Table 8.2 Chemical Composition of Typical Glasses (in percent)

No.°	SiO_2	B_2O_3	Al_2O_3	Fe_2O_3	As_2O_3	CaO	MgO	Na_2O	K_2O	PbO	ZnO	BaO	Sb_2O_3	LiO_2	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	72.5		1.4			13.3		14.0							
4	73.0		0.8			12.7	0.2	12.7							
5	71.8		1.4	0.1		8.9	3.3	14.3							0.3
6	70.6		0.8	0.1		10.6	0.1	17.0							0.8
7	72.7		0.5	0.1		13.0		13.2					0.2		0.4
8	72.0		2.1			10.2		14.9							0.8
9	72.4		0.8	0.4		5.3	3.7	17.4							
10	66.4	4.0	2.4				5.2	15.6			6.2				
11	81	12.5	2.0					4.5						1.0	
12	72.4		1.0	0.1		8.1	0.2	18.1				0.2			
13	67.2				0.5	0.9		9.5	7.1	14.8					
14	96.3	2.9	0.4												
15	100														
16	55	10	14			13	5	0.5				1			

°Notes: 1, Egyptian, 1500 B.C.; 2, Pompeian window; 3, window, American cylinder, 19th century; 4, window, Machine cylinder, 1920; 5, window, Fourcault, 1929, American; 6, window, Fourcault, European; 7, plate with SbO_2; 8, soda-lime container, American 1949; 9, electric lamp bulb; 10, Jena laboratory, before 1910; 11, Pyrex laboratory; 12, tableware—soda-lime; 13, tableware—lead crystal; 14, 96% silica, Vycor; 15, fused silica; 16, "E" glass for fibers

SOURCES 1 and 2—Blau, Chemical Trends, *Ind. Eng. Chem.* 32 1429 (1940); 3-16—Scholes and Greene, *Modern Glass Practice*, Cahners, Boston, Mass., 1975

which impart high thermal resistance and permit it to be used beyond the temperature ranges of other glasses. This glass is also extraordinarily transparent to ultraviolet radiation.

2. *Alkali silicates.* Alkali silicates are the only two-component glasses of commercial importance. Sand and soda ash are simply melted together, and the products designated sodium silicates,[3] having a range of composition from $Na_2O \cdot SiO_2$ to $Na_2O \cdot 4SiO_2$. A knowledge of the equilibrium relations[4] in these two-component systems has aided the glass technologist in understanding the behavior of more complicated systems. Silicate of soda solution, also known as *water (soluble) glass*, is widely consumed as an adhesive for paper in the manufacture of corrugated-paper boxes. Other uses include fireproofing. The higher-alkaline varieties are used for laundering as detergents and as soap builders.

3. *Soda-lime glass.* Soda-lime glass constitutes 95 percent of all glass manufactured. It is used for containers of all kinds, flat glass, automobile and other windows, tumblers, and tableware. There has been a general improvement in the physical quality of all flat glass, such as increased flatness and freedom from waves and strains, but the chemical composition has not varied greatly. The composition as a rule lies between the following limits (Table 8.2): (1) SiO_2, 70 to 74%; (2) CaO, 8 to 13%; (3) Na_2O, 13 to 18%. Products of these ratios melt at relatively low temperatures. They are sufficiently viscous that they do not devitrify and yet are not too viscous to be workable at reasonable temperatures. The great improvement has been in the substitution of instrument-controlled mechanical devices for the hand operator. Similarly, in container glass, the progress has been largely of a mechanical nature. However, the influence of the liquor trade has created a tendency among manufacturers to make glassware particularly high in alumina and lime and low in alkali. This type of glass melts with more difficulty but is more chemically resistant. The color of container glass is much better than formerly because of the improved selection and purification of raw materials and the use of selenium as a decolorizer.

Applications of phase-rule[5] studies have explained many of the earlier empirical observations of the glassmaker, have led to some improvements (such as more exactness in the manufacture of soda-lime glass), and have laid the basis for new glass formulations. The phase diagrams for many systems are known and have been published, and the system Na_2O–CaO–SiO_2 has been particularly detailed.

4. *Lead glass.* By substituting lead oxide for calcium oxide in the glass melt, lead glass is obtained (see No. 13 in Table 8.2). These glasses are of very great importance in optical work because of their high index of refraction and dispersion. Lead contents as high as 92% (density 8.0, refractive index 2.2) have been made. The brilliance of good "cut glass" is due to its lead-bearing composition. Large quantities are used also for the construction of electric light bulbs, neon-sign tubing, and radiotrons because of the high electrical resistance of this glass. It is also suitable for shielding from nuclear radiation.

5. *Borosilicate glass.* Borosilicate glass usually contains about 10 to 20% B_2O_3, 80 to 87% silica, and less than 10% Na_2O. This type of glass has a low expansion coefficient, superior resistance to shock, excellent chemical stability, and high electrical resistance. The laboratory glassware made from this glass is sold under the tradename Pyrex. In recent years, however, the name Pyrex has been applied to many glass objects made from other compositions, such

[3]See Chap. 12 for fuller descriptions.

[4]Morey, *The Properties of Glass*, 2d ed., Reinhold, New York, 1954.

[5]Morey, *Data of Geochemistry*, Geological Survey Paper 440L, U.S. Govt. Printing Office, 1964; Shahid and Glasser, Phase Equilibrium in the System Na_2O-CaO-SiO_2, *Phys. Chem. Glasses* **12** 50 (1971).

as alumino-silicate glass for top-of-the-stove ware. Uses of borosilicate glasses, in addition to laboratory ware, are high-tension insulators and washers, pipelines, and telescope lenses such as the 500-cm disk at Mt Palomar

6. *Special glasses.* Colored and coated, opal, translucent, safety, optical, photochromic glasses, and glass ceramics are special glass. All of these have varying compositions depending upon the final product desired

7. *Glass fibers.* Glass fibers are produced from special glass compositions that are resistant to weather conditions. The very large surface area of the fibers makes them vulnerable to attack by moisture in the air. This glass is low in silica, about 55%, and low in alkali (see No. 16, Table 8.2).

RAW MATERIALS.[6] In order to produce these various glasses, large tonnages of glass sand are used in the United States each year. Soda ash, salt cake, and limestone or lime are required to flux this silica. In addition, there is heavy consumption of lead oxide, pearl ash (potassium carbonate), saltpeter, borax, boric acid, arsenic trioxide, feldspar, and fluorspar, together with a great variety of metallic oxides, carbonates, and the other salts required for colored glass. In finishing operations, such diverse products as abrasives and hydrofluoric acid are consumed.

Sand for glass manufacture should be almost pure quartz. A glass-sand deposit has, in many cases, determined the location of a glass factory. Its iron content should not exceed 0.45% for tableware or 0.015% for optical glass, as iron affects the color of most glass adversely.

