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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

**GLASS  
AND  
GLASS MAKING**



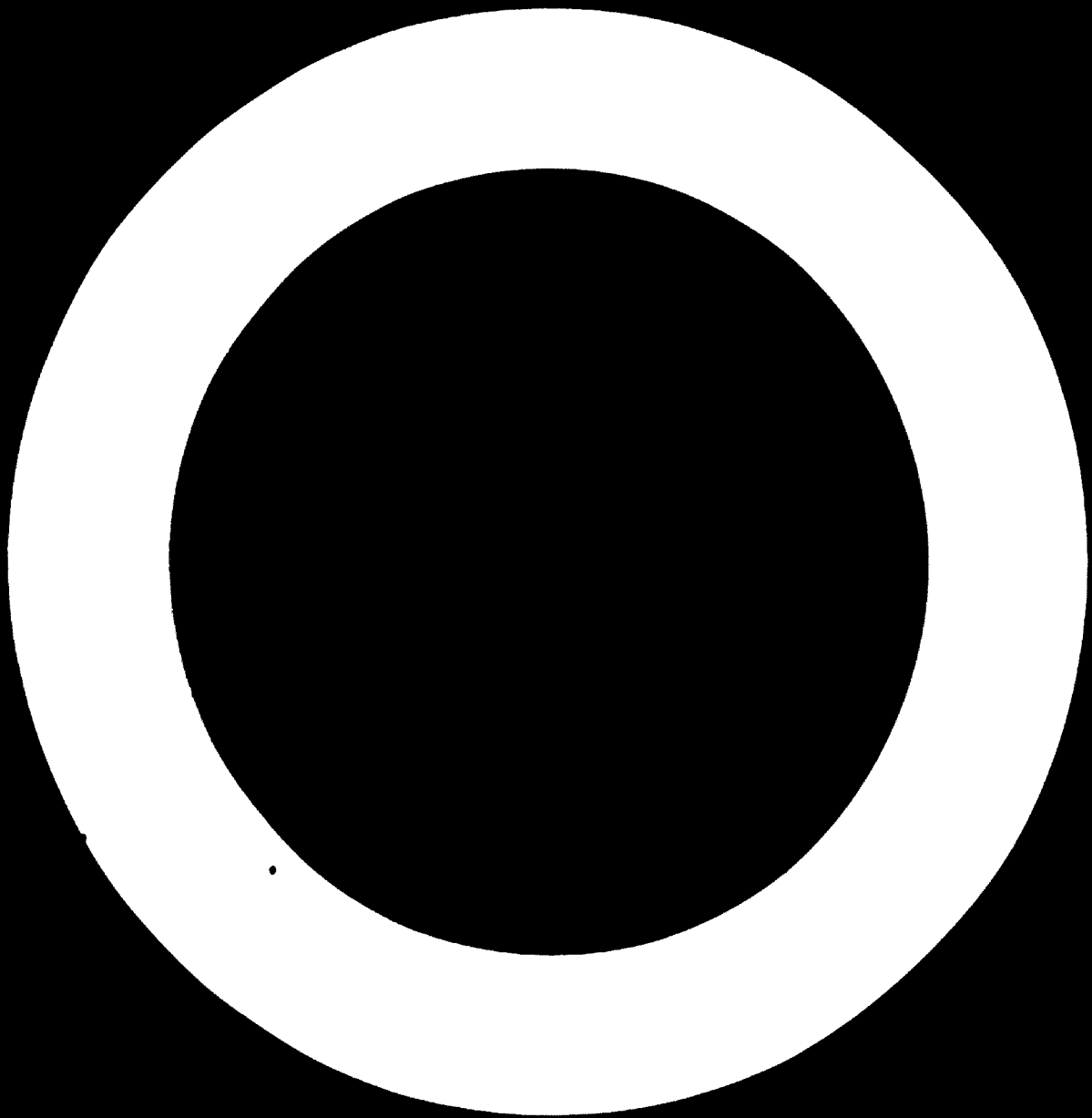
UNITED NATIONS

**UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION**  
Vienna

**GLASS  
AND  
GLASS MAKING**



**UNITED NATIONS**  
New York, 1977



Explanatory notes

References to dollars (\$) are to United States dollars, unless otherwise stated.

References to "tons" are to metric tons, unless otherwise specified.

The following forms have been used in tables:

Three dots (...) indicate that data are not available or are not separately reported

A dash (-) indicates that the amount is nil or negligible

A blank indicates that the item is not applicable

Totals may not add precisely because of rounding.

Besides the common abbreviations, symbols and terms, the following have been used in this report:

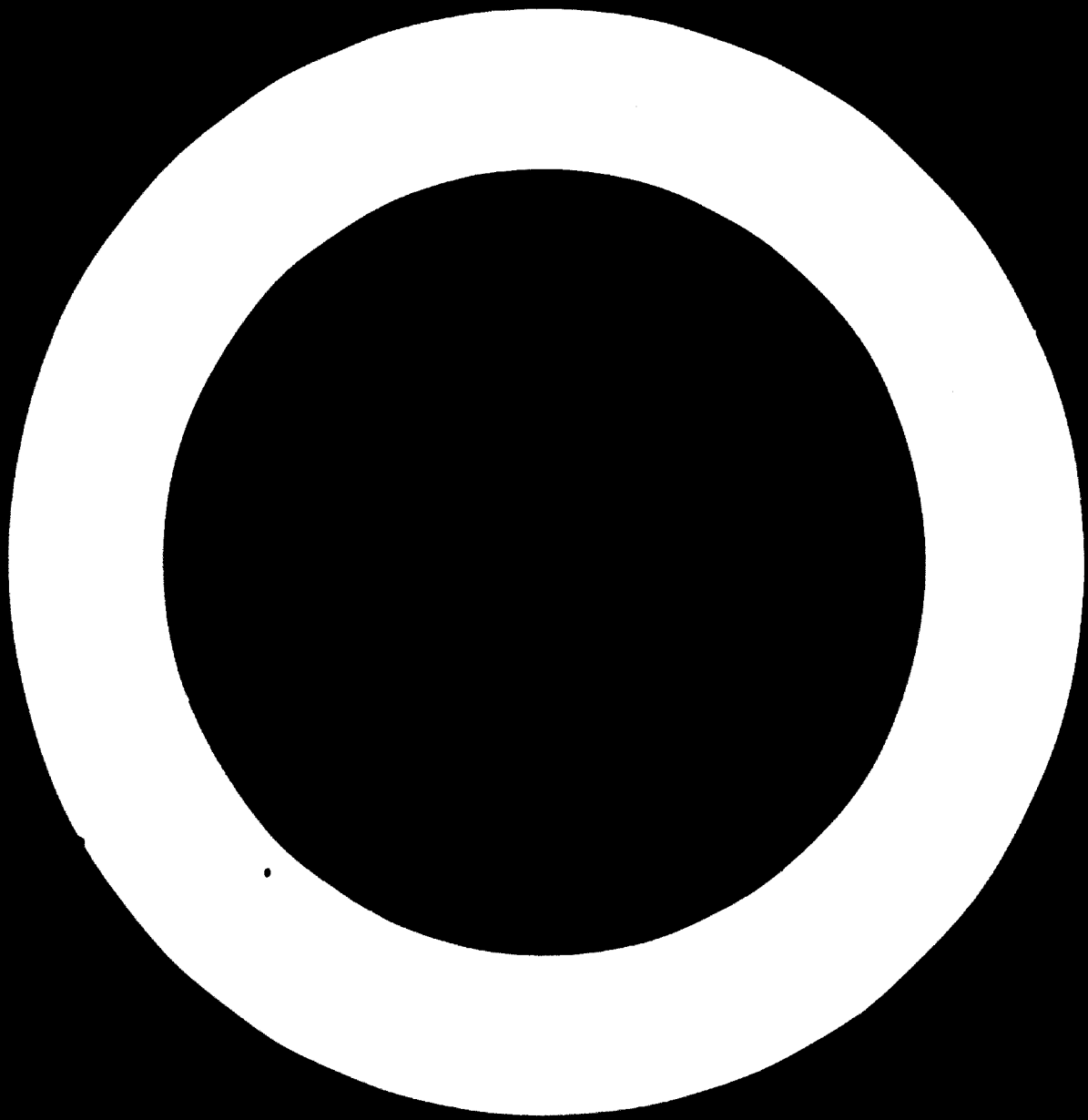
Å	angstrom = $10^{-8}$ cm
psi	pound-force per square inch
n	viscosity

