# Glass packaging materials

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# INTRODUCTION

- Glass has been defined by **ASTM** (American Society for Testing and Materials) as **"an amorphous, inorganic product of fusion that has been cooled to a rigid condition without crystallizing."**

- Although glass is often regarded as a **synthetic material**, it was formed naturally from **common elements in the earth's crust** long before the world was inhabited.

- Glass exists in a vitreous or glassy state in which molecular units have a disordered arrangement but sufficient cohesion to produce mechanical rigidity.

- Although glass has many of the properties of a solid, it is **really a highly viscous liquid**. During cooling, glass undergoes a reversible change in viscosity, the **final viscosity being so high as to make the glass rigid** for all practical purposes.

# HISTORY

- The first glass vessels were probably sculpted from solid blocks about 3000 BCE.

- In about 1000 BCE, the **techniques of pouring molten glass** were developed, resulting in the formation of crude but useful glass objects.

- The **real revolution in glassmaking** came around 200 BCE with the introduction of the blowing iron.

- Blowing through one end of the iron causes the viscous liquid to balloon at the other end, leading to the production of hollow glass objects.

- By 200 CE, articles of glass were in fairly common use in households.

- However, **glass remained expensive** until improved techniques in the **eighteenth and nineteenth centuries** brought down the price of bottles and jars to a relatively affordable level.

# New developments

- **Mechanization of glass container manufacture** was introduced on a large scale in **1892**, and several important developments occurred over the next few decades.

- These included the **first fully automated machine for making bottles** built in **1903** by Michael J. Owens at the Toledo, Ohio.

- **Automatic production processes** in **1923** with the development of the **gob** (mass or lump of molten glass) feeder, which ensured the rapid supply of more consistently sized gobs in bottle production.

- Soon afterward, in **1925**, the **Hartford Empire Company** developed its IS (inventors- Ingersall and Smith) blow and blow (B&B) machine.

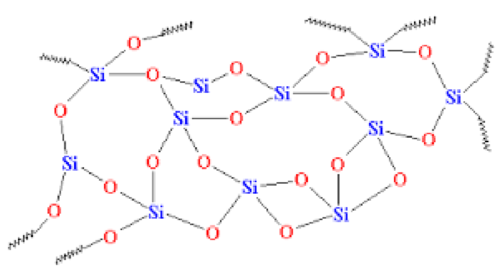
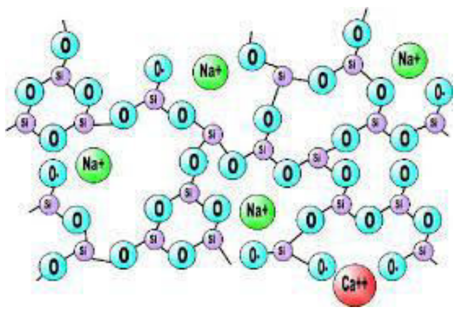
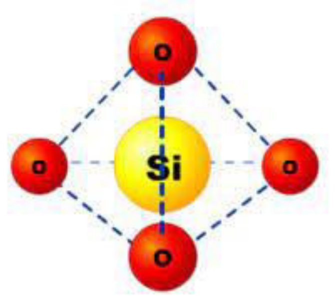
- Used in **conjunction with the gob feeders, IS (individual section) machines** allowed the simultaneous production of a number of bottles from one piece of equipment.

- Further developments have occurred, resulting in the production of a wide range of glass containers for packaging.

- The **two main types** of glass container used in food packaging are **bottles** (which have narrow necks) and **jars** (which have wide openings).

# COMPOSITION AND STRUCTURE

- The principal ingredient of glass is **silica** derived from sand, flint or quartz.
- Silica can be melted at very high temperatures (1723°C) to form fused silica glass.
- For most glass, **silica is combined with other raw materials** in various proportions.
- **Alkali fluxes** (commonly sodium and potassium carbonates) **lower the fusion temperature and viscosity** of silica.
- **Calcium and magnesium carbonates** (limestone and dolomite) act as **stabilizers**, preventing the glass from dissolving in water.

