (K, Ca) ^f		Ultramarine, (zinc) stearate and oxalate, aluminum hydroxide? (1122 cm ⁻¹)	Heat-bodied drying oil, P/S 1.1, P/S 1.2, Zn	French ultramarine in slightly heat-bodied oil, aluminum hydroxide, and zinc stearate and oxalate
	Blue	Al, Ca, P, Co (Cl)				Cobalt blue and bone black
Karel Appel, <i>Grand Fleur de la Nuit</i> (1954)	Blue	Na, Al, Si, S, Mg		Oil, ultramarine, aluminum hydroxide? (1122 cm ⁻¹), oxalate? (1322 cm ⁻¹)		French ultramarine blue, aluminum hydroxide, unidentified magnesium compound(s) in oil
Robyn Denny, <i>Painting 6</i> (1961)	Light blue	Co, Ti, Mg, Al, Si, Pb, S (Na, Cl, K, Sn)	Quartz, hydrocerussite, cobalt oxide, titanium-dioxide (anatase), sodalite/ultramarine, magnesium carbonate	Oil, magnesium carbonate, chalk, barium sulfate	Drying oil, P/S 1.8	Cerulean blue, lead white, French ultramarine, titanium dioxide (anatase), unidentified aluminum compound(s), magnesium carbonate in oil
Robyn Denny, <i>October 1958</i>	Dark blue	Al, Si, Ca, P, Ti, Pb, S, Ba, Zn, Na				French ultramarine, bone black, titanium white, lead white, and lithopone
Borlase Smart, <i>Seascape at Clodgy</i> (1935)	White ground	Ca, Pb				Calcium carbonate and lead white
	Blue	Al, Pb, Zn, Co		Drying oil + zinc oxalate?	Drying oil, P/S 2.0	Cobalt blue, lead white [+ red lake (Al substrate)], and zinc (oxalate?) in oil
	Yellow	Pb, Cr, Ca, Zn, Al, Si, K, Cu				Lead (zinc) chromate yellow and viridian

Note: Samples were analyzed at the Courtauld Institute of Art, University of London, using scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX) and studied with light microscopy and EDX in cross section, unless stated otherwise. X-ray diffraction (XRD), gas chromatography/mass spectrometry (GC/MS), and Fourier transform infrared (FTIR) spectroscopy were carried out at ICN; direct temperature resolved mass spectrometry (DTMS) was done at Shell Research and Technology Centre, Amsterdam.

^a Heat-bodied or stand oil, interpreted on the basis of DTMS results. GC/MS result in *italics*; see text for discussion.

^b Taken from reverse of yellow panel.

^c Based on analysis results of bulk of paints; see text.

^d Based on information on the tube label (obtained from Alun Foster, Winsor & Newton, e-mail message June 2006).

^e Stand oil or heat-bodied oil was not used by Winsor & Newton (A. Foster, e-mail message, Sept. 2006).

^f Microscopy and EDX results at ICN by Matthijs de Keijzer.

^g Water-soluble efflorescence at the surface was identified as a combination of ammonium iron sulfate and ammonium zinc sulfate (Hallebeek 2005). It was hypothesized that material had formed on the surface, as no evidence was found for this material in the bulk of the paint.

^h Absorptions at 1268 and 1251 cm⁻¹ seem to be related to chrome green pigment (Stefan Zumbühl, Berne University of the Arts, e-mail message to K. J. van den Berg, June 2006).

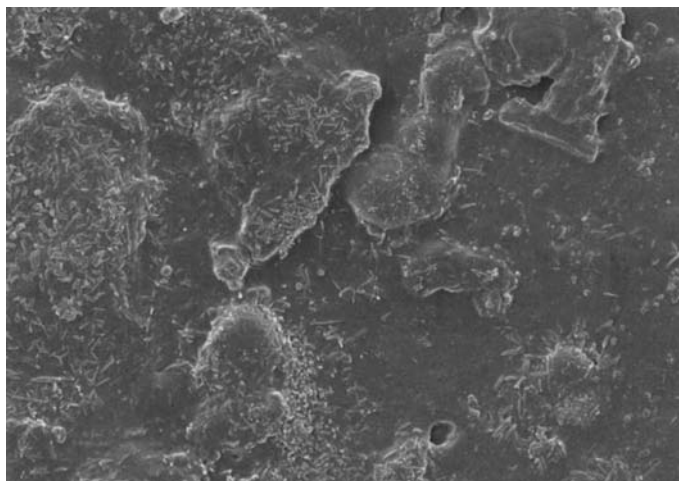


FIGURE 4 SEM image (1500 \times magnification) of a sample of blue paint from Jasper Johns's *Untitled* triptych showing crystal-like structures on the surface.

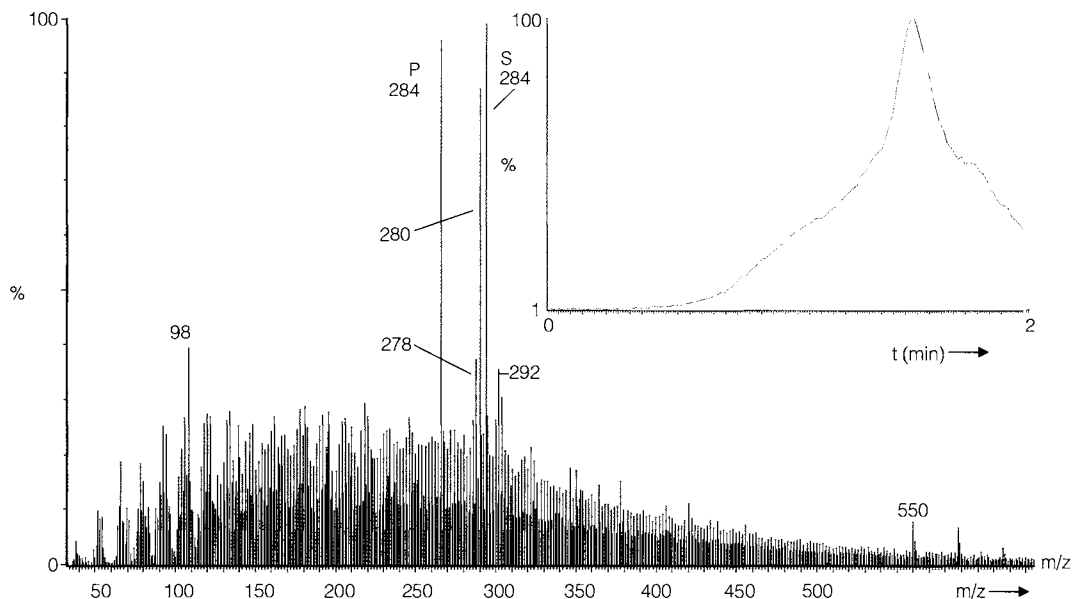
the Jasper Johns is shown in the SEM image magnified 1500 \times in figure 4. The most water-sensitive paints showed the greatest concentration of these surface structures, although they were present in small amounts on the surface of some of the less water-sensitive paints.

Oil media were identified in all paints. The palmitate/stearate (P/S) ratios for gas chromatography/mass spectrometry (GC/MS) and direct temperature resolved mass spectrometry (DTMS) analyses were generally below 2, which could indicate linseed oil, although P/S ratios alone cannot provide absolute proof of oil type, particularly in modern oil formulations.⁴ Although DTMS analysis established the presence of heat-bodied oil in some cases (fig. 5),⁵ no relationship was seen between the degree of heat pretreatment of the oil and the water sensitivity of the paint film. Lipid compounds were the only organic components detected in the paintings, making it unlikely that other media or additives were present in large quantities.

Jasper Johns's *Untitled* (1964–65)
All the paints on the triptych are well bound, and their surfaces are glossy in passages, made matte only by particles of surface dirt. Exceptionally, passages of cadmium yellow paint also exhibited slight ochre-colored spotting, which has been linked with deterioration of the pigment (Leone et al. 2005). Trials for surface cleaning using aqueous agents suggested that paints of all colors were sensitive to water and polar solvents but not to relatively nonpolar solvents, including mineral spirits and iso-octane (Wijnberg et al., forthcoming).

LM examination at low magnification (20–200 \times) of unmounted fragments from the painting and SEM images showed a skin of medium at the paint surface in yellow (fig. 6), blue, red, purple, orange, and green paints, while other colored

FIGURE 5 DTMS spectrum of chromium oxide green paint from Appel's *L'homme*. The peaks at m/z 256 and 284 (palmitic and stearic acid, P/S ratio of 1.0) indicate the presence of drying oil, most likely linseed oil, but this will also be influenced by the presence of aluminum stearate (see text and table 1). The strong peaks at 278, 280, and 292 indicate a strongly heat-bodied paint, most likely stand oil.



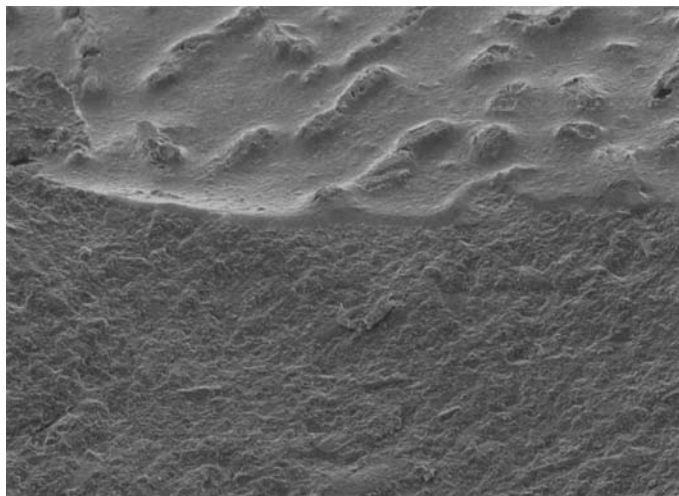


FIGURE 6 SEM image (1200 \times magnification) of a sheared sample of cadmium zinc yellow paint from Jasper Johns's *Untitled*, showing a skin of medium on the surface.

paints used for the work appeared more uniformly bound throughout the layer and were relatively medium-rich.

Crystal-like structures were present on the surface of all the colored areas examined. These were either needle-like or rod shaped, and ranged from approximately 200 nm to 2 μ m in length. Figure 4 illustrates these features on the surface of a sample from the blue-painted area of the painting. Material of closely similar morphology is also found to varying degrees in the bulk paint film. Elemental aluminum—sometimes associated with magnesium—was found concentrated in the structures on the surface and in similar materials within the layer of yellow, red, and blue paints from the Johns. The aluminum content may be associated with aluminum stearate or hydrated alumina [aluminum hydroxide $\text{Al}(\text{OH})_3$], an extender used in twentieth-century paints (Mayer 1991, 184–87). Although these compounds were not identified with FTIR, it should be noted that aluminum stearate would be present only in very small quantities in a paint formulation, and that the main feature in the spectrum of aluminum hydroxide (the O–H stretching region at 3200–3650 cm^{-1}) is often masked by the O–H stretching of other ingredients.

In general, the pigments used for the upper paint were of one hue, and may reflect Johns's use of a single paint tube for each section of the paint.⁶ Inorganic analysis using energy dispersive X-ray analysis (EDX) and X-ray diffraction (XRD) suggests that cadmium red and yellow paints and purple made from cobalt violet and red lake are extended with barium

sulfate or lithopone, whereas cadmium orange, ultramarine-cobalt blue paint, and viridian contain silica.

Analysis of the paints used by Johns in *Untitled*, 1964–65, showed inclusion of elemental zinc and aluminum in the red, yellow, green, and purple paint. In addition, FTIR showed that several of the paints contain barium sulfate and magnesium carbonate in addition to the elements associated with the pigments identified in the paint (fig. 7A). While the compounds identified by FTIR are not in themselves water absorbing, some zinc-containing materials such as ZnO and hydrated alumina, if present, may influence the moisture sensitivity of the paint.

Samples of blue paint from Johns's *Untitled* and Robyn Denny's *Painting 6* contain a combination of ultramarine and cobalt blue, with titanium dioxide in the unstable ultraviolet (UV)-absorbing anatase form (as established with XRD). This unstable pigment may be linked with deterioration of the binder and its sensitivity to water.⁷

Paints from tubes of Winsor & Newton Cadmium Yellow (dated 1971) and Vermillion (dated 1970) artists' oil paints were selected for comparison to potentially similar paints used by Johns.⁸ The paints were chosen because the base pigments should not contain aluminum. Separation of pigment from medium had occurred in the spills of the vermilion paint on the outside of the tube, and this was thought worthy of investigation, as similar separation was observed in a work by Karel Appel.

Analysis of the cadmium yellow tube paint and the cadmium yellow samples from the Johns showed similar results. EDX analysis showed significant elemental aluminum as well as magnesium in the bulk paint, suggesting that a combination of compounds that contain these elements was added. FTIR analyses confirmed the presence of barium sulfate and magnesium carbonate in drying oil (fig. 7B). In the vermilion paint, no barium sulfate was detected.⁹ Again, the aluminum compounds could not be characterized. Although it is possible that the aluminum compounds are degradation products of aluminum stearate that cannot be precisely characterized using the methods employed in this study, this seems less likely, since Winsor & Newton did not use aluminum stearates in their paints.¹⁰ Ultramarine-containing oil paints, for example, included alumina hydrate rather than stearate to control the consistency of the paint.¹¹

The presence of aluminum hydroxide in the Winsor & Newton paints is possible, but not in substantial amounts, since the typical absorptions in the FTIR spectrum at 3200–3650 and 1120 cm^{-1} do not stand out.¹²

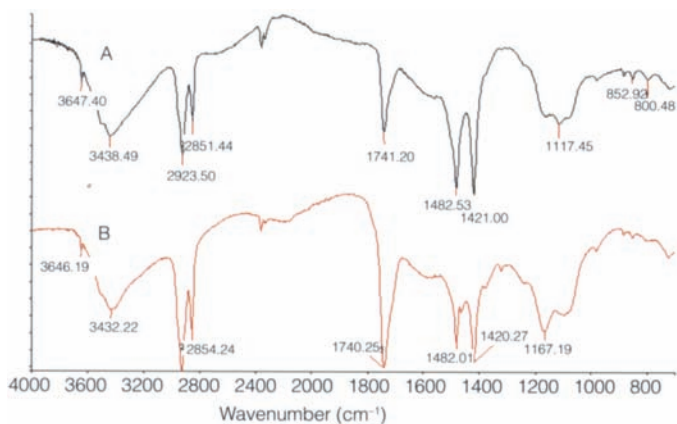


FIGURE 7 FTIR spectra of (A) Jasper Johns's *Untitled* and (B) dried Winsor & Newton Cadmium Yellow Deep paint (ca. 1971). Absorptions at 1740 cm^{-1} indicate oil, 1482 and 1421 cm^{-1} magnesium carbonate, and 1000 – 1200 cm^{-1} barium sulfate. There was no indication of aluminum stearate or hydroxide.

Karel Appel's *L'homme* (1953)

Karel Appel's *L'homme* (fig. 2) was painted in 1953, with paint squeezed directly from the tube. Most of the paints appeared to be water sensitive, yet the degree of sensitivity varied considerably. The ochre/umber containing brown and green paints was relatively insensitive to water, whereas a yellow earth/umber and zinc white-containing paint was considerably more sensitive. The order of increasing sensitivity of paints to water, saliva, and 1% triammonium citrate in water was ochre/umber brown, ochre/umber and Prussian blue-green, chromium oxide green, yellow ochre/umber/zinc white, ultramarine.

The painting contains at least three different blue paints, including French ultramarine, cobalt blue (mixed with bone black), and a dark green containing Prussian blue and umber. The ultramarine blue is the most unstable, and the medium has separated from part of the paint. The paint is extremely sensitive to water; in contact with a moist swab, the structure collapsed readily. FTIR analysis of the clear organic material that had separated from the pigment indicated the presence of zinc stearate and heat-bodied oil. The remaining fraction contained the pigment, the heat-bodied oil medium, and material tentatively identified as zinc oxalate (see table 1) and is hygroscopic.

A yellow/brown paint that exhibited water sensitivity almost as strong as that of the ultramarine paint also contained zinc stearate. The absorption peak in the paint residue at

1122 cm^{-1} (in addition to the one at 3200 – 3650 cm^{-1} , see above) could possibly be associated to hydrated alumina $[\text{Al}(\text{OH})_3]$, which could have been added to control the consistency of the paint. Its presence was also indicated in the ultramarine blue paint from *Grande fleur de la nuit*.

FTIR and DTMS analysis of a sample of a slightly less water-sensitive green paint indicated the presence of chromium oxide in stand oil, and aluminum stearate was positively identified.

The cobalt blue and umber paints showed areas where efflorescent material has aggregated to form crusts on the surface. SEM micrographs of the blue paint showed crystal-like structures in the paint (fig. 8), similar to those found in Johns's paints, and EDX showed the crusts to contain significant elemental aluminum, but its composition could not be identified. The soluble efflorescence at the surface of the brown paint was identified using XRD as a combination of ammonium iron sulfate and ammonium zinc sulfate (note to table 1; Hallebeek 2005). A water-sensitive paint containing ultramarine in oil from *Grande fleur de la nuit* showed similar efflorescence. FTIR analysis indicated the presence of an oxalate.

Robyn Denny's *Painting 6* (1961) and *October 1958*

The paintings by Denny discussed here have recently been investigated (Gayler 2006). They are large in scale and painted on canvas, and they both comprise broad passages of blue

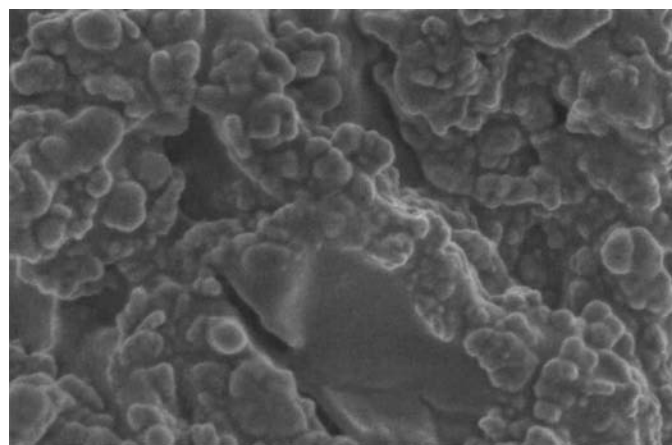


FIGURE 8 SEM image ($70,000\times$ magnification) of aggregated efflorescence on sample of blue paint from Karel Appel's *L'homme*.

paint that exhibited water sensitivity. Pigments identified include cobalt blue and French ultramarine, and both paints contained higher levels of elemental aluminum than would be expected for the pure pigment.

SEM images of the blue paint from these works show crystal-like surface structures of inorganic composition similar to that found in Johns's blue paint. The surface has no skin of medium, but the pigments are well bound in oil and also responded to moist swabs. Magnesium carbonate was identified in the bulk paint film by FTIR, comparable to the results for the Johns paints.

Borlase Smart's *Seascape at Clodgy* (1935)

The blue and yellow paints in the Borlase Smart painting showed sensitivity to water and saliva swabs. Analysis identified chrome yellow (with viridian) and cobalt blue pigments in the paint, along with another aluminum-containing compound that was not positively characterized. Significant amounts of zinc found in inorganic elemental analysis might be associated here with zinc oxalate in the paint film; zinc stearate was not detected. SEM images of the surface of the water-sensitive paints showed a skin of medium with soft flow properties.

Characterization of Water-Soluble Additives to Paint

To characterize water-soluble paint additives that could account for the water sensitivity, water extracts were made from red paint removed by swabs from the Jasper Johns and the green paint (containing Prussian blue and ochre) from Karel Appel's *L'homme*. Tests for the swab extracts were compared to results for water extracts from Winsor & Newton Cadmium Yellow Deep paint (sampled from spills on the outside of the tube). The water extracts were dried and analyzed.

Whereas EDX analysis showed a variety of elements that can, in part, be related to dirt, analysis of the water extracts with DTMS and GC/MS indicated low concentrations of fatty acids and diacids. The diacids, which are more soluble in water than fatty acids, are relatively high in concentration. In contrast, FTIR analysis of the water extracts shows broad absorption peaks at 1600–1620, 1350–1415, and 1120–1140 cm^{-1} , which suggests the presence of inorganic salts. These results indicate the presence of small amounts of water-soluble soaps and salts on the surface of the paints. No contribution of other water-soluble paint additives was detected.

Discussion and Conclusions

This study suggests that water sensitivity in the works studied here is related to phase separation of components in the original paint formulations, as exemplified by the blue paint of Karel Appel's *L'homme*. A more common occurrence is the formation of a skin of medium on the paint surface, as exemplified by the surface of passages of paint from Jasper Johns's *Untitled* triptych. Sensitivity can also occur in less medium-rich paints, where removal of paint is due to sensitivity of the medium rather than mechanical action on underbound paint.

In general, hygroscopic pigments—those poorly wetted by oil—are affected most. These include ultramarine and other blues and chrome and cadmium yellows, but the water sensitivity is certainly not limited to these paints, as demonstrated by the range of colors used by Jasper Johns for the oil painting in this study.

Samples from all the paintings in this study, as well as the Winsor & Newton oil tube paints from 1970–71, show elemental aluminum in high concentration. Although literature from twentieth-century manufacturers of oil paint suggests that aluminum stearates were added as pigment dispersants, positive identification of the compound was realized only in the sample from *L'homme*. However, zinc stearate, which has also been used as a dispersant, was detected in the two most water-sensitive paint samples from the same painting.

The extender hydrated alumina [$\text{Al}(\text{OH})_3$], which could be an alternative source for the presence of elemental aluminum, was detected only in the ultramarine blue paints from the two Appel paintings.

Although detected in only one sample, an excess of aluminum stearate may be consistent with the findings from qualitative EDX analysis. Paint-manufacture literature stresses the danger of adding excess aluminum stearate, which may lead to a nondrying paint and vulnerability to water. Water absorption of the paint may be enhanced by the inclusion of water-absorbing inorganic materials, in particular zinc compounds and perhaps magnesium carbonate (which were also found in several of the paints, including those from works by Robyn Denny and Borlase Smart) or hydrated alumina.

The universal presence of an aluminum-containing compound on the surface of the paint, in the form of crystal-like structures that could not be characterized as hydrated alumina or aluminum stearate, could suggest that the surface material is a degradation product of the stearate. It is postulated that aluminum stearate soaps may hydrolyze on aging to form hydrated alumina and free fatty acids or soluble

fatty acid soaps. Partially hydrolyzed aluminum stearate has surfactantlike functionalities and could potentially form micelles with external hydroxyl polar functional groups that may facilitate water wetting during cleaning. If present in excess, the hydrolyzed additive may, as a consequence of its polarity, demonstrate a water affinity, which could explain the sensitivity of the paint to polar solvents and water. This would occur more readily in paints that contain hygroscopic pigments, or in an alkaline or acid media that might be influenced by the condition of the oil binder or by pigments. These hypotheses require evidence from further technical investigations.

Using FTIR, magnesium carbonate was also found in several samples, and in some cases the magnesium is associated with the surface structures. Although it was not possible to identify the surface structures containing elemental aluminum in the present study, the application of improved X-ray or electron surface diffraction techniques might usefully be applied in future investigations.

Morphological evidence from SEM images of paint samples suggests that the crystal-like structures are present in varying proportions. If these structures are related to degradation products of aluminum stearates, the variation in the amount present may reflect manufacturing specifications for individual paints, and concomitant water sensitivity.

There may be a relationship between the separation of pigment and binder observed in this study, the degradation of metal stearates, and the resulting efflorescence. Efflorescence has been linked with migration of fatty acids or metal soaps from the oil medium to the surface. This may be exacerbated if paint manufacturers add free fatty acids to facilitate wetting of the pigments.

The present study is a first attempt to document the specific water sensitivity of well-bound oil paints used in a small selection of twentieth-century paintings. Other examples of water-sensitive paints reported in the literature include works by Marc Chagall, Brice Marden, and Willem de Kooning. Study of works by these artists and other works made in oil media that exhibit similar sensitivity might clarify the cause more reliably.

Acknowledgments

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Appendix: Experimental Details

SEM/EDX

Analysis was carried out on carbon-coated samples using a JEOL S100 scanning electron microscope (SEM) with an Oxford Instruments light element detector and Inca software. Elemental analysis was executed on uncoated samples using a Hitachi S3400N ESED instrument. Samples from *L'homme* were examined with a JEOL JSM 5910 LV scanning electron microscope and a Noran Vantage energy-dispersive X-ray spectroscopy system with a Pioneer Norvar detector. Images taken of uncoated samples with the Hitachi S3400N ESED and high-resolution topographic images were produced using a Philips XL30 FEG SEM, with a field-emission electron source, low-acceleration voltage, and high vacuum (10^{-9} mBar). Samples were coated with 20 nm of gold palladium (80% Au/20%Pd) palmitate using a Cressington sputter coater 208HR.

XRD

XRD was carried out using a Debye-Scherrer powder camera; $2r = 57.3$ mm, Philips PW 1024. The X-ray generator was a Philips PW 1830. The X-ray film used was double-coated CEA REFLEX 25. Exposure conditions were Kv 40, mA 30, time 300 minutes, copper tube.

FTIR

A PerkinElmer Spectrum 1000 FTIR spectrometer with Autoimage System FTIR microscope was used, and a diamond anvil cell with type IIa diamonds.

GC/MS

GC/MS was carried out on a ThermoQuest GC8000 Top Voyager GCMS combination. GC conditions were ZB5 column (0.25 mm ID., 0.25 mm film thickness), helium carrier gas, flow 0.8–1.0 ml/minute, electron impact ionization (70 eV), and mass range of m/z 45–480. Data were acquired

and processed with Masslab 1.4. Samples were mixed and sonicated with Methprep II (Alltech) and benzene (½ v/v) before injection.

DTMS

Analyses were performed using a JEOL SX102 sector mass spectrometer. Samples suspended in methanol were inserted directly on a Pt/Rh filament probe and a current ramped at 0.5 A/minute for 2 minutes to 800° C. Desorbed molecules were ionized (16 eV) at 200° C and accelerated to 8 keV. The mass spectrometer was scanned from *m/z* 40 to 800, with a cycle time of 1 second. A JEOL MP-7000 data system was used for data acquisition and processing.

Notes

- 1 *Untitled* (1964–65), by Johns, and *L'homme and Grande fleur de la nuit*, by Appel, are from the Stedelijk Museum Amsterdam. The Robyn Denny paintings are from the Gulbenkian Centre for Modern Art in Lisbon, and were examined in a technical study by Courtauld student Stephen Gayler. The painting by Borlase Smart is property of the St. Ives Library, Cornwall, and was examined in a technical study by Courtauld student Nadine Power.
- 2 Private communication with Alun Foster, Winsor & Newton, May 16, 2006.
- 3 The technical grades are partly aluminum hydroxides. Gas chromatography/mass spectrometry analysis of a 1993 aluminum stearate (technical grade, British Drug Houses Ltd., ICN collection) gave a palmitate/stearate (P/S) ratio of 0.4.
- 4 P/S ratios of less than 2 indicate linseed oil in traditional oil paints, but other oils sometimes used in modern oil paints—such as sunflower, dehydrated castor or tung oil—have similar ratios. Moreover, such additives as metal stearates or free fatty acids also influence P/S ratios, making assignment of the oil type very difficult.
- 5 The diagnostic value of these molecular markers for heat-treated oils was suggested by J. J. Boon, FOM Institute for Atomic and Molecular Physics (personal communication, September 2005). We believe that the temperature of formation (slightly lower than the temperature of pyrolysis of the oil network) and the degree of unsaturation of the markers suggest that the molecules are retro-Diels-Alder products of dimerized polyunsaturated fatty acid moieties during heat treatment (Perkins, Taubold, and Hsieh 1973).
- 6 Johns recently stated that he might have used Winsor & Newton oil paint, but couldn't be sure (Wijnberg et al., forthcoming).
- 7 *Painting 1937* by William Nicholson contains a square of yellow pigment mixed with titanium dioxide (anatase) in oil media that exhibits blooming. SEM images have been used to suggest that UV

absorption of anatase has caused the degradation of the binder by disrupting the pigment-binder interface (unpublished research by A. Burnstock). A similar mechanism may have occurred here.

- 8 The paints were from the collection of the Stedelijk Museum Conservation Department and were dated from information on the tube label by Alun Foster, Winsor & Newton (e-mail message to K. J. van der Berg, June 2006).
- 9 Barium sulfate is often added to cadmium pigments by pigment manufacturers to control the strength of batches to a standard, according to Alun Foster, Winsor & Newton (e-mail message to K. J. van der Berg, September 2006).
- 10 Alun Foster, e-mail message to K. J. van der Berg, September 2006.
- 11 Bronwyn Ormsby, Tate, e-mail message to K. J. van der Berg, June 2006.
- 12 Positive identification is complicated by the fact that several forms of hydrated alumina seem to be possible. FTIR spectra show differences in O–H stretching vibrations at 3200–3650, and different absorptions at 1120 cm⁻¹ or 1025 cm⁻¹, the former of which can be masked by BaSO₄.

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Wet Cleaning Acrylic Emulsion Paint Films: An Evaluation of Physical, Chemical, and Optical Changes

Bronwyn A. Ormsby, Thomas J. S. Learner, Gary M. Foster, James R. Druzik, and Michael R. Schilling

Abstract: *An extensive study on the effects of cleaning acrylic emulsion paint films with aqueous systems and organic solvents has been made. In particular, the relationship between changes in the paints' properties and the removal/extraction of surfactant from the surface or bulk of the films has been examined. The methodology involved several analytical and visual techniques to monitor a number of chemical, physical, and optical properties prior to and after surface cleaning treatments, as well as natural and accelerated aging. These included various forms of thermal analysis, Fourier transform infrared spectrometry and microscopy, as well as color and gloss measurements. Results indicate that there is a clear link between changes in physical properties, such as glass transition temperature, with the extraction of surfactant from the bulk film resulting from immersion in aqueous-based systems. However, more realistic simulated treatments, such as swab-rolling with aqueous systems for short periods of time, removed only the surfactant that had collected on the paint's surface and had a negligible effect on the physical properties of the bulk film. Optical changes include a slight increase in gloss with swabbing treatments, occasional pigment removal, and an increase in the surface area of some cleaned films. Interestingly, the use of aliphatic hydrocarbon solvents, such as Stoddard solvent, consistently left the surface surfactant and physical properties unaffected. In general, the changes in properties caused by wet treatments were minimal when compared to those caused by changes in ambient temperature and relative humidity.*

Introduction

Conservators have expressed a number of concerns regarding the conservation of acrylic emulsion paints (Jablonski et

al. 2003; Murray et al. 2001; Ormsby et al. 2006). One of their priorities is to evaluate changes in the properties of acrylic emulsion paints caused by commonly used conservation treatments such as surface cleaning, and in particular, to identify any potential long-term detrimental consequences.

The wet cleaning systems used by conservators for surface cleaning acrylic emulsion paints have been adapted from methods established for oil paintings, and expertise and knowledge has built up through hands-on experience and information exchange. However, it is now known that aqueous-based cleaning risks the removal of surfactant from the surface of emulsion films, and potentially from the bulk film. Surfactants are present in every emulsion paint formulation as emulsifiers, dispersants, and wetting agents. Specifically, polyethylene oxide-based surfactants, such as Triton X-405, have been identified in acrylic emulsion paints (Learner, Chiantore, and Scalarone 2002; Digney-Peer et al. 2004; Smith 2005), and small amounts of other types have also been detected (Smith 2005).

Other concerns include pigment removal and swelling in organic solvents and aqueous systems. In a dry film, the swelling process is driven primarily by the absorption of solvent by hygroscopic materials such as surfactants, which remain trapped within the bulk film as agglomerates, in addition to exuding to the air and substrate interfaces during the drying process. Water also exists as an independent entity within the bulk film, and these water domains can act as channels for water diffusion. The hydrophilic nature of the surfactants suggests that the structures on the film surface may act as potential water diffusion pathways, as can traces of surfactant left in channels created by water evaporation during drying (Agarwal and Farris 1999). The polymer blend composition can also have

an effect on water affinity, with a decrease in water absorption occurring with an increase in the hard phase of the copolymer (the methyl methacrylate [MMA] component).

It is of primary importance to establish whether the loss of these hydrophilic components contributes to any subsequent deterioration of the paint films. Previous studies have focused on the use of particular analytical techniques or paint properties, often using one brand or type of paint. However, the collaborative nature of this research has facilitated a multifaceted approach encompassing several paint brands and analytical techniques and benefiting from the expertise of each participant.

This paper explores changes in several properties of acrylic emulsion paint films treated with wet cleaning systems, with an emphasis on the effects of surfactant removal and extraction. Physical properties include glass transition temperature, flexibility, and film density. Chemical properties focus on the identification of surfactant on the paint surface, and optical properties include color and gloss, as well as surface morphology. The effects of cleaning were also compared to accelerated aging, and free films were compared to equivalents on canvas substrates.

Methodology

Sample Preparation

Paints

Films were cast directly from professional-grade artists' acrylic emulsion paints, both *n*-butyl acrylate/MMA (*n*BA/MMA) and ethyl acrylate/MMA (EA/MMA), as listed in table 1. Four pigments were used: titanium white (PW6) because of its ubiquitous use; azo yellow (PY3) and phthalocyanine green (PG7) as examples of solvent-sensitive organic pigments; and burnt umber (PBr7), which can be difficult to suspend—hence the paints may contain more surfactant. Samples incorporating common artists' modifications (i.e., water dilution [1:1 v/v] and added gloss medium [1:1 v/v]) were also prepared. Each gloss medium was identified as a p(*n*BA/MMA) copolymer; however, the identity of the majority of the additives used in these paints remains proprietary information.

Film Casting

Films were cast onto Teflon-coated stainless steel plates or 10-ounce acrylic primed cotton canvas using a Sheen Instruments adjustable film caster to a dry thickness of $110 \pm 20 \mu\text{m}$. Films were stored in dark ambient conditions, monitored with loggers, and had 4–30 months' drying time prior to testing.

Accelerated Aging

A group of samples were thermally aged in a Fisons 185 HWC environmental oven (60° C; 55% RH) for 16 weeks. Others were light aged at 15,000 lux for 16 weeks under Philips TLD 58W/840 daylight tubes with the UV component filtered by Perspex. Assuming reciprocity, this is equivalent to ~50 years of exposure under normal museum conditions.

Surface Cleaning Treatment Simulation

The majority of samples were tested with deionized water; however, solutions of 0.5% Triton X-100/XL-80N, 2% triammonium citrate, 10% ethanol, neat ethanol, acetone, and Stoddard solvent were also used. Most samples were immersed for between 5 seconds and 24 hours, removed with tweezers, lightly blotted, and transferred onto silicone release paper to dry for at least a week prior to testing. Other samples were swab rolled for 30 or 60 seconds with sterile cotton swabs and left to dry under the same conditions.

Sample Preconditioning

Dynamic mechanical analysis (DMA) revealed that ambient relative humidity (RH) levels affected data repeatability; hence samples were preconditioned to test %RH levels prior to analysis. For differential scanning calorimetry (DSC), cut-to-size free-film samples were placed in a desiccator for 7 days prior to analysis. For humidity-controlled DMA, free-film samples were placed either into a sealed saturated-salt chamber set at ~50% RH using a saturated solution of magnesium nitrate for at least 24 hours, or into glass jars containing silica gel beads, sealed, and left for at least 48 hours prior to testing. After transfer from the humidity chamber or jars to the DMA, samples were equilibrated within the environmental chamber at the test RH for at least 5 minutes.

Instrumentation

Fourier Transform Infrared (FTIR) Microscopy

The pigment, filler, and medium content of the paints were identified with a Nicolet Avatar 360 spectrometer using a diamond cell and Spectra Tech IR plan microscope. One hundred twenty-eight scans were collected at a resolution of 4 cm^{-1} , and the data were processed using Omnic 6.2 software (Nicolet).

Scanning Electron Microscopy/

Energy Dispersive X-ray Analysis (SEM/EDX)

The elemental composition of the pigments and fillers was determined using a Hitachi S3000 SEM/EDX instrument. Samples were attached to SEM stubs with carbon-filled adhe-

Table 1 Characterization of four brands of acrylic emulsion paints and gloss media with FTIR microscopy, EDX analysis, and PyGC/MS.

Brand	Color	Pigment ID (EDX and FTIR)	Filler ID (EDX and FTIR)	Medium ID (FTIR and PyGC/MS)
Liquitex High Viscosity Colors	Titanium White	PW6	None	BA/MMA
	Hansa Yellow	PY3	None	BA/MMA
	Phthalocyanine Green	PG7	None	BA/MMA
	Burnt Umber	Natural umber + bone black?	None	BA/MMA
	Gesso	PW6	Chalk, kaolin	BA/MMA
	Gloss Medium and Varnish	–	–	BA/MMA
Talens Rembrandt Acrylic Colours	Titanium White	PW6, zinc oxide/sulfate		BA/MMA
	Azo Yellow Lemon	PY3		BA/MMA
	Phthalocyanine Green	PG7		BA/MMA
	Burnt Umber	Mars brown?	Chalk	EA/MMA
	Gesso	PW6	Chalk, kaolin	BA/MMA
	Acrylic Medium Glossy	–	–	BA/MMA
Winsor & Newton Finity Acrylic Colours	Titanium White	PW6	None	BA/MMA
	Lemon Yellow	PY3	Kaolin?	BA/MMA
	Phthalocyanine Green	PG7 + PY3?	None	BA/MMA
	Burnt Umber	Natural umber + bone black?	Chalk?	BA/MMA
	Gesso	PW6	Chalk	BA/MMA
	Acrylic Gloss Medium	–	–	BA/MMA
Golden Heavy Body Colors	Titanium White	PW6	Kaolin?	BA/MMA
	Hansa Yellow	PY3, PW6	None	BA/MMA
	Phthalocyanine Green	PG7	None	BA/MMA
	Burnt Umber	Natural umber	Chalk	BA/MMA
	Gesso	PW6	Chalk, kaolin	BA/MMA
	Polymer Medium (Gloss)	–	–	BA/MMA

sive discs and sputter-coated with carbon. EDX conditions of 20 kV and working distance of 15 mm were used.

**Pyrolysis Gas Chromatography/
Mass Spectrometry
(PyGC/MS)**

Paint binders were characterized using a GSG Pyromat Curie point pyrolyzer interfaced to a Varian Saturn 2000 GC/MS.

- Pyrolysis conditions: 625° C for 10 seconds

- GC conditions: Held at 40° C for 2 minutes, ramped to 320° C at 10° C/minute, then held for a further 2 minutes at 320° C
- Injection: 30:1 split
- Column: Phenomenex Zebron ZB-5 column (30 m length; 0.25 mm internal diameter; 0.25 µm film thickness)
- MS conditions: EI mode (70 eV), scanned 40–399 amu every 0.49 second

Fourier Transform Infrared Spectrometry Attenuated Total Reflection (FTIR-ATR)

Two instruments were used: (1) a Nicolet Avatar 360 FTIR and Germanium ATR crystal, wavenumber range of 4000–600 cm^{-1} at 4 cm^{-1} resolution for 200 scans, with Omnic 6.2 (Nicolet) data processing; and (2) a Bruker Vector 22 and Matrix, Golden Gate Diamond ATR, wavenumber range of 4000–600 cm^{-1} , resolution 4 cm^{-1} and 32 scans/minute, with OPUS-NT Optics 3.1 beta (Bruker) and Omnic 6.2 (Nicolet) data processing.

Differential Scanning Calorimetry (DSC)

The DSC method was based on the ASTM E1356 standard (ASTM n.d.) using a Mettler Toledo DSC822e instrument, operated with Star software. Analysis was carried out under nitrogen over a temperature range of -60° – 100° C, at a rate of 10° C/minute. Three layers of paint were used and weighed prior to analysis. Glass transition temperature (T_g) values were taken from the inflection point of the second heating ramp and averaged from three runs.

Dynamic Mechanical Analysis (DMA)

All DMA analysis was carried out using a Polymer Labs MkIII DMTA instrument in tensile mode. Sample free length was 5 mm from samples measuring 10 ± 0.5 mm wide \times 22.5 mm total length. For in situ creep DMA, the instrument was mounted vertically downward, and the clamps immersed. Analysis was carried out under ambient isothermal conditions, with a static load of 0.01 N, clamp torque at 30 cNm, with no averaging.

The RH-controlled system consisted of a polycarbonate chamber sealed with rubber washers, with separate dry and 100% RH supplies regulated and mixed before being put in the chamber. Temperature was maintained with a water jacket and by placing the pipe work and bubbler inside a water bath. A sensor inside the environmental cell controlled RH. Scan heating rate was 1.5° C/minute, thermal scan from 15° to 60° C, and RH set at 50%. Frequency was set at 1 Hz, strain of 2 (~ 32 μm peak to peak), starting load of 0.1 N in reducing force mode, clamp torque at 10 cNm, with no averaging and no clamp retightening at low temperature. Data were collected using PlusV v5.42 (Rheometrics) and plotted using Origin software v7.5 (OriginLab).

Atomic Force Microscopy (AFM)

The AFM instrument was an NT-MDT (Molecular Devices and Tools for Nano Technology), NTEGRA Prima multi-functional scanning probe microscope with a high-resolution

noncontact tapping mode “Golden” Silicon Cantilever (NSG10) series with a typical tip-curvature radius of 10 nm, cantilever resonance frequency of 255 kHz, and spring constant k at 11.5 N/m. Tapping conditions included “free” amplitude A_0 and set point value A_{sp} . Images were recorded simultaneously in topographic and phase modes, with scan sizes from 5 to 50 μm .

Gloss and Color

Gloss values were obtained using a Sheen Instruments Gloss Meter at a 60-degree angle, with five readings per sample. Color was measured using a Minolta CM-2600d Spectrophotometer and CIELab colorspace, with at least three readings per sample, processed using Minolta Spectra Magic 3.6 software.

Results and Discussion

Chemical Properties

FTIR-ATR Analysis

The surfactant in emulsion paints can appear on the surface of films as small round spots or crystals (Digney-Peer et al. 2004; Owen, Ploeger, and Murray 2004) via a number of debated mechanisms—including interfacial tension reduction, diffusion, and capillary forces—and similar structures were observed on many of the free-film samples prepared for this study. FTIR-ATR analysis was used to explore the surface chemistry of these samples and confirmed that a polyethylene oxide-based surfactant (probably Triton X-405) was present on the surface of most paint films. However, surfactant was also present on paints with no obvious spot crystals, that is, where it had formed a coherent film.

Table 2 lists the results of the FTIR-ATR analysis of the air surface of each paint type taken after twelve and thirty months of natural aging in dark, ambient conditions. The p(*n*BA/MMA) copolymer paints tend to have minor or trace amounts of surfactant on the surface compared to major amounts identified on the Talens p(EA/MMA) paints. It was clear that the amount of surface surfactant increases over time, and that the films on canvas followed a similar pattern, with slightly less surfactant due to the porous nature of the canvas.

Surface surfactant was also monitored during treatment with several aqueous systems and Stoddard solvent. Figure 1 shows a detail of several Liquitex titanium white samples on canvas before (lower group) and after (upper group) swab-rolling for one minute. The 1090–1130 cm^{-1} region corresponds to the largest surfactant peak, with the apex typically at ~ 1110 cm^{-1} . The before-cleaning detail confirms that the

Table 2 FTIR-ATR analysis for the presence of polyethylene oxide surfactant on the air surface of several acrylic emulsion free films after twelve and thirty months of natural aging in dark conditions.

Brand	Titanium White		Azo Yellow		Phthalocyanine Green		Burnt Umber		Gesso	
	12 months	30 months	12 months	30 months	12 months	30 months	12 months	30 months	12 months	30 months
Liquitex	Trace	Trace	Trace	Trace	n/a	Major	n/a	Moderate	None	None
Talens	Major	Major	Major	Major	Major	Major	Major	Major	Major	Major
Winsor & Newton	Trace	Minor	Trace	Moderate	Trace	Trace	Trace	Trace	n/a	Moderate
Golden Artist Colors	Trace	Minor	n/a	Major	n/a	None	n/a	None	n/a	Trace

surfactant is present on all controls, and the magnified after-cleaning detail reveals that the surfactant was removed by all aqueous systems and not the Stoddard solvent. This trend was consistent throughout the cleaning tests and confirms that this surface surfactant will be at least partially removed by short aqueous (and probably other polar solvent) treatments, regardless of pigment type or brand. There was no evidence that the addition of surfactant (e.g., Triton) and chelating agents (etc.) to the water had any additional influence on surfactant removal.

Several titanium white and azo yellow paints were also immersed from 1 minute to 24 hours using the same systems. Surface surfactant was fully removed in every case except the Liquitex titanium white sample immersed for 1 minute, where removal appeared to be partial. Extraction of surfactant from

the bulk film occurred for the full range of samples when they were subjected to 24-hour water immersions. The extracts were analyzed using transmission-mode FTIR, and in every case the major component was polyethylene oxide based. Interestingly, after further dark storage, additional surfactant appeared on the surfaces of many of the cleaned samples, indicating that the exudation process is ongoing.

Table 3 FTIR-ATR analysis for monitoring the presence of polyethylene-oxide surfactant on the surface of white and yellow paints immediately after aging and after six months of dark storage.

Paint	Aging Regime	Amount of Surfactant on Air Side	
		After Aging	After 6 Months' Dark Storage
Liquitex Titanium White	12 months natural	Trace	Trace
	Light	None	None
	Thermal	None	Major
Talens Titanium White	12 months natural	Major	Major
	Light	None	None
	Thermal	None	Major
Liquitex Azo Yellow	12 months natural	Trace	Trace
	Light	None	None
	Thermal	None	Major
Talens Azo Yellow	12 months natural	Major	Major
	Light	None	None
	Thermal	None	Moderate

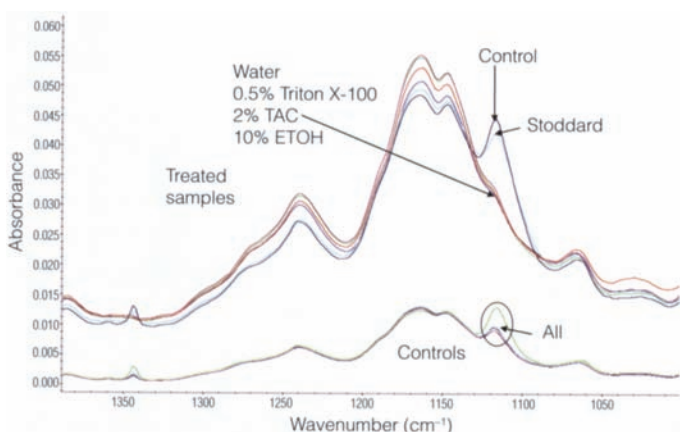


FIGURE 1 FTIR-ATR analysis—monitoring the effect of swabbing treatments on the surface of Liquitex Titanium White films on canvas. The FTIR spectra region at 1090–1130 cm^{-1} characterizes the main surfactant peak.

Accelerated aging of a selected group of samples, shown in table 3, confirmed that light aging also removed surfactant from the exposed surface, possibly through an oxidation mechanism. Thermal aging removed surfactant from *both* surfaces, probably due to the exuded surfactant melting at $\sim 45^\circ\text{C}$ and reentering the paint film. This is consistent with the reappearance of surfactant in large amounts on the surface after further dark storage.

Physical Properties

One of the important concerns about wet cleaning acrylic emulsion paints is whether the cleaning process causes any short- or long-term changes in physical properties (or both), such as decreased flexibility, and whether these changes contribute to long-term deterioration. Both DSC and DMA quantify T_g , with DSC also providing information on melting and crystalline transitions within the sample and DMA offering information on film flexibility and cross-link or polymer chain density.

Differential Scanning Calorimetry

DSC was carried out on Liquitex titanium white free-film samples, comparing the effects of 1-minute swabbing and 1-hour immersion treatments with commonly used aqueous systems and Stoddard solvent. A selection of data (fig. 2), confirms that swabbing treatments caused a slight increase in T_g , ranging

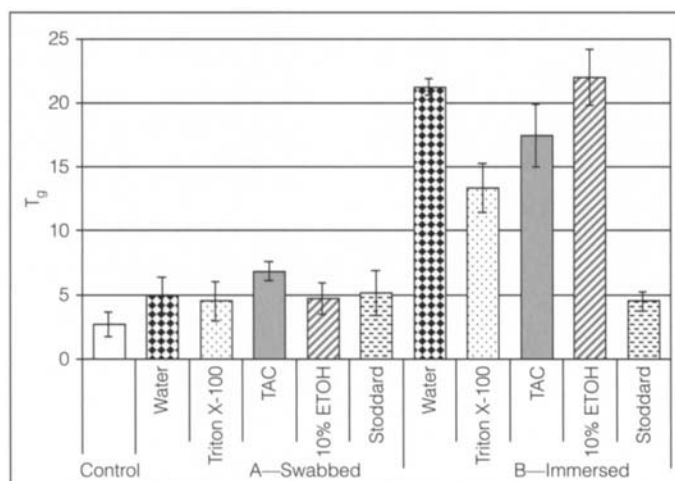


FIGURE 2 DSC analysis—the effect of cleaning treatments on T_g values (degrees Celsius) for Liquitex Titanium White free films: (A) swabbed for 1 minute, (B) immersed for 1 hour. (Systems: water, 10% ETOH, 2% TAC, 0.5% Triton X-100.)

from 2.0° to 3.5°C . This reflects the surfactant removal from the surface film, as assessed by FTIR-ATR, and the paints did not feel any less flexible when manipulated by hand. The larger T_g increase of up to 20°C resulting from the immersion treatments reflects the extraction of surfactant (and possibly other material) from the bulk film, and as expected, the paints were less flexible, although still not enough to crack when sharply folded. The T_g of the Stoddard-treated samples did not significantly change with increased exposure time, suggesting that the extraction of hygroscopic material is primarily responsible for changes to physical properties.

The untreated controls in figure 3 demonstrate the natural variation in T_g for samples cast from one paint. The highest T_g values (~ 10 – 11°C) for the paints that were thermally aged and those with gloss medium helped to contextualize the minimal changes caused by swabbing. The increased T_g of the thermally aged sample may be due to the loss of surfactant; however, it is also possible that aging also induced greater particle coalescence (Snuparek et al. 1983). Similarly, the increased T_g of the gloss medium–modified paint is primarily due to the higher T_g of the gloss medium copolymer.

Figure 3 also shows the results of the 1-hour water immersions for each control. The naturally aged, light-aged, and diluted samples all responded similarly to immersion, suggesting substantial surfactant content. The thermally aged and added-gloss samples showed a reduced response to immersion, confirm-

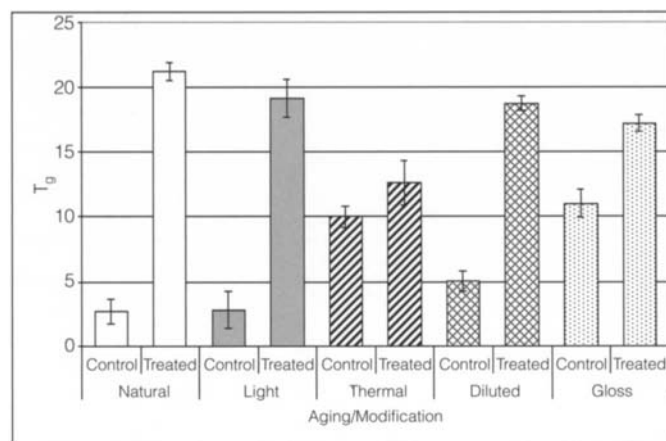


FIGURE 3 DSC analysis—the effect of aging, modification, and 1-hour water immersions (treated) on T_g (Liquitex Titanium White free films).

ing that reduced surfactant content, increased coalescence, and harder copolymer blends all reduce the effect of aqueous or polar solvent treatments.

Dynamic Mechanical Analysis

For immersion or creep DMA, the instrument is inverted (Foster, Ritchie, and Lowe 2003), and the clamped sample immersed into a beaker of water or organic solvent. The displacement percentage data refer to the distance the clamps move apart while maintaining a constant load on the sample during immersion, and represent the relative combined swelling and plasticizing effect of the solvents on these paint films.

Table 4 includes the maximum displacement percentage values for a series of 5-second water immersions of several naturally aged paints, and shows that the majority of the Liquitex paints were displaced to a greater extent than the other brands, with Winsor & Newton paints displacing the least. This suggests that swelling is primarily dependent on brand, rather than pigment, and therefore must relate to differences in paint formulation, such as copolymer composition and quantities of hygroscopic material. The fact that the clamps were displaced by up to 34 percent during a 5-second immersion clearly illustrates that water has a potentially severe swelling effect on these paints, and that contact with aqueous solutions should be kept to a minimum.

Table 4 DMA analysis of the effect of 5-second water immersions on maximum displacement percentage data for several free films.

