# Colloidal stabilisation of beer

**Colloidal instability in beer is caused through the interaction of proteins and polyphenols. To understand the mechanisms that underlie beer stabilisation it is necessary to examine the main changes which inevitably accompany the natural ageing of beer, and affect both its taste and clarity.**

**Technical Summary 1**

**The first of a new series of technical summaries for the Institute & Guild's AME candidates. By Tim O'Rourke.**

Professor J. De Clerck[1] attributes three principal changes which occur in beer and which are brought about by the presence of polyphenols and tannins.

- Increase in haze caused by the precipitation of protein substance.
- Increases in harsh or unpleasant after taste in beer
- Increases in colour, particularly following oxidation.

The first manifestation of the loss of colloidal stability is observed as chill haze, which is a reversible association between small low polymerised polyphenols and proteinaceous material. The tendency to form chill haze progressively increases over time.

Oxidation of some polyphenols – flavanoids in particular, lead to the formation of condensed (polymerised) products. These are active precursors in haze formation, leading to permanent (irreversible) haze formation (see illustrations below).

To avoid colloidal haze production the brewer has to control the brewing by the selection of brewing materials and production and storage of packaged beer. These steps can be divided into:

- Controlling the protein content of the beer

- Controlling the polyphenol content in the beer

- Controlling the physical conditions in the brewing process

## Controlling protein content

Proteins in beer come from malt and some adjuncts such as wheat and barley. It is broken down during malting and mashing to produce haze precursors but is also the source of the amino acids necessary for yeast growth, hydrophobic proteins which produce beer foam and protein which give beer texture and mouthfeel.

The brewer has to strike a balance between reducing protein content to improve colloidal stability and affecting fermentation and beer quality.

Typical ways of reducing the protein content of a beer are:

- Selecting malts low in nitrogen (typically 1.6 to 1.8% nitrogen)

- Using adjuncts which are low or free from nitrogen e.g. maize flakes or brewing syrups.

- Using under-modified malts thereby reducing the amount of protein extracted, this will be counter balanced by proteolysis in the mashing programme.

- Proteins are also removed from the brewing process with the spent grains and as hot or cold break after wort boiling, during cooling and cold conditioning. The efficiency of separation will depend on the quality of boiling, performance of the whirlpool, and temperature of cold storage.

- The performance of break separation can be improved through using kettle finings

It is principally the acidic hydrophilic proteins containing prolein which bond with polyphenols to produce haze.

## Controlling polyphenol content

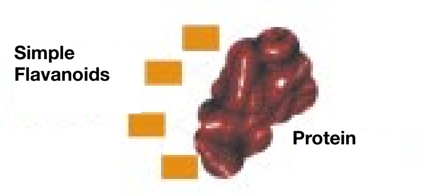
Polyphenols come from hops and husk of the malt. The polyphenols from hops are generally highly polymerised and are precipitated with hot and cold break before filtration and hence have little adverse effect on beer stability.

The malt polyphenols are extracted during mashing and wort separation. During the brewing process may give beer some anti-oxidant protection, however there is little evidence that malt polyphenols protect bright beer from oxidation in package.

Typical ways of reducing the polyphenol content in beer are by:

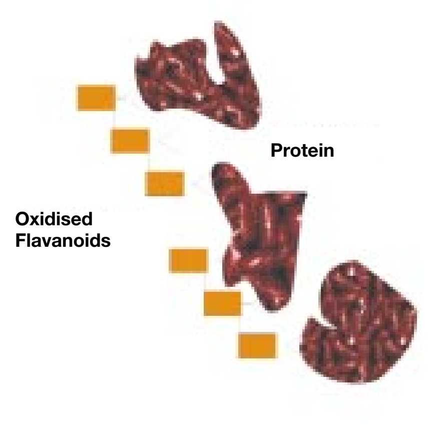
- The use of adjuncts to dilute the amount of polyphenols coming from the malt.

- Most malt polyphenol is extracted towards the end of the runoff. Extraction can be reducing by avoiding running to a low gravity



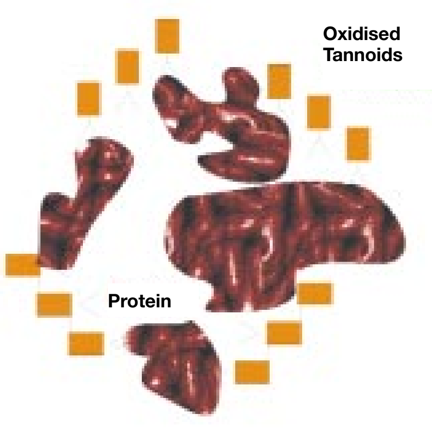

**Haze free**

*In freshly packaged beer there is no chill haze (<0.6 EBC) and the polyphenol haze precursors exist as simple flavanoid molecule which bond with proteins by hydrogen bonding.*




