

# GLASS INDUSTRY

## Definition

Glass is a hard material that is usually transparent made by cooling certain molten materials in such a way that they do not crystallize but remain in amorphous state. Glass is considered to be a super cooled liquid, i.e. the solid in which the molecules are present as aggregates as in liquid, and are not present in any definite pattern. Glass is completely a vitrified product which has no definite composition. The major ingredients form over 90% of all types of glasses is *Lime* ( $\text{CaCO}_3$ ), *Sand* ( $\text{SiO}_2$ ) and *soda ash* ( $\text{Na}_2\text{CO}_3$ ). The raw materials used in the manufacture of glass can be broadly divided into the following categories:

1. Acidic oxides
2. Basic oxides
3. Cullets
4. Coloring matter

## 1. ACIDIC OXIDES

A large variety of acidic oxides can be used. The choice depends upon the quality of glass to be made. The various acidic oxides that can be used are as follows:

- **Sand ( $\text{SiO}_2$ ).** It forms silicates on fusion with the other ingredients. The sand used in glass manufacture should be pure and free from iron as it imparts color to the glass. The sand is washed before its use in order to make it free from impurities. The sand used should not be too fine as it makes the reaction violent. It should not be too coarse either because it makes the reaction slow.
- **Borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ).** It is a minor ingredient which supplies  $\text{B}_2\text{O}_3$ . Besides its high fluxing power, borax lowers the coefficient of expansion of glass and adds to its chemical durability.
- **Phosphorus(V) Oxide,  $\text{P}_2\text{O}_5$ .** It is used as  $\text{Na}_2\text{HPO}_4$  or  $\text{Ca}_3(\text{PO}_4)_2$  and is added in tableware glass for imparting bright appearance.
- **Arsenious oxide,  $\text{As}_2\text{O}_3$ .** It is generally used to remove air bubbles from the glass.

## 2. BASIC OXIDES

Some of the basic oxides used are as follows:

**Limestone (CaCO<sub>3</sub>).** It provides CaO. Sometimes burnt dolomite containing CaO and MgO is employed as a substitute of lime.

- **Feldspar.** It is a naturally occurring mineral with a formula Na<sub>2</sub>O. Al<sub>2</sub>O<sub>3</sub>. 6SiO<sub>2</sub>(soda feldspar) or K<sub>2</sub>O.Al<sub>2</sub>O<sub>3</sub>.6SiO<sub>2</sub> (Potash feldspar). It is cheap, pure and easily fusible. Feldspar is used as a flux, *i.e.*, to lower the melting point, and to retard denitrification of glass.
- **Lead oxide.** Litharge (PbO) or red lead (Pb<sub>3</sub>O<sub>4</sub>) is used for the production of heavy and high quality flint glass, which is used in optical instruments, tableware and decorative articles.

### 3. CULLET

It is the crushed glass from imperfect or defective articles or their trimmings. It makes the melting easy and also utilization of waste.

### 4. COLOURING MATTER

Coloured glasses are obtained by adding certain metallic oxide or salts in the fused mass. Various coloring agents and the corresponding shades are grouped as follows:

**Red:** CdO (1.4%), Se (1 %)

**Ruby red:** (i) Colloidal gold or ruby gold, (ii) Cu<sub>2</sub>O

**Light yellow:** Cerium oxide (2%), Titanium oxide (TiO<sub>2</sub>)

**Deep blue:** Cobalt oxide (CoO) (0.1%)

**Greenish blue:** Copper (II) oxide, CuO

**Emerald green:** Cr<sub>2</sub>O<sub>3</sub> (0.15%), CoO (0.001%)

**Amber:** FeS (0.3%)

**Black:** MnO<sub>2</sub> + Fe<sub>2</sub>O<sub>3</sub>

**Yellow:** CdS

## Types of Glass

Glass is classified in a number of ways on the basis of its chemical composition, properties, manufacturing process or its use. Some important types of glass are as follows.

### 1. Soft Glass or Soda -Lime Glass

Soft glass or Soda glass also known as window glass, is an ordinary glass which is a mixture of sodium silicate and sodium calcium silicate. It mainly consists of 71%-75% (SiO<sub>2</sub>), 12%-16% (Na<sub>2</sub>O), 10%-15% (CaO)

*Use:* Bottles, Jars, Drinking Glasses and Window Glass.