Brand	Pigment	Maximum % Displacement
Liquitex	Titanium White	34
	Azo Yellow	22
	Burnt Umber	22
	Phthalocyanine Green	14
Talens	Titanium White	16
	Azo Yellow	8
	Phthalocyanine Green	14
Golden Artist Colors	Titanium White	17
	Titanium White	7.5
Winsor & Newton	Titanium White	4
	Burnt Umber	4

Note: Films were naturally aged for four to five months prior to testing. Film thicknesses of 109.7 ± 10.6 μm were used.

Five-second immersions comparing the effect of various solvents are summarized in table 5, and confirm that polar solvents cause the greatest displacement and that Stoddard solvent has a negligible effect. The response varied slightly by brand: Liquitex samples displaced the most with ethanol; Golden samples, with water. It is clear that polar solvents such as acetone and ethanol severely swell acrylic emulsion paints, and they are rarely used by conservators on these paints.

Controlled RH DMA thermal scans were carried out on two titanium white paints: a highly RH-responsive example (Liquitex, BA/MMA, unfilled) and a relatively unresponsive example (Talens, EA/MMA, chalk filler). The samples were swabbed with water for 1 minute and immersed for from 1 minute to 24 hours. Figure 4 includes the tan δ curves for the Liquitex titanium white control and treated samples, which provide information on T_g (temperature at the peak apex) and cross-link density (height at the peak apex).¹ The control and swabbed samples are conjunct, suggesting that swabbing treatment had little effect on the T_g or cross-link density; in other words, the removal of surface surfactant does not cause significant changes in bulk film properties.

The immersed samples all show a decrease in tan δ peak height and an increase in T_g (a peak apex shift to the right), which concurs with the DSC results. A decrease in tan δ peak height traditionally refers to an increase in cross-link

Table 5 DMA analysis of the effect of various 5-second solvent immersions on maximum displacement percentage data for Golden and Liquitex titanium white free films.

Immersion Solvent	Maximum % Displacement after 5 Minutes	Maximum % Displacement after 45 Minutes
Liquitex Titanium White		
Deionized water	32	40
1% Triton X-100	36	23
Ethanol (1)	58	N/A (sample broke)
Ethanol (2)	52	N/A (sample broke)
Acetone	28	25
Stoddard solvent	1	5
Golden Titanium White		
Deionized water	27	18
Ethanol	13	8
Acetone	18	21
Stoddard solvent	1	3

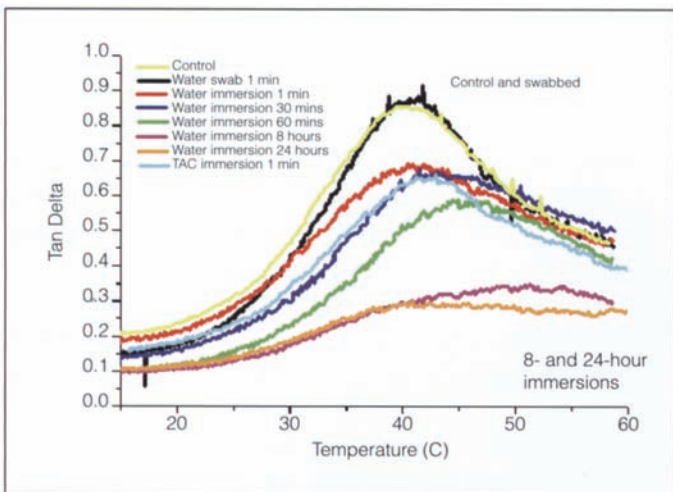


FIGURE 4 Controlled RH DMA—exploring the effect of water treatments on Liquitex Titanium White free films (tan δ data).

density; however, it can also reflect the loss of material from a film, in this case the surfactant, resulting in increased polymer chain density. The corresponding displacement percentage data confirm that swabbing has little effect on flexibility, and that the loss of bulk film surfactant with increasing immersion time resulted in decreased flexibility. The Talens Titanium White paints have lower tan δ peak height values than the Liquitex samples, reflecting the decreased viscous response of these paints, which is primarily caused by the chalk filler.

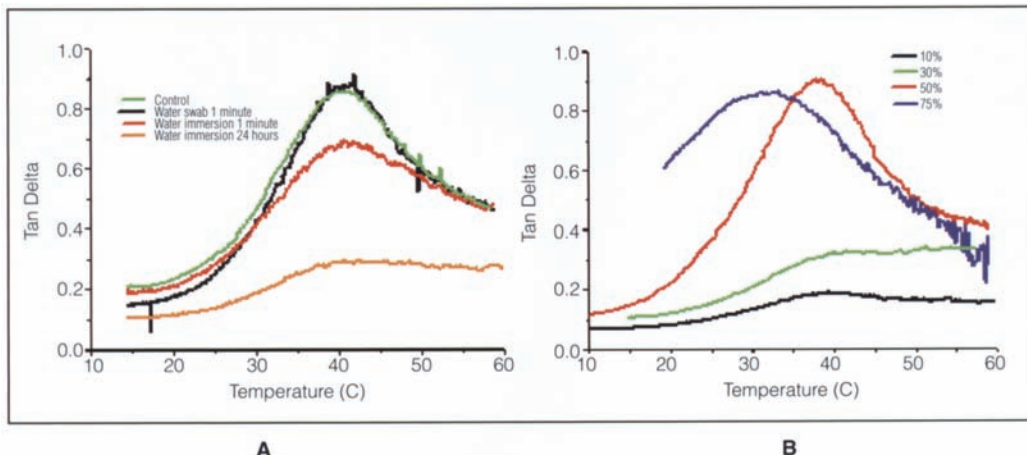
To assess the possible effects of the addition of surfactant or chelating agents to the water, several naturally aged

titanium white samples were immersed in solutions of 10% ETOH, 0.5% Triton X-100, 2% TAC, water, and Stoddard solvent for 1 minute. The representative TAC data included in figure 4 illustrates that the additional agent does not significantly affect the data (i.e., that the extraction effect is primarily due to water).² A selection of aged titanium white samples were also immersed in water for 1 minute and 1 hour. As for the DSC results, the light-aged samples responded similarly to the naturally aged samples, and the thermally aged samples showed a decreased response to treatment. The untreated thermally aged paints also had higher T_g values and decreased tan δ peak heights, suggesting that a significant amount of material (surfactant) was removed by aging or that increased polymer coalescence had occurred, or both.

Acrylic emulsion paints are also highly responsive to changes in relative humidity (Ormsby et al. 2007; Erlebacher, Mecklenburg, and Tumosa 1992). Figure 5 compares the tan δ data for Liquitex Titanium White free films treated with water to the effect of changing relative humidity. It is clear that the data for the 8- and 24-hour water immersions are similar to the 10% RH data: a decrease in RH from 50% to 10% produces changes in physical properties similar to those caused by long water immersions, albeit temporarily.

When combined, the DSC and DMA data suggest that aqueous conservation treatment exposures such as swabbing have little effect on the physical properties of these paints, despite the accompanying removal of surface surfactant. Mechanical testing studies carried out thus far on acrylic paints confirm that acrylic emulsion paint films do not suffer a significant decrease in flexibility when subjected to short aqueous treatments (Hagan and Murray 2005).

FIGURE 5 Controlled RH DMA analysis—comparing the effect of (A) “cleaning” with changes in (B) relative humidity (Liquitex Titanium White free films, tan δ data).



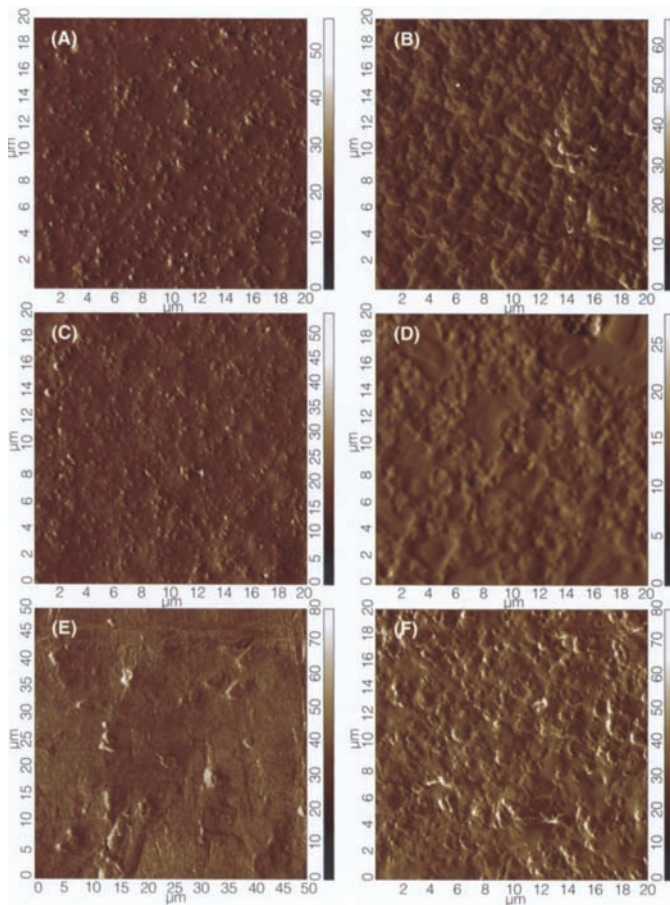


FIGURE 6 AFM phase images of Liquitex and Talens titanium white paint free films: (A) Liquitex control, (B) Liquitex 30-second water swab, (C) Liquitex 1-minute water swab, (D) Liquitex 1-minute water immersion, (E) Talens control, (F) Talens 1-minute water swab.

Optical Properties

Surface Imaging

Thin surface surfactant layers and their removal during cleaning were documented with AFM. Figure 6 shows Liquitex and Talens Titanium White free films before and after cleaning by swab-rolling and/or short immersions in water. The phase mode images (which highlight subtle differences in material properties) show distinct differences in the surface of the two brands. The thick, formless layer evident on the Talens control (fig. 6E) is surface surfactant, and while the surface is slightly smoothed on the Liquitex control (fig. 6A), the surfactant layer is not particularly evident. This concurs with the FTIR-ATR data, where significantly more surfactant was detected on the Talens paints.

The image of the 30-second-swabbed Liquitex sample (fig. 6B) suggests that the surfactant layer has swollen and been affected by mechanical action. In contrast, the 1-minute-swabbed sample (fig. 6C) appears similar to the control, suggesting the surface surfactant has been fully removed by this stage. The 1-minute-immersed sample surface (fig. 6D) suggests that the surfactant layer has been partially removed, confirming that mechanical action plays a role in removal.³ The swabbed (fig. 6F) and immersed (not pictured) Talens samples were similar and confirmed that the surfactant layer was fully removed in both cases.

One possible consequence of the removal of surface surfactant other than changes in gloss (see the following section) is a possible increase in surface area. This was assessed via roughness measurements derived from AFM analysis (listed in table 6). The data suggest some brand dependency; for example, the Liquitex paints had the same roughness after

Table 6 AFM roughness measurements for Liquitex and Talens titanium white free films—controls and water treatments.

Sample	Treatment	Average Roughness (nm)	Standard Deviation (n = 3)
Liquitex	Control	49.3	5.8
	Water swabbed for 30 seconds	152.8	120.2
	Water swabbed for 1 minute	45.0	12.9
	Water immersed for 1 minute	48.9	9.4
Talens	Control	48.3	26.9
	Water swabbed for 1 minute	138.5	59.1
	Water immersed for 1 minute	144.4	26.2

cleaning, but the Talens paints showed a significant increase, presumably due to the presence of chalk filler.

Gloss and Color Change

The range in gloss levels for the four control titanium white paints varied significantly (from 5 to 65 gloss units), and generally decreased with canvas substrates. Accelerated light aging tended to cause a slight decrease in gloss, with a usual further slight decrease with thermal aging. Cleaning experiments revealed that changes in gloss are dependent on pigment, substrate, and brand; however, a general trend was discernable—the higher the inherent gloss, the greater the potential change from cleaning/aging, and vice versa.

The data in Figure 7 illustrate that swabbing treatments on free films caused negligible changes in gloss for each system. However, the aqueous immersions resulted in significant decreases in gloss, and the Stoddard solvent, regardless of the treatment, resulted in minor decreases in gloss. The Talens films were much lower in gloss, and any changes were therefore less pronounced. Equivalent samples on canvas revealed that the aqueous systems caused slight increases in gloss (a maximum of three units) and that Stoddard solvent had a negligible effect. This concurs with previous findings regarding films on glass substrates (Digney-Peer et al. 2004) and free films (Ploeger et al. 2005).

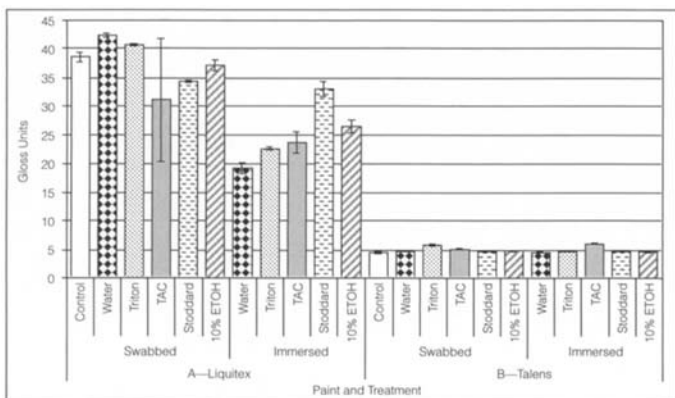


FIGURE 7 Gloss measurement (taken at a 60-degree angle to the paint surface) of (A) Liquitex and (B) Talens Titanium White free films, swabbed for 1 minute and immersed for 1 hour in various aqueous systems and Stoddard solvent.

The color stability of acrylic emulsion paints is high when compared to other artists’ paints (Learner, Chiantore, and Scalrone, 2002). Both titanium white and azo yellow paints were assessed for color change with aging and cleaning, and the substrate did not appear to influence the results (fig. 8). Light aging did not result in significant color change ($\Delta E < 0.4$). However, the thermal-aging regime visibly yellowed some titanium white paints, particularly the Talens samples, with ΔE values of up to +2.4, corresponding primarily to increased Δb^* values. Yet none of the cleaning treatments produced changes detectable to the eye. The highest ΔE , of +0.1, occurred for the samples treated with Stoddard solvent, which was also noted to remove color from the organic-pigmented films more readily than any of the aqueous systems.

Conclusions

A number of analytical and optical tools were employed to assess and evaluate the effects of using wet surface cleaning techniques on acrylic emulsion paint films, to aid conservators in their decision-making and treatment processes. The study focused on assessing the relationship between the polyethylene oxide–based surfactants (e.g., Triton X-405) within and on the surface of these films and any changes to physical, chemical, and optical proper-

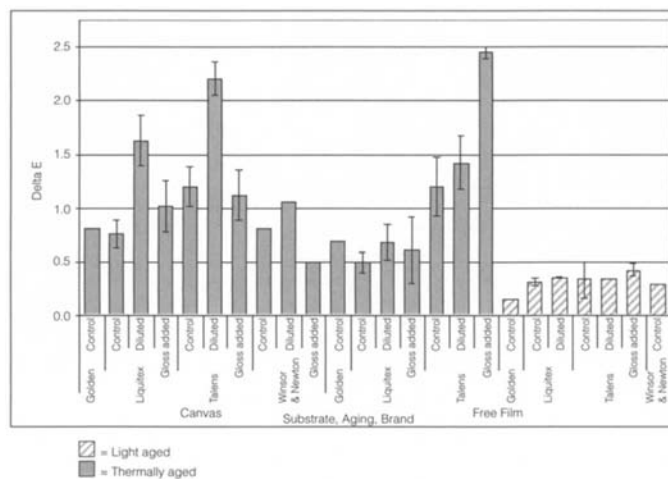


FIGURE 8 $\Delta E^{(94)}$ color-change measurements of four brands of accelerated aged titanium white free films and canvas samples.

ties. Each method provided insight into the response of these paints to surface cleaning and accelerated aging.

After film formation, surfactants migrate to the surface and form crystals and/or coherent layers that can be monitored. On a dry film surface, surfactant appears to attract and retain dirt, contributing to changes in gloss that can be visually distracting. Whereas the surfactant remaining within the bulk film facilitates the absorption of moisture and contributes to the swelling behavior of these paints when exposed to aqueous systems, polar solvents, and water vapor.

It should be expected that all aqueous cleaning methods, including swab-rolling, will at least partially remove the surface surfactant layer, which can result in small increases or decreases in gloss, depending on the original gloss of the paint. Encouragingly, several thermal analytical techniques have shown that acrylic emulsion paint films are exceptionally flexible and that minor changes caused by swabbing for a relatively long period (one minute) and light aging to the equivalent of fifty years in a museum environment do not affect the critical physical properties of these paints. As expected, longer exposures to aqueous/polar systems and thermal aging regimes cause changes in physical properties, such as increases in T_g , and film density, as well as a decrease in flexibility, that need to be further assessed for significance over time and/or with repeated treatment.

It has also been shown that after treatment and/or aging regimes, surfactant remaining within the bulk film will continue to migrate to the surface; hence new surfactant layers may form as part of an ongoing process. This will naturally lead to small changes in physical properties, which have thus far proven to be insignificant to the longevity of these paint films. Indeed, this ongoing process may be somewhat advantageous, as the paint films become slightly harder and less responsive to moisture over the long term, perhaps decreasing the tendency to collect and imbibe dirt and reducing swelling potential during wet cleaning treatments and fluctuations in relative humidity.

As an alternative to aqueous and polar systems, nonpolar aliphatic solvents may be considered, particularly where the removal of original material is of concern, as these systems do not appear to disturb the surface or bulk film surfactant and have minimal effect on physical properties. However, organic pigmented films exhibit an increased tendency for pigment removal when nonpolar solvents are used. The relationship between surfactant content and changes in relevant properties will continue to be explored over the next few years, and cleaning efficacy will be studied in more detail. Equally importantly,

the evaluation of the surface cleaning treatment of several acrylic emulsion paintings, in close collaboration with painting conservators, will be undertaken.

Acknowledgments

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Materials and Suppliers

Acrylic Emulsion Paints

ColArt International Holdings Ltd. (Winsor & Newton, Liquitex),
Whitefriars Avenue, Wealdstone, Harrow, Middlesex HA3 5RH,
UK; www.colart.com

Golden Artist Colors, Inc., 188 Bell Road, New Berlin, NY 13411,
USA; www.goldenpaints.com

Royal Talens B.V., P.O. Box 4, 7300 AA Apeldoorn, The Netherlands;
www.talens.com

Film Caster

Sheen Instruments Ltd., Unit 4 St Georges Industrial Estate,
Richmond Road, Kingston-Upon-Thames, Surrey, KT2 5BQ, UK;
www.sheeninstruments.com

Fredrix 10-Ounce Primed Cotton Duck Canvas

Russell & Chapple, 68 Drury Lane, London, WC2B 5SP, UK;
www.russellandchapple.co.uk

Solvents (Triton X-100, Triammonium Citrate, Ethanol, Stoddard Solvent)

VWR International Ltd., Hunter Boulevard, Magna Park,
Lutterworth, Leicestershire LE17 4XN, UK; uk.vwr.com

Teflon-Coated Stainless Steel Plates

Corus Firststeel Coated Strip Ltd., Brockhurst Crescent, Walsall, West
Midlands WS5 4AX, UK

Notes

- 1 There is often a significant difference between the T_g when measured by DMA and DSC. This is due to several factors: (1) Heating rate/calibration—the DSC uses a small sample and the machine is thermally calibrated, whereas DMA uses a large sample and the air temperature near the sample is measured (i.e., a kinetics problem). (2) Calculation method—with DSC the inflection or midpoint temperature is typically measured, and if the DMA storage modulus onset temperature was used, it would lie closer to DSC values than the $\tan\delta$ peak values. (3) Test frequency—for each decade of increase in frequency, T_g increases by $\sim 6^\circ\text{C}$.
- 2 Some evidence from DSC and DMA analysis suggests that the use of Triton-based surfactants may minimize the extraction of surfactant from the bulk film. This may result from the similar chemistry of the surfactant (Triton X-405) and the Triton X-100 solution—extraction may be slowed by the presence of the Triton in the water if the mechanism is primarily driven by a concentration gradient. This effect requires further exploration.
- 3 This was also confirmed by FTIR-ATR analysis, where surfactant was detected on the sample that had been immersed for 1 minute but not on the swabbed sample. Alternatively, drying effects may have resulted in uneven surfactant redeposition, rather than the partial removal of surfactant during immersion.

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Morphological Changes and Rates of Leaching of Water-Soluble Material from Artists' Acrylic Paint Films during Aqueous Immersions

Rebecca Ploeger, Alison Murray, Simon A. M. Hesp, and Dominique Scalarone

Abstract: *The leaching and identification of water-soluble material from artists' acrylic paint films and the associated paint chemistry has been researched over the past ten years. These studies have helped identify paint ingredients that are problematic with respect to conservation, but no studies have focused on the rate of the leaching processes. In this study, surface tension and conductivity measurements of water in which paint films had been immersed over a period of time showed the rate of leaching of surfactants and ionic species. In addition, thermo-mechanical analysis (TMA) of the paint films during an aqueous immersion period showed the rate of swelling of these films. The results of these experiments revealed that the period of greatest leaching of the components was during the first five minutes. Two experimental Golden Artist Colors (GAC) formulations (Naphthol Red Light and Bone Black), the polymer emulsion used for the experimental formulations (Rhoplex AC-234), and a commercial GAC formulation (Ultramarine Blue) were investigated. All the formulations showed similar leaching rates, but the Rhoplex AC-234 showed only a change in surface tension, indicating that the ionic species' leaching and swelling are almost completely due to the paint manufacturer additives. The surface morphology of the paint films was monitored with atomic force microscopy (AFM), and a change in surface roughness was observed for each film after immersion. The changes in the observed properties occurred almost immediately upon exposure to water, thus conservators should be mindful that distilled water can rapidly remove material from paint films.*

Introduction

Acrylic polymer coatings have been available since the 1930s; however, it has only been in the past fifty years that acrylic

paints have become popular and widely used in industrial, consumer, and artistic applications (Crook and Learner 2000). Acrylics are an important coating material because of their durability, clarity, and overall resistance characteristics.

Artists' acrylic paints are complex chemical systems, consisting of a number of different performance-enhancing additives, such as surfactants, protective colloids, antifoaming agents, thickeners, and stabilizers. This complexity is increased by the variability of paint formulations by manufacturer (in both the acrylic polymer and the acrylic paint), color, and manufacturing date. Studies have shown that noticeable changes to color, gloss, and surface morphology of artists' acrylic paint films occur after aqueous immersion with distilled water (Owen, Ploeger, and Murray 2005; Ormsby 1992), and there is also evidence of some changes in the mechanical properties (Hagan 2004; Hagan and Murray 2005). Owen and colleagues showed that swabbing caused little or no change in color but slight changes in gloss in some samples; however, more significant changes in color and gloss were observed for many of the immersed samples (Owen, Ploeger, and Murray 2005). Hagan and Murray (2005) showed that an increase in strength and stiffness and a decrease in elongation of samples occurred after immersion, but these changes were smaller than those associated with environmental changes (i.e., relative humidity and temperature).

These changes in properties vary significantly between colors and manufacturers. Unfortunately, little has been published about artists' acrylic paints that would allow conservators to care confidently for acrylic artworks. Currently, water, saliva, and detergent or surfactant solutions are recommended with caution as cleaning treatments for acrylic works of art (Murray et al. 2001; Scalarone and Chiantore 2004). However,

temporary swelling of the surface, an increase in tint, and the removal of water-soluble additives at and near the paint surface have all been observed with these treatments (Jablonski, Hayes, and Golden 2001; Jablonski et al. 2003). In contrast, nonpolar, hydrocarbon-based solvents have been observed to cause fewer of these negative effects (Ormsby et al. 2006).

This paper addresses the rates at which certain additives are leached from an artists' acrylic paint film during an aqueous immersion. The surface tension and conductivity of the immersion water were monitored, and thermomechanical analysis (TMA) was used to monitor the rate of swelling of the paint films. These leaching rates are important for conservators as they give some insight into the amount of time an acrylic painting may safely be exposed to a water treatment, and also some indication of what may occur in a disaster situation, like a flood. Atomic force microscopy (AFM) was also used to monitor surface morphology changes due to the removal of material on the film surface.

Experimental Method

The paints and polymer sample were supplied by Golden Artist Colors (GAC). The paint colors investigated were Naphthol Red Light, Bone Black, and Ultramarine Blue. These colors were chosen for this study because they are commonly used by artists and give a range of chemical nature (organic and inorganic pigments). The red and black paints were prepared from formulae published by Rohm and Haas specifically for research purposes (Ploeger 2005), using a pre-1995 formulation of Rohm and Haas Rhoplex AC-234, a copolymer blend of 34% methyl methacrylate (MMA) and 66% ethyl acrylate (EA) (Stringari and Pratt 1993). Pure Rhoplex AC-234 was also investigated. The blue paint was a commercial (GAC) formulation and was later shown with pyrolysis gas chromatography/mass spectrometry (PyGC/MS) to be a copolymer blend of *n*-butyl acrylate (*n*-BA) and MMA. The two experimental acrylic paint films and raw polymer were cast on Mylar sheets and aged naturally at Queen's University, while the ultramarine blue was cast on Mylar and naturally aged at the Smithsonian Institution in Washington, D.C. The Naphthol Red and Bone Black samples were cast on May 1, 2003; the Ultramarine Blue on February 25, 1999; and the Rhoplex AC-234 samples on February 25, 2004. The Mylar was carefully peeled from the acrylic film samples, and in some cases cooling with ice was needed to aid this process.

The sample size used for the capillary rise and conductivity experiments was 15 × 60 mm, with an average thickness

of approximately 0.2 mm. The films used in the post-immersion AFM studies were cut from the capillary rise samples after the experiments. The capillary rise and conductivity experiments were repeated five times and three times for each film for the thermomechanical analysis (TMA) and AFM studies, respectively. Further details concerning the experimental setups and procedures are located in the appendix to this paper.

All the aqueous immersions in distilled water were one hour in duration, and the samples were allowed to dry on a mesh surface for at least 72 hours before post-immersion studies. From a conservation perspective, this length of immersion time appears to be excessive; however, it provides some important insights into the leaching processes and their rates.

Results

Rate of Change

Surface tension and conductivity measurements of the immersion water and TMA analyses of the paint films showed that the rate of change—both leaching and three-dimensional swelling—was greatest in the first 5 minutes of the experiment. After the first 5 minutes, the rate of leaching and swelling began to decrease and approached an equilibrium state. It appears that two main events occurred during the immersion period. First, within 5 to 10 minutes, water penetrated the surface of the film and then rapidly washed away excess surface material, such as surfactant and ionic salt crystals. Second, after 5 to 10 minutes, the penetration of water plasticized the film and released similar materials from within the bulk of the paint film. A similar initial rapid leaching rate was observed by Learner and colleagues for the extraction of organic material in aging experiments of acrylic paints (Learner, Chiantore, and Scalarone 2002). The results of the rate studies are shown in figures 1–4 and summarized in table 1.

In the Rhoplex AC-234 film, the swelling was not as significant, which suggests that it is primarily caused by the thickeners or other additives that are added by the paint manufacturer, and are therefore not present in the base emulsion. There was also no significant increase in the conductivity of the immersion water containing the Rhoplex AC-234 films, which supports studies that have identified nonionic surfactants as some of the major leached additives (Scalarone and Chiantore 2004; Ploeger et al. 2005; Smith 2005). A nonionic surfactant material would have no effect on the conductivity of the immersion water; however, it would cause a decrease in the surface tension. This is also an indication that a significant amount of the ionic materials leached are additives

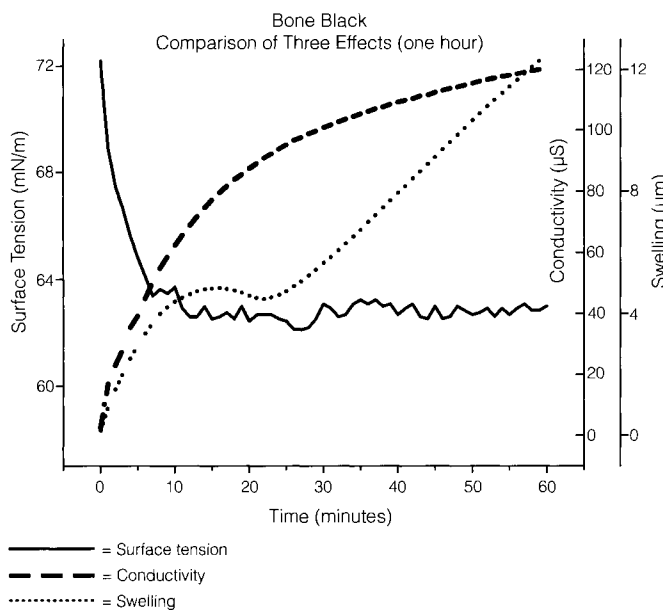


FIGURE 1 Rate of leaching and swelling for Bone Black paint films. Surface tension, conductivity, and swelling rates are compared.

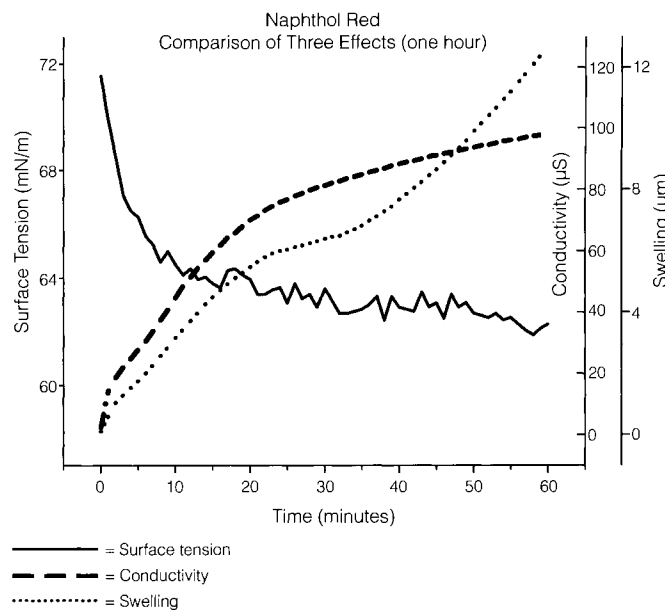


FIGURE 2 Rate of leaching and swelling for Naphthol Red paint films. Surface tension, conductivity, and swelling rates are compared.

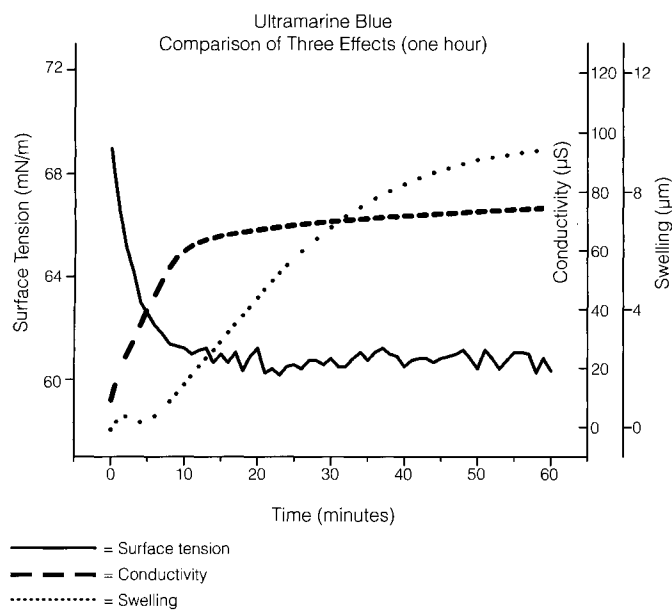


FIGURE 3 Rate of leaching and swelling for Ultramarine Blue paint films. Surface tension, conductivity, and swelling are compared.

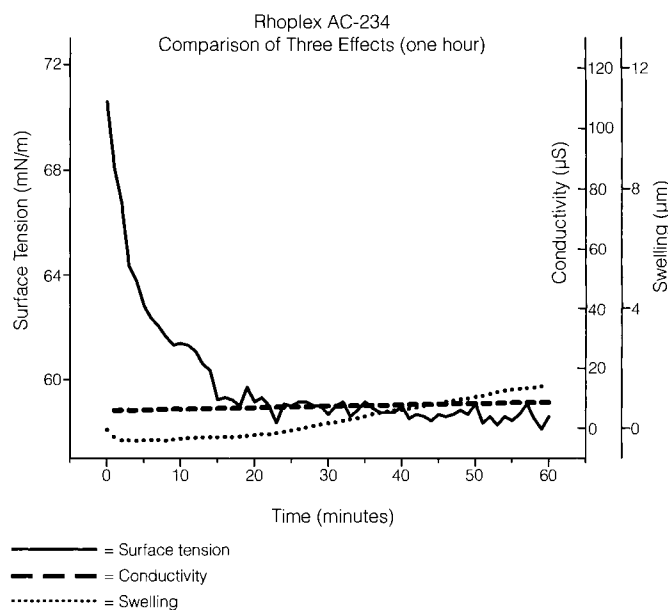


FIGURE 4 Rate of leaching and swelling for Rhoplex AC-234. Surface tension, conductivity, and swelling rates are compared.

Table 1 The rates of change in surface tension, conductivity, and swelling are given for the first five minutes of each experiment.

Film	Surface Tension (mN/m·minute)	Conductivity (μ S/minute)	Swelling (μ m/second)
Naphthol Red	-1.08	4.44	5.40×10^{-3}
Bone Black	-1.36	6.69	9.10×10^{-3}
Rhoplex AC-234	-1.55	0.04	2.00×10^{-4}
Ultramarine Blue	-1.27	5.81	4.90×10^{-3} 3.90×10^{-3}

Note: The ultramarine blue samples' swelling rates are reported for 0–100 seconds and 300–500 seconds, due to a bump in the data between 100 and 300 seconds that distorts the rate data.

added by the paint manufacturer, such as a dispersing agent. For example, in the red and black paints, Tamol 850, a sodium salt of a polyacrylic acid (Rohm and Haas 2006), was added. The second step in the leaching process is slower than the first, because the rearrangement of the bulk of the film and diffusion of water into the film is a much slower process than the initial wash-off at the surface.¹ The water then can interact with the additives within the film and continue the process of swelling and the leaching of additives.

The rates of change for the pigmented films are similar for each experiment. The surface tension and conductivity

changes are similar; however, the swelling rate is lower for the Ultramarine Blue film. This is likely due to the higher hydrophobicity of the p(*n*BA/MMA) polymer used in the ultramarine paint compared to the p(EA/MMA) used for the other two colors, although it could also be caused by differences in chain entanglement and cross-linking, as well as the additives present. The equilibrium swelling of the ultramarine blue is also slightly less than that of the other pigmented films.

It will be noticed that in all the pigmented films, a “bump” occurs in the swelling curve, followed by more swelling. This is an artifact of the experiment, perhaps due to the 2 grams of force that must be applied to the film surface to avoid probe slippage during the experiment. At some point, the weight of the probe takes over briefly as hygroscopic pressure continues to build. There may also be some buoyancy effects, since water will alter the force exerted on the sample.

Morphological Changes

AFM analyses indicated that there was an increase in the roughness for the Naphthol Red and Bone Black paint films after the samples were immersed in water (figs. 5 and 6) and a statistical difference was measured between the two. In contrast, the roughness of the Ultramarine Blue films *decreased* after immersion. The Ultramarine Blue films were made from a commercial paint formulation, which used a different polymer—p(*n*BA/MMA)—and different additives, and this

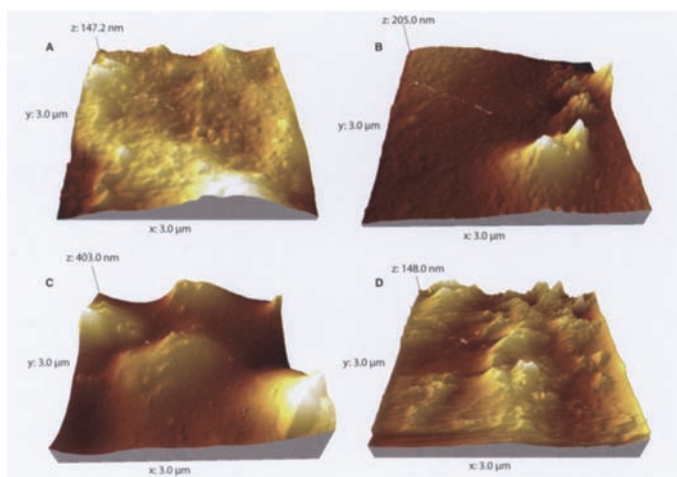


FIGURE 5 AFM images ($3 \mu\text{m} \times 3 \mu\text{m}$) of before-immersion film surfaces: (A) Naphthol Red, (B) Bone Black, (C) Ultramarine Blue, (D) Rhoplex AC-234 film. (Rhoplex AC-234 films were softer, and it was more difficult to obtain good AFM images.)

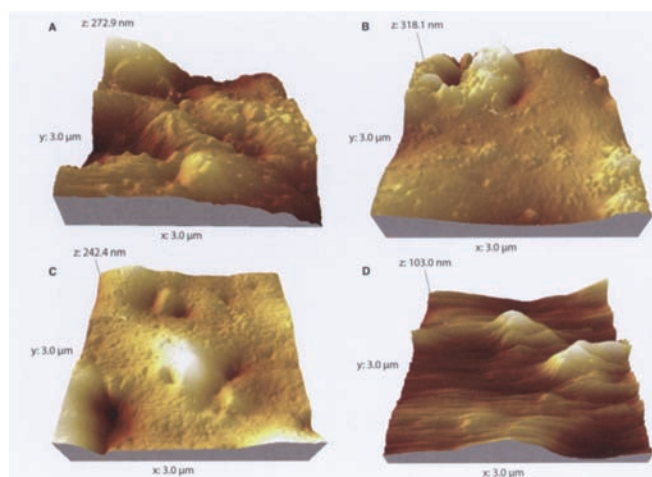
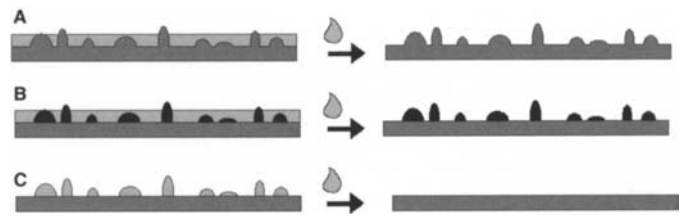


FIGURE 6 AFM images ($3 \mu\text{m} \times 3 \mu\text{m}$) of after-immersion film surfaces: (A) Naphthol Red, (B) Bone Black, (C) Ultramarine Blue, (D) Rhoplex AC-234 film. (Rhoplex AC-234 films were softer, and it was more difficult to obtain good AFM images.)



This work must be combined with other studies to determine adequate conservation treatments for conservators. For these experiments, in which the samples were totally immersed in water, the most rapid leaching occurs at the start of the aqueous exposure period. Even a limited exposure to water immersion may cause some irreversible leaching, and there may be visual changes to the paint film surface, but more work is needed to determine this. The majority of the leached materials are paint manufacturer additives; thus reactive or nonmigratory additives could be investigated in the future by manufacturers to minimize the loss of material. Studies need to be performed using typical conservation treatments to determine if there are similar leaching effects and the rate at which they occur. In addition, other studies are required to investigate the long-term effects of additive leaching on the chemical, mechanical, and visual properties of artists' acrylic paint films.

Acknowledgments

We would like to thank Ana Delgado and Dr. Ralph Paroli at the National Research Council of Canada labs (NRC-CNRC); Professor Oscar Chiantore and his group at the University of Torino, Italy; Mark Golden and James Hayes from Golden Artist Colors; Dr. Marion Mecklenburg at the Smithsonian Institution; and Dr. H. F. Shurvell at Queen's University for all their help and support throughout these studies. We would also like to acknowledge partial financial support from the Natural Sciences and Engineering Research Council of Canada.

Appendix

Capillary Rise Experiments: Rate of Change of Surface Tension of Immersion Water

Surface tension measurements were performed with a glass capillary rise apparatus. Equilibrium was achieved from upper and lower approaches in the capillary tube with distilled water before the start of every experiment. The film samples were completely immersed in 25 mL of distilled water and gently stirred with a magnetic stirrer. The height of water in the capillary tube was measured with a ruler at a precision of 1 mm every minute for one hour, for upper and lower approaches, and the average of the values was used in the calculation for the surface tension values. Five repeats were performed for each type of film. The experiments were all performed at room temperature, $22^{\circ}\text{C} \pm 1^{\circ}\text{C}$.

Conductivity Experiments: Rate of Change of Ionic Strength of Immersion Water

Conductivity experiments were performed with Vernier software conductivity probes, and data was recorded every 30 seconds for one hour with Logger Pro software. The system was calibrated with a 200 μS NaCl calibration standard before each experiment. The conductivity probes are suitable for basic laboratory experiments, and the accuracy was reported to be $\pm 1\%$ of the full-scale reading. The film samples were completely immersed in 25 mL of gently stirred distilled water in a small cylinder, and the conductivity probe was lowered into the distilled water. The experiments were all performed at room temperature, $22^{\circ}\text{C} \pm 1^{\circ}\text{C}$.

Thermomechanical Analysis Experiments: Rate of Sample Swelling

A TMA SSC/5200 Seiko Instrument balance and TMA/SS 120C Seiko Instrument unit were used. All experiments were performed at 25°C in distilled water (with an air gas flow) and under 2 g of pressure to prevent probe slippage. Data were recorded every second for 90 minutes with Seiko Instruments software. The samples (circular in shape with a diameter of 3 mm) were placed in a custom-made glass container and aligned before the addition of distilled water at the start of the experiment. These experiments were performed on the untreated samples.

Atomic Force Microscopy Experiments

AFM experiments for Rhoplex AC-234, Naphthol Red, and Bone Black were performed with a Park Scientific Instruments Autoprobe unit, and the images were recorded with Pro Scan software. Experiments for the Ultramarine Blue were done with a Di Digital Instruments/Veeco Metrology Group MultiMode atomic force microscope, and the images were recorded with NanoScope software. Data analysis was performed using Image Metrology Scanning Probe Image Processor (SPIP) software. Images were recorded in contact mode with a silicon tip and at the $3 \times 3 \mu\text{m}$ size. Larger images were difficult to obtain due to the rough surface morphology and the loss of surface contact with the probe. AFM data were recorded for untreated and water-treated paints (from $5 \times 5 \text{ mm}$ samples). The surface roughness averages were analyzed with the AFM software. A third-order polynomial plane fit was performed before the images were analyzed. Roughness calculations were performed using three images for each sample and taking the average of the three. (It is recommended that these studies be repeated in a tapping mode or another operational mode to avoid drag marks on the surface from the probe.)

Notes

- ¹ According to Michael Bender, Rohm and Haas, in an e-mail message dated January 24, 2006.

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Laser Cleaning of a Study Painting by Ad Reinhardt and the Analysis/Assessment of the Surface after Treatment

Carol Stringari, Christopher W. McGlinchey, Kristalia Melessanaki, Sjoerd Postma, and Corey D'Augustine

Abstract: *A long-term collaborative project that focused on the possibilities for treating a damaged and heavily restored black square from 1960–66 by Ad Reinhardt was completed in 2005. The successes and failures of the methodologies used to treat the surface and characterize the original paint are discussed in this paper. Ethical and philosophical issues are also addressed. After careful studies, the painting was treated at Art Innovation, Oldenzaal, in November 2005. Art Innovation has developed and built an advanced, large-format workstation for controlled laser cleaning of paintings. This mechanized easel consists of an ultraviolet excimer laser (248 nm) and a LIBS detection system for online control of the cleaning process. The surface of the painting was compared to and evaluated against untreated Reinhardt paintings. Interviews and conversations with a range of scholars, artists, and conservators were conducted to record their responses to the cleaning. Characterizing the pigment composition of the original Reinhardt surface that lies below the restoration layers was challenging. A number of analytical techniques, including scanning electron microscopy/energy dispersive X-ray analysis (SEM/EDX), Fourier transform infrared (FTIR) analysis, and polarizing light microscopy were used to try to definitively distinguish one black square from another. This is essential in ascertaining whether the laser cleaning arrived at the surface of the painting or penetrated to a layer below. It is also crucial for evaluating the aesthetic success and value of the treatment.*

Introduction

Ad Reinhardt's *Black Painting* (1960–66) was in a private collection insured by AXA Art Insurance Corporation when it was seriously damaged. After a series of unsuccessful conser-

vation treatments, the painting was declared a total loss and the insurance company paid out the full value of the painting. AXA Art Insurance then generously donated the painting to the study collection of the Guggenheim museum and funded the present research undertaken by members of the Guggenheim and Museum of Modern Art (New York) conservation departments. Previous investigation of the artist's materials and techniques helped to identify extensive past restoration campaigns on the AXA painting and to evaluate alternative approaches for removal of the restorations, such as treatment with lasers (Stringari, Pratt, and McGlinchey 2004, 165–69). Current research further investigates the use of laser ablation techniques and focuses on a modified approach to the removal of restoration layers from the AXA painting via laser ablation. This phase of the project illustrates that it is sometimes difficult to distinguish between original and restoration layers and that it is just as challenging to obtain homogeneous surfaces on monochromatic works with laser techniques as it is with more traditional cleaning methods.

Ad Reinhardt's Black Paintings

Ad Reinhardt (1913–1967) was a New York School painter, theorist, comic, and critic. Reinhardt, who was known equally for his black paintings and black humor, methodically developed an oeuvre that moved from abstract expressionism through overall abstraction to increasingly close-valued, monochromatic work. After 1957, Reinhardt painted exclusively cruciform grids in a palette of chromatic blacks, with minute additions of red, blue, and green, which slightly changed the blacks, allowing the almost imperceptible squares to be distinguished. Described by the artist as “just the last paintings that anyone can make” (Rose 1975), these “black” paintings were

paradoxically almost indistinguishable from one another and never truly black at all. They include several works irreverently titled *Ultimate Painting* and numbered. The paintings defy both interpretation and reproduction, and when Reinhardt sought a logical conclusion to a lineage of reductive art tracing back through Josef Albers, Piet Mondrian, and Kasimir Malevich, he heralded a new generation of perceptual art, including work by artists as diverse as Agnes Martin, James Turrell, and Shirazeh Houshiary.

When in good condition and properly lit, the black paintings operate at the threshold of the viewer's perception by necessitating a prolonged and fixed attention whereby their subtle tonal variation gradually becomes apparent as the grid emerges into focus. For Reinhardt, this emphasis on perception carried moral overtones, since it demanded a personal withdrawal—however fleeting—from the co-mingling of art and commerce he reviled as “Pepsi-Cola philosophy” (Rose 1975, 148). Toward this end, Reinhardt recognized that an extremely matte, close-valued, and richly pigmented surface could intensify the viewer's perceptual involvement, and he designed a systematic technique to exploit this connection. Dissolving his tube oil paints in turpentine, drawing off the solvent and dissolved medium, and repeatedly stirring to ensure an even dispersion of paint, Reinhardt brought color to its greatest intensity by applying the underbound pigment in thin, semiopaque layers.¹ While attempting to eliminate all brushwork and the “hand” of the artist, he, ironically, used a traditional technique to obtain his end.

Unfortunately, the black paintings' extension of the perceptual process comes at the expense of their surfaces' longevity—a problem of which Reinhardt was acutely aware. Because he used extremely lean paint, the surfaces are easily scratched and burnished and readily absorb oils from skin, leaving disfiguring saturated marks. Reinhardt wrote in 1960,

The painting leaves the studio as a purist, abstract, non-objective object of art, returns as a record of everyday (*surrealist, expressionist*) experience (“*chance*” spots, *defacements, hand-markings, accident—“happenings,” scratches*), and is repainted, restored into a new painting painted in the same old way (*negating the negation of art*), again and again, over and over again, until it is just “right” again. (Rose 1975, 83)

While such repainting sometimes meant local retouching done by Reinhardt himself with jars of paint that he stored precisely for this purpose, subsequent conservators' efforts at

retouching have never recaptured the black paintings' rich, homogeneous surface. Because the paint is so underbound, any wet inpainting or cleaning technique can readily cause tide lines, which are especially disfiguring on Reinhardt's uniform surface. And because such marks impair Reinhardt's intended all-over optical effects by drawing attention to discrete areas of the painting, these damages may be considered more severe than similar damages within more relational compositions. In short, damaged Reinhardt paintings are among the most difficult conservation challenges due to their extremely unforgiving surfaces.

The Damaged Painting

In the case of the AXA painting, previous restoration treatments had ultimately resulted in repainting the entire work to conceal the damaged surface. As described elsewhere (Stringari, Pratt, and McGlinchey 2004), scanning electron microscopy/energy dispersive X-ray (SEM/EDX) analysis was used to identify up to eleven restoration layers (measuring approximately 120 microns in total) applied over Reinhardt's original paint structure. While many of these layers appear to be richly pigmented, several layers at the top of the stratigraphy have a very low concentration of pigment. In addition, a thin, unpigmented organic layer (or one with a very low concentration of pigment) was identified at the interface of the original and restoration layers—likely used as a sealant over Reinhardt's porous paint film. Fourier transform infrared (FTIR) analysis characterized all of the restoration layers as synthetic, principally polyvinyl acetate (PVA) in the layers immediately above the original, and an acrylic emulsion similar to Rhoplex AC-34 in the upper layers.

Tests using traditional conservation techniques for removing restoration layers included the use of solvents, poultices, gels, enzymes, and heat, but none were successful in achieving a uniform surface. All of the approaches had some visible effect on the original surface, and of equal importance, none was able to achieve an even cleaning. Due to its potential for uniform cleaning, laser ablation was investigated on mock-ups that simulated the painting. The work was done at the Los Angeles County Museum of Art (LACMA) with an Nd:YAG laser (McGlinchey, et al. 2005). After the appropriate wavelength, fluence, pulse duration, and overlap in both the x and y dimensions were experimentally identified, laser testing provided very promising results. When viewed under stereo magnification, the exposed original surface appeared to be uniform, matte, and indistinguishable from the surfaces of other, untreated works in Reinhardt's black paintings series.

Initial testing on the AXA painting took place at the Institute of Electronic Structure and Laser at the Foundation for Research and Technology-Hellas (FORTH) in Crete, where both ultraviolet excimer (KrF 248 nm, pulse duration 35 ns) and infrared lasers (Nd:YAG 1064 nm, pulse duration 15 ns) were used. At the conclusion of this work, the ultraviolet excimer laser was determined to be the most suitable instrument for use on the AXA painting (McGlinchey et al. 2005). Research demonstrated, as expected, that the ultraviolet laser can provide excellent spatial resolution and is therefore more likely to permit a higher degree of control during cleaning. Specifically, nanosecond excimer laser ablation is advantageous for the removal of thin surface layers, due to its high accuracy (on the order of 0.5–1 μm thickness per pulse), and moreover, any heating effect on the paint layer, expressed in terms of the thermal diffusion length, is estimated to be of the same order of magnitude (Georgiou 2004).

During the investigations with the infrared laser, pigment alterations were observed. This would be a likely consequence of heat generation on the surface and large penetration depth, both of which are characteristics of infrared laser ablation mechanisms. Nevertheless, some tests with the infrared laser quite effectively broke the bond between a transparent acrylic polymer emulsion (in our mock-up samples) and the oil layer below. The unpigmented acrylic layer could be easily removed following cleaning to reveal the layer below. This suggests that further research should be done to study the possibilities for utilizing such laser systems for the removal of acrylic varnishes or intractable, clear acrylic coatings.

Laser Cleaning Methodology

Laser cleaning is based on the phenomenon called ablation, defined as the removal of material with the application of an intense laser source on the surface of the object. This can occur through a variety of photochemical, photothermal, and thermal mechanisms. When the material surface is ablated, a plume is created that contains the removed material in the form of small molecular fragments and both neutral and charged particles. To prevent these materials from becoming deposited on the instrument or the ablated surface, a vacuum or inert gas flush is sometimes used for clearance.

The laser's penetration depth is dependent on the beam intensity, laser wavelength, pulse duration, and the material's ablation threshold, or the fluence required to achieve ablation. Every material will have a unique ablation threshold at a specific wavelength and pulse duration.

The beam's intensity is defined as the peak power divided by the exposed area. Furthermore, a beam's fluence is measured in total energy of a pulse per unit area, with increased ablation occurring at higher fluence. At a specific wavelength and pulse duration, fluence is responsible for the amount of ablation, since it must exceed the ablation threshold of any material to be removed. A summary of these values is as follows:

$$\text{Intensity} = \text{Peak Power} / \text{Area}$$

$$\text{Fluence} = \text{Pulse Energy} / \text{Area} \quad (F = \text{J}/\text{cm}^2)$$

$$\text{Peak Power} = \text{Pulse Energy} / \text{Pulse Duration}$$

The AXA painting was particularly difficult, since the underlying original was pigmented oil, while the restoration layers were pigmented acrylic polymers—quite different chemical compositions, but of similar ablation thresholds and thus exhibiting similar reactions to the laser. Many of the restoration layers (fig. 1) differed quite dramatically in pigment composition and pigment-to-binder ratio (Stringari, Pratt, and McGlinchey 2004). This difference in pigment composition allowed the optimization of laser cleaning procedures.

