Beer Aromas: Where They Come From, Whey They Go

Packaging Perspective

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Packaging Material Properties that Effect Beer Aroma & Flavor Stability

Aroma & Gasket Interactions

Oxygen Control

Beer Aroma Issue & Packaging Property

<table>
<thead>
<tr>
<th>Beer Aroma Issue</th>
<th>Packaging Property</th>
</tr>
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<tbody>
<tr>
<td>Staling &amp; Oxidation</td>
<td>Oxygen control, barrier &amp; scavenger</td>
</tr>
<tr>
<td>Flavor &amp; Aroma Scalping</td>
<td>Gasket chemistry and polarity</td>
</tr>
<tr>
<td>Contamination from packaging</td>
<td>Gasket and coating formulations and sources of materials</td>
</tr>
<tr>
<td>Contamination from the environment</td>
<td>Gasket barrier properties</td>
</tr>
</tbody>
</table>

Points for Discussion

- Oxygen control
- Aroma & Flavor Scalping
- Packaging contamination
- Environmental Contamination
- Sensory evaluation

Oxygen Controll
### Staling and Oxidation Requirements & Prevention

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Source</th>
<th>Prevention</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel or reagent</td>
<td>Beer</td>
<td>Optimize formulation and process to improve masking and resistance to oxidation</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Initial</td>
<td>Optimize transfer, filling and sealing process</td>
</tr>
<tr>
<td>Ingress</td>
<td></td>
<td>Package selection</td>
</tr>
<tr>
<td>Energy</td>
<td>Heat</td>
<td>Refrigeration</td>
</tr>
<tr>
<td>Light</td>
<td></td>
<td>Tinted bottles, sealed boxes</td>
</tr>
</tbody>
</table>

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### Estimated Quantity of Oxygen in Beer Bottles per Source

<table>
<thead>
<tr>
<th>Operation</th>
<th>Poor Oxygen Control</th>
<th>Good Oxygen Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tanks and Transfers</td>
<td>100 ppb</td>
<td>25 ppb</td>
</tr>
<tr>
<td>Bottling</td>
<td>150 ppb</td>
<td>25 ppb</td>
</tr>
<tr>
<td>Closing</td>
<td>250 ppb</td>
<td>50 ppb</td>
</tr>
<tr>
<td>Closure ingress over 4 months*</td>
<td>700 ppb</td>
<td>60 ppb</td>
</tr>
<tr>
<td>Refrigeration</td>
<td></td>
<td>Slows reaction &amp; ingress</td>
</tr>
<tr>
<td>Total after 4 months</td>
<td>1200 ppb</td>
<td>160 ppb</td>
</tr>
</tbody>
</table>

*Area with largest potential for improvement

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### Oxygen Ingress Determination

- Most polymers’ barrier properties suffer as heat and humidity increase
- Many oxygen scavengers are activated by heat and humidity
- Packages have to be tested filled with non-reactive liquid (stabilized water)
- Packages are filled at low and consistent oxygen levels
- Oxygen in packages measured over time
- Packages can be stored in various environments or abused
  - Warehouse stacking
  - Drop impact
  - Transportation
  - etc.

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### Oxygen Concentration in Beer

### Oxygen Concentration in Water

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### Barrier Materials

- Early barrier = Aluminum disk over cork
- In shell molder barrier polymers
- Multi-layer polymers & foil
- Barrier additives to enhance polymer performance
Crown Closures

- Twist-off Crown
  - Also used for pry-off
  - In shell molded
- Pry-off crown
  - In shell molded

Barrier Closures and Sealants

- Effective at reducing the ingress of oxygen, nitrogen and contaminants
- Reduces the loss of carbon dioxide
- Barrier properties dependent on
  - Sealant barrier properties
  - Sealant physical properties
  - Closure design
  - Closing conditions

Oxygen Ingress Through Crown Liners

Barrier Closures and Sealants

- Effective at reducing the ingress of oxygen relative to the standard closure and sealant
- Oxygen scavenger can be added to the sealant, closure or plastic bottle
- Performance dependent on the activation of the scavenger and path of oxygen ingress
- Has potential to reduce oxygen in package
- Shelf-life of scavenger containing materials is limited

Oxygen Scavenger Sealants

- Effective at reducing the ingress of oxygen relative to the standard closure and sealant
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- Has potential to reduce oxygen in package
- Shelf-life of scavenger containing materials is limited

Oxygen Scavengers Used in Closures

<table>
<thead>
<tr>
<th>Material</th>
<th>Catalyzed Available</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td></td>
<td>Fast triggered</td>
<td>Color pickup</td>
</tr>
<tr>
<td>Ascorbate</td>
<td>Yes</td>
<td>Controlled speed TDA GRAS</td>
<td>Color, Odor</td>
</tr>
<tr>
<td>Sulfite</td>
<td>Yes</td>
<td>Controlled speed, High process temp, TDA GRAS</td>
<td>Bad press for corrosion in crowns</td>
</tr>
</tbody>
</table>

Oxygen Scavenger Schematic

- moisture activated scavenger particle
- Inactive scavenger particle
- oxygen molecule
Oxygen Scavenger Effect in Crown Liners