**Chill haze**

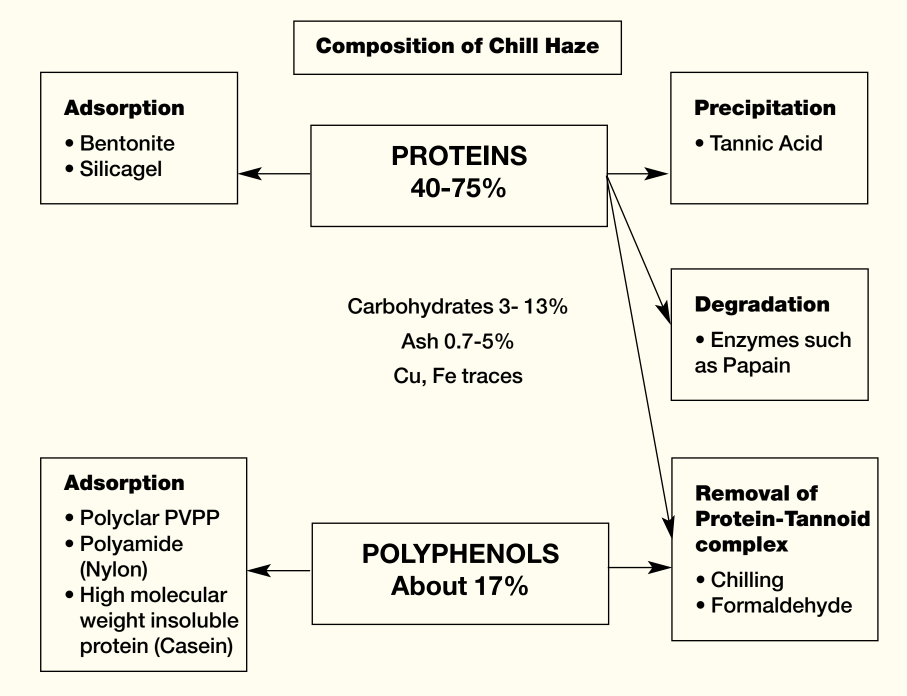
*Oxygen catalyses the polymerisation of simple flavanoids which become three to four units long, and which are able to bond with a number of proteins via hydrogen bonds to form chill haze.*




**Permanent haze**

*As the polyphenols continue to oxidise larger complexes are formed, and some of the polyphenol/protein hydrogen bonds are replaced by more permanent ionic bonds. These bonds no longer break when the beer is heated and leads to the formation of permanent haze.*

## TABLE 1: Summary of techniques used in colloidal stabilisation of beer




## Summary of stabilisation control during processing

| Area of Application | Polyphenol Reduction | Protein Reduction | Process Optimisation |
|---|---|---|---|
| Barley / Malt | Proanthocyanadin free barley | Low protein barley | Low malt modification |
| Mashing | High adjunct ratio | High adjunct ratio | High temperature mash |
| Mash separation | High cut off gravity<br>Low sparge pH | Bright worts run off | |
| Wort boiling | Avoid wort & trub recycling | | Time and vigour of boil |
| Wort clarification | Time of hop addition<br>Hot break removal | Kettle finings<br>Hot break removal | Whirlpool efficiency |
| Fermentation | Cold break removal | Cold break removal | |
| Maturation | Lack of agitation | Sedimentation<br>Auxiliary finings | Time and temp. of cold storage |
| Filtration | Stabiliser addition | | Cold filtration<br>Oxygen pick up<br>Metal ions |
| Stabilisation | PVPP | Silica gel<br>Tannic acid<br>Enzyme | Contact time<br>Temperature<br>Contact |

## Summary of stabilisation control during packaging

| Area of Application | Causative Factors | Preventative Factors |
|---|---|---|
| Packaging and distribution | Metal ions<br>High storage temperatures<br>High in package oxygen<br>Shaking/agitation | Soften water<br>Cool storage<br>Low process oxygen<br>Anti oxidants |
| Trade | Stock rotation<br>Extended shelf life<br>High temperatures<br>Direct sunlight | BBD/Package date<br>Beer fresh in time<br>Direct deliveries<br>Refrigerated storage & distribution |

(greater than 1004 or 1° Plato) and keeping the sparge pH low (below 7). Operations such as weak wort recycling may increase the concentration of extracted polyphenols.

• Proteins and polyphenols form complexes at low temperatures, and hence are removed during cold maturation and cold filtration.

• A new variety of malt (proanthocyanidin free) has been developed by Carlsberg and is now commercially available. This may permanently solve the polyphenol problem for the brewers.