Ablation of some pigments induces either a temporary or permanent color shift that has been associated with reversible reduction mechanisms, changes in hydration, phase changes, and decomposition of pigments into their constituent elements (Pouli et al. 2001, 2003; Chappé et al. 2003). However, this phenomenon was not anticipated to be problematic for the AXA painting, as none of the pigments known to undergo ablation-induced color shifts were identified on the surface of the Reinhardt. But it must be stressed that this technique may not be suitable for certain pigments on paintings, such as vermilion or lead-containing pigments.

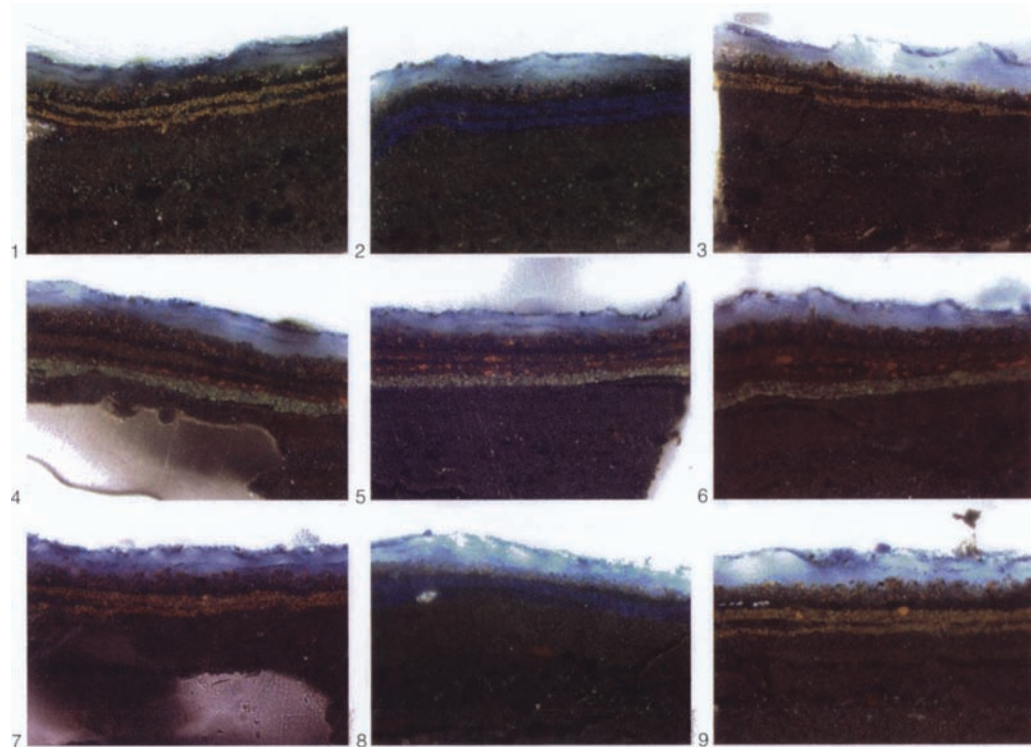
Specifications

Continued research on the use of laser ablation on the AXA painting took place at the laboratories of Art Innovation in Oldenzaal, the Netherlands. The goal of this work was to investigate various approaches to laser treatment while working on a larger area of the painting; this was facilitated by a mechanized easel that moves the laser arm across the surface of the painting in a fully controllable manner. This facility was chosen for its large-format workstation, which employs a KrF ultraviolet excimer laser (Lambda Physik COMpex 205) with the following specifications:

- Wavelength: 248 nm.
- Pulse duration: 25 ns.

FIGURE 1 Cross sections from the AXA Reinhardt painting showing the numerous layers of inpaint (all the colored top layers); 280× magnification, visible illumination, images overexposed to reveal black layers. The layers below are original artist-applied layers.

Photo: James Martin, Orion Analytical, © Solomon R. Guggenheim Museum.



- Pulse energy: 0–650 kJ/pulse.
- Repetition rate: 1–50 Hz.
- The fluence can be varied according to the material to be ablated; in this case, it was 0.8–1.2 J/cm².

The “optical arm” of the mechanized easel scans the laser beam over the surface of the painting horizontally. The arm employs parallel mirrors in a configuration similar to that of a periscope. In this way, the laser spot properties are kept constant over the 1400 × 1900 mm working area. The head of the arm also contains an autofocusing optic system, a digital camera, and a visible laser beam that is used to accurately position the arm (fig. 2).

The laser spot on the surface is Gaussian in shape in the x direction (the scanning direction). It requires an overlap in this direction to achieve an even distribution of energy over the scanned surface. The overlap in the x direction is determined by the beam width (w) and the step size (dx) in the x direction; overlap in x = $[1 - (dx / w)] \cdot 100\%$. An overlap of 80% and one pulse per position implies that each part of the surface is irradiated five times.

In the y direction the laser spot is more of a “top hat” shape; in this direction there is no overlap. At the beginning of the project, the laser beam scanned the object, making a

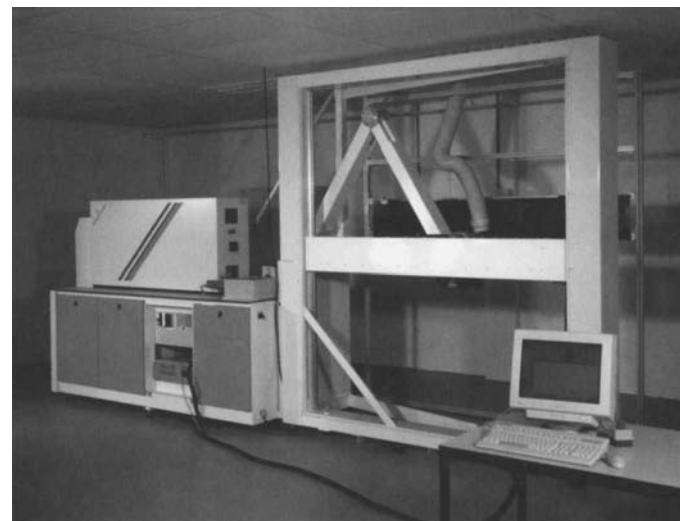


FIGURE 2 Laser cleaning station, with easel and control system, Art Innovation, Oldenzaal, the Netherlands. Photo: Art Innovation.

horizontal motion along a specific y coordinate. Every horizontal line had a certain y coordinate that corresponded to this line. At the next line, the y coordinate was either increased or decreased with the beam height. In this way a whole area can be filled with the same energy. However, the vertical register for the top of the beam in one line and the bottom of the beam in the previous line created a horizontal stripe.

During the project, this horizontal scanning strategy was changed to minimize a striping pattern that was observed during cleaning trials. This change was achieved with a software alteration. A horizontal movement with random y coordinates eliminated the striping effect—at every x position a different, random y coordinate was used. Moreover, at every new line the same random series of y displacements was used. In this way, the vertical alignment of the laser beam can be ensured at every horizontal position. In addition, the vertical alignments in one line are all at different y positions, leaving no visible striping effect (fig. 3). The resulting effect is similar to feathering an edge of a varnish during cleaning or breaking up a line of damage during inpainting.

An online detection system based on laser induced breakdown spectroscopy (LIBS) is intrinsically linked to the laser. This consists of a range of fibers and a spectrograph with a fast intensified charge coupled device camera (Oriel MS260i, Instaspec V ICCD). LIBS spectra are continuously recorded in a preselected spectral region. The ablated plasma plume can be analyzed after every laser pulse (the pulse rate is limited to two pulses per position per second; without the LIBS function the repetition rate can be increased).

LIBS spectra were run on standards prepared at the Guggenheim lab, utilizing the pigments that had been analyzed through FTIR, SEM, and polarized light microscopy (fig. 4). These spectra were used to guide the interpretation of the LIBS results during the cleaning procedure, in order to monitor the extent of cleaning within the painting's layer structure (Anglos, Couris, and Fotakis 1997; Anglos 2001).

Experimental Method

As noted above, initial tests using the laser to remove the restoration layers left a striped appearance due to use of a heterogeneous beam; since the intensity of the laser was heterogeneous over the width of the beam, the depth of ablation was similarly uneven. After the edges of the beam were masked to ensure the painting's exposure to only the homogeneous portion of the beam, this striping effect was eliminated. However, a far subtler artifact was still observable, and it was not con-

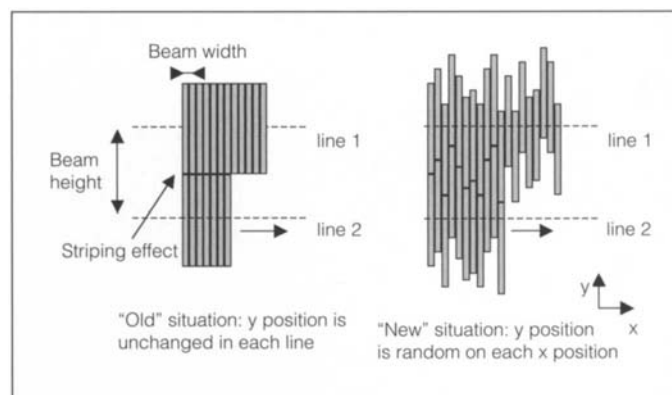


FIGURE 3 Diagram of random pattern laser scanning program for cleaning the Reinhardt with “feathered edges.” Illustration: Sjoerd Postma, Art Innovation, Oldenzaal, the Netherlands.

sidered acceptable for the cleaning of the painting. While the surface within the beam was cleaned evenly, either marginally insufficient or excessive overlap of successive passes of the laser left thin areas that were under- or overcleaned. Yet it was important that the laser beam at no point be allowed to ablate the original surface.²

Horizontal lines at the top and bottom of each pass could be observed due to this subtle imprecision in vertical overlap, where minute areas were ablated either by both or neither of successive passes. Instead of the wide bands caused by the previous strategy, the surface now exhibited thin parallel stripes closely resembling pencil lines, which disfigured Reinhardt's homogeneous surface.

Since these lines comprised a closely packed series of unevenly cleaned points created during each of the laser pulses, the visible effect of the imprecise overlap could be minimized by scattering them evenly over the surface of the painting, where they would simply resemble the evenly dispersed dark spots of the canvas's warp and weft. In other words, although traces of the undercleaned spots of laser ablation would remain, they would be distributed in such a way as to mimic the painting's original appearance. A new computer program to deliver the laser beam was written that simulated this all-over “random” path of the beam. It introduced a Δy value of ± 5 mm for each lateral step, effectively allowing the line 10 mm of deviation in the vertical direction. Within this range, 256 y values were paired with successive x values and were repeated across the canvas;

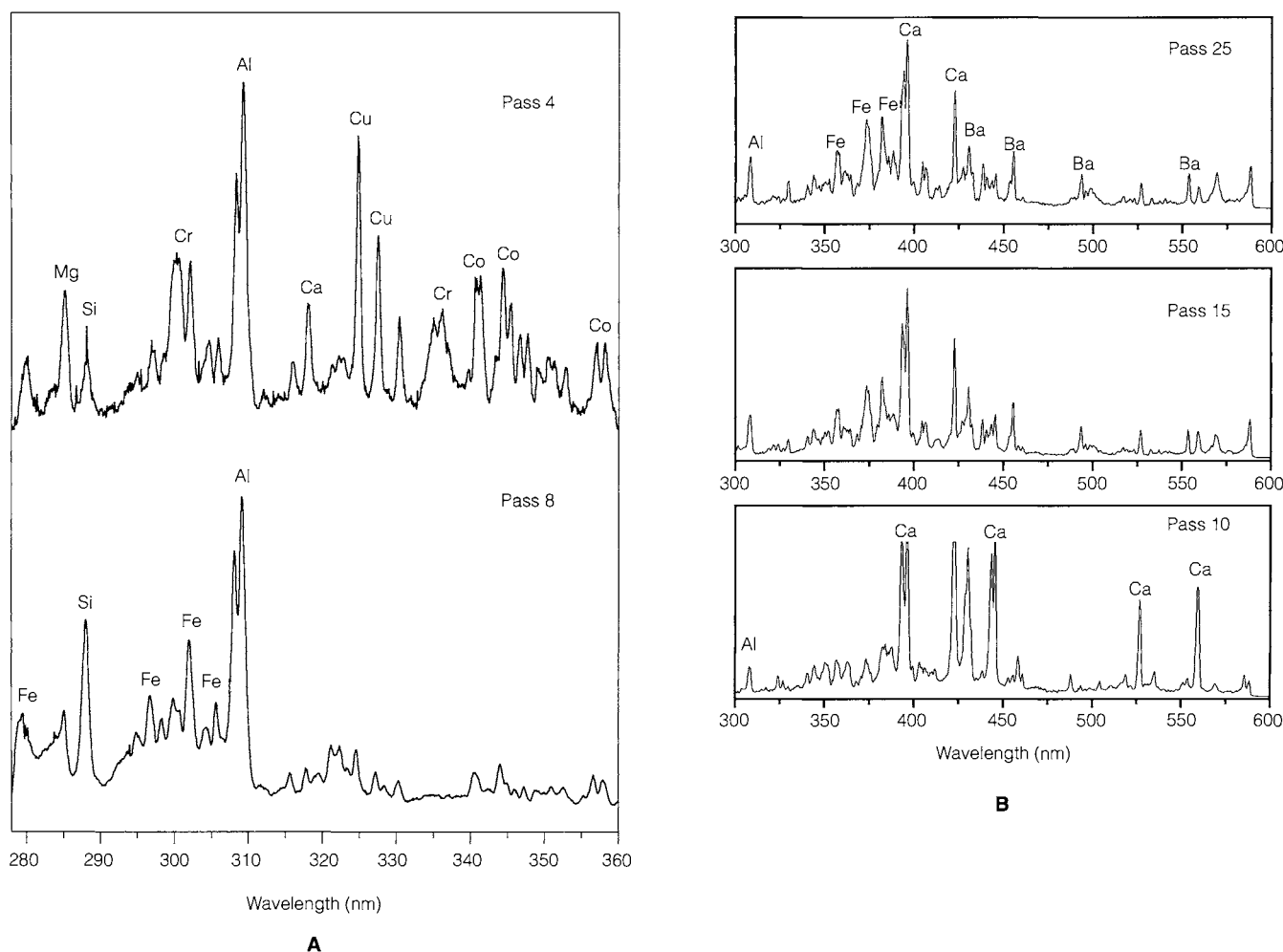


FIGURE 4 LIBS analysis during cleaning of the AXA Reinhardt painting: (A) Square 8, laser pass 4: presence of Co, Cu, and Al. Square 8, laser pass 8: presence of Fe indicates breakthrough into an iron-rich layer. (B) Square 2: increase in Fe as the laser penetrated the first iron-rich layer. Illustration: Kristalia Melessanaki, IESL FORTH.

each horizontal pass of the laser interlocked into those above and below it.

Due to the added movement in the y dimension, the cleaning time required for one square of the painting increased by more than double, to ten and a half hours, but tests of the program were extremely promising: traces of the laser's path were barely discernable to the eye without magnification. The endpoints of each laser pulse appeared as discrete black dots that closely resembled the recesses of a darkly painted canvas.

This new program resolved the most problematic visual effect of the cleaning seen up to that point.

To maximize this scattering effect, the program was subsequently rewritten to employ Δy values of ± 10 mm. Because the total amount of vertical linear deviation equals the beam width (20 mm), the program allowed for "feathering," or even scattering of the laser's endpoints over the treated surface area. In essence, while this technique did not obliterate all traces of the laser beam, use of this randomized program creates a surface that very closely simulates the appearance of an original black Reinhardt surface.

Restoration layers from one of the painting's nine squares were treated with this approach. With each pass of the laser, old damages progressively became apparent. These included a long curving scratch, a large fill over a loss, and small local areas of cracking. This was an encouraging sign that the laser cleaning was not changing the topography of the surface, and

that the laser was indeed very controllable, removing small amounts of material with each pass. It was known, based on earlier reports, that the painting had suffered damages in the past, and that this was most likely the reason for the extensive repainting. However, the damage had not been visible using conventional methods of examination, such as X radiography or infrared examination techniques. These abrasions and rubs might be easily accepted today as a natural result of a painting's life, if the painting were lit to minimize their appearance. It might also be possible to sufficiently disguise such damage by interrupting the forms with minimal inpainting or solvents.

Several unanticipated phenomena were observed during the laser cleaning.

- A temporary shift in surface appearance was noted immediately after ablation, thus indicating a lag in the "stabilization" of the surface of approximately four hours. Upon exposure to the laser, the surface appeared somewhat lightened, although this may simply indicate a transitory period of increased reflectivity. In every case, these lighter areas darkened overnight to match the areas previously cleaned.
- With repeated laser exposure, the physical characteristics of the acrylic polymers changed: they became increasingly brittle.
- Each pass of the laser resulted in less ablation than the previous pass, suggesting a certain self-limiting effect from redeposits on the surface.
- The hardened surface became extremely difficult to wet with polar solvents after exposure to the laser.

Results of Analysis

Scanning electron microscopy was used to characterize the surface morphology of areas subject to laser ablation (fig. 5). Unexpectedly, the resulting surface exhibited a pattern of conical masses extending outward from the surface. The mechanism of their formation is not understood at this time; it is possible that they derive from a self-limiting effect caused by the laser ablation threshold of the pigment versus the binder. Another explanation may be that these cones form as the material cools: the acrylic emulsion polymers heat up very quickly and are thermoplastic. It is possible that the layers beneath the ablated layer heat up quickly, and when they are cooling this surface is created. Analysis performed on samples of this hard material suggest that the cones contain inorganic matter, and elemental

maps exhibit calcium and phosphorous overlaps consistent with the presence of bone black, which was present in the ablated restoration layer. Calcium carbonate was also identified.

There is a theory that the organic-rich component readily vaporizes but either redeposits or leaves behind a certain amount of inorganic compounds. In the first case, the conical shape of the material could develop as the redeposited material fuses with the heated organic binder on the paint surface and locally tapers off until the temperature becomes insufficient to bind the material. In the latter, the shape could relate to material found behind an inorganic compound with a high ablation threshold; this compound would effectively shield underlying materials from exposure to the laser. This phenomenon requires further study, and future testing will be carried out where the ablation site is cleared with a pressurized inert gas to remove any material that could potentially redeposit on the surface. In the present configuration, only a weak vacuum is pulled near the plume, which may provide insufficient clearance to prevent redeposit. Nonetheless, more fundamental investigations must be carried out, and further research on analogous materials should be considered, in order to better understand this curious phenomenon.

Mechanical cleaning was performed after each pass of the laser cleaning, in an attempt to remove the surface deposits with moisture. However, it proved difficult to wet out the remaining part of the repainted surface after the laser treatment, and it appeared that this surface became more brittle and

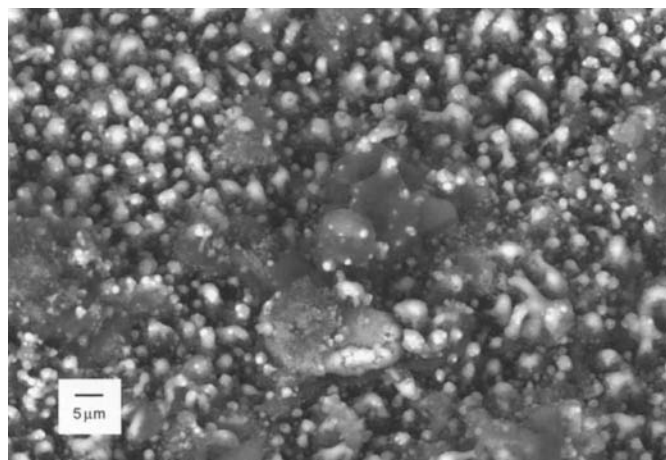


FIGURE 5 SEM image of cone structure on surface after laser cleaning of the overpainted areas.

less porous. This light surface cleaning with moisture resulted in tide lines on the surface, but removal of “redeposits” did enhance the laser activity, which had slowed down considerably as the residues grew thicker. After repeated passes, the laser gradually was able to remove the tide lines. It may be necessary to remove these redeposits regularly as the surface is being cleaned. Tests should also be done with a variety of solvents through tissue and with very soft sponges, to assess whether the wetting and resulting tide lines can be further diminished.

Throughout the treatment, LIBS analysis was used to monitor the elemental composition of the ablated material contained in the plume, and to guide the laser cleaning application. LIBS relies on the analysis of the plasma plume that is created by focusing a pulse of a laser in the material surface. The result of the analysis is an atomic emission spectrum with characteristic peaks that leads to the determination of the elements contained in the material ablated, reflecting the local elemental composition. The fiber system was positioned approximately 3 cm from the painted and ablated surface, at such an angle as to be away from the laser-treated area. A library of spectra was developed by collecting LIBS spectra from a series of relevant pigments in both oil and acrylic binders. This library was used to identify pigments in spectra collected during ablation. When used in conjunction with cross-section samples from each of the nine squares and corresponding EDX spectra, LIBS effectively monitored the depth of the laser’s penetration and corresponding layer removal. LIBS allows us to stop the cleaning at any point and gauge the position of the cleaning within the structure of the painting (fig. 4). This procedure is the main form of controllability with laser cleaning, essentially telling the conservator when to stop. It sets the limits of the original structure and, as a result, the limits of cleaning treatment.

Ethical Considerations

The standard approach for laser cleaning of paintings is to combine its use with traditional cleaning techniques. For example, the laser is used to remove a portion of an intractable polymerized varnish, and then solvents or other cleaning materials may be used to remove the remaining unwanted material. The Reinhardt project was particularly challenging because the original surface is extremely sensitive and cannot tolerate solvent and/or mechanical actions. A decision was made to use the laser to reveal a small area of the original sur-

face in order to compare this to the ablated areas where a thin layer of restoration material was left intact.

Importantly, the results of laser ablation appear visually acceptable; the surface where thin layers of the restoration remain can also be brought to a very matte, nonreflective appearance, closely resembling an original Reinhardt surface. However, the original surface is not affected in any way and remains covered. Although it was not possible to thoroughly remove the restoration layers, this may be an appropriate concession for the moment, allowing for further refinement of the technique and potentially allowing the painting to be exhibited again.

Conclusions

The laser cleaning technique is clearly applicable to certain problems on modern paintings that are too easily harmed by traditional conservation practice. The primary breakthrough of this research was to adjust the software in order to simulate the methodology that a conservator uses when cleaning by hand. The striping pattern observed is not a function of the laser itself but rather reflects our current inability to deliver the laser through traditional software. The random pattern enabled us to achieve a much more even surface. Such homogeneity over the surface—even if the painting is not completely cleaned—is arguably the most important aspect of a successful cleaning of a monochromatic artwork. This ability to achieve an even cleaning is crucial to the conservator’s work. Further research should be done on the engineering and delivery of the laser in order to enhance the overall system.

A major advantage of the ultraviolet laser system for the cleaning of modern paintings is the high spatial resolution that can be achieved for removing unwanted layers. No such resolution can be achieved by any mechanical or chemical means. In recent experiments at FORTH, the use of femtosecond lasers (lasers emitting UV pulses of several 10^{-15} second) has proven effective for cleaning modern paintings, since the spatial resolution is improved and photochemical effects are not observable. The Reinhardt would be an excellent candidate for testing with these extremely controllable lasers.

Time and funding proved to be a factor in the research, and we were forced to stop after cleaning two squares with very promising results. Presently, we are devising a plan to continue refining this technique to achieve the most subtle results. In essence, the methodology used was sound and the research was advanced considerably. We feel that this cleaning

approach has significant potential, but the research must continue in order to achieve the finest results.

Acknowledgments

AXA Art Insurance generously donated the painting and funding for the research; special thanks go to Dietrich von Frank, Christiane Fischer, and Vivian Ebersman. We would like to thank numerous colleagues who have participated in the project: C. Fotakis, V. Zafropoulis, and D. Anglos at the Institute of Electronic Structure and Laser (IESL) of the Foundation for Research and Technology, Hellas (FORTH); the staff at Art Innovation, Oldenzaal; McCrone Inc.; James Martin at Orion Analytical; and colleagues Ellen Pratt, Christa Haiml, Meg Abraham, and Isabel Duvernois.

Notes

- 1 Information on Reinhardt's technique was gathered from his writings (Rose 1975), photographs of him working in his studio, and discussions with the artist's ex-wife, Rita Reinhardt, Lucy Lippard, and various studio assistants and artists working contemporaneously to Reinhardt.
- 2 The standard, responsible approach to laser ablation of unwanted material on painted surfaces is to remove or alter no part of the original; instead, a selective undercleaning is preferred. This was carried out in the laser cleaning of the AXA Art Reinhardt painting at IESL-FORTH and Art Innovation. It is the choice of the conservator to select alternative and appropriate methods for the removal of residues if this is judged to be necessary.

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Penetration of Liquid Water through Waterborne Acrylic Coatings

Paul M. Whitmore, Hannah R. Morris, and Val G. Colaluca

Abstract: *The water sensitivity of waterborne acrylic paint films is well known, and this property is critical to the protective function of the coating as well as to its resistance to staining during application or in subsequent accidents. The paint's pronounced tendency to absorb and transport water also has a significant effect on its response during aqueous surface cleaning. In this study, the penetration of liquid water through films of artists' waterborne acrylic gessoes (Daler-Rowney, Daniel Smith, Golden, Grumbacher, Lascaux, Liquitex, Bob Ross, and Utrecht) and paints (Liquitex Titanium White, Phthalocyanine Green, Burnt Umber, Hansa Yellow, and Cadmium Red) has been measured. The water penetration appears to be a simple diffusion process, with a rate governed by a diffusion coefficient in the range of $1-8 \times 10^{-7}$ cm²/second. The water permeability of these paints is strongly influenced by the amount of water-soluble components incorporated into the dried film. Extraction of those ingredients by prolonged water immersion lowers the diffusion coefficient to about 25–50 percent of its original value. Aqueous surface cleaning (simulated by wet swab-rolling) had a much smaller effect, but calculations indicate the uppermost 50 μ m of a paint film will be saturated with water during the first 10 seconds of a cleaning treatment. It remains to be determined whether the leaching of water-soluble material from this thin surface layer will significantly affect the paint film's behavior.*

Introduction

The penetration of liquid water into and through acrylic coating films plays a major role in their performance, preservation, and conservation treatment. The so-called waterborne acrylic paints, formulated with water-based polymer dispersions rather than solutions of the acrylic polymer media, dry to form

films that are particularly permeable to water, as compared to oil-based paints. Waterborne acrylic dispersion paints are thus poor barriers for protecting water-sensitive substrates such as metals (Pérez et al. 1999).

Aqueous surface cleaning of waterborne acrylic paint films has also come under scrutiny because of concerns about control of the treatment. These acrylic coating films contain substantial quantities of water-soluble ingredients, most of which were included to aid in the polymer synthesis and formulation of the paint (Jablonski et al. 2003). Water penetration in the paint film risks extraction or movement of those ingredients during aqueous cleaning treatments. As with solvent leaching of oil paints during cleaning, the removal of such water-soluble components can affect the appearance, physical properties, and possibly the future aging of the film. The removal of these water-soluble additives from the interface with underlying paint layers also raises the possibility that adhesion might be affected by the surface cleaning. Water migration through the acrylic paint layer could also move stains or soluble additives laterally away from the cleaned area, affecting larger areas of the paint than intended and possibly redepositing material at interfaces or tide lines. Several studies have been examining these side effects of aqueous surface cleaning on waterborne acrylic coatings (Digney-Peer et al. 2004; Jablonski et al. 2003; Murray et al. 2002). Removal of water-soluble ingredients has been observed; less well understood is the location in the acrylic paint film where these ingredients originated.

Finally, transported water can also carry discoloration into or through these coatings. The phenomenon known as "support-induced discoloration," the staining of top coats from the movement of water-soluble discoloration from the substrate,

is an example of such a problem (Hamm et al. 1993). Waterborne colored matter applied to the surface of these paints will also tend to be readily absorbed, and such stains can be very difficult to remove because of their deep penetration into the paint.

All of these processes are controlled by the rate of liquid water penetration into and transport throughout the paint layer. This paper describes a study in which the penetration of liquid water has been measured directly on free films of waterborne acrylic artists' gessos and paints. The rates of penetration for different commercial artists' paint products and the changes in water penetration with film thickness and with age of the coating films were examined. Changes in water penetration with extraction of water-soluble ingredients are described. Finally, the changes that occur as a result of aqueous surface cleaning are explored.

Experimental Method

All samples of artists' acrylic paints and gessos were purchased from 2000 to 2005 and were used without any dilution or other modification. Eight brands of artists' acrylic gesso were included in this study: Daler-Rowney, Daniel Smith, Golden, Grumbacher, Lascaux, Liquitex, Bob Ross, and Utrecht. Two commercial waterborne acrylic sealer-primers—Masterchem Industries' KILZ Premium and Zinsser's Bulls Eye 1-2-3—were also tested for comparison. Five colors of high-viscosity acrylic artists' paints—Liquitex Titanium White, Phthalo Green, Burnt Umber, Hansa Yellow, and Cadmium Red—were tested, in order to explore a range of formulations of these inorganic and organic pigments. Free films of artists' acrylic coatings were made by drawing down the fluid paints on Teflon sheets with a doctor blade. After drying overnight, the coating films were carefully peeled from the substrate and replaced upside down on the Teflon sheet to continue drying at 23° C and 50% relative humidity (RH) until ready for testing. Dry film thicknesses were measured with a micrometer (Ames). Just before water penetration testing, a piece of the coating film was cut off and removed from the Teflon support.

Water penetration measurements were made with a conventional method that uses a Fourier transform infrared (FTIR) spectrometer to detect breakthrough of water through a coating film (Nguyen, Bentz, and Byrd 1995). An accessory made expressly for this purpose was used, a Multi-Reflection Edge Seal Liquid Cell (Harrick Scientific). In this technique, a 1.5 × 5.5 cm piece of coating film was placed on a zinc selenide attenuated total reflectance (ATR) crystal (fig. 1). The ATR crystal bearing the acrylic coating was then assembled into

the accessory, becoming one wall of an enclosed liquid cell, which has an inlet and an outlet for filling. Aluminum foil was used on the back of the ATR crystal to isolate the elastomer O-ring and from the coating. Once assembled, this device was inserted into the sample compartment of an FTIR spectrometer (Thermo-Electron Nicolet Magna 550, controlled with Omnic 5.2a software), in which the infrared (IR) beam travels through the ATR crystal and records the spectrum of the material in contact with the crystal surface.

The test consisted of rapidly filling the water cell, collecting IR spectra repeatedly after the water introduction, and determining the time when the IR spectrum displayed the absorption peak at 3400 cm⁻¹, indicating that water had reached the ATR crystal surface. The FTIR was set up to collect spectra through the ATR crystal in the region of 2500–4000 cm⁻¹, the portion of the infrared spectrum including the water absorption band at 3400 cm⁻¹. Spectra were collected with 4 cm⁻¹ resolution; 32 scans were collected and averaged for each data point. Data collection and software processing allowed data to be recorded every 40–60 seconds. (For the tests of the Masterchem commercial sealer-primer, which had breakthrough times of around 14 hours, the instrument was programmed to collect spectra every 15 minutes.)

A background spectrum was first taken with the water cell assembly in the spectrometer, but without the coating on the ATR crystal and with no water in the cell. The accessory was then removed from the spectrometer, the coating was applied to the ATR crystal, and the device was reassembled and replaced in the spectrometer. The water cell was quickly filled with deionized water by injection with a syringe, and collection of the FTIR spectra was immediately initiated. Typical spectra collected during a water penetration test are shown in figure 2,

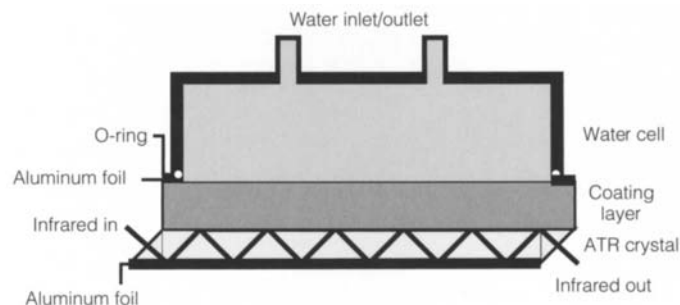


FIGURE 1 Schematic of the test apparatus, with the coating film mounted in the Multi-Reflection Edge Seal Liquid Cell (relative dimensions not to scale).

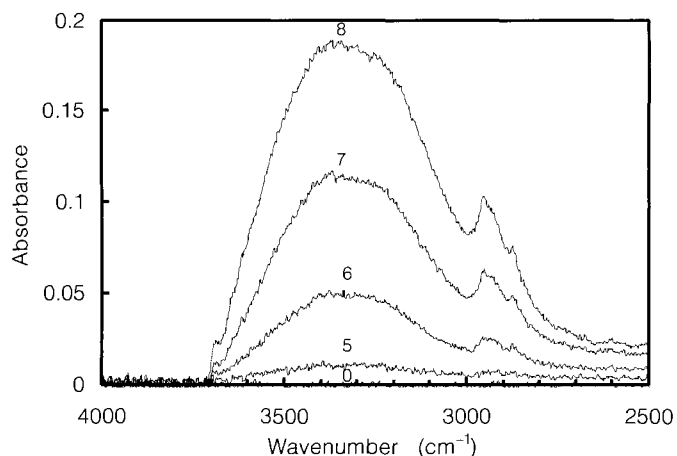


FIGURE 2 Typical infrared spectrum of acrylic coating on ATR crystal, measured at 0, 5, 6, 7, and 8 minutes after water introduction into the cell. Increase in absorbance at 3400 cm^{-1} indicates emergence of water through the bottom of the coating film.

and the increase in absorbance at 3400 cm^{-1} , indicating water penetration to the bottom layer of the coating during the collection period, is illustrated in figure 3. The breakthrough time for the water reaching the lower surface of the film was determined to be the time when the measured absorbance at 3400 cm^{-1} had shown an increase for three consecutive readings.

In order to study the effect of removal of water-soluble ingredients on the film properties, measurements were made on films that had been soaked in deionized water for three days, with changes of the water every day, and subsequently dried to constant weight.

While there is no “standard” protocol by which aqueous cleaning treatments are performed on paintings, the technique known as “swab-rolling” is frequently employed (see Hamm 2004, for example). In that method, a cotton swab dampened in a cleaning fluid (in this case water) is rolled over the surface of a paint film. Depending on the efficiency of the cleaning observed, this treatment may be repeated, sometimes with slight pressure. In this study, a swab wetted with water was rolled over the coating film (a two-year-old Liquitex acrylic gesso, $350\text{ }\mu\text{m}$ thick), the treatment was repeated with a second wet swab, and after the paint film had dried, a water penetration test was run. A second trial was performed on a separate sample, this time with three separate swab-rolling treatments before drying and subsequent water penetration measurement. The total contact time of liquid water on the coating film

surface was judged to be approximately 7 seconds (two swabs) and 10 seconds (three swabs).

Results and Discussion

The measured water breakthrough times for Liquitex acrylic gesso films of various thicknesses are shown in figure 4. The breakthrough times (i.e., when water appeared in the first spectrum measured after filling the water cell) ranged from 1 to 25 minutes, depending on the thickness of the film. The increase in the breakthrough times with greater film thickness suggests a roughly parabolic relationship. This is verified by the linear dependence shown in figure 5, in which the water breakthrough times are plotted against the square of the film thickness. This linear relationship is characteristic of diffusion behavior, in which all the measured films share a single value of the diffusion coefficient (Crank and Park 1968), which is related to the slope of the line by the following equation (Nguyen, Bentz, and Byrd 1995):

$$\text{slope} = 1 / (6 \times \text{diffusion coefficient})$$

The diffusion coefficient describes the rate at which mass is transported across a barrier (here, an acrylic paint film) in order to equalize a concentration gradient on either side of the barrier (in this case, water on one side of the film, no water on

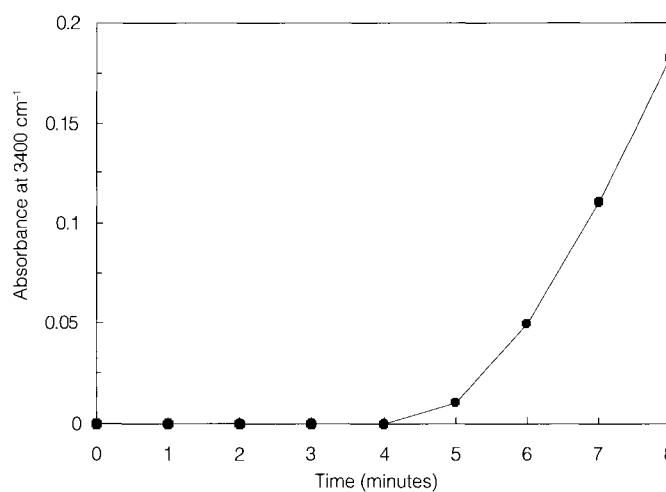


FIGURE 3 Absorbance at 3400 cm^{-1} versus time after water introduction into the cell (values taken from spectra of figure 2).

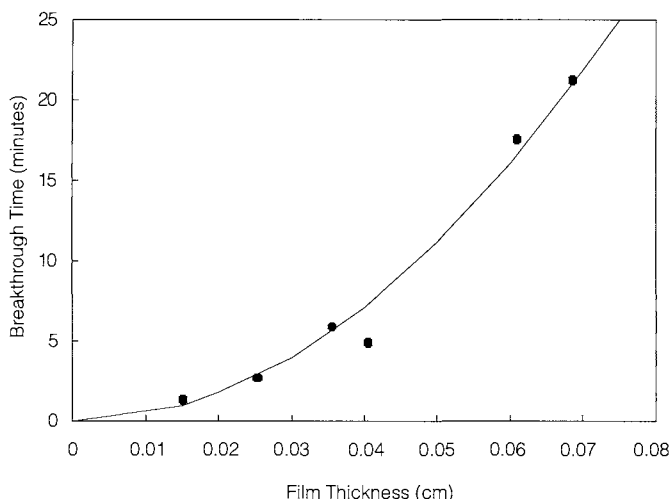


FIGURE 4 Water breakthrough times versus coating film thickness for Liquitex acrylic gesso (10–11 weeks after film preparation).

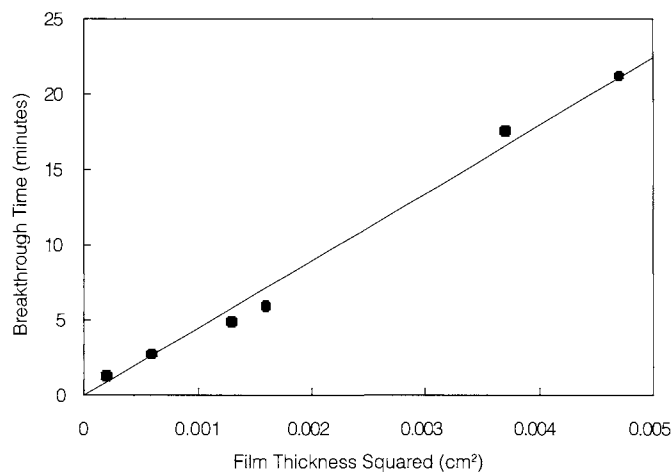


FIGURE 5 Water breakthrough times for Liquitex acrylic gesso films (data from fig. 4) plotted against the square of the film thickness. The slope of the fitted line is related to the diffusion coefficient by the equation slope = $1 / (6 \times \text{diffusion coefficient})$. The R^2 value for the least-squares fit is 0.99.

the other side). Thus, the greater the diffusion coefficient, the more rapidly water is transported through the film. In the case of the Liquitex gesso films shown in figure 5, the results for all the films fall on or near the line ($R^2 = 0.99$), which indicates that all of the films transport water with approximately the same diffusion coefficient. This suggests that film formation in the thin films tested (150 μm) is not so different from that of thicker films.

Because the acrylic coating films were found to be characterized by a single value of the diffusion coefficient regardless of film thickness, measurements of the water breakthrough time for an individual film can be used to calculate the effective diffusion coefficient with the following equation (Nguyen, Bentz, and Byrd 1995):

$$\text{diffusion coefficient} = (\text{film thickness})^2 / (6 \times \text{time})$$

Diffusion coefficients calculated using this second equation for individual films of Liquitex acrylic gesso at different times following casting are shown in figure 6. The high permeability of the very fresh film ($1.59 \times 10^{-6} \text{ cm}^2/\text{second}$ for a two-day-old film) decreases rapidly as the film forms a more continuous barrier during film formation from the acrylic dispersion. The value of the diffusion coefficient measured after about fifty days (about $5 \times 10^{-7} \text{ cm}^2/\text{second}$) seems to remain

roughly constant for the next year. This development time for ultimate water diffusion properties is consistent with previous measurements of the time for developing ultimate physical properties for this type of waterborne acrylic paint vehicle (Whitmore and Colaluca 1995). Diffusion coefficients for dif-

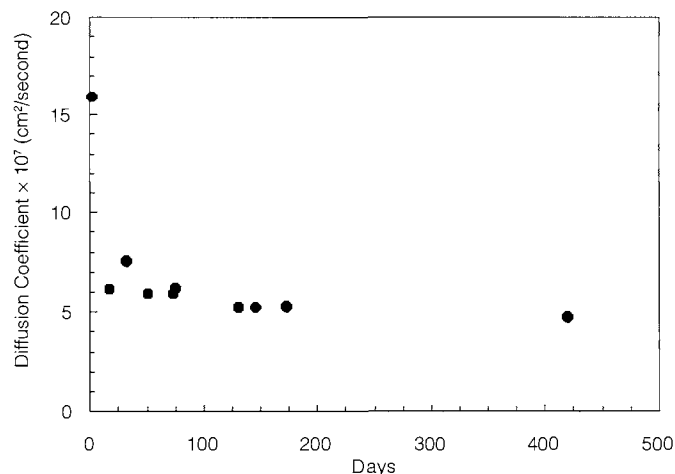


FIGURE 6 Water diffusion coefficients for films of Liquitex acrylic gesso (610–685 μm thickness) measured at various times after film preparation.

ferent products described in the following comparisons were all measured after the films had been cured at least fifty days, so that their ultimate values had presumably been reached.

Water diffusion coefficients measured for different acrylic artists' gessos are listed in table 1. There is a relatively small difference between the measured water diffusion coefficients for the various products, which range from about 1.6×10^{-7} cm²/second for Utrecht gesso to about 6.6×10^{-7} cm²/second for the Liquitex gesso. Diffusion coefficients for water penetrating through several acrylic paints are also shown in table 1. Diffusion coefficients for these acrylic artists' paint films were in the same approximate range as those found for the acrylic gessos. The last entries in table 1 are the diffusion coefficients for the commercial sealer-primers, Zinsser and

Masterchem, which are at least an order of magnitude lower than those measured for the acrylic artists' coatings. These values can be compared to the measured diffusion coefficients (taken from Nguyen, Bentz, and Byrd 1995) for an alkyd paint and an epoxy paint, which are not waterborne and are usually used for protection of water-sensitive substrates. As expected, the measured water diffusion coefficients for these paints are much lower than those of the waterborne acrylic artists' coatings.

These high water diffusion coefficients found for the waterborne acrylic artists' coatings may be related to the water-soluble ingredients, mainly surfactants, which are known to be incorporated in these films cast from polymer dispersions (Whitmore, Colaluca, and Farrell 1996). Workers studying aqueous cleaning of acrylic paints have observed the removal of such water-soluble ingredients during water application (Digney-Peer et al. 2004; Jablonski et al. 2003; Murray et al. 2002). Those studies did not determine whether these ingredients were removed from the surface of the paints or from the interior of the paint layer. If the latter, one might expect that such water extraction would leave the coating film, depleted in these water-soluble components, with a decreased water diffusion coefficient.

The water diffusion coefficients shown in table 2 indicate that, indeed, removal of the water-soluble components with prolonged exposure to water (in this case, immersion for three days) can reduce the permeability of the film. Two acrylic gesso films were tested, one a very fresh application that had dried for only three days and was likely to be incompletely cured. The second film was cured about two years, and represents behavior believed representative of a very well-developed film. As reported above, the three-day-old film displays a water diffusion coefficient of 8.1×10^{-7} cm²/second, slightly higher than the value measured for the two-year-old film, 5.9×10^{-7} cm²/second. Following immersion in deionized water for three days, the water penetration of the coating film was tested again. The results shown in table 2 indicate a significant reduction in the water diffusion coefficient, to 25 percent of the original value for the three-day-old film, and to 50 percent for the two-year-old film. The larger percent reduction of the diffusion coefficient for the very new film is consistent with the earlier observation that the young acrylic coating films have greater ease of extractability due to there being a less tightly knit polymer network at very early curing times (Whitmore and Colaluca 1995). (Indeed, the water diffusion coefficient for the extracted three-day-old film is slightly lower than that for the extracted two-year-old film.)

Table 1 Measured diffusion coefficients for acrylic artists' gessos and paints and commercial sealer-primers and paints. Films were ten to eleven weeks old, 100–150 μ m thick.

Coating	Diffusion Coefficient (10^{-7} cm ² /second)
Acrylic gessos	
Liquitex	6.6
Daniel Smith	5.9
Lascaux	3.5
Grumbacher	3.3
Daler-Rowney	2.2
Bob Ross	2.0
Golden	1.7
Utrecht	1.6
Acrylic paints (Liquitex)	
Titanium White	7.6
Phthalo Green	5.8
Burnt Umber	5.5
Hansa Yellow	3.3
Cadmium Red	3.1
Commercial sealers, primers, and paints	
Zinsser	0.15
Masterchem	0.02
Alkyd paint ^a	0.33
Epoxy paint ^a	0.30

^a Data from Nguyen, Bentz, and Byrd 1995.

Table 2 Change in water diffusion coefficients of Liquitex acrylic gesso films from aqueous extraction and washing. Water extractions were performed by three-day immersion of 3-day-old and 793-day-old films of Liquitex acrylic gesso (230 μm thick). Cleaning tests were done by rolling a moist swab two or three times over a film of Liquitex acrylic gesso (799 days old, 340 μm thick).

Acrylic Gesso Age and Treatment	Diffusion Coefficient ($10^{-7} \text{ cm}^2/\text{second}$)
3 days old, not immersed	8.1
3 days old, water extracted	2.3
793 days old, not immersed	5.9
793 days old, water extracted	3.3
799 days old, unwashed	5.9
799 days old, swab-rolled twice	5.0
799 days old, swab-rolled three times	5.3

This finding suggests that the content of these water-soluble components in the film have a great influence on its water permeability. Consequently, a measurement was made to detect any change in the water diffusion coefficient as a result of very brief water contact during aqueous surface cleaning of two-year-old films, using brief swab-rolling as a simulation of a common cleaning practice. The results of this aqueous surface cleaning simulation are shown in table 2. As observed previously, extraction by prolonged water immersion reduced the diffusion coefficient by roughly 50 percent. The swab treatments, on the other hand, had very little effect, perhaps a 10–15 percent reduction of the diffusion coefficient. This result suggests that for acrylic coating films the brief contact with water during surface cleaning is unlikely to severely alter the water permeability of the paint.

There is reason to be cautious in interpreting this last finding in this way, however. As was shown in the data of figure 4, it takes approximately five minutes for water to completely penetrate a 350 μm gesso layer. For contact times of only seven to ten seconds, then, it is unlikely that the coating strata deep beneath the surface would have experienced water contact at all, and thus transport of water-soluble material out of those layers would not have occurred. But the data of figure 4 suggest that briefer contact times might have affected a layer just below the surface, perhaps substantially extracting material from it

and altering its water permeability. If that thin layer had been affected, testing of a thinner film might have produced a more significant change in the diffusion coefficient.

Unfortunately, such a test of a very thin film is not possible with the current measuring technique, which is limited to measuring water breakthrough times longer than about one minute (the time for the instrument to collect the first data point). Instead of probing the effect of water on very thin films experimentally, however, one can use the measured diffusion coefficient for an acrylic paint (roughly $5 \times 10^{-7} \text{ cm}^2/\text{second}$ according to the results reported in table 1) to calculate the extent of penetration of water into the coating film at very short times using the equation described above: $\text{diffusion coefficient} = (\text{film thickness})^2 / (6 \times \text{time})$. The result of that calculation is shown in figure 7. According to this diffusion model, based on the measured behavior of artists' acrylic coatings, about ten seconds after applying water to the surface, the water has reached 50 μm deep into the film. A film thickness of 5–50 μm is typical for a very thin paint application, which just hides the underlying paint (Johnston-Feller 1986). Thus, for the thinnest of paint films, aqueous cleaning is likely to affect the entire thickness of the coating layer. It remains unknown whether water penetration itself is sufficient to allow significant extraction of water-soluble components from the film in such a brief period of wetness.

This examination of aqueous cleaning of acrylic paints suggests that water penetrates exclusively in a downward

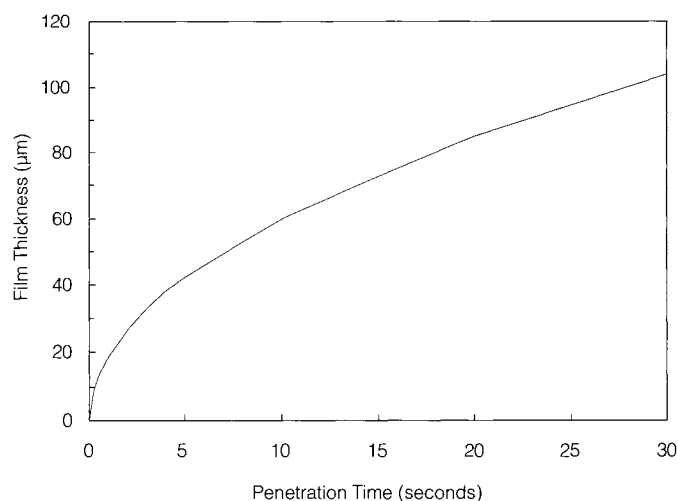


FIGURE 7 Calculated water penetration time for an artists' acrylic coating film having a diffusion coefficient of $5 \times 10^{-7} \text{ cm}^2/\text{second}$.

direction through the paint layer structure. This perspective derives mainly from the method by which the measurements have been made, which detects the emergence of water on the bottom side of the coating film. However, water diffusion is a three-dimensional process, and once the water has entered the film, it travels laterally away from the wetted area as well as down into the depth of the film. Nonetheless, the results of this study indicate that the lateral movement of water in the acrylic paint is very small for brief water contact times, which are representative of typical surface cleaning regimens. Local cleaning would cause water to travel about 50 μm beyond the edge of the wetted area (absent any capillary action through paint cracks or a canvas support). Such lateral movement would probably be so small as to be imperceptible.

Conclusions

The findings of this study allow a more quantitative description of the well-known water sensitivity of artists' waterborne acrylic paints. The penetration of water into the coatings appears to be governed by simple diffusion behavior, despite the obvious tendency of the films to absorb water and swell. The diffusion coefficient that describes the rate of water transport is in the range of $1\text{--}8 \times 10^{-7} \text{ cm}^2/\text{second}$, at least ten times greater than the values for waterborne commercial sealer-primers and for alkyd and epoxy paints that are formulated to be effective water barrier coatings. For these highly permeable artists' acrylic paints, water applied to the surface of the film can completely penetrate thin paint films (10–50 μm) within a few seconds and thicker films (100–200 μm) within a minute. Transport of discoloration from the support (support-induced discoloration) is easily rationalized (since drying paint films can hold water for several hours), and staining from external sources is likely to penetrate to significant depths in the paint layer.

The water permeability of the waterborne acrylic paint films appears to be strongly influenced by the content of water-soluble components retained in the dried film. It is likely that some of the residues observed to be removed during aqueous surface cleaning of acrylic paints have come from this thin layer beneath the surface. Removal of those components reduces the water sensitivity of the paint, lowering the diffusion coefficient to about 25–50 percent of its original value, but even extensive extraction of those ingredients does not leave the film impermeable to water. Aqueous surface cleaning is likely to leach some of those components from the uppermost 50 μm of a paint film. Whether the very slight reduction in water sensitivity and flexibility has a significant impact on

performance or aging of the paint film must be addressed in future research.

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PART SIX

Behavior and Properties

Factors Affecting the Mechanical Properties of Modern Paints

Eric Hagan, Maria Charalambides, Thomas J. S. Learner, Alison Murray, and Christina Young

Abstract: *It is well known that modern artists use many types of paint in their work, and they frequently experiment with products outside of those sold by art supply retailers. As a result, museums acquire paintings that are highly variable in composition. It is useful to understand trends in the mechanical properties of both artist-grade and household paints to properly care for objects containing such materials.*

For this study, a selection of white paints commonly used in the United Kingdom was prepared for chemical and mechanical analysis. The aim was to identify their compositions and relate this information to their respective mechanical properties. Several materials were included in the analysis: an artists' emulsion, household (matte, eggshell, silk) emulsions, an artists' alkyd, household alkyds, a traditional oil, and a water-mixable oil. Pigment and filler ingredients were identified by Fourier transform infrared (FTIR) spectroscopy, and in some cases inorganic components were verified by energy dispersive X-ray analysis (EDX). Binder resins were identified for the solvent and waterborne paints using pyrolysis gas chromatography/mass spectrometry (PyGC/MS).