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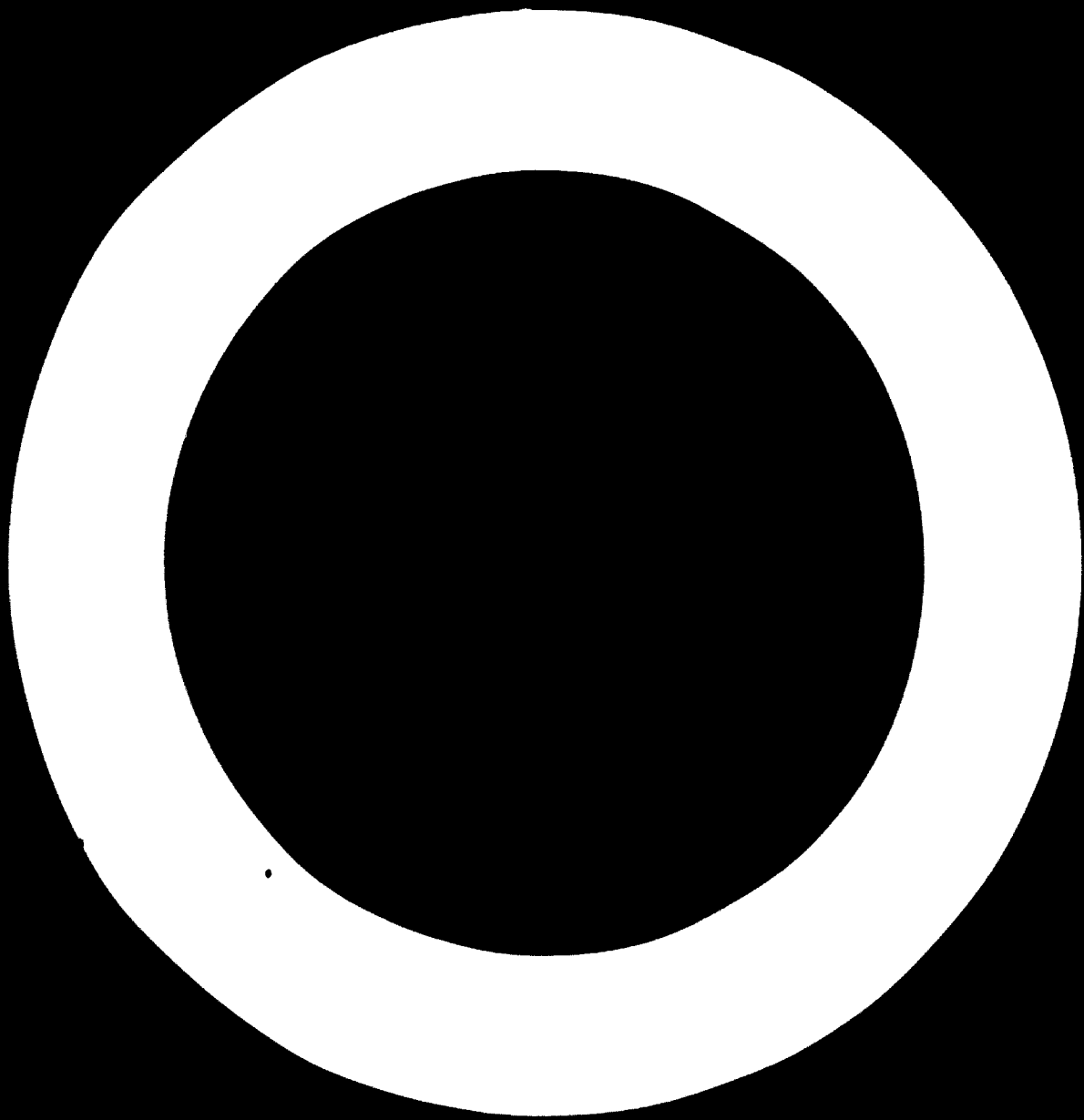
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## INTRODUCTION

Glass making, one of the oldest of industries, has had a fascination for man throughout the ages. The transmutation of common sand and earth into a gem-like, rigid, transparent material has all the romance of alchemy. Today, by far the greater volume of glass is made by fully automatic means, and a visit to a modern bottle factory, for example, might lead one to suppose that the industry is now simply a question of engineering; but a look behind the scenes will show that glass making is still very much a matter of art rather than science. The glass technologist is the alchemist behind the scenes who must daily exercise his art, assisted by science, to ensure that the machines are capable of functioning properly.

Glass cannot be shaped by brute force alone, as is the case with metals or plastics: it must be persuaded into shape by encouragement or constraint so that, like a perverse mule, its movement complies with its own inclination and yet is in the right direction. In this respect the glass technologist's job is similar to that of the chief executive, a major portion of whose time is taken up, not with routine administration, but in dealing in one way or another with the recalcitrance of human nature. The trouble is however that these two persons seldom speak the same language. This is particularly true in new glass industries in developing countries, where the formal training for the two jobs is often quite different. Thus, one of the purposes of this monograph is to provide insights into glass making that will provide a common ground of understanding for both the technologist and the executive.

It is an interesting reflection that in the highly competitive glass business the large, elaborate and highly organized glass manufacturers are often operating at marginal viability, whereas some small family firms, ill-equipped and with little formal organization, manage to operate successfully. Is it perhaps that in the latter case the glass technologist and the chief executive are often one and the same person?

Much of the mechanics, in both literal and figurative senses, is standard practice, standard engineering, standard costing, and it is easy for an experienced manager coming to the industry for the first time to believe that this is just another manufacturing industry and that his production engineering textbook would be equal to all occasions. The differences are subtle and insidious, and it may be years before he realizes that he has been trying to drive the mule with a steering-wheel and that he and the mule just happened to have been going the same way.

