Beer Stabilization Technology
- clearly a matter of choice

Mustafa Rehmanji, Chandra Gopal and Andrew Mola

International Specialty Products
1361 Alps Road
Wayne, NJ 07470
U.S.A.
Scope of Presentation

• Mechanism of Haze Formation
• Upstream Stabilization: Polyclar Brewbrite
• PVPP
• Silica Gel
• Tannic acid
• Papain
• Admixture: Silica +PVPP
What is Beer Stability?

Beer stability is the extent to which a beer tastes and looks as good after aging as it did when it was first packaged. Stability is assessed by:

- Changes in colloidal stability (HAZE)
- Flavor stability (oxidation and staling)
- Color increase
- Microbial stability

Reference: Jean De Clerck, A Text Book of Brewing
# Beer Stabilization Guidelines

<table>
<thead>
<tr>
<th></th>
<th>Drinking Life</th>
<th>Stabilization Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CASK BEER</strong></td>
<td>(UK) 4 weeks</td>
<td>None - Low</td>
</tr>
<tr>
<td><strong>KEG BEER</strong></td>
<td>10 weeks</td>
<td>Low - Medium</td>
</tr>
<tr>
<td><strong>EXPORT KEG</strong></td>
<td>36 weeks</td>
<td>Medium</td>
</tr>
<tr>
<td><strong>SMALL PACK</strong></td>
<td>Bottle up to 52 weeks</td>
<td>High</td>
</tr>
<tr>
<td></td>
<td>Cans up to 75 weeks</td>
<td>High</td>
</tr>
</tbody>
</table>

The extent to which a beer requires colloidal stabilization depends on the raw materials, process, required shelf life and storage conditions.
Non-Biological Haze in Beer

- **Protein-Polyphenol** complexes - chill & permanent haze
- **Carbohydrates** - starch & β-glucans
- **Oxalates**
- **Other constituents** - metal hazes, collapsed fob, PGA, filter aids, iso-α-acids etc.
Change in Polyphenols and Flavanoids During Brewing

Total Polyphenols mg/l

<table>
<thead>
<tr>
<th>Step</th>
<th>Polyphenols</th>
<th>Flavanoids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mash in</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Last runnings</td>
<td>1,600</td>
<td>800</td>
</tr>
<tr>
<td>Copper cast</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fermenter</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mash end</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper up</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Whirlpool</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maturation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Total Flavanoid mg/l

- Polyphenols = EBC 9.9.1
- Flavanoids = EBC 9.9.2

Brewing Process

Step 1 – avoid use of very weak wort (<1.5 P)
Model for Protein – Polyphenol Interaction

Polyphenols are depicted as having two ends that can bind to protein. Proteins are depicted as having a fixed number of polyphenol binding sites.

Courtesy: Karl Siebert, Cornell University

Chill-Haze Development & Shelf-Life Model (Forced Aging at 37°C) for a Stabilized Standard Lager Beer

- Total Haze (°EBC)
- Correlation co-efficient $r = 0.9915$
- Haze Development Rate = 0.47°EBC units/week
- Lag Phase
- Shelf life (Time to develop haze = 2°EBC)
- Permanent or background haze
- Storage Time (weeks)
Relative Haze Formation

Beer stabilized with 100 g/hl PVPP to remove reactive polyphenols

Catechin Haze EBC

Tannic Haze EBC

Step 2 – minimize oxygen pick-up! < 0.1 ppm
Carbohydrate Hazes

- **Prevention** - raw material selection
  - complete starch conversion
  - process effects — identify sources of ‘shear’ damage

- **Remedies** - enzymes - β-glucanase, amylases, dextrinases
Oxalate Haze - ‘Green Haze’

• ‘Beer stone’ - calcium oxalate
• Octahedral crystal
• Check oxalic acid levels in malt
• Treated by addition of calcium salts ($\text{CaSO}_4$) to brewing liquor to precipitate oxalate
# Raw Material & Process Strategies to Optimize Colloidal Stability