Mechanical properties were determined through measurements of stress-strain curves under controlled environmental conditions. Results showed a wide range of properties due to different levels of pigment and filler in the paint systems. This was especially true for the household emulsions, which are manufactured with many different pigment volume concentrations (PVC) to modify optical properties. Tensile tests were also performed on specific materials to illustrate the plasticizing effect of water. These data were complemented by measurements of hygral expansion strains caused by attraction of water to hydrophilic formulation ingredients.

Introduction

The types of binder, pigment, and additives and their relative amounts determine the structural behavior of a paint film and its response to surrounding conditions. These conditions may involve stress that is externally applied, or stress induced by environmental changes. Mechanical analysis has previously been applied to painting materials to understand the effects of age (Mecklenburg, Tumosa, and Erhardt 2005), environmental conditions (Erlebacher et al. 1992; Hagan and Murray 2005), transportation (Mecklenburg and Tumosa 1991), and conservation treatments (Tumosa et al. 1999; Young and Ackroyd 2001). An understanding of the mechanical behavior of materials is essential for minimizing the risk of immediate or long-term damage to collections.

It is expected that structural properties vary greatly within the range of decorative household paints as a result of the variability in filler content. A comparison of these products with their artist-grade counterparts will provide useful information about the materials present in modern paintings. In this paper, the primary focus is given to emulsion paints, with a secondary focus on alkyd and oil-based products. Restricted use of solvents has created a market for water-mixable oil (WMO) paints, and these were also included in the study. A brief review of the factors influencing the properties of paint films is presented next, as background for the experimental data.

Factors for Consideration

Temperature

Temperature changes can adversely affect the stress-strain behavior of a paint film, especially at values below the glass

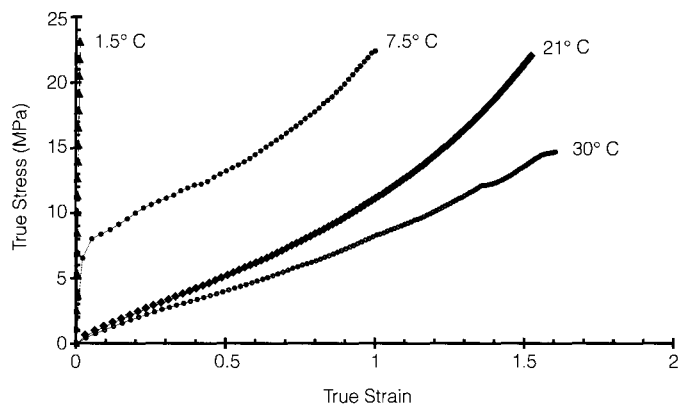


FIGURE 1 Effect of temperature on a p(EA/MMA) bone black emulsion paint.

transition temperature of the binder resin. Figure 1 illustrates the severe embrittlement of a seven-month-old poly(ethyl acrylate-co-methyl methacrylate) [p(EA/MMA)] bone black emulsion paint as temperature was decreased below 7.5° C. Tests at the three highest temperatures were performed under 50% relative humidity (RH), and the 1.5° C sample was preconditioned to 50% RH at 21° C before testing. Similar results for acrylic paint films were shown by Erlebacher and colleagues (1992) in an investigation of climate effects on modern paints.

Water Content

All paint films absorb water to some degree, and the effect on emulsion paints is currently receiving significant attention (Scalarone, Chiantore, and Learner 2005; Ploeger et al. 2005). At high moisture content, these materials are at risk for surfactant migration and dirt pickup. Risk of brittleness from additive leaching seems minimal; however, the long-term effects must still be considered. The behavior of emulsion paints is extremely complex due to the mechanism of film formation and the large number of additives present in the formulations.

Emulsion films are formed by water evaporation and the subsequent coalescence of spherical latex particles called micelles. These latex particles are bundles of high-molecular-weight polymer that are typically dispersed in water by surfactant molecules adsorbed on their surfaces (Steward, Hearn, and Wilkinson 2000). The extent of coalescence is determined by the nature of the polymer and additives. The dry film usually contains a nonhomogeneous distribution of surfactants because of their high surface activity and limited compatibility

with the binder. Distribution of surfactants in latex films is difficult to quantify and has been extensively studied by Urban (1997, 2000). Ethoxylated surfactants are known to behave as partial plasticizers for acrylic emulsions, and their partial compatibility is shown by a slight lowering of glass transition temperature (Belaroui et al. 2003).

The high concentration of hydrophilic functional groups in emulsion paints provides the means for water diffusion. Kelly (2003) showed that the water sensitivity of emulsion paint was effectively reduced through the use of hydrophobic polymers and dispersants, and by limiting the level of water-soluble thickener. To understand how water interacts with a paint film, it is useful to consider early research into the water absorption of rubber. Lowry and Kohman (1927) showed that water-soluble inclusions in rubber increased the uptake of water. The driving force for water absorption, or desorption, was the difference in vapor pressure between the surrounding environment and the water-soluble species within the bulk material. Water absorption increased dramatically when the vapor pressure of the surrounding environment was raised above that of a saturated solution of the inclusions (about 75% RH). Increased stiffness of the rubber resulted in a decrease in the amount of water absorbed due to hydrostatic pressure on the water cells creating a higher internal vapor pressure. Washing the rubber prior to testing was shown to remove water-soluble additives and decrease the water sensitivity of the material. The similarity of water's effects on natural rubber and emulsion polymer films was first discussed by Brown and Scullin (1953).

Pigment Volume Concentration (PVC)

The amount of pigment and filler greatly influences the properties of a paint film. Perera (2004) reviewed the effect of pigment particles on several factors: tensile properties, thermal expansion, internal stress, and water transport. Pigment particles add constraint to the polymer binder and decrease its mobility, which is similar to the presence of cross-link sites in a dry linseed oil. If good adhesion exists between binder and pigment, the stiffness will increase until a critical pigment volume concentration (CPVC) is reached. The specific level at which this occurs is characteristic of the type of binder and filler present. At the CPVC there is just enough binder to hold the pigment particles together, and beyond this point structural support is lost between particles. Films above the CPVC show characteristics such as low tensile strength, low failure strain, and poorly bound pigment. Matte household emulsion paints are typically formulated near or over the CPVC, to increase surface rough-

ness and light scattering. Base coats are formulated similarly; however, in this case the motive is to increase “tooth,” allowing the subsequent layer to better adhere. For a given color, paints with the lowest PVC are those with the highest gloss—typically household alkyd top coats. High gloss is achieved when the polymer is deposited from a solvent and pigment is sufficiently covered. Typical formulations for these products are available in reference texts for organic coatings (Morgans 1990).

Materials and Methods

Materials

A summary of the decorative paints selected for testing is provided in tables 1 and 2 for the artist materials and household products, respectively. All artist-grade paints were labeled titanium white and included information about the type of binder used, whereas the household products were simply labeled “pure brilliant white.” This necessitated the use of chemical analysis to obtain information about the paint compositions.

Table 1 Artist-grade paints prepared for analysis.

Manufacturer	Binder
Winsor & Newton	Safflower oil
Griffin (Winsor & Newton)	Alkyd
Artisan (Winsor & Newton)	Water-mixable oil
Golden Artist Colors	Acrylic

Table 2 Household paints prepared for analysis.

Manufacturer	Medium	Gloss	Application
ICI: Dulux (Trade)	Solvent	High gloss	Interior/exterior, wood and metal
ICI: Dulux (nondrip)	Solvent	Gloss	Interior/exterior, wood and metal
Crown (nondrip)	Solvent	Gloss	Interior/exterior, wood and metal
ICI: Dulux (Trade)	Water	Silk	Interior walls and ceilings
ICI: Dulux (Trade)	Water	Eggshell	Kitchen and bathroom
ICI: Dulux (Trade)	Water	Matte	Interior walls and ceilings
Crown	Water	Matte	Interior walls and ceilings

Density

The densities of the films were measured in an effort to determine their pigment volume concentrations. Strips of paint were weighed and then immersed in a narrow graduated cylinder containing water, and the volume change was observed. An estimate of the PVC was calculated using the density of the binder resin and that of the appropriate pigment/filler. Binder densities were determined from separate measurements on nonpigmented resins or published literature (Clark and Tschentke 1929).

Chemical Analysis

Fourier transform infrared (FTIR) analysis was performed on paint samples using a Nicolet Avatar 360 spectrometer with a diamond cell and Spectra Tech IR plan microscope. Each spectrum was collected using 128 scans at a resolution of 4 cm⁻¹.

Pyrolysis gas chromatography/mass spectrometry (PyGC/MS) was carried out with a GSG Pyromat Curie point pyrolyzer interfaced to a Varian Saturn 2000 GC/MS. The GC column was a Phenomenex Zebron ZB-5 column (30 m length, 0.25 mm inside diameter, 0.25 mm film thickness). Conditions used were as follows:

- Pyrolysis: 625° C for 10 seconds
- GC: Maintained at 40° C for 2 minutes, then ramped to 320° C at 10° C/minute and held for a further 2 minutes at 320° C
- MS: EI mode (70 eV); scanned 40–399 amu every 0.49 second

Scanning Electron Microscopy (SEM)

Images of paint microstructure were obtained using a Jeol JSM 5300 scanning electron microscope in high vacuum mode with electron beam energy of 20 keV. Paint samples were fractured at room temperature to expose pigment particles on the viewing surface. Energy dispersive X-ray analysis (EDX) was performed on some samples to verify inorganic components.

Tensile Testing

Tensile tests were performed on free films at a constant speed of 5 mm/minute, under environmental conditions maintained at 21° C, 50% RH. Deviations from these conditions were made only when investigating effects of displacement rate or moisture content. Samples were preconditioned in enclosures containing silica gel for at least two days to ensure equilibrium moisture content prior to testing. Thickness and width were measured three times along the gauge length with both a

micrometer and a Vernier caliper. Nominal sample dimensions were 40 mm gauge length, 13 mm width, and 0.15 mm thickness. The age of the films was approximately three months at the time of testing.

Experimental error was reduced by discarding samples showing flaws or large deviations in thickness. Tabs of paper were bonded to the gripping ends of the samples with cyanoacrylate adhesive to minimize slipping and stress concentrations. Slipping is a common problem in tensile testing, which results in apparent stiffness values that are too low and extensions that are too high. Stress concentrations from grip pressure commonly give premature failure in tensile tests.

Load-displacement data were converted to true stress and strain values using the relationship

$$\varepsilon = \ln \frac{L}{L_0}$$

for true strain, and

$$\sigma = \sigma_{eng} \cdot e^\varepsilon$$

for true stress. In these equations, L is the instantaneous length during testing, L_0 is the gauge length, and σ_{eng} is the engineering stress (load divided by initial cross-sectional area).

Most published tensile data for paint films are presented as engineering stress-strain. At strains below 0.1 the engineering and true values are essentially equal. The correction at high strains gives a more accurate description of conditions experienced by a ductile sample. Such high strains are not likely to be encountered in paintings; however, data presented in this manner are very useful for interpreting the behavior of materials.

Hygral Expansion

Hygral swelling was measured using six tensometer devices enclosed in Perspex cases where relative humidity was controlled with silica gel at 23° C. Samples with gauge lengths of 100 mm were clamped in grips similar to those used for the tensile test device. A movable grip was manually displaced to measure the film lengths at various moisture contents. Incremental changes of 10–15% RH were performed every two days for a complete sorption-desorption cycle. The difference in length from the dry condition was used to calculate swelling strain as

$$\varepsilon_\beta = (L - L_0)/L_0$$

where L is the sample length at a specific moisture content and L_0 is the gauge length at the dry condition.

Results

Paint Compositions

Tables 3 and 4 summarize the binder, pigment, and extender ingredients found in the artist-grade and household paint products. Pigment and extender components were identified with FTIR and EDX, and binders were identified with PyGC/MS. FTIR analysis was aided by a database of known spectra as well as published literature on modern paint analysis (Learner 2004).

The ratio of peak heights to areas observed in the FTIR spectra provided additional information about the levels of ingredients present in the formulations. Binder peaks in the household alkyd spectra were much stronger in the C=O stretching region when compared to the Griffin artist alkyd. This was a result of the lower pigment volume concentration used in the household products to achieve maximum gloss. Similarly, the emulsion paints with the highest gloss showed the strongest peaks in this region. Extender peaks dominated the spectrum of each matte emulsion.

Tensile Tests

Figure 2 shows the stress-strain curves of the white emulsion paints. Both matte emulsions failed at very low strains as a result of their high filler content. Ductility of the Dulux eggshell emulsion was comparable to that of the Golden artists' acrylic. FTIR analysis indicated that both of these paints contain a significant level of binder resin. High failure strains are explained by a combination of moderate pigment volume concentration and the strong binding power (polymer-pigment adhesion) of the acrylic resins. The Dulux silk emulsion failed at an intermediate strain, which was unexpected since it is

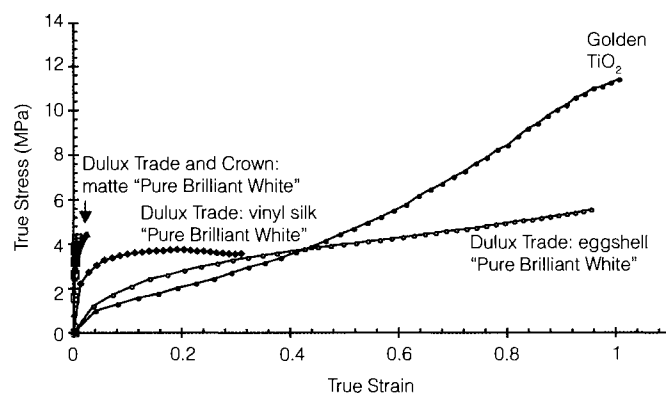


FIGURE 2 Stress-strain curves for white emulsion paints.

Table 3 Summary of ingredients found in the artist-grade paints.

Manufacturer	Binder	Pigment(s)	Extender(s)
Winsor & Newton	Safflower oil	TiO ₂ , ZnO	BaSO ₄ , MgCO ₃
Griffin (Winsor & Newton)	Orthophthalic-based alkyd	TiO ₂	Dolomite
Artisan (Winsor & Newton)	Safflower oil	TiO ₂ , ZnO	-
Golden Artist Colors	Acrylic copolymer (BA/MMA)	TiO ₂	-

Table 4 Summary of ingredients found in the household paints.

Manufacturer	Medium	Gloss	Binder	Pigment	Extender(s)
ICI: Dulux (Trade)	Solvent	High gloss	Orthophthalic-based alkyd	TiO ₂	-
ICI: Dulux (nondrip)	Solvent	Gloss	Orthophthalic-based alkyd	TiO ₂	-
Crown (nondrip)	Solvent	Gloss	Orthophthalic-based alkyd	TiO ₂	-
ICI: Dulux (Trade)	Water	Silk	Styrene-modified PVA	TiO ₂	Kaolin
ICI: Dulux (Trade)	Water	Eggshell	Styrene-modified acrylic (BA/STY/MMA)	TiO ₂	Kaolin, CaCO ₃
ICI: Dulux (Trade)	Water	Matte	Acrylic terpolymer (BA/EHA/MMA)	TiO ₂	Kaolin, CaCO ₃
Crown	Water	Matte	PVA	TiO ₂	Talc

higher in gloss than the eggshell product. It is possible that the binder in the silk emulsion contains a greater amount of hardening monomer to give a stiffer polymer matrix.

Another important difference between the materials shown in figure 2 is the effect of strain rate on the measured properties. Organic coatings are visco-elastic materials to varying degrees, meaning that stress is dependent on the rate of applied strain. Figure 3 shows the modulus versus strain-rate data on a log-log plot for the Golden and Crown emulsion paints. These tests were performed at various speeds and the strain rate over the modulus region was assumed constant. A straight line through each set of data points in figure 2 indicates that the power law

$$E = kR^n$$

is obeyed, where E is the modulus (stiffness), k is the y-intercept, R is the strain rate, and n is the slope of the line. A value of n = 0 signifies an ideal elastic solid (no viscous component), while n = 1 indicates a liquid. Intermediate values relate to varying degrees of visco-elastic behavior. In this case, the Crown matte

emulsion is close to an elastic solid, with n = 0.09, and the Golden product is more visco-elastic, with n = 0.34. In order to obtain data under equilibrium conditions, the Mecklenburg and colleagues' results are presented at a very low strain rate

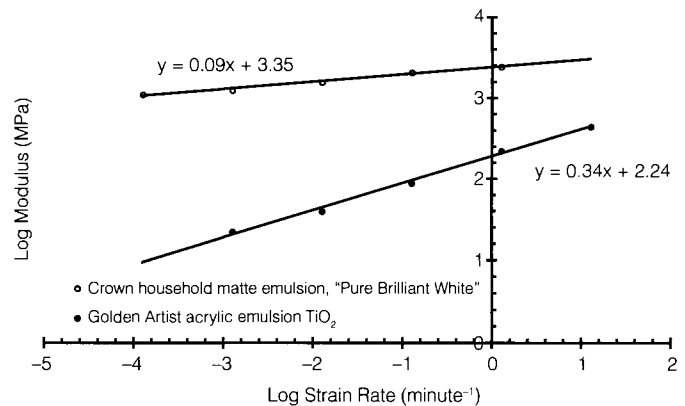


FIGURE 3 Effect of strain rate on the modulus of two emulsion paints.

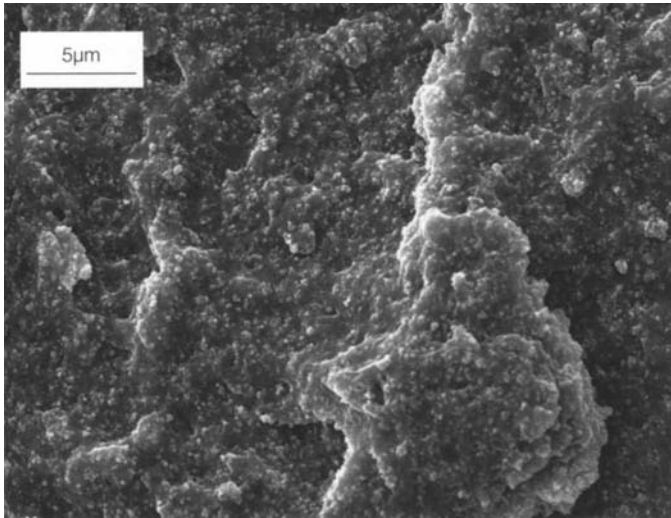


FIGURE 4 SEM image of the Golden artists' emulsion paint.

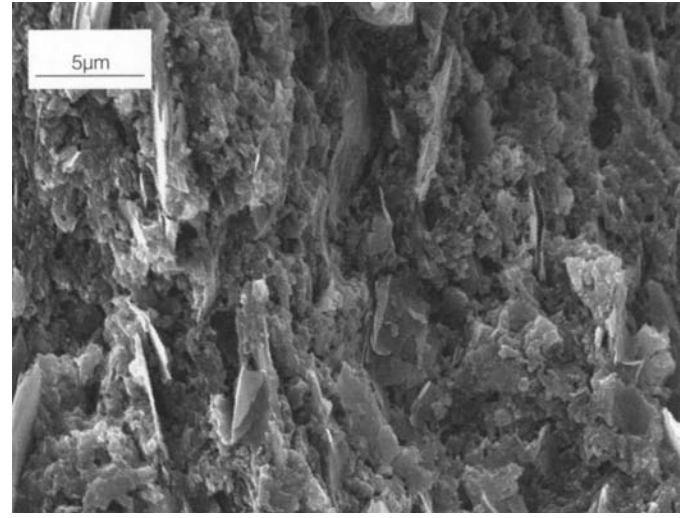


FIGURE 5 SEM image of the Crown matte emulsion paint.

(Mecklenburg, Tumosa, and Erhardt 2005). This is useful for understanding material interactions under environmental changes. For the purposes of this investigation, a higher strain rate was used to compare full stress-strain curves of ductile materials in a shorter amount of time.

Data in figure 3 emphasize that the high filler content in the matte emulsion paint constrains the paint binder and resists polymer flow upon loading. The result is that the stiffness of the highly filled paint film is much higher, and the failure strain is lower. As mentioned previously, the restraint imposed on the polymer by pigment particles is similar to that given by cross-linking in other paint systems; therefore, oil paints are expected to have a lower n value than emulsions (at ambient temperature).

Relative amounts of filler and binder in the Golden and Crown emulsion paints, respectively, are shown by the SEM images in figures 4 and 5. The fracture image of the Golden artist emulsion indicates a binder-rich film with small TiO₂ particles (~ 0.2 μm diameter). A similar image for the Crown product shows a high level of talc filler (the plate-like particles; identified by FTIR) and very little binder. This paint contains a wide particle-size distribution; the small particles between the talc plates are likely to be TiO₂.

Figure 6 shows stress-strain curves measured from each of the alkyd paints. The household products are all significantly more ductile than the Griffin artist alkyd. FTIR spectra suggest that more binder was present in each of the household paints.

An approximation of pigment volume concentrations from density measurements gave about 15 percent for the household alkyds and about 30 percent for the Griffin alkyd. This explains the higher stiffness and lower failure strain of the artist material; however, it is possible that the resin properties also differ. The large extensions observed for the household alkyds are likely to decrease with age as the binder cross-links further.

The effect of moisture content on the Golden emulsion paint is shown in figure 7. Films were preconditioned to equilibrium moisture content and tested under respective relative humidity levels at 21° C. It is apparent that water has a strong softening effect on the latex, as shown by the decreased

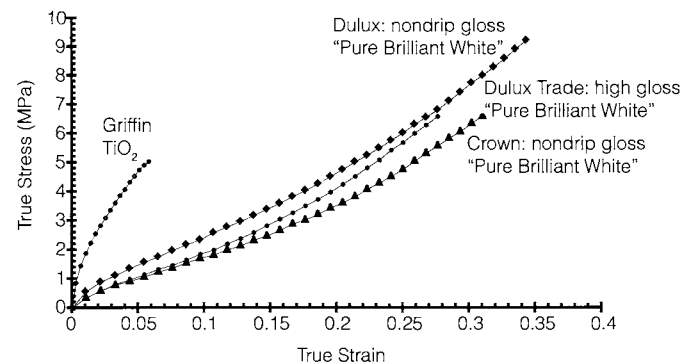


FIGURE 6 Stress-strain curves for white alkyd paints.

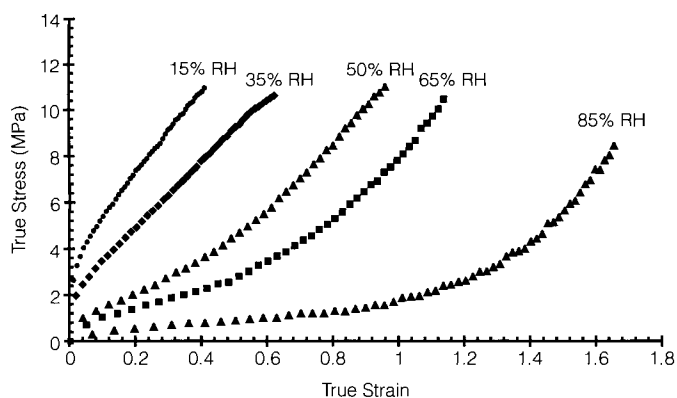


FIGURE 7 Effect of moisture content on the Golden acrylic emulsion paint.

stiffness and increased elongation at high RH. These data are similar to results shown in previous work for a bone black emulsion paint containing a p(EA/MMA) binder (Hagan and Murray 2005).

A greater J-shape in the true stress-strain curves at high moisture content is due to increased flow of the polymer chains. Water disrupts hydrogen bonding between film components and increases the free volume through swelling. The polymer becomes more mobile under strain until limits are reached at chain entanglements and pigment particles. Several other factors may also have this effect, including increased temperature, low polymer interdiffusion, presence of surfactants, and presence of coalescing solvents. All of these affect the interaction of polymer chain segments, and the shape of the true stress-strain curve is a useful indicator of changes that occur in the bulk film.

Another product that showed a significant softening with increased relative humidity was the Artisan water-mixable oil (WMO). Hydrophilic additives used to make the WMO binder compatible with water are the expected cause of moisture sensitivity, which is likely to diminish as the polymer cross-links further. The water sensitivity of both materials will be monitored as they age further, and more detailed results will be given in future work.

Hygral Expansion

Hygral expansion strains were measured for several paint products at 23°C. Results for a full desorption-sorption cycle are presented in figure 8 for the Golden and Crown emulsions. These two materials were chosen for comparison due

to their contrasting filler content. Emulsion paints generally have a high affinity for water due to the presence of hydrophilic additives that aid in latex stabilization and film formation; however, swelling strains were extremely low for the Crown matte emulsion. This is because the matte paint is formulated near the CPVC, so less binder is present to absorb water. Nearly identical results were obtained for the Dulux matte emulsion. All other emulsions showed very high swelling above about 65% RH; values were similar to those of the Golden product. Swelling strains of the alkyd and oil paints were at intermediate levels between the two paints shown in figure 8. It was not possible to accurately measure swelling of the water-mixable oil films because they became excessively soft at moderate levels of moisture and the measuring instrument required a certain amount of sample stiffness to obtain valid data.

Conclusions

A wide range of mechanical properties was evident within the emulsion and alkyd paint materials. Decorative household emulsions are formulated with optical properties ranging from very matte to semigloss. This directly affects the mechanical properties because of differences in pigment volume concentration. Matte emulsion paints were shown to fail at very low strains as a result of the constraint imposed on the binder by filler particles. Similarly, the Griffin artist alkyd was stiffer and less ductile than the household alkyd products. The artist paint was lower in gloss, and results suggested that it contained a higher amount of inorganic filler.

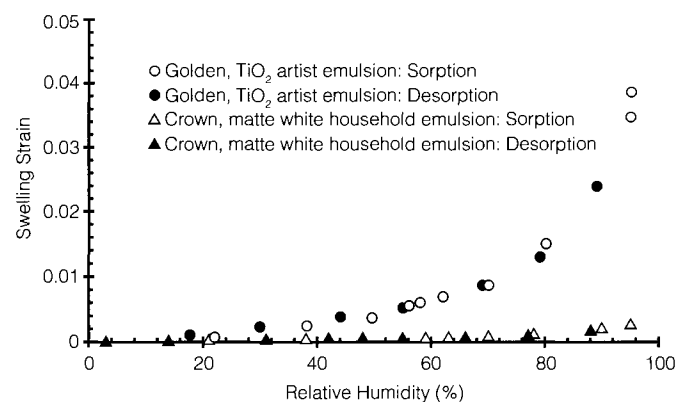


FIGURE 8 Hygral expansion strains for the Golden and Crown (matte) emulsions versus relative humidity at 23°C.

The effects of water were measured through hygral expansion and stress-strain experiments on the materials. Emulsion paints absorbed more water than the other paint systems in all cases except the matte products. This was due to the high proportion of filler in the matte paints, so that less binder was available to swell. The softening effect of water on the paint films was illustrated with tensile data. A strong affinity for water resulted in a significant decrease in the stiffness of both the artist emulsion and the water-mixable oil at high RH. The high level of hydrophilic components explained softening in these paint systems.

The results presented in this paper are part of ongoing research on the structural properties of modern paint materials. Future work will involve studying the effects of temperature and monitoring the aging properties of each product.

Acknowledgments

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Aging Characteristics of a Contemporary Acrylic Emulsion Used in Artists' Paints

Gregory D. Smith

Abstract: *Thin films of Rhoplex AC-2235, an n-butyl acrylate-co-methyl methacrylate dispersion marketed for use in artist-quality acrylic paints, were artificially aged using simulated "indoor sunlight" (i.e., simulated sunlight through window glass). Analysis of the unpigmented films during aging provided insight on the aging characteristics of this dispersion medium. Chemical analysis suggests a dominant aging mechanism based on cross-linking for the acrylic polymer over very long exposures. However, the glass transition temperature was found to remain relatively constant, indicating that the flexibility of the films is largely retained. Colorimetry of the unpigmented films indicated an initial yellowing that rapidly bleached, resulting in largely colorless films. Short-term changes in the films were found to be complex, yet correlated across all analyses. The water-extractable additives in the unpigmented polymer, mainly surfactant, were found to be largely unaffected by the light aging. Triton X-405, the primary emulsifier, was found to exude to the surface of the films and remain over the entire aging regime. A sixteen-year-old, naturally aged acrylic gel medium that had been exposed to window-filtered sunlight was also found to have significant deposits of exuded surfactant on its surface.*

Introduction

Acrylic polymers enjoy catholic use by artists and conservators due to their widespread availability from industrial sources, tunable physical properties, affordability, ease in handling, and purported stability over time. The aging characteristics of solvent-borne acrylics, which are used as adhesives, consolidants, and varnishes, and occasionally as paint binders, have received significant attention since the pioneering work of Robert Feller (Whitmore 2002). Interest in the aging of these

materials has not waned (Amoroso and Furlan 1975; Whitmore and Bailie 1990; Melo et al. 1999; Lazzari and Chiantore 2000; Chiantore and Lazzari 2001; Bracci and Melo 2003; Spathis, Karagiannidou, and Magoula 2003; Toniolo, Casadio, and Cariati 2004). By comparison, acrylic emulsions have only recently attracted the attention of conservation scientists. Only four detailed chemical studies of their aging behavior have appeared in the literature (Whitmore and Colaluca 1995; Learner, Chiantore, and Scalarone 2002; Digney-Peer et al. 2004; Scalarone, Chiantore, and Learner 2005), although a few additional reports surveying the suitability of various acrylic dispersion media for conservation purposes have appeared in conference proceedings (de Witte, Florquin, and Goessens-Landrie 1984; Howells et al. 1984), bulletins (Parker 2005), and peer-reviewed journals (Duffy 1989; Horton-James, Walston, and Zounis 1991; Down et al. 1996). Additional focus is warranted due to the pervasive use of these dispersion materials in industry, art, and conservation. Moreover, the prominence of waterborne coatings in artwork is expected to increase as restrictions on volatile organic compounds (VOCs) are enacted for environmental reasons. This study expands on the current knowledge concerning the aging of these aqueous coatings by examining the visual, physical, and chemical changes induced in a contemporary acrylic emulsion when exposed to simulated "indoor sunlight" (i.e., simulated sunlight through window glass).

Whitmore and Colaluca (1995) exposed films of a commercial ethyl acrylate-co-methyl methacrylate (EA/MMA) gel medium to thermal aging and artificial-light aging using three fluorescent light exposure systems: UV-B, UV-A, and simulated daylight. Their results suggested that heat merely accelerated the aging process observed at room temperature

in the dark—increased haziness, yellowing, and insolubility of the polymer. Observations consistent with the slow migration of residual surfactant to the film surface (Whitmore, Colaluca, and Farrell 1996) and gradual cross-linking of the films were noted. Analysis of aging under UV-B fluorescent lamps ($\lambda_{\text{peak}} = 315 \text{ nm}$) showed initial changes similar to heat aging, but these rapidly reversed, yielding loss of haziness, color, and tensile strength as well as increased polymer solubility. The latter process dominated the aging and was attributed to chain scission photochemistry resulting from the intense UV exposure. Longer-wavelength UV-A radiation ($\lambda_{\text{peak}} = 350 \text{ nm}$) followed these same general trends, but more slowly. A limited-duration exposure to simulated-daylight fluorescent lamps showed an initial increase in insolubility, but a reversal was never observed during the short duration of the experiment.

Learner and his co-workers have examined the aging of commercial acrylic paints based on EA/MMA as well as *n*-butyl acrylate-co-methyl methacrylate (*n*BA/MMA) (Learner, Chiantore, and Scalarone 2002; Digney-Peer et al. 2004; Scalarone, Chiantore, and Learner 2005). Their results, based on thermal and fluorescent-light aging with no UV component, concluded that these materials are quite resistant to yellowing compared to other artists' media. In their study, paints based on an *n*BA/MMA binder became increasingly insoluble in tetrahydrofuran (THF) with aging, whereas EA/MMA paints occasionally increased in solubility. These results may indicate slight differences in the dominant degradation pathway of the two acrylic copolymers. An equally significant finding, however, was the reported loss of water-soluble additives with visible light aging. Surfactants, which are used as emulsifiers and wetting agents in acrylic dispersion paints (Jablonski et al. 2003), are thought to be responsible for many of the conservation concerns surrounding these artworks, including their optical clarity, water sensitivity, and surface tackiness (Digney-Peer et al. 2004; Butler, Fellows, and Gilbert 2005).

This research examines the aging characteristics of Rhoplex AC-2235, which is likely to be very similar to many unpigmented commercial acrylic emulsion artists' mediums. These are often used in a pure form by artists as isolation layers or clear coats (Hayes, Golden, and Smith 2007) and by conservators as adhesives (Down et al. 1996). Furthermore, as Rhoplex AC-2235 is a raw ingredient in acrylic emulsion paint manufacture, it was hoped that the results could be generalized to many current artists' paints.

The aging conditions were chosen to bridge the gap between the previously mentioned studies; simulated indoor sunlight contains only a small fraction of the short-wavelength

UV radiation used by Whitmore and Colaluca (1995) while incorporating the complete visible spectrum used by Learner and co-workers (Learner, Chiantore, and Scalarone 2002; Digney-Peer et al. 2004; Scalarone, Chiantore, and Learner 2005). The aging behavior of acrylics exposed to this wavelength range is particularly important, since the vast majority of acrylic artwork does not reside in museums with filtered lighting, but rather is exposed to indoor sunlight while hanging in residences, studios, and galleries. This study provides frequent snapshots of aging in its early stages, allowing for an assessment of the status of paintings early in their life. It will also allow comparisons to be made as the paintings continue to age over several centuries. When one considers that the oldest acrylic emulsion paintings are now approaching only fifty years old, the complex aging that occurs early in an artwork's history when exposed to "typical" exposure conditions is particularly germane.

Experimental Method

Samples

Rhoplex AC-2235 was supplied to the author by Golden Artist Colors (GAC), which purchased the product directly from the manufacturer, Rohm and Haas. To facilitate the preparation of films of constant thickness, a small batch of the watery dispersion was thickened by the addition of 1.5% (w/w) hydroxyethylcellulose (HEC). This material was cast as a film ($4 \times 12 \text{ cm}$) on thin, rectangular soda-lime glass plates utilizing a 100 mil Mylar template and a drawdown bar. A dry film thickness of $109 \pm 6 \mu\text{m}$ was measured using a digital micrometer. All films were allowed to dry at laboratory conditions of 23°C and 50% relative humidity (RH) for several weeks prior to artificial aging, extraction, or analysis.

Although not reported here, Rhoplex AC-2235 was confirmed to be an *n*BA/MMA dispersion using a published pyrolysis gas chromatography/mass spectroscopy (PyGC/MS) protocol (Learner 2005). The major emulsifier was identified as an oligomeric octylphenol polyethoxylate surfactant, Triton X-405, using a published liquid chromatography/mass spectroscopy (LC/MS) technique for identifying water-soluble additives in acrylic paints (Smith 2005). Although not confirmed by analysis, the dispersion as received from the manufacturer is also expected to contain a biocide in very low concentrations, perhaps Rocima 551 or Kathon LX. The samples were unpigmented and did not include any further known additives aside from the HEC thickener.

Naturally aged films of commercial acrylic dispersion gel media were also available from an earlier support-induced

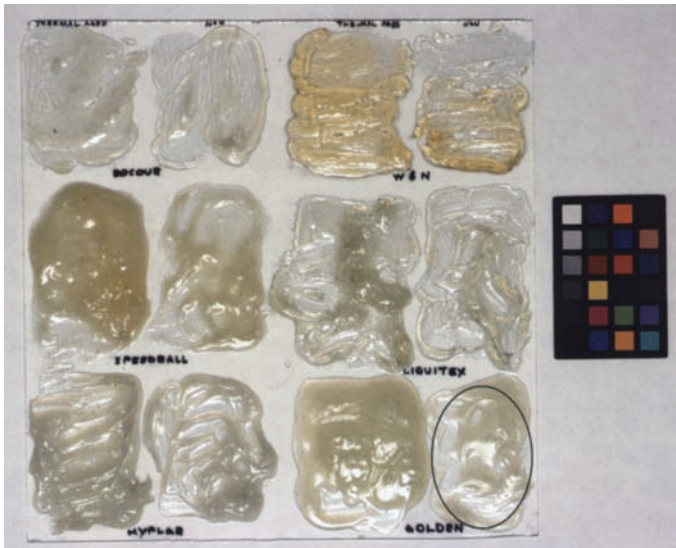


FIGURE 1 Test panels of commercial acrylic dispersion gels for SID study (Hamm et al. 1993) aged naturally by sunlight through window glass for sixteen years. The oval denotes the Golden Artist Colors gel used in this study.

discoloration (SID) study conducted at Buffalo State College in 1989 (Hamm et al. 1993) (fig. 1). Thick pours of the gels were arrayed on a soda-lime glass plate and aged naturally under studio conditions of approximately 23° C and 50% RH while laid flat on a laboratory shelf. These films have received unfiltered sunlight through north- and west-facing plate glass windows for approximately sixteen years. One of the pours, a Regular Gel Medium (Golden Artist Colors), was used in this study.

Artificial Aging Regime

Rectangular sample films of Rhoplex AC-2235 were artificially aged on their glass supports using simulated sunlight through window glass in an Atlas Ci65 Xenon Arc Weather-Ometer that had both soda-lime and borosilicate glass filters. Figure 2 shows the scaled irradiance spectrum of the arc source (solid line) compared to Arizona sunlight (dashed line). The effect of the window glass filter is seen in the reduced intensity of the arc source below 400 nm. Power to the arc lamp was controlled to maintain an irradiance at 420 nm of 0.9 W/m²/nm. The illuminance was calculated to be 74,425 lux. The aging chamber environment was maintained at an average temperature of 35° C and 40% RH. Thin strips of polymer were removed from a single sample film at periodic stages to create a series of time-

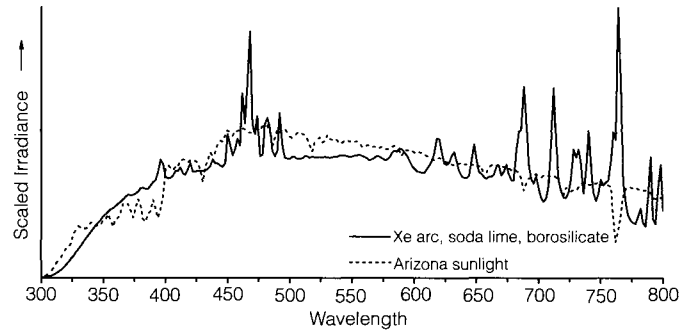


FIGURE 2 Scaled irradiance spectrum of the Xe arc source filtered by soda-lime and borosilicate glass filters (solid line) compared to unfiltered Arizona sunlight (dashed line). The effect of the window glass filter is seen in the reduced intensity of the arc source below 400 nm.

resolved aged samples. Based on Whitmore and Colaluca’s (1995) reciprocity approximation regarding average museum exposures (2950 hours/year at 150 lux), the longest artificial aging period of 1196 hours is equivalent to over two hundred museum years, although the small UV-A component below 400 nm used in this study would not normally be found in museums using filtered lighting. Table 1 lists all the sample aging times and their equivalent in museum years using the above approximation.

Table 1
Relationship between hours of exposure to artificial simulated indoor sunlight and equivalent years of exposure to museum lighting, assuming reciprocity.

Artificial Aging ^a (hours)	Equivalent Museum Aging ^b (years)
22	3.7
44	7.4
110	18.5
202	34.0
436	73.3
796	133.9
1196	201.2

Note: Museum lighting calculations taken from Whitmore and Colaluca 1995.

^a Irradiance = 74,425 lux.

^b Assumes reciprocity, 2950 hours/year at 150 lux.

Colorimetry and Gloss

CIELab color measurements excluding the specular component were made on the glass-mounted films using an UltraScan XE colorimeter (Hunter Lab) with 10-degree observer and D65 illuminant. A standard white tile was placed behind the glass substrate. Change in the b^* axis (yellow-blue) in comparison to the initial reading was used to indicate degree of yellowing with age. Gloss measurements at 60 degrees were performed using a BYK Gardner Micro Tri-Gloss meter. In order to eliminate reflections from the back of the supporting glass substrates, a black cloth was placed behind the sample. Values for both tests are shown as the average of six measurements across the sample, with error bars indicating one standard deviation ($\pm 1\sigma$).

Differential Scanning Calorimetry (DSC)

Glass transition temperatures (T_g) were measured using a Q1000 calorimeter (TA Instruments). Round samples were cut from free paint films using a 7 mm diameter hole punch, weighed on a 0.1 μg sensitive balance (Mettler Toledo UMX2), and sealed in crimped aluminum sample pans. The samples were then heated at a rate of 10° C/minute from -60° to 80° C under a nitrogen purge. The T_g was calculated using Universal Analysis software (TA Instruments) as the inflection point along the step transition. Triplicate measurements were made using new sample material for each run. Reported values are the average, with error bars indicating $\pm 1\sigma$. All samples showed an endothermic peak at approximately 46° C on the first heating due to the melting of exuded surfactant crystals. Subsequent measurements on the same sample showed no endotherm, but did indicate a reduction in the T_g by several degrees, suggesting the plasticizing role of the reincorporated surfactant.

Polarized Light Microscopy (PLM)

An E400 Eclipse PLM microscope (Nikon) was used to document the surface morphology of acrylic films in transmitted light at high magnification (100 \times). Anisotropic crystalline material on the surface of the amorphous polymer was visualized under crossed polarizers. Image capture was achieved using a C-mounted DS-5M digital camera and DS-L1 control unit (Nikon).

Weight Change and Solubility

Weight change was assessed using a single acrylic film on its glass substrate. The sample was weighed periodically during the aging regime using a microgram-sensitive balance (Denver

Instruments A-200DS). Change in weight was calculated by subtracting the initial weight from subsequent measurements. Percent weight change in the film alone could not be calculated due to the presence of the glass substrate and its inexact dimensions.

Solubility tests were conducted by sampling a film using a 7 mm diameter hole punch. The circular samples were then weighed on a 0.1 μg sensitive balance (Mettler Toledo UMX2) and placed in clean glass vials to which 0.5 mL of water was added. After 20 hours of extraction, the residual polymer was removed and allowed to dry for several days before being reweighed. The same samples were then placed in new vials (which had been weighed), to which 1 mL of unstabilized THF was added. After 20 hours of extraction, the fraction that was soluble in THF was removed by syringe and stored for molecular weight analysis (see below), and the vial and residual gel were dried before being reweighed. The water and THF extraction results are represented as the percent weight loss following each extraction and are the average of triplicate measurements, with error bars representing one standard deviation ($\pm 1\sigma$).

Gel Permeation Chromatography (GPC)

GPC separations were performed on a GPC-20 chromatograph (Polymer Labs) with a Midas autosampler using unstabilized THF as the mobile phase. The THF-soluble fractions described above were diluted with mobile phase as necessary to achieve an approximately 1% (w/w) solution. A single 50 μL injection for each sample was introduced onto two serial 5 μm particle size PLGel Mixed D size (300 \times 7.6 mm) exclusion columns (Polymer Labs) at ambient temperature (approximately 23° C). Total run times were 25 minutes with a flow rate of 1 mL/minute. Eluting components were detected by a refractive index detector and processed using Cirrus GPC software (Polymer Labs). Weight-average molecular weights (M_w) were determined by reference to a set of polystyrene standards run under identical conditions.

Fourier Transform Infrared (FTIR) Spectroscopy

Surface infrared spectra were collected using a Continuum microscope with a germanium (Ge) micro-attenuated total reflection (μATR) accessory coupled to a Nexus 670 FTIR spectrometer (Nicolet). A pressure-sensitive monitor was used to achieve a consistent sample contact with the ATR accessory. Based on the refractive index of Ge, the depth of analysis was less than 1 μm . The spectra are the average of 64 scans at 4 cm^{-1} spectral resolution. Infrared (IR) absorption bands for the

acrylic binder (1731 cm^{-1}) and for Triton X-405 surfactant (1343 and 1109 cm^{-1}) were identified by comparison to pure reference materials. Changes in the relative surface composition during aging were measured by comparison of the ratios of acrylic to surfactant absorption band areas ($1731/1343$ and $1731/1109$).

A “transfection” FTIR analysis was performed on material extracted from the surface of the naturally aged SID sample. A micropipette was used to deliver $10\ \mu\text{L}$ of deionized water onto the surface of the GAC regular gel medium. After 5 seconds, the drop was re-collected and deposited onto a MirrIR reflective slide (Kevley Technologies), where it was left to dry in a desiccator. Multiple extraction experiments were performed to determine that approximately $18\ \mu\text{g}$ of material is removed by this procedure. The tide line formed by extracted material was analyzed using the FTIR microscope in reflectance mode with a $15\times$ objective. The spectrum, which is the result of a double transmission through the sample, was compared to reference spectra to identify the extracted material.

Results and Discussion

Thin films of Rhoplex AC-2235 were exposed to intense simulated indoor sunlight for 1196 hours; periodic sampling of the films was used to establish a series of increasingly aged samples. A battery of analytical tools were employed to characterize changes in physical and chemical properties of the acrylic polymer. The fate of water-soluble additives was also investigated through aqueous extraction and subsequent characterization of the extract solution.

Physical Changes

Figure 3 shows the results for colorimetry, gloss, and T_g for the polymer film, which had a barely perceptible yellowness when compared to a white standard immediately after coalescence and before aging ($b^* = 0.74$). The data shown in figure 3A for the change in the b^* value with increasing light exposure indicate that yellowing rose sharply in the first few hours of artificial aging, but quickly reversed, ultimately yielding a film that was slightly less colored than the starting material ($b^* = 0.70$). These results are entirely consistent with previous observations that note the slight yellowing of acrylic emulsion materials with age and the bleaching effect that accompanies light exposure (Whitmore and Colaluca 1995; Whitmore, Colaluca, and Morris 2002). It is worth noting that, although yellowing does occur when acrylic emulsion media are stored in the dark, this effect is far less serious than for other artists’ paint media (Learner, Chiantore, and Scalarone 2002).

Prior to aging, the films appeared semiglossy, optically transparent, with a slight haziness when viewed at an angle. The semigloss designation was confirmed by a 60-degree gloss measurement, which yielded an initial value of 65 gloss units (fig. 3B). Measurements made over the course of the aging test showed a rapid loss of gloss, which later stabilized before dropping even further. Loss of gloss could be due to erosion of the binder at the film-air interface or to the exudation to the surface of mobile materials from within the bulk. To resolve this issue, the surface morphology was observed using PLM under crossed polarizers. PLM has been noted as a means of identifying crystallized surfactant materials that are known to exude to the film-air interface upon coalescence of the acrylic dispersion (Whitmore and Colaluca 1995; Whitmore, Colaluca, and Farrell 1996; Digney-Peer et al. 2004). Small domains of crystalline material were identified as residual surface surfactant by their characteristic “Maltese cross” patterns when viewed under crossed polarizers (Whitmore, Colaluca, and Farrell 1996). Inspection of aged samples showed that these crystallites grew in number and size with increasing light aging. A photomicrograph (fig. 4) reveals the almost total coverage of the film’s surface after 1196 hours of aging. The crystallites were estimated to range in size from less than $10\ \mu\text{m}$ to approximately $100\ \mu\text{m}$.

The persistence of the surfactant material when irradiated with simulated indoor sunlight was surprising in light of

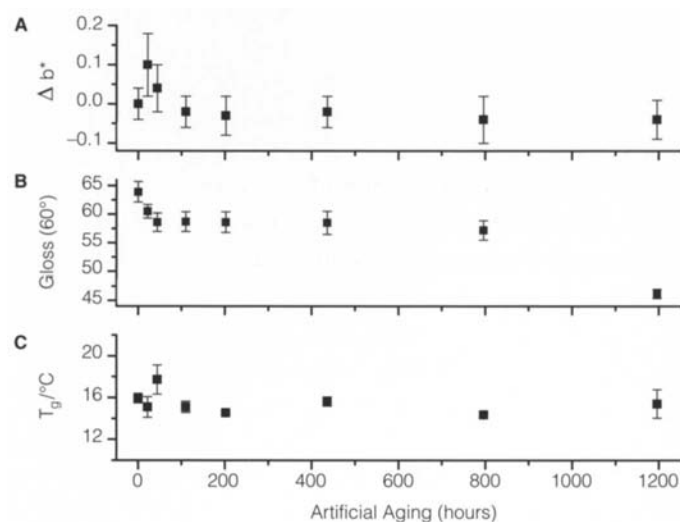


FIGURE 3 Results for changes in (A) yellowness, (B) 60-degree surface gloss measurements, (C) glass transition temperature during aging.

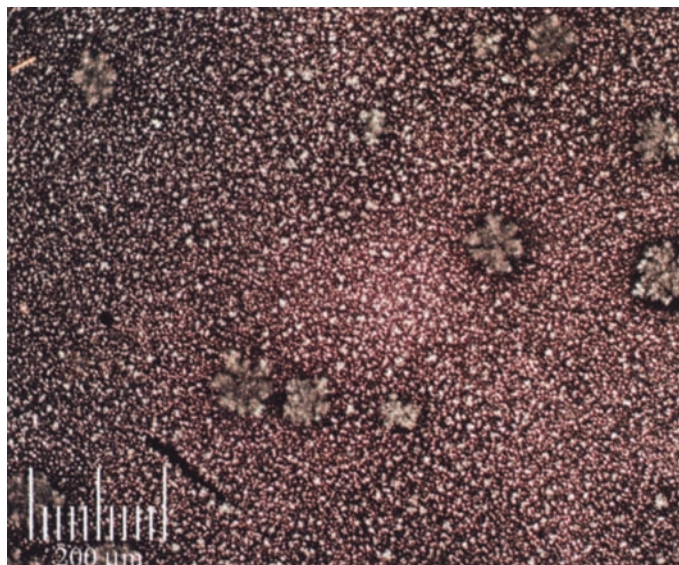


FIGURE 4 Transmitted polarized light photomicrograph with crossed polarizers of Rhoplex AC-2235 film surface following 1196 hours of artificial aging.

previous studies. Others have noted that surfactants in thinly applied acrylic paints were reduced by visible-light aging without a UV component (Digney-Peer et al. 2004; Scalarone, Chiantore, and Learner 2005). The more energetic UV-B radiation used by Whitmore and Colaluca (1995) in the aging of a commercial acrylic emulsion artists' medium was also reported to dissipate surface haze, supposedly through photolysis and evaporation of the polyether surfactant. The Xe arc chamber and filters used in this study included a small portion of UV-A between 400 and 310 nm, which would be expected to be more aggressive in terms of surfactant photolysis than visible light alone. Although visual inspection suggested that the surfactant remained in the films, it was perhaps possible that the surface material was being photolyzed, but that a sufficient reservoir existed in the film's bulk to replace any surface material degraded by light exposure. Further analysis was performed to confirm the fate of the water-soluble additives (see below).

Figure 3C plots the polymer T_g , as measured by the inflection point in a DSC thermogram, over the course of the aging test. The glass transition is actually a temperature range over which the polymer changes from being a hard, glassy material (at temperatures below T_g) to being a soft, rubbery material (at temperatures above T_g). A polymer's T_g

is often used as an indicator of brittleness, flexibility, or tackiness, depending on its relationship to the ambient temperature (Schilling 1989). An increase in T_g indicates that the polymer is becoming more firm and less flexible, whereas a decrease would suggest a tackier, softer film. Changing environmental conditions such as relative humidity can affect the T_g , as can the loss of plasticizing components.

Rhoplex AC-2235 is a flexible material at room temperature with a very slight surface tackiness. The softness of the polymer increases with increasing RH (Erlebacher, Mecklenburg, and Tumosa 1992), and extraction of plasticizing surfactants by water washing can cause increased firmness (Hayes, Golden, and Smith 2007). The data shown in figure 3C indicate that the flexibility of the film is largely retained. Only modest deviations from the average T_g of approximately 15° C are observed, and these do not show a relationship to increasing light exposure.