Soda (Na_2O) is principally supplied by dense soda ash (Na_2CO_3). Other sources are sodium bicarbonate, salt cake, and sodium nitrate. The latter is useful in oxidizing iron and in accelerating the melting. The important sources of *lime* (CaO) are limestone and burnt lime from dolomite ($CaCO_3 \cdot MgCO_3$), the latter introducing MgO into the batch.

Feldspars have the general formula $R_2O \cdot Al_2O_3 \cdot 6SiO_2$, where R_2O represents Na_2O or K_2O or a mixture of these two. They have many advantages over most other materials as a source of Al_2O_3, because they are cheap, pure, and fusible and are composed entirely of glass-forming oxides. Al_2O_3 itself is used only when cost is a secondary item. Feldspars also supply Na_2O or K_2O and SiO_2. The alumina content serves to lower the melting point of the glass and to retard devitrification.

Borax, as a minor ingredient, supplies glass with both Na_2O and boric oxide. Though seldom employed in window or plate glass, borax is now in common use in certain types of container glass. There is also a high-index borate glass that has a lower dispersion value and a higher refractive index than any glass previously known and is valuable as an optical glass. Besides its high fluxing power, borax not only lowers the expansion coefficient but also increases chemical durability. Boric acid is used in batches where only a small amount of alkali is wanted. Its price is about twice that of borax.

Salt cake, long accepted as a minor ingredient of glass, and also other sulfates such as ammonium and barium sulfate, are encountered frequently in all types of glass. Salt cake is said to remove the troublesome scum from tank furnaces. Carbon should be used with sulfates to reduce them to sulfites. *Arsenic trioxide* may be added to facilitate the removal of bubbles. *Nitrates* of either sodium or potassium serve to oxidize iron and make it less noticeable in the finished glass. Potassium *nitrate* or carbonate is employed in many better grades of table, decorative, and optical glass.

[6]ECT, 3d ed., vol. 11, 1980, pp. 807–880.

Cullet is crushed glass from imperfect articles, trim, and other waste glass. It facilitate melting and utilizes waste material. It may be as low as 10 percent of the charge or as higl as 80 percent.

Refractory blocks for the glass industry have been developed especially because of th severe conditions encountered. *Sintered* zircon, alumina, mullite, mullite-alumina and *elec trocast* zirconia-alumina-silica, alumina, and chrome-alumina are typical of those for glas tanks. See electrocast refractories, Chap. 6 The latest practice in regenerators utilizes basi refractories because of the alkali dust and vapors. Furnace operating temperatures are limite mainly by silica-brick crowns, which are economical to use in the industry

CHEMICAL REACTIONS. The chemical reactions involved may be summarized

$$Na_2CO_3 + aSiO_2 \rightarrow Na_2O \cdot aSiO_2 + CO_2 \quad (1$$

$$CaCO_3 + bSiO_2 \rightarrow CaO \cdot bSiO_2 + CO_2 \quad (2$$

$$Na_2SO_4 + cSiO_2 + C \rightarrow Na_2O \cdot cSiO_2 + SO_2 + CO \quad (3$$

The last reaction may take place as in equations (4) or (5), and (6):

$$Na_2SO_4 + C \rightarrow Na_2SO_3 + CO \quad (4$$

$$2Na_2SO_4 + C \rightarrow 2Na_2SO_3 + CO_2 \quad (5$$

$$Na_2SO_3 + cSiO_2 \rightarrow Na_2O \cdot cSiO_2 + SO_2 \quad (6$$

The ratios Na_2O/SiO_2 and CaO/SiO_2 are not molar ratios. The ratio may be of the type $Na_2O/1.8SiO_2$, for example. In an ordinary window glass the molar ratios are *approximately* 1.5 mol Na_2O, 1 mol CaO, and 5 mol SiO_2. Other glasses vary widely (Table 8.2).

Typical manufacturing sequences can be broken down into the following.

Transportation of raw materials to the plant
Sizing of some raw materials.
Storage of raw materials.
Conveying, weighing, and mixing raw materials, and feeding them into the glass furnace
Burning of the fuel to secure temperature needed for glass formation.
Reactions in the furnace to form glass.
Saving of heat by regeneration or recuperation
Shaping of glass products
Annealing of glass products.
Finishing of glass products.

To carry out these steps, modern glass factories are characterized by the use of materials-handling machinery supplying automatic and continuous manufacturing equipment, in contrast to the "shovel and wheelbarrow" methods of older factories. In spite of the modernization of plants, however, the manual charging of small furnaces is still carried on, though a dusty atmosphere is created. The trend, however, is toward mechanical batch transporting and mixing systems so completely enclosed that practically no dust is emitted at any stage of the handling of glass or raw materials.

METHODS OF MANUFACTURE

The manufacturing procedures may be divided (cf. Fig. 8.1) into four major phases: (1) melting, (2) shaping or forming, (3) annealing, and (4) finishing.

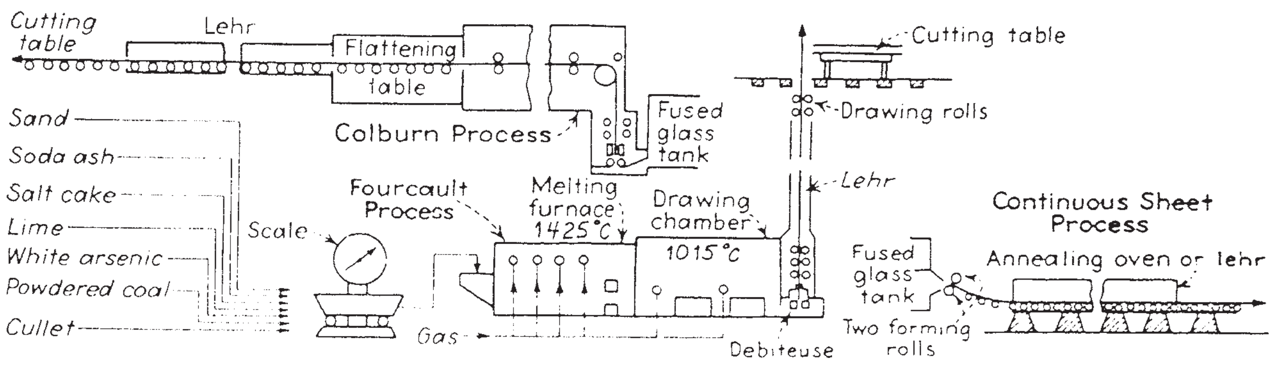
MELTING. Glass furnaces may be classified as either pot or tank furnaces (cf. Fig. 8.2, of a tank furnace). *Pot furnaces*, with an approximate capacity of 2 t or less, are used advantageously for the small production of special glasses or where it is essential to protect the melting batch from the products of combustion.[6a] They are employed principally in the manufacture of optical glass and art glass by the casting process. The pots are really crucibles made of selected clay or platinum. It is very difficult to melt glass in these vessels without contaminating the product or partly melting the container itself, except when platinum is used. In a *tank furnace*, batch materials are charged into one end of a large "tank" built of refractory blocks, some of which measure 38 x 9 x 1.5 m and have a capacity of 1350 t of molten glass. The glass forms a pool in the hearth of the furnace, across which the flames play alternately from one side and the other. The "fined"[7] glass is worked out of the opposite end of the tank, the operation being continuous. In this type of furnace, as in the pot furnace the walls gradually corrode under the action of the hot glass. The quality of the glass and the life of the tank are dependent upon the quality of the construction blocks. For this reason, much attention has been given to glass furnace refractories.[8] Small tank furnaces are called day tanks and supply a day's demand of 1 to 10 t of molten glass. They are heated either electrothermally or by gas.

