Reasons to Fine

- Adjust Flavor
  - Remove astringency
- Adjust Color
- Remove unwanted aroma
- Enhance wine Stability
  - Remove additive such as an enzyme
Classes of Fining Agents

• Proteins
  • Gelatin
  • Casein
  • Egg-whites
  • Others
• Charcoal
• Copper
• Polymers
  • Polyvinyl poly pyrrolidones
• Bentonite
• Polysaccharides
• Silica Gel
**How fining agents Work**

- Positive charge
- Negative charge
- Phenolic compound

<table>
<thead>
<tr>
<th>Haze</th>
<th>Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protein</td>
<td>&quot;+&quot;</td>
</tr>
<tr>
<td>Tartaric Acid</td>
<td>&quot;-&quot;</td>
</tr>
<tr>
<td>Copper/Iron</td>
<td>&quot;+&quot;</td>
</tr>
<tr>
<td>Phenolics</td>
<td>&quot;-&quot;</td>
</tr>
<tr>
<td>Polysaccharides</td>
<td>&quot;-&quot;</td>
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Van der Walls forces

- Weak molecular interactions not arising from ionic or covalent bonds
- Mechanism for fining
- Also a reason for instability
Brief overview of options
Activated Charcoal (Carbon)

- Non selective
- Adsorption occurs due to van der Waals interactions
- Useful for making a simple “base” wine
- To remove wine faults
- Clean up bad fruit before fermentation
- Different types depending on goal
Protein fining agents

• Rationale: softening red wines
  • Removal of polyphenols and tannins
• Used to remove color compounds that might lead to instabilities (white wines)
• *Positive* charge in wine
  • Protein/tannin interaction = hydrogen bonding
• Residue concerns
  • 20% of casein may remain
 Iso-electric Point

- Depending on pH a protein can change charge
- Wine
- Impacts effectiveness and solubility
- At wine pH most proteins are net positive
Protein - Egg albumin (whites)

- Composed mostly of ovalbumin
  - Isoelectric point – 4.6
  - Other proteins in albumin range from 4.1-14.3
- 3.6% proline by mol
- Used to decrease astringency in red wines
  - Less efficacious than gelatin (see %proline)
- Less “fruit” character lost
• Primarily using casein as fining agent
• However special because micelle has been stabilized on introduction
• Fat may also play role (potential off aromas)
• Used To remove phenolic compounds or excessive oak
Casein

- Milk protein (3% as Ca caseinate)
  - Isoelectric point – 4.6
  - 8% proline by mol
- Used in white wines to remove:
  - Color, browning compounds
- Recommended for press wines
- Can reduce Cu and Fe (oxidation implications?)
PVPP Trial
Thiol Removal through copper fining

$$
\text{Cu}^{2+} + \text{H}_2\text{S} \rightarrow 2\text{H}^+ \text{ CuS (insoluble)}
$$

$\text{CuSO}_4$ About 25% copper by weight
Fate of H$_2$S in wine

Hydrogen Sulfide (1-10 µg/L)

Mercaptans (0.3-1 µg/L)

Disulfides (1-5 µg/L)

* Not removable with copper
• Early intervention key
• Must know H2S concentration otherwise may exceed legal limits for copper
• Addition limit 6.0ppm but Residual limit 0.5ppm
So you have made it to the end!

- Fermentation is finished
- ML completed
- Acid Adjustments have been made
- Blending Finished
- Additions
  - Sugar
  - Tannins
  - \( \text{SO}_2 \)
  - Pixie Dust, Love and Snake Oil
- The wine is just how you like it (or close), but what can you do to keep the consumer from ruining it
Removing Proteins

- Over time proteins can denature causing a haze
- More likely when a wine is heated (think of cooking an egg)
Bentonite

- Non-pure silicone volcanic clays
  - Montmorillonite
- High swelling & ion exchange capacity
- Two common forms: Na+ & Ca++
  - Na+ - USA (not legal in EU) – too much Na+ to wine
  - Ca++ - EU (less swellable)
- Negative charge (some positive too)
Bentonite sub-structure

- *Positive* edges, *negative* interior
- Overall more *negatively* charged
Bentonite

- Used for absorptions & adsorptions
- Removes protein non-specifically
  - Haze and foam active proteins
  - Implications for beer and sparkling wine???
- Bench trials conducted for dosing rate – Heating wine after fining
- Potential loss of metals into wine
Bentonite Trials

Control  0.5 g/L  1.0 g/L  1.5 g/L  2.0 g/L
Heat Stability testing

- Primarily testing for protein instability
- Many variants
  - simple method you heat wines at 80 C for 6 hours
- Some methods also use reagents to simulate storage
- Ultimate goal to predict what gets to the consumer
Cooling matters

![Graph showing the relationship between cooling time and turbidity for different wines and cooling rates. The graph indicates that cooling time affects the turbidity, with different rates affecting the outcome. The x-axis represents cooling time (hours), and the y-axis represents turbidity (Δ NTU). The graph shows the pass and fail criteria for each wine and rate combination.](image-url)
Heat Stability: Turbidity

• Formazine Turbidity Unit (FTU)
• Light source = High Emission Infrared LED
  ➢ Wavelength peak at 890nm
Cold Instability

- Consumers are terrified because of “broken glass” in their wine
- Caused by tartrate instability
  - Usually potassium bitartrate precipitation
  - Rarely calcium tartrate can be an issue as well
What is needed for tartrate crystal formation

- Solution needs to be saturated
  - Lower solubility at low temperatures
  - Lower solubility at high alcohol
- Cations need to be present (potassium, to a lesser extent calcium)
- Initial nucleation needs to happen
  - Without nucleation even a super saturated solution maybe ok
Titratable acidity

- Great metric for how we perceive wine but not much else
- Diverges greatly from total acidity due to grape cation uptake
Total Acidity

- Useful for understanding the chemistry of a wine, but hard to measure in a winery
- The amount of protons that the organic acids would contain if they were all disassociated
- Total acidity = [H+] titratable + [K+] + [Na+] (Boulton 1980)
Cold stabilization

- Basic idea is to mimic worst case scenario during transport and storage.
- Without nucleation precipitation will not occur
  - Pre-seed with potassium bitartrate
Importance of pH
Other remedies

- Stop nucleation
  - Cellulose
  - Mannoproteins

- Potential concerns with heat stability
- Longevity?
Other Methods

- Remove Substrate for crystal formation
  - Electro dialysis
  - Cation Exchange
    - Rather then removing tartrate, removes Cations
Assessing Cold Stability
Cold Stability

Freeze/Thaw test
- Centrifuge – removes pre-existing insoluble materials
- Freeze (-20°C)
- Thaw
- Compare change in pH before and after (tartrate loss)
  - pka

Figure 1. Tartrate Solubility Curve. Courtesy of Dr. Roger Beulon.
Other Methods

- Conductivity
  - Measure conductivity saturate at temp, measure again
- CP Test- Need ethanol, potassium and tartrate calculations
Prevention

- Cation additions add up
  - Calcium carbonate, potassium mettabisulfite
Order of Finishing a wine

1. Complete fermentation
2. Additive additions
3. Heat stabilization
4. Cold Stabilization*
5. Filtration
6. Bottling