Chemical Changes

Figure 5 shows the results of increasing light exposure for weight change, percent of polymeric material that is insoluble in THF, and the weight-average molecular weights (M_w) for the THF-soluble fraction of films of Rhoplex AC-2235. The acrylic polymer loses a small amount of material very rapidly in the earliest stages of artificial aging. Considering the slightly

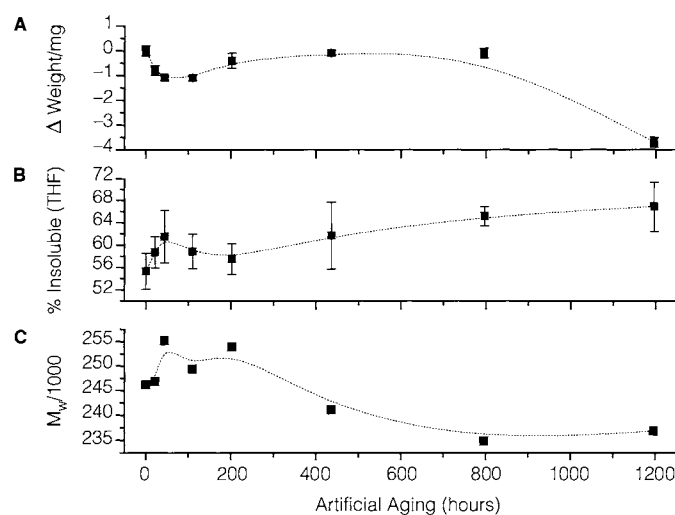


FIGURE 5 Results for changes in (A) sample weight, (B) percent polymer film insoluble in THF, (C) weight-average molecular weight of the soluble fraction in THF during aging. Dashed lines indicate trends suggested by the data.

warm conditions of the aging chamber (approximately 35° C) and the relatively fresh polymer films, this change is likely to be due to evaporation of low-molecular-weight additives and residual polymerization components. Down and colleagues (1996) report the release of various volatile esters, water, acetic acid, alcohols, and ethers during the aging of acrylic dispersions. The exact nature of the lost material here is not known, however, and it is impossible to rule out the potential for rapid weight loss due to photolysis of chemically labile parts of the polymer. The decrease in weight is eventually reversed, and most of the previously lost weight is regained by the five hundredth hour of aging. Weight gain is expected when oxidation of the polymer backbone or emulsion additives occurs. The longest aging periods show again a drop in sample weight. The reduction in weight can be accounted for by elimination of side groups along the polymer chain during polymer cross-linking, or by the loss of small molecules due to chain scission of the polymer or reactions of other additives, such as hydrolysis of the HEC thickener side chains. The percentage of weight change for the polymer itself could not be calculated due to the presence of the glass support; however, the differences measured with respect to the overall polymer film weight can be classified as very small (<1 percent), in agreement with previous studies (Howells et al. 1984). This observation corresponds well with cross-linking, rather than chain scission, being the dominant aging mechanism for films of *n*BA/MMA dispersions exposed to simulated indoor sunlight.

Freshly coalesced films of Rhoplex AC-2235 are known to be nonreversible in water and are also surprisingly insoluble in even strong organic solvents. The lower solubility of this polymer dispersion in organic solvents when compared to its solvent-borne counterpart, Acryloid B-48S, is believed to be due to the much higher molecular weight in emulsion-based coatings and a slight amount of cross-linking during the manufacture of the dispersion product. The initial M_w of the THF-soluble portion of Rhoplex AC-2235 was measured here to be approximately 246,000, compared to 48,000 for B-48S solution reported elsewhere (Lazzari and Chiantore 2000). Figure 5B reveals that 55% of the initial polymer remains as an insoluble gel after twenty hours immersed in THF. The likelihood that cross-linking is a dominant aging mechanism is supported by the 10% overall increase in insoluble material during the artificial aging test.

Figure 5B shows complex behavior in the earliest aging periods, but the results are well correlated with those observed in the measurement of weight change (fig. 5A). The percentage of insoluble material initially increases rapidly at the

same time that the film is quickly losing weight. Loss of low-molecular-weight additives that would normally be soluble in THF satisfactorily explains this rapid increase in the percentage of insoluble material, especially if one assumes that an underlying process of polymer cross-linking is occurring simultaneously. The initial increase in insoluble material is then reversed momentarily at the same point as the temporary weight gain. Increased polymer solubility may be a response to the brief increase in oxidation believed to be responsible for the increase in sample weight.

Figure 5C reveals the M_w of the polymer fraction that was soluble in THF. The overall trend with aging is a decrease in the molecular weight of this fraction. Although such an observation might lead one to conclude an aging mechanism based on chain scission was in operation, the results are actually also consistent with dominant cross-linking (Lazzari and Chiantore 2000), as suggested by minimal weight loss and increasing insolubility of the polymer film in THF. As the polymer material increases in molecular weight due to cross-linking, at first an increase in the molecular weight of the soluble fraction is observed. However, the larger molecules eventually increase in size, to the point that they can no longer be extracted, thereby leaving only the fragments with the smallest molecular weight in the THF solution analyzed by GPC. Hence, the average molecular weight for this fraction diminishes.

Fate of Water-Soluble Additives

Residual surfactant present in pigmented acrylic paints and commercial acrylic mediums has been shown previously to be degraded and volatilized by visible light aging (Digney-Peer et al. 2004; Scaroni, Chiantore, and Learner 2005). The observed persistence of crystallized surfactant on the surfaces of these unpigmented acrylic dispersion films over extended exposure to even more energetic simulated indoor sunlight appeared to contradict those results. Although the size and number of the surface features observed by PLM appeared to grow throughout the aging experiment, molecular analysis of the surface was undertaken using μ ATR-FTIR to determine the relative surface composition. Applying identical contact pressure between the ATR crystal and the aged samples' surfaces made possible a semiquantitative assessment of the surface surfactant compared to bare acrylic polymer.

The IR spectra of *n*BA/MMA and Triton X-405 have appeared in the literature (Learner 2005). Figure 6 shows the change in the ratio of band areas for the acrylic ester peak at 1731 cm^{-1} and two peaks at 1343 and 1109 cm^{-1} , which are attrib-

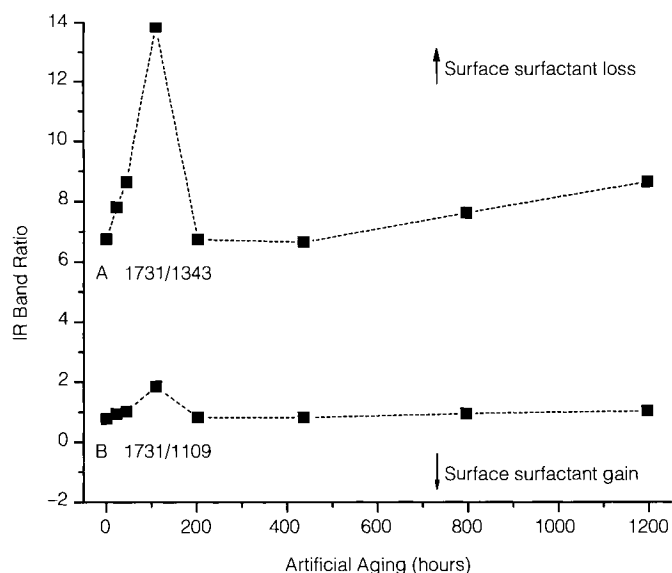


FIGURE 6 Ratios of the band areas for the acrylic ester peak at 1731 cm^{-1} and two surfactant ether peaks at (A) 1343 cm^{-1} and (B) 1109 cm^{-1} from $\mu\text{ATR-FTIR}$ measurements of the surfaces of artificially aged films of Rhoplex AC-2235. Dashed lines indicate trends suggested by the data. Increasing ratio indicates reduced surface surfactant, whereas a lower ratio signifies increasing concentration of surfactant on the surface.

utable to the ether functional groups of Triton X-405. Both data sets reveal identical compositional data with increasing exposure time. A rapid increase in the ratio at the earliest stages of aging indicates a surface being depleted of surfactant. This change can result from loss of surfactant at the surface due to photolysis and evaporation, but it might also result from surfactant retreating into the bulk of the acrylic film, perhaps as a result of increased mobility in the slightly warm chamber. In light of the coinciding loss of weight, the former is perhaps more likely. By the two hundredth hour of aging, a resurgence of surfactant to the surface has almost exactly replaced the lost material. Only minimal change in the ratio occurs over the remainder of the aging protocol.

To assess further the fate of water-soluble additives in the bulk of films of unpigmented Rhoplex AC-2235, aqueous extractions were performed. Figure 7 shows the percentage of water-extractable material in the acrylic films over the course of the light-aging test. Initially, 4.5 percent of the polymer film is soluble in room-temperature water. This value is consistent with the dry weight of nonionic surfactant emulsifier present in films of acrylic dispersion media. The insolubility of the

acrylic monomers and polymers in water rules out their contribution to the weight loss following aqueous extraction, and previous analyses of the aqueous extracts of HEC-thickened acrylic emulsion films by LC/MS found no indication of the cellulosic thickener (Smith 2005). The HEC thickener is of sufficient molecular weight that it is assumed to be completely entangled in the insoluble polymer matrix. The amount of water-soluble material diminishes by 0.25 percent following the initial period of light exposure, but the water-extractable component remains relatively high and constant throughout the rest of the artificial-aging test. The exact composition of the lost material is not known; however, the rapidity and duration of the decrease in the water-soluble component matches well the initial weight loss data shown in figure 5A as well as the change in the amount of surface surfactant indicated in figure 6.

Importantly, the presence of significant amounts of water-soluble material throughout the aging test, combined with the visual and molecular assessments of persistent surfactant crystallites at the film-air interface, indicates that simulated indoor sunlight is incapable of eliminating the bulk of the residual surfactant in clear coats of acrylic dispersion medium. The role played by pigments and other additives that are added to paint formulations, as well as the thicknesses of the films, has not been ascertained, although the differences

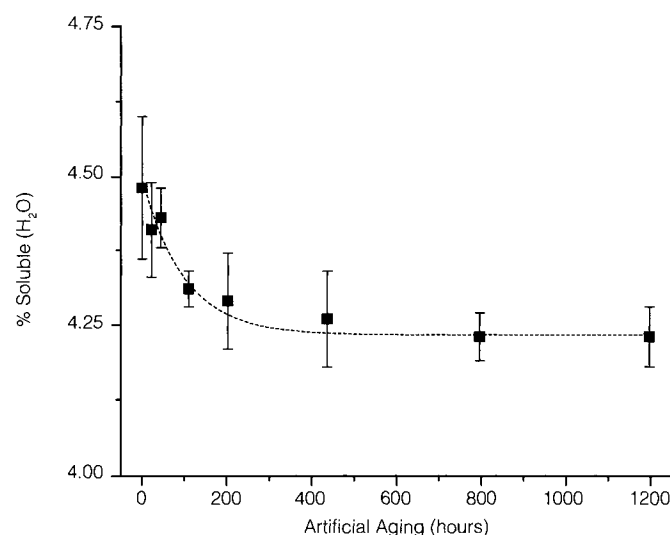


FIGURE 7 Percentage of water-extractable material in films of Rhoplex AC-2235 during aging. The dashed line indicates the trend suggested by the data.

between the samples used here and those studied in previous tests may account for the seemingly contradictory data. It has been shown that some pigments catalyze the oxidation of the acrylic binder (Scalarone, Chiantore, and Learner 2005), a chemical change not observed here for unpigmented acrylic medium. A similar photocatalytic effect may play a role in the degradation of polyether surfactants in pigmented acrylic paints. Moreover, the previous studies utilized sample films that were often one-third as thick as those used in the current research. Thin films may be more susceptible to extensive surfactant degradation, and they also have a smaller reservoir of residual surfactant. It has been noted that even in light-aged films that saw a decrease in the surface surfactant concentration, new surfactant exuded to the film-air interface after artificial aging (Digney-Peer et al. 2004).

The ability of artificial-aging experiments to replicate the aging effects that occur under natural conditions is always in question, although reasonably similar aging behavior for simulated and natural outdoor weathering of solvent-borne acrylics has been demonstrated recently (Bracci and Melo 2003). To confirm the stability of surface surfactant on clear acrylic dispersion films, an FTIR analysis of surface material on a naturally aged acrylic gel medium exposed to indoor

sunlight for sixteen years was undertaken. Figure 8A shows the IR spectrum of residue from a very brief aqueous surface extraction of the naturally aged gel medium. When compared to figure 8B, which shows the IR reference spectrum for Triton X-405, figure 8A confirms that the residual emulsifier has endured harsh indoor lighting for nearly two decades without detectable degradation.

Conclusions

Films of Rhoplex AC-2235 show complex chemical and physical changes in the early stages of simulated indoor-sunlight aging, probably as a result of volatilization of low-molecular-weight additives. However, over the long term, trends toward cross-linking ultimately dominate, as suggested by the increasing insolubility of the coalesced polymer in strong organic solvents. Despite an increase in molecular weight with age, the films remain very flexible and slightly tacky. This is indicated subjectively by handling and objectively by measuring the T_g of the aged films, which remains at a value slightly below room temperature. The photostability of the *n*BA/MMA dispersion is confirmed by the constancy of its IR spectrum and the lack of evidence for significant weight gain or loss. This observation covers Rhoplex AC-2235, and probably most other *n*BA/MMA emulsions of similar composition—the “Feller Class A” rating like that attributed to the commercial EA/MMA emulsion studied previously (Whitmore and Colaluca 1995). Although the sample films yellowed slightly initially, this trend was rapidly reversed by further illumination, thereby demonstrating the potential of simulated indoor daylight to bleach discoloration in clear acrylic emulsion media.

Thin films of Rhoplex AC-2235 were found to become hazy almost immediately after casting. PLM and FTIR microscopy revealed that this is due to the exudation of surfactant emulsifiers following film coalescence. Observations of gloss and surface composition over the course of the artificial-aging test indicate that the exuded surfactant persists despite harsh simulated indoor lighting conditions. Data recorded here with regard to the fate of water-soluble additives in unpigmented dispersion films, both artificially and naturally aged, indicate that they are not significantly reduced, which is at odds with earlier reports on acrylic paint samples. However, these discrepancies are likely to be the result of differences in the samples, the presence of pigments and additives in the acrylic paints, and the aging conditions.

The stability of polyether surfactants in clear films of contemporary acrylic emulsions has a bearing on conservation

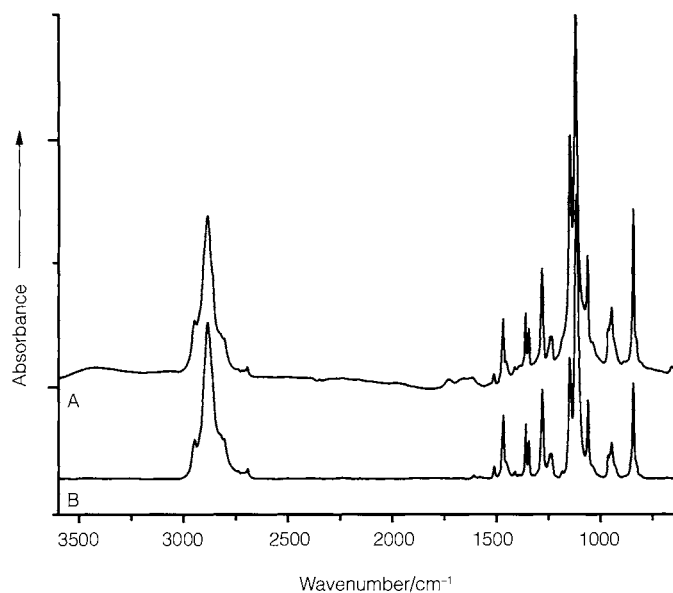


FIGURE 8 Comparison of FTIR spectra from (A) water extract residue from the surface of the naturally aged sample, (B) reference sample of Triton X-405. The absorbance axis has been offset to assist in comparison.

concerns regarding these waterborne coatings. Surfactants have been blamed for problems with adhesion, loss of optical clarity, dirt pickup, and water sensitivity. The long-term persistence of these additives will require conservators to deal with surfactants in artworks bearing clear coats of acrylic medium throughout the life of the objects. This conclusion suggests that further study of these components of acrylic emulsions is warranted to provide conservation professionals a better understanding of their chemistry, their effects on acrylic binders, and best practices in treating works composed of acrylic emulsion media.

Acknowledgments

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Interfacial Interactions of Modern Paint Layers

Christina Young

Abstract: *This paper reports on experimental work to measure the adhesion, flexibility, and onset of cracking of modern paint layers. The objective was to investigate systematically and in greater detail the most significant findings of previous research into the mechanical characterization of composite paint layers with different media on canvas substrates. First, testing of layered alkyds and acrylics indicates that at low strains the mechanical properties of the composites can be predicted by combining the properties of the individual layers in proportion to their thickness. However, at higher strains this is not the case. After the failure of an alkyd layer, the stiffness is higher than what would be predicted assuming the load was taken by the acrylic layer only. Second, acrylic primings reduce the amount of cracking in the alkyd top layers, appearing to retard their normal brittle behavior. Conversely, failure of alkyd primings occurs but the acrylic top layer remains visually intact. Samples consist of commercially available oil, alkyd, and acrylic primings with subsequent paint layers of different pigments in oil, acrylic, and alkyd media. The priming and paint layers were prepared as composites on canvas and as free films. Mandrel and fold tests were performed to measure flexibility; the tensile force needed to detach the upper paint layer from a composite was used to measure adhesion. Crack initiation/propagation were captured using a CCD. The acquired data will result in a better understanding of interfacial interactions and potential failure modes of modern paint-layer combinations.*

Introduction

The combinations of paints that may be chosen for the execution of a painting has expanded dramatically as new paint media have been developed by the coatings industry and then

adopted by artists. However, the majority of artists working in a two-dimensional format still use canvas as their main support. Much of the research into the potential problems with modern paints has focused on the use of industrial paints as part of the design layer, whether it has been applied directly onto the canvas or on top of a priming layer. In modern and contemporary works, there has been very little discussion about the role of the canvas or the priming and the possible influences these might have on the longevity of the work and observed mechanical cracks or delamination.

This paper focuses on the properties of artists' alkyd and acrylic primers. It describes how their physical behavior is altered when used in combination with oil, alkyd, and acrylic paints. The research has two aims: first, to investigate layered structures as free films and on canvas, and second, to understand how the mechanical properties of each layer and the adhesion between them affect the behavior of combined layers. This work forms part of the author's continuing research into the applicable methods of measuring interfacial interactions of artists' materials (e.g., peel and shear forces, adhesion, and delamination), with the long-term objectives of predicting problems and finding the most appropriate approaches to mitigate them.

The choice of paints for testing was based on those paints that are most readily available commercially and are among the best selling at the main art suppliers in London for students and professionals. The primers tested were Spectrum Thixotropic Alkyd, a Winsor & Newton alkyd, Golden Acrylic Gesso, and Roberson Oil Primer and Acrylic (table 1). The top paint layers consisted of Michael Harding Artists oils, Liquitex acrylics, Golden acrylics, and Winsor & Newton Griffin alkyds (table 2).

Table 1 Primer samples tested.

Primer Brand and Name	Pigment	Binder ^a	Extender ^a	Manufacturer's Recommended Use
Golden Gesso Primer	TiO ₂	p(BA/MMA) acrylic	Silica	Priming all surfaces for oil and acrylic paint
Winsor & Newton Oil Painting Primer	TiO ₂	Alkyd	Aluminum silicate	Priming all surfaces for oil and alkyd
Spectrum Thixotropic Alkyd	TiO ₂	Alkyd	None detected	Priming all surfaces for oil and alkyd
Roberson Oil Primer	TiO ₂	Modified oil alkyd	Aluminum silicate	Priming canvas and wood for oil
Roberson Acrylic Primer	TiO ₂	p(BA/MMA) acrylic	Calcium carbonate	Priming all surfaces for oil, acrylic, and tempera

^a Identified by FTIR.

Table 2 Paint samples tested.

Artist Paint	Stated Pigment	Media
Liquitex High Viscosity	Cadmium selenosulfide (red)	Acrylic emulsion
Liquitex High Viscosity	Copper phthalocyanine (blue)	Acrylic emulsion
Golden Heavy Body	Cadmium red	Acrylic emulsion
Golden Heavy Body	Phthalocyanine blue	Acrylic emulsion
Winsor & Newton Finity	Cadmium red	Acrylic emulsion
Winsor & Newton Finity	Phthalocyanine blue	Acrylic emulsion
Winsor & Newton Griffin	Cadmium sulfoselenide (red)	Long-oil modified alkyd (extender dolomite ^a)
Winsor & Newton Griffin	Copper phthalocyanine (blue)	Long-oil modified alkyd (extender dolomite ^a)
Michael Harding Artists	Cadmium sulfoselenide (red)	Acid-refined linseed oil
Michael Harding Artists	Chlorinated copper (blue)	Acid-refined linseed oil

^a Identified by FTIR.

Interestingly, those primers that are recommended for use with oil and alkyd paint layers on a variety of supports—canvas, fiberboard, wood, and metal—are alkyd based. Alkyd artists' paints formulated for the upper paint layers are often used by artists because of their short drying times, and sometimes as a method to block-in the design on top of the primer before returning to oil paint for the final design layers. Both alkyd and oil media are known to become brittle with age, and hence if they are used together on a canvas support, which can undergo large deformations, there is a substantial possibility of cracking in both preparation and design layers.

Sample Preparation

The oil, alkyd, and acrylic primings were prepared with subsequent paint layers of phthalocyanine blue and cadmium red

in oil, acrylic, and alkyd media. The priming and paint layers were prepared as composites on canvas and as free films.

Free films were cast onto polyester sheets, and composites were prepared on stretched 12 ounce cotton duck using a paint film applicator. The priming and paint layers were applied at thicknesses of 100 and 200 microns, respectively. The samples were left to dry for six days in ambient conditions, after which free films were produced by peeling the polyester sheet away from the paint film and the composites on canvas were removed from their stretchers. Both were cut into 25 × 150 mm strips.

In addition, a previous set of samples had been prepared on stretched canvas, with the layers applied by brush in accordance with the manufacturer's instructions. The crack initiation results only from these earlier samples are reported in this paper. The full results from that work are reported elsewhere (Gregg 2002; Young et al. 2004).

Investigating the mechanical properties of paints necessitates an artificial aging program to evaluate their long-term properties. This is especially true where curing or aging leads to cross-linking or increased crystallinity of the molecular structure. These changes are likely to cause important changes to the macro-mechanical properties of the materials. For the films on canvas, half of the samples were aged in the dark as controls, while the other half underwent thermal and light aging (60° C for 91 days, of which 30 days included exposure to 14,000 lux). For the free films, only thermal aging was undertaken. Three sets were aged at 60° C and 55% relative humidity (RH). One set was the control and the other two were aged for 50 and 122 days, respectively. All samples were preconditioned for 72 hours at 55% RH before testing.

The data for the 122-day thermal aging are what is considered in this paper. This aging regime was chosen because it enabled a direct comparison with data from research into the mechanical properties of traditional nineteenth-century oil grounds (Carr et al. 2003).

Tests

The interfacial interaction between the layers of a painting depends upon stiffness, strength, flexibility, and adhesion. In relation to canvas paintings, these terms can be understood as follows: *Stiffness* relates to how taut a painting is when tensioned. *Ultimate tensile strength* (UTS) is the resistance to fracture under tension. Both properties are measured by tensile testing. *Flexibility* is the ability to bend without fracture; it was tested using a mandrel test (Bend Test BS 3900) for paint and varnishes, and for fabric by determining the bending length and flexural rigidity using test BS 3356:1990. *Adhesion* is the resistance to delamination between layers; it was tested by Cross-Hatch BS EN 3900-E6/Pull-Off BS EN 24624.¹

Tensile testing was performed on an Instron 4301 at a speed of 5 mm/minute at 20° C ± 2° C and 55% RH ± 2%. Sample size was the same for free films and composites. Films were tested to 20% strain or to their UTS, whichever occurred first. Composites were tested to UTS. For the canvas composite samples, the strain at which cracks first appeared was recorded as the crack initiation (CI), based on careful observations during the testing (fig. 1).

The mandrel tests used a rig consisting of metal rods (mandrels) with diameters from 1 to 23 mm. Each sample was bent around the rods to an angle of 180 degrees for 2 seconds with the primer layer inside. Samples were deemed to have failed at the largest diameter at which cracking occurred. If a

sample had not cracked on the mandrels, it was subjected to a 180-degree fold test. The test procedure was to fold the sample back on itself in one direction and then in the other direction repeatedly for up to 100 folds or until failure, whichever occurred first. Because the maximum tensile and compressive strains this test exerts are on the free surfaces, cracking was assessed by visual inspection for a surface crack in either the primer or pigmented layer. From the previous tests it had been found that larger-diameter rods resulted in very few failures and hence there was no discrimination between samples. Further mandrel tests and 180-degree fold tests were repeated on the samples after an additional two years of natural aging with rod diameters of 1–6 mm.

Adhesion tests were performed using the cross-hatch method. The two-layer free films were adhered to a flat steel plate with Permabond E32A8B and left to cure for 24 hours. The upper paint layer was then cut into small squares using a tool with serrated teeth equally spaced 2 mm apart. This method reduces the lateral bonding within the layer and promotes delamination between the layers. The degree of delamination of the layer is classified by a visual assessment of the degree of paint loss from each square compared to a standard. The pull-off test was used for comparison of two sample types. The test consisted of a free film sample with primer and paint layers adhered with Permabond E32A8B onto two stubs, which were then coupled to a tensile tester. Tensile testing was performed on an Instron 4301 at a speed of 5 mm/minute at 20° C ± 2° C and 55% RH ± 2%. The test measured the tensile force required to separate the two paint layers.

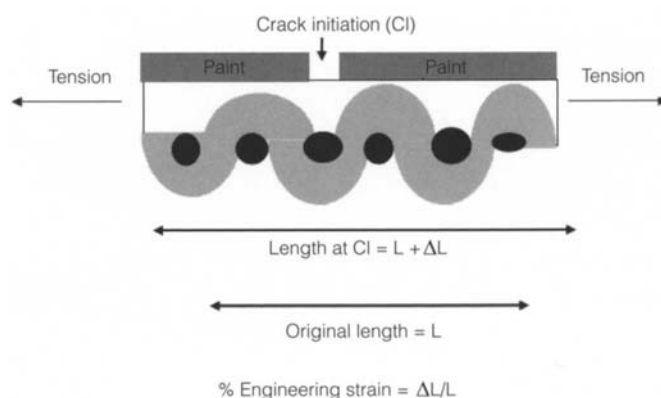


FIGURE 1 Crack initiation.

Results

This paper concentrates on the analysis of the results from the free films with a red paint layer and compares it to data from previous testing of the same layer structure on cotton duck canvas, the full results of which are published elsewhere (Young et al. 2004). Stress and strain were calculated from the load extension data of each sample, using the initial gauge length and the measured thickness.³ For most external forces exerted on a stretched painting, typically the strain experienced will be on the order of 0.1–10%. In this strain range, calculation of engineering strain is appropriate (see fig. 1). The results are plotted in figures 2–6, grouped by the primer. As would be expected from visco-elastic materials, there is no clearly defined linear region from which to calculate the elastic modulus.³ Therefore, the secant modulus at 0.5% and 5.0% strain⁴ has been calculated from the stress-strain plots (summarized in table 3). The percentage of strain at which crack initiation occurs for the composite samples and the mandrel and fold test results for the free films are also summarized in table 3. (For clarity, all paint film layers that are not primer are described below by their media, rather than by manufacturer, as there is only one in each case.)

Acrylic Gesso–Acrylic Paint Samples

Comparison of the secant modulus at 5% strain shows that Golden Gesso Primer (fig. 2) and Roberson Acrylic Primer (fig. 3), with an acrylic paint layer, had the lowest stiffness of all the paint combinations, in the range 0.02–0.04 MPa. After aging, there appears to be a very slight increase in stiffness, but this change is within the error of the experimental measurement. For all these samples, cracks were not observed after mandrel tests or after 100 folds of a fold test. Thus, it is considered that a significant change in flexibility did not occur after aging. This result is consistent with the composite sample results, for the same paint combinations, where crack initiation did not occur before failure of the complete composite. It is worth noting that the cotton duck canvas without primer or paint layers typically exhibits a strain of approximately 25% before failure. This sets an upper limit on the percentage strain for crack initiation.

Acrylic Gesso–Oil Paint Samples

The results for the unaged Golden Gesso with an oil paint layer are similar, with a secant modulus at 5% strain of 0.03 MPa, no failure after 100 folds, and no crack initiation before composite

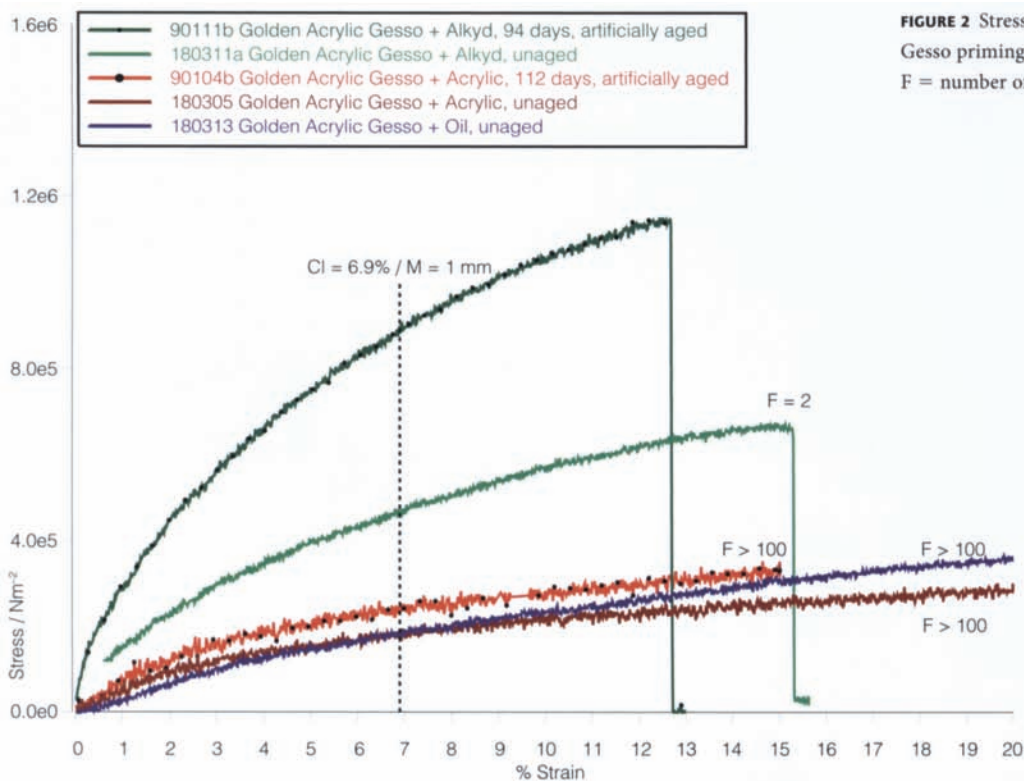


FIGURE 2 Stress-strain curves for Golden Gesso priming plus one paint layer. F = number of folds.

Table 3 Testing results.

Priming Layer	Paint Layer	Thermal Aging (days)	Secant Modulus (MPa) at 0.5% Strain (error ± 0.03 MPa)	Secant Modulus (MPa) at 5.0% Strain (error ± 0.02 MPa)	Crack Initiation Strain (error $\pm 1\%$)	Mandrel Failure Diameter (mm)	Folds to Failure
Golden Acrylic Gesso	Winsor & Newton Griffin Alkyd	94	0.36	0.15	6.9%	1	N/A
Golden Acrylic Gesso	Winsor & Newton Griffin Alkyd	None	0.21	0.08	None	No failure	2
Golden Acrylic Gesso	Liquitex Acrylic	112	0.11	0.04	None	No failure	>100
Golden Acrylic Gesso	Liquitex Acrylic	None	0.06	0.03	None	No failure	>100
Golden Acrylic Gesso	Michael Harding Artists Oil	112; remains attached to substrate	Not tested	Not tested	Not tested	Not tested	Not tested
Golden Acrylic Gesso	Michael Harding Artists Oil	None	Insufficient data above baseline	0.03	None	No failure	>100
Roberson Acrylic Primer	Winsor & Newton Griffin Alkyd	94	0.08	0.11	1.4%	No failure	1
Roberson Acrylic Primer	Winsor & Newton Griffin Alkyd	None	0.08	0.09	8.0%	No failure	1
Roberson Acrylic Primer	Liquitex Acrylic	112	Insufficient data above baseline	0.04	None	No failure	>100
Roberson Acrylic Primer	Liquitex Acrylic	None	Insufficient data above baseline	0.02	None	No failure	>100
Winsor & Newton Alkyd Primer	Winsor & Newton Griffin Alkyd	64	1.06	Failed at 4% strain	1.8%	1	N/A
Winsor & Newton Alkyd Primer	Winsor & Newton Griffin Alkyd	None	0.24	0.17	1.9%	4	N/A
Winsor & Newton Alkyd Primer	Liquitex Acrylic	112	Insufficient data above baseline	0.14	1.4%	Not tested	N/A
Winsor & Newton Alkyd Primer	Liquitex Acrylic	None	Insufficient data above baseline	0.05	19.0%	No failure	3
Spectrum Alkyd Primer	Winsor & Newton Griffin Alkyd	94	0.07	0.18	3.3%	Not tested	N/A
Spectrum Alkyd Primer	Winsor & Newton Griffin Alkyd	None	0.05	0.01	8.0%	No failure	1
Spectrum Alkyd Primer	Liquitex Acrylic	112	0.17	0.08	3.3%	4	N/A
Spectrum Alkyd Primer	Liquitex Acrylic	None	0.05	0.05	None	No failure	2
Spectrum Alkyd Primer	Michael Harding Artists Oil	82	Insufficient data above baseline	0.4	9.4%	1.5	N/A
Spectrum Alkyd Primer	Michael Harding Artists Oil	None	Insufficient data above baseline	0.1	11.6%	1.5	N/A

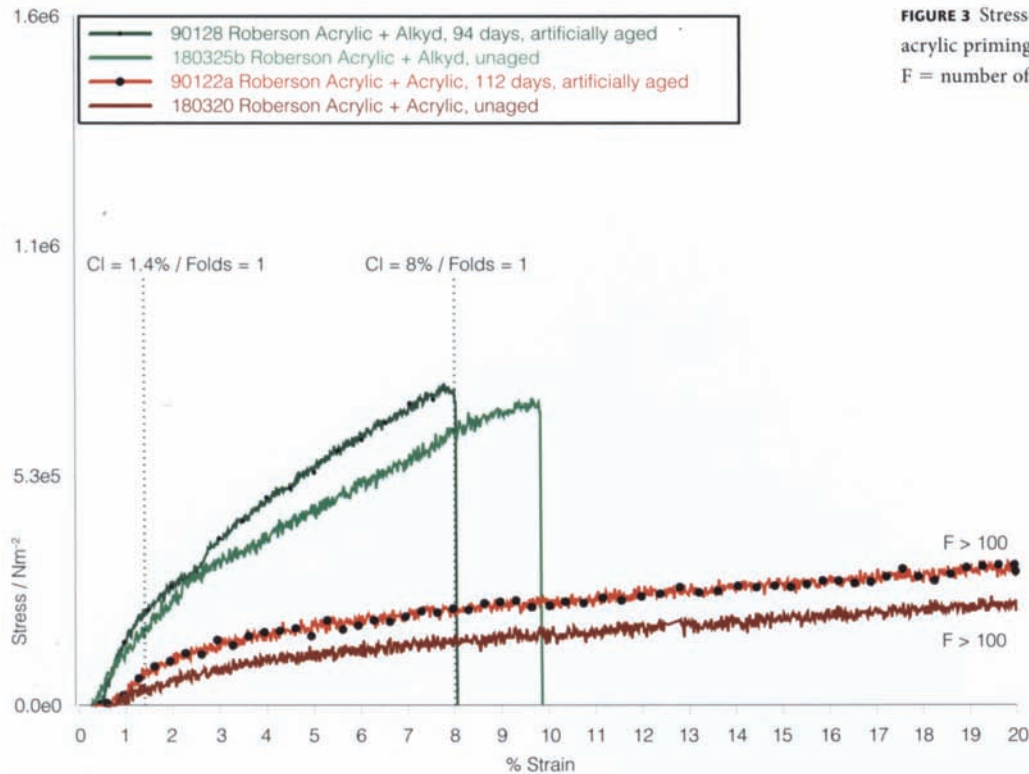


FIGURE 3 Stress-strain curves for Roberson acrylic priming plus one paint layer. F = number of folds.

failure. This would be expected, because at the time of testing (twenty-one days and two years), the oil paint film can still be considered to be “young,” and therefore not fully cross-linked, and when young, oil paint’s stress-strain behavior is similar to that of acrylic films. Unfortunately, the artificially aged acrylic primer–oil films could not be detached from the polyester substrate (for reasons yet to be investigated), and therefore, no direct comparison could be made with aged acrylic primers with acrylic films. However, from the previous testing of the oil paint film, one would have expected the two-layer samples to have increased in stiffness and reduced in flexibility (Carr et al. 2003).

Acrylic Gesso–Alkyd Paint Samples

For the samples of alkyd paint layers on Golden Gesso, there was a doubling in stiffness, to 0.08 MPa, when compared to the acrylic, and a further increase after aging to 0.15 MPa. At 0.5% strain, a similar trend can be seen (fig. 2). Strain to failure of the aged sample was at 12.7% strain. Crack initiation at 6.9% strain occurred for the equivalent canvas composite sample. Strain to failure of the unaged sample was at 15.4% strain. Thus, although the acrylic primer can withstand over 25% strain without failure, the addition of the alkyd layer causes

premature failure. The unaged alkyd sample failed after two folds of a fold test; the aged sample failed at a diameter of 1 mm on the mandrel tester. Thus, as expected, significant increase in stiffness and reduction in flexibility had occurred with the addition of an alkyd layer.

For the Roberson Acrylic Primer (fig. 3), the addition of the alkyd paint did not cause a change in stiffness after aging (0.08 MPa at 0.5% strain). At 5% strain, an increase in stiffness, to 0.09 MPa, did occur when compared to the acrylic (0.02 MPa), and a small increase occurred after aging (0.11 MPa). But it can be seen from the curve for the aged acrylic-alkyd sample in figure 3 that some failure in the sample is occurring at approximately 2.5% strain, where a dip in the curve occurs, and thus the stiffness at 5% corresponds to a sample with a cracked top coat. This correlates with the observed crack initiation of the canvas composite at 1.4% strain. Although no obvious dip occurs for the unaged sample, the strain to failure is 10%, which is close to the observed crack initiation value for the composite at 8% strain. The alkyd layer has caused premature failure in the acrylic layer, which has reduced the strain to failure. Interestingly, this alkyd paint layer has had a greater influence on the Roberson primer than on the Golden Gesso Primer, which could be the result of

greater interfacial interaction and therefore better adhesion between the paint and the Roberson primer. Both unaged and aged samples failed after one fold of the fold test. Overall, the Roberson Acrylic Primer–alkyd combination produces a less extensible paint film than the Golden Gesso equivalent. This could be caused by higher levels of calcium carbonate extender, higher pigment volume concentration, and greater interfacial interaction between the two layers.

Alkyd Primer–Alkyd/Acrylic/Oil Samples

One can see from comparison of the curves for Winsor & Newton alkyd primer (fig. 4) and Spectrum alkyd primer (fig. 5), both of which had a Winsor & Newton alkyd paint layer on top, that some failure in the samples has occurred at approximately 1–3% strain, where dips or inflections in the gradient occur. Thus, it is very hard to discern a valid place to compare the secant modulus. Nevertheless, if one assumes failure has not occurred before 1%, then it can be seen with reference to figures 4–5 and table 3 that Winsor & Newton alkyd primer with a Winsor & Newton alkyd paint layer results in the stiffest combination, at 0.5% strain with moduli of 0.24 MPa unaged and 1.06 MPa aged. Surprisingly, the Spectrum alkyd primer has a stiffness (0.05 MPa) close to that of the acrylic

primers when unaged. This could be explained by the fact that no extender was detected in the primer by Fourier transform infrared (FTIR) analysis.⁵ Once the primer is aged, the stiffness increases to 0.07 MPa, which is not significant, but the reduced strain to failure and observed cracking implies this value is inaccurate. The observed crack initiation for the Winsor & Newton alkyd-alkyd and Winsor & Newton alkyd-acrylic canvas composites are at 1.4% and 1.8%, respectively, which correlates very well with the observed inflections of the free-film curves at 1.4% and 1.6%, respectively (fig. 4). The aged free films failed after mandrel tests at a diameter of 1 mm for Winsor & Newton alkyd-alkyd and 4 mm for Winsor & Newton alkyd-acrylic and Spectrum alkyd-acrylic. Unaged equivalents all failed after one fold of the fold test. The observed crack initiation for both the Spectrum alkyd-alkyd and Spectrum alkyd-acrylic canvas composites is at 3.3%, this correlates with the observed inflections of the free film curves at 0.8% and 3.2%, respectively (fig. 5).

The curves shown in figure 6 compare samples with oil and acrylic layers on top of Spectrum alkyd primer. As before, the stress-strain curve for the unaged oil is similar to that of the acrylic film. However, for the aged sample, the stiffness at 5% strain is 0.1 MPa, which is significantly different than for

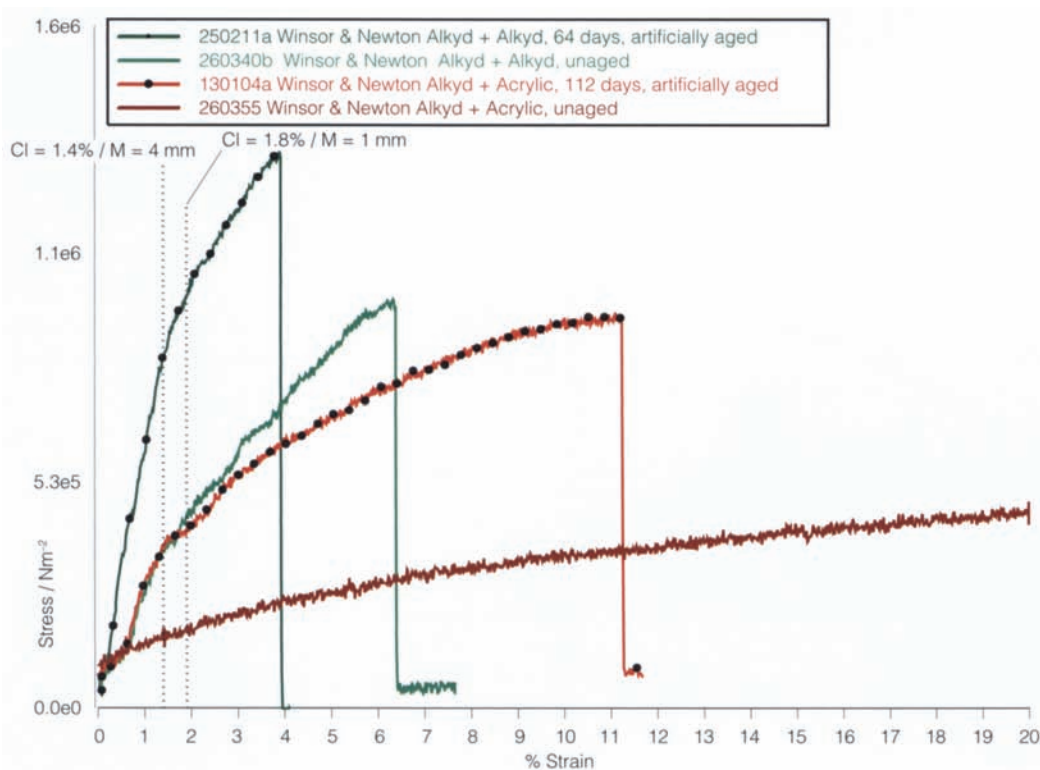


FIGURE 4 Stress-strain curves for Winsor & Newton alkyd priming plus one paint layer. F = number of folds.

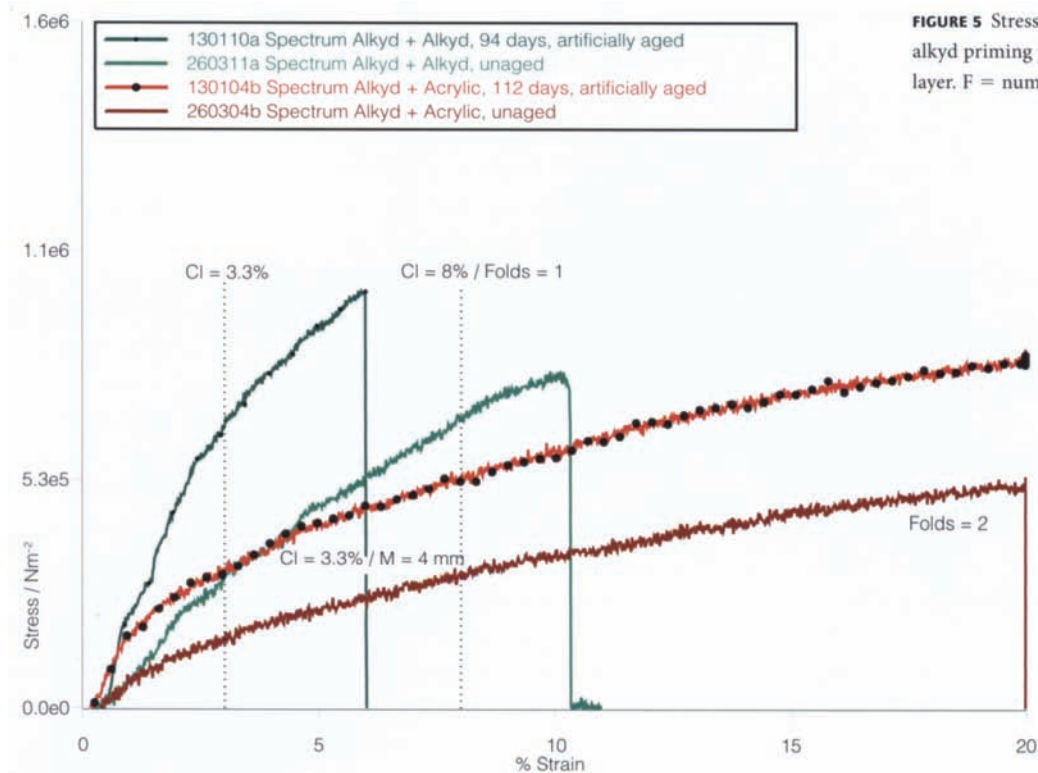


FIGURE 5 Stress-strain curves for Spectrum alkyd priming plus alkyd or acrylic paint layer. F = number of folds.

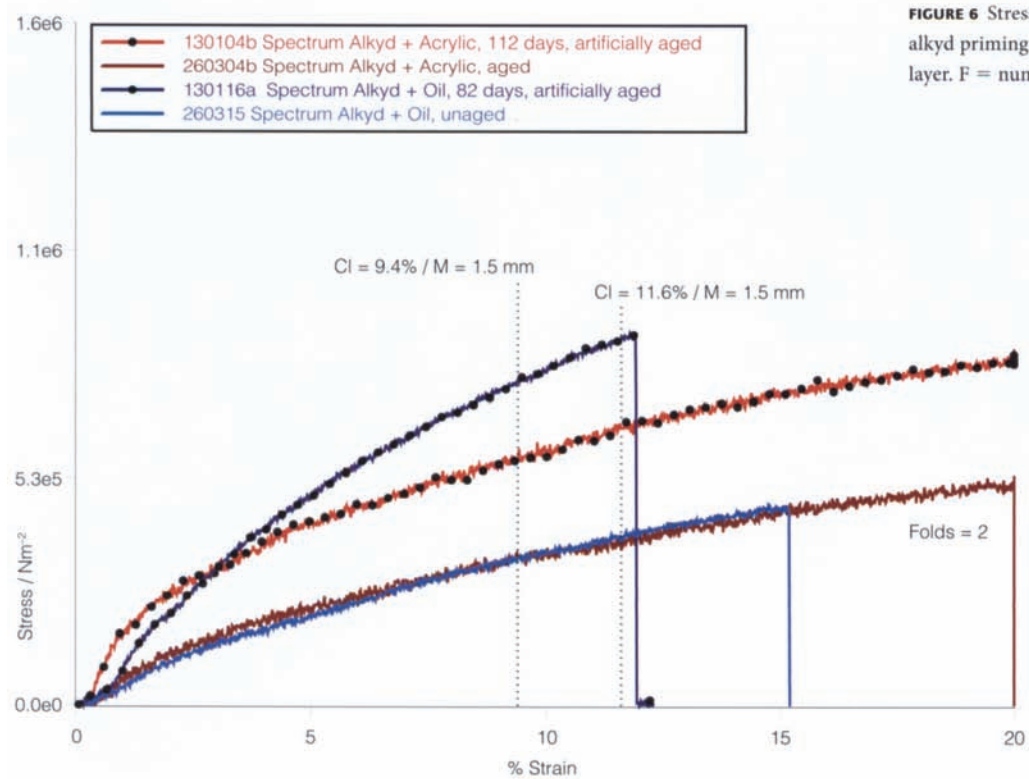


FIGURE 6 Stress-strain curves for Spectrum alkyd priming plus acrylic or oil paint layer. F = number of folds.

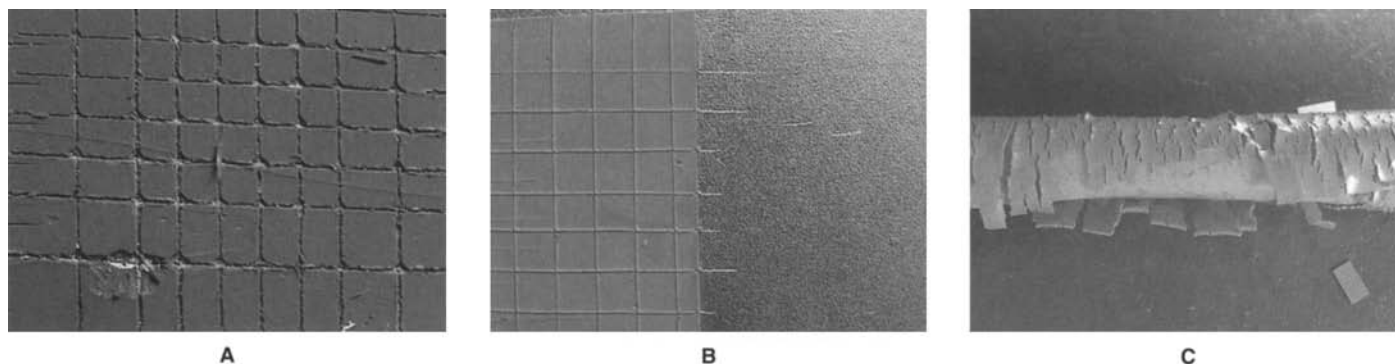


FIGURE 7 (A) Crosshatch adhesion, unaged oil-acrylic.
 (B) Crosshatch adhesion, unaged acrylic-acrylic.
 (C) Tensile testing, unaged oil-acrylic.

an acrylic layer. The acrylic-alkyd primer combination went beyond 20% before the complete composite failed, whereas the oil-alkyd primer failed at 12% (aged) and 15.5% (unaged), which correlates well with the crack initiation for the canvas composites of 9.4% strain and 11.6% strain, respectively.

Adhesion Tests

The results from the adhesion tests (two examples are shown in figures 7A and B) were unsatisfactory, as in all but a few cases there was no significant difference in the crosshatch results. The test is difficult to reproduce systematically. The oil paint films were the only ones to show any difference in the degree of loss of paint, whether unaged or aged. This difference was consistent with observations from the tensile testing of these films, where peeling away of the oil film from the primer occurred in the unaged samples (fig. 7C). This behavior was also observed for the composite samples. The pull-off tests were also inconclusive. Bubbles or unevenness in the films or in the adhesion to the stubs led to premature failure. At this stage more testing is continuing to find an experimental procedure that is reproducible. So far, the mandrel bend tests have given a greater understanding of the adhesion between layers, as this test encompasses adhesion, flexibility, and extensibility.

Discussion

There is no obvious incompatibility when combining layers of the different media tested, such as separation of media or stress drying cracks. Acrylic films have the lowest stiffness and least tendency to fracture. A significant change in proper-

ties was not found for aged acrylic emulsions. They survived multiple bending and high strains with eventual failure above 25% strain (above the breaking strain of the canvas), resulting in ductile fracture.

Initially, alkyd primers are not significantly stiffer than acrylic primers, but they are less flexible. They do increase in stiffness with aging, and aging reduces the strain to failure of the acrylic paint layer. Significant increase in stiffness and reduction in flexibility occur with the addition of an alkyd layer. As would be expected, acrylic-alkyd films exhibit brittle fracture at low strains when aged. Reduction in stiffness resulting from fracture in the alkyd or oil layer in the free films corresponds to cracking in the same paint layer of the canvas composite, at approximately the same strain. The load is then shared between the cracked and complete extensible acrylic layer—in all cases premature fracture on the acrylic layers occurs when free films are tested. These fractures occur at relatively low strains and are not visible if there is an acrylic paint layer on top; thus they present an underlying problem.

“Young” oil paint films have stress-strain behavior similar to that of acrylic films. It is suggested that delamination due to poor adhesion with an alkyd or acrylic primer might present more of a problem when they are in this stage of maturation. Once they have aged, oil paint films cause premature failure of the acrylic primer. This correlates with the adhesion tests, which show the unaged paint films to have relatively poor adhesion. However, adhesion improves as the film matures, thus increasing the interfacial interaction and tendency to promote and propagate fractures.

Conclusions

Bend tests in conjunction with tensile tests have been found to be more useful than cross-hatch tests for understanding the interfacial interaction of these films because they encompass adhesion, flexibility, and extensibility. They highlight combinations of materials that are particularly vulnerable and require further and detailed analysis. Also, the tests replicate more closely a painting on a stretcher, for instance, the bending of the tacking margin around a stretcher member. Visual observation during testing was invaluable for understanding the mechanisms of failure and cannot be underestimated. Such observation also is the crucial link with the real paintings encountered by conservators.