Most of the difficulties stem from the peculiar nature of glass. At high temperatures, liquid glass begins to behave like the ideal universal solvent: it is a problem to find a chemically-resistant refractory material capable of containing it. But the most significant feature of glass is that it changes gradually from a syrup-like liquid at a melting temperature of about  $1500^{\circ}\text{C}$  to a rigid solid when cooled to about  $500^{\circ}\text{C}$ , where it loses its red glow. During the change, its viscosity changes by a factor of six million million. Some idea of this colossal change in working characteristics is given by representing the viscosity of the glass during melting in the glass-melting furnace on a graph by a line 1 in. (2.5 cm) long. Glass withdrawn from the furnace ready for working (at about  $1100^{\circ}\text{C}$ ) has a viscosity corresponding to a line 2 yd (18.3 cm) long. During working to the desired shape, whether by machine, hand or mouth-blowing, the line representing viscosity stretches to about 2 mi (3.2 km). Finally, the glass must be annealed to remove any stresses introduced during the forming of the article. This is effected by controlled cooling to a temperature where the viscosity corresponds to the distance from the earth to the sun, 93 million miles (150 million kilometres).

The flow characteristics of glass make it possible to work the glass in a variety of ways: by blowing to make bottles and jars; by pressing to make tableware; by drawing to make window glass and tubing; and by rolling to make plate glass.

It might be thought that it is a simple matter to specify the flow characteristics by means of viscosity measurements at various working temperatures and to set the glass-forming machines according to ordinary engineering principles. That is not so. Viscosity is a measure of the resistance to flow or change of shape at static temperatures; but in glass forming the temperature is far from static. The glass loses temperature at a rate that varies significantly with, e.g., the presence of trace impurities and their state of oxidation. Below about  $200^{\circ}\text{C}$  glass is a good thermal insulator, but at higher temperatures radiation predominates in heat transfer and the transparency of the glass lends it a high heat-transfer rate, depending to some extent on its colour. Therefore minor differences in cooling rate mean major differences in flow characteristics.

The viscosity variation of glass is only one aspect of many which make it impractical to specify a glass-making process completely. In the end, there is an element of art and craft, and that is where the glass technologist is needed. By training, he is taught to apply his art scientifically and his science artfully.

This monograph is intended not only for those entering the industry for the first time in whatever capacity, whether it be as entrepreneur or office messenger, but also to those experienced technologists who have never had a formal grounding in their subject, but who even today are often the key persons in successful glass making. The glass technologist fresh from college may also find something interesting here.

The scope of the work is quite broad, as can be gathered from an inspection of the table of contents. It proceeds from the history of the industry, through a technical discussion of the theory and practice of glass making and a consideration of the economical problems involved in setting up a glass factory, to a survey of current trends in the industry.

It is said that good glass making is a matter of getting things right and keeping them right. The glass technologist plays a major part in both these respects. As the chief troubleshooter, he must know how to modify the raw-material mix, often on a daily basis, to maintain or improve the performance of the furnaces and machines and yet maintain the quality of the product. He must make the best economic use of the raw materials available and compensate for natural variations that occur in them. Finally, he must have an appreciation of the over-all economic operation of the plant. It is in this last regard that the glass technologist is often poorly informed. Often, economic controls are imposed from the top and seem illogical and arbitrary to the technical man who is concerned with the glass in the furnace today that is to be worked tomorrow; what happened last week is largely irrelevant to him. In many cases that view is justified. Often the systems for recording production, quality and performance are designed primarily for the highest level of management who receive the figures too late to take effective remedial action - what one might call post mortem control. The figures would be no less valuable to the administration if they were designed primarily to guide the technical person in immediate control and only secondarily as a record of performance. That is particularly true of the factories in developing countries that have been built on the assumption that a glass industry can be bought as a turn-key operation.

If the chief executive and the glass technologist can learn to see the whole glass-making operation with the same eyes, then the best use can be made of the machines, equipment and procedures involved in production and the glass factory can be operated as a coherent, independent complex.

In dealing with some of the scientific aspects of the nature of glass, the author has sometimes used concepts that are not universally accepted. His excuse is that he himself has found them useful. If a knowledgeable reader feels inclined to challenge them, so much the better, for the author's intention is to be thought-provoking.

## I. THE EVOLUTION OF THE GLASS INDUSTRY

It seems to be the fashion for historians to dismiss as myth the story related by Pliny in the first century A.D. concerning the discovery of glass making. Nevertheless, these historians have been unable to substitute anything but the vaguest supposition and seem to ignore the significant build-up to the story. Pliny relates:

"In Syria there is a region known as Phoenice ... In this district, it is supposed, rises the river Belus, which after a course of five miles, empties itself into the sea near the colony of Ptolemais. The tide of this river is sluggish ... Full of slimy deposits, and very deep, it is only at the reflux of the tide that the river discloses its sands, which agitated by the waves, separate themselves from their impurities and so become cleansed ... The story is, that a ship, laden with nitre, being moored upon this spot, the merchants, while preparing their repast upon the sea-shore, finding no stones at hand for supporting their cauldrons, employed for the purpose some lumps of nitre which they had taken from the vessel. Upon its being subjected to the action of the fire, in combination with the sand of the seashore, they beheld transparent streams flowing forth of a liquid hitherto unknown: this, it is said, was the origin of glass."

Perhaps not the origin of glass, but it could fairly have been the start of glass industry. Green glazes, i.e., glass coatings on pottery, have been dated back to about 12000 B.C., and it is inevitable in the ancient civilizations of that time, in which the making of earthenware pots was commonplace, that glass would from time to time to "discovered". But it would be unlikely that any of these discoveries would contain all three of the significant elements present in Pliny's story: (1) the combination of nitre and fire generating a high temperature; (2) the use of well-washed sand giving glass a spectacular clarity; (3) the discovery being made by merchants, the entrepreneurs of the age, who would surely wish to exploit such an exciting prospect.

A particular feature of the long history of glass making is the existence of long dormant periods between developments of new techniques. Thus, some 1700 years elapsed between the development of glazed earthenware and the making of cored glass vessels, which might be said to be the first true glass articles. These vessels were made by building a coating of glass on a core of moulded sand mounted on a stick and scratching out the sand as the glass was setting. This technique, by which most ancient glass vessels were made, survived for about 1000 years before it was abruptly supplanted about 500 B.C. by the technique of blowing, which persists today.

With the advent of the blowing technique the industry expanded rapidly, not only because of the great improvement in the technique used, but also, no doubt, because of the commercial stability of the Roman Empire. In Rome itself, blown-glass vessels were highly prized and thus commanded high prices. Pliny records the sale of two cups for 6000 sesterces (about £50). However, with the rapid growth of competition the prices were considerably reduced. Glass vessels entered the utility market and were no longer only a luxury in the same class as those of silver and gold. In 220 A.D., there were so many glass workers in Rome that a section of the city was assigned to them and Alexander Severus put a tax on the glass makers - a not unusual kind of reward for success.

Improvements in both the technical and the aesthetic quality of glass took place over the years, of course, but it was not until the nineteenth century that any major technological breakthrough was made.

The first known treatise on glass technology is on some cuneiform tablets excavated at Nineveh. Its estimated date is 640 B.C. This is an excerpt:

"When thou settest out the ground for a furnace ... thou shalt seek out a favourable day in a fortunate month ... thou shalt bring in embryos (born before their time) ... thou shalt offer the due libations before them."

(If one takes development banks as being the modern equivalent of those "born before their time", that last command makes good sense even today.) After having thus explained how to propitiate the powers-that-be, the text gives very practical advice: use of dry wood for fuel etc.

