The Nature, Formation & Prevention of Beer Hazes

Ian L Ward

Cloudy Beer

Beer haze may be defined as an insoluble or semi-soluble particulate matter which is small enough to form a colloidal suspension in beer, (typically <2µm). These particles scatter transmitted light and are observed as a degradation in the transparency of the beer. This visible observation may be quantified by measurement of reflected and transmitted light through the sample against an accepted standard. Instrumentation has developed over the years from the early haze meters to highly sensitive machines, with computer controlled reagent dosing and data logging, capable of providing predictive information on beer shelf life.

Permanent Post Filtration Beer Haze

Presentation spoilt by the development of permanent post filtration haze due to high tannin (polyphenol) / protein content prior to (left) and following forced storage.

The Origin of Beer Particles

The table below categories the nature of common beer hazes which occur prior to and post filtration. Although yeast and bacteria can give rise to hazes in beer, their presence in finished beer is also likely to cause severe flavour degradation. Microscopic examination will confirm the presence of an undesirable organism. Although both filtration and finings have been used to remove biological haze the only real solution is to attend to good hygiene practices to prevent the initial infection occurring.

BIOLOGICAL PARTICLES	NON-BIOLOGICAL PARTICLES (NMP)
Brewers Yeast	Particulate Proteinaceous Protein-Polyphenolic Carbohydrate-Starch (β-glucan) Lipids
Wild Yeast Bacteria	
CLARIFICATION & PACKAGING	
Brewers Yeast Wild Yeast Bacteria	Proteinaceous Protein-Polyphenolic Carbohydrate Addition Related

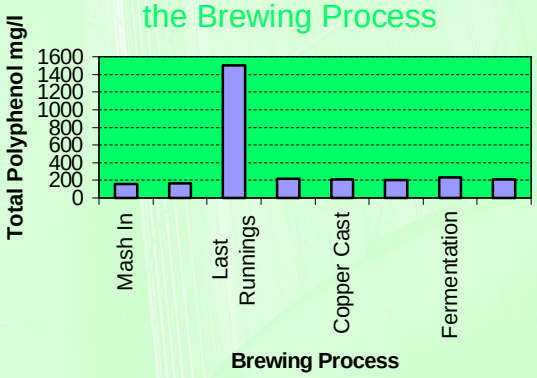
Particles through the Brewing Process

Turbidity causing Non Microbiological Particles (NMP), are formed and removed throughout the brewing process. Good brewing practice favours the removal of these particles at the earliest opportunity. This serves to facilitate effective final clarification, whether by centrifugation, filtration or fining. In addition, good brewing practice, such as efficient boiling and care to avoid over-sparging, limits the concentration of soluble haze precursors which are responsible for virtually all post-filtration hazes.

Mashing - Milling of grist materials results in the generation of numerous fine dusty starch and husk particles. These are usually removed during mash separation. However, if the wort is not recirculated through the mash bed prior to run-off, or excessive pressures are applied to a mash filter, these grist particles will carry through into the sweet wort. This is particularly true in the case of lautering, where frequent, rapid, or excessively deep raking will disturb the mash bed, releasing the numerous entrapped particles. In addition, it is not unknown for lauter plates to become damaged, warped or even incorrectly re-laid, allowing the passage of larger particles into the wort. Inadequate mash stand, poor quality malt or poor control of mash temperature can result in poor conversion and residual starch and / or β-glucan.

β-glucan, although not strictly a haze causing material or precursor can have a severe negative impact upon the filterability of beers. Over-sparging has also been shown to wash excessive levels of undesirables, such as lipids and polyphenolic material from the mash, which have a deleterious effect upon particle levels and overall beer haze stability.

Changes in Total Polyphenol Levels During the Brewing Process



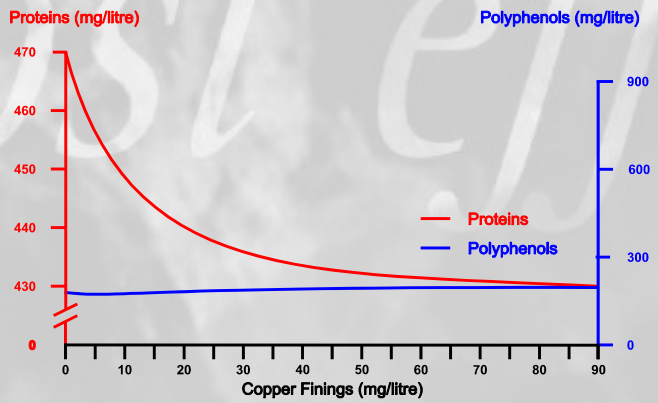
High concentrations of reactive haze precursor polyphenols are found in last runnings. It is therefore important to avoid over-sparging.