The foregoing types are *regenerative* furnaces and operate in two cycles with two sets of checkerwork chambers. The flame gases, after giving up some of their heat in passing across the furnace containing the molten glass, go downward through one set of chambers stacked

[6a] t = 1000 kg.

[7] "Fining" is allowing *molten* glass sufficient time for the bubbles to rise and leave or dissolve in the glass.

[8] See Electrocast Refractories in Chap. 9.



The charge entering the furnace contains (in kilograms) approximately

Sand	15.4	Lime	6.8
Soda ash, dense	16	Cullet	22.7
Salt cake	4.5	Other	0.5–1.0
Powdered coal	0.2		

Fig. 8.1. Flowchart for flat glass manufacture

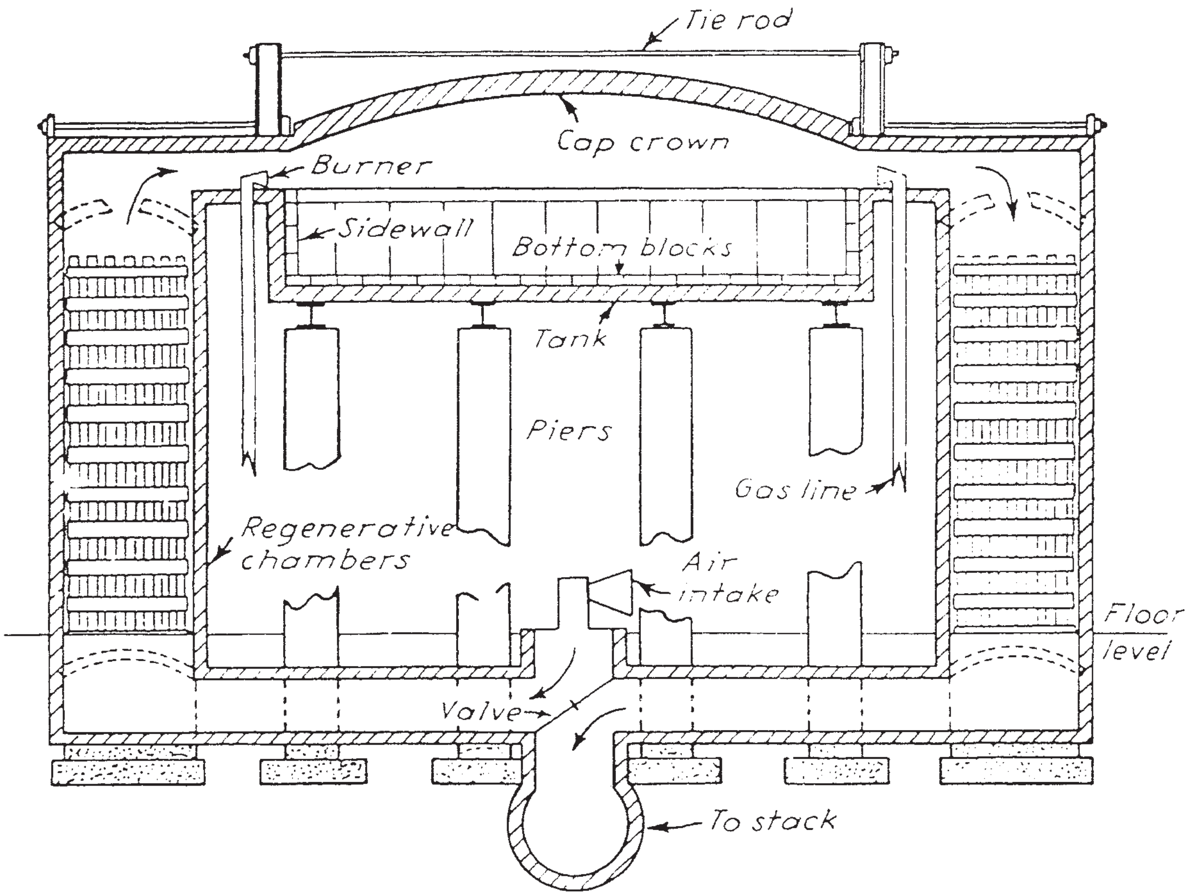


Fig. 8.2. Cross section of glass tank furnace showing regenerative chambers

with open brickwork or checkerwork. A great deal of the sensible heat content of the gases is removed thereby, the checkerwork reaching temperatures ranging from 1500°C near the furnace to 650°C on the exit side. Simultaneously, air is preheated by being passed up through the other previously heated regenerative chamber and is mixed with the burned fuel gas,[9] the resulting flame being of a higher temperature than would have been possible if the air had not been preheated. At regular intervals of 20 to 30 min, the *flow* of the air-fuel mixture, or the cycle, is reversed, and it enters the furnace from the opposite side through the previously heated checkerwork, passing through the original checkerwork, now considerably cooled. Much heat is saved by this regenerative principle, and a higher temperature is reached.

The temperature of a furnace just starting production can be raised only certain increments each day, depending upon the ability of the refractory used to stand the expansion. Once the regenerative furnace has been heated, a temperature of at least 1200°C is maintained at all times. Most of the heat is lost by radiation from the furnace, and a much smaller amount is actually expended in the melting. Unless the walls are allowed to cool somewhat by radiation, however, their temperature would become so high that the molten glass would dissolve or corrode them. To reduce the action of the molten glass, water cooling pipes are frequently placed in the furnace walls.

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[9]If the fuel is producer gas, it is preheated also, but rarely if a higher energy type is employed, such as natural gas or oil.

