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.

Professor J. De Clerck\textsuperscript{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.

Technical Summary 1

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

- 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.

- 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.

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

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.

At 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

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<th>Polyphenol Reduction</th>
<th>Protein Reduction</th>
<th>Process Optimisation</th>
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<td>High adjunction ratio</td>
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<td>Cold break removal</td>
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<td>PVP</td>
<td>Silica gel Tannic acid Enzyme</td>
<td>Contact time Temperature Contact</td>
<td>High storage temperatures</td>
<td>Beer activity and services</td>
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**PROTEINS**

- **Adsorption**
  - Bentonite
  - Silicalg

- **Precipitation**
  - Tannic Acid

- **Degradation**
  - Enzymes such as Papain

- **Removal of Protein-Tannoid complex**
  - Chilling
  - Formaldehyde

**POLYPHENOLS**

- **Adsorption**
  - Polycar PVP
  - Polyamide (Nylon)
  - High molecular weight insoluble protein (Casein)

- **Removal of Protein-Tannoid complex**
  - Chilling
  - Formaldehyde

(greater than 1004 and 1° Plati) and keeping the sparge pH low (below 7). Operations such as weak wort recirculation 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 catalysed by metal ions (particularly Fe++ and Cu++) 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:

- Poly saccharides 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 beer 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 (Polyglucol alginate)

- Lack of calcium in the mash can result in the formation of calcium carbonate, 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 stabilisation regime.

Further Reading

- Tim O’Rourke Back to Basics, Brewers Guardian February 2000 – p29
- De Clerck J: Brewers Digest August 1970 p62 – 64
- McMurrough I at “Effect of PVPV dosage on the skyline 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% & semigels 5% moisture. ACTION: Adsorbs proteins based on selective control of pore diameter – removes <40,000 MW. DOSAGE: Add to ICT at run down to up to 50g/l. ADVANTAGES: Insoluble – easy to use DISADVANTAGES: Moderately expensive. Generally suitable if a shelf life < 9 months is required. |
| Tannic acid | SOURCE: Natural gallotannins extracted from Chinese gall nuts or Shumac leaves. ACTION: Has many hydroxyl groups, attracts proteins – bonds with nucleophilic (OH & NH) protein groups in a similar manner to natural beer polyphenols to produce insoluble precipitate. DOSAGE: 5 to 8 g/l to cold rough beer ADVANTAGE: Very efficient stabiliser DISADVANTAGE: Requires 5 to 10 minutes contact Produces voluminous bottoms |

**Enzyme Contact**

- Tannic acid
- Temperature

**Auxiliary**

- Finings Whirlpool
- Finings of cold storage

**Chilling**

- Metal ions
- Oxygen pick up
- Efficiency

**SOURCE:** Cross linked PVP – made synthetically.

- 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

- ADVANTAGE: Survives normal pasteurisation <20 PU’s Continues in bright beer may effect foam

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**ACTION:** Hydrolyses proteins. (Beer foam is protein)

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**DisADVANTAGE:** Continues in bright beer may effect foam.