Molded Liner Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Pry crown</th>
<th>Twist crown</th>
<th>Aluminum</th>
<th>Plastic</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>TPR/TPE</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>EVA</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>LDPE</td>
<td>*</td>
<td>*</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Butyl</td>
<td>*</td>
<td>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barrier Materials</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butyl</td>
<td>*</td>
<td>*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Accelerated Flavor Testing for Oxidation

- Fill at low initial oxygen levels
- Test oxygen ingress not heat aging
- Heat aging = long term pasteurization
- Accelerated oxygen ingress = flavor shelf-life
- Bottles are placed in pure oxygen atmosphere for approximately 5X acceleration

Aroma & Flavor Scalping

Absorption of aromas & flavors by the packaging (gasket).

Scalping Parameters

- Chemistry and polarity of the polymers (plastics, rubber, paint) in contact with the beer.
- Size and polarity of the aromas and flavors
- Non-polar flavors have been studied greatly for the citrus industry
- Silicone > LDPE > HDPE > PP > PET > Saran
- Scalping can be used to remove undesirable aromas and flavors [TCA, TBA, TeCA, …]
Scalping Evaluation

- Scalping of mixed aromas & flavors can be selective based on concentrations, kinetics, thresholds, capacity to scalp, etc.
- Scalping usually happens quickly (hours, days)
- Avoid accelerated tests
- A gasket that is good or bad for one beer may be the opposite for another.
- Crown gasket materials are mixtures of many ingredients

Scalping Reference

- Effects of flavour absorption on foods and their packaging materials, Remco W.G. van Willige
- Many others available with an internet search

Packaging Contamination

Migration of plastic and coating ingredients into the beer

Sources for Migration and Contamination

- Crown gasket or liner
- Coatings, paints and inks on the crown
- Plastic bottles
- From the degradation of the packaging materials
- Hoses and gaskets in the brewery

Packaging Material Contaminants

- Change in “typical” odor and flavor of the plastics
- Minor additives - antioxidants, heat stabilizers, antistats, process aids
- Major ingredients – lubricants, plasticizers, scavengers
- Dust collected on the inside surfaces (paint, metal fines, dirt, etc.)
- Food law compliance does not insure NO contamination nor good flavor properties

PVC Crown Liner

- PVC – polymer, antioxidants, catalysts, emulsifiers in plastisol resins
- Plasticizers – DOP, DiOP, Didp, epoxidized soybean oil (ESO)
- Heat stabilizers – Ca & Zn fatty acids, ESO, antioxidants
- Blowing agents – degradation products
- “Kickers” – Zn soaps, fatty acids
- Lubricants – waxes, fatty acids, oils, etc.
- Oxygen scavengers – degradation products, catalysts
- Pigments
- Process aids – waxes, soaps, oils, etc.
Coatings (paints)

- Resins
- Plasticizers
- Crosslinking agents
- Catalysts
- Pigments
- Waxes and slip agents
- Emulsifiers (in water-borne and organosols)
- Flow control agents – surfactants of all kinds

Sources of Packaging Degradation

- Empty package
  - Excess heat and shear from manufacturing
- Empty and Filled package
  - Heat and moisture during transportation and warehousing
  - Oxidation and degradation of scavengers
  - UV light exposure

Material Degradation Contaminants

- Bottles
  - Acetaldehydes, antioxidants
- Closures/liners
  - Aldehydes, ketones, oxidized fatty acids and plasticizers
- Oxygen scavengers
  - Water soluble scavengers and byproducts
  - Low molecular weight oxidation products

Environmental Contaminants

- Oxygen
- Nitrogen
- UV
- TCA
- Solvents
- Exhaust fumes
- Perfumes
- Etc.

Detection & Identification of Contaminants

- Appearance
- Odor
- Sensory
- Qualitative analysis
- Quantitative analysis
- Spiked or dosed controls
- Knowledge of packaging materials and chemistry
Environmental Contamination

- Chemical contamination from materials in atmosphere where the bottle is located
- Relative barrier performance determined by storing filled bottles in concentrated environment
- Analysis for chemical in beverage by appropriate method (GC, HPLC, SPME, etc)

UV Ingress or Exposure

- UV effects on beer already known
- UV also degrades plastics and additives used in packaging
- This degradation causes flavor problems
- European mineral water industry has established the “Light Box Test”
- Light Box Test exposes filled bottles to fluorescent or Xenon light for one week
- Analysis by sensory evaluation
- Typical contaminants include aldehydes and ketones
- Unpigmented plastic closures are extremely prone to this problem

Packaging Material Realities

- No package or material is perfect
- All plastics/polymers are permeable and have extractables, but are they detectable and manageable?
- Temperature and humidity can greatly effect barrier performance
- The number of potential contaminants is endless
- PVC or Phthalate-free tells you what the gasket is not.

Bottom Line on Packaging

- No bottle or closure is perfect
- Be aware of the potential problems
- Determine properties and thresholds that are critical to your product
- Evaluate and specify performance properties
- Sensory performance is the bottom line