Other ingredients are added to give glass certain physical properties. For example-

- **Lead gives clarity and brilliance** although at the expense of softness of the glass.

- **Alumina increases hardness and durability.**

- The addition of about **6% boron to form a borosilicate glass reduces the leaching of sodium** (which is loosely combined with the silicon) from glass.

As a **consequence of the sodium** in glass being loosely combined in the silica matrix, the glass surface is subject to three forms of **“corrosion”:**

- **Etching** is characterized by alkaline attack, which slowly destroys the silica network, releasing other glass components.

- **Leaching** is characterized by acid attack in which hydrogen ions exchange for alkali or other positively charged mobile ions. The remaining glass (principally silica) usually retains its normal integrity.

- **Weathering** is **not a problem in commercial glass** packaging applications since it may take centuries to become apparent.

# Composition

**Typical Formula for a 1 Tonne Batch of Soda-Lime Container Glass**

| Material | Weight (kg) | Oxides Supplied (kg) $SiO_2$ | $Al_2O_3$ | $CaO$ | $Na_2O$ | $FeO$ | LOI[a] (kg) |
|---|---|---|---|---|---|---|---|
| Sand $SiO_2$ | 300 | 299.3 | 0.2 | | | 0.3 | 0.5 |
| Soda ash $Na_2CO_3$ | 100 | | | | 58.3 | | 41.7 |
| Aragonite $CaCO_3$ | 90 | | | 49.0 | | 0.02 | 40.7 |
| Feldspar ($SiO_2 \cdot Al_2O_3$) | 40 | 26.4 | 7.6 | 0.4 | 1.3 | 0.03 | 0.1 |
| Salt cake NaCl | 4 | | | | 2.1 | | 1.9 |
| Cullet | 460 | 333.7 | 9.2 | 48.8 | 67.2 | 1.03 | 0.1 |
| Total | 994 | 659.4 | 17.0 | 98.2 | 128.9 | 1.95 | 85.0 |
| Yield of glass | 909 | | | | | | |
| Wt% oxides | | 72.6 | 1.9 | 10.8 | 14.2 | 0.1 | |

*Source:* Adapted from Boyd, D.C. et al., Glass, in: *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edn., Kroschwitz, J. (Ed.), Vol. 12, John Wiley & Sons, New York, pp. 555–628, 1994.

[a] Loss on ignition (also referred to as fusion loss).

- A typical formula for soda-lime glass is given in Table. In practice, however, the quantities vary slightly; for example,

  silica ($SiO_2$) 68%-73%,
  calcia (CaO) 10%-13%,
  soda ($Na_2O$) 12%-15%,
  alumina ($Al_2O_3$) 1.5%-2% and
  iron oxides (FeO) 0.05%-0.25%

depending on the glassmaker and the raw materials being used.

- The **loss on ignition or fusion loss** (generally the oxides of carbon and sulfur) can vary from 7% to 15%, depending on the quantity of cullet (i.e., scrap or recycled glass) used.

- The greater the quantity of cullet there being less fusion loss .

# PHYSICAL PROPERTIES

## MECHANICAL PROPERTIES

The mechanical strength of a glass container is a **measure of its ability to resist breaking** when forces or impacts are applied. Glass deforms elastically until it breaks in direct proportion to the applied stress.

Because of its **amorphous structure, glass is brittle** and usually breaks because of an applied **tensile stress**. It is now generally accepted that **fracture of glass originates at small imperfections or flaws**.