The beginnings of a more scientific approach are seen in the classic work L'arte vetraria by A. Neri, a priest living in Florence, Italy. It was first published in 1612 and translated into English, French, German and Latin. It was a time of great development and glass factories were multiplying throughout Europe. By 1600, the art of out glass had been well developed. In 1615, the use of coal instead of wood for firing glass furnaces was pioneered in England, and flint glass was invented there in 1675. It was called flint glass because its silica content was derived from flints (nodules of silica found in chalk deposits). It also contained lead oxide, which gave it a brilliance not seen in glass before that time. The term "flint glass" is now also used for any clear, colourless glass.



With some notable exceptions, glass technology was poorly served by scientists until recently. In the first place, glass was regarded by them as an anomalous material, not conforming to the simple concept that matter exists in only three states: gas, liquid and solid. In the second place, glass science was severely hampered by the acceptance of the phlogiston theory, which was based on false ideas about calcination and combustion, phenomena of obvious importance in making a material like glass that consists primarily of oxides. On the other hand, the development of the science of optics, in which glass plays such a large part, brought a great deal of experimentation that was indirectly of service to glass technology.

On the practical side, the fundamental processes of glass melting and working cannot be scaled down to laboratory trials satisfactorily because of the nature of glass. A modern glass-melting furnace, for example, represents a heavy capital investment and is expected to last from four to eight years. It therefore requires a great act of faith to make any major change that cannot be proved except on a large scale. For this reason developments in technology have been necessarily slow, with the minimum commitment being made at each stage. The semi-automation and then complete automation that developed at the turn of the century started as a mechanical copying of the skillful manipulations of the glass maker. Later, the machines were designed primarily on mechanical principles to achieve the end-product in the most direct way, and production speeds some hundred times greater were achieved.

Window glass made by hand was formed either by the crown or the cylinder process. In the crown process, a necked sphere was blown and the neck removed to leave a hole. The hole was opened out by spinning the reheated glass until it became a disc with a bulbous centre where it was supported by the spinning rod. The central "bull's-eye", regarded as the main disadvantage of the process, has now become so popular as a collector's item that the process is still in existence to meet this demand. The cylinder process was more productive. The cylinder was blown, its ends detached, and, after splitting it along its length, the cylinder was flattened out in an oven. In the modern process, a variant of the Fourcault process introduced in 1902, the flat glass is drawn directly from the melt as a continuous strip, often more than 2 m wide.

Modern bottle-making machines have also departed from the hand-production sequence. In the hand process the glass was gathered on a hollow tube and

blown in two stages. The neck was formed as a finishing step after the blowing iron was removed. Today the neck of the bottle is still called the "finish", although it is in fact the first part to be formed. A measured quantity of molten glass, the "gob", is fed automatically to the machine and the entire blowing sequence, annealing, and often inspection and packing are fully automatic.

These developments have allowed the glass manufacturer to sell a much improved product at about the same nominal price as hand-produced glass despite the serious reduction in the real value of currency over the years.

Glass containers and drawn sheet represent about 83% of the world production of glass at the present time. Table 1 gives figures for France and the Federal Republic of Germany, taken together, as representative of the industry as a whole.

Table 1. Glass production by type in France and the Federal Republic of Germany 1973

Type	Production volume (million)	Proportion of total (%)	Per capita production (kg)	Annual growth rate (%)
Safety glass	0.536	7.8	4.8	3.72
Plate and rolled	0.628	9.4	5.7	2.36
Drawn sheet	0.627	9.4	5.7	1.28
Containers	4.920	73.4	44.6	5.56

The relative growth rates for plate and rolled glass and for drawn sheet suggest that the former type was overtaking the latter in 1973. Although more recent figures are not available, it is more than likely that this has really happened, not because of a change of market but because of the invention of a new technique for rolling glass (the float process) with a vastly superior surface finish. Not only is float glass an inexpensive substitute for ground and polished plate glass, but it is invading the conventional market for thick drawn sheet.

It has been suggested that the invention of glass windows was a major factor in the drift of civilizations to more northerly climates. Certainly there is today a close correlation between the per capita production of flat glass and the mean mid-winter temperature (see figure). In any case, the

growth rate of window-glass production continues to be phenomenal. Over 1963-1972, the production of 27 countries, representing a population of 1551 million people, increased at the rate of 5% per annum (from 685 million to 990 million square metres).

Flat glass can be densely packed for shipment, and large amounts of it are moved in international trade. Production figures are not therefore a good measure of the producing country's consumption, and straight consumption figures are not easy to obtain. Table 2 is an attempt to calculate the consumption of seven countries from production, import and export data.

Table 2. Consumption of drawn sheet glass in various countries, 1971

Country	Production (t)	Imports (t)	Exports (t)	Consumption (t)	Population (million)	Per capita consumption (kg)
Denmark	24 000	22 294	15 847	30 000	5	6
France	216 000	33 553	60 970	189 000	51	3.7
Germany, Federal Republic of	370 138	95 005	107 077	358 066	61.3	5.84
Italy	562 000	68 190	91 245	539 000	54.5	9.9
Japan	1 145 000	1 785	363 855	783 000	103	7.6
Sweden	52 000	30 786	-	83 000	8	10
Turkey	62 700	6 480	5 080	64 100	36	1.8

Sheet glass ranges typically between 2 and 8 mm in thickness with an average of about 3.5 mm. One ton of 3.5-mm glass corresponds to 114.3 m<sup>2</sup> (1230 ft<sup>2</sup>).

The bulky nature of glass containers militates against their easy export, so that production figures are more likely to reflect consumption. However, indirect exports, in which the bottles or jars are used to contain a product that is being exported, may be significant in some cases. Table 3 gives the production of 17 countries representing about 19% of the world population. Also given is an approximate indication of how bottles are used, based on experience in the United Kingdom of Great Britain and Northern Ireland.

Table 3. Per capita production of bottles in various countries and approximate distribution of use, 1970

Country	Population (million)	Per capita production (kg)	Annual growth rate (%)	Use	Proportion of total (%)
United States	202	65.0	3.7		
Bulgaria	3.3	43.0	10.5		
United Kingdom	55.0	40.0	2.8		
France	50.0	35.0	8.5		
Germany, Federal Republic of	60.0	35.0	8.2		
Sweden	7.8	35.0	5.8	Food	35.0
Italy	53.0	23.0	7.3	Beverages	32.8
Hungary	10.2	19.3	11.0	Pharmaceuticals	17.0
Austria	7.3	18.0	8.5	Toiletries	8.1
Japan	100.5	14.6	8.2	Miscellaneous	4.1
Spain	32.0	14.4	10.7	Direct export	<u>3.0</u>
Poland	32.1	13.2	4.7	Total	100.0
Romania	19.3	12.7	9.2		
Finland	4.8	12.5	6.9		
Cuba	7.9	11.3	5.3		
Portugal	9.2	10.9	9.3		
Yugoslavia	19.6	10.5	10.0		

In spite of competition from plastics and cans, the growth rate for containers is rather greater than that for flat glass.

These dry statistics, which are in any case useful in making a preliminary estimate of market potential, may spark some interest when it is realized that they predict that, if the growth rates are sustained, new production capacity for about 800 000 t of bottles and 160 000 t of sheet glass will need to be added world wide every year. If, for example, one assumes that a glass factory of minimum viability must have an annual output of 20 000, some 50 new glass factories will be needed throughout the world every year. Even though most of the additional business will be absorbed by existing plants and by greater operating efficiency, and even though it is true that a minimum factory can rarely be matched with a local market, it is clear that there is room for many new enterprises in the ever expanding field of glass making.