## **2. Refractory Potassium Glass**

It is a mixture of potassium silicate and calcium silicate. It has high refractive index. 54%-65% ( $\text{SiO}_2$ ), 13%-15% ( $\text{Na}_2\text{O}$ ). This glass is used for and decorative glass wear.

*Use:* Drinking Glasses, Vases, Bowls, making prism, lenses and Decorative Items

## **3. Borosilicate Glass**

The main constituents of Pyrex Glass are boroxide 7%-13% ( $\text{B}_2\text{O}_3$ ) and silica 70%-80% ( $\text{SiO}_2$ ). , 4%-8% Sodium oxide ( $\text{Na}_2\text{O}$ ) 2%-7% ( $\text{Al}_2\text{O}_3$ ). This glass has no chemical durability and is soluble even in water.

*Use:* Cooking Wear, Headlamps, Laboratory Glass (Pyrex)

## **4. Water Glass**

Water glass is just a sodium silicate, which is prepared by the reaction of sodium oxide ( $\text{Na}_2\text{O}$ ) and silica ( $\text{SiO}_2$ ). This glass has no chemical durability and is soluble even in water.

## **5. Colored Glass**

Colored glass is prepared by adding certain transition metal oxides. For example copper oxide ( $\text{CuO}$ ) gives light blue coloured glass, where as cobalt oxide ( $\text{CoO}$ ) gives dark blue color, chromium oxide ( $\text{Cr}_2\text{O}_3$ ) gives green colour and zinc oxide ( $\text{ZnO}$ ) give red colored glass.

## **6. Photochromic Glass or Photosensitive Glass**

Photochromic glass produces darkness on exposure to bright sunlight but becomes clear again in absence of light. This glass contains silver chloride or silver bromide salts which is sensitive to light, in presence of light, the salt is decomposed to give finely divided black silver, in absence of sunlight, silver and chloride recombine to reform  $\text{AgCl}$ . This glass is used in sunglasses.

## **7. Optical Fibers**

Optical fibers are thin fibers of silica glass of high purity. They have excellent optical transparency. This glass is used to transmit T.V Programs, Telephone conversion, Computer output etc. It is also used to make a design on glass. This process is called Etching.

# Preparation of Glass

## Glass melting

Glass can be made by variety of methods, but in most cases, it is produced by melting raw materials at an elevated temperature. This process involves raw materials selection, weighing, mixing of components in appropriate proportion and removal of impurities to get a homogeneous melt. Large scale commercial melting takes place in refractory tanks which are further connected to series of glass forming machines. The melting of batch components takes place in furnaces. The selection of furnace depends upon the quantity and type of glass being produced. Most of the furnaces are made up of refractory blocks which can work at temperatures more than 1500°C.

The different types of furnaces commonly used are *unit melter*, *recuperative melter*, *electric melter* and *regenerative furnace*. The batch materials to manufacture glass can be divided into following five categories according to their role in the process: glass former, flux, modifier, colorant and fining agent. Glass formers are one of the most important components present in any glass. Silica ( $\text{SiO}_2$ ), boric oxide ( $\text{B}_2\text{O}_3$ ) and phosphoric oxide ( $\text{P}_2\text{O}_5$ ) are the most common type of glass formers present in oxide glass. The use of silica glass is wide but melting temperature of silica is too high (1600-1725°C). To reduce the processing temperature of silica, different types of flux such as  $\text{Na}_2\text{O}$  and  $\text{PbO}$  can be used. The addition of fluxes to silica reduces the overall cost of glass processing but results in degradation of properties. To overcome this problem, different property modifiers or intermediates such as boron, sodium, magnesium, titanium, and calcium can be used to modify the properties of glass. Colorants are used to control the color in the final glass. The amount of iron oxides (impurities) present in the glass results in unintentional change in color of glass. The other types of colorants used are gold and silver.