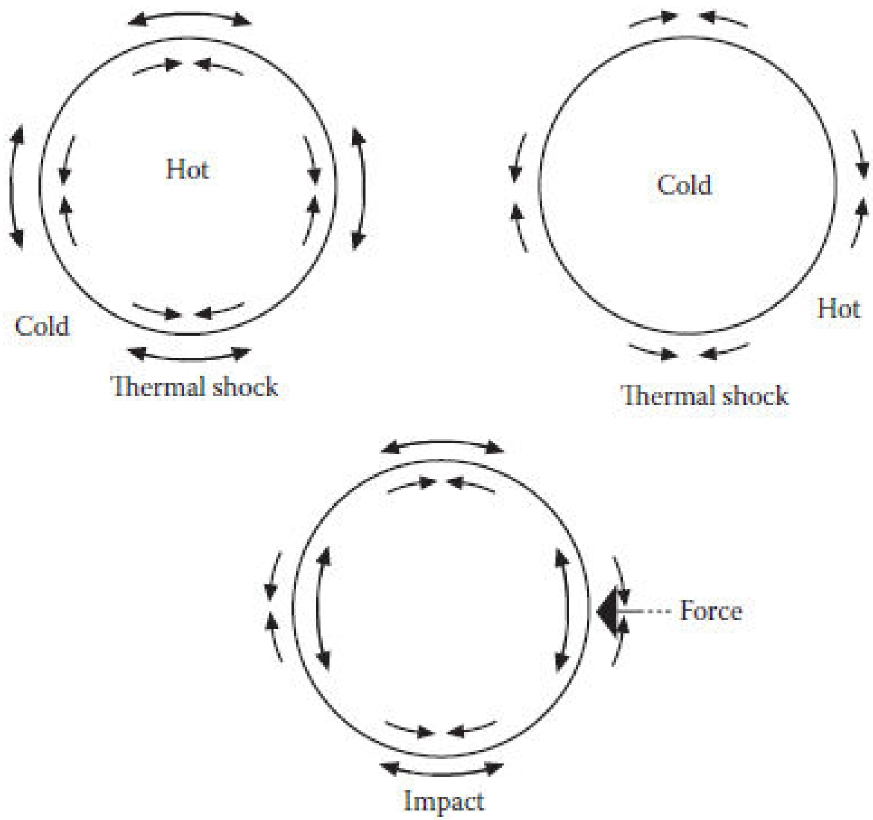
These small imperfections or flaws cause a **concentration of stress** that may be many times greater than the nominal stress at the section containing them.

Thus, it is the ultimate tensile strength of a glass surface which determines when a container will break. The fracture formula is

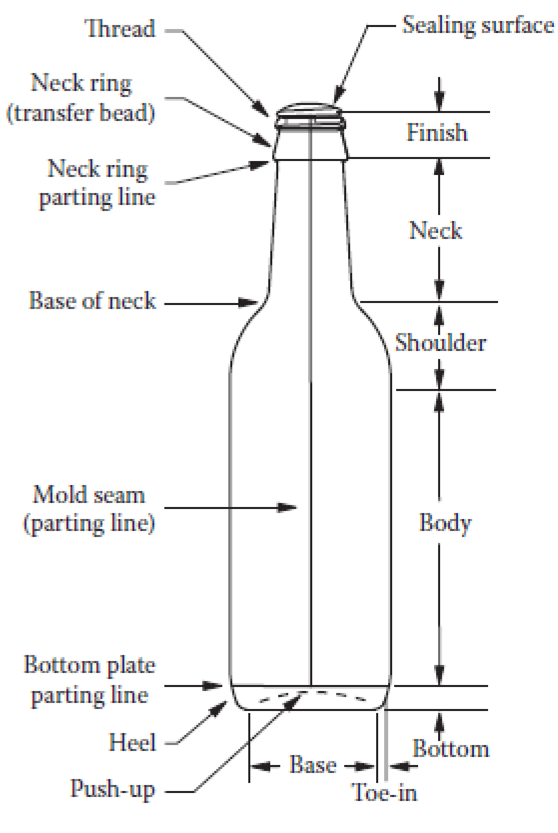
Tensile Stress + Stress Concentrator = Fracture

**The principles of fracture analysis** or diagnosis of the cause(s) of glass container breakage have been described by **Moody (1977)**. The following four aspects are important:

**1. Internal pressure resistance:**
This is important for **bottles produced for carbonated beverages**, and when the glass container is likely to be processed in boiling water or in pressurized hot water. Internal pressure produces bending stresses at various points on the outer surface of the container.



**2. Vertical load strength:** While glass can resist severe compression, the **design of the shoulder is important** in minimizing breakage during high-speed filling and sealing operations.



**3. Resistance to impact:** Two forms of impact are important- a moving container contacting a stationary object (as when a bottle is dropped) and a moving object contacting a stationary bottle (as in a filling line). In the latter situation, **design features are incorporated into the sidewall to strengthen contact points**. A cross section of a round bottle illustrating the ways in which tensile stresses on the inside and outside surfaces vary at various points around the bottle circumference is shown in Figure.

**4. Resistance to scratches and abrasions:** The overall strength of glass can be significantly impaired by surface damage such as scratches and abrasions. This is especially important in the case of reduced wall thickness bottles such as **“one-trip”** bottles.

# THERMAL PROPERTIES

The thermal strength of a glass container is a measure of its ability to **withstand sudden temperature change**. In the food industry, the behavior of glass with respect to temperature is of major significance, glass has the least resistance to temperature changes.

The resistance to thermal failure depends on the

- type of glass employed
- the shape of the container
- the wall thickness

When a glass container is suddenly cooled (e.g., on removal from a hot oven), tensile stresses are set up on the outer surfaces, with compensating compressional stresses on the inner surface.

# OPTICAL PROPERTIES

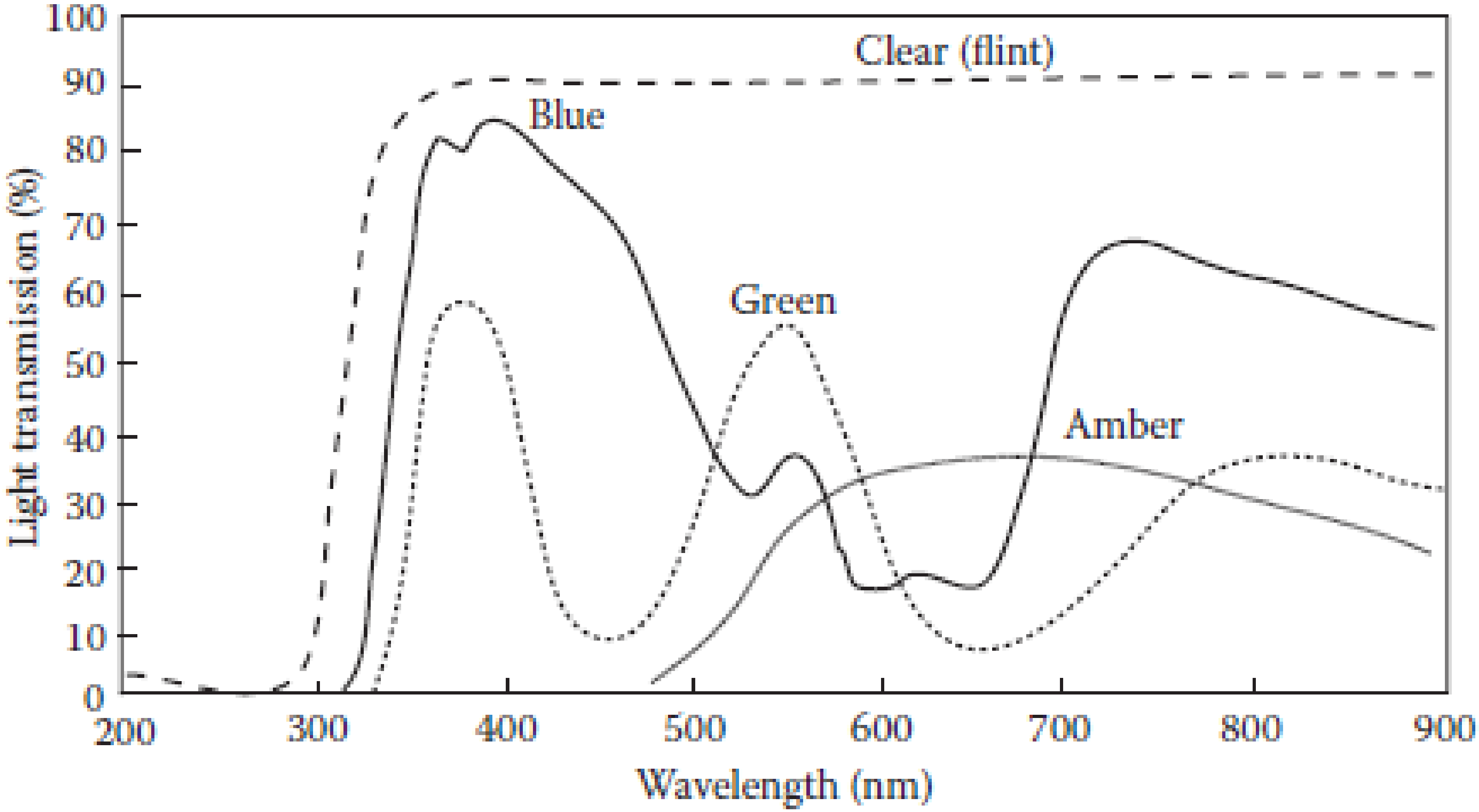
In silicate glasses, transmission is limited by the absorption of silica at approximately **150 nm in the UV** and at **6000 nm in the IR region**.

**Iron impurities** further **reduce transmission** in the UV and near-IR regions.

**Transmission may be controlled by the addition of coloring additives** such as metallic oxides, sulfides or selenides and the compounds that are frequently used are listed in Table.

### Coloring Agents Used in Glass

| Effect | Oxide |
|---|---|
| Colorless, UV absorbing | $CeO_2$, $TiO_2$ |
| Blue | $Co_3O_4$, $Cu_2O + CuO$ |
| Purple | $Mn_2O_3$, $NiO$ |
| Green | $Cr_2O_3$, $Fe_2O_3 + Cr_2O_3 + CuO$, $V_2O_3$ |
| Brown | $MnO$, $MnO + Fe_2O_3$, $TiO_2 + Fe_2O_3$, $MnO + CeO_2$ |
| Amber | $Na_2S$ |
| Yellow | $CdS$, $CeO_2 + TiO_2$ |
| Orange | $CdS + Se$ |
| Red | $CdS + Se$, Au, Cu, $Sb_2S_3$ |
| Black | $Co_3O_4$ (+ Mn, Ni, Fe, Cu, Cr oxides) |




Typical light transmission of common container glasses.

Glasses and other transparent materials **tend to darken and lose much of their ability to transmit light** when bombarded by high energy radiations such as those used in food irradiation.

**There are two principal causes of this coloration of glass.**

**First,** the impact of the **radiations may displace electrons**, which can become lodged in holes in the structure, forming color centers.

**Second**, changes produced in the **valence of bivalent or multivalent metal oxides** may result in the increased absorption of light in the visible range.

This second effect forms the basis of the process to protect glass from this coloration where a **metal oxide is included in the composition of the glass**.

Provided that the oxide is free from serious light absorption bands in both valences, protection from discoloration may be obtained.

The **addition of $CeO_2$** (it is reduced to $Ce_2O_3$ by the radiations) in glasses in amounts up to **1.5%** has proved an effective means of **reducing coloration**. Unfortunately, it is a **very expensive** oxide, so glass containers treated this way are significantly more costly than standard containers.

# MANUFACTURE

## MIXING AND MELTING

The largest constituent **(68%–73%) is silica**; the second largest constituent **(15%–50%) is cullet**, originating both as glass scrap from the factory and recycled glass from consumers (so-called *postconsumer glass).*

The use of **cullet can cause problems with the production of some types of glass** unless there is good separation of colored glass.

In addition to the **problem of color mixing, ceramic and metal contamination** can also limit the use of cullet in glass manufacturing.

However, the use of **cullet is economically desirable** since less energy is required to melt cullet than new raw materials.

Cullet also **reduces the amount of dust and other particulate matter** that often accompanies a batch made exclusively from new raw materials.

**Glass-melting furnace**, which is maintained at a temperature of approximately **1500°C**.

Here, they are converted into molten glass that is **chemically homogeneous** and virtually **free of gaseous inclusions**.

The melting process consists of two phases:
(1) changing the solids into a liquid and
(2) refining or "clearing up" of the liquid.

During the refining process, gases (principally CO2, SO2 and water vapor) produced by the chemical reaction rise to the surface of the furnace and are removed.