The research is continuing with development of the pull-off adhesion tests and steady-state peel testing. The BS adhesion tests are essentially performance tests for a defined set of samples. Other adhesion tests, such as the tapered double cantilever beam (TDCB) test (Moore, Pavan, and Williams 2001), enable the data to be compared with adhesion theory and, although these tests do not represent the real situation, they allow predictions to be made under a defined set of conditions. An investigation into their applicability for conservation mechanics is under way.

Although not directly measured in these tests, it is clear that creep in the acrylics at room temperature and brittle fracture at low temperatures are more of an issue than straining or bending of the films. However, the next phase of the research will entail characterization of a greater range of artists' acrylics and comparison with household acrylic emulsions as composite layers to corroborate the findings reported in this paper. Similarly, a comparison of artist alkyd primers and household alkyds used as artists' materials will be made. In addition, an investigation will be made into the change of properties and degradation of the canvas when acrylic emulsions of differing formulations and dilutions are used directly on the canvas.

Acknowledgments

The author would like to thank Rebecca Gregg, Tom Learner, Maria Charalambides, and Roy Moore.

Notes

- 1 The fold tests did not follow a standard.
- 2 Stress = Force divided by the loading area of the sample. Strain = Change in length of the sample under a load, normally expressed as a percentage of the original length.
- 3 The elastic modulus is a ratio of stress, within proportional limit, to corresponding strain.
- 4 The secant modulus is not restricted within the proportional limit; it is the slope of a line from the origin to a specified point on the stress-strain curve:
 $1 \text{ MPa} = 1 \times 10^6 \text{ Nm}^{-2}$
- 5 FTIR was carried out on a Nicolet Avatar 360 FTIR spectrometer using a diamond cell placed in a Spectra Tech IR plan microscope. Sixty-four scans were performed at 4 cm^{-1} resolution.

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Solvent Action on Dispersion Paint Systems and the Influence on the Morphology—Changes and Destruction of the Latex Microstructure

Stefan Zumbühl, Francesca Attanasio, Nadim C. Scherrer, Wolfgang Müller, Nicolai Fenners, and Walter Caseri

Abstract: Binding systems based on aqueous dispersions produce heterogeneous microstructures on film formation. Depending on the system and additives, the original morphology of latex particles can still be recognized after the drying process, despite interdiffusion of the polymer chains. This leads to characteristic physical properties, including a potentially high sensitivity to solvents. The current work tested the action of fifty solvents on three commercially available aqueous dispersion paint systems sold as artists' paint colors. The systems tested are based on acrylic copolymer, acrylic/styrene-copolymer, and polyvinyl acetate/versatate-copolymer components. An immersion-swelling test was applied to quantify the time-dependent swelling capacity. Extractable components were qualified by Fourier transform infrared (FTIR) analysis and quantified by gravimetry. Particular emphasis was given to structural changes within the film as well as surface morphology, documented with scanning electron microscopy (SEM) on cryo-prepared samples. The degree of latex destruction was quantified by a light-scattering technique. Polymer composition and type of additives strongly influence the sensitivity of paint films to solvents. A lot of solvents largely destroy the latex structure, leading to irreversible changes in optical and mechanical properties. Extraction of various mobile components occurs within several discriminate sections along the polarity scale, and thus only specific and narrow windows of selected solvents can be regarded as suitable for conservation treatments. These were evaluated for each of the systems investigated.

Introduction

Acrylic and other dispersion binding systems are widely used in modern paints, and conservators are aware of their high

degree of sensitivity to solvents. The film formation process of these paints has an important influence on their resulting physical and mechanical properties (Provdor, Winnik, and Urban 1996), due to the production of heteromorphic microstructures. Despite the interdiffusion of polymer chains, part of the original latex structure is retained in the dried film, with a continuous network of additives between the compact polymer spheres, and this is primarily responsible for their high sensitivity to solvents. In general, the film properties of latex paints are affected not only by the nature of the polymer, but also by the complex system of binder and additives, as well as film preparation and conditioning. These circumstances generate new demands on techniques for the conservation of acrylic paints (Jablonski et al. 2003). In this context, the action of fifty solvents on aqueous dispersions paint systems was investigated. Focus was given to three types of commercially available artists' paint. Several aspects of the solvent action were investigated, such as swelling capacity, leaching effects, morphological changes in the film core, and modification of the surface structure, as well as the mechanical and physical consequences for paint films treated with solvents.

Film Formation of Latex Binder

Latex paints are complex systems containing several additives and processing aids to optimize the film formation process (Wang et al. 1992; Waters 1997; Kittel 1998; Zohorehvand 2001; Jablonski et al. 2003). The principle of film formation of latex binders is not comparable to that of solution systems. According to the literature, the drying and film formation process can be described by a simplified model with three distinct stages (Eckersley and Rudin 1990; Richard 1997; Kittel 1998): In the

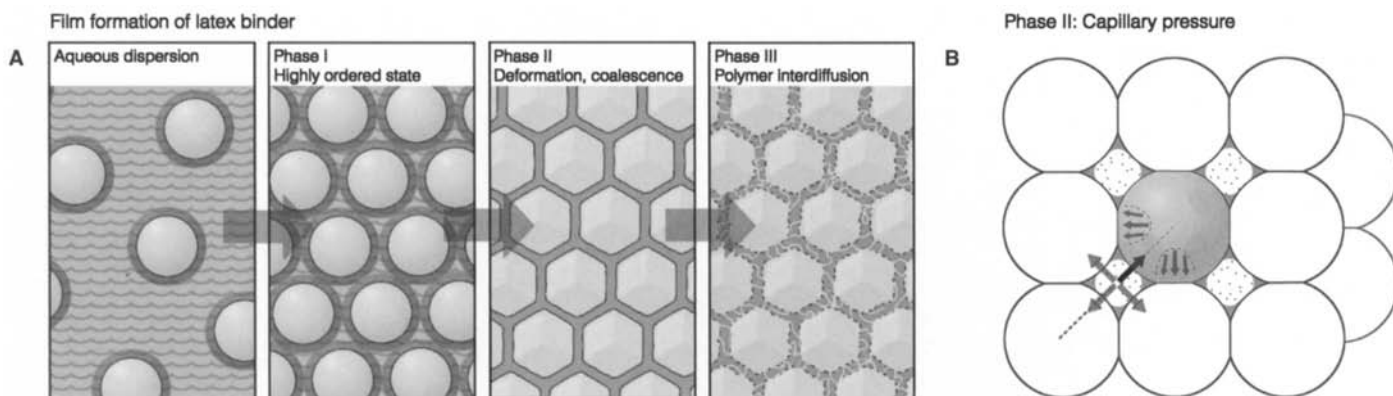


FIGURE 1 (A) In a simplified model, the drying and film formation process can be described by three distinct stages. (B) One of the driving forces is the capillary pressure leading to deformation of the particles and subsequent coalescence. The interdiffusion of polymer chains between particles leads to the stabilization of the system. Based on the film formation process of aqueous dispersions, these binding systems lead to heteromorphic microstructures.

wet state, the solid latex particles are dispersed in water and stabilized by a surrounding layer of surfactants. Electrostatic and steric forces between the charged polymer and the end-chain groups of surfactants keep the spheric particles apart and stabilized in the surrounding aqueous media. These forces are overcome by the evaporation process of the water phase. Film formation is initiated by the coalescence of individual latex particles (Kittel 1998) (fig. 1).

During the first phase of the drying process, water evaporates from the surface, which leads to a concentration and compaction of latex particles. This continues until the polymer fraction has reached about 60–70 percent volume, at which point the particles are in a highly ordered state (Verduyn et al. 2001). The second phase of film formation is initiated by the irreversible coalescence of individual latex particles and accompanied by a distinct reduction of the overall rate of evaporation (Eckersley and Rudin 1996). The drying process during this phase has important consequences on the resulting film, due to the limited time remaining to pack the spherical particles into an ordered structure prior to flocculation.

From then on, compaction continues with particle deformation and the filling of interparticular capillary channels (Dobler and Holl 1996). Different models have been proposed

to describe this process (Dillon, Matheson, and Bradford 1951; Brown 1956; Voyutskii 1958; Bradford and Vanderhoff 1972; Kendall and Padget 1982), but extended research during the 1980s and 1990s arrived at a combination of different factors (Provdar, Winnik, and Urban 1996). One of the driving forces is the polymer-water interfacial tension, leading to the deformation of particles during the drying process. The coalescence arises from a disequilibrium, whereby the capillary forces must overcome the forces of resistance to deformation (Nicholson and Wasson 1990) (fig. 1B). The capillary force is strongly influenced by the particle size and the surface tension of these lattices (Vanderhoff et al. 1966; Vanderhoff 1970; Armstrong and Wright 1992). In conclusion, the theory of coalescence considers film formation as a process whereby physical forces hold the deformed particles together (Voyutskii 1958, 1963). The third phase is initiated by the formation of a continuous film. This process is dependent on mutual interdiffusion of polymer chains between the particles (Kim and Wool 1983; Chevalier et al. 1992; Zhao and Heckmann 1996). The intermigration is primarily dependent on the nature of the polymer structure and the orientation of the chains (Hahn et al. 1986; Hahn, Ley, and Oberthür 1988; Yoo et al. 1990, 1991). In summary, the sintering or capillary processes, as well as the polymer chain interdiffusion, influence the specific coalescence mechanisms. The participation or dominance of either of those processes consequently depends on various factors.

The development of a homogeneous film from latex is a strongly idealized view. Since the glass transition temperature (T_g) of the polymer is so near room temperature, the interdiffusion of polymer chains is strongly dependent on volatile coalescing aids (Wang and Winnik 1991; Kittel 1998), with other additives effectively working against film formation (Holl et al. 2001). In practice, the resulting polymer film has a heteromor-

phic microstructure, with a continuous network of additives separating the latex particles still retained after film formation (Distler and Kanig 1978; Kast 1985; Zhao and Heckman 1996). This observable fact has important consequences regarding the material properties and the film's behavior on interaction with solvents.

Experimental Setup

Several aspects characterizing the action of fifty solvents on aqueous dispersions paint systems were investigated. Focus was put on three commercially available artists' paint colors based on an acrylic copolymer (Schmincke PRIMAcryl), an acrylic-styrene copolymer (Schmincke Akademie Acryl), and a polyvinyl-versatate copolymer (Lefranc & Bourgeois Flashe) with different proportions of latex to additives (refer to the appendix to this paper for details).

Under specific conditions the swelling capacity of a material can be an idealized indicator of the degree of solvent interaction. It is therefore a useful tool to describe the solute-specific interactions. Although the assumptions made are not fully adequate for the investigated systems, the swelling behavior still delivers important information to the conservator in practice. In this context, sample films of the three commercial paint media were subjected to immersion, and their swelling capacity was plotted against time. The test applied followed the principle described by Phenix (2002) with minor modifications (Zumbühl 2005). The morphological changes induced by immersion in solvents were visualized by scanning electron microscopy (SEM) on cryoprepared samples. The freeze-fracture method was chosen to investigate the internal structure of a dried film (Roulstone et al. 1991; Wang et al. 1992), whereby the paint samples were cooled in a liquid nitrogen atmosphere and broken under specific conditions. The uranyl-acetate contrasting method (Kanig and Neff 1975; Distler and Kanig 1978) was applied to selectively mark the additives and make them visible in back-scattered electron (BSE) mode. This approach enabled the investigation of the migration and diffusion of additives into the polymeric material, induced by solvent interaction. The total light scattering (TLS) method was applied to investigate the degree of destruction qualitatively. Furthermore, component extracts of the three paint systems were characterized by Fourier transform infrared (FTIR) spectrometry and quantified by gravimetry. Finally, the influence of solvent action on the morphology and the mechanical behavior of paint films were tested by stress-strain measurements. (Detailed information on the experimental setup is given in the appendix.)

Results

Swelling Capacity

The results from the swelling tests indicate that the swelling capacity of such paint films is enormous, exceeding the swelling capacity of an oil film by a factor of approximately ten (fig. 2A). Over a broad part of the polarity scale, the swelling volume is beyond 100 percent. Normalizing the data, it becomes evident that the investigated paint films document a high sensitivity to solvents over a broad range along the polarity scale, with maximum swelling capacities for solvents inducing strong dispersive interaction, such as chlorinated solvents, as well as polarizable molecules such as aromatics (fig. 2B). The swelling behavior is consistent with the theoretically expected solvent interaction on acrylic polymers. Solvents with minimal swelling action for both acrylic paint types can be found only near the upper and the lower ends of the polarity scale. Highly apolar solvents, such as aliphatic hydrocarbons, as well as very polar solvents, including water, seem to be the least dangerous in this context. Significant differences in the solvent sensitivity were observed for the class of alcohols (fig. 2C). Further investigations on other acrylic paint systems confirmed that the solvent sensitivity regarding alcohols varies considerably among different products, so it is not possible to infer general conclusions about this class of solvents. In contrast to the acrylic latex paint, the matte Flashe-PVAc paint reacts only with highly polar solvents. This material is sensitive to water, formamide, and methanol—all solvents with strongly associated hydrogen bonding. All other solvents, including most of the alcohols, have no swelling action on this paint film (fig. 2D).

The swelling process generally runs extremely fast in acrylics (fig. 3). Swelling begins within the first seconds of immersion, and the largest increase in volume takes place within the next thirty seconds. This behavior is clearly different from that of an oil paint film. Within the first ten seconds of immersion, the increase in volume exceeds 200 percent for the majority of solvents tested. Only the strongly apolar and strongly polar solvents at either end of the scale, including the alcohols, show moderate and slow interaction. The Akademie paint demonstrates this behavior in a much more accentuated way than the PRIMAcryl. Despite the lower swelling capacity overall, the process runs much faster in this system. These results suggest that the film quality after drying strongly influences the penetration of solvents in dried latex paint. Based on the general model of film formation, the penetration is favored in latex structures with limited

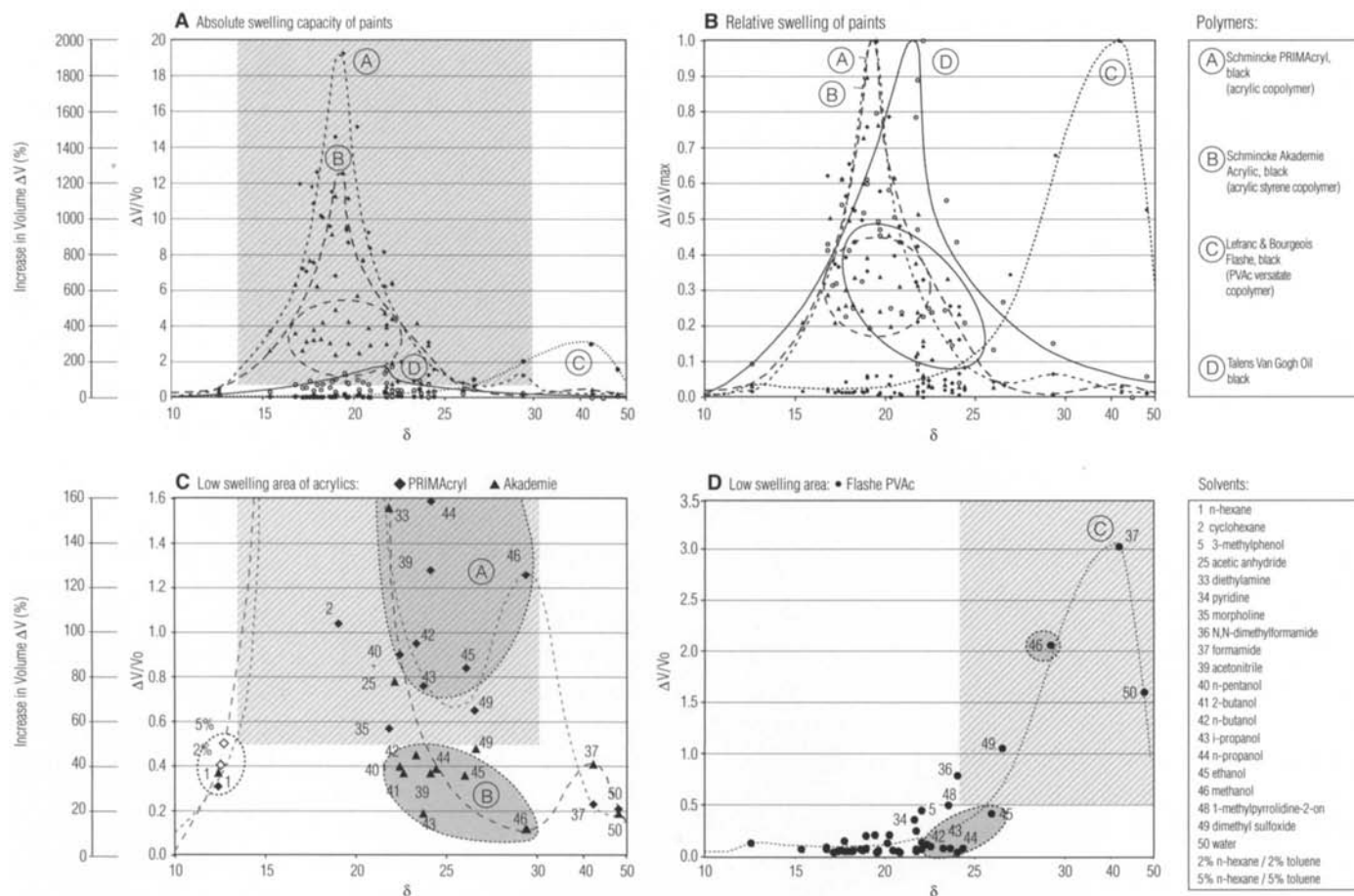


FIGURE 2 (A) The absolute swelling values of latex paint films on immersion in solvents spread along the polarity scale. (B) The relative spectral values show a high sensitivity to solvent interaction over a broad range along the polarity scale, with maximum swelling capacities for solvents inducing strong dispersive interaction. (C) and (D) Enlargement of (A) and (B), respectively, localizing potentially useful solvents with minimal swelling action. Significant differences in the solvent sensitivity were observed for the class of alcohols highlighted in the graphs.

film formation. It is highly facilitated by the interparticular network of incorporated additives, resulting in near-simultaneous swelling action throughout the microstructure. In contrast, in a well-homogenized film, the penetration propagates following a pseudo-Fickian model, similar to the classical penetration of solvents into solid material. The resultant swelling front moves from the surface into the material. There, the

penetration is strongly influenced by the nature of the polymeric material.

Changes in the Latex Microstructure

The solvent action and solvation of polymeric material leads to fundamental changes of the inner microstructure of the latex binder. SEM revealed that coalescence and homogenization are limited under normal film formation conditions, and individual particles are still clearly distinguishable after complete drying (fig. 4A). Solvent treatment by immersion for thirty seconds destroyed the latex morphology to various degrees (figs. 4B–H). In most solvents, the polymeric material of the latex particles is obviously dissolved completely (figs. 4C–G). During the subsequent evaporation process, film formation follows the classic model of dissolved systems, whereby the previous microstructure is irreversibly destroyed. This results in an amorphous and homogeneous film on complete redrying. Solvents with high evaporation pressures and low retention times are less destructive, retaining a still-recognizable

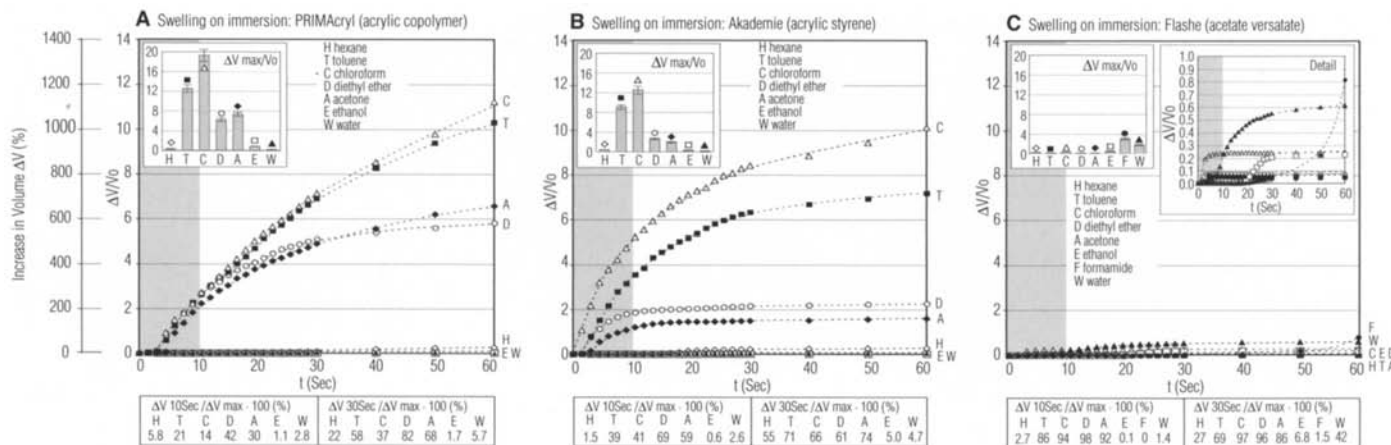


FIGURE 3 Plotting the time-dependent swelling capacity of a selection of seven solvents along the polarity scale reveals the speed of the swelling action. Within the first 5–10 seconds, an enormous swelling power was observed for most solvents.

relic latex structure. Solvent uptake within an equivalent immersion time would thus be relatively low. Nevertheless, the resulting film structure is no longer original, having been more or less destroyed, and is not comparable to the untreated reference.

Only low-swelling solvents, such as aliphatic hydrocarbons, caused no visible changes to the inner microstructure, and the character of the spherical latex particles also seems unaffected (fig. 4B). Very polar solvents at the other end of the polarity scale, such as water, do not dissolve the acrylic latex binder, and so the spherical shape of the latex particles also remains intact after aqueous treatment (fig. 4H). The solvent interaction with water is determined by the additives, particularly by the readily soluble surfactants, which include different kinds of wetting agents, stabilizing agents, and thickeners. The latex structure itself remains unaffected with these solvents. And, although the

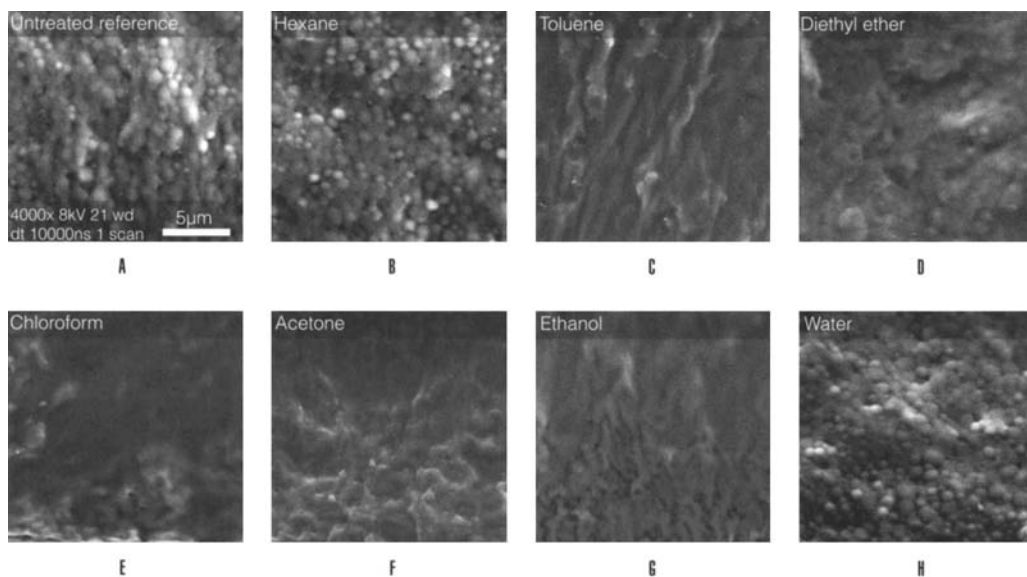


FIGURE 4 SEM images (in secondary electron mode) of freeze-fractured surfaces showing the inner microstructure of an acrylic latex film. The influence of seven solvents spread across the polarity scale is visualized, showing varying degrees of destruction of the morphological structure.

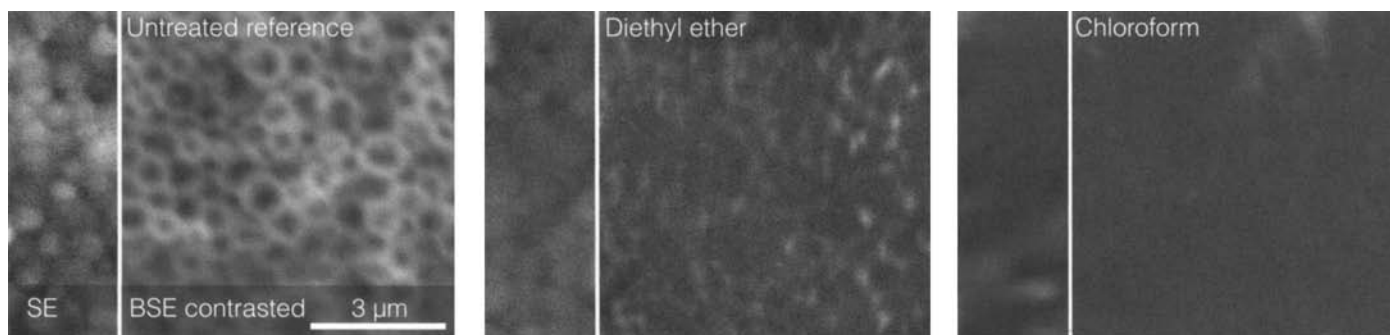


FIGURE 5 SEM-BSE images of sample sections contrasted with the uranyl-acetate method. The additives are selectively marked with uranium and thus become visible through atomic number contrast in BSE mode. In the reference sample, the additives form a continuous network filling the space between distinct and closely packed latex spheres. Diffusion of additives into the dissolved polymer material correlates with the solvating power.

structure seems packed more densely than the reference sample, this is probably the result of the partial leaching of additives that filled the network structure. Films treated with alcohols show varying degrees of destruction, but in all sample cases, the original morphology was modified to some degree.

In samples contrasted with uranyl acetate, the additives are selectively marked and can be made distinctly visible in BSE mode (fig. 5). Looking at the reference sample (no solvent treatment), it is obvious that additives fill the space between distinct latex spheres, forming a polygonal network. When the films are treated with solvents, the additives start to diffuse into the dissolved polymeric material. Depending on the solvating power, additives may become enriched in separated accumulations. Applying moderate solvents having high evaporation pressure leads to various degrees of partial destruction of the original microstructure. Treatment with powerful solvents causes the additives to disperse completely into the polymer matrix. The original structure is totally destroyed through this homogenization process.

These interpretations can be verified by the total light scattering (TLS) method (fig. 6). It is well known that latex binders have a milky appearance when rewetted, becoming transparent again on drying. This event is caused by the existence of separated spherical particles that have a different refractive index than the surrounding liquid phase. Depending on particle size, either Rayleigh or Mie diffraction occurs. TLS delivers qualitative information about the existence of distinct

latex particles within the film structure (i.e., not homogenized). Treatment with solvents, which leads to the dissolution of latex particles, results in films' remaining transparent after rewetting. Of the fifty solvents applied, only the apolar aliphatic hydrocarbon hexane had no influence on the latex structure (fig. 6B). All other solvents were highly destructive, except for some highly polar solvents.

Solvent Extraction

The leaching process in acrylic paint films runs extremely fast. After one minute of immersion time, there was no significant leaching detectable. Over a broad section across the polarity scale, polymeric material was the main constituent of analyzed leachates (fig. 7). But even in solvents with low swelling capacities, several components were leached out in minor quantities. The aliphatic hydrocarbon hexane, for example, dissolved a saturated hydrocarbon component, possibly a colloid stabilizer from the binding system. Water dissolved various additives, such as surfactants, as well as thickeners and processing aids. For the Akademie paint (fig. 7B), similar results can be observed, while the amount of leached components is reduced when compared with the PRIMAcryl results (fig. 7A). Here, ethanol removed a polyethylene oxide derivative and a polyurethane thickener. Most of these components are added during the paint manufacturing procedure.

Despite the very limited swelling, extremely high amounts of material were extracted from the Flashe paint film (fig. 7C). Over a broad range of the polarity scale, polymeric material was leached out. In this particular case, the elimination of components can be understood as a kind of washing-out effect. Very polar solvents such as formamide and water exhibit high dissolution rates of the polyethylene oxide additive. Only for the aliphatic hydrocarbon hexane was no significant extraction of hydrocarbon components observed.

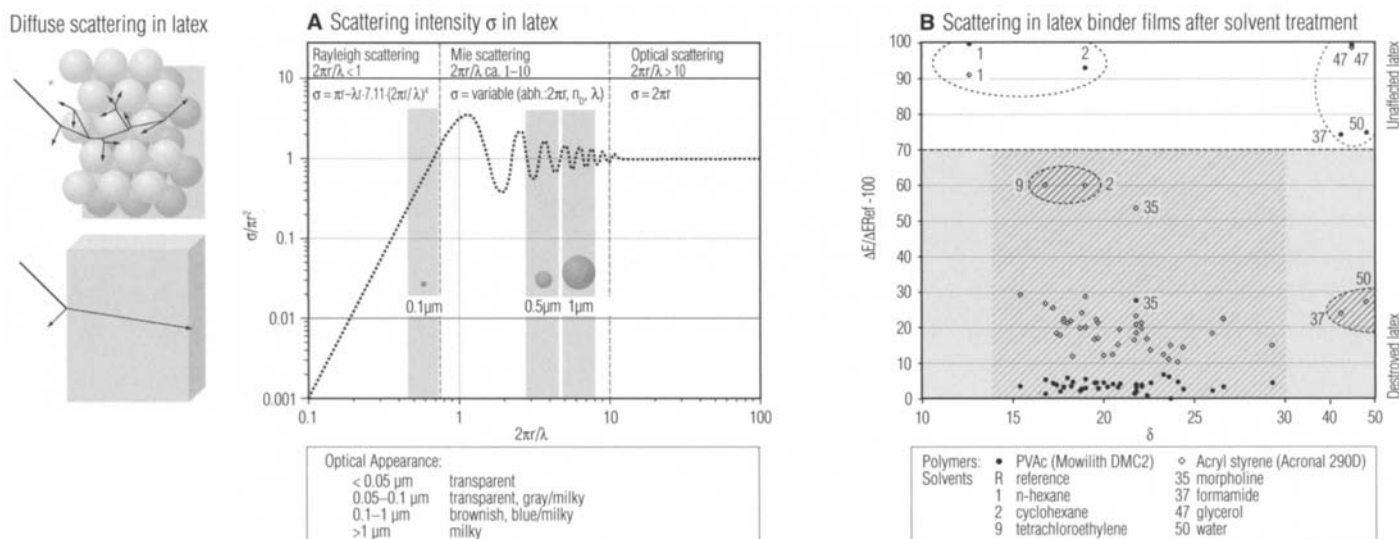


FIGURE 6 (A) The diffuse visible light scattering on rewetted films delivers qualitative information on the existence of distinct latex particles. The light reflection depends on the sphericity of the particles and the refractive index of the material. (B) This graph gives an overview of all results for two binding systems: Mowilith DMC2 and Acronal 290D. On the y-axis, 100% represents the equivalent light scattering in relation to the nontreated reference sample; 0% represents a fully transparent film with minimal water uptake, representing a completely destroyed latex microstructure. The latex particles in Plextol B500 were too small to be differentiated by this method.

Alteration of Mechanical Properties

The solvent treatment of acrylic paint films has a decisive influence on the mechanical properties of the film (fig. 8). The stress-strain measurement of the untreated reference shows a highly elastic and elastoplastic behavior. This characteristic is well known for such binding systems, and is described by the elastic deformability of the latex particles in the film (Distler and Kanig 1978; Rharbi et al. 1996). Differences between the selected products can be explained by the variable nature of the latex material and varying proportions of additives. After paint films were immersed for ten seconds in the solvent and allowed to dry completely, the mechanical properties of the films altered very significantly, becoming much more rigid. This strongly correlates with the swelling capacity. Stiffness increases in parallel with the rate of dissolution, followed by a rapid decrease in the case of extremely powerful solvents. But even films treated with solvents that cause minimal swelling and apparently leave the latex microstructure unaffected are subject to significant

alterations. In contrast to the PRIMAcryl paint (fig. 8A), the Akademie acrylic paint (fig. 8B) shows an extremely heterogeneous behavior and breaks down much faster. This material only retained its homogeneous properties after treatment when low-swelling solvents, such as hexane and water, were used.

The Flashe-PVAc color is different. This paint is much more rigid and has no mechanical strength (fig. 8C). The reference material breaks down after an elongation of only 2%, possibly due to the high level of additives that inhibit full film formation. The extraction of polyethylene oxide additives by polar solvents consequently leads to a somewhat higher elasticity. Immersion treatment with most other solvents leads to the complete loss of any mechanical strength whatsoever. The breaking power is minimal, with films failing at an elongation around 0.5%.

Discussion

The results of this research generate a consistent image of the physical alterations induced by solvent interaction on acrylic latex paint films. The properties of latex paints are strongly dependent on the film formation process. The degree of latex coalescence and polymer interdiffusion is responsible for the latex microstructure. In particular, additives such as thickeners interrupt this process and significantly influence the paint properties. Such materials, for example, display an extremely high sensitivity to solvent interaction. Most of the solvents destroy the microstructure and lead to the formation of a new film. This is comparable to a molecularly dissolved binding system, which results in a film with densely intertwined polymer chains. These irreversible morphological changes lead to a strong increase in

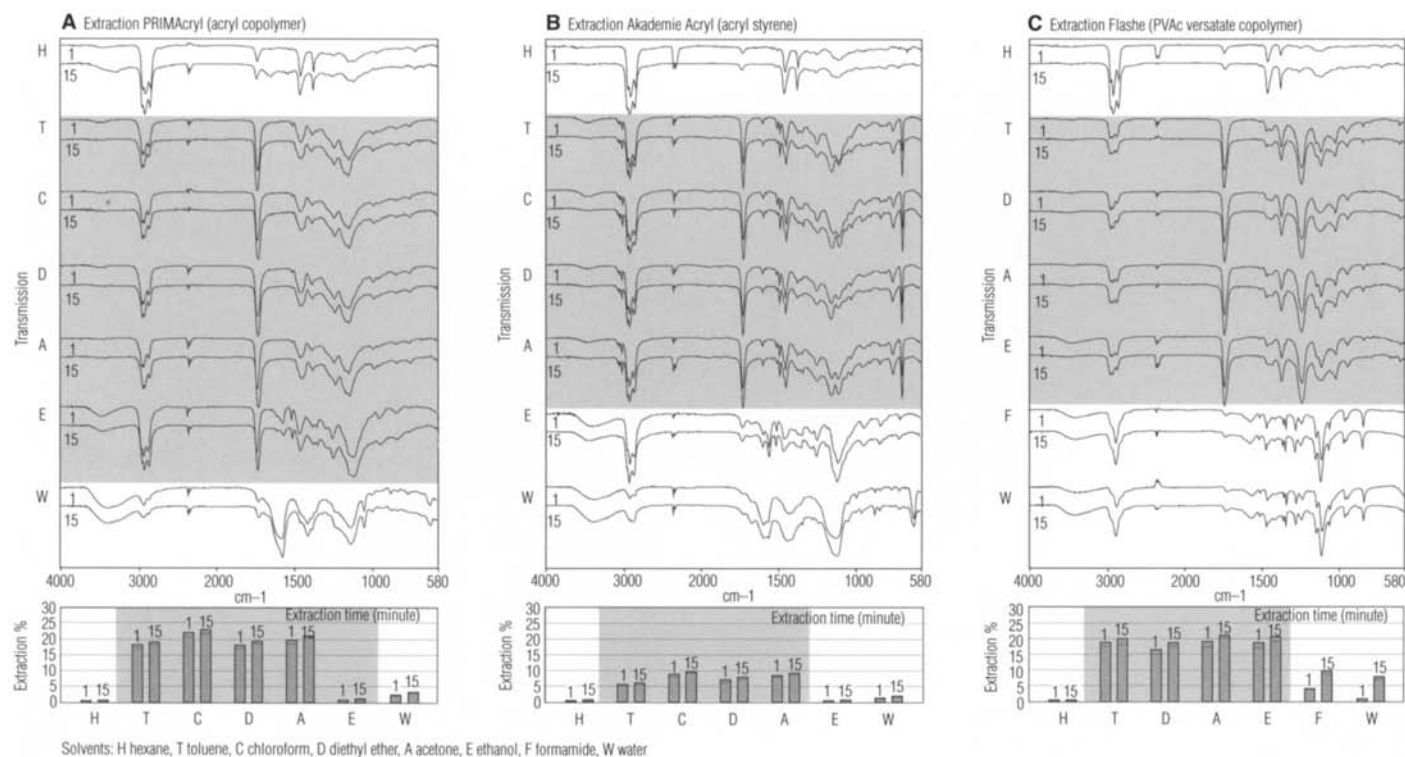


FIGURE 7 This graph shows the leached components after 1 minute and 15 minutes of extraction time for each of the three paint systems: (A) PRIMAcryl, (B) Akademie, (C) Flashe. Extracts were characterized by FTIR and quantified by gravimetry. Varying amounts of different components were leached along the polarity scale. The marked area highlights leaching of polymeric binder material.

stiffness of these paint films. In highly swollen systems, diffusion processes are facilitated, and an accumulation of binding material along the surface was observed. This segregation phenomenon leads to a further decrease in mechanical strength, as well as visible changes in the optical appearance. The homogenization is disturbed by a large volume of additives, such as thickeners. The resulting material properties are therefore strongly influenced by these components. In this context, the Flashe paint color is an extreme case, since film formation is inhibited by the enormous volume of polyethylene oxide additive. The binder is therefore easily washed out by solvent interaction, which results in powdery films without any mechanical strength whatsoever, even with highly polar solvents.

Overall, only aliphatic hydrocarbons and highly polar solvents, such as water and, in some cases, alcohols, left the latex microstructure unaffected. While inducing minimal mor-

phological alterations, treatment with hexane or water does affect the mechanical properties. However, a quite different mechanism seems responsible for the structural changes: these solvents are not able to dissolve the acrylic polymer, but they penetrate the core shell of the latex particles and locally act as a plasticizer (Sullivan 1975; Vezin and Florence 1981; Wang and Winnik 1991, 1993; Baumstark and Schwartz 2001). Interaction with water has a similar effect (Sperry et al. 1994; Kast 1985; Levine and Slade 1985). This kind of effect is well known from the action of film formation aids. For example, lowering the glass transition temperature enhances polymer interdiffusion and leads to an optimized interparticular stability (Hoy 1973; Richard 1996; Juhué and Lang 1994). In the case of water, repetitive treatments have the same effect (Schwartz and Kossmann 1997). The accompanying leaching of additives leads to a further enhancement of this process. After the hydrophilic additives are leached out, the water affinity is reduced (Snuparek 1996; Steward et al. 1996). The extent of structural changes caused by treatment with water is thus not comparable to the dissolved systems described above. A similar effect regarding structural modifications was observed by an increase in temperature (List and Kassis 1982; Hahn et al. 1986; Hahn, Ley, and Oberthür 1988; Eckersley and Rudin 1993). An optimized interdiffusion also leads to greater stiffness of the material.

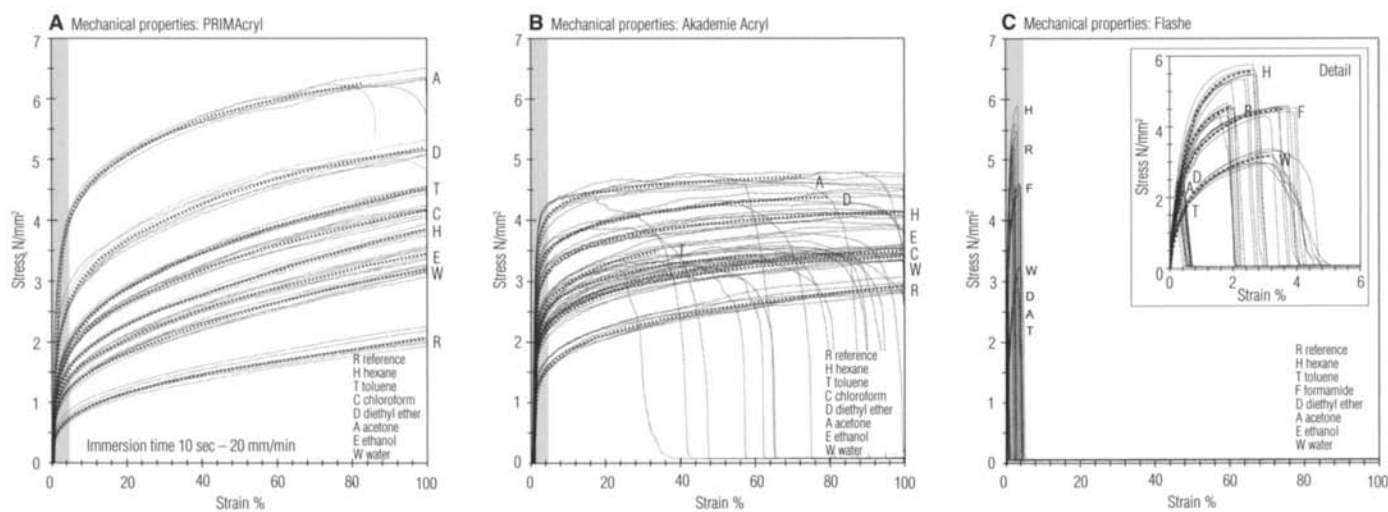


FIGURE 8 After paint films are immersed for 10 seconds in solvent and then completely dried, the mechanical properties of the films are subject to significant alterations. After treatment with solvents, all films were much more rigid, with some samples exhibiting heterogeneous mechanical behavior. This effect strongly correlates with the swelling capacity.

Conclusions

These findings suggest that the composition of latex paint systems has a major influence on film formation and the resulting morphological microstructure, as well as the physical properties of these films. Overall, latex paints are extremely sensitive to solvent interaction. The specific effect not only depends on the nature of the polymer but is strongly influenced by the morphological microstructure. Interaction with solvents leads to variable modifications of this structure and, in many cases, to its total destruction. Only very apolar solvents seem to leave the microstructure more or less unaffected. Thus, only a very small selection of solvents may be considered as suitable for conservation treatments.

Acknowledgments

Sample preparation support from Dr. Walter Heckmann, Department of Polymer Physics, BASF, Ludwigshafen, Germany, is greatly acknowledged. Volker Schaible from the National Academy of Arts Stuttgart, Germany, is thanked for fruitful discussions.

Appendix

Materials

- Schmincke PRIMAcryl professional—pigment: PBk11 PBk7; acrylic copolymer; additive content: 2% (thickener: 1%); pigment volume concentration (PVC): 60%; minimal film formation temperature (MFT): 13° C
- Schmincke Akademie Acryl—pigment: PBk11, PBk7; acrylic-styrene copolymer; additive content: 4% (thickener: 2%); PVC: 50%; MFT: 19° C
- Lefranc & Bourgeois Flashe—PVAc versatate (Veova) copolymer; pigment: PBk 11, PBk 7; additive content: 5%–10%; MFT: 18° C
- Plextol B500 (Rohm)—acrylic copolymer
- Acronal 290D (BASF)—acrylic-styrene copolymer
- Mowilith DMC2 (Höchst)—PVAc maleinic acid dibutyl ester copolymer
- Solvents—All solvents supplied by Merck apart from 1,1-dichloroethane and 2-ethoxyethanol (Grogg Chemie) and dichloromethane, 1,2-dimethoxyethane, 4-hydroxy-4-methyl-2-pentanone, and acetophenone (Fluka)

Instrumentation and Preparation

The immersion-swelling test (modified from Phenix 2002) was carried out on free films (300 μm thick, 14 mm wide) prepared with an Erichsen GmbH preparation tool. Films were allowed to dry for 92 days. Segments (1 mm wide) were then fixed in a circular glass holder (inner diameter 4 mm), designed to inhibit lateral deformation (Zumbühl 2005).

The swelling power of solvents was documented using a Wild M5 microscope + Nikon Coolpix 5000 camera mounted on a ProMicron ocular adapter. Timed sequential images were controlled with a Nikon Remote Cord MC-EU1. Swelling power was quantified by ImageJ image-processing software. The scanning electron microscope (SEM), secondary electron (SE), backscattered electron (BSE) images, and X-ray maps were produced on a CamScan 4 (Cambridge). Samples were carbon coated using a Baltec Med 020 (C-thread, flash mode). Samples for SE images were prepared by the freeze-fracture method described in Roulstone et al. (1991). Samples were left for 21 days after solvent treatment.

SE images were collected at 8 kV, 21 mm working distance, 4000 \times magnification, 10,000 ns dwell time. Samples for BSE imaging were cut using a Diatome diamond blade under cryogenic cooling and treated with uranyl acetate (Kanig and Neff 1975; Distler and Kanig 1978). A 5% solution of uranyl acetate (Merck) was filtered with a Millipore Millex-GV hydrophilic PVDF 0.22 μm filter. A drop was put on a Parafilm sheet. After immersion for 60–120 seconds, samples were rinsed twice with distilled water. BSE images were collected at 20 kV; 21 mm WD, 10,000 \times magnification; 10,000 ns dwell time, and one to three averaged frames.

The total light scattering procedure was used, as described in Bohren and Huffman (2004) and Van Tent and te Nijenhuis (1992a, 1992b). Latex binder films were immersed for 60 seconds. VIS light reflection was measured with photo spectrometer Minolta CM-2022 (d8/SCI). Samples were dried for 19 days after solvent treatment. Leaching was measured by infrared spectrometry and quantified by gravimetry. Paint film samples (500 mg) were immersed in 50 ml of solvent for 1 minute and 15 minutes. Samples then dried for 7 days after solvent evaporation. Measurements were carried out on μ -FTIR Perkin Elmer System 2000 with a Cassegrain-microscope, with samples leveled onto a CVD diamond window. Settings used were transmittance mode, 32 averaged scans with 2 cm^{-1} resolution. For quantitative analysis, two spectra with less than 4% deviation were collected.

Stress-strain measurements were carried out on Zwick tensile tester Z2.5/TN1S in controlled room conditions of 54%–56% relative humidity (RH) and 17°–18° C. Free paint films (14 mm wide, 100 mm effective length) were made by brushing paint onto Teflon-coated foil. Samples were immersed in solvent for 10 seconds, dried for 23–24 days, and then removed from the foil. Seven replicates per paint type were tested. Zwick settings were elongation speed, 20%/minute; maximum elongation, 100%.

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PART SEVEN

Posters

Summaries and illustrations from posters shown at the symposium appear on the following pages.

The Effects of Ultraviolet Light Aging on the Mechanical and Physical Properties of Artists' Acrylic Paints

Judith Bannerman

Long-term exposure to ultraviolet (UV) light and environmental conditions play major roles in the damage caused to acrylic paint films over time. With this in mind, an investigation was undertaken into the effects of UV light aging on free films of artists' acrylic paints, with a focus on titanium dioxide white, gesso, phthalocyanine green, and acrylic resin. Artificially aged and naturally aged acrylic paint samples were tested over time in a controlled environment for changes in mechanical and chemical properties. Both light exposure and relative humidity were found to affect the transition temperature at which the paint films change from a brittle to ductile behavior. Results showed that increasing relative humidity lowered the transition temperature and reduced the risk of damage to the free film. However, the plasticizing effect of the water also made the paint more susceptible to the detrimental effects of light aging. Thus, light degradation will occur over time, but controlling the environmental conditions allows this process to be slowed and the risk of long-term damage reduced.

Art in Bad Times

Eva Brachert

Who needs art in a time when everybody needs something to eat and a roof above the head, but you have the urge to paint?

—GUSTEL STARK (2005)

The high degree of devastation in day-to-day life in the Rhein-Main area of Germany after World War II created the possibility of a new beginning in everyday occurrence as well as in artistic expressions. Despite this being a time of general shortage, with suitable artistic materials difficult to obtain, artists were able to experiment by using house paints and other non-art materials.

A group of young artists, including Gustel Stark, Gustel Stein, Heinz Prüstel, and Willy Fuegen, formed the New Group Rheinland-Pfalz in May 1954; their main goal was to create abstract art showing the strained relationship of concentrated color and tight shape in front of a wide, indefinite space. They were oriented westward, and particularly influenced by French artists from Léger to Braque. The latter was a key player beside Willi Baumeister, who was condemned by the Nazis. Research has been undertaken to collect oral, written, and technical information about paintings created by this group.

Our interviews with the artists revealed that they all had traditional academic artistic educations. They were capable of making and applying their own oil priming to prevent absorption of the binding medium of the colors too quickly while working. Sometimes they preferred quick-drying binding media to facilitate the application of subsequent paint layers. They often wiped away upper layers or used a stencil to achieve the impression of three dimensionality by revealing underlayers while keeping the contour clear. To earn money they sometimes decorated walls of cooperative housing projects with abstract compositions of plane and color (fig. 1).



FIGURE 1 Gustel Stein (German, b. 1922), *Summer, 1955*. Wall painting with plaster, disperse colorants (Caparol), and glass mosaics embedded, 400 × 250 cm (157 × 98% in.). Mainz, Germany. Published with permission of the artist.

They also tried to imitate the rough character of walls on their canvases (fig. 2). As Gustel Stark describes it, “Our paintings on canvas are wall paintings manqué” (interview with author in November 2005). On both, they worked with

oil, casein, and plaster paste, structural plaster, glass, quartz, and other fillers in synthetic resin, to give each part of the painting an individual structure. In addition to artists’ colors, they used colors from the German Amphibolin Company (Deutsche Amphibolin Gesellschaft) in combination with adhesive mortar to embed glass mosaic pieces. In other cases, they used transparent polymer resin as a binder for pigments, to get deeper color effects on the wall and the canvas. Pigments were dispersed into a glue when more brilliant colors were desired, although these lean layers were more susceptible to mechanical damage and bleaching. In all cases, a coating of Capaplex (German Amphibolin Company) was applied as protection.

However, the decorative layers and coatings have become dull and brownish on aging. These changes affect the visual balance of color, line, and structure, and therefore the potential exists for losing important information about this movement.



FIGURE 2 Gustel Stark (German, b. 1917), *Malerei 50/55, 1955*. Oil, clay, and sand on canvas, 75 × 175 cm (29½ × 68% in.). Mainz, Germany, Landesmuseum, 86/156.

Cleaning *The Café Balzac Mural*

Anne Carter

Debate has ensued about whether to clean the dark yellow patina from *The Café Balzac Mural* (fig. 1) since its acquisition by the Queensland Art Gallery in 1988. The mural was painted in situ in 1962, in the Melbourne café that gives the work its name, by three Australian and New Zealand artists: Colin Lanceley, Mike Brown, and Ross Crothall. For twenty-six years the mural hung in the café, developing its patina of organic material, most likely cigarette smoke and cooking residue. The painting is collaged from locally sourced materials (commercial paint and adhesives) and found objects (artists' paint, magazine cuttings, paint lids, and wine labels).

Following discussion with one of the artists, cleaning tests were undertaken in 2005, and it was decided to remove the dirt layers. Water-based cleaning options were explored, with low-concentration triammonium citrate and methyl cellulose gels found to be most effective. However, while the paint cleans up well and reveals a stunning array of colors, the paper elements remain dark and degraded. FTIR analysis revealed that the glue used to adhere some of the paper components is a polyvinyl acetate (PVA), which has become very dark and disfiguring. Treatment decisions required consideration of whether the darkened PVA should be reduced and how the paint/collage tonal balance would be affected.

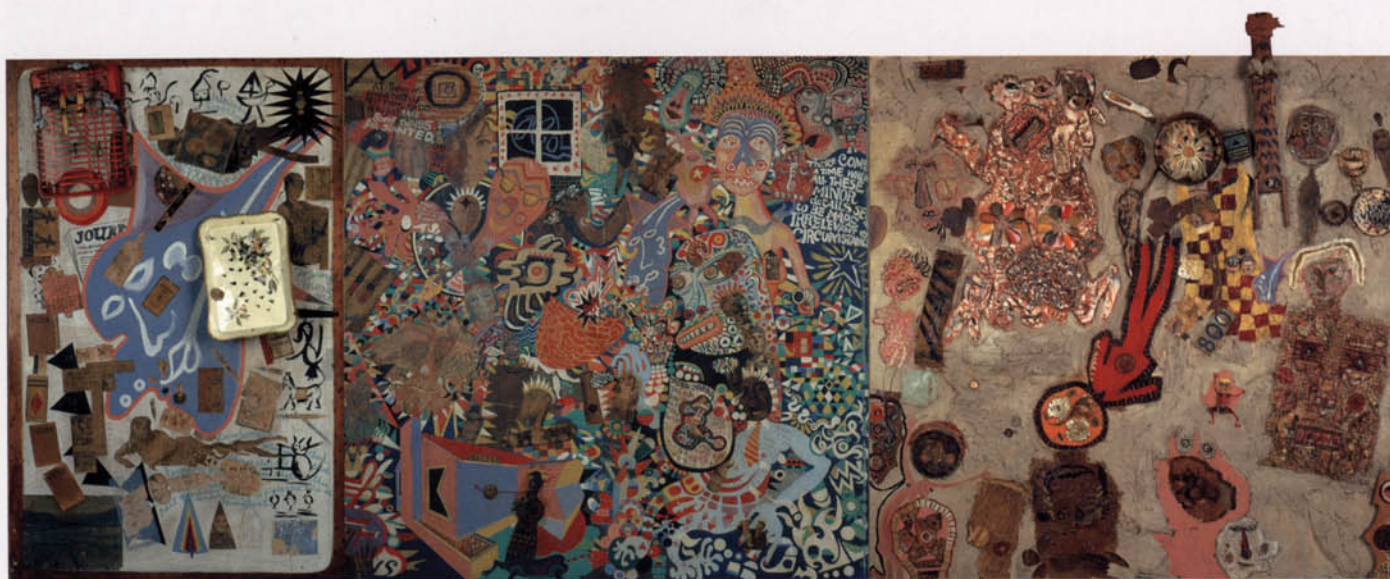


FIGURE 1 *The Café Balzac Mural*, 1962. Ross Crothall (Australian, b. 1934) [left panel], Mike Brown (Australian, 1938–1977) [center panel], Colin Lanceley (Australian, b. 1938) [right panel]. Left and center panels: oil, synthetic polymer paint, and mixed-media collage; right panel: car Duco, enamel paint, sand and plaster, oil, synthetic polymer paint, and mixed media collage on plywood panels. Triptych overall: 195.3 × 487.4 cm (77 × 192 in.). Brisbane, Australia, Queensland Art Gallery. Purchased 1988. Published with permission.

The Identification of Some of the Painting Materials at Museo d'Arte Contemporanea all'Aperto di Maglione

Oscar Chiantore, Rebecca Ploeger, and Antonio Rava

Maglione, in Italy, is host to a unique outdoor contemporary art gallery, the Museo d'Arte Contemporanea all'Aperto di Maglione (MACAM). Established in 1985, this evolving gallery contains about 160 in situ works of art: paintings, sculpture, and installations (see www.macam.org for more information). Materials used range from paints (polymeric and natural), to marble, metals, wood, and ceramics. As a result of inconsistent supports, such as plaster facades on houses and cement on newer buildings, traditional techniques are rarely employed for the museum's wall paintings.

What makes MACAM so unique is that it is entirely outdoors and has no protection from the environment (natural elements and man-made pollution) and no security to prevent vandalism. It is hoped that our study will draw more attention to MACAM and some of the conservation concerns about the works of art there. Many studies on modern artistic materials have focused on materials under indoor rather than outdoor display conditions, and it is hoped that a conservation program will be initiated to help prevent further deterioration and loss of more of the outdoor works. Our study focused on ten unique pieces throughout the village and aimed to identify the binders used by the artists using Fourier transform infrared spectroscopy attenuated total reflectance (FTIR-ATR) and pyrolysis gas chromatography/mass spectrometry (PyGC/MS), with and without derivatization with TMAH (trimethylammonium hydroxide), as outlined in previous publications (Learner 2004; Scalarone and Chiantore 2004).

Come ti modello il cielo (1991), by Antonio Carena, is a painting on sheet metal measuring 155 cm × 100 cm, mounted on the side of a building (fig. 1). It has not changed drastically since it was originally created. A sample of blue paint from behind one of the metal curls was identified as polyvinyl acetate (PVA), containing VeoVa, a vinyl ester of Versatic acid (a highly branched C₉ or C₁₀ structure).



FIGURE 1 Antonio Carena (Italian, b. 1925), *Come ti modello il cielo*, 1991. Maglione (Italy), Museo d'Arte Contemporanea all'Aperto di Maglione (MACAM). Photo taken in January 2006. Published with permission of MACAM and the artist.

The nine other works are summarized in table 1. In several cases, there were multiple layers of paint or painting material, and in those cases they were analyzed separately and identified. Also, in some samples it appears that there could have been mixed binders, or the blending of layers.

Table 1. The binders used (determined by analysis) in nine selected works of art at MACAM.

Artist, Title, and Painting Details	Colors and Binder Identification
Armando Testa, <i>Untitled</i> (1988), painting on plaster	Red: acrylic (EA/MMA); maybe also PVA/VeoVa present
Piero Ruggeri, <i>Untitled</i> (1988), painting on galvanized iron	Red: alkyd (evidence of fatty acids)
Maurizio Matrone, <i>Untitled</i> (1987), painting on plaster	White: PVA with other unknown binder/material
Salvo, <i>Capriccio</i> (1988), painting on plaster	Green: acrylic (EA/MMA)
Concetto Pozzati, <i>Pane bianco quotidiano: Fantasmagoria</i> (1986), painting on plaster	White: acrylic (EA/MMA)
Alik Cavaliere, <i>Omaggio a Maurizio</i> (1991), sculpture: paint on anodized metal	Red: acrylic with styrene
Gian Franco Asveri, <i>Untitled</i> (1991), painting on plaster	Red (top layer): PVA/VeoVa White (bottom layer): acrylic (EA/MMA)
Franco Guerzoni, <i>Archeologia della notte</i> (1989), painting on plaster	Blue (top layer): alkyd White (bottom layer): acrylic with styrene
Ugo Nespolo, <i>Untitled</i> (1986), painting on plaster	Pink (top layer): acrylic (EA/MMA) White (bottom layer): acrylic with styrene

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The Complexities of *Woman in a Courtyard* (1933) by Julian Trevelyan

Maureen Cross

Throughout the career of Julian Trevelyan (1910–1988), his style and media changed constantly. *Woman in a Courtyard* (Tate Collection, T07833; fig. 1), from 1933, is an important work of the artist's Surrealist period. It was found abandoned in his studio and had suffered extensive damage, but the opportunity to study the artist's materials and techniques resulted in a successful restoration.

From 1931 to 1934, Trevelyan lived in Montparnasse, enrolling at the Académie Moderne and producing paintings that combined free-floating geometric forms with taut architectural backgrounds. Trevelyan began the painting by making pencil "scribbles," then worked quickly and spontaneously, combining both artists' oils and household paints in varying consistencies. Trevelyan's palette comprised Prussian blue, synthetic ultramarine, vermilion, and earth colors, with black and white to alter the hue, and he created textures by adding wood chips and sawdust. The black gloss paint of the signature and date is thought to be a commercial paint, due to the relatively high amount of extenders.

Trevelyan's unorthodox and often unstable materials, combined with the poor storage conditions, made the conservation treatment complex. Structural work involved consolidation and the local removal of extensive hard-edge planar distortions on a low-pressure table. Treatment was further complicated by the presence of a previous composition beneath the visible layers (confirmed by infrared reflectography and X radiography). To give the painting the best continual support over time, the canvas was reattached to an aluminum honeycomb board. An interleaf of MicroChamber archival paper was used because it contains molecular sieves and buffers that trap and neutralize the damaging by-products of deterioration. Losses were filled with a pigmented Mowiol GE4-86 chalk mixture and textured to mimic surrounding paint.

As a result of the diverse paint effects favored by Trevelyan, no single approach to inpainting was appropri-

ate. Losses in the high-gloss, black paint were toned using Gamblin Conservation Colors and inpainted with dry pigments dispersed in Regalrez 1094. Matte areas were retouched using watercolors, and the medium-rich oil paint required dry pigments dispersed in MS2A.

The use of nontraditional materials that characterizes Trevelyan's work presents challenges to both art historians and conservators. With technical study of this key work, significant insight into his working methods has been gained.



FIGURE 1 Julian Trevelyan (British, 1910–1988), *Woman in a Courtyard*, 1933. Oil, enamel, and graphite on canvas, 72.5 × 72.5 cm (28½ × 28½ in.). London, Tate, T07833. © Tate, London, 2007.

Study of the Influence of Synthetic Organic Pigments on the Thermal and Photodegradation of Linseed Oil by FTIR/ATR Spectroscopy

*Julio M. del Hoyo-Meléndez and
María Teresa Doménech-Carbó*

The main objective of this research project was the characterization of changes undergone by linseed oil when combined with synthetic organic pigments. The pigments selected for the study were PR3, PY74, PR170 (azo), PG7 (phthalocyanine), PV19 (quinacridone), PR83 (anthraquinone), and PY110 (isoindolinone).

Thermal- and light-aging treatments were applied on model paints prepared by binding the above-mentioned pigments with linseed oil at three different concentrations: 10%, 25%, and 50% (w/w). Attenuated total reflectance (ATR) spectra of test specimens were acquired before and after the accelerated-aging treatments.

Two different behaviors were observed on the aged model paints. A group of binary specimens exhibited a decrease of the shoulder of the carbonyl band at approximately 1712 cm^{-1} . This shoulder is associated with the carboxylic acids present in the oil. Interestingly, the second group of model paints exhibited the opposite behavior: a slight increase of the shoulder. This effect was also observed in pure linseed oil specimens. These results suggest that some pigments might have an inhibitory effect on the long-term aging processes of the drying oil.

What Makes the Color Field? A Technical Examination of Magna Paint

Glenn Gates, Tatiana Ausema, and Susan Lake

Magna paint is a solution of poly(*n*-butyl methacrylate) resin in solvent that was developed by Leonard Bocour and Sam Golden in the mid-1940s. Like oil paint, Magna could be thinned with turpentine and diluted with additional acrylic resin. Unlike oil, Magna dries very quickly. Morris Louis manipulated these characteristics of Magna as he developed his technique of pouring paint to stain canvas.

Although early Magna paint suited Louis's work well, the loose consistency of the paint caused Bocour to change the formula in 1958, giving the paint more body, reportedly by adding beeswax. This formulation change made the paint harder to disperse in solution, causing Louis to complain of being "none too happy with the present Magna since it doesn't particularly lend itself to my purposes." Therefore, in April of 1960, Bocour began to make a thinner form of Magna, reportedly without beeswax, specifically for Louis (Upright 1985).

The primary objective of this study was to use pyrolysis gas chromatography/mass spectroscopy (PyGC/MS), to characterize the Magna paint used by Louis before and after this modification date. A number of paint colors from four paintings in the Harvard University Art Museum collection were studied: *Blue Veil* (1958, DU#126), orange, green, and three blue paints; *Orange Column* (1960, DU#300), red and orange paints; *Tau* (1960 DU#339), green and orange paints; and *Color Barrier* (1961, DU#430), yellow, red, and two green paints.

All the pyrograms from these paints confirmed the presence of poly(*n*-butyl methacrylate). In addition, they all indicated higher-order methacrylates, including octyl, decyl, dodecyl, and tetradecyl methacrylates. This is consistent with similar analyses from two other Louis paintings: *Alpha Phi* (1960–1961, DU#400) and *VAV* (1960, DU#175) (Learner 2004).

The presence of long-chain alkanes—suggestive of wax—was also clearly observed in the pyrogram of the red

paint from *Orange Column* (1960), specifically eicosane (C_{20}), heneicosane (C_{21}), docosane (C_{22}), tricosane (C_{23}), and tetracosane (C_{24}). In the red paint sampled from *Color Barrier* (1961), only C_{22} – C_{24} were observed, and at lower intensity. In *Blue Veil* (1958), although these three alkanes were detected in the orange paint, they were absent in the blue.

For all four paintings, long-chain alkanes were detected only in red and orange paints, all of which contained cadmium sulfoselenide pigments. Clearly, further paintings need to be analyzed before we can conclude whether there was an overall formulation change, or whether the wax was added just to cadmium red/orange pigments (to improve stability or dispersion), or whether the wax has come from another source.

Analytical Details

- CDS 1500 pyroprobe, interface (at 300° C) to an Agilent Technologies 6890N Network GC System with a 5973 Network MSD
- Pyrolysis: 750° C for 10 seconds
- Column: 30 m DB-5
- Carrier gas: Helium at 60 cm/second
- GC program: 40° C for 1 minute; 10° C/minute to 120° C; 15° C/minute to 300° C; isothermal for 10 minutes
- Transfer line temperature: 240° C
- MSD source temperature: 200° C

References

- Lerner, T. 2004. *Analysis of Modern Paints*. Los Angeles: Getty Conservation Institute.
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Modern Standards for Modern Paints: The Activities of ASTM D01.57

Mark Gottsegen and Ross Merrill

ASTM International—originally the American Society for Testing and Materials—is one of the world's largest voluntary standards-writing organizations, with more than thirty thousand members. Most of the members come from industry and government organizations. People who volunteer their time, expertise, and laboratory use for standards development write all ASTM's standards: artists, conservators, manufacturers' representatives and their laboratory personnel, chemists, color scientists, and interested third parties—even nonmembers who do not have a vote participate in ASTM standards development. Most of ASTM's standards are adopted by the organizations (industry, government, academic) for which they are written. A few are codified into U.S. federal law.

This poster offers some detail about the activities of ASTM's Subcommittee D01.57, Artists' Paints and Related Materials. Since 1978, D01.57 has focused on providing guidance to artists and manufacturers about the testing and formulation of artists' materials, mainly paints and other coloring materials. Information is also given about meetings and memberships: voting, nonvoting, and student.

Since 1983, ASTM International has published some fifteen standards from D01.57. These include the most well-known standard for labeling art materials for chronic health hazards (ASTM D 4236)—incorporated into U.S. law as part of the Federal Hazardous Substances Act: the Labeling for Hazardous Art Materials Act. D01.57's most important standard, ASTM D 4303, details the methods used for accelerated instrumental testing of colored art materials for lightfastness using natural and simulated daylight. Other standards, or specifications, provide information about formulation, test methods, colorant selection, and labeling for seven types of artists' paints: oils, resin-oils, alkyds (D 4302), acrylic dispersions (D 5098), transparent watercolors (D 5067), gouache paints (D 5724), and colored pencils (D 6901). These standard specifications apply only to

professional artists' paints, and do not address "student" "sketching," or "economy" grades. Other standards include supporting test methods and practices for the specifications, such as how to make a drawdown of paste paints, a highly scientific tinting strength test method, a test method for determining the autocombustibility (potential for spontaneous combustion) of natural drying oils, and a solubility test for the metal-colorant content of paints.

Current and ongoing work is focused on revising the lightfastness test methods to make them more applicable to nontraditional coloring systems (colored pencils, pastels, printed digital media, and other colored inks; fig. 1), developing a more user-friendly method for determining tinting

strength in oil and acrylic dispersion paints, a very large project to set some standards for primers/grounds, and a specification for artists' pastels.

It is important to understand a significant aspect of ASTM International's standards: they are living, changing documents. They all must undergo a five-year review and then are either reapproved or dropped. They are all subject to revision at any time: some of D01.57's standards have had several major revisions since the first date of publication.

All of ASTM International's standards are available in printed and electronic form from www.astm.org. ASTM D01.57's standards are in Volume 06.02 of the Annual Book of Standards.

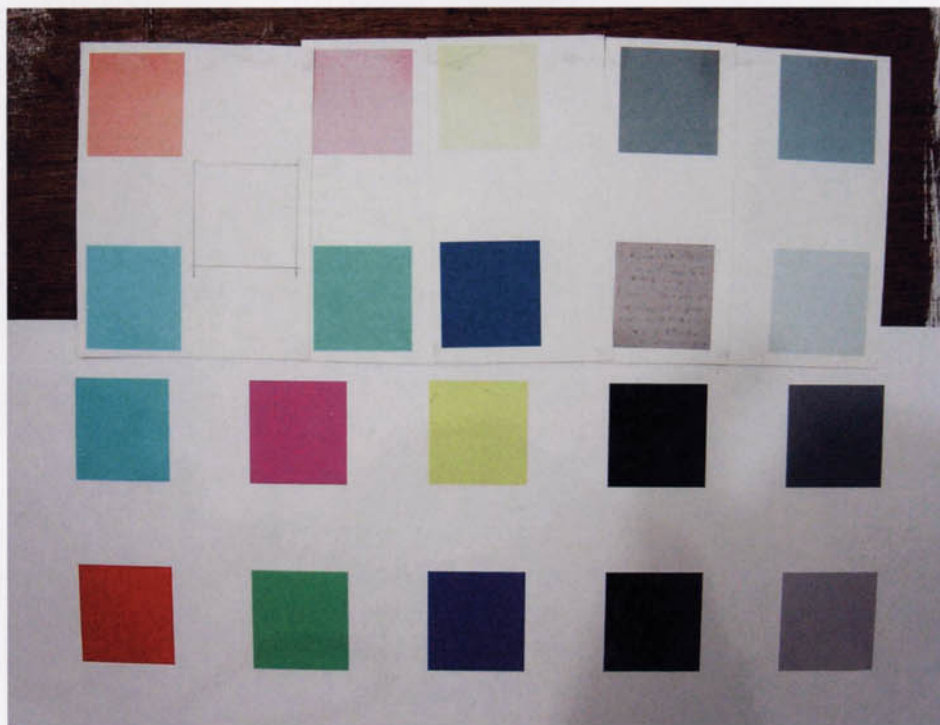


FIGURE 1 Accelerated lightfastness test results of some dye-based digital inks. The top group is after exposure; the bottom group is before.

Analyzing Visual Change in a Painting by Josef Albers

James Hamm, Gregory D. Smith, and Aniko Bezúr

A Josef Albers painting from 1955 titled *Homage to the Square: Dedicated* has undergone a dramatic shift in half of its outer band of color. Albers meticulously recorded the materials used for his paintings in ink directly on the reverse of the support, and this color is described as barium yellow in oil from Permanent Pigments. This shift was investigated using various analytical techniques, including X-ray fluorescence (XRF), Fourier transform infrared (FTIR) microscopy, polarized light microscopy, and other standard examination techniques, with the aim of understanding why the change is limited to only half of the color band and whether the change is dependent on the pigment itself, the medium, or another factor.

A further complication resides in the need to determine which half is the correct color and which has changed. Albers varnished this painting using a methacrylate resin applied by spray overall, as noted on the support's reverse. This resin may have altered the saturation of the paint to such an extent that Albers felt compelled to intervene. At present, it is clear that the varnish had been removed inexpertly from the entire band of barium yellow. Despite the present visual discrepancies, it must be assumed that the painting once met with his stringent visual approval, since it was sgraffito signed and sold as a finished work.

A Painter's Paradise

Sarah Hillary and Thomas J. S. Learner

The art of Colin McCahon (1919–1987) focused on New Zealand landscapes and questions of faith and doubt in a secular world, and his work became increasingly abstract over time (fig. 1). Severe shortages during World War II made it difficult to obtain art materials, so McCahon made paints following recipes in artists' manuals and experimented with paints intended for household decoration. However, when artist-quality materials reappeared for general consumption in the 1950s, McCahon continued to use household materials, combining them with the higher-grade materials. Not only did the commercial paints have different properties that could be exploited, but McCahon considered that scientific innovation had facilitated the painting process and made the era "a paradise for beginners" (McCahon 1971).

Questions about McCahon's paint compositions resulted in a study of eight paintings from 1955 to 1969, from the Auckland Art Gallery. The paint media were analyzed by pyrolysis gas chromatography/mass spectrometry (PyGC/MS) and Fourier transform infrared (FTIR) spectroscopy, and pigment analysis was carried out using energy dispersive X-ray analysis (EDX).

Analysis confirmed that McCahon began using alkyds as early as 1954, and that these and oleoresinous paving paints were often mixed with artist-quality and household-standard oils. The addition of sand and sawdust provided texture, and dry pigments were included to increase the range of colors. In the 1960s and 1970s, he quickly adopted PVAs and acrylics (table 1). Further variations in surface texture and reflectance were achieved with brushwork, layering, and additives and with localized varnishes. Varnishes were also found between layers, indicating that modifications had taken place.

A range of conservation concerns have been identified for McCahon's paintings made with these "nontraditional" materials.

Table 1. Use of paint media.

Decade	Lead-Based Oil	Oleoresinous	Alkyd	PVA	Acrylic
1930s	X	X			
1940s	X	X			
1950s	X	X	X	X ^a	
1960s	X	X	X	X	
1970s			X	X	X
1980s				X	X

^aLate 1950s.



FIGURE 1 Colin McCahon in his studio. From *New Zealand Woman's Weekly*, March 27, 1961. Published with permission of the Colin McCahon Research and Publication Trust and *New Zealand Woman's Weekly*.

- Varnishes applied by the artist have discolored, affecting the overall color balance of the paintings. However, removing original varnishes from household paints can be problematic and would alter the surface qualities.
- A number of oil-modified alkyd and oleoresinous paintings kept in uncontrolled environments with high temperatures (and possibly high light levels) have developed severe traction cracking, whereas paintings kept in stable museum environments do not appear to be affected. The development of cracking may be related to the rosin detected in the paint.
- Surface cleaning with water was found to leave dull streaks on the surface of PVA paintings from the 1960s, possibly due to the crystallization of emulsifiers such as polyoxyethylene-type compounds.
- Many of McCahon's paintings are on unstretched canvas supports, allowing a great deal of movement, which causes cracking in the paint layer. Although most of these paintings are painted in acrylic or PVA, in some cases more inflexible paints such as oil and alkyd have been used, resulting in raised cracks.

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Liquefying Oil Paint in Some Late-Twentieth-Century Paintings

Frank G. Hoogland,
Jerre van der Horst, and Jaap J. Boon

Several oil paintings in private, corporate, and museum collections made from 1990 to 1995 by F. van H.¹ presently show a disturbing paint defect that started in the year 2000. Although the flesh-colored paint dried initially, it developed a molten appearance and a viscous, sticky layer on its surface about six years after its application. This phenomenon smooths the sharp edges of the impasto and results in long drips that originate from the sticky surface layer (fig. 1). Other colors applied in the same manner are not affected

by this phenomenon. We were able to obtain samples of the original flesh-colored, commercial artists' oil paint used in these paintings, and have been able to perform comparative analytical studies of the tube paint, two draw-downs (thin and thickly applied) from 2002, and samples from two paintings that show areas of dripping paint.

Comparative studies were performed with direct temperature resolved mass spectrometry (DTMS), Fourier transform infrared (FTIR) spectroscopy, gas chromatography/



FIGURE 1 A painting by F. van H. shows disturbing paint defects of melting impasto and vertical flesh-colored drips caused by physical separation of paint components after an initial drying period of six years. Published with permission of the artist.

mass spectrometry (GC/MS), electrospray ionization–mass spectrometry (ESI-MS), and X-ray diffraction (XRD). All paints used for the impastos were shown to be oil paints with no unusual components. Pigments in the flesh-colored paint were identified as titanium white, cadmium yellow, and cadmium red. Additional components included calcium carbonate (filler), beeswax, and aluminum stearate. The oil appears to be a mixture of sunflower and linseed oil (9:1, based on ESI-MS data [unpublished]), with a very low drying index of 73 (>70 is required for drying). The absence of unsaturated fatty acids and the presence of diacids and midchain oxygen-functionalized C₁₈ fatty acids in the painting samples imply that chemical drying (i.e., oxidation of unsaturated fatty acid moieties) had taken place. The GC/MS data show that, besides hydrolysis, renewed esterification is taking place, and compositional differences between the flesh-colored paint on the painting, the drips, and the reference materials points to differences in the degree of hydrolysis in these samples.

Thin sections prepared at low temperature (5° C) and analyzed by FTIR transmission microscopy (fig. 2) show a 20–40 μm thick organic top layer, while the main paint layer is rich in calcium carbonate with discrete particles of aluminum stearate. DTMS and ESI-MS analyses of these layers show that the major organic components of the paint layer are saturated fatty acids (with aluminum stearate causing a high stearic acid content), whereas those of the top layer are oil oxidation and hydrolysis products.

We propose that during the drying of this paint, the unsaturated fatty acid moieties of the oil in the paint are insufficiently cross-linked and instead oxidize directly to azelaic acid moieties and other high-polarity products that are incompatible with the paint mass. A physical separation mechanism ensues, which leads to a poorly consolidated surface film that is unable to dry and therefore begins to drip down the painting.²

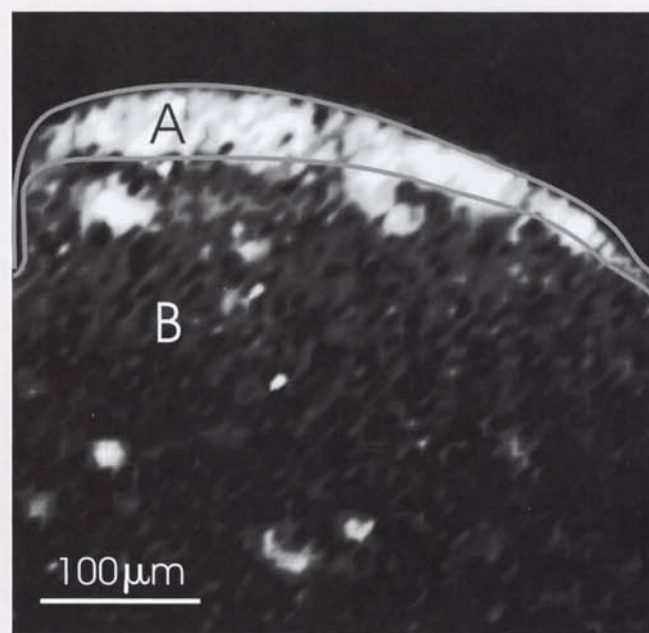


FIGURE 2 Transmission FTIR image (2940–2850 cm⁻¹) of a thin section of the affected paint showing (A) a layer of oil-derived oxidation products on top of (B) the paint layer. Areas of white correspond to high levels of absorbance.

Notes

- 1 Artist's full name protected at artist's request.
- 2 H. Schmincke & Co., the manufacturer of the flesh-colored paint, refutes the results of this investigation (personal e-mail from Stadermann Luiten, the lawyers in Rotterdam that represent the company).

Dictated by Media: Conservation and Technical Analysis of a 1938 Burlap Painting by Joan Miró

Ashley M. Johnson, Elma O'Donoghue,
and Marc S. Walton

A small burlap-canvas painting, created by Joan Miró in 1938, was recently treated at the Los Angeles County Museum of Art to stabilize severely flaking paint. This paint exfoliation was confined to areas of matte red, green, and yellow paints. These paints were also characterized by soft spherical protrusions. Analysis corroborated what Miró described in his letters and studio notes about his working methods and materials, including his use of supports, his grounds, underdrawings, and paint layers.

Extensive nondestructive analysis of the painting, including infrared reflectography, X-ray fluorescence (XRF), and digital microscopy, was carried out. XRF, gas chromatography/mass spectrometry (GC-MS), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy established that the painting's ground was calcium carbonate in animal glue (a commercially prepared painter's plaster) and that the paint media consisted of various types of drying oils. Interestingly, scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM-EDX) revealed a zinc white imprimatura underneath areas of vermilion and verdigris paints, which were flaking and had spherical protrusions. These spherical protrusions were identified as zinc palmitate soaps. The soaps were probably a result of zinc white in the imprimatura layer reacting with slow-drying poppy seed oils in the overlying paint layers. Miró's meticulous studio notes show he used house paints (made by Ripolin), as did Picasso and Kandinsky, and that he frequently combined traditionally incompatible media. The analysis results also suggest that he added his own oils to standard artists' oil colors.

This painting proved to be an informative example of Miró's techniques from a period of great experimentation—the time of his exile in Paris during the Spanish Civil War. For more detailed information, see the authors' subsequent publication "Dictated by Media: Conservation and Technical Analysis of a 1938 Joan Miró Canvas Painting," in *The Object in Context, IIC Munich Congress* (2006).

Paints and Coatings Used in Outdoor Murals

Jessica Keister, Joyce Hill Stoner, and Joseph Weber

The Winterthur/University of Delaware Program in Art Conservation has launched a five-year project to test paints currently used by outdoor muralists in Philadelphia (2500 outdoor murals) and other U.S. cities. The authors have surveyed key murals, from eight to twenty years old, and gathered observations regarding fading, chalking, and flaking. Based on paints and coatings suggested by artists and conservators on the task force for the new Heritage Preservation/National Institute for Conservation initiative Rescue Public Murals, 922 3 × 3-inch sample squares have been prepared to test acrylic paints from Golden, NovaColor, and Sher-Cryl and potassium silicate paints from Keim. Red, yellow, and blue paints taken directly from the containers or mixed with white have been applied to the prepared supports in order to study their photostability and the photocatalytic effect of titanium dioxide on fading. The following coatings are also being tested: Paraloid B-72 and NovaColor varnish (both with and without CIBA 777), Golden Artist Colors MSA varnish with UVLS, and Triangle catalyzed polyurethane "antigraffiti" coating (required by some mural arts commissions).

Samples are placed on south-facing racks at a 45-degree angle to the ground (fig. 1); spectra and color change of each sample are measured every three months by microspectrophotometry and colorimetry. We hope to increase awareness among arts administrators regarding the importance both of planning for future maintenance and of involving conservators, the original artists, and members of the community. A higher-cost paint may save money in the long run.



FIGURE 1 Jessica Keister on the Winterthur Museum property with samples of paint used by mural artists. Photo: Joyce Hill Stoner.

Squeeze Up Close

Kathrin Kinseher

Prompted by the lack of information about the working properties and visual qualities of different commercial oil and acrylic paints, the Munich Art Academy aimed to develop a practical tool to demonstrate the surface characteristics of different types and brands of paint. During this study, carried out in 2002 with students Ingrid Floss, Julia Schimtenings, and Oleksiy Koval, a total of thirty-eight different ranges of acrylic paints from numerous manufacturers were compared. These included Daler-Rowney, Golden Artist Colors, Kreul, Lascaux, Liquitex, Lukas, Maimeri, Nerchau, Schmincke, Schutzmann, Talens, and Winsor & Newton, as well as lower-price brands.

Our study confirmed many of the expected differences between artist- and student-quality ranges. Artists' acrylics contain higher concentrations of pigment (including those that have only recently been developed and/or are of higher cost) and a high-quality acrylic emulsion binder, whereas student acrylics are softer and more fluid and often contain mixtures of pigments and higher levels of extenders (Seymour 2003, 413).

Within each range, three colors were painted out in four different ways: mass tone (unmodified), diluted, tint (mixed with white), and impasto. Titanium white (PW 1), ultramarine blue (PB29), and black (different pigments: PBk7, PBk9, PBk11) were applied to primed canvas and test cards. Figure 1 demonstrates a selection of the paint-outs and clearly shows some of the differences between the various brands. Some of the most striking differences are the intensity of the color tone and the surface characteristics of impasto. For example, ultramarine paints display a huge variety of opacities and brightness of color. The paint-outs with titanium white vary in opacity and also in tinting strength. The results of mixing white with black vary considerably, from very bright to very dark grays, both warm and cool. Figure 2 shows some of the black paints, where differences in gloss are particularly apparent.

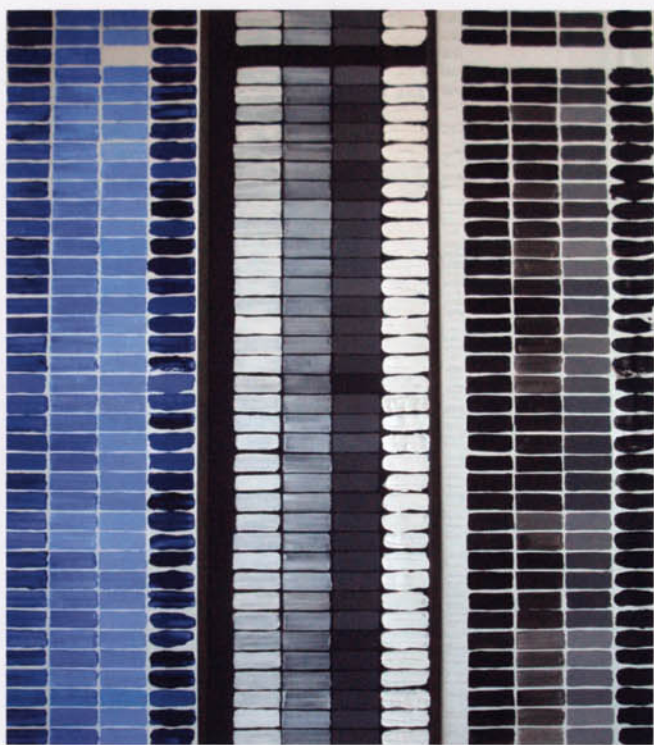


FIGURE 1 A selection of color paint-outs of various brands.

Great differences in consistency were also apparent when the paint was applied to create impasto, ranging from stiff, buttery paint to thin paint that dripped off the spatula. We observed that it was not only those brands labeled “high flow” that exhibited a very fluid consistency. It was also evident that many impasto applications failed to maintain their structure. Some applications show an inhomogeneous surface: cracking, granularity, or separation of binder and pigment. Our study shows significant differences in appearance between the various brands of acrylic paint, especially between student- and artist-quality paints.



FIGURE 2 Black paints (from top to bottom): Golden Fluid, Guardi, Kreul Solo Goya Acrylic Pastos, Kreul Solo Goya Acrylic Fluid, and Kreul Solo Goya Triton (cracks), with addition of white impasto.

References

- Seymour, P. 2003. *The Artist's Handbook: A Complete Professional Guide to Materials and Techniques*. London: Arcturus Publishing.

A Simple Solution to a Complex Problem: The Consolidation of Joan Miró's *Portrait of a Young Girl*

Christina Milton O'Connell

Finding an appropriate adhesive to consolidate a matte, unvarnished painting can be a challenge. Add to that a range in solvent sensitivity among different colors in the painting, considerable variation in paint thickness, and a painted inscription on the raw fabric of the verso, and the decision concerning adhesives becomes more complicated. The treatment of Joan Miró's *Portrait of a Young Girl* (fig. 1), painted in 1966, prompted the search for an adhesive that did not readily saturate or darken the matte colors or change the gloss of the varied surfaces, did not penetrate the support and markedly darken the fabric (which could be visible from the front through thin paint and ground layers) or interfere with the legibility of the inscription on the verso, and had enough adhesive strength to hold both thinly applied and more impastoed layers of paint.

Once the solvent sensitivity range was determined for each color, a variety of aqueous and solvent-based adhesives were empirically tested to determine which met the desired properties. Of the adhesives tested (including gelatin, sturgeon glue, Aquazol, BEVA D-8, Lascaux P550-40TB, and BEVA 371), Aquazol was the only one that successfully fit all the criteria. Aquazol (Polymer Chemistry Innovations) is composed of poly(2-ethyl-2-oxazoline). Its properties made it possible to use different molecular weights (MW) of the adhesive and alter the diluents so that the same consolidant could be used throughout the painting. Ten percent concentrations of Aquazol 50 (MW = 50,000), 200 (MW = 200,000), and 500 (MW = 500,000) were applied by brush in mixtures consisting of water, isopropanol, acetone, and ShellSol 135, depending on the specific sensitivity of each color or medium. For better penetration, Aquazol 50 was applied first, followed by Aquazol 200, and then Aquazol 500 where greater adhesive strength was needed. A hot-air tool and silicone brushes were used to realign and set down raised flakes of paint (fig. 2).



FIGURE 1 Joan Miró (Spanish, 1893–1983), *Portrait of a Young Girl*, 1966. Private collection, Indianapolis. Published with permission. © 2007 Successió Miró/Artists Rights Society (ARS), New York/ADAGP, Paris.



FIGURE 2 Raking light detail of figure 1 taken before treatment, showing extensive flaking between the paint and the porous ground layer. © 2007 Successió Miró / Artists Rights Society (ARS), New York / ADAGP, Paris.

In addition to successfully meeting the criteria listed above, Aquazol should not interfere with any future analysis of the artist's materials. The compatibility of Aquazol with a wide variety of materials, from traditional protein glues to waxes, also makes the painting easily retreatable.

Conservation Treatment of Ultramarine Oil Paint on Michael Craig-Martin's *Full Life*

Julia Nagle and Miguel d'Almeida

There are some things that gracefully age and other things that just look a mess.

—MICHAEL CRAIG-MARTIN (2003)¹

Full Life (1985; Tate T07392) is a sculpture made of a wooden support with welded steel elements and a painted aluminum panel attached (fig. 1). The layer sequence on the aluminum is as follows: two-part etching primer, white acrylic gesso primer, titanium white oil paint, pencil drawing, compositional elements masked with tape, Winsor & Newton ultramarine artists' oil color rolled on, masking tape peeled off to reveal white.²

Prior to conservation, the flat blue paint surface looked unevenly saturated and dusty: whitish spots, reminiscent of mold, were scattered throughout. Other damages included cotton wool fibers caught in the paint, abrasion around the edges caused by handling that exposed yellowish priming, and, where masking tape had been cut away with a scalpel, some lifting of white paint and ground from the support.

Under magnification, the "mold" spots appeared as a crystalline material that had exuded from the ultramarine blue paint, particularly around the peaks created when it was rolled on (fig. 2). There was more exudate toward the bottom of the painting, where the corrosion of the steel elements was also worst. The corrosion indicated *Full Life* had been subjected to high humidity levels.

To date, the cause of the exudate is unclear. Analysis by Fourier transform infrared (FTIR) spectroscopy, gas chromatography/mass spectrometry (GC/MS), and energy dispersive X-ray analysis (EDX) has identified only synthetic ultramarine pigment and linseed oil. The underlying white paint consists of titanium white and chalk (EDX). Imaging under a scanning electron microscope showed no obvious differences between damaged and undamaged areas of blue paint, and both white and blue paint films appeared very lean.



FIGURE 1 Michael Craig-Martin (British, b. 1941), *Full Life*, 1985. Oil on aluminum and steel, 211 × 261 cm (83 × 102¾ in.). London, Tate, T07392. © Tate, London, 2007. © Michael Craig-Martin.

However, EDX has revealed levels of sulfur and aluminum that are too high to be accounted for just by the ultramarine pigment. One potential source of the excess aluminum could be alumina hydrate, which was added to Winsor & Newton's ultramarine artists' oil color to control the consistency.³

The blue paint blanched on contact with water and polar solvents, but was unaffected by low aromatic hydrocarbons. Loose dirt was cleared with a soft brush and Groomstick molecular trap. Other accretions, such as cotton wool fibers, were removed mechanically under magnification. Raised paint was consolidated with Paraloid B72 in ShellSol A, and damages around the edges were retouched with pure ground synthetic ultramarine in 1% Regalrez 1094.

The firmly anchored exudate could only be removed mechanically, which resulted in a polishing of the paint surface. Therefore, a 1% solution of Regalrez 1094 in naphtha

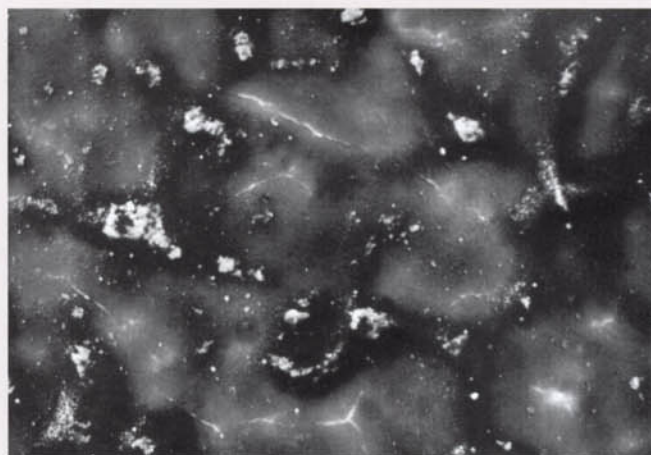


FIGURE 2 Magnification of blue paint in figure 1.

was applied to affected areas with an airbrush. The low boiling point of the naphtha reduced the gloss of the resin, and the airbrush enabled controlled, localized application. This reversible process was repeated until the hue and saturation appeared even across the panel.

Notes

- 1 Interview with Michael Craig-Martin by Tate Sculpture Conservation, 2003.
- 2 Conversation between M. Craig-Martin and author, 2004.
- 3 Correspondence with Alun Foster, chief chemist, Winsor & Newton, 2004.

Eugène Leroy's Painting: A Moving Matter

Grazia Nicosia



FIGURE 1 Eugène Leroy (French, 1910–2000), *G* (detail), 1995. Oil on canvas, 193 × 131 cm (76 × 51¾ in.). Paris, Collection du Fonds National d'Art Contemporain, Ministère de la Culture et de la Communication. Published with permission of the Eugène Leroy Estate.

Approximately forty paintings by Eugène Leroy (1910–2000), a French artist emblematic of “matter painting,” were examined. Eugène Leroy painted in oil without any added siccatives on stretched canvas. The painted matter is sometimes more than 4 cm (1.6 inches) thick (fig. 1). Although the materials used are traditional, the implementation is unusual. The paint’s weight and thickness, and the strong smell of linseed oil emanating from the pictorial layer, are characteristic of Leroy’s paintings. The pictorial matter polymerizes only on its surface, while the deep layers remain viscoplastic. The painted matter is thus solid yet soft and develops a mobile behavior (fig. 2), leading to complications in discerning and defining their surfaces.

Studying the artist’s intention permitted only a theoretical reconstruction of the original state. The viscoplastic

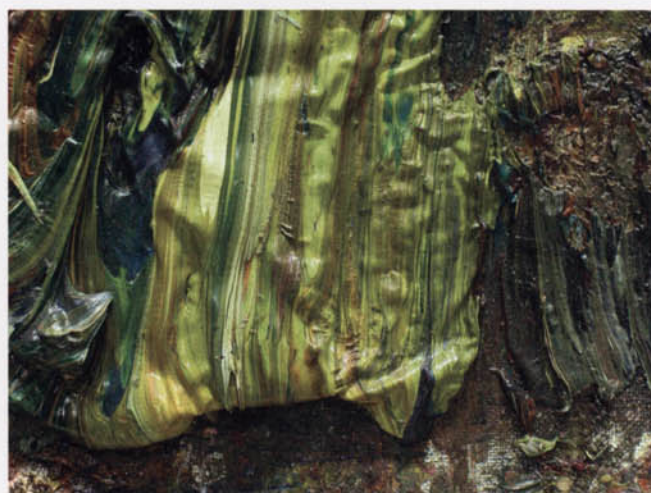


FIGURE 2 Eugène Leroy (French, 1910–2000), *Pour Maxime* (detail), 1987–90. Oil on canvas, 162 × 130 cm (63¾ × 51¼ in.). Paris, Collection du Fonds National d'Art Contemporain, Ministère de la Culture et de la Communication. Published with permission of the Eugène Leroy Estate.

state of the matter makes the work itself changeable. While these changes are intrinsic to its material, they do not correspond to the intention of the artist. An illustrated typology of the material alterations in paintings with heavy impasto on stretched canvas was developed, including the movements of painted matter, and preventive conservation measures that are specific to the storage and display of this type of work were suggested. For example, it requires specific space and light conditions to assert itself as a three-dimensional work of art—the shadow shed by the matter’s relief becomes a “moving” color of its own.

Acknowledgments

Thanks to Sylvie Dassiou for her translation of this abstract.

Tate AXA Art Modern Paints Project: Evaluating the Effects of Cleaning Acrylic Paintings

Bronwyn A. Ormsby, Thomas J. S. Learner, Patricia Smithen, and Thomas Wessel

For the conservation profession, there are a number of potential concerns when cleaning acrylic emulsion paints, including paint film softness, solvent sensitivity, swelling with aqueous systems, extraction of soluble components, ingrained dirt and fingerprints (fig. 1), surface changes (such as uneven gloss, tide lines, and burnishing), unknown long-term and aging effects, and a general lack of specific training among conservators.

Tate has been involved in a long-term research strategy to address some of these concerns. To date, over six hundred samples have been prepared, on canvas and as free films, using four pigment types and gesso from four brands of paint, as well as examples with added gloss medium (1:1 v/v) and dilution with water (1:1 v/v) (fig. 2). The properties of these paints have been monitored and compared after cleaning tests and artificial-aging regimes, including their physical properties, such as flexibility, stiffness, and response to relative humidity (RH); chemical properties, such as surface chemistry and extracted material; and optical properties, including changes in color, gloss, and surface morphology.

The research so far has shown that acrylic emulsion paints are flexible and degradation resistant after accelerated aging, compared to oils and alkyds, and that these paints are very responsive to changes in temperature and RH. Swabbing tests of up to one minute with aqueous systems were proven to remove surface surfactant but had little effect on physical properties, whereas cleaning with nonpolar organic solvents did *not* remove surfactant from the paint surface or bulk film. Removal of bulk film surfactant (by immersion in polar solvents or thermal aging) was shown by thermal analytical methods to render these paints less responsive to moisture and to increase film stiffness. Any visual changes caused by surface cleaning were minimal, with potential for only minor changes in gloss.

The Tate AXA Art Modern Paints Project (TAAMPP) aims to build on this research by addressing some of the

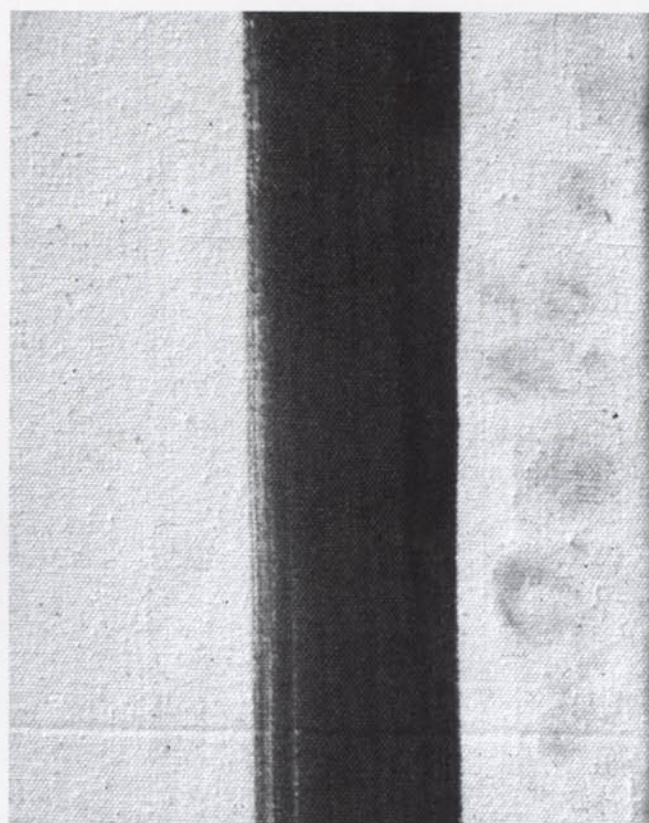


FIGURE 1 Ingrained dirt and finger marks in the acrylic gesso of a painting.

more practical aspects of the conservation of acrylic emulsion paints. While investigation into general paint properties such as swelling and permeability will continue, the next three years will focus on complementary aspects, such as cleaning efficacy (i.e., assessing the effects of dirt removal) and the assessment, improvement, and development of cleaning methods (including nonpolar, aqueous, and dry methods, as well as new developments), exploring issues around the soiling of these paints, and the cumulative effects



FIGURE 2 Assortment of paint samples ready for cleaning treatments.

of treatment and aging. In addition to this, five acrylic emulsion paintings in the Tate Collection will be surface cleaned and the treatments evaluated as case studies.

The benefits of TAAMPP will aid both preventive conservation and practical treatments by providing further clarification of the long-term effects of surface-cleaning treatments and aging on paint properties, exploring dirt deposition and retention, building understanding of how surface cleaning may affect resoiling, enabling conservators to choose and modify cleaning systems with possible new treatment options to tackle some of the difficult cleaning issues, and providing credible examples as case studies—which will take the research directly to practicing conservators.

Alterations in Unvarnished Contemporary Paint in Spain: A Visual Approach

*Maria Teresa Pastor Valls and
Maria del Carmen Pérez García*

The conservation and restoration of contemporary works involves investigation of the concept of the work, unusual materials and techniques employed, causes that contribute to the appearance of alterations, and the artist's role and legal rights regarding any intervention that may modify the aesthetic or conceptual aspects of the work.

This poster describes initial results from a research project entitled Unvarnished Contemporary Paint Stabilization Systems and Treatments Research: Criteria and Methodology of Intervention. For this project, it was considered necessary to carry out a preliminary field study that permitted a visual approach to the problem in order to establish the bases to be developed in the experimental phase. In this way, different forms of aging have been observed in the relationship between binding media and surface alterations.

The objectives of the project were to

- define different forms of alterations for unvarnished paint layers, in relation to the materials employed;
- know which alterations are more frequent and which need intervention or treatment;
- understand the main factors and causes of the alterations;
- survey the opinion of conservators regarding these alterations;
- establish guidelines for carrying out tests in the future.

Data were obtained and collected from photographs, a field record sheet, and a survey form for conservators (sent to different contemporary art museums and Spanish educational institutions). A database was designed to handle all the incoming data. Paintings from a selection of local museums in Valencia were also included, as examples where measures of preventive conservation are lacking and unfavorable display conditions are experienced.

The main factors responsible for the alterations found were incorrect environmental conditions (i.e., high temperatures, low relative humidity, strong lighting, lack of fresh air), incorrect handling, and factors derived from the technique employed.

Figure 1 shows the number of instances of each type of alteration in each of the main types of paint (oil, acrylic, gouache, vinyl, and mixed techniques).

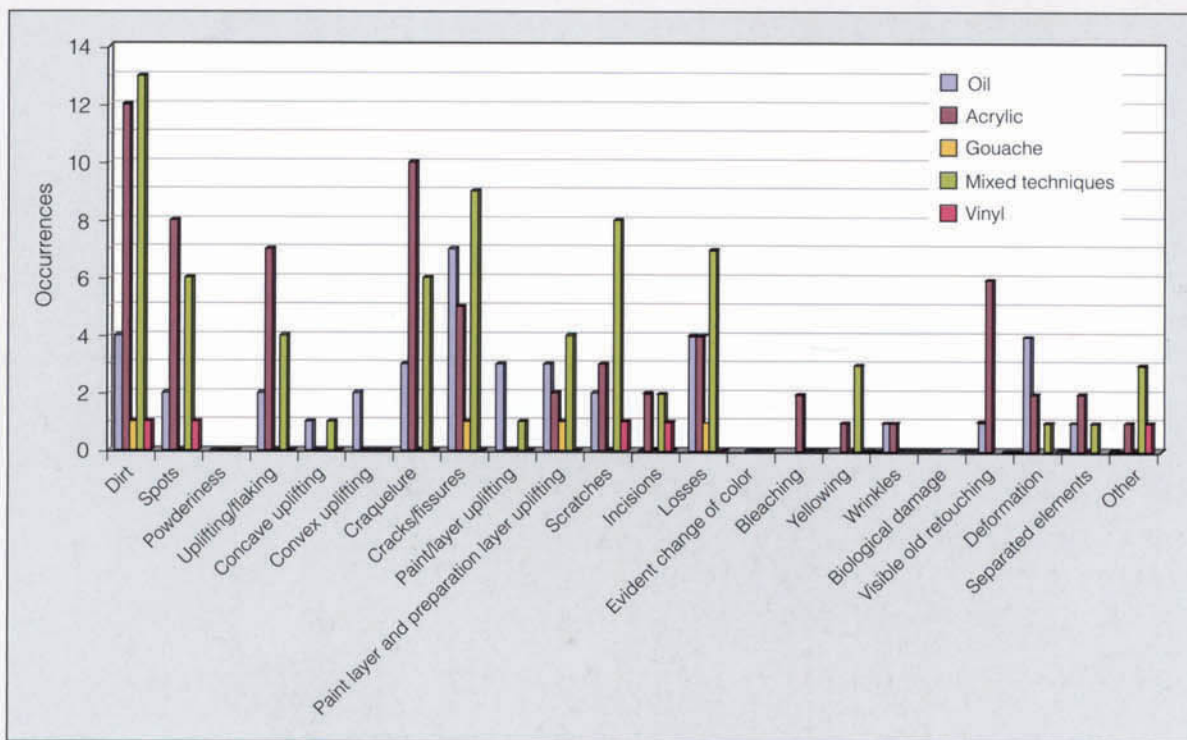


FIGURE 1 Occurrences of various alterations in five types of paint.

Our conclusions can be summarized as follows:

- Of the 304 works studied, a high percentage presented some type of alteration.
- The most frequent alterations detected were dirt accumulation, spots, craquelure, cracks/fissures, losses, and lifting or flaking paint or ground.
- The alterations needing urgent intervention included lifting (paint layer separating from the preparation layer, and ground separating from the support) and the areas of loss.
- All alterations usually appear in localized areas.
- Mixed techniques presented the greatest stabilization problems, followed first by oils and then by acrylics.
- Factors that most affected appearance include accidents and deliberate damage, adverse environmental conditions, and the technique employed (e.g., loss of adhesion between layers, weakening of the adhesive, and use of stiff and thick mixtures).
- Preventive conservation measures have a significant positive impact on the condition of the paintings.

Acknowledgments

The study was subsidized by Fundación ICO, Instituto de Crédito Oficial, with a grant for the cited thesis project (2003–4, 2004–5).