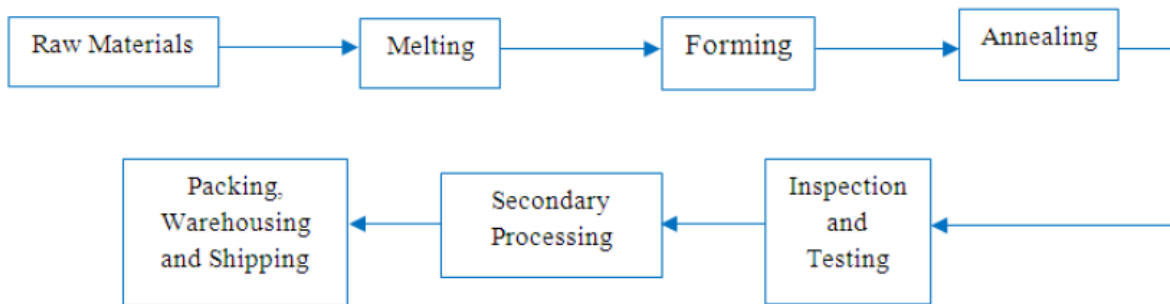
These types of colorants change glass color by forming colloids in glasses. Finally, fining agents such as arsenic, antimony oxides, potassium and sodium nitrates are added to raw materials to remove bubbles from the melt. As the raw materials melt and react inside the furnace, carbon dioxide and water emission takes place which causes formation of bubbles. The high temperature and low viscosity is maintained to raise the gas bubbles at the upper surface of the melt and hence removed from the melt. Fining is important because it controls the

homogeneity of glass by eliminating bubbles. Batch particles size and their mixing in proper proportion are other factors that provide homogeneity in glass structure.

Nowadays, large scale production of glass industries uses computers to control mixing of different constituents and feeding of mixture into the furnace. In recent years, oxygen is typically used in glass making to enhance the combustion of glass. The benefits of using oxygen are improved furnace effectiveness, reduced pollution, good quality glass and longer furnace life.

### **Glass forming**

Glass forming is an intermediate stage in glass manufacturing process. It comes in between glass melting and annealing. Manufacturing of almost all commercial glass comprises of different stages. The stages of glass manufacturing are illustrated in Figure 1.



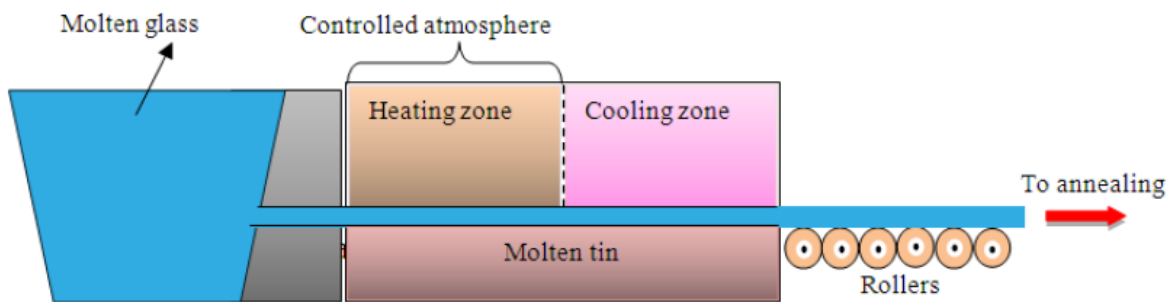
**Figure 1.** Schematic of typical glass manufacturing process.

In forming stage of glass manufacturing, viscosity of molten glass changes gradually with temperature. Glass forming permits molten glass to be shaped into flat sheets and filaments by controlling the viscosity. For example, viscosity of the glass must increase slowly as the temperature drops to produce full lead crystal and the viscosity of the glass must increase rapidly as the temperature drops to manufacture glass fiber. Depending upon the applications, there are different processes of forming the glass. The most common type of glass forming process can be categorized as:

### **Flat glass**

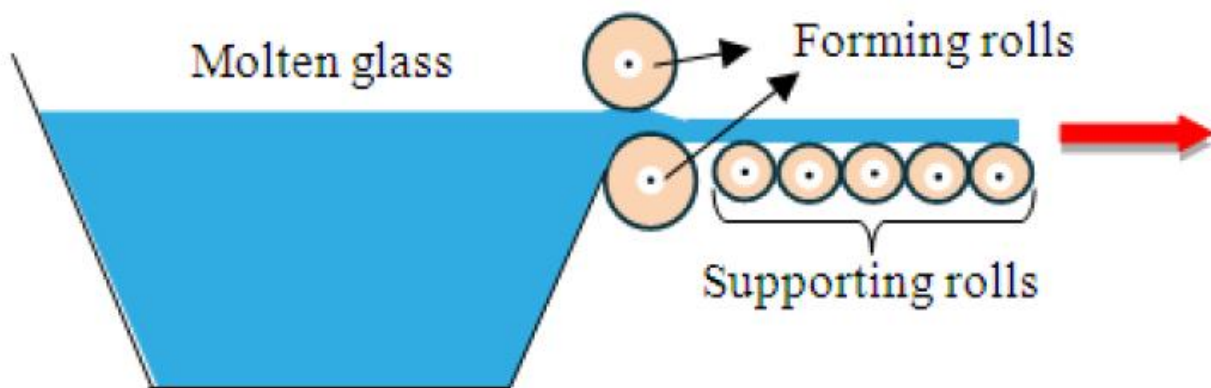
Flat glass, sheet glass, or plate glass is made by two processes. The processes are float glass process and rolled glass process. Both of these processes are continuous method. Thickness of the glass plate formed by these processes ranges from 0.8 to 10 mm. In float glass process

(Figure 2), a ribbon of glass is made by pouring molten glass from the furnace to a bed of molten metal such as tin, lead and low melting point alloys under controlled atmosphere. The molten glass floats on a thin bath of molten metal and then moves through the temperature-controlled kiln (also known as Lehr) and solidifies. The temperature of glass is maintained at 1000°C for a long period of time to separate irregularities and to get the desired flat surface. Glass produced by this technique has uniform thickness, smooth surface and does not require any further grinding and polishing.



**Figure 2** Float glass process of forming flat glass.

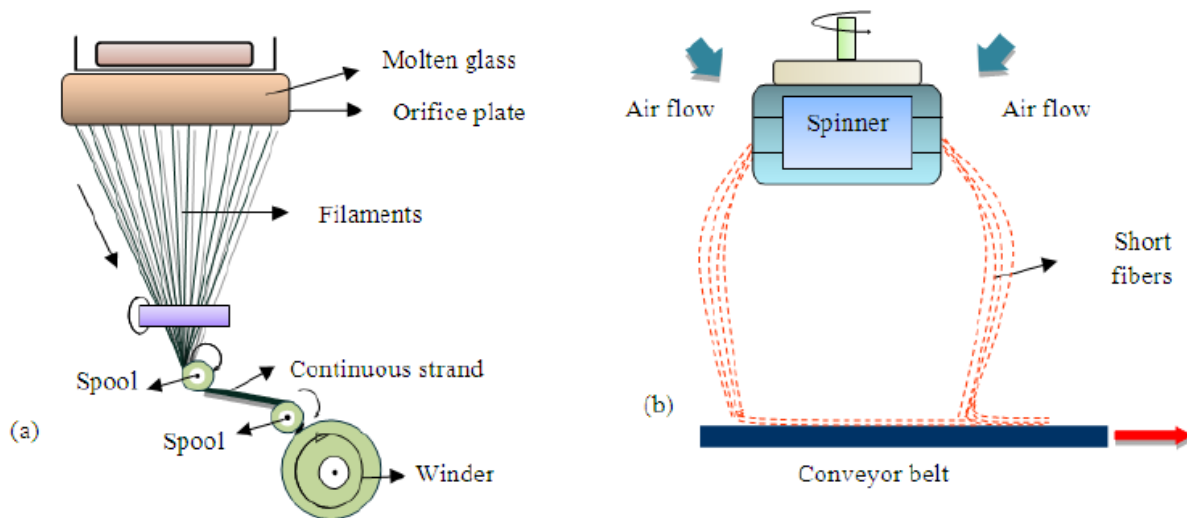
In the drawing or rolling process (Figure 3), the continuous stream of molten glass from a furnace passes through a pair of water cooled rollers. Generally, this process is used to make patterned glass and wired glass. The patterned glass is made by passing the glass through the rollers at a temperature of 1050°C. This type of glass is made in a single pass process. Gap between the rollers are adjusted to get the desired thickness of flat-sheet glass. Similarly, wired glass is made by meshing steel wire into molten glass by rolling process. It is used for making low cost fire resistant glass which automatically breaks at high temperatures.