SHAPING OR FORMING. Glass may be shaped by either machine or hand molding. The outstanding factor to be considered in *machine molding* is that the design of the glass machine should be such that the article is completed in a very few seconds. During this relatively short time the glass changes from a viscous liquid to a clear solid. It can therefore be readily appreciated that the design problems to be solved, such as flow of heat, stability of metals, and clearance of bearings, are very complicated. The success of such machines is an outstanding tribute to the glass engineer. In the following discussion the most common types of machine-shaped glass, i.e., window glass, plate glass, float glass, bottles, light bulbs, and tubing, are described.

Window Glass. For many years window glass was made by an extremely arduous hand process that involved gathering a gob of glass on the end of a blowpipe and blowing it into a cylinder. The ends of the latter were cut off, and the hollow cylinder split, heated in an oven, and flattened. This tedious manual process has now been entirely supplanted by continuous processes or their modifications, the Fourcault process and the float process, as outlined in the flowchart in Fig. 8.1.

In the *Fourcault* process a drawing chamber is filled with glass from the melting tank. The glass is drawn vertically from the kiln through a so-called "débiteuse" by means of a drawing machine. The débiteuse consists of a refractory boat with a slot in the center through which the glass flows continuously upward when the boat is partly submerged. A metal bait lowered into the glass through the slot at the same time the débiteuse is lowered starts the drawing as the glass starts flowing. The glass is continuously drawn upward in ribbon form as fast as it flows up through the slot, and its surface is chilled by adjacent water coils. The ribbon, still traveling vertically and supported by means of rollers, passes through a 7.5-m-long annealing chimney or lehr. On emerging from the lehr, it is cut into sheets of desired size and sent on for grading and cutting. This is shown in Figs. 8.1 and 8.3.

PPG Industries operates a modified Fourcault process that produces *Pennvernon* glass. Sheets of glass 3 m wide and up to 0.55 cm thick are made by varying the drawing rate from 96 cm/min for single-strength[10] to 30 cm/min for 0.55 cm. This process substitutes for the floating débiteuse a submerged draw bar for controlling and directing the sheet. After being drawn vertically a distance of 8 m, most of which is in an annealing lehr, the glass is cut. For thicknesses above single and double strength, a second annealing is given in a 36-m standard horizontal lehr.

Plate Glass. Between 1922 and 1924 the Ford Motor Co. and PPG Industries independently developed a continuous automatic process for rough-rolled glass in a continuous ribbon. The glass is melted in large continuous furnaces holding 1000 or more tons. The raw materials are fed into one end of the furnace, and the melted glass, at a temperature as high as 1595°C, passes through the refining zone and out the opposite end in an unbroken flow. From the wide refractory outlet the molten glass passes between two water-cooled forming rolls, which give it a plastic ribbon configuration. The ribbon of glass is drawn down over a series of smaller water cooled rolls running at a slightly higher surface speed than the forming rolls. The stretching effect of the different speeds and the shrinking of the glass as it cools flatten the ribbon as it enters the annealing lehr. After annealing, the ribbon may be cut and

[10]Single-strength window glass has a thickness of 2.2 to 2.5 mm; double-strength glass measures 3 to 3.35 mm.

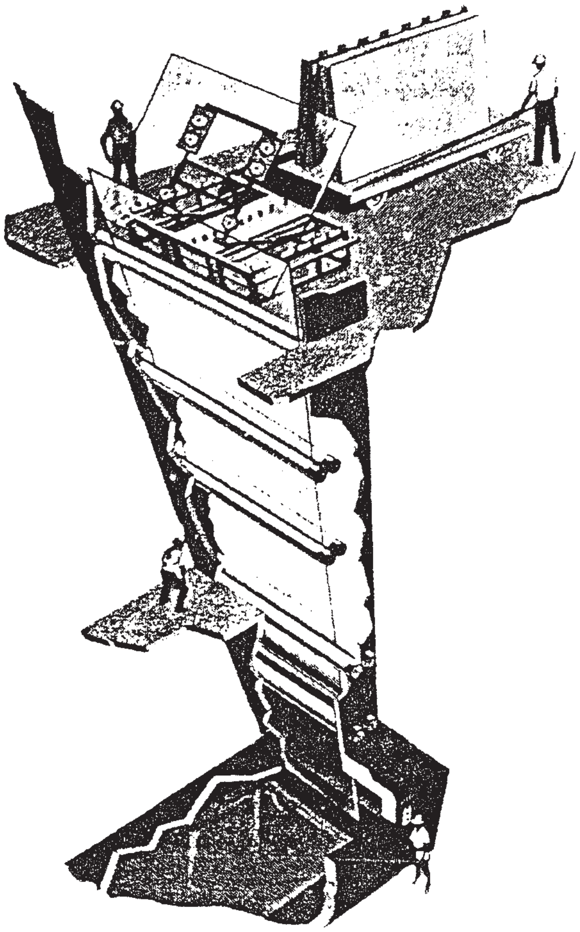

Fig. 8.3. Pictorial flowchart of modified Fourcault process for flat glass. Here the glass is continuously drawn vertically by rolls through the lehr to an automatic cutter. *(American-Saint Gobain Corp.)*

sheets for grinding and polishing, or it may progress automatically for 50 to 100 m, undergoing annealing, grinding, polishing, and inspection before it passes through cutting machines and is reduced to salable plates. Grinding and polishing removes about 0.8 mm of glass from each surface. About 30 years later this system was substantially modified by the grinding and polishing of both sides of the continuous ribbon simultaneously.

Float Glass.[11] Float glass was developed by Pilkington Brothers in England. It is a fundamental improvement in manufacturing high-quality flat glass. It has long been known that a fire-polished glass has superior reflectance and wear qualities. The float process employs the tank furnace melting system (Fig. 8.2) in which raw materials are fed into one end of the furnace and the molten glass passes through the refining zone into a narrow canal that connects the furnace with the bath (Figs. 8.4 and 8.5). Rate of flow is precisely controlled by automatically raising or lowering a gate that spans the canal. The molten glass is conducted onto and along the surface of a pool of molten tin in a nonoxidizing atmosphere under closely controlled conditions of temperature. The controlled heating melts out all irregularities and produces a glass with both sides flat and parallel.

In 1975 PPG Industries[12] made a substantial improvement in the Pilkington process by having the stream of molten glass from the melting furnace be of the desired width (usually about 4 m) as it flows onto the molten bath. This minimizes the effects of flow from a thick, unshaped mass to the sheet which introduces optical distortion.

[11]Pilkington, Flat Glass: Evolution and Revolution over 60 Years, *Glass Technol.* **17** (5) 82 (1976).

[12]ECT, 3d ed., vol. 11, 1980.

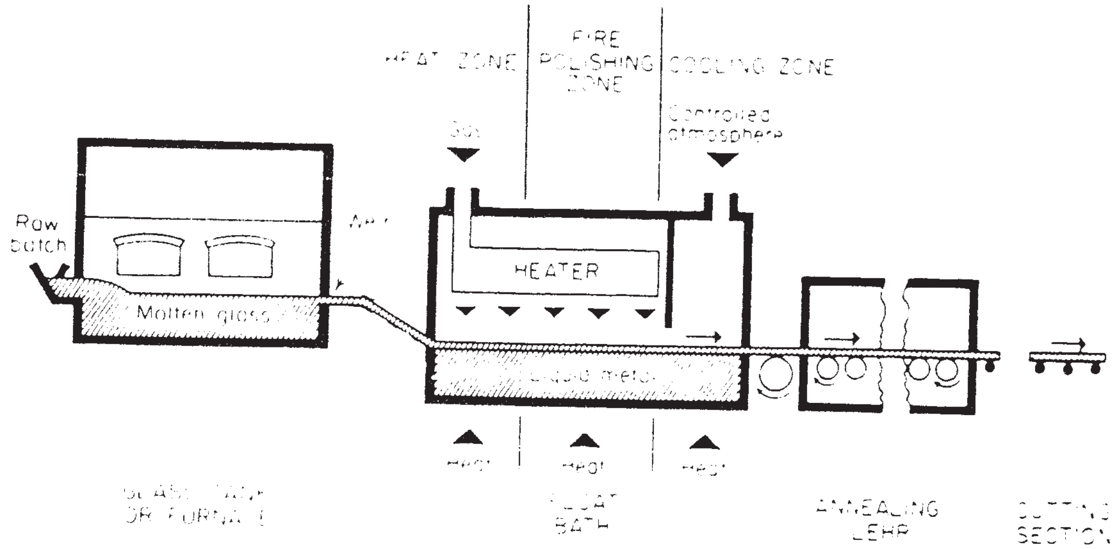

Fig. 8 .4. Flowchart of a continuous process for the manufacture of float glass. (*PPG Industries.*)

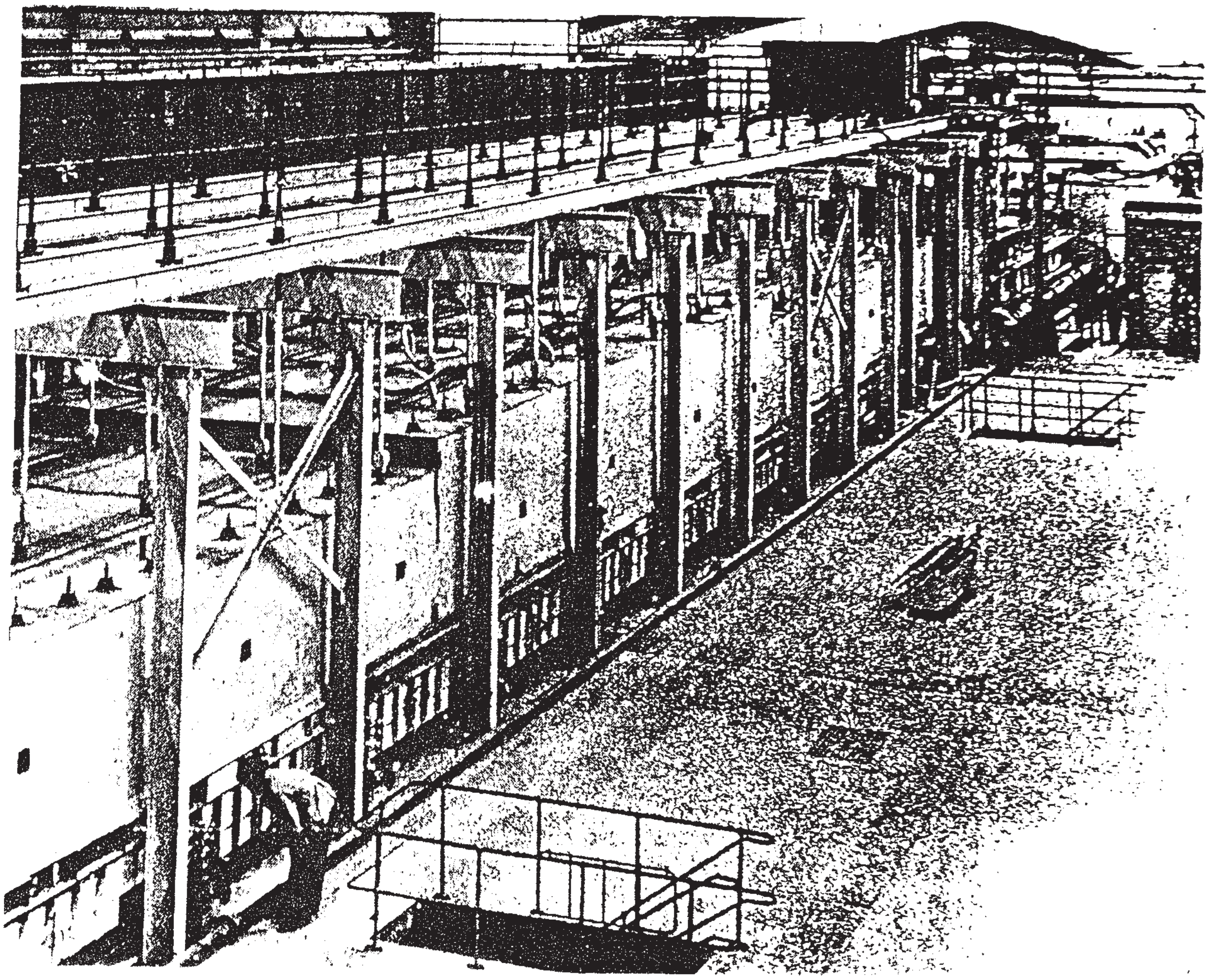

Fig. 8 .5. Photograph of the Pilkington *float-bath* section in which the 2.5-m-wide glass ribbon is formed at the Pilkington Bros float-glass process plant at St. Helens, Lancashire, England. The operating temperatures in the melting section are from about 1500 to 1200°C [*Chem. Eng.* 71 (3) 38 (1964)]. (Courtesy *Pittsburgh Plate Glass Co.*)

The glass is cooled down while still on the molten metal until the surfaces are hard enough to enter the lehr without the lehr rollers spoiling the bottom surface. About 50,000 m^2 day of float can be produced in thicknesses from 3 to 19 mm and in widths of 3 to 3.5 m. This process has practically eliminated the production of ground and polished plate glass.

Wired and Patterned Glass. In patterned glass manufacture, the molten glass flows over the lip of the furnace and passes between metal rolls on which a pattern has been engraved or machined. The rolls form the glass and imprint the pattern in a single operation. Such glass diffuses the light and ensures a certain amount of privacy, which recommends it for use in rooms, doors, and shower enclosures. Such glass can be reinforced with wire during the initial forming for special safety needs, e.g., for windows near fire escapes. Both operations are pictured in Fig. 8.6.