## II. NATURE OF GLASS AND ITS PROPERTIES

### Constitution

When a liquid cools, a critical temperature, the freezing point, is usually reached at which its component atoms or molecules, which have been moving about chaotically, settle into the orderly arrangement characteristic of a crystalline solid. When the solid is reheated, the atoms break away from the crystal pattern quite abruptly at the same critical temperature, now called the melting point, and chaos - fluidity - is restored. This behaviour suggests that to crystallize a liquid three things are necessary: loss of the energy of random motion, time for the atoms to be marshalled in conformity to the pattern and a pattern to which to conform. That is quite true. For example, if a liquid is cooled so rapidly that insufficient time for marshalling is allowed, and if care is taken to exclude specks of dirt or contact with surfaces with a microscopically orderly arrangement that might provide a pattern and so nucleate crystal growth, the liquid may be supercooled below its normal freezing point.

Usually, the degree of supercooling that is possible is quite small. Nuclei can develop spontaneously and the liquid suddenly crystallize as a consequence. But there are some liquid compositions that can be supercooled very easily and permanently. The most important supercooled liquid known is based on fused quartz, which is made from silica sand or silicate minerals, among the most abundant and widespread natural materials known.

Of course we are speaking of glass. Is, then, this material really a liquid - although supercooled? In most respects it is more "solid" than accepted solids, by virtue of its brittleness, for example. Is it then a solid? In fact, the question only arises because early scientists dictated that there were only three states of matter: solid, liquid and gas. Glass is a "glass", and there are at least 100 000 t of it melted every day to justify the existence of a fourth state of matter - the glassy state.

The glassy state is peculiar in many ways. There are states within the state. We find that time is an important factor, so that the properties of the glass may depend on its previous history. Fortunately, the practical man can largely ignore these effects, provided he accepts that within a certain temperature range, the "transformation" range, the situation is not normal but can be handled by rather crude rules-of-thumb.

Let it be supposed that we are dealing with a typical bottle glass containing about 15% sodium oxide ( $\text{Na}_2\text{O}$ ) and 10% lime ( $\text{CaO}$ ), the remainder being substantially 75% silica ( $\text{SiO}_2$ ). The appropriate relative populations of ions in this glass are 60% oxygen, which are relatively large in size; 26% silicon, which are rather small; 10% sodium; and 4% calcium. The  $\text{Na}_2\text{O}$  is added to help to "flux" the glass, i.e., dissolve the silica and allow melting at a lower temperature (about  $1500^\circ\text{C}$ ), for silica alone has too high a melting point to be melted in available refractory containers. The lime is also a fluxing agent, but its major role is to make the final glass insoluble in water and everyday liquids. In view of the large number and volume of the oxygen ions, we can visualize the molten glass as a conglomerate of oxygen ions held loosely together by the tiny silicon ions, each of these forming bonds with the four nearest oxygen ions, and the calcium and sodium ions scattered at random throughout, having lost their original share of oxygen ions to the general conglomerate. Because of this picture, the silicon ion and others like it are often called network formers and the scattered ions, network modifiers.

At high temperature the sodium ions, and to a lesser extent the calcium ions, are extremely active - like dogs in a flock of sheep. There is little to hold them in any one place and they charge energetically around tending to break up the network of oxygens strung together by the silicons, that is, they help to flux or melt the glass. As the temperature is lowered, the calcium ions, which are larger and carry twice the electric charge, lose their mobility long before the sodium ions. The properties of the glass, e.g., the fluidity and specific volume, broadly conform with this picture, that is to say they are what one would expect on the basis of balance in a conflict between the mobile ions trying to disperse the oxygens and the silicon ions trying to hold them together.

At about  $1000^\circ\text{C}$ , when this glass has the viscosity of a thick syrup, the contest and the mobility are such that a crystalline phase may form if the glass is held there for any length of time. The phenomenon is called devitrification. To avoid it during manufacture it is necessary to take the glass from the furnace above  $1000^\circ\text{C}$  and cool it rapidly during the shaping process to about  $750^\circ\text{C}$ , when the danger will have passed. At this temperature the glass is about as soft as butter; the calcium ions are virtually at rest, but the sodium ions are still active and from time to time they win in the contest with the silicons and the glass can be made to change shape slowly.

At about 600°C the transformation range of temperature begins. The behaviour here is anomalous. Just as time is necessary for the ions to be marshalled into crystalline formations, so also time is required for a mobile ion to find a suitable environment for retirement from its active role. In theory there is always a suitable niche, for although the ions are electrically charged the glass as a whole is neutral, so that there must be vacant sites surrounded by oppositely charged ions. But the ion may be far removed from a niche and for this reason alone condemned to wander long after its "bed-time". Thus, time is required to reach the equilibrium or balance appropriate to each temperature, and during this time the physical properties will change. At high temperatures, equilibrium is established so quickly that any change goes unnoticed. At 600°C, however, it takes seconds to stabilize, at 550°C, minutes, at 500°C, hours and at 450°C, days. Thus it happens that the physical properties at room temperature are not uniquely defined by the chemical composition of the glass but depend also to some extent on the cooling treatment it has received.

In practice, after most shaping operations, the glass is left with a temperature distribution so far from uniform that if it is allowed to cool the differential stresses that build up because of differential contraction are likely to break the glass. The glass is therefore annealed by holding it at a uniform temperature high enough to yield under these stresses, and so disperse them, but not high enough for the glass to distort under its own weight, and then cooling it without introducing significant temperature differences. The annealing temperature is usually in the middle of the transformation range so that this process tends to define the equilibrium condition or "fictive" temperature of the glass also and therefore create reproducible room-temperature properties.

The two features, a temperature range where devitrification is likely and a transformation range of temperatures where physical properties vary with time, appear to be a characteristic of all glasses. There is another phenomenon of considerable technical importance which occurs only in glasses of particular composition. This is known as "phase separation" or "glass-in-glass" separation. Many glass systems are apparently as incompatible as oil and water at low temperatures and yet will melt together as a single liquid at the usual melting temperature. Articles produced from such a melt may seem in no way

exceptional as far as physical properties are concerned and yet it may be found that their resistance to chemicals is much less than anticipated and critically dependent on the length of heat treatment around 600°C. What has happened is that the melt has separated into two different glasses on a sub-microscopic scale, i.e. on a scale too fine to be seen by eye. The average physical properties are unchanged, but nevertheless there are two glasses present, one of which may be soluble in water. The technologically important borosilicate glasses have limitations on this account, but on the other hand the effect has been turned to good account in the production of glasses of unique properties (e.g., Vycor) and the development of the whole new technology of glass-ceramics.

#### Physical properties

Historically, the constitution of glass has been inferred from studies of its physical properties, but for the purposes of this publication the opposite course will be taken. In the first place, the structure is ionic, i.e., it consists of electrically charged particles but has no free electrons. All the electrons are tightly bound to their respective ions and cannot absorb visible light as conduction electrons do. The material is therefore transparent. Since there are no free electrons to carry heat and no periodic structure to propagate elastic waves, there is no easy way of conducting heat, so that glass is a thermal insulator. At low temperatures there is no means of conducting electricity and the glass is a good electrical insulator. (When the temperature is high enough for sodium ions to be mobile, an electrolytic current can develop.) Certain special glasses that break these rules can be melted, e.g., glasses that do have free, light-absorbing conduction electrons, but these must be considered exceptional.

The random structure means that glass is isotropic down to the atomic scale; its properties are the same in all directions. Nor is there any possibility of the existence of gliding planes as in metals, where groups of atoms can slide relative to one another and make the material ductile. The glass therefore remains elastic up to the limit of its strength. One cannot conceive of such a structure being broken under purely compressive stress; in fact, ultimate failure occurs under tension only.



The spherical noble-gas structure of the individual ions means that they have been stripped of most of the properties that made the atoms from which they came distinctive. Their properties arise simply from their electrical charge, physical volume and weight, so that one would expect the numerical value of any physical property of the glass to be the simple sum of contributions from each of the component ions according to the numbers of each present. Although that is not necessarily true of properties such as electrical conductivity, chemical resistance and viscosity, which involve movement of ions within the structure, it is substantially true of those properties that depend on static structure only, such as density, thermal expansion, specific heat and elasticity. Thus, a knowledge of the charges, sizes and weights of ions and certain simple additive rules for combining them are of great value to the glass technologist in formulating his batch (raw-material mixture) to make the best use of available materials or to achieve some modification of the physical properties of his glass. Tables 4, 5 and 6 are designed to provide guidance for batch formulation in a convenient form.

The left-hand side of table 4 gives the electrical charges, sizes and weights of the ions commonly used in glass formulation. The scale of the glass structure is set by the largest and most numerous of the ions, the oxide ( $O^{-2}$ ) ion, which has an ionic crystal radius of 1.40 Å. Close packing of spheres of that size would leave two sizes of sites for other ions. The smaller of these could hold a positive ion of radius 0.315 Å, which would then have four oxide ions as nearest neighbours. The larger could hold an ion of 0.58 Å radius with six nearest neighbours. The silicon ion ( $Si^{+4}$ ) is too large to fit into the smaller site, although it could form a stable, electrically neutral structure with four nearest-neighbour oxygens. The result is a distortion of the orderly pattern that close packing would give. The boron ion ( $B^{+3}$ ), on the other hand, is so small that it can fit anywhere in the structure, so that one might expect that the addition of  $B_2O_3$  to the batch would give some unusual effects.

These sites should not be thought of as closed cavities; indeed, small atoms like helium can migrate from one vacant site to another provided the way is not blocked by (say) sodium or calcium ions, which tend to lodge in them.

Table 4. Structural properties of ions and ionic equivalents of their oxides

Ion	Radius (Å)	Atomic weight	Formula of oxide	Ionic equivalent <sup>a/</sup>
B <sup>+3</sup>	0.22	10.8	B <sub>2</sub> O <sub>3</sub>	1.73
4-0 site	0.32			
P <sup>+5</sup>	0.34	31.0	P <sub>2</sub> O <sub>5</sub>	0.85
Be <sup>+2</sup>	0.37	9.0	BeO	2.40
Si <sup>+4</sup>	0.42	28.1	SiO <sub>2</sub>	1.00
As <sup>+5</sup>	0.47	74.9	As <sub>2</sub> O <sub>3</sub>	0.61
Al <sup>+3</sup>	0.53	27.0	Al <sub>2</sub> O <sub>3</sub>	1.18
6-0 site	0.58			
V <sup>+4</sup>	0.60	50.9	V <sub>2</sub> O <sub>5</sub>	0.66
Ti <sup>+4</sup>	0.62	47.9	TiO <sub>2</sub>	0.75
Fe <sup>+3</sup>	0.67	55.8	Fe <sub>2</sub> O <sub>3</sub>	0.75
Li <sup>+1</sup>	0.68	6.9	Li <sub>2</sub> O	4.03
Cu <sup>+2</sup>	0.70	63.5	CuO	0.76
Mg <sup>+2</sup>	0.71	24.3	MgO	1.49
Zn <sup>+2</sup>	0.74	65.4	ZnO	0.74
Na <sup>+1</sup>	0.98	23.0	Na <sub>2</sub> O	1.94
Ca <sup>+2</sup>	0.98	40.1	CaO	1.07
Cd <sup>+2</sup>	1.00	112.4	CdO	0.47
Sr <sup>+2</sup>	1.15	87.6	SrO	0.58
Pb <sup>+2</sup>	1.26	207.2	PbO	0.27
F <sup>-1</sup>	1.33	19.0		
K <sup>+1</sup>	1.33	39.1	K <sub>2</sub> O	1.28
Ba <sup>+2</sup>	1.35	137.3	BaO	0.39
O <sup>-2</sup>	1.40	16.0		

<sup>a/</sup> The ratio of the number of positive ions furnished by a given weight of the oxide to the number furnished by the same weight of SiO<sub>2</sub>.

The weight of the ion is of little consequence except in its effect on the density of the glass. It is given in table 4 for a practical reason: the glass technologist normally deals with the weights of oxides in his batch formulation and may forget that equal weights of, say, CaO and MgO do not

contain the same number of ions. The right-hand side of table 4 gives the ionic equivalent of each oxide, i.e., the number of metal ions in a given weight of the oxide relative to the number of  $\text{Si}^{+4}$  ions contributed by the same weight of  $\text{SiO}_2$ . The number given for  $\text{CaO}$  is 1.07 and for  $\text{MgO}$ , 1.49. Thus, if the technologist wishes to substitute magnesia ( $\text{MgO}$ ) for lime ( $\text{CaO}$ ) without upsetting the proportion of alkaline earths in the batch, he must use a smaller amount of  $\text{MgO}$  since it furnishes more ions per gram than the  $\text{CaO}$ . The ratio of the weight of  $\text{MgO}$  to that of  $\text{CaO}$  for an equal number of ions is then  $1.07/1.49$ .

Although not so logical, factors based on the weight percentage of oxide in the batch are more convenient to use than those based on the mole percentage (as the ionic equivalent is). The factors given in table 5, which are in that form, are applicable for calculating the thermal and elastic properties of common soda-line glasses. They are not accurate for large departures in composition, however.

It is of course vital to have some idea of the effect of substitutions on the working characteristics of the glass. Viscosity is a dynamic property and is therefore not expected to be a truly additive function of the static properties of the glass constituents. Nevertheless, in dealing with such a complex problem it is helpful to assume that each component makes its own independent contribution. Table 6 gives the increase (+) or decrease (-) in temperature required to maintain the viscosity at its initial value when one weight percentage unit of the silica is replaced by another oxide. Because of the huge variation of viscosity of glass with temperature, it is more convenient to refer to the logarithm of the value of the viscosity  $\eta$  (in poises) rather than the value itself. A viscosity of  $\log \eta = 2$  corresponds roughly to the melting temperature, 3.5 to the temperature at which the glass is withdrawn from the furnace, and 13 to the annealing temperature. The temperature interval between  $\log \eta = 3.5$  and  $\log \eta = 5.5$  is the "working range" of the glass and extends from about  $1080^\circ\text{C}$  to  $350^\circ\text{C}$ .

#### Anomalies

In addition to the anomalies that occur in the region of the annealing temperature, there are two well-known anomalies connected with batch formulation: the borate anomaly and the mixed-alkali anomaly.

Table 5. Calculation of physical properties of soda-lime glass from its oxide composition

(a) Factors (per unit of weight percentage)

Oxide	Coefficient of thermal expansion (a) (10 <sup>-7</sup> per °C)	Specific volume (v) (10 <sup>2</sup> cm <sup>3</sup> /g)	Surface tension (γ) (dyne/cm)	Young's modulus (e) (kilobar)	Specific heat	
					f	g
SiO <sub>2</sub>	0.05	0.44	3.25	6.9	.000463	0.1657
Li <sub>2</sub> O	6.56	0.350				
Na <sub>2</sub> O	4.32	0.324	1.27	9.8	.000829	0.2229
K <sub>2</sub> O	3.9	0.357		6.9	.000335	0.2019
MgO	0.45	0.322	5.77	3.9	.000514	0.2142
CaO	1.63	0.231	4.92	6.9	.000410	0.1709
BaO	1.40	0.122	3.7	6.9		
B <sub>2</sub> O <sub>3</sub>	-0.66	0.460	0.23	5.9	.000635	0.198
Al <sub>2</sub> O <sub>3</sub>	0.14	0.373	5.98	14.7	.000453	0.1765
ZnO	0.70	0.168		9.8		
ZrO <sub>2</sub>	0.23	0.173				
PbO	1.06	0.093				

(b) Formulas

If the factors a, v etc. and weight percentages p corresponding to the oxide constituents are labelled with the subscripts 1, 2, ..., the formulas for the properties of the glass are as follows:

Coefficient of linear thermal expansion:  $a = a_1p_1 + a_2p_2 + \dots$

Specific volume = 1/density:  $v = v_1p_1 + v_2p_2 + \dots$

Surface tension:  $\gamma = \gamma_1p_1 + \gamma_2p_2 + \dots$

Young's modulus:  $E = E_1p_1 + E_2p_2 + \dots$

Mean specific heat, 0°-t° C:  $s = \frac{ft + g}{0.00146 + 1}$

where  $100f = f_1p_1 + f_2p_2 + \dots$ ,

and  $100g = g_1p_1 + g_2p_2 + \dots$

Table 6. Temperature change required to restore initial viscosity and change in working range when one weight percentage unit of the  $\text{SiO}_2$  is replaced by another oxide ( $^{\circ}\text{C}$ )

Replacement oxide	Initial viscosity ( $\log \eta$ )			Change in working range ( $\log \eta = 3.5 - 5.5$ )
	2	3.5	13	
$\text{Na}_2\text{O}$	-17.0	-12.5	-3.5	-4.3
$\text{MgO}$	-9.0	-5.0	+3.3	-3.5
$\text{CaO}$	-20.0	-11.8	+8.0	-5.6
$\text{B}_2\text{O}_3$	-20.0	-11.6	+7.3	-7.0
$\text{Al}_2\text{O}_3$	+12.5	+9.6	+2.8	+2.6
$\text{Fe}_2\text{O}_3$	-11.5	-8.0	-	-3.4
$\text{PbO}$	-12.4	-9.8	-2.9	-2.3

The borate anomaly strikes the eye immediately in table 5:  $\text{B}_2\text{O}_3$  is the only oxide that makes a negative contribution to thermal expansion. The explanation is as follows. Except for its charge, an ion confined at a site in a solid is like a gas molecule at extremely high pressure, i.e., confined to an extremely small volume. It bombards the "walls" of its site and pushes them outwards, leading to expansion of the whole solid. However, the ion carries a positive electric charge and is surrounded by negative charges. If the positive charge is fully compensated, the resulting electro-static forces tend to contain the ion and reduce its thermal motion. In glass, singly charged ions are not fully compensated, and their contribution to thermal expansion is therefore large. That is borne out in table 5; the singly charged alkali ions  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  make by far the largest contribution. Moreover, because of their high mobility, they can even escape into sites that carry no electric charge, so that their contribution to thermal expansion becomes even greater. Thus, most of the thermal expansion of the glass is attributable to the alkali ions, and at temperatures in the region  $500^{\circ}\text{C}$ - $600^{\circ}\text{C}$ , where their mobility greatly increases, the thermal expansion increases rapidly.

Now, the most natural position to find a boron ion ( $0.22 \text{ \AA}$ ), with its charge of +3, is in the very small space left ( $0.21 \text{ \AA}$ ) when three oxygen ions come together, i.e., in one of the small channels that join the regular sites in glass. That is the kind of site they occupy in fused  $\text{B}_2\text{O}_3$ , which has a high thermal expansion. If, however, alkali ions occupy neighbouring sites, the

boron ions are repelled by their positive charge into a 4-0 site, i.e., the kind of site occupied by silicon in low-expansion fused silica. Thus, the first addition of  $B_2O_3$  to a glass containing alkali lowers the expansion coefficient, just as increasing the silica content would. If too much boron is added, however, it may form its own glass system in rivalry with silicon, and phase separation might occur. The effect of boron addition is therefore not simple; its small size allows it to adopt several roles.

The mixed-alkali anomaly is that properties such as electrical and chemical resistivity, which involve the movement of mobile ions, change to much higher values if a mixture of two alkalis is added than if either alkali is added alone in the same mole proportion. The probable explanation is that the smaller the ion, the more easily does it pass through channels in the structure but the less easy is its removal from a charged site to become mobile, because the electrostatic field is greater. Thus, at a given temperature, a lithium glass would have a certain number of highly mobile ions, while a sodium glass would have more mobile ions but of lower mobility. In both cases, of course, there are as many vacant charged sites as there are mobile ions that vacated them, but these vacancies are characterized by their static structure and not the nature of the ions that had just occupied them. If now the two glasses are mixed, the more mobile lithium ions quickly occupy the many sites vacated by the less mobile sodium ions, leaving only these slow ions free to wander. It is like a game of musical chairs, in which the more agile player wins.

#### Service performance

The man in the street is not concerned with the constitution or chemical composition of glass. His concern is that his windows or bottles retain their transparency and do not break easily. In short, he is concerned with their chemical, mechanical and thermal durability. The manufacturer, provided he meets these requirements, has considerable scope in formulating the glass to suit his own conditions.

#### Chemical durability

The structure of a soda-lime glass, as we have seen, is predominately one of large oxygen ions held together like a bunch of grapes by small silicon ions and a scattering of sodium and calcium ions. As far as chemical durability is

concerned, the oxygens are passive: they play much the same role as they do in anodized aluminium, where they provide a protective skin on this otherwise extremely reactive metal. Although a liquid in contact with glass may have a short-range structure very similar to the glass itself, the mobility of ions in it is much greater. If the liquid contains alkali ions these tend to migrate into the glass, diluting the silica content, possibly to the extent that the surface layer becomes soluble in water. Sodium ions, for example, form a layer of soluble sodium silicate (water-glass) on the surface. When the surface layer dissolves, the layer below is exposed to attack. Thus, the attack of an alkaline solution will continue as long as it remains unspent and in contact with the glass. The extent of the attack is in part determined by the mobility of ions in the glass and in part by the chemistry of the alkali-enriched surface layer. When the attack is interrupted, insoluble lime may be left on the surface as a gray deposit, giving the glass an etched appearance.

If the solution contains no alkali ions or if it is water or acid, the alkali ions diffuse out of the glass and are replaced by small hydrogen ions (often hydrated), so that the surface layer becomes a hydrogen-silicate glass rather than water-glass. This surface layer remains integral and acts as a barrier against further attack. Eventually, it may become detached because of strains arising from the difference in structure. If it flakes off, a new surface is presented for renewed attack. This kind of attack is therefore intermittent.

The initial reaction of water with a glass surface is remarkably rapid. If two bottles are taken hot from a lehr (annealing oven) and rubbed together, the glass will be abraded. If the bottles are allowed to stand for an hour or two, the rubbing friction is greatly reduced. Apparently the glass picks up an invisible film of moisture from the air, which lubricates the surface. The film seems to be a surface gel; stains caused by metallic ions, e.g. iron and copper, that have diffused into the film are difficult to remove.

It has been found that bottles that show a bloom (a cloudy film) after having been in an oil-fired lehr have improved durability after the bloom has been washed off. The bloom is a deposit of sodium sulphate produced by the attack of the  $\text{SO}_2$  coming from the combustion of sulphur-containing fuel oil on the surface of the glass. As suggested above, the removal of sodium ions from the surface of glass improves its chemical durability.

The action of hydrofluoric acid (HF) is exceptional. Since HF dissolves silica, attack is immediate; a ground glass surface can be polished by dipping it in the acid. Most cut-glass is now polished in this way in a fraction of the time that was formerly taken to polish it mechanically.

Apart from ion mobility and chemistry there are other complications. An increase in temperature may increase the rate of attack relatively more for one glass than another; an accelerated test conducted at high temperature may put glasses in a different order of chemical resistance than a test conducted at normal temperatures. Any tendency for phase separation in a glass will usually lower its chemical resistance. That can reverse the expected effect of some additions. For example, the substitution of some of the CaO by BaO in such a glass, which at first sight seems to be a step in the wrong direction, may greatly improve the durability because it reduces the tendency for phase separation. Some of the elements initially leached from the glass into the attacking solution may increase (alkalis) or hinder ( $\text{Al}_2\text{O}_3$ , ZnO) further attack. The problem of improving the chemical durability of the product with additives is therefore highly complex, and only a rough indication of the influence of particular additives can be given. In the following list, the number is the percentage increase or decrease (-) in durability that can be expected when a 1% addition of the oxide is made to a normal bottle glass composition.

$\text{Na}_2\text{O}$	-50
$\text{MgO}$	28
$\text{CaO}$	12
$\text{BaO}$	9
$\text{ZnO}$	7
$\text{PbO}$	2

$\text{K}_2\text{O}$ , by itself, has a figure similar to  $\text{Na}_2\text{O}$ , but if the two alkalis are mixed the durability is better than if either is added alone.  $\text{Al}_2\text{O}_3$  has a positive factor of about 22%, but only up to about 2% total alumina in the glass.  $\text{B}_2\text{O}_3$ , if substituted for  $\text{Na}_2\text{O}$ , has a positive effect up to about 4% substitution because of the reduction in  $\text{Na}_2\text{O}$  content.



### Mechanical durability

The mechanical properties of glass, which determine its robustness in service, are peculiar. Although the tensile strength of glass is intrinsically about 1000 times greater than that of steel, the value that must be used in prudent design is 10 times smaller, i.e., 1000 psi. The reason for that huge margin is that the designer must take the weakness of the surface of the glass into account. Also, the strength depends on the duration of the test and the size of the test sample. These factors so dominate the mechanical behaviour of glass that differences in chemical composition are comparatively insignificant and for practical purposes can be ignored.

There are two main theories that attempt to explain these features. One attributes the effects to a reaction between the glass and atmospheric moisture during breakage. The other is more fundamental and will be discussed here.

The complete homogeneity of glass makes it an ideal material to which to apply the mathematical theory of elasticity. According to this theory, if a material containing a flaw is subjected to tension the tensile stress will be intensified near the flaw to an extent depending on the size and shape of the flaw. If the intensified stress is great enough to cause the flaw to become larger, the stress will be further increased, leading to progressive and catastrophic breakage. Unlike most other physical properties, the strength of glass is therefore expected to depend on the presence of local abnormalities of structure rather than the average structure as a whole. That is easily demonstrated, of course; the glazier "cuts" glass by starting a crack at a scratch made with a hard (e.g. diamond) point. The odd fact is that glass seems to behave as if it contained many small flaws - large enough to be seen under the microscope, but in fact never seen. These hypothetical flaws are known as "Griffith flaws" after the man who first used the concept.

Above, we likened the action of mobile ions in molten glass to that of dogs in a flock of sheep, breaking silicon-oxygen bonds from time to time because of their activity. This action still persists at annealing temperatures, and the question arises as to whether this bond-breaking activity could be significant enough at the much lower room temperatures for such broken bonds to constitute a Griffith flaw? At first sight it would seem that such an

event would be so rare as to be of no significance, but when one remembers that there are about one million million million sodium ions in each cubic centimetre of glass and each has many opportunities every second to try its strength against the silicon-oxygen bonds, the chances of success are not negligible. On this dynamic picture it might be said that Griffith flaws would be born, and probably immediately disappear, again and again throughout the glass, at random, many times each second. Microscopic examination would of course not reveal them. If, however, the glass is under sufficient stress, one of these flaws could become "frozen" in place, whereupon the stress-intensifying action would cause it to propagate until macroscopic breakage occurred.

Actually, not one, but several, of these events acting in unison would be necessary to develop into a self-generating flaw. That affects the probability of flaw formation considerably. If, on the other hand, the site of the flaw is on the surface of the glass, far fewer of these events are necessary so that the chance of breaking from the surface is very much greater than the chance of breaking from deep within the glass.

If this is the correct explanation of the strength behaviour of glass, there are a number of features that one would expect to find: glass would always break from a surface. The greater the surface area the greater the chances of breakage. The longer the duration of the stress the greater the chances of breakage. There would be an inherent variation in test results on identical samples because failure is a matter of probabilities. The strength would increase at very low temperatures as the mobile ions lose their mobility. Finally, and somewhat surprisingly, the strength would not vary much with the number of mobile ions.

All these features are in fact found. Glass always breaks from a surface although this may be an internal surface at the boundary of a bubble or at a stony inclusion. Test samples of very small surface area have a high strength; fine glass fibres are exceptionally strong. Glass is about three times stronger under impulse loading than under a stress maintained for a long time. Tests on identical samples show a coefficient of variation of about 13%. At liquid-nitrogen temperatures the strength of glass is much higher. The strength of fused silica, which contains only traces of sodium, is less than twice the strength of a soda-lime glass with about 15%  $\text{Na}_2\text{O}$ .

It seems that the only practical way to achieve high strength is to protect the surface. Boro-silicate glasses usually give a better service performance because they resist scratching. Bottles are sometimes given a titanizing treatment, a thin-film deposit of  $TiO_2$  or  $SnO_2$  on the surface, for much the same reason. Any process that can induce a permanent compressive stress into the surface layers will increase the strength to the extent that this stress must first be overcome before a tensile stress can break the glass from the surface. Of course a corresponding tension must occur elsewhere in the glass to balance the compression, but that can be in the body of the glass, where the strength is much greater. Toughened, or tempered, glass is made by utilizing this principle. Instead of being annealed, the glass is heated to a uniform temperature almost high enough to distort it and then cooled rapidly by an air blast applied uniformly over the surface. The resultant parabolic temperature distribution creates a parabolic stress distribution when the temperature finally evens out, with the compressive stress in the surface approximately twice the maximum tensile stress introduced in the central layers. The strength can be increased by a factor of 2.5-5 by this means. If the glass ultimately breaks, it breaks into small square-edged pieces that are much less likely to cause injury than the sharp slivers from broken annealed glass. Even greater practical strengths can be obtained by grading the surface structure in an after-process, in which, for example, the surface alkalis are exchanged by soaking the glