Lecture #2

History of the Glass Industry

Terminology and Definitions

Formulation and Uses of Glass
History of Glass

- Glass in Egypt (1500 B.C.)
  - First Formula (60 parts sand, 180 parts ashes of sea, 5 parts chalk)
  - Used as Vessels and Jewelry
- The Glassblowing Pipe (200 B.C. Syria)
  - Simple, Round Objects
  - Thin Walled, Multi-shaped Glasses
  - First example of flat glass (windows)
- MnO₂ and Improved Oven Technology (Romans)
  - Clear and Better Quality Glass
- Germans Ernst Abbe and Otto Schott (1876)
  - Glass Research
  - Thermometer, Optical Glasses, Cooking Wear
History of Glass Manufacturing in the U.S.

- Mixed Traditions of English and German Glassmaking
- Earliest Efforts Introduce Annealing (1740’s)
- Three Major Centers in the U.S. (19th Century)
  - South Jersey- Waldglass
  - Pittsburgh, Ohio
  - Northern New York/New England
- Glassmaking in the 20th Century
  - Growth of American Optical Glass Industry
  - Industrial and Consumer Glasses (Owens-Illinois)
History of Flat Glass

1680 - plate process (rolled on tables after annealing, grinding and polishing)

1750 - cylinder glass by blowing

1840 - mechanical blowing

1903 - continuous sheet drawing

1914 - Fourcault (first vertical drawing)

1925 - Pittsburgh vertical drawing process

1960 - Float process
ASTM Definition of Glass

“...an inorganic product of fusion that has cooled to a rigid condition without crystallization”
Glass... the Material

Other Definitions:

“Glass is an inorganic product of melting, which when cooled without crystallization, assumes a solid state”

“Glass includes all materials which are structurally similar to a liquid but which have a viscosity so great at normal ambient temperatures that they can be considered as solids”
System 1 - Crystallization
System 2 - Glass Formation

Ts - melting point
Tg - transformation point
Tr - room temperature

Factors affecting Glass Formation

- The movement of the structural elements
  
  Viscosity \( \eta = 10^{13} \) Poise (P) - [Tg]
  
  (in comparison, water = 10^{-2}, olive oil = 10^2 and honey = 10^4 Poise)

- Glass must be heated to \( \sim 10^2 \) to achieve homogeneous melt -Glass forms \( \sim 10^3-10^8 \)

- Speed of Cooling

- Number of components
Glass Types and their Uses

- **Soda-Lime Glass**
  71%-75% Sand, 12%-16% Soda, 10%-15% Lime
  Use: Bottles, Jars, Drinking Glasses and Window Glass

- **Lead Glasses**
  54%-65% SiO₂, 18%-38% Lead Oxide (PbO), 13%-15% Soda
  Use: Drinking Glasses, Vases, Bowls and Decorative Items

- **Borosilicate Glasses**
  70%-80% SiO₂, 7%-13% B₂O₃, 4%-8% Na₂O, 2%-7% Al₂O₃
  Use: Cooking Wear, Headlamps, Laboratory Glass (Pyrex)

[Sand: SiO₂, Soda: Na₂O or K₂O, Lime: CaO]
Classification of Components

- **Network Formers**: SiO$_2$, B$_2$O$_3$
- **Intermediate Formers**: Al$_2$O$_3$, ZrO$_2$
- **Modifiers**: Na$_2$O, CaO, MgO
- **Colorants**: Fe$_2$O$_3$, Cr+, Se+
- **Decolorants**: As$_2$O$_3$, MnO$_2$, CoO
- **Refining Agents**: As$_2$O$_3$, CaSO$_4$
## Formers, Intermediates and Modifiers

<table>
<thead>
<tr>
<th>Formers</th>
<th>Intermediates</th>
<th>Modifiers</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>Al$_2$O$_3$</td>
<td>Na$_2$O</td>
</tr>
<tr>
<td>B$_2$O$_3$</td>
<td>PbO</td>
<td>CaO</td>
</tr>
<tr>
<td>GeO$_2$</td>
<td>Sb$_2$O$_3$</td>
<td>K$_2$O</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>ZnO</td>
<td>MgO</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>TiO$_2$</td>
<td>Li$_2$O</td>
</tr>
<tr>
<td>As$_2$O$_3$</td>
<td>BeO</td>
<td>BaO</td>
</tr>
</tbody>
</table>
Standard Terminology of Glass

- ASTM designation C 162 - 94 (pp 29-40)

- Standard terms used by Glass industry
Terminology

- Divitrification - Crystallization
- Cullet - scrap glass cullet
  - foreign cullet (from an outside source)
  - domestic cullet (from within the plant)
- Annealing - Controlled cooling process
- Stones - unrefined grains of various sizes
- Straie (Cord) - inhomogeneous streaks of different RI which produce distortion
Raw Materials

- All are either directly or indirectly (cullet) geologically derived. (inherent impurities)
- 20 million tons of raw material are used annually in North America for glass industry
- Impurities can be a function of individual mining locations
## Glass Batch Raw Materials

<table>
<thead>
<tr>
<th>Major Ingredients</th>
<th>Minor Ingredients</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica Sand</td>
<td>Borates</td>
</tr>
<tr>
<td>Soda Ash</td>
<td>Salt Cake</td>
</tr>
<tr>
<td>Limestone</td>
<td>Slag</td>
</tr>
<tr>
<td>Dolomite</td>
<td>Potassium Carbonate</td>
</tr>
<tr>
<td>Feldspar</td>
<td>Sodium Nitrate</td>
</tr>
<tr>
<td>Nepheline Syenite</td>
<td>Lithium Carbonate</td>
</tr>
<tr>
<td>Aplite</td>
<td>Lithium Minerals</td>
</tr>
<tr>
<td>Kaolin</td>
<td>Litharge</td>
</tr>
<tr>
<td>Cullet</td>
<td>Barium Carbonate</td>
</tr>
<tr>
<td></td>
<td>Strontium Oxides</td>
</tr>
<tr>
<td></td>
<td>Coloring Oxides</td>
</tr>
</tbody>
</table>
Silica

- 12 million tons of Quartz sand are used annually in North America
- High transportation costs limit distance from source to plant (about 100 miles)
- Grain size (proper melting conditions) and Fe contamination limit the sources of sand
- Over 100 glass sand mines in North America
Soda Ash

- $\text{Na}_2\text{CO}_3$ is the main source of sodium oxide
- 3 million tons are used annually in North America
- Wyoming is main source of “Trona”
- Soda Ash is recrystallized prior to use to remove iron impurities
Limestone Calcia (CaO) and Magnesia (MgO)

- Contribute to the chemical durability of glass and control the viscosity during forming.
- MgO enhances the flow process during the float process (found in high quantities in float glass)
- Mixture of MgO and CaO reduces energy costs
- 1.5 million tons of lime is consumed by the glass industry in North America annually
Glass Classification

Types                      Applications

Soda-Lime                  Windows and Containers
Lead                       Housewares and Decorations
Borosilicate               Industry, Lamps, Cookware
Special                    Optical, Electronics, TV
Soda - Lime Glasses

- By far the greatest number of industrially produced glasses
- Composed of 71%-75% sand, 12%-16% soda and 10%-15% lime
- Magnesia (MgO) replaces some CaO in float process
- Potassium sometimes replaces sodium
Lead Glasses

- Lead Oxide replaces much of the lime resulting in a glass type known as *lead crystal*
- Composed of 54%-65% SiO₂, 18%-38% PbO, and 13%-15% Soda Ash or potash
- Exhibit very high refractive index, suited for decorative purposes
Borosilicate Glasses

- Higher percentage of SiO$_2$ than other glass
- Composed of 70%-80% SiO$_2$, 7%-13% B$_2$O$_3$, 4%-8% Na$_2$O and K$_2$O and 2%-7% Al$_2$O$_3$
- Posses a high resistance to chemical corrosion and temperature change
Specialty Glasses

- Quartz Glass
- Industrial Grade Borosilicates (chemical plant pipes)
- Glasses for the electronic industry
- Glasses for television tubes (x-ray absorption)
- High voltage insulators, electron conductive and semi-conductive
- Optical and Ophthalmic glass
Manufacturing Processes for Glass

Batch, Container, Float Glass

Tempered Glass and Windshield Manufacture
The Glassmelt

- Batch Melting
  - Pot Melts (1300 °C - 1600 °C)
  - Tank Melts (Two step process)

- Continuous Tanks
  - Manufacturing of Flat Glass
  - 40 - 100 meters long
Glass Manufacture

- Sand
- Limestone
- Soda
- Other

- Mixing

- Furnace
  - Melting
  - Homogenizing
  - Refining

- Forming
- Annealing
Agricola Oven
Modern Tank Design

1 - Hopper (mixing)
2 - Introduction of materials
3 - Further Mixing, Initial Melting
4 - Fusion
5 - Passage to refining
6 - “Working end” (refining)
7 - Exit area

Overhead view of melt tank

9 - Heat regeneration

Refractory Walls composition: Zr - Al - Si (ZAS) bricks

The Float Glass Process

- Molten glass is introduced into a controlled atmosphere chamber of liquid tin.
- At the entrance, the temperature of the tin is ~1000 °C and at the exit it is ~ 600 °C.
- Rollers at the exit side “pull” the glass and the speed of the roller determines the thickness of the glass output.
- Thicknesses between 1.5 and 20 mm are possible.
Glass Melt Tank

6 - 12 feet wide
30 - 120 feet long
Output: 100 - 400 tons/day

The largest tanks hold 2500 tons of molten glass
a - glassmelt
b - melt tank
c - transport rollers
d - float bath
e - molten tin

“Suck-Blow Process”