<table>
<thead>
<tr>
<th>Process</th>
<th>Polyphenol Reduction</th>
<th>Protein Reduction</th>
<th>Process Optimization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material selection</td>
<td>Low proanthocyanidin malt</td>
<td>Low protein barley</td>
<td>Low malt modification</td>
</tr>
<tr>
<td></td>
<td>Hop extract</td>
<td></td>
<td>Coarse grind of malt</td>
</tr>
<tr>
<td>Brewhouse</td>
<td>High adjunct ratio</td>
<td>Mashing process pH, temperature</td>
<td>Vigorous kettle boil for &gt;60 min.</td>
</tr>
<tr>
<td></td>
<td>Avoid weak worts</td>
<td></td>
<td>Avoid excess mineral salts</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Good hot break</td>
<td>Cold wort filtration</td>
</tr>
<tr>
<td>Fermentation/ Maturation</td>
<td>Rapid onset to fermentation</td>
<td>Early yeast removal</td>
<td>Minimum 7 days maturation at -1ºC</td>
</tr>
<tr>
<td>Filtration</td>
<td></td>
<td></td>
<td>Low solids count</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Filter at -1ºC</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Avoid O₂ Pick up</td>
</tr>
</tbody>
</table>

➢ Step 3 – check & verify cold storage temperatures
Colloidal Stabilization of Beer

Composition of Chill Haze

PROTEINS
40-75%
- Tannic acid
- Papain

POLYPHENOLS
About 17%
- Polyclar Plus (PVPP-Si composites)
- Resins
- Polyclar (PVPP)
- PVP or PVP-silica

Adsorption:
- Silica gel

Precipitation:
- Polyclar Plus (PVPP-Si composites)
- Resins

Degradation:
- Papain

Other Polyphenol:
- Chilling

Adsorption:
- Polyclar (PVPP)

Carbohydrates 3-13%
Ash 0.7 - 5%
Cu,Fe Traces

Protein-Tannoid complex:
- Chilling
What is Polyc Mahar Brewbrite?

It is a proprietary composite of a selected Carrageenan and micronized PVPP.

**Kappa Carrageenan**

[Chemical structure of Kappa Carrageenan]

- β-D-galactose 4 sulfate 3,6-anhydro-α-D-galactose

**Marine polysaccharide of galactose & galactose sulfate monomers**

**PVPP**

[Chemical structure of PVPP]

- 2-pyrrolidinone, 1-ethenyl-, homopolymer

**Cross-linked polyvinylpyrrolidone**
Step 4 – wort clarity is very important and is related to beer clarity
Increase in Wort Yield - Commercial Trial

• Polyclar Brewbrite gave 3.2% increase in cold wort collected in FV as compared to untreated wort
Decrease in Fermentation Time with Polyclar Brewbrite - Commercial Trial

Polyclar Brewbrite gave 10% reduction in fermentation time as compared to untreated.
Analysis of Packaged Beer - Commercial Trial

Accelerated Forcing Test

Cycle = 24 hours at 60°C followed by 24 hours at 0°C
No. of Cycles (to reach 2.0 EBC Units) = month of predicted shelf life
Summary of Trial Results with Polyclar Brewbrite

- Enhances clarity of wort & beer
- Increases wort production
- Decreases fermentation time
- Improves total productivity of plant
- Extends shelf life of packaged beer
  - Longer shelf life requires PVPP treatment at filtration
- PVPP helps reduce astringency in beer*

* Measuring Astringency of Beverages using a Quartz-Crystal Microbalance
PVPP - Methods of Use

- **Single use**
  - Added prior to primary filtration and removed at the filtration stage

- **Regeneration**
  - Used after primary filtration on a horizontal leaf filter or candle filter and then recovered for re-use
Stabilization with PVPP

- Slurried in deaerated water (8 - 10% wt/wt)
- Hydrated for 1 hour (maximum efficacy)
- Added to beer during transfer
- **Single use** - usually added before DE filter
  - 5-10 min. contact time
- **Regeneration grade** - added after DE filtration
Possible Injection Points for Polyclar Plus and Polyclar PVPP

- Inlet Buffer Tank
- Dosing Tank
- DE Stabilizer
- DE Filter
- Bright Beer Tank
- Trap/Bag Filter
- Polish Filter
- Buffer Tank
- Packaging

Flow diagram showing the possible injection points for Polyclar Plus and Polyclar PVPP in a brewing process.
Tannoid Reduction with PVPP

- Untreated 10 g/hl
- 10 g/hl
- 30 g/hl
- 50 g/hl

Detection limit 10 - 12 mg/l

➢ Step 5 – reduce the tannoids with PVPP
Increase in Shelf Life of PVPP

- Treated Beer

![Bar chart showing the predicted shelf life of treated beer with different concentrations of Polyclar 10 (g/hl).]
# Hydrogels vs. Xerogels

<table>
<thead>
<tr>
<th>Hydrogel</th>
<th>Xerogel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contain 30-50% water</td>
<td>Contain 5% water</td>
</tr>
<tr>
<td>Easier to disperse</td>
<td>Harder to hydrate &amp; disperse (more dusty)</td>
</tr>
<tr>
<td>Used at up to ~150 g/hL</td>
<td>Used at up to ~80 g/hL</td>
</tr>
<tr>
<td>Less effective than xerogels</td>
<td>More effective than hydrogel</td>
</tr>
<tr>
<td>Greater permeability than xerogel</td>
<td>Greater microbial stability</td>
</tr>
<tr>
<td>Less microbial stability</td>
<td></td>
</tr>
</tbody>
</table>
Action of Silica gel

Protein adsorption follows three sequential steps:

- **Diffusion** of proteins from the beer matrix to the surface of the silica gel (relatively fast step)
- **Attraction**: Surface adsorption of proteins to the hydrated silica gel (relatively fast step)
- **Penetration** of the surface adsorbed proteins into the silica gel (rate determining step)
Protein Stabilizers - Tannic Acid

• From (Chinese) gallnuts
• Complexes with haze-active proteins
• Used at low dosage rates 4-10g/hL
• Added between FV & MV, or,
• In-line to DE filter
• Minimum contact time 10 min.
• Cannot be used at the same time as PVPP, but can be used sequentially – *tannic first, then PVPP*
Protein Stabilizers - Papain

- Proteolytic enzyme - from papaya
- Four iso-enzymes
- Degrades proteins - non-specific
- Used at low concentrations 1-6 g/hL
- Added at maturation or beer filtration
- Activated during pasteurisation
- Persists in beer
- Adverse impact on beer foam
What is Polyclar® Plus?

A proprietary composite of micronized Polyvinylpolypyrrolidone (PVPP) and selected Silica Xerogel
Predicted Shelf Results - Plant Trial with Polyclar Plus 730

(Composite 70%Si + 30%PVPP)

- **Step 6** – Balanced stabilization is efficient and cost effective
Brewery Trials – Filter Pressures, Run Lengths & Beer Stability with Polyclar Plus

<table>
<thead>
<tr>
<th>Stabilizer</th>
<th>Dose rate (g/hl)</th>
<th>ΔP/hr*</th>
<th>Filter Run Time (hr.)</th>
<th>Total Haze** (EBC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xerogel only</td>
<td>35.8</td>
<td>0.49</td>
<td>6.4</td>
<td>6.9</td>
</tr>
<tr>
<td>PVPP only</td>
<td>12.6</td>
<td>0.35</td>
<td>7.4</td>
<td>3.6</td>
</tr>
<tr>
<td>Polyclar Plus 730</td>
<td>33.0</td>
<td>0.25</td>
<td>12.0</td>
<td>1.2</td>
</tr>
</tbody>
</table>

*Pressure increase at steady state
**Total haze measured at 0°C after 5 days incubation at 60°C
Beer Transport

➢ Step 7 – don’t forget the beer after it leaves the brewery!
Seven Steps to Colloidal Stability

1. Avoid use of very weak wort (<1.5 P)

2. Minimize O₂ pickup throughout the brewing process (<0.1 ppm dissolved O₂ in beer ex-fermenter and into package)

3. Cold store, transfer & filter beer at 0°C, or below

4. Wort & beer clarity are important – optimize finings & filter aid use

5. Ensure that the tannoids are reduced (removed) from fresh beer – use PVPP

6. Balanced stabilization is efficient and cost effective – silica + PVPP

7. Consider beer transport & storage
Thank You!