Wort Boiling - during the wort boiling process, thermal denaturation causes coagulation of protein and polyphenolic material to form a hot break. Efficient coagulation is favoured by a high wort pH, the presence of sufficient protein, and good wort boiling conditions, i.e. a minimum of 102°C at atmospheric pressure, of sufficient duration (minimum one hour) and vigour (a good rolling boil), to maximise denaturation. Under these conditions, the hot break is formed as large flocs which are relatively easily removed in the whirlpool or hop-back as trub. If

coagulation is inefficient, fine flocs will be formed which may remain in suspension and be carried over into subsequent stages of the brewing process. Alongside the removal of protein and polyphenolic material from the wort, further polyphenolic material is extracted from the hops. The contribution of hops to the total polyphenol level of wort depends upon the variety used. It has been reported that the derivation of high proportions of bitterness from extracts or oils, at the expense of plant material, can lead to sufficiently low levels of polyphenols as to cause poor protein removal during cold break formation.

Wort Cooling - On cooling, further wort proteins and polyphenols interact and precipitate as cold break. This material consists of very fine particles that are slow to settle and consequently are likely to remain in suspension until final clarification. Taken in combination, boiling and wort cooling remove 17-35% of the total protein content, depending upon the malt variety and hop product/variety used. Cold break formation is temperature dependent, only forming in significant quantities below 20-30°C, and increasing dramatically in quantity as the temperature is further decreased. The removal of these cold break particles can be facilitated and enhanced by kettle finings allowing the removal of up to a further 20% of malt derived protein.

Protein Removal in Wort by Kettle Finings



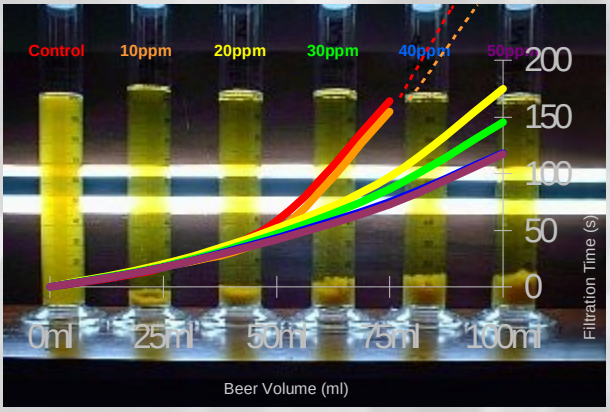
Assay of the protein and polyphenol levels in wort illustrate the removal of protein from the wort as the concentration of kettle finings is increased.

Fermentation - Several physical changes occur, which both produce particles, and facilitate their removal. Yeast reproduction starts, resulting in an increase in the number of yeast cells in the beer; the pH is reduced from pH 5 to 4, facilitating the interaction of protein and polyphenol moieties to form NMP. This results in the removal of 45-65% of the soluble proteins and 20-30% of the soluble anthocyanogen content of the bitter wort. Streaming current measurements suggest that acidic proteins (average iso-electric point <3.5) are selectively removed at this stage. In addition, as the concentration of alcohol increases, the viscosity and density of the wort are reduced, so increasing the rate of sedimentation of any particles present as given by Stokes' Law. This, together with the long period of time associated with fermentation, permits the removal of a certain amount of cold break with the yeast cone / fermenter bottoms.

Beer Cooling - at the end of fermentation, as beer is chilled, yeast flocculates and settles to the bottom of the fermenting vessel or cold storage tank carrying with it other particulate material as it sediments. The density of a yeast cell is approximately 1.160 g/cm^3, giving a typical rate of sedimentation of approximately 18 cm/day for a single cell, or 72 cm/day for a floc of six cells. In addition, cooling causes the further interaction of protein and polyphenol moieties to form further NMPs. The density of an NMP is not known, but has been estimated to be intermediate between that of beer and a yeast cell. However, unlike yeast cells, which are generally of uniform size (~5µm), NMPs have a very broad size distribution, ranging from < 1µm up to ~ 30µm. This results in a wide range of sedimentation rates; 0.8 cm/day for particles of radius 1µm; 40 cm/day for particles of radius 7µm. Particle removal at this stage is augmented by isinglass and auxiliary fining agents.

Clarification - The final removal of particulate matter from beer is the subject of a related but separate discussion , suffice it to say that the correct choice of clarification aids, filter and filter media have a profound effect upon filter efficiency and performance. The illustration below shows the effect of cold wort clarity on final beer filter performance.

Effect of Kettle Fining on Filtration

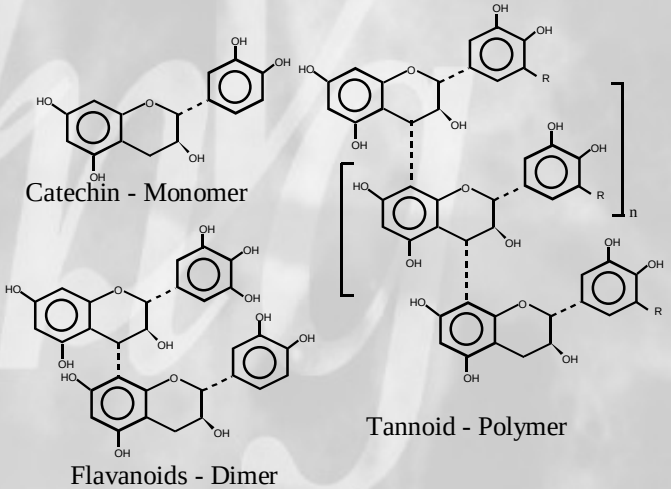


As the rate of kettle coagulent increases the cold wort clarity improves. This improvement is accompanied downstream by both an increase in the volume of beer through the filter and a decrease in the time taken to filter a given volume.

Development of Haze in Filtered Beer

By far the most common form of haze formation or colloidal instability in packaged beer is the agglomeration of protein and polyphenolic materials. Upon analysis of isolated beer haze deposits, it is typically found that the largest fraction of haze material is protein., (40-75%), where polyphenols make up a smaller component (~17%). The balance is typically carbohydrate and ash. Despite the relative concentrations of these species it is thought that the polyphenolic materials being the more reactive species trigger the haze formation. Polyphenolic materials found in beer can be categorised into three types dependant upon the degree of oxidation and polymerisation.

Structures of Polyphenols Found in Beer

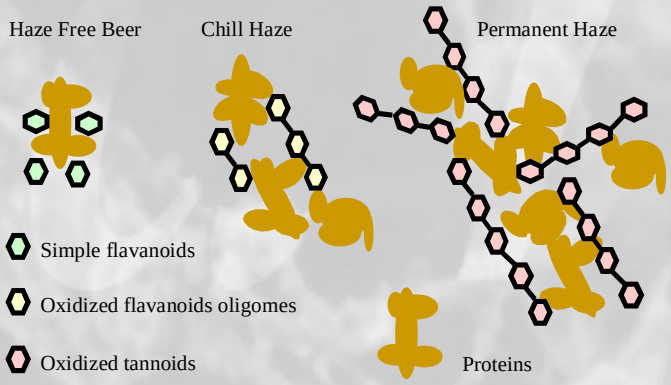


Haze and Polyphenol Polymerisation

Simple flavanoids present in beer do not produce haze since the polyphenol protein agglomeration is of suffiently low molecular weight as to be and remain soluble and hence invisible. As the beer ages however, the flavanoids oxidise and begin to polymerise. The oligomeric polyphenol produced is able to crosslink protein molecules and produce a much less soluble entity. As the temperature of the beer is reduced, the agglomerate precipitates and is observed as a chill haze. Upon warming the precipitate dissolves and the haze disappears.

With prolonged storage the oxidised flavanoids continue to polymerise and become known as tannoids. Tannoid protein agglomerates are of such a size (>60,000 Daltons), as to be insoluble in beer even at ambient temperatures and hence give rise to permanent haze.

Formation of Beer Haze



Several factors affect the speed of polyphenol polymerisation and hence haze formation.

Factors Affecting Haze Development

- Polyphenol concentration
- Haze forming hydrophilic protein concentration
- Oxygen
- Heat
- Particulates, carbohydrates
- Transition metal ions (Cu, Fe)
- Light

Clearly concentration of haze precursors has a profound effect upon haze formation. Limiting the concentration of either one or both of these species can be used as strategies to control haze formation. The availability of oxygen, accelerates the oxidative polymerisation of polyphenols in beer. Quite apart from the deleterious affects on beer flavour, oxygen catalyses the conversion of flavanoids to tannoids, and hence the development of permanent haze. Transition metal ions such as copper and iron have been implicated as redox catalysts in the oxidation of flavanoids to tannoids. Exposing the beer to heat simply serves to accelerate the oxidation / polymerisation reactions, according to standard chemical kinetics.

The presence of certain carbohydrate materials, especially alginic acid, which is a contaminant of propylene glycol alginate, (PGA) used for foam stabilisation, has been found to accelerate haze formation. This is typically characterised by a large visible particulate matter in the beer. If PGA is used and a particulate haze is observed; staining with thionin reveals a pink colouration with acidic polysaccharides such as alginates.

Beer Haze Prevention Strategies

The factors affecting haze development suggest a number of strategies to limit haze formation. The brewer can take steps throughout the brewing process to favour the production of a haze free and stable beer.

Brewing Practises Favouring Haze-Free Beer

- Selection of raw materials
  Avoidance of high protein or β-glucan malt
  Limit use of high nitrogen adjuncts
  Use of low polyphenol or polyphenol free malts
  Care in the use hop extracts and oils
- Correct mashing regimes
  Correct and controlled mash temperature
  Avoidance of over-sparging or over-raking
- Vigorous rolling boil
- Long cold conditioning times (-1°C for 3 weeks)
- Correct fining / filtration regimes
- Scrupulous limitation of oxygen ingress

The demands for beer to be served ever colder and, in the case of packaged beer, to remain bright throughout an extended shelf life, means even fastidious attention to the above is unlikely to produce adequate stability alone.

Processing Aids and Beer Haze Control

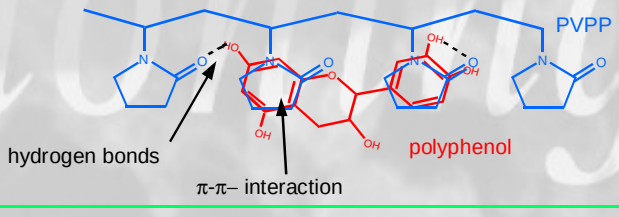
Over the years a number of processing aids have been developed to tackle the issue of enhancing beer haze stability. All the technologies centre on either reduction of hydrophilic beer proteins or polyphenol levels, or more recently, a combination of both. Each technique has its own pros and cons, and many are used routinely in combination, to suit the brewers own requirements and plant constraints. There are three routes for the control of protein levels and two for the control of polyphenols. It has been known for all techniques to be used in combination, but recently a combination of adsorption of protein and polyphenol materials have become the favoured techniques.

Silica gels are amorphous silicon dioxide which upon hydration forms polysilicic acid on the silica particle surface. The presence of -Si(OH)- groups enables the adsorption of proteins by hydrogen bonding, with the hydrated silica gel acting as the H donor and proteins as the H acceptors. The binding mechanism favours hydrophilic, (haze forming) proteins over hydrophobic proteins, known to be important in beer foam, although at high dose rates there is some evidence of beer foam loss.

Polyvinylpolypyrrolidone, (PVPP) is a highly cross linked synthetic polymer which adsorbs polyphenols by a combination of H-bonding, π-bond overlap between pendant pyrrolidone rings and phenol rings, polar and hydrophobic interactions. The spatial arrangement and multiplicity of bonding gives highly specific binding of polyphenols.

Both of these techniques in isolation suffer from diminishing returns. As the dose rate of adsorbent is increased the effectiveness begins to tail off. Consequently the notion of using low dose rates of both or a combined material has found to be more cost effective than a single target approach.

PVPP / Polyphenol Binding Interactions



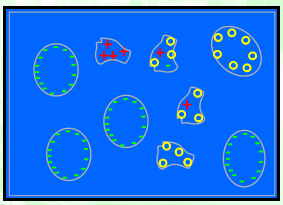
Comparison of Colloidal Stabilisation Process Aids Available

Technique Process / Aid	Usage	Negative Aspects of Use	Positive Aspects of Use
Precipitation Kettle finings Typical use rates 3-5 g/hl	Used in the kettle to form a cold break which is separated with the yeast cone.	Stabilisation effect limited. Primary function is to improve filterability Equivalent to approx. 20 g/hl of silica gel	Gives improvements in beer filterability. May be used in combination with down stream adsorption techniques.
Precipitation Tannic Acid Typical use rates 1-5 g/hl	Used in conditioning vessel to complex protein material in an analogous reaction to haze formation. Concept is to precipitate all haze forming protein material prior to filtration.	Tends to give a diffuse sediment which can present severe filtration difficulties if sediment is fed to the filter.	Effective stabilisation obtained for intermediate shelf life
Degradation Proteolytic Enzyme Typical use rates 1-4 g/hl	A derivative of papaya as a standardised preparation into fermentation or conditioning vessel.	Enzyme remains active in the beer Has been implicated in poor foam retention and flavour changes.	Effective stabilisation over long shelf life.
Adsorption Silica Gel - Protein Typical use rates 80-200 g/hl	Silica gels adsorb soluble hydrophilic proteins Used in conditioning tank or on filtration.	High dose rates required if used alone which can impact upon foam retention.	Effective method of stabilisation. Totally removed from beer on filtration.
Adsorption PVPP - Polyphenols Typical use rates 20-60 g/hl	An insoluble synthetic polymer which removes the reactive species in haze formation. Used in conditioning vessel or on filtration.	Expensive in use although may be regenerated with appropriate plant.	Effective method of stabilisation. Totally removed from beer on filtration. Reduces beer aging astringency.
Adsorption Combined Protein/Polyphenol Typical use rates 40-100 g/hl	Silica gel and PVPP used together or in combination in conditioning vessel to adsorb a portion of both protein and polyphenol materials.	More expensive than silica alone, but without the impact on foam retention since dose rates are lower.	Very effective stabilisation. Totally removed by filtration.

Hazes in Unfiltered Beers

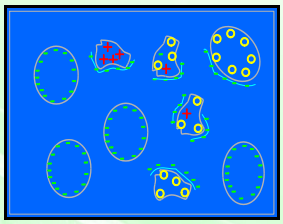
For beer in keg, serving tank, or cask the cost of adsorptive beer stabilisers may be uneconomic. Indeed in the case of cask conditioned beers quite inappropriate. These beers although less prone to age related haze formation, since they are generally consumed younger, can still throw chill haze and protein hazes. Indeed, for unfiltered cask conditioned and serving tanked beers, protein haze is a major problem since isinglass fining systems alone rarely remove excess protein completely.

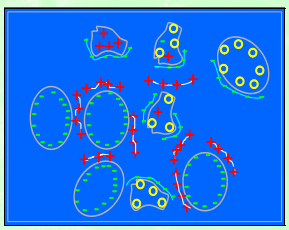
Clarification strategies for unfiltered beer have been developed to overcome this.



In an unfiltered beer, yeast cells tend to carry a net negative charge. Protein and yeast cell debris may carry a positive or no net charge. Isinglass being positively charged tends only to react with yeast cells and where there is a large excess of protein, incomplete clarification results.

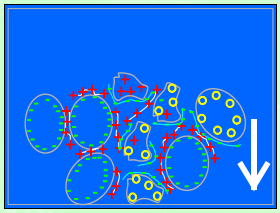
By the application of a solution of protein adsorbent, strongly negatively charged polymer, prior to isinglass treatment, all the particles present are effectively labelled with a negative charge. These solutions are known as Auxiliary Finings and are made from either acidified polysaccharides or polysilicic acid solution.





Once isinglass is added, all the particulates are available to react and complete clarification is obtained. The combined auxiliary and Isinglass flocs then settle as given by Stokes Law, leaving a bright supernatant beer.

The choice of Auxiliary type depends upon, the beer for no obvious analytical reason and is determined by empirical observation and experimentation



An extreme example of haze formation in cask conditioned beers, is found as a result of dry hopping. The addition of whole leaf or pelletised hop material into the cask at racking imparts a spicy aroma and an exquisite hop flavour to the beer, but almost always produces a beer which proves extremely difficult to clarify. In almost all cases, a silicate auxiliary fining agent is effective in producing a haze free beer. The phenomenon is still under investigation as to what chemical component causes the turbidity and why silicate auxiliaries solve the problem.

Clear Beer?

By careful observance of practices which favour the production of haze stable beers, as outlined herein, and the application of appropriate stabilisers, a beer in small pack can be made to have a colloidal stability in excess of 12 months, far longer than the flavour stability. For a cellar tanked, cask or keg beer it is possible, and should be the norm, to produce beers which remain bright for the life of the product even when served at colder temperatures.

Should you require any further information, please contact us at the address below.

BREWERS SUPPLY GROUP

Brewers Wholesale Supply Inc.
312 Connell Hwy
Newport
RI 02840
Tel (800) 816 8542
Fax (401) 845 6746
www.brewerswholesale.com