### Controlling the brewing process.

Attention to the brewing process can reduce the level of the protein and polyphenols finishing up in the final beer, thus reducing the tendency to produce colloidal instability. The principal changes which improve beer stability are:

• Cold storage and cold filtration of the beer encourages the formation of chill haze. It is essential once cooled, the beer remains cold particularly in line to the filter as the chill haze can rapidly re-dissolve. Lower temperatures (-2°C) are better for final beer stability.

• Haze is produced as a result of oxidation of polyphenols, and hence eliminating oxygen, particularly in package will reduce the rate of haze formation and increase beer shelf life.

• Oxidative reactions are catylised by metal ions (particularly $Fe^{2+}$ and $Cu^{2+}$) reduction of metal ion improve beer stability. Similar oxidative processes also accelerate staling in beer and colloidal instability is often associated with aged beer flavours.

• The protein/ polyphenol interactions are dependent on electrostatic attractions between the two compounds. It is found that beers with higher pH, above 4.2, show better colloidal stability.

### Process aids to reduce proteins or polyphenols.

By optimising the brewing process it is possible to produce good which are stable for up to three months without additional treatment.
However, if a longer shelf life is required chemical stabilisers are recommended. See Table 1, above left.

### Other possible causes of haze in bright beer

As well as colloidal instability there are other hazes found in bright beer:

• Polysaccharides such as starch and beta glucans not broken down during mashing, can produce a fine haze or cast in finished beer. As well as haze the presence of the complex carbohydrates often cause filtration problems.

• Poor filtration and hygiene can lead to particles in the bear either as a result of a breakthrough from the filter or filter aid.

• Poor beer handling or over carbonation, particularly when using reduced hop compounds, can result in particulates due to collapsed foam floating in the beer.

• Poorly hydrolysed foam stabiliser (Polyglycol alginate)

• Lack of calcium in the mash can result in the formation of oxalic acid crystal, which can also lead to gushing.

The brewer has to control the whole process to produce small pack beer with the required shelf life. It is not possible just to rely on chemical treatment at the end of the process to consistently achieve the colloidal stability. It is also found that a balanced chemical treatment removing both proteins and polyphenols provides a more efficient and more cost effective stabilization regime. ■

***Further Reading***

•Tim O' Rourke et al from poster presented at Perth Convention – *Ferment* June 1998 – p189
• Tim O' Rourke Back to Basics, *Brewers Guardian* February 2000 – p29
• Mike O'Neill – Advances in Beer Stabilisation *The Brewer* July 1998 – p293 and August – p 353
• De Clerck J. *Brewers Digest* August 1970 p 62 – 64
• McMurrough I et al "Effect of PVPP dosage on the flavanoid content of beer and consequences for beer quality" *Brew Digest* 59 (10) 1984.

## Summary of the properties of different beer stabilisers

**Silica Gel**
SOURCE: Made by acidic polymerisation of silicate solutions. Two forms: hydrogels-70% & xerogels 5% moisture.
ACTION: Adsorbs proteins based on selective control of pore diameter – removes <40,000 MW
DOSAGE: Add to CT at run down up to 50g/hl
Add to filter powder slurry up to 100g/hl
ADVANTAGES: Insoluble – easy to use
DISADVANTAGE: Moderately expensive.
Generally suitable if a shelf life < 9 months is required.

**Proteolytic enzyme**
SOURCE: Usually Papain produced from the latex of *Carica papaya*.
ACTION: Hydrolyses proteins. (Beer foam is protein)
DOSAGE: 2 to 6 mls/hl to rough or bright beer
DISADVANTAGE: Survives normal pasteurisation <20 PU's
Continues in bright beer may effect foam

**Tannic acid**
SOURCE: Natural gallotannins extracted from Chinese gall nuts or Shumac leaves.
ACTION: Has many hydroxyl groups, attracts proteins – bonds with nucleophylic (SH-& NH-) protein groups in a similar manner to natural beer polyphenols to produce insoluble precipitate.
DOSAGE: 5 to 8 g/hl to cold rough beer
ADVANTAGE: Very efficient stabiliser
DISADVANTAGE: Added in line cold 0 to -10C
Requires 5 to 10 minutes contact
Produces voluminous bottoms

**Polyvinylpolypyrrolidone**
SOURCE: Cross linked PVP – made synthetically.
ACTION: Preferentially bonds with polymerized polyphenols (tannins) through hydrogen and multi-site bonding.
DOSAGE: Single use 10 to 30 g/hl.
Regeneration 25 to 50 g/hl
ADVANTAGES: Very effective stabiliser
Selective for problematical polyphenols
Insoluble – easy to use
DISADVANTAGE: High cost for single use.
Capital investment for regeneration system.