Julião Sarmiento, a Portuguese Artist at Work: Study of *Just a Skin Affair* (1988)

Ana Isabel Pereira, Stephan Schäfer,
and Maria João Melo

To date, only a few technical studies have been done on Portuguese contemporary and modern art and artists. Julião Sarmiento (b. 1948) is a Portuguese contemporary artist who has received international recognition. In our project, a detailed study of the materials and techniques used by the artist in the 1988 painting *Just a Skin Affair* (fig. 1) was carried out. An interdisciplinary approach involved an extensive artist interview and collaboration with the Portuguese manufacturer of the materials used by the artist. The painting illustrates Sarmiento's working methods in the 1980s. At that time, Sarmiento mixed dry pigments with an aqueous dispersion of polyvinyl acetate sold under the trade name Vulcano V7. For this practice he would have drawn on the time he spent in 1969 as assistant to Joaquim Rodrigo (1912–1997), who was already using this painting technique, as well as on his academic training, which included using conventional methods (according to Sarmiento, "We had to



FIGURE 1 Julião Sarmiento (Portuguese, b. 1948), *Just a Skin Affair*, 1988. Polyvinyl acetate emulsion on canvas, 120.7 × 140.5 cm (47½ × 55¼ in.). Lisbon, Fundação Calouste Gulbenkian—Centro de Art Moderna. Photo: Angel Ordiales. Published with permission of the artist.

use oil paints, egg temperas made by ourselves”).¹ Sarmiento said that this method “was much cheaper, and that was important for me.”

For *Just a Skin Affair*, Sarmiento worked on bare cotton canvas, building up a variable number of paint layers. The medium used by Sarmiento in this painting has been confirmed as a polyvinyl acetate using Fourier transform infrared (FTIR) microspectroscopy (fig. 2). The pigments identified by FTIR and X-ray fluorescence (XRF) microspectrometry are mostly inorganic, with the exception of an organic yellow and red. Furthermore, “The colors seen in this painting, more than colors, are ‘dirty’ colors that are obtained through paint residues. I would grab the remains of other paints and add all of them together.”

At least one layer was literally dirty—made with dust and PVA. As described by Sarmiento, this brown layer was “garbage—I swept the studio’s garbage and got a brown pow-

der mixed with branches and trash.” By this time it was usual for the artist to create textured surfaces by adding various kinds of substances to the paints. He explained that “the canvas surface had to be tactile for me. I realized that I could change it using many tricks like sand, badly dissolved pigments, tobacco.”

According to Sarmiento, at the time he had adopted an “experimental and spontaneous attitude” in the creation of his works of art. He chose his material based on aesthetic quality first, and then durability. In his own words, “If the works disappear, they disappear. I will not modify one inch of my work thinking about durability. The work ages. They get the look of time passing by, which is also important.”

Acknowledgments

We would like to thank the artist, Julião Sarmiento, and Dr. Ana Vasconcelos, curator of the Calouste Gulbenkian Foundation, Center of Modern Art, in Lisbon.

Analytical Details

- FTIR: Nexus and Continuum-Nicolet FTIR microspectroscopy in transmittance mode, spectral region 4000–650 cm^{-1} , diamond anvil cell
- XRF: ArtTAX XRF microspectrometer equipped with a polycapillary lens and Silicon-DRIFT detector

Notes

- 1 All quotations come from an interview with Sarmiento conducted by Ana Isabel Pereira in the artist’s studio in Sintra, Portugal, in 2003.

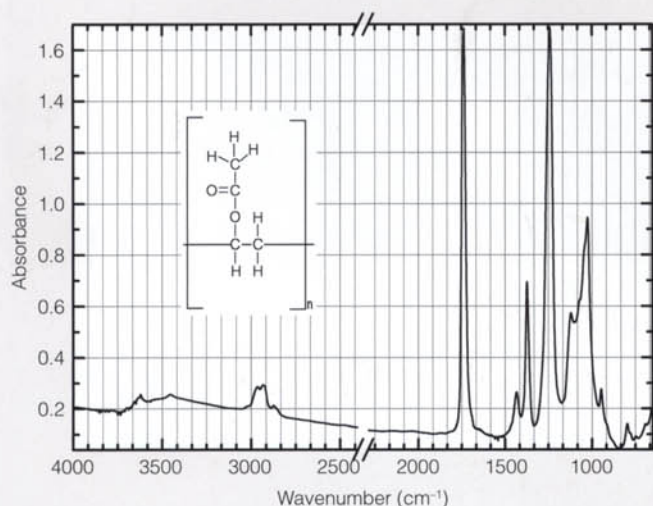


FIGURE 2 FTIR spectrum of the binding medium from a sample of Sarmiento’s *Just a Skin Affair*, showing the characteristic absorption bands of polyvinyl acetate.

Fluor-S-Art, Northern Lites, DayGlo: Daylight Fluorescent Pigments, Their Development, Use, and Performance

Sarah Eleni Pinchin and Jia-sun Tsang

An American invention, daylight fluorescent pigments are seen everywhere in modern life, from Warhols to Tide detergent cartons. Created in 1934 by the brothers Robert and Joseph Switzer, founders of the DayGlo Color Corporation, these pigments (fig. 1) have influenced the public's consciousness of color. Because of the additive effect in which radiation is absorbed and reemitted at longer wavelengths, daylight fluorescent pigments are extremely bright—in fact, brighter than white, as seen in Ken Kesey's "Acid Test" Signboard (fig. 2).



FIGURE 1 Switzer Brothers pigments, ca. 1950.



FIGURE 2 Ken Kesey (American, 1935–2001) and the Merry Pranksters, "Acid Test" Signboard, ca. 1964. Painted paper on plywood, 173.7 × 96.5 cm (68 × 38 in.). Washington, D.C., National Museum of American History, Smithsonian Institution, 1992.0413.01. Published with permission.

These pigments were originally made by suspending a small amount of fluorescent dye in resin, and the process has deviated little from the basic formula over time, making object-condition surveys from that seventy-year period particularly relevant for contemporary works. Based on interviews and materials from the archives of DayGlo Color, our study provides a review of fluorescent paint production, which should assist conservators in the physical assessment of these paints.

Because these bright colors are extremely fugitive when exposed to light, the original color is sometimes completely lost, and there is no easy way to determine whether the object was once Arc Yellow or Neon Red. Indeed, due to the fading process, these colors may not look fluorescent at all. To preserve this material (bearing in mind that it is not possible to adequately document the extent of fluorescence in photographic prints), conservators need to know how to characterize these pigments using ultraviolet light and provide appropriate guidelines to mitigate prolonged light exposure.

Rescue Public Murals!

William Shank and Timothy Drescher

Today, many of the hundreds of masterpieces of mural art, especially those from the 1970s and 1980s, are in serious disrepair. These murals constitute a major piece of the United States' artistic heritage (fig. 1). Many were created by Chicano, Asian American, and African American artists for neighborhoods lacking in established cultural resources, and they will soon disappear unless steps are taken to save them.

Rescue Public Murals was formed in April 2004, when a group of distinguished muralists, art historians, conservators, and arts administrators met in Los Angeles, courtesy of the Getty Conservation Institute and the Getty Research Institute, to explore ways to locate and save public murals. It is sponsored by Heritage Preservation, which is guided by its highly successful Save Outdoor Sculpture! program (see www.heritagepreservation.org/programs/sos).

Priorities for Rescue Public Murals are to

- prepare a list of “highly endangered murals,” which will be widely publicized—these will be murals that are artistically significant are endangered, and enjoy support in their communities;
- conduct assessments of the most endangered murals—using teams of artists and conservators and working with members of the local community—to provide recommendations and budgets for saving them;
- work with communities to generate funds to save murals, through matching grants and additional fund-raising;
- develop an illustrated national online database of community murals; and
- develop and disseminate guidelines for maximizing the longevity of mural materials and caring for extant murals.

While community murals offer a relatively untouched field for conservators, special circumstances require unusual

approaches. What sets community murals apart from easel paintings and the great Mexican (and other) frescoes is that they are primarily social. The word *community* refers to the daily audience of the mural as well as its producers, including artists and sponsors, whoever owns the wall underlying the

mural, and sometimes official or semiofficial groups, boards, commissions. The daily audience whose interests generated a mural comes first (otherwise it is not a community mural), and people in communities, including artists, change their attitudes, their likes and dislikes. Their murals reflect this



FIGURE 1 Dewey Crumpler (American, b. 1949), *The Fire Next Time I*, 1977. (Destroyed in 2007.) Acrylic emulsion on concrete, 11 × 13.7 m (36 × 45 ft.). San Francisco. Published with permission of the artist.

variability and dynamism. For community mural preservation, the most important factors are the determinant social contexts surrounding each mural—multiple social contexts of which the mural is a dynamic, vital artistic record.

For conservators, this requires a different approach than the usual. Traditionally, a conservator's job has been to protect static objects, but community murals are not static. This does not mean conservators have no role in their restoration, only that their role must be reconceived in light of community murals' distinctive characteristics—most importantly as part of a social process inflected by artistic and technological concerns.

While in traditional conservation the goal is often to restore the original state of the painting—or what is left of it—the conservation of community murals must meet the desires of the mural's surrounding audience, community, and history. It is the brave new world of conservation.

The Art Materials Collection and Study Center

Michael Skalka

The Art Materials Collection and Study Center at the National Gallery of Art in Washington, D.C., was created in 1994 to archive paints, literature, and related art products so that future generations would have unadulterated, primary resource material for study. More than seventeen thousand items have been catalogued in this growing collection. In addition, materials from well-known artists and gifts of nineteenth-century wooden watercolor boxes enhance the strength of the collection. An electronic catalogue on compact disc of the holdings in the collection is available; it serves as an item locator and provides extended information on the history and development of art material product lines.

Materials, Techniques, and Artist's Intention in the Geometric Works of José María Yturralde

*Ioseba I. Soraluze Herrera and
Rosario Llamas Pacheco*

The surfaces of the geometric paintings by the Spanish artist José María Yturralde (b. 1942) are particularly important to their meaning. *Prisma 4* (1972) is a work from the *Figuras Imposibles* series and is executed on a plywood support with nails that have rusted, causing the paint to crack and peel. X-radiography confirmed the location of the nails, and chemical analyses—cross-section, Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy/energy dispersive X-ray (SEM-EDX)—identified the different pigments and media used. Colorimetric studies were also performed and the types of wood used were identified.

Because *Prisma 4* is a monochromatic work, any variation on its surface would interrupt the reading of the work, and retouching would have been noticeable. Following an in-depth interview with the artist, overpainting the damaged work was considered the best option. The paint that Yturralde used in 1972 is no longer on the market; however, the original manufacturer prepared special batches of three different types of “matt blue synthetic washable paint” that would be similar to the paint from that period. Yturralde solved the problem with the nails and overpainted his own painting under the guidance of the foundation's conservation department. The ultimate aim of this study is to show that the meaning of this work prevails over the authenticity of the physical structure; in a conceptual piece of this kind, the final aesthetic finish is more important than the original material.

Problems with the Cleaning of Textured Modern Paintings

*Iwona Szmelter, Andrzej Koss,
Jan Marczak, and Marek Strzelec*

The cleaning and conservation of textured modern painted surfaces is highly problematic. Challenges encountered include controlling the penetration of solvents (even when dispersed in a gel or soap), the toxicity of the majority of efficient solvents, the insolubility of many materials, the need for great dexterity and lengthy mechanical interventions, and the need to search for alternative techniques, based on the newest scientific achievements. As restoration practices must be nondestructive, the cleaning of textured painting is a delicate, painstaking job.

This poster presents preliminary results of the project Laser Renovation of Works of Art, carried out in Poland at the Interacademy Institute for Conservation and Restoration of Works of Art (AFA), and the Institute of Optoelectronics, Military University of Technology, Warsaw, under the aegis of the COST G7 Action, EU.

Information about the technique and identification of binding media, pigments, support materials, fillers, and so forth was gathered through interviews with artists (using the model adopted by the International Network for the Conservation of Contemporary Art) and by applying different diagnostic systems on analytical techniques, including laser induced breakdown spectroscopy (LIBS) using a Mechelle 5000 system with an iStar DV434 camera (fig. 1) and Raman spectroscopy (R-3000, Raman Systems, Inc.). Optical coherence tomography was used to control laser ablation. Pilot tests of cleaning were executed at different fluencies of the Er:YAG laser. For example, figure 2 shows a detail of cleaning tests on exposed canvas. One of the most critical parameters of laser cleaning is the substrate ablation threshold, which should always be determined in order to prevent the unwanted removal of underlying layers.

As a primary result, laser cleaning has been evaluated as a most promising technique, particularly for paintings characterized by high nonuniformity of facture. The advantage of laser cleaning is the lower risk of damage to the top

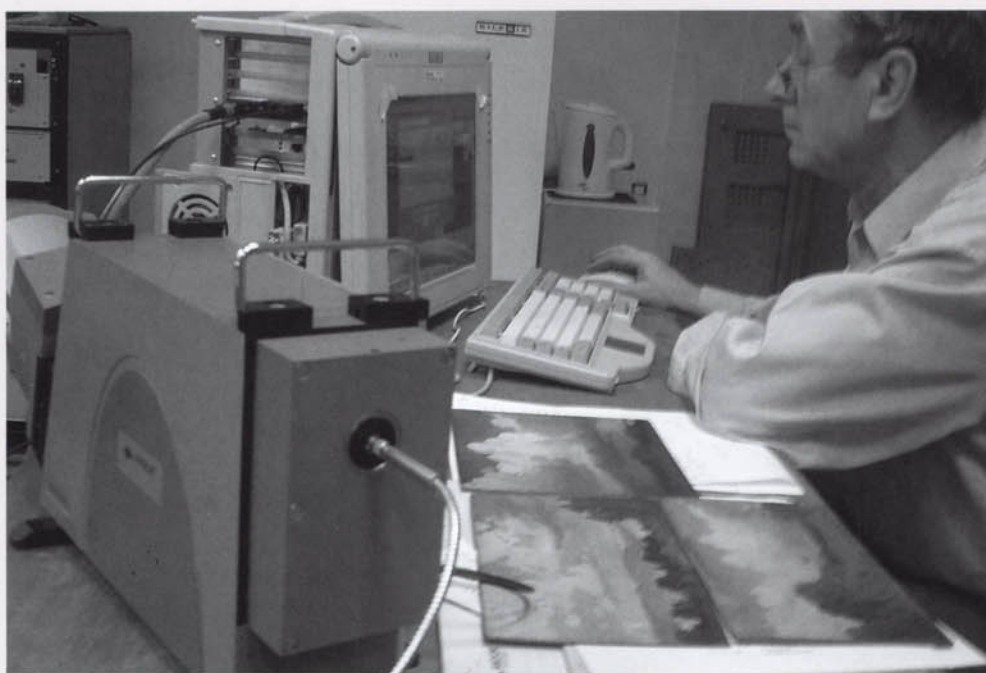


FIGURE 1 Using the LIBS Mechelle spectrometer with iStar DV434 camera to make in situ measurements on paintings.



FIGURE 2 Detail of cleaning tests on the canvas of a painting (*Landscape 1*), by Peter Potworowski. Published with permission of Jan Potworowski, Foundation of P. Potworowski.

layers. A laser has the ability to focus on very small areas, with greater control over the amount and type of material removed, and it is an environmentally friendly technique. However, much more investigation for the laser parameters and the induced chemical and mechanical changes for all applications is still required, because of the broad spectrum of media, pigments, and supports that are encountered.

Acknowledgments

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Symposium Participants

Affiliations of participants are given as of the date of the symposium.

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Adler	Richard	Vitra Design Museum	Weil am Rhein	Germany
Aggerholm	Dorthe	Fælleskonserveringen	Aarhus	Denmark
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Amann	Sandra	Amann+Estabrook Conservation Associates	New York	USA
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Bamforth	Nigel	Victoria and Albert Museum	London	UK
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Barker	Rachel	Tate	London	UK
Barraclough	Graeme	Courtauld Institute of Art	London	UK
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Bushart	Elisabeth	Private practice	Munich	Germany
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Duff	Natasha	Tate	London	UK
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Gayler	Steve	Courtauld Institute of Art	London	UK
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Goris	Ruth	Tate	London	UK
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Hagan	Eric	Tate/Imperial College, London	London	UK
Haiml	Christa	The Menil Collection	Houston	USA
Hale	Tom	White Cube	London	UK
Haner	Paul	St. Louis Art Museum	St. Louis	USA
Harrison	Lynne	The British Museum	London	UK
Harva	Kirsti	Kiasma Museum of Contemporary Art	Helsinki	Finland
Havermark	Katarina	Moderna Museet Stockholm	Stockholm	Sweden
Hayes	James	Golden Artist Colors	New Berlin, New York	USA
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Hons	Sandra	University of Applied Science	Bern	Switzerland

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Izzo	Carolina	Te Papa	Wellington	New Zealand
Jones	Rica	Tate	London	UK
Jónsson	Olafur	National Gallery of Iceland	Reykjavik	Iceland
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Kaltenbruner	Gerda	Akademie der Bildenden Künste	Vienna	Austria
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Keneghan	Brenda	Victoria and Albert Museum	London	UK
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Khandekar	Narayan	Straus Center for Conservation, Harvard University Art Museums	Cambridge	USA
Khanjian	Herant	Getty Conservation Institute	Los Angeles	USA
King	Annette	Tate	London	UK
Kinseher	Kathrin	Akademie der Bildenden Künste	Munich	Germany
Kirsch	Kathrin	Restauratieatelier Amsterdam SKRA	Amsterdam	Netherlands
Konefal	Irene	Museum of Fine Arts	Boston	USA
Krist	Gabriela	Universität für angewandte Kunst	Vienna	Austria
Kristiansen	Susanne	People's History Museum	Manchester	UK
Krueger	Jay	National Gallery of Art	Washington, D.C.	USA
Kunzelman	Diane	Opificio delle Pietre Dure & Laboratri de Restauro di Firenze	Florence	Italy
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Lang	Ulrich	Museum of Modern Art (MMK)	Frankfurt	Germany
Learner	Thomas	Tate	London	UK
Levenson	Rustin	Rustin Levenson Art Conservation Associates	Miami	USA
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Lowry	Kate	National Museum Wales	Cardiff	UK
Mack	Abigail	National Gallery of Art	Washington, D.C.	USA
Mackinnon	William	Private practice	London	UK
Madzarac	Nada	Museum of Modern Art	Ljubljana	Slovenia
Mancusi-Ungaro	Carol	Whitney Museum of American Art	New York	USA

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Martins	Elizabeth	Unversidade Nova de Lisboa	Almada	Portugal
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McDonald	Elizabeth	Tate	London	UK
McSharry	Carolyn	Victoria and Albert Museum	London	UK
Menu	Michel	Louvre	Paris	France
Miettinen	Marianne	Espoo Museum of Modern Art (EMMA)	Helsinki	Finland
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Miller	Rose	Courtauld Institute of Art	London	UK
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Milton O'Connell	Christina	Indianapolis Museum of Art	Indianapolis	USA
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Morrison	Rachel	Courtauld Institute of Art	London	UK
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Perry	Roy	Tate	London	UK
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Phillips	Glenn	Getty Research Institute	Los Angeles	USA
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Poisson	Marie-Chantale	San Francisco Museum of Modern Art	San Francisco	USA
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Preusser	Frank	Los Angeles County Museum of Art	Los Angeles	USA
Pullen	Derek	Tate	London	UK
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Ramsay	Barbara	Artex Fine Art Services	Landover	USA
Rava	Antonio	Studio Rava	Turin	Italy
Richardson	Clare	Tagar Stonor Richardson	Uxbridge	UK
Richenberg	Jennifer	Royal Academy of Arts	London	UK
Ridge	Jacqueline	Tate	London	UK
Rivers	Shayne	Victoria and Albert Museum	London	UK
Rogala	Dawn	Buffalo State College Art Conservation Program	Buffalo, New York	USA
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Ryder	Nicole	Private practice	London	UK
Saltmarsh	Polly	Courtauld Institute of Art	Cambridge	UK
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Saunders	David	The British Museum	London	UK
Saunders	Linnaea	Los Angeles County Museum of Art (LACMA)	Los Angeles	USA
Scalisi	Lucia	Private practice	London	UK
Schaening	Anke	Akademie der Bildenden Künste	Vienna	Austria
Scheidemann	Christian	Contemporary Conservation, Ltd.	New York	USA
Schilling	Michael	Getty Conservation Institute	Los Angeles	USA
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Scholte	Tatja	Instituut Collectie Nederland (ICN)	Amsterdam	Netherlands
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Skalka	Michael	National Gallery of Art	Washington, D.C.	USA
Skopek	Matthew	Museum of Modern Art	New York	USA
Smit	Ingebord	Rijksmuseum Twenthe	Amsterdam	Netherlands
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Smith	Margaret	Private practice	Anstey	Bermuda
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Smithen	Patricia	Tate	London	UK
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Standeven	Harriet	Royal College of Art/ Victoria and Albert Museum	London	UK
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Steele Pullman	Dawne	Private practice	Honolulu	USA
Stenger	Jens	Straus Center for Conservation	Cambridge	USA
Stevenson	Lesley	National Galleries of Scotland	Edinburgh	UK
Stonor	Katherine	Courtauld Institute of Art	London	UK
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Szmelter	Iwona	Academy of Fine Arts	Warsaw	Poland
Tager	Sharon	Tel Aviv Museum of Art	Hod Hasharon	Israel
Tallent	Carolyn	Private practice	Santa Monica, California	USA
Taor	Sally	Courtauld Institute of Art	London	UK
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Thornton	Vic	White Cube	London	UK
Townshend	Piers	Tate	London	UK
Tsukada	Masahiko	Tokyo National Museum	Tokyo	Japan
Turnbull	Rachel	National Museum Wales	Cardiff	UK
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Vernaza Albisser	Clemencia	Solomon R. Guggenheim Museum	New York	USA
Von Imhoff	Hans-Christoph	Private practice	Vicosoprano	Switzerland
Walsh	Valentine	Private practice	London	UK
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Weilhammer	Ulrich	Tainan National University of the Arts	Tainan County	Taiwan
Welch	Stephan	Getty Research Institute	Los Angeles	USA
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Whalen	Timothy	Getty Conservation Institute	Los Angeles	USA
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Whitmore	Paul	Carnegie Mellon University	Pittsburgh	USA
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Willisch	Susanne	Doerner Institut	Munich	Germany
Winkelmeyer	Iris	Lenbachhaus München	Munich	Germany
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Author Biographies

Biographies are current as of the date of the symposium.

Francesca Attanasio holds an FH degree (diploma) in conservation and restoration from the University of Applied Science, Bern, Switzerland. Since 2004, she has been a freelance conservator, and she is currently working on various paint conservation projects in Germany.

María Jesús Ávila holds a PhD in art history from the Extremadura University (1995), and from 1995 to 1999 she was a professor in the department from which she graduated. Ávila is now a curator at Chiado Museum, National Museum of Modern Art in Lisbon, where she has commissioned several exhibitions. Her research is concerned with Portuguese modern and contemporary art, and she has also contributed to catalogues and specialty magazines.

Mauro Bacci is director of research at the Institute of Applied Physics, Nello Carrara (IFAC-CNR), Florence. His main interest is in spectroscopy, from both a theoretical and an applied point of view. For many years, he has been developing totally nondestructive spectroscopic techniques for the study of the works of art.

Jaap J. Boon was trained in geology and chemistry at the Universities of Amsterdam and Utrecht and at Delft Technical University. He started in 1983 as a research associate at the Foundation for Fundamental Research on Matter (FOM), Institute for Atomic and Molecular Physics (AMOLF), and was made head of molecular physics there in 1987. He became a professor of molecular paleobotany at the University of Amsterdam in 1988, and a professor of analytical mass spectrometry at the university in 2003. Boon initiated the Netherlands Organization for Scientific Research (NWO) priority project MOLART

(Molecular Aspects of Ageing in Art), granted in 1995, and the De Mayerne Program in 2002. Presently, he is the head of the Molecular Paint Research Group at AMOLF, which focuses on the chemical microscopy of pigments and binding media and their interactions in paintings. He is the author or a co-author of more than 350 research papers, and has supervised more than thirty PhD theses.

Aviva Burnstock is head of the Department of Conservation and Technology at the Courtauld Institute of Art, London, where she took a PhD (1991) and a diploma (1984) in the conservation of easel paintings. She has been a Joop Los Fellow at the Institute for Atomic and Molecular Physics (FOM/AMOLF in Amsterdam since 2003, and from 1986 to 1992 she worked in the Scientific Department of the National Gallery, London, following a year as a practicing conservator with the Regional Galleries Association of New South Wales, Australia. Burnstock also has a BSc in neurobiology from the University of Sussex, England.

Walter Caseri has a doctorate in chemistry and has been active as a senior scientist since 1996 at the Institute for Polymers, Swiss Federal Institute of Technology ETH, Zürich. He is involved in both research and teaching.

Maria Charalambides, PhD, has been a senior lecturer in the Mechanical Engineering Department of Imperial College, University of London, since 2004, and a member of the academic staff since 1997. Prior to this, she was a senior scientist at the National Physical Laboratory. She has published approximately forty papers, on topics including material characterization of soft solids; food processing, such as rolling, extrusion,

and cutting; repair of fiber-reinforced polymer composite materials and strength prediction of adhesively bonded joints; delamination in composite materials; development of inverse methods for material characterization; properties of particulate-filled polymer systems; and mechanical properties of paint coatings.

Oscar Chiantore is a professor of chemistry and technology of polymers at the University of Torino, Italy, where he also teaches chemistry of conservation and degradation of materials. His scientific activity is principally directed toward the analysis and characterization of organic materials in works of art and the investigation of degradation mechanisms and stability of polymers and other film-forming materials. One of Chiantore's ongoing interests is conservation problems in modern and contemporary art, and he is consequently involved in studies of modern artists' paints, particularly acrylics and alkyds, and on plastic materials in artworks. He has recently published *Conservation of Contemporary Art* (in Italian), co-authored with Antonio Rava, a restorer specializing in this field.

James Coddington, a graduate of Reed College, Oregon, and the Winterthur/University of Delaware conservation program, is the Agnes Gund Chief Conservator at the Museum of Modern Art (MoMA), New York. A paintings conservator, he has published and lectured on a range of topics concerning the preservation and conservation of modern art. These have included the theory and practice of modern art conservation, structural restoration of paintings, infrared imaging of modern works of art, and the materials and techniques of Jackson Pollock. He was also a co-editor, with Maryan Ainsworth, of the summer 1995 issue of *Art Journal*: "Conservation and Art History."

Val G. Colaluca received a BS in biology from Point Park University, Pittsburgh. He is an associate scientist at the Art Conservation Research Center, Carnegie Mellon University, Pittsburgh.

Dana Cranmer received her BA in fine arts from Scripps College, Claremont, California, in 1970 and an MA in fine arts from Hunter College, New York, in 1975. She worked at the Solomon R. Guggenheim Museum from 1970 until 1981, when she became the conservator of The Mark Rothko Foundation. In 1988, she founded Cranmer Art Conservation, Inc., located in New York.

Stuart Croll is a professor in the Department of Coatings and Polymeric Materials at North Dakota State University. His principal research interest is the photodegradation of coatings during weathering, but he also works on colloidal stability and phase separation in pigment and latex suspensions and nanoscale characterization of coatings. Croll was previously with Millennium Inorganic Chemicals, a manufacturer of titanium dioxide pigments, where he was the director of the Pigment Research and Analytical departments. He earned a degree in physics from the University of London, and subsequently completed a doctorate in physics at the University of Leeds. He then worked in England for a time, moving later to the Division of Building Research in the National Research Council of Canada, where he studied the internal stresses in coating films that arise during curing. He spent fourteen years at the Sherwin-Williams paint company, where he studied film formation in aqueous and nonaqueous coatings, application rheology, weathering of coatings, and a variety of other topics, eventually becoming director of research and head of the Analytical Department in the Coatings Division.

Corey D'Augustine is the Kress Fellow at MoMA, New York. His primary interest is in the conservation and technical art history of modern and contemporary painting.

Suzan de Groot studied analytical chemistry at the Hogeschool, Amsterdam, graduating in 1996. She has worked at the Netherlands Institute of Cultural Heritage (ICN) since 1996, and is currently engaged in FTIR analyses of materials used in objects of cultural heritage, carrying out artificial aging experiments and testing physical and mechanical properties of paper. She is also responsible for the ICN quality standards for archival materials.

James R. Druzik is a senior scientist at the Getty Conservation Institute, where he has worked since 1985. Previously, he worked at the Los Angeles County Museum of Art and the Norton Simon Museum. His interests have been centered on preventive conservation research, beginning in the late 1970s on gaseous and particulate air pollution effects on materials of cultural value. For the ten-year period from 1988 to 1998, he and Pamela Vandiver, Smithsonian Institution, organized five symposia through the Materials Research Society entitled "Materials Issues in Art and Archaeology." Since the late 1990s, his interests in environmental risks to cultural materials have been supplemented by an active research interest in environmental influences on material properties and reducing photo-

chemical risks in museum lighting. He has a BSc in chemistry from the University of Santa Clara.

John A. Escarsega is a research chemist for and leader of the Coatings and Corrosion Team, Materials Application Branch for the U.S. Army Research Laboratory, and is the commodity manager for chemical agent resistant coatings for the Department of Defense (DOD) for military tactical vehicles, aircraft, and support equipment. He received his BS in chemistry from the University of Mary Washington, Fredericksburg, Virginia. Escarsega has been active in coatings research for the DOD since 1981, and is the primary patent holder for the novel water-dispersible coating that is currently being implemented on Army and Marine Corps assets. He is also the author of more than fifty publications and an active member of the American Chemistry Society and the Federation for Coatings Technology, Baltimore.

Nicolai Fenners trained as a painter and varnisher and studied at the University of Applied Sciences in Stuttgart-Vaihingen at the faculty of paint, varnish, and synthetic materials. Since 1994, he has worked in the laboratory of artists' color manufacturer H. Schmincke & Co. GmbH on research and development of oil and acrylic colors.

Joana Lia Ferreira graduated in conservation and restoration from the New University of Lisbon (2001), and is currently a PhD candidate in conservation science at the same university. Her research project, *Liaisons Dangereuses, Conservation of Modern Art: A Study of the Synthetic Binding Media in Portugal*, is focused on the molecular characterization of acrylic and vinyl emulsion paints used by Portuguese artists since the 1950s and the study of those media's photodegradation and evolution with time. As an intern and a professional conservator she has worked at several conservation sites, including two mural paintings of Estrela Faria (1910–1976), a Portuguese modern artist.

Alun Foster has held the job of chief chemist at Winsor & Newton since 1977, having started at the company in 1968. Equally interested in both art and chemistry, Foster chose chemistry and graduated with an external London BSc in chemistry and physics in 1967. Combining the two interests enables him to understand artists' needs and relate their requirements to the formulation of the products. Currently responsible for toxicology, he is also involved in research and development, technical services, quality control, labeling, and enquiries.

Gary M. Foster received his PhD from the University of Exeter in 2006. He is a member of the Thermal Methods Group (Royal Society of Chemistry), and his research interests include novel applications of thermal, rheological, spectroscopic, and mechanical techniques, which he has applied to a wide variety of materials, including thermoplastics, composites, adhesives, paints, rubbers, metals, and ceramics.

Mark Golden, CEO of Golden Artist Colors, has twenty-plus years of industry experience and was most recently elected to the board of directors of the New York Foundation for the Arts (NYFA), one of the country's largest providers of funding and services to individual artists. Golden received one of NYFA's 2005 Inspiration awards, and was also recently honored by the Manufacturers Association of Central New York with a 2005 Wall of Fame award. He has been a guest lecturer at the Smithsonian Institution, the Getty Museum, the Tate Gallery, the College Arts Association convention, and colleges throughout the United States, Europe, and Japan. He has co-authored several technical papers on issues dealing with conservation of acrylic paint and paintings.

Pia Gottschaller did her undergraduate studies in art history at Ludwig-Maximilians-Universität in Munich (BA 1994) and her postgraduate studies in the conservation of easel paintings at the Courtauld Institute of Art, University of London (diploma 1997). From 1997 to 1998 she held an advanced-level internship at the Straus Center for Conservation, Harvard University Art Museums, where she participated in a research project on Max Beckmann's painting technique. From 1998 to 2000 Gottschaller was an Andrew W. Mellon Fellow at the Menil Collection in Houston, participating in a project conserving the series of mural paintings in the Rothko Chapel. Subsequently, she was a PhD candidate at Technische Universität in Munich, doing a project on Palermo's painting technique. From 2003 to 2005 she was an associate conservator at the Whitney Museum of American Art, New York. Since that time, she has been a postdoctoral research fellow at Bibliotheca Hertziana, Max Planck Institute for Art History, Rome, and an Habilitation candidate at Technische Universität, Munich, researching Lucio Fontana's artistic process.

Mary H. Gridley received her BA with distinction in art history from Yale University in 1980. After a year as a Syracuse University Florence Fellow studying early Italian Renaissance art, she worked at Christie's in New York. She received a diploma in the conservation of easel paintings from the

Courtauld Institute, London, in 1992. She specializes in contemporary art conservation, and has been at Cranmer Art Conservation since 1995.

Eric Hagan graduated with master's degrees in mechanical engineering and art conservation at Queen's University, Kingston, Ontario, in 2002 and 2004, respectively. He is currently entering his second year of PhD studies at Imperial College, University of London, with funding from the Tate Gallery and the Natural Sciences and Engineering Research Council of Canada. His thesis involves the mechanical characterization of a wide range of modern artists' paints.

Christa Haiml received an MA in art history and French at the University of Vienna, in 1995, and a postgraduate diploma in the conservation of easel paintings from the Courtauld Institute of Art, London, in 1999. Subsequently she was awarded a two-year advanced internship at the Guggenheim Museum in New York and worked in the Netherlands at the Kollektief in Amsterdam, the Kröller-Müller Museum in Otterloo, and the Netherlands Institute of Cultural Heritage (ICN) in Rijswijk. She recently completed a two-and-a-half-year fellowship at the Menil Collection in Houston.

James Hayes, technical director at Golden Artist Colors, plays an integral role in the company's research and development efforts, creating numerous product improvements and innovative new products. He has helped both to implement several computer systems to track the quality efforts and to create a database of all research and development efforts. He also works with the Production Department to improve processes and solve problems and oversees the technical support area, which is responsible for the company's technical writing efforts as well as answering the questions from customers that come in daily.

Simon A. M. Hesp is an associate professor and the coordinator of graduate studies in the Department of Chemistry, Queen's University, Kingston, Ontario. Hesp's work concentrates on the investigation of brittle and ductile failure properties of visco-elastic and purely elastic materials, with a particular focus on modified asphalt materials for road construction. A related interest deals with the application of this work to better understanding the properties of painting materials.

Frank G. Hoogland received an MSc in analytical sciences from the University of Amsterdam in 2004. He is presently

engaged in PhD research on analytical mass spectrometry of paints in the Molecular Paintings Research Group of Professor Jaap Boon at the Foundation for Fundamental Research on Matter (FOM), Institute for Atomic and Molecular Physics (AMOLF), in Amsterdam.

Narayan Khandekar received a BSc (1986) and a PhD (1991) from the Department of Organic Chemistry, University of Melbourne. He then completed a postgraduate diploma in the conservation of easel paintings from the Courtauld Institute of Art, University of London, in 1992. Khandekar was a teacher of theory and a research scientist at the Hamilton Kerr Institute, Fitzwilliam Museum, University of Cambridge, from 1992 to 1994; a conservator of paintings, University of Melbourne, 1995–1996; and a scientist in the Museum Research Laboratory of the Getty Conservation Institute from 1997 to 2001. He is currently senior conservation scientist in the Straus Center for Conservation, Harvard University Art Museums. His principal interest is the technical examination of paintings and painting materials.

Diane Kunzelman received her master of arts in art history from Syracuse University in 1970. Since 1977, she has been senior painting restorer at the Fortezza da Basso Laboratory of the Opificio delle Pietre Dure, in Florence. Kunzelman specializes in conservation treatments of panel and canvas paintings, research into innovative methods of noninvasive investigation and conservation of artworks, and computer simulation of restoration interventions.

Thomas J. S. Learner is currently a senior scientist and head of contemporary art research at the Getty Conservation Institute; at the time of the symposium he was a senior conservation scientist at Tate. He joined the Conservation Department of the Tate Gallery in 1992, and has focused on researching and setting up analytical techniques for the identification and characterization of twentieth-century painting materials. His principal research interests are improving methods of analysis, examining the physical properties of modern paints, assessing the effectiveness of cleaning treatments, studying the materials and techniques of painters in the 1960s, and assessing the long-term aging properties of modern paints. He has published widely, including two books, *The Impact of Modern Paints* (2000), co-authored with Jo Crook, and *Analysis of Modern Paints* (2004). He earned a PhD in chemistry from Birkbeck College, University of London, in 1997; a master's degree, also in chemistry, from Oxford University, in 1988;

and a diploma in the conservation of easel paintings from the Courtauld Institute of Art, University of London, in 1991.

Suzanne Quillen Lomax received her PhD in organic chemistry from the University of Maryland in 1984. Her thesis explored the photochemistry of iminium salts. She performed postdoctoral research in organic photochemistry at Northwestern University. In 1986, she joined the Scientific Research Department of the National Gallery of Art as an organic chemist. She has been a speaker for the American Chemical Society Speaker Service since 1990. Her main areas of work include identification of paint binders, varnishes, waxes, and synthetic organic pigments.

Abigail Mack has been an object conservator at the National Gallery of Art in Washington, D.C., for the last seven years. One of her responsibilities was the recent installation of the gallery's outdoor Sculpture Garden, and much of her current work focuses on the maintenance and conservation of these sculptures. Mack has also worked in the art conservation departments of the Brooklyn Museum of Art, Denver Museum of Natural History, Peabody Museum at Harvard University, and the Field Museum. She received a master's degree in art conservation from the State University of New York College at Buffalo, and a bachelor of fine arts from the School of the Art Institute of Chicago.

Donata Magrini is working on her master of science degree in technologies for conservation and restoration of cultural heritage at the University of Florence. Her work is focused on noninvasive spectroscopic investigation of modern pigments.

Carol Mancusi-Ungaro holds a joint appointment as associate director of conservation and research at the Whitney Museum of American Art and founding director of the Center for the Technical Study of Modern Art, Harvard University Art Museums. She has written on the techniques of Mark Rothko, Jackson Pollock, and Barnett Newman, and continues to engage in research documenting the materials and techniques of living artists as well as other issues pertaining to the conservation of modern art.

Joy Mazurek has worked as a laboratory research associate at the Getty Conservation Institute since 1998. She specializes in the identification of organic materials by gas chromatography/mass spectrometry. She is currently obtaining her master's degree in biology, with an emphasis in microbiology,

and developing methods that use antibodies to identify binding media.

Christopher W. McGlinchey is conservation scientist at the Museum of Modern Art (MoMA), New York, and has worked in the field since 1983. In addition, he serves as adjunct professor of conservation science at the New York University Center for Conservation. At MoMA he is engaged in the development of conservation techniques specifically for the treatment of modern art, and is responsible for the development of analytical tools to characterize the broad spectrum of media found in the collection.

Kristalia Melessanaki is a conservator and has been employed at the Institute of Electronic Structure and Laser of the Foundation for Research and Technology-Hellas (IESL-FORTH), Heraklion, Crete, since 1998. She has been involved in numerous research projects and applications related to the use of laser techniques for cleaning and analysis of art, and is the co-author of more than ten scientific articles. Her main activity has focused on laser spectroscopic techniques (LIF and LIBS), for the analysis and characterization of art and archaeological objects ranging from Minoan pottery to works by El Greco. She is particularly involved in the conservation of modern paintings.

Maria João Melo holds a PhD in physical chemistry (1995), and is an assistant professor in the Conservation Unit at the New University of Lisbon. Her research interests include the conservation of modern artworks, in particular, the study of polymer photodegradation. Her main scientific area of research is chemistry, and other areas of interest include color in art and nature, polymers in conservation, and molecular-level devices for molecular information processing.

Julian Miller is the owner and operator of Sublime Restorations, Inc., which he established in Rowley, Massachusetts, in 1995. He purchased his first classic car at age fifteen, and in the late 1980s began his formal training in classic and collectible automotive restoration at Paul Russell & Co., Essex, Massachusetts. He has been involved with best-of-show winners at many national and international competitions, including the Pebble Beach Concours and Meadow Brook Concours. He has restored cars from the Ralph Lauren collection, some of which were on exhibit at the Museum of Fine Arts, Boston, in 2005, as well as many others. He was contracted by the Whitney Museum of American Art to restore the finish on the Donald Judd sculpture *Untitled* (1965).

Hannah R. Morris received a PhD in analytical chemistry from the University of Pittsburgh, where her research focused on materials characterization in complex polymer blends using spectroscopy and chemical imaging techniques. Since 2000, she has been deputy director of the Art Conservation Research Center at Carnegie Mellon University, Pittsburgh.

Wolfgang Müller trained as a laboratory assistant in organic chemistry at the University GH Essen. Since 1990, he has worked in the painting industry, primarily with artists' colors. In 2003, he became head of the laboratory of H. Schmincke & Co. GmbH, responsible for research and development and quality management.

Alison Murray is an associate professor in the Art Conservation Program at Queen's University, Canada. She received her BSc from McGill University and her MSc and PhD degrees from a joint program between Johns Hopkins University and the Smithsonian Institution. She is currently conducting a research program for characterizing and conserving modern materials, including acrylic paints and grounds; this research integrates information derived from sources including mechanical testing data, chemical analysis, and surface analysis.

Eleonora Nagy, MFA, MAC, is a conservator specializing in modern and contemporary sculpture. She has been recognized as a leading conservator for conservation issues on Donald Judd's sculptures. Extensively publishing on the topic since 1997, Nagy has pioneered new methods for conservation of Judd's works. Her special interests include unusual conservation problems, research into their causes, and their practical resolution and treatment, as well as industrial production, its infusion into artworks, and fabrication methods. She is the chair of the Advisory Committee for Conservation and Restoration (ACCR) for the Donald Judd Foundation. Her institutional experience includes the Canadian Conservation Institute, the Guggenheim Museum, the Whitney Museum of American Art, and the Tate Gallery.

Bronwyn A. Ormsby received a bachelor's of applied science degree in the conservation of cultural materials from the University of Canberra, Australia (1992). She then worked at the National Gallery of Australia (NGA) as a painting conservator from 1993 to 1998. During her employment at the NGA, she was granted leave to complete a two-year postgraduate internship in conservation science and the conservation of

easel paintings at the Hamilton Kerr Institute (1995–1997), researching the saponification of oil paints by alkalis. In 2002, she received a PhD from Northumbria University, England; her dissertation was entitled "The Materials and Techniques of William Blake's Tempera Paintings." From 2003 to 2005 Ormsby was the Leverhulme Fellow in Conservation Science at Tate, London, and she is now the AXA Art Research Fellow at Tate, continuing her research into the evaluation of the effects of surface cleaning of acrylic emulsion paintings.

Marcello Picollo is a researcher at the Institute of Applied Physics Nello Carrara (IFAC-CNR) in Florence. He holds an MS in geology from the University of Florence, and has been working on spectroscopic investigations of works of art since 1991. His main area of interest is the development and application of noninvasive UV, Vis, and IR spectroscopic techniques for the study of artists' materials, using both spectrophotometric and imaging systems. At the end of 2005, he became Asia and Australia chairperson of the Infrared and Raman Users Group Organization.

Rebecca Ploeger has bachelor's (2003) and master's (2005) degrees in engineering chemistry from Queen's University, Canada. Her research focused on the effects of aqueous immersion on the chemical, visual, and morphological properties of artists' acrylic paint films. In November 2005, she started her PhD in chemical sciences at the University of Torino, Italy, and is continuing to work in the artists' paint field, focusing on alkyd paint films.

Sjoerd Postma is an engineer employed by Art Innovation, Oldenzaal, Netherlands, where he has been involved in numerous laser-cleaning projects. He holds a master's degree in technical physics, and before his employment at Art Innovation he received a PhD in laser-welding application.

Bruno Radicati is a technician at the Institute of Applied Physics Nello Carrara (IFAC-CNR) in Florence. His main activity is developing specific software for spectroscopic studies and color analysis of artworks, as well as characterizing pigments using noninvasive spectroscopic devices.

Ana Maria Ramos holds a PhD in polymerization kinetics from the New University of Lisbon (1993), where she now is assistant professor. She is involved in research projects dealing with polymer characterization, specifically, in the study of average molecular weights, polydispersity, and characteristic

transition temperatures and their relationship with polymer structure and aging phenomena.

Dominique Scalarone received her PhD in chemistry from the University of Torino (2001) with a thesis on characterization and aging studies of natural and synthetic organic painting materials. From 2002 to 2005 she was involved in research projects on the design, development, and characterization of polymers for high-performance protective coatings. Since 2005, she has been a university researcher (assistant professor level) in the Department of Inorganic, Physical, and Material Chemistry of the University of Torino, where she teaches chemistry and gives courses in the science and technology for cultural heritage curricula. Her scientific activity is focused on structural and molecular characterization of natural and synthetic macromolecular compounds, stability and degradation of complex polymer systems, and the morphology, surface properties, and stability of organic coatings from waterborne dispersions.

Nadim C. Scherrer holds a BSc degree in physical geography from the University of New England, Australia, and a PhD in earth sciences from the University of Bern, Switzerland. He has been working for the art technological laboratory within the Department of Conservation and Restoration at the Bern University of Applied Sciences since 2001.

Michael R. Schilling earned his BS and MS degrees in chemistry from the California State Polytechnic University, in Pomona. He has worked at the Getty Conservation Institute (GCI) since 1983, and presently holds the position of senior scientist and head of the Analytical Technologies section. He oversees and coordinates a wide variety of projects that are conducted by the scientists in his section: applied research in materials analysis, scientific support to GCI's field conservation projects, study of museum collections, evaluating the air quality in museums, and assessing safe levels of lighting in museum galleries. One of Schilling's main research interests is the characterization of organic materials using gas chromatography/mass spectrometry, and he has taught numerous workshops to inform conservation professionals about qualitative and quantitative analysis of natural organic binding media. Since 1997, he and his staff have been studying the materials and techniques of modern and contemporary artists, focusing on the analysis of modern synthetic binding media and synthetic organic pigments.

Gregory Smith received a BS in anthropology/sociology and chemistry from Centre College, Danville, Kentucky, before pursuing graduate work at Duke University, ultimately earning his doctorate in physical/analytical chemistry. His postgraduate training included investigations of pigment degradation processes and palette studies of illuminated manuscripts at the British Library and the Victoria and Albert Museum, development of synchrotron infrared microscopy facilities at the National Synchrotron Light Source, and researching cleaning issues related to artists' acrylic emulsion paints at the National Gallery of Art, Washington, D.C. In 2004, Smith joined the faculty of the conservation training program at Buffalo State College as the first Andrew W. Mellon Assistant Professor of Conservation Science.

Patricia Smithen, graduate of Queen's University, Canada with a master's in art conservation (1993), is a conservator of modern and contemporary paintings at Tate. She joined the Conservation Department in 1999, and assisted in the preparation of works for display at Tate Modern's opening in 2000. Her research interests include the use of infrared reflectography on modern paintings; technical studies on works in the Tate Collection, including mixed-media works and Surrealist paintings; and developing new treatment options for modern works. She is currently a member of the Tate AXA Art Modern Paints Research Project and will be undertaking surface-cleaning studies and treatments on acrylic paintings from the Tate Collection.

Harriet Standeven graduated with an MA in paintings conservation from the University of Northumbria in 2000. She received her PhD from the Royal College of Art/Victoria and Albert Museum Conservation Program in 2004; her research examined the historical and technical development of gloss house paints, with reference to their use by twentieth-century artists. She is now employed as a tutor on the RCA/V&A Conservation Program, and works as a freelance conservator, specializing in the care of modern and contemporary art.

Carol Stringari, senior conservator of contemporary art at the Solomon R. Guggenheim Museum, has worked at the museum for fourteen years and oversees the treatment and care of the contemporary permanent collection. She has overseen conservation projects on minimalist and monochromatic paintings by artists Ad Reinhardt, Robert Ryman, and Robert Mangold.

She was a key member of the team for the preliminary design and execution of the inaugural exhibition of the Guggenheim Museum Bilbao and the museum's conservation lab. Prior to working at the Guggenheim, Stringari was at the Museum of Modern Art, New York, where she did an extensive survey of the acrylic paintings in the collection. She teaches and lectures on contemporary conservation and ethical considerations in various university programs as an adjunct professor. She is also a founding member of the International Network for the Conservation of Contemporary Art. Her special interest is in issues of the ethics and integrity of unconventional artworks.

Shelley Sturman is head of the Object Conservation Department at the National Gallery of Art in Washington, D.C. She received her BA and MA from Brandeis University, and holds an MS in conservation from the University of Delaware. She is actively involved in the American Institute for Conservation, of which she is a fellow and a former director; the International Institute for Conservation, where she is also a fellow; and the Washington Conservation Guild, of which she is a past president. In her spare time, Sturman teaches preventive conservation to graduate students of museum studies at George Washington University. She has published widely on a variety of conservation topics, has lectured at major universities and international meetings, and is a co-author of *Degas at the Races*, co-editor of *Saint-Porchaire Ceramics*, and a contributor to many National Gallery catalogues, including *Western Decorative Arts* and *Nineteenth Century French Sculpture*. Areas of special interest to Sturman include working with living artists, discovering the mysteries of the Degas waxes, researching the casting techniques of Renaissance bronzes, and developing durable coatings for outdoor sculpture.

Giorgio Trumpy received his BS in technologies for conservation and restoration of cultural heritage at the University of Florence, in 2004. His thesis, written in collaboration with the Institute of Applied Physics Nello Carrara (IFAC-CNR), was focused on spectroscopic and colorimetric investigation of white artists' pigments.

Masahiko Tsukada is a conservation scientist in the Conservation Division, Department of Cultural Properties, Tokyo National Museum (formerly at the National Museum of Western Art). He works mostly on preventive conservation of the museum collection, and his main research interests include the characterization of painting materials.

Klaas Jan van den Berg received his PhD in chemistry at the University of Amsterdam in 1994. From 1995 to 1999 he was a project leader at MOLART in charge of the development of strategies for chemical analysis (both bulk and surface) of painting materials. Since 2000, he has been at the Netherlands Institute of Cultural Heritage (ICN), where he is responsible for paintings research. His main interest is the study of material changes in nineteenth- and twentieth-century painted art.

Jerre van der Horst was trained as a chemical technician at the higher laboratory school of Hogeschool Alkmaar, Netherlands. For the past ten years he has been employed as a research chemical engineer in charge of mass spectrometry and microscope spectroscopy in the Molecular Paintings Research Group at the Foundation for Fundamental Research on Matter (FOM), Institute for Atomic and Molecular Physics (AMOLF), in Amsterdam.

Paul M. Whitmore has a BS in chemistry from the California Institute of Technology (Caltech) and a PhD in physical chemistry from the University of California at Berkeley. He has worked in art conservation science for his entire professional career, starting at the Environmental Quality Laboratory at Caltech, and then moving to the Fogg Art Museum at Harvard University. Since 1988, he has been at Carnegie Mellon University, directing the Research Center on the Materials of the Artist and Conservator (recently renamed the Art Conservation Research Center). His current research interests are in material degradation chemistries, intrinsic and environmental risk factors for those processes, and chemical sensors for material aging processes and risk factors. He has published on many conservation areas, including acrylic paint media stability and the physical damage to acrylic coatings from shrinkage stresses during drying, fading of colorants from air pollutant exposure, fading of transparent paint glazes from light exposure, and projects utilizing a new nondestructive probe of light stability for colored artifact materials.

Louise Wijnberg studied art history and conservation and restoration of art at the Sorbonne and received her PhD in 1988 at the National Center for Scientific Research (CNRS), Thiais, France. She has been paintings conservator of the Stedelijk Museum of Amsterdam since 1986, and a lecturer in the Restoration and Conservation Program of the University of Amsterdam since 2005.

Christina Young is a conservation scientist and lecturer in easel painting conservation at the Courtauld Institute of Art. She has a BSc in physics from Imperial College, University of London, and an MSc in applied optics. In 1994 she was awarded the Gerry Hedley Research Scholarship and gained her PhD in 1996 with a thesis entitled “Measurement of the Biaxial Tensile Properties of Paintings on Canvas.” Before joining the Courtauld she was Leverhulme Research Fellow at Tate Britain from 1997 to 2000. Her main areas of research are the measurement of the physical properties of canvas and panel paintings and the development of methods and materials used for structural conservation treatments.

Stefan Zumbühl studied conservation at the University of Applied Science in Bern, Switzerland, receiving his certificate in 1996 with a thesis focused on MALDI-MS of terpenes. He then worked on a number of different scientific projects at the Swiss Institute for Art Research, Zürich; the Swiss National Library, Bern; and the Swiss Federal Institute of Technology, Zürich. Since 2000, he has been a lecturer at the University of Applied Science in painting conservation and at the university’s analytical laboratory.

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