Blown Glass. Glass blowing, one of the most ancient arts, until the last century depended solely upon human lungs for power to form and shape molten glass. Modern demands for blown glass, however, have required the development of more rapid and cheaper methods of production.[13] The machine making of bottles is only a casting operation that uses air pressure to create a hollow. Several types of machines produce *parisons*, partly formed bottles or bottle blanks. One is the suction-feed type used, with certain variations, in bulb and tumbler production. Another is the gob-feed type, which has been applied to the manufacture of all types of ware made by pressing, blowing, or a combination of "press and blow."

In the suction-feed type, glass contained in a shallow, circular revolving tank is drawn up into molds by suction. The mold then swings away from the surface of the glass, opens, and drops away, leaving the parison sustained by the neck. The bottle mold next rises into position around the parison, and a blast of compressed air causes the glass to flow into the mold. The latter remains around the bottle until another gathering operation has been performed; it then

[13] Scholes and Greene, *Modern Glass Practice*, Cahners, Boston, Mass., 1975, chap. 15.

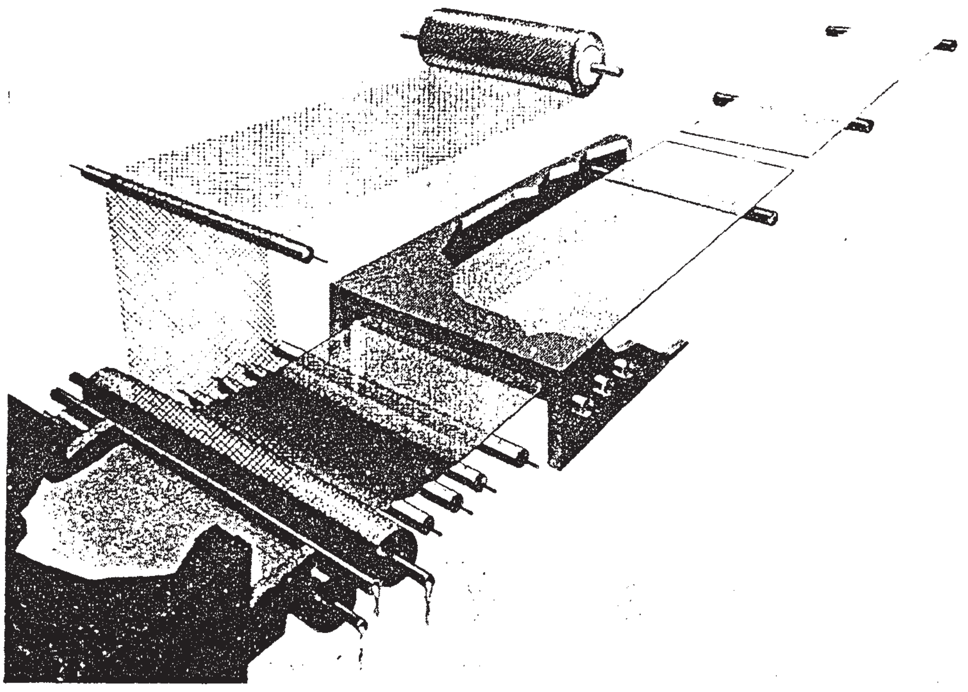

Fig. 8.6. Pictorial flowchart of a 1.5-m ribbon of wired and patterned glass. *(American Saint-Gobain Corp.)*

drops the bottle and rises to close around a fresh parison The operations are completely automatic, and speeds of 60 units per minute are not uncommon.

The gob feeder represents one of the most important developments in automatic glassworking. In this operation the molten glass flows from the furnace through a trough, at the lower end of which is an orifice The glass drops through the orifice and is cut into a gob of the exactly desired size by mechanical shears. It is delivered through a funnel into the parison mold, which starts the formation of the bottle in an inverted position, as shown in Fig. 8.7. A neck pin rises into place, and another plunger drops from the top, whereupon compressed air in the "settle blow" forces the glass into the finished form of the neck. The mold is closed on top (bottom of the bottle), the neck pin is retracted, and air is injected in the "counter

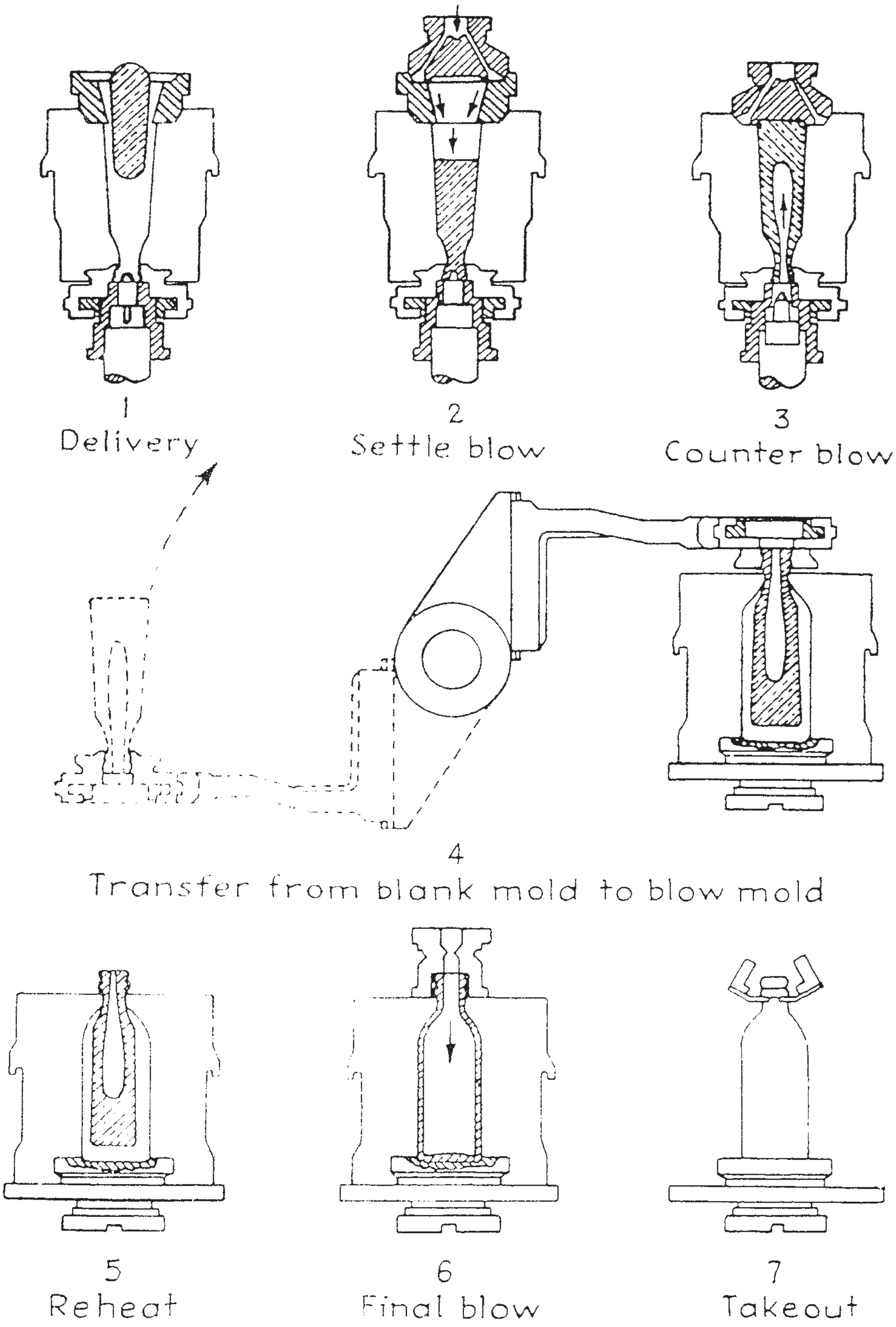

Fig. 8.7. Automatic bottle manufacture by an I-S machine *(Glass Packer.)*

blow" through the newly formed neck to form the inner cavity. The parison mold opens, and the parison is inverted as it passes to the next station, so that the partly formed bottle is then upright. The blow mold closes around the parison, which is reheated for a brief interval. Air is then injected for the final blow, simultaneously shaping the inner and outer surfaces of the bottle. The blow mold swings away, and the bottle moves on the lehr.

Automatic bottle-blowing machines usually consist of two circular tables, known as the *parison-mold* table and the *blow* table. As the glass moves around the periphery of the table, the various operations described above take place. Table movement is controlled by compressed air which operates reciprocating pistons, and the various operations occurring on the table are coordinated with table movement by a motor-timing mechanism. This latter device constitutes one of the most vital and expensive parts of the equipment.

Light Bulbs. The blowing of a thin bulb differs from bottle manufacture in that the shape and size of the bulb are determined initially by the air blast itself and not by the mold. The molten glass flows through an annular opening in the furnace and down between two water-cooled rollers, one of which has circular depressions that cause swellings on a glass ribbon coinciding with circular holes on a horizontal chain conveyor onto which the ribbon moves next. The glass sags through these holes by its own weight. Below each hole is a rotating mold. Air nozzles drop onto the surface of the ribbon, one above each of the glass swellings or conveyor holes. As the ribbon moves along, these nozzles eject a puff of air which forms a preliminary blob in the ribbon. The spinning mold now rises, and a second puff of air, under considerably less pressure than the first, shapes the blob into the mold and forms the bulb. The mold opens, and a small hammer knocks the bulb loose from the ribbon. The bulbs drop onto a belt which carries them to the lehr rack, where they slip neck down between two parallel vertical strips which support them as they are annealed. The total time for the entire series of operations, including annealing, is about 8 min. Machine speeds as high as 2000 bulbs per minute have been attained.

Television Tubes. Television tubes are now made as large as 68 cm across and consist of three principal parts, the face phosphorescent screen, on which the picture is produced, the envelope, and the electron gun. The phosphor is applied to the face screen of the envelope either by settling or dusting. Manufacture of the glass envelope was difficult until centrifugal casting was invented, which uses a revolving mold to produce a much more uniform wall thickness. The glass parts are sealed together, using a gas flame or gas and electricity. For *colored* television tubes, the phosphor is applied to the inner surface of the screen. A perforated mask is mounted behind the screen to direct the electron beams properly. The high temperature involved in sealing cannot be employed here, since this would cause deterioration of the phosphor.

Glass Tubing. In the Danner process the molten glass flows onto the top end of a revolving, hollow clay rod inclined at about 30°. Air is blown through it and the glass on the rod slowly flows toward the bottom end where it is pulled off to form a tube. A pair of belts grip the tubing and draw it at a uniform speed. The diameter and wall thickness are controlled by the temperature, speed of drawing, and volume of air that is blown through the rod. Tubing does not require annealing.

Glass tower plates and bubble caps, prisms, and most other optical glass, most kitchenware, insulators, certain colored glasses, architectural glass, and many similar items are *hand-molded.* The process consists essentially in drawing a quantity of glass, known as the *gather*, from the pot or tank and carrying it to the mold. Here the exact quantity of glass required

is cut off with a pair of shears, and the ram of the mold driven home by hand or by hydraulic pressure. Certain glass forming is carried out by semiautomatic methods which involve a combination of the machine- and hand-molding processes previously described. Volumetric flasks and cylindrical Pyrex sections for towers are fabricated in this manner.

ANNEALING. To reduce strain, it is necessary to *anneal all glass* objects, whether they are formed by machine- or hand-molding methods. Briefly, annealing involves two operations: (1) holding a mass of glass above a certain critical temperature long enough to reduce internal strain by plastic flow to less than a predetermined maximum and (2) cooling the mass to room temperature slowly enough to hold the strain below this maximum. The lehr, or annealing oven, is nothing more than a carefully designed heated chamber in which the rate of cooling can be controlled so as to meet the foregoing requirements. The establishment of a quantitative relationship[15] between stress and birefringence caused by the stress has enabled glass technologists to design glass to meet certain conditions of mechanical and thermal stress. With the foregoing data as a basis, engineers have produced continuous-annealing equipment, with automatic temperature regulation and controlled circulation, which permits better annealing at a lower fuel cost and with less loss of product.

FINISHING. All types of annealed glass must undergo certain finishing operations which, though relatively simple, are very important. These include cleaning, grinding, polishing, cutting, sandblasting, enameling, grading, and gaging. Although all these are not required for every glass object, one or more is almost always necessary.

MANUFACTURE OF SPECIAL GLASSES

Research and development are at the heart of the new and improved types and properties of glass. This section illustrates some of the new glass products that have resulted.

FUSED SILICA GLASS. Fused silica glass, or vitreous silica, may be made by fusing pure silica, but such products are usually blebby and difficult to produce in transparent form. It is now manufactured by Corning[16] by vapor-phase high-temperature pyrolysis of silicon tetrachloride. This type of process lends itself naturally to controls which permit chemically pure SiO_2. The raw silica produced in this manner is in the form of plates, or boules. The high temperature of the reaction tends to drive off undesired contaminants, giving fused-silica impurities in the order of 1 part in 100 million. This fused-silica glass has remarkable properties (Table 8.3) and has the lowest ultrasonic absorption of any material. Because of its low thermal expansion it is used for telescope mirrors, e.g., in a 158-cm mirror for a telescope at the U.S. Naval Observatory.

HIGH-SILICA GLASS. This product, known as Vycor,[17] constitutes an important advance toward the production of a glass approaching fused silica in composition and properties. This has been accomplished with the avoidance of former limitations on melting and forming.

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[15]Shand, op. cit., pp. 103–109.

[16]ECT, 3d ed., vol. 11, 1980, pp. 807–880.

[17]Corning Glass Works, U.S. Patent 2,106,744 (1938), and 2,221,709 (1940).

The finished articles contain approximately 96% silica and 3% boric oxide, and the rest is alumina and alkali. Borosilicate-glass compositions of about 75% silica content are used in the earlier stages of the process, in which the glasses are melted and molded. After cooling, the articles are subjected to heat treatment and annealing, which induce the glass to separate into two distinct physical phases. One of these phases is so high in boric and alkaline oxides that it is readily soluble in hot acid solutions, whereas the other is rich in silica and therefore insoluble in these solutions. The glass article is immersed in a 10% hydrochloric acid (98°C) bath for sufficient time to permit the soluble phase to be virtually all leached out. It is washed thoroughly to remove traces of the soluble phase, as well as impurities, and subjected to another heat treatment that serves to dehydrate the body and to convert the cellular structure to a nonporous vitreous glass. In the course of these processes the glassware undergoes a shrinkage in linear dimensions amounting to 14 percent of its original size. Table 8.3 compares its properties with those of other glasses. This method of glass manufacture furnishes a product that can be heated to a cherry red and then plunged into ice water without any ill effects. Also, this glass has high chemical durability and is extremely stable to all acids except hydrofluoric, which, however, attacks this glass considerably more slowly than others. Its shrinkage is also proportionately even, so that the original shape is preserved.

COLORED AND COATED GLASSES. Although for many centuries they were used merely for decoration, today transparent colored glasses are essential for both technical and scientific purposes and are produced in many hundreds of colors. Colored glass may be one of three types: (a) Color is produced by the absorption of certain light frequencies by agents in solution in the glass. The coloring agents of this group are the oxides of the transition elements, especially the first group, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu. This class can be subdivided into those in which the color is due to the chemical structural environment and those in which the color is caused by differences in state of oxidation. As an example of the former, NiO dissolved in sodium-lead glass yields a brown color, but in a potash glass it produces heliotrope. In the latter, chromium oxides produce colors ranging from green to orange, depending on the proportion of the basic oxide Cr_2O_3 to the acidic oxide and the composition of the glass, i.e., whether it is basic or acidic. (b) Color is produced by colloidal particles precipitated within an originally colorless glass by heat treatment. The classic example is the precipitation of colloidal gold, producing gold-ruby glass. (c) Color is produced by microscopic or larger particles which may be colored themselves, such as selenium reds (SeO_2) used in traffic lights, lantern globes, etc., or the particles may be colorless, producing opalescent glass.

Coated glasses are made by depositing transparent metallic films on the surface of clear or colored glass. The films are designed to provide specific transmission and reflection characteristics, which are important to the architect today.

Opal, or translucent, glasses are clear when molten but become opalescent as the glass is

***Table* 8.3** Comparative Properties of Glasses

	Common Lime	Pyrex Borosilicate	Vycor 96% Silica	Fused Silica	Pyroceram
Softening point °C	715	746	1530	1525	1250
Annealing point °C	527	450	1020	1085	
Specific gravity	2.50	2.23	2.18	2.20	2.60
Young's modulus GPa	70		68		

SOURCE: ECT, 3d ed., vol. 11, 1980, p. 830

worked into form, because of the separation and suspension of minute particles of various type, size, and density in the medium, which disperse the light passing through.

Opal glass is often produced by growing nonmetallic crystals from nucleated silver particles developed from an original clear glass containing silver. It is employed for architectural effects, e.g., in window louvers, for transmission of specified wavelengths, and for tableware.

SAFETY GLASS. Safety glasses[18] may be grouped into two general classes: laminated safety glass and heat-strengthened (or tempered) or case-hardened safety glass. Wired glass may also be considered safety glass (Fig. 8 .6).

Laminated safety glass, which is the most widely used in this country, consists of two sheets of thin plate glass, each of which is about 3 mm thick, with a sheet of nonbrittle plastic material between. The plastic and glass are washed, and an adhesive is applied to the glass (if the plastic used requires it, such not always being the case). The glass and plastic sheet are pressed together under moderate heat to seal the edges. The glass is subjected to moderate temperatures and hydraulic pressures in an autoclave, in order to bring the entire interlayer into intimate contact, after which the edges of the sandwich may be sealed with a water-resistant compound.

The glass used in the manufacture of laminated safety glass has the same physical properties as ordinary glass, so that the safety features depend solely upon the ability of the plastic interlayer to hold fragments caused by accidental breaking of the glass itself. The first plastic used commercially was cellulose nitrate, which was replaced by cellulose acetate. Now practically all laminated safety glass uses polyvinyl butyral resin. This vinyl plastic is more elastic than cellulose acetate, since it stretches under relatively low stresses up to its elastic limit, after which considerable additional stress is necessary to make it fail. It remains clear and colorless under all conditions of use, is not affected by sunlight, and does not need adhesives or water-resistant compounds in manufacturing.

Tempered, or strengthened,[19] *glass* is very strong and tough. It is used for doors and windows of automobiles and for pipe. It possesses high internal stresses and, if the surface is broken, shatters into many pieces. Its manufacture involves controlled heat annealing whereby the nonuniform stresses in glass are replaced by controlled, uniform, low-level stresses. Such glass is really very strong in compression and very weak in tension. *Physical tempering* is an outgrowth of the study of annealing and is less drastic than the quenching process long used for making Prince Rupert drops. The already-formed glass vessel or sheet to be strengthened by tempering or annealing is heated to some temperature, e.g., 425°C, just below its softening point, and then quenched in air, molten salt, or oil. During this tempering, a sandwich effect results when the exterior, or skin, of the glass cools rapidly and becomes hard and the interior cools more slowly and continuously and contracts after the exterior has become rigid. Thus the interior pulls on the *outside* surface, *compressing* it, whereas the *interior* develops compensating *tension* and provides a threefold increase in strength. Chemcor[20] is *chemically strengthened* glass that may have three to five times the strength of even physically tempered products. It duplicates the stresses just described by physical means (controlled quenching). This has been done by ion exchange with the outer

[18]Randolph, Evolution of Safety Glass, *Mod. Plast.* 18 (10) 31 (1941); cf. Weidlein, History and Development of Laminated Safety Glass, *Ind. Eng. Chem.* 31 563 (1939).

[19]Olcott, Corning Glass Co., Chemical Strengthening of Glass, *Science* **140** 1189 (1963).

[20]Corning Chemical Engineering Achievement, *Chem. Eng.* **70** (23) 233 (1963); **71** (1) 36 (1964).