When the molten glass **becomes free of gas** (seed-free), it is then **ready for forming into containers**.

At this point, the temperature of the melt has been lowered from 1250°C to 1350°C to approximately 1100°C.

# Energy Source for the furnace

The **preferred energy source** for glassmaking is **natural gas**, although alternate fuels such as oil and propane are used in some plants. With increasingly stringent environmental regulations limiting the emissions of $NO_x$ from glass container furnaces, various systems have been introduced using natural gas and $O_2$ as the furnace fuel.

**Advantage**

When air (78% $N_2$) is subjected to very high temperatures, various oxides of nitrogen are formed. By using natural gas and $O_2$ as the furnace fuel, there is **no $N_2$ to be oxidized**.

In addition, there are **improvements in energy efficiency** since only two volumes of O2 are needed to burn 1 volume of natural gas compared to 10 volumes when air is used.

# FORMING PROCESSES

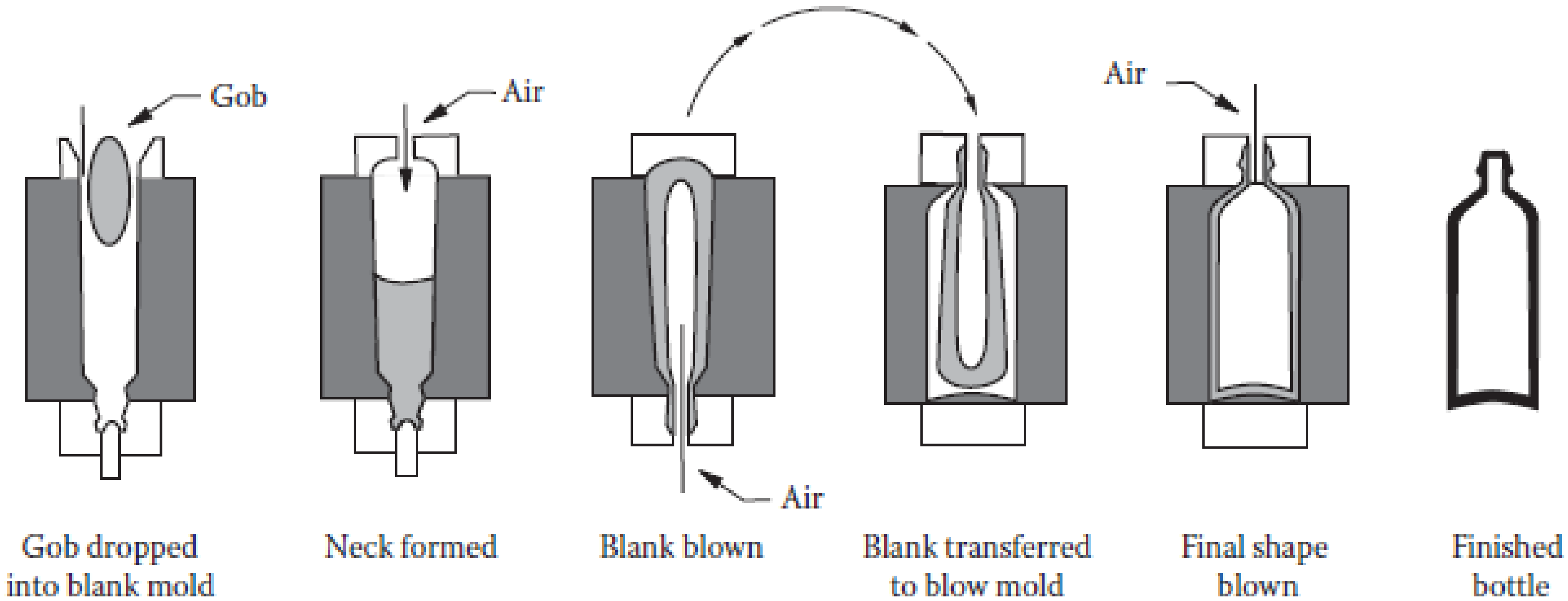
- The glass exits in a continuous, viscous stream which is **cut by rapidly moving, horizontal steel blades** to form what is known as a **"gob"** (i.e., a mass or lump of molten glass).

- Precise **control of temperature and shape during the formation of the gob** is required for the high-speed production of accurately formed glass containers.

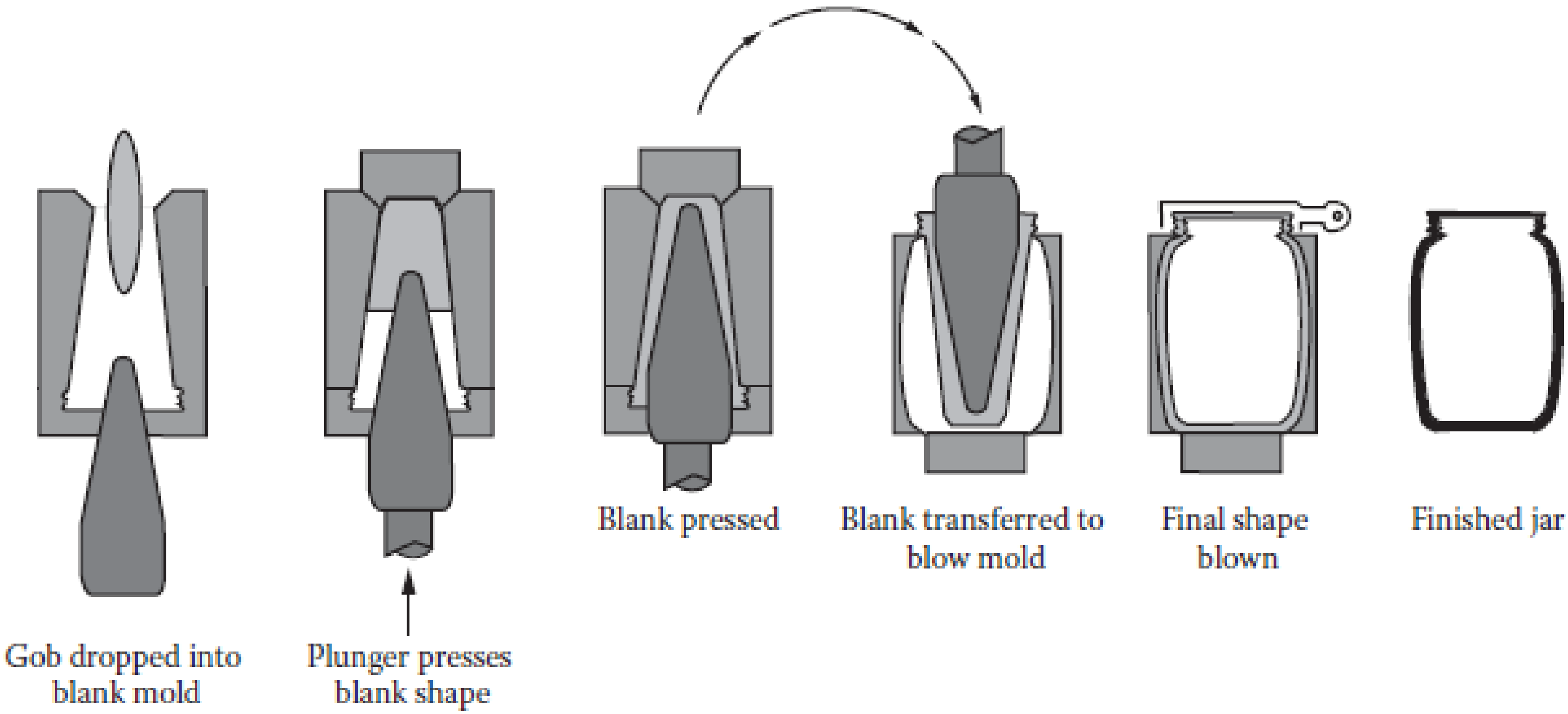
- Temperatures in the vicinity of 1100°C.

- The process of converting a cylindrically shaped gob of glass into a bottle or jar is called **forming** and it is essentially a controlled cooling process.

# Blow and Blow



# Wide Mouth Press and Blow

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