CL-304

Chemical Process Technology

GLASS MATERIALS

Production and Applications

Group:22

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Introduction

Glass is an essential material in modern construction because it's hard, see-through, and resistant to chemicals. It also bends light, can withstand pressure, and expands under heat. Improving glass in recent years has mostly been about controlling these features, especially its hardness, transparency, and chemical resistance. Glass experts work on tweaking these traits to make glass more useful in different ways.

History

The history of glass dates to ancient times, with references to its discovery around 6,000 or 5,000 B.C. Venice dominated glassmaking until the 16th century when it spread to Germany and England. Window glass was mentioned in A.D. 290, and plate glass emerged in France in 1688. In America, glassworks were established in Jamestown in 1608 and Salem, Mass., in 1639. Significant advancements in glass technology occurred in the late 19th century, driven by innovations like continuous sheet glass drawing processes. The rise of the automobile industry further spurred advancements, leading to rapid evolution in glass manufacturing. Today, the industry is highly specialized, incorporating modern science for production and product development.

Uses and Economics

The glass industry serves multiple sectors:

1. **Construction**: Used in windows, facades, and partitions for transparency and insulation.
2. **Automotive**: Essential for windshields and windows, enhancing safety and driving experiences.
3. **Electronics**: Critical for high-resolution displays in smartphones, tablets, TVs, and monitors.
4. **Packaging**: Preserves food and beverage quality, valued for sustainability.

5. **Medical and Scientific**: Essential for maintaining substance purity in laboratory equipment.
6. **Art and Design**: Offers creative possibilities for sculptures and decorative pieces.

Glass types include flat glass, containers, and specialty glass, with prices varying based on production method and quality. For example, construction glass ranges from $3 to $15 per square foot, while specialized glass for electronics commands higher prices. Overall, the glass industry is a significant economic contributor driven by innovation and sustainability.

Chemical Composition of Typical Glass

No.	SiO_2	B_2O_3	Al_2O_3	Fe_2O_3	As_2O_3	CaO	MgO	Na_2O	K_2O	PbO	SO_3
1	67.8	.....	4.4	....	....	4.0	2.3	13.7	2.3	....	1.0
2	69.4	.....	3.5	1.1	....	7.2	....	17.3			
3	70.5	.....	1.9	0.4	....	13.0	....	12.0	1.9		
4	71.5	.....	1.5	....	....	13.0	....	14.0			
5	72.88	.....	0.78		....	12.68	0.22	12.69			
6	72.9	.....	0.7		....	7.9	2.8	15.0			
7	72.68	.....	0.50	0.07	....	12.95	....	13.17	.....	....	0.44
8	74.50	.....	0.81	0.09	....	5.5	4.1	15.0			
9	72.4	.....	0.8	0.4	....	5.3	3.7	17.4			
10	73.88	16.48	2.24		0.73	.....	....	6.67	Trace		
11	74.2	0.4	....	....	0.2	4.3	3.2	17.7			
12	67.2	.....	....	....	0.5	0.9	....	9.5	7.1	14.8	
13	69.04	0.25	....	....	....	12.07	....	5.95	11.75		
14	64.7	10.6	4.2	....	....	0.6	....	7.8	0.3		
15	80.75	12.00	2.20		0.40	0.30	....	4.10	0.10		
16	80.9	12.6	1.8	....	....	....	....	4.4			
17	96.0	3.6									

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1. Egyptian from Thebes (1500 B.C.) (Blau).

2. Pompeian window (Blau).

3. German window (1849) hand-blown (Blau).

4. Representative window and bottle glass of nineteenth century (Sharp).

5. Machine cylinder glass (Sharp).

6. Fourcault process sheet with 0.7 per cent BaO (Sharp).

7. Polished plate with 0.18 per cent Sb_2O_3 (Sharp).

8. Owens ,machine bottle (Sharp).

9. Electric light bulb (Sharp).

10. Jena, incandescent gas chimney (Sharp).

11. Tableware, lime crystal (Sharp).

12. Tableware, lead crystal (Sharp).

13. Spectacle with 0.9 per cent Sb_2O_3. (Sharp).

14. Jena with 10.9 percent ZnO, 1911 laboratory (Sharp).

15. Corning Pyrex laboratory (Sharp).

16. Laboratory Pyrex 774 (Blau).

17. 96 per cent silica No. 790 (1940) (Blau).

Manufacturing of Flat Glass

Glass is a rigid, undercooled liquid with no specific melting point and high viscosity, preventing crystallization. Chemically, it forms from fused non-volatile inorganic oxides resulting from decomposed alkali and alkaline earth compounds, sand, and other constituents, creating a completely vitrified product or containing minimal no vitreous material.

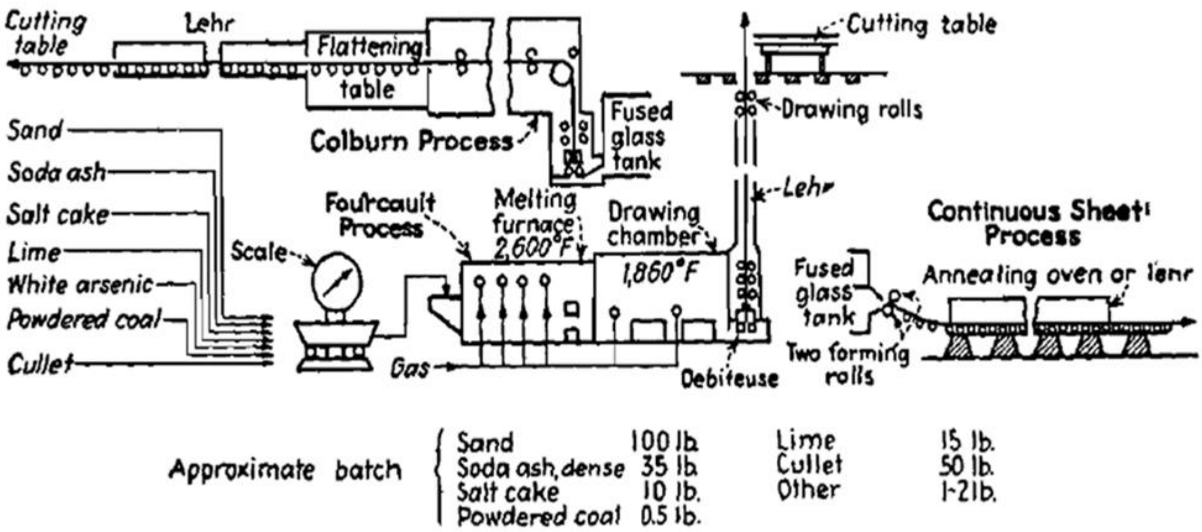

FIG. 1. Flow sheet for flat-glass manufacture.

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Composition

The glass industry has seen numerous developments over the past thirty years, yet lime, silica, and soda still make up over 90% of all glass production, much like they did 2,000 years ago. However, there have been minor changes in major ingredients or significant changes in minor ingredients. Commercial glasses generally fall into six classes:

1. **Vitreous Silica**: Made from pure silica without a flux, offering high thermal and chemical resistance.
2. **Alkali Silicates**: Water-soluble glasses used as solutions, mainly sodium silicates.
3. **Lime Glass**: Widely used for windows, fixtures, and containers, made from soda-lime-silica.
4. **Lead Glass**: Used for decorative and optical purposes due to its high index of refraction and dispersion.
5. **Borosilicate Glass**: Contains boric oxide and silica, known for optical and scientific applications.
6. **Special Glass**: Includes coloured, translucent, safety, fiberglass, photosensitive, phosphate, and borate glasses.

Coloured glass, opal glass, safety glass, fiberglass, high-silica glass, photosensitive glass, and phosphate glass serve various specialized purposes within these categories.

Raw Materials

The glass industry relies on various raw materials for production:

- Over 5,000,000 tons of glass sand are used annually in the United States, along with 1,500,000 tons of soda ash, 113,000 tons of salt cake, and 875,000 tons of limestone or equivalent lime.
- Other materials include lead oxide, pearl ash, borax, boric acid, arsenic trioxide, feldspar, and fluorspar, as well as a variety of metallic oxides, carbonates, and salts for coloured glass.
- Sand for glassmaking should be nearly pure quartz, with low iron content to avoid affecting glass colour adversely.

- Soda, mainly supplied by dense soda ash, is crucial for glassmaking, along with sodium bicarbonate, salt cake, and sodium nitrate for oxidizing iron and accelerating melting.
- Lime is primarily sourced from limestone and burnt lime from dolomite, introducing magnesium oxide into the batch.
- Feldspars are used for aluminium oxide supply, contributing sodium oxide or potassium oxide and silica, while lowering the glass melting point and preventing devitrification.
- Borax and boric acid provide sodium oxide and boric oxide, enhancing fluxing power, lowering expansion coefficient, and increasing chemical durability.
- Other additives like salt cake, sulphates, arsenic trioxide, and nitrates serve various purposes, such as removing scum, reducing bubbles, or oxidizing iron.
- Gullet, or crushed glass waste, is sometimes added to the batch to aid melting and utilize waste materials.
- Refractory blocks, including electro cast alumina, zirconia-alumina, mullite, magnesia-alumina, and chrome-alumina combinations, are used in glass tanks due to the severe conditions encountered, with a trend towards basic refractories in regenerators and recuperators for alkali dust management.

Chemical Reactions

The chemical reactions involved in glassmaking can be summarized with the following equations:

1. $Na_2CO_3 + aSiO_2 \rightarrow Na_2O \cdot aSiO_2 + CO_2$ (1)
2. $CaCO_3 + bSiO_2 \rightarrow CaO \cdot bSiO_2 + CO_2$ (2)
3. $Na_2SO_4 + cSiO_2 + C \rightarrow Na_2O \cdot cSiO_2 + SO_2 + CO$ (3)
4. $Na_2SO_4 + C \rightarrow Na_2S + CO$ (4)
5. $2Na_2SO_4 + C \rightarrow 2Na_2S + CO_2$ (5)
6. $Na_2SO_4 + cSiO_2 \rightarrow Na_2O \cdot cSiO_2 + SO_2$ (6)

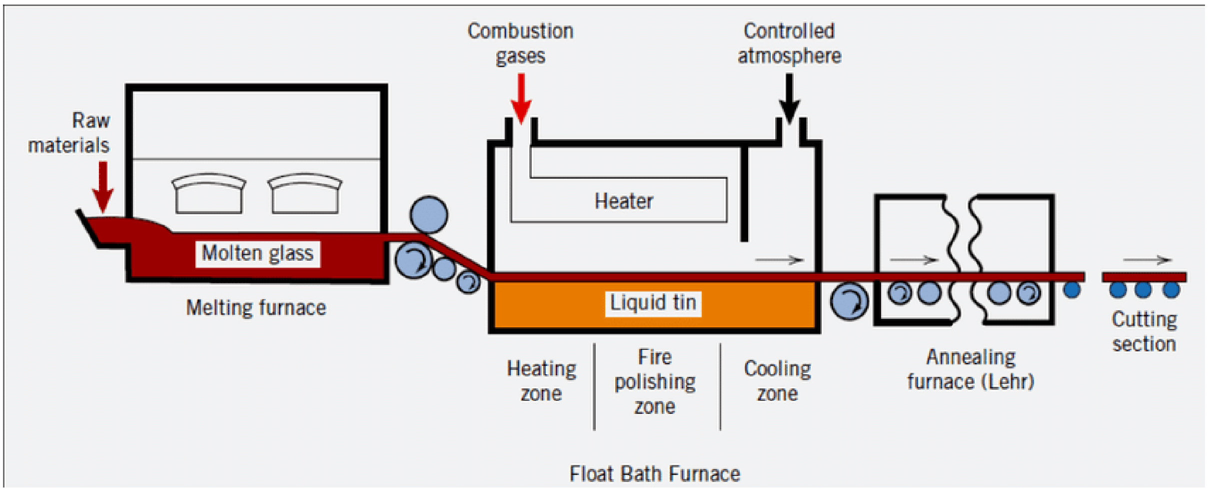
It's noted that the ratios of Na_2O/SiO_2 and CaO/SiO_2 in the compounds formed need not be 1:1 molecular ratio, and the molecular ratios typically found in ordinary window glass are approximately 2 moles of Na_2O, 1 mole of CaO, and 5 moles of SiO_2.

Unit Operations and Unit Processes

In glass manufacturing, the process involves:

1. **Transporting raw materials**: Materials are brought to the plant.
2. **Sizing and storing**: Some materials are sized, then stored until needed.
3. **Feeding raw materials into the furnace**: They are conveyed, weighed, and fed into the furnace.
4. **Glass formation**: Materials react in the furnace to form glass.
5. **Heating with fuel**: Fuel is burned to achieve the necessary temperature.
6. **Heat saving**: Techniques like regeneration save energy.
7. **Shaping**: Molten glass is shaped into products.
8. **Annealing**: Controlled cooling relieves stress in the glass.
9. **Finishing**: Final touches are added.

Modernization includes machinery for handling materials and automatic manufacturing, reducing manual labour and dust emissions to meet stricter regulations.



Elkersh, Hussein. (2014). Innovative Cleaner Production Technique: Foam Glass Production from Lead Crystal Glass Sludge. 10.13140/RG.2.1.4850.9849.

Methods of Manufacturing

The manufacturing process can be categorized into four main phases: melting, shaping, annealing, and finishing.

Melting

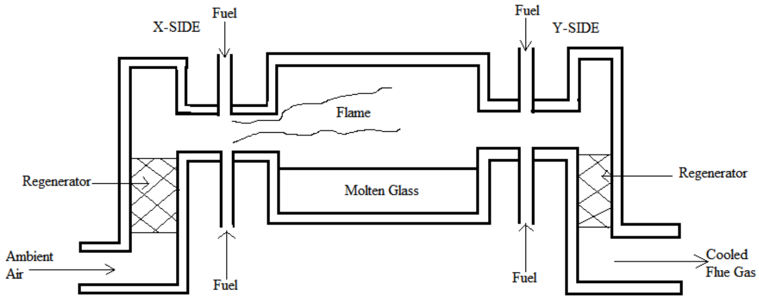
Glass furnaces are divided into pot and tank furnaces, further categorized as regenerative or recuperative.

1. **Pot Furnaces**: These are small, typically holding up to 2 tons of glass. They're used for specialized glasses like optical or art glass, where protecting the melting batch from combustion products is crucial. Pots are made of clay or platinum crucibles.
2. **Tank Furnaces**: Batch materials are charged into a large tank, forming a pool of molten glass. Flames play across the hearth, and the refined glass is continuously worked out from the opposite end. The quality of the glass and furnace life depend on the quality of refractory blocks used.

Both types of furnaces can be:

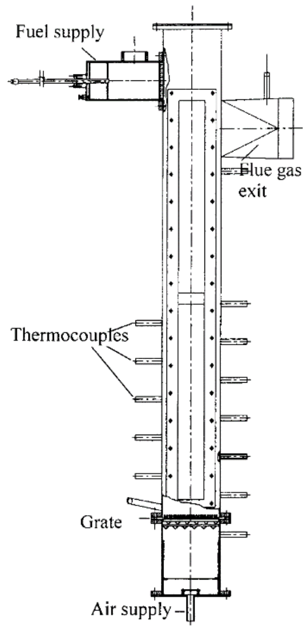
- **Regenerative**: Operating in cycles with two sets of checker work chambers, where flame gases give up heat and preheat incoming air, achieving higher temperatures and saving heat.
- **Recuperative**: Achieving the same preheating effect but with continuous flow in one direction, passing hot gases through passages and preheating air in adjacent passages. However, they face challenges with leaking and clogging compared to regenerative furnaces.

Maintaining furnace temperature is crucial, with regenerative furnaces typically kept at least at 2200°F. Melting costs about $2 per ton of glass, with most heat lost through radiation. Water cooling pipes are often used in furnace walls to reduce the corrosive action of molten glass.



Tank furnace Diagram

Basu, Amlan & Mohanty, Sumit. (2016). FOPID Controller for Heating Furnaces. 10.13140/RG.2.1.1887.1921.



Pot furnace Diagram

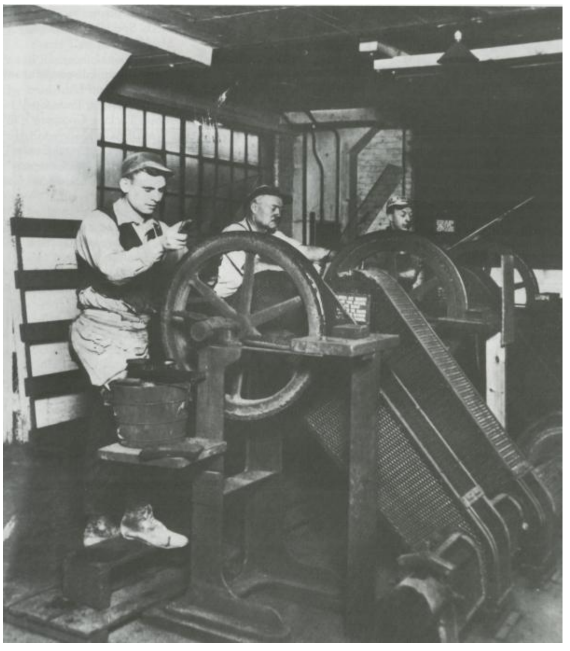
Horttanainen, Mika & Saastamoinen, J. & Sarkomaa, P.. (2002). Operational Limits of Ignition Front Propagation against Airflow in Packed Beds of Different Wood Fuels. Energy & Fuels - ENERG FUEL. 16. 10.1021/ef010209d.

Shaping or forming

Glass shaping techniques encompass both machine and hand molding. Machine molding demands meticulous design to ensure swift completion of the article as the glass swiftly solidifies. Notably, the design intricacies involve considerations such as heat flow, metal stability, and bearing clearance, highlighting the complexity of the engineering involved.

Window Glass: The traditional manual process of window glass production, involving blowing a gob of glass into a cylinder and flattening it, has been replaced by continuous methods like the Fourcault and Colburn processes. In the Fourcault method, glass is vertically drawn through a debiteuse and cooled by water-cooled coils to form a ribbon, subsequently cut into sheets. On the other hand, the Colburn process involves vertical drawing followed by heating and bending over a horizontal roller before flattening into sheets.

Plate Glass: Historically, plate glass was crafted by pouring molten glass onto flat tables and rolling it into uniform plates, a process that required precise coordination to avoid imperfections. This manual method has been supplanted by continuous processes pioneered by the Ford Motor Company and the Pittsburgh Plate Glass Company. These processes involve melting glass in large furnaces and forming sheets between water-cooled rolls, ensuring uniformity and efficiency.



Pittsburgh Glass Factory glass polishers, Ford City, PA, 1926. source

Bottle Production: Bottle manufacturing employs machines for casting, with suction-feed or gob-feed methods being prevalent. Suction-feed machines draw glass into molds using suction, followed by blowing and shaping. Conversely, gob-feed machines deliver molten glass through a trough to molds, where it is shaped using air pressure. These automated processes allow for high-speed production, with machines capable of producing up to 60 units per minute.

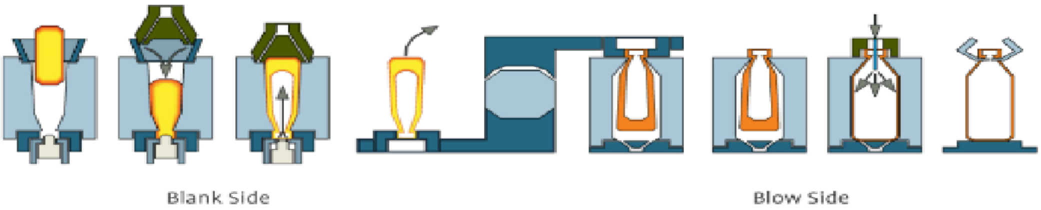


Figure 1. Blow and Blow Process [2].

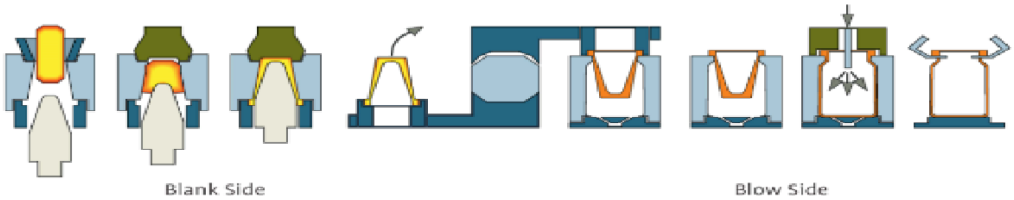


Figure 2. Press and Blow Process [2]

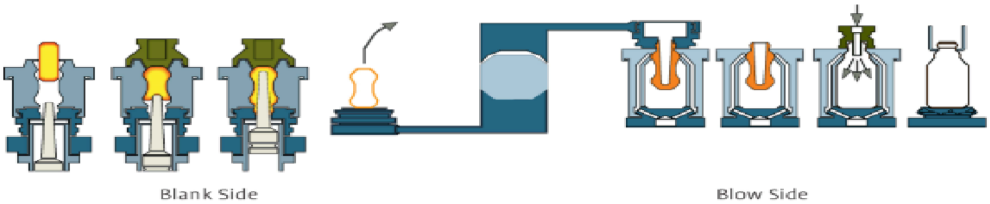
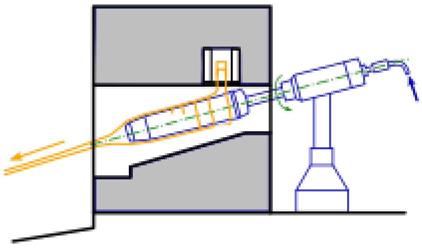


Figure 3 Narrow Neck Press and Blow Process [2]

Singhtaun, C., & Nutchaphan, T. (2019). An Application of Production Scheduling Problems with Sequence-Dependent Setup Time in a Glass Bottle Forming Process. Proceedings of the 2019 International Conference on Management Science and Industrial Engineering - MSIE 2019.

Light Bulbs: Machine blowing of light bulbs utilizes air pressure to shape thin bulbs swiftly. In this process, molten glass flows through an opening in the furnace and between water-cooled rollers, forming swellings on a glass ribbon. Subsequently, air nozzles eject puffs of air onto the ribbon, shaping preliminary blobs that are then formed into bulbs using rotating molds. These automated machines boast speeds of up to 700 bulbs per minute.

Glass Tubing: Glass tubing production predominantly relies on machine processes such as the Danner or Vello methods. In the Danner process, molten glass flows into a constant-level trough before being drawn off as tubes or rods using a rotating mandrel. Conversely, the Vello process involves vertical dropping of molten glass through an annular space surrounding a rotating rod or blowpipe, maintaining air pressure to produce tubing of desired dimensions.



Machine (Danner) for automatically and continuously drawing glass tubing or rods. source

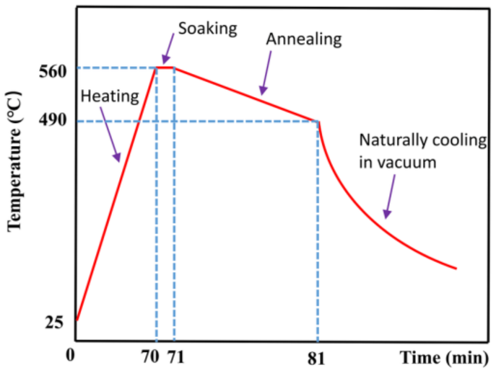
Hand-Molded Glass Items: Certain glass items, like tower plates and bubble caps, continue to be hand-molded. In this process, glass is drawn from pots or tanks and shaped manually or with hydraulic pressure. Despite advancements in automation, hand-molding remains essential for crafting specialized glass products. The manual process allows for intricate designs and customization, catering to specific needs in various industries.

Annealing

- Annealing is essential for reducing strains in glass objects, regardless of whether they are formed by machine or hand molding methods.
- Annealing involves two main operations:

  1. Holding the glass above a critical temperature to reduce internal strain through plastic flow.
  2. Slowly cooling the glass to room temperature to maintain strains below a predetermined maximum.

- A lehr or annealing oven is used for this purpose, providing a carefully controlled heated chamber where the cooling rate can be managed to meet specific requirements.
- Quantitative relationships between stress and birefringence caused by stress have enabled glass technologists to design glass to withstand mechanical and thermal stress conditions.
- Engineers have developed continuous annealing equipment with automatic temperature regulation and controlled circulation, enabling better annealing at lower fuel costs and minimizing product loss.



Annealing temperature graph.

Li, Lihua & Yang, Gao & W.B., Lee & Ng, Man & Chan, Kin. (2019). Carbide-bonded graphene-based Joule heating for embossing fine microstructures on optical glass. Applied Surface Science. 500. 144004. 10.1016/j.apsusc.2019.144004.

Finishing

Every form of annealed glass requires specific finishing procedures, which, although straightforward, carry significant importance. These procedures encompass cleaning, grinding, polishing, cutting, sandblasting, enamelling, grading, and gaging. While not all these processes are mandatory for every glass item, at least one or more are typically essential.

Manufacture of Special Glasses

Optical Glass

1. Optical glass is distinguished by its high homogeneity and specific composition, tailored for precise optical characteristics required in scientific instruments.
2. Stringent requirements include low viscosity, resistance to devitrification, minimal coloration without decolorizing agents, absence of bubbles and striae, favourable properties for grinding and polishing, and durability under various climatic conditions.
3. Melting pots for optical glass are made from high-purity clays and sometimes platinum. Raw materials are meticulously selected and compounded for purity and composition.
4. The melting process involves gradual heating of pots to high temperatures before charging the batch and cullet. Stirring is

performed with a clay tube until the glass reaches the desired viscosity.

5. After melting, the glass is slowly cooled to break into large chunks, which are then inspected and prepared for molding into blanks.
6. Blanks undergo inspection using liquid immersion to reveal subsurface imperfections before annealing and final inspection.
7. New developments include reusable platinum pots, resulting in higher-quality optical glass, and the use of small platinum-lined tank furnaces for continuous melting.

These processes ensure the production of high-quality optical glass with precise optical properties suitable for scientific instruments.

Safety Glass

1. **Laminated Safety Glass:**

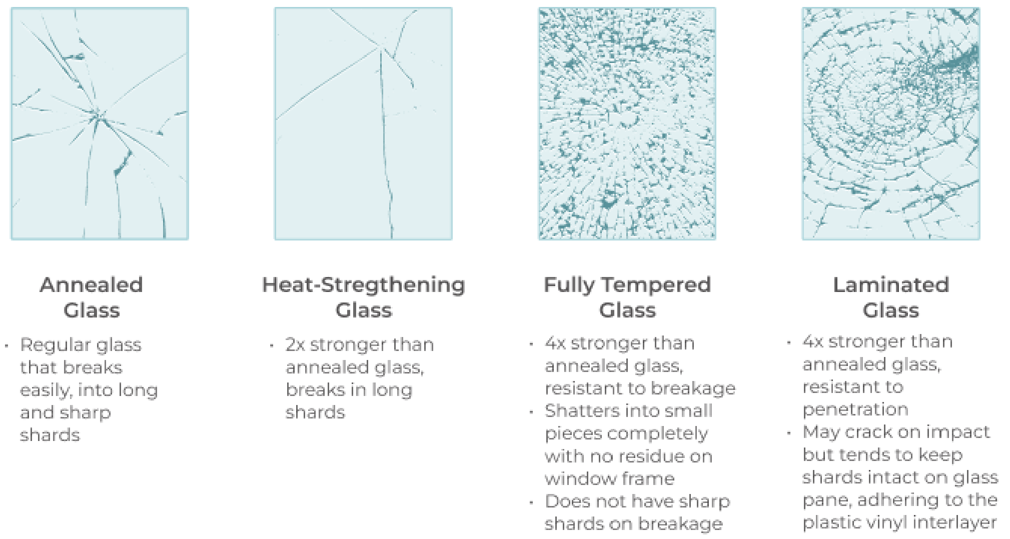
   - Consists of two thin sheets of plate glass separated by a layer of nonbrittle plastic material.
   - Manufacturing involves washing the glass and plastic, applying adhesive (if needed), pressing them together under heat, and subjecting to high temperatures and pressure in an autoclave.
   - Typically uses polyvinyl butyral resin as the plastic interlayer, which holds the glass fragments upon breakage.
   - Polyvinyl butyral resin offers elasticity, clarity, colourlessness, resistance to sunlight, and does not require additional adhesives or water-resistant compounds.

2. **Tempered Safety Glass:**

   - Comprises a single sheet of glass heat-treated to induce compression on the outer surface upon cooling.
   - Resistant to bending forces but weaker against high-velocity impacts, causing the glass to shatter into small, safer pieces upon breakage.

3. **Structural Wire Glass:**

- Used primarily as a fire retardant.
- Manufactured by placing steel wire netting on soft lime glass fresh from the furnace and passing between rolls.
- The continuous operation results in wire-reinforced glass, with the glass being shaped by bending the wire.



source

High-silica Glass

1. **Composition and Properties:**

- The product aims to approach fused silica in composition and properties.
- Contains approximately 96% silica, 3% boric oxide, and the remaining alumina and alkali.
- Utilizes borosilicate glass compositions with around 75% silica content in the initial stages.

2. **Process Overview:**

    - Glasses are melted and molded using borosilicate glass compositions.
    - After cooling, heat treatment is applied, causing the glass to separate into two distinct physical phases.
    - One phase, high in boric and alkaline oxides, is soluble in hot acid solutions, while the other, rich in silica, is insoluble.
    - The glass articles are then immersed in a 10% hydrochloric acid bath to leach out the soluble phase.
    - Thorough washing removes traces of the soluble phase and impurities.
    - Subsequent heat treatment dehydrates the body and converts the cellular structure to a nonporous vitreous glass.

3. **Properties and Characteristics:**

    - Undergoes a 14% shrinkage in linear dimensions during the processes.
    - Exhibits high durability, being able to withstand heating to a cherry red and rapid cooling without damage.
    - Demonstrates excellent chemical stability, resisting most acids except hydrofluoric acid, which attacks it more slowly than other glasses.

Chemical Engineering Applications

1. **Forms of Use:**

    - Bulk: Used in large equipment pieces like pipes, towers, and pumps.
    - Coating: Applied over steel and cast iron in tanks, reactors, and pipes.
    - Fibers: Employed in insulation, fabrics, tower packings, and plastic laminates.

2. **Preferred Types:**

- Borosilicate glass, high-silica glass, and pure fused silica are primarily used in process industries.
- These materials offer improved chemical resistance and mechanical properties due to advancements in glass formulas.

TABLE 3. COMPARATIVE PROPERTIES OF GLASSES[a]

	Common lime	Pyrex No. 774	96 per cent silica No. 790	Fused quartz
Softening point, °C.....	696	819	1442	1667
Annealing point, °C....	510	553	931	1140
Strain point, °C........	475	510	857	1070
Maximum temperature for use (for limited periods), °C..........	....	500–550	1000–1090	1400
Specific gravity.......	2.47	2.23	2.18	2.01
Coefficient of linear expansion (per °C.)...	92×10^{-7}	$32\text{–}33 \times 10^{-7}$	$7.8\text{–}8 \times 10^{-7}$	$5.5\text{–}5.95 \times 10^{-7}$

[a] BLAU, Chemical Trends, *Ind. Eng. Chem.*, **32**, 1419 (1940); *cf.* PERRY, *op. cit.*, p. 1548. The coefficient of linear expansion in the change in length (centimeters) per unit of length (centimeters) per centigrade degree change in temperature.

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Rock or Mineral Wool

1. **Production Process:**

- Mineral wool is produced through the melting of suitable rock or furnace slag.
- The preferred composition of wool rock includes silica, alumina, lime, and magnesia in specific ratios to facilitate fiber formation.
- The rock is melted in a cupola at around 3000°F and blown into fibers using steam at high pressure.
- Centrifugal action from a rapidly revolving disk aids in creating fine fibers.

2. **Properties and Uses:**

- Mineral wools, including rock wool and slag wool, offer excellent heat and sound insulation properties.
- They have a low coefficient of heat transfer, do not attract moisture, and are fireproof and vermin proof.
- Mineral wools are used in loose form or shaped into blankets for insulating homes, railroad cars, and refrigerators.
- They are relatively inexpensive and can be fabricated wherever suitable rock is available.
- Around 100,000 tons of rock wool are manufactured annually, along with additional quantities of slag and glass wool.
- Mineral wool usage is increasing in chemical construction, particularly in outdoor plants.

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