**Figure 3.** Rolling of flat glass.

## Glass fibers

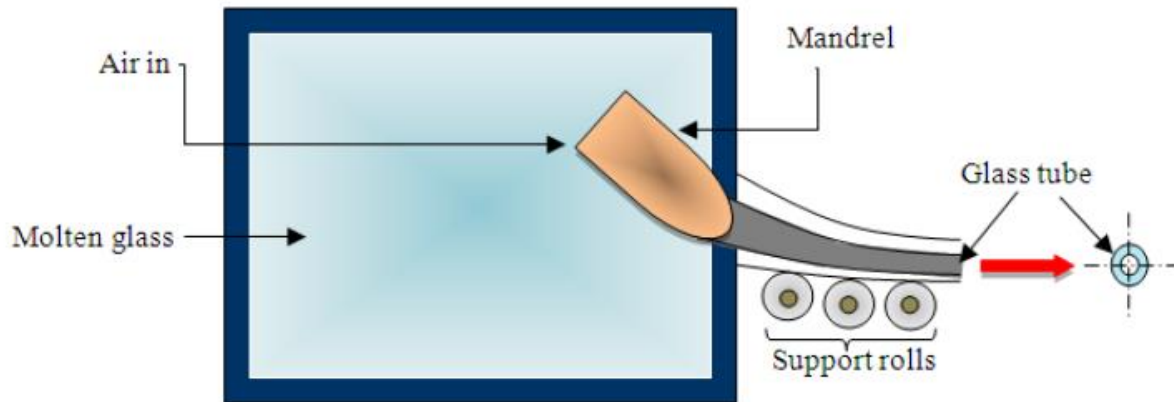
Fiber glass is available in two types: continuous glass fiber and short glass fiber (glass wool). The first one is used in fabrication of composite materials and latter one is used for thermal insulation. Continuous glass fiber is produced by drawing molten glass through multiple orifices. The speed during drawing can be upto 500 m/s. Fibers of small diameter ( $2\mu\text{m}$ ) can be produced by this process. The process is schematically shown in Figure 4 (a). In glass wool process (Figure 4 (b)), the molten glass is ejected from a rotating head by centrifugal spraying process. The rotating head or spinner cup contains more than 2000 holes. Since the holes diameter of spinner is very small, only fine fiber is formed. Air is supplied from the top to direct the fiber downward and to reduce the temperature. As the fibers descend, the binder is mixed to achieve the required wool criteria. The amount of binder decides the mechanical properties of wool. In this process, the diameter of the fiber can be achieved from  $20\text{-}30\mu\text{m}$ .



**Figure 4.** Glass fiber processing: (a) continuous glass filament process; (b) glass wool process.

## Glass tubing

In this process, molten glass flows around a rotating hollow cone-shaped or cylindrical mandrel through which air is supplied continuously to avoid the collapsing of glass tube while the glass is drawn out by set of rollers. The temperature and flow rate of blown air determine the diameter and thickness of the glass tube. The process is shown in Figure 5.



**Figure 5.** Continuous glass tubing process.

### **Toughened or tempered glass**

Glass can fracture due to stress concentration. To avoid the fracture of glass, local high compressive stresses are induced near the surfaces. This is done by thermal toughening of glass.

Initially, the glass plate is heated to 650°C after which the outer surface is rapidly cooled by air blasts. Due to which thin compressive layer is created at the outer surface and the center of the glass becomes the region of tensile stresses. This causes the self-equilibrium. The glasses used in glazed door and making table tops are made by this process and is termed as toughened or safety glass.

### **Laminated glass**

It is made by bonding of two or more pieces of safety glass. The adhesive mostly used for bonding is polyvinyl butyral (PVB). Depending upon the number of safety glass layers, the strength of the glass may be increased or decreased. Nowadays, laminated glass is produced by bonding number of annealed glass layers with plastic interlayers. This type of glass is used in automobile windshields where strength is one of the key issues.

### **Properties of glass**

Following are the properties exhibited by glass.

1. Capacity to absorb different colors without effecting transparency.
2. Hardness.
3. Chemically inert.
4. High refractive index
5. Amorphous
6. Brittleness
7. Transparency and translucence
8. Dispersion.
9. Vitrification.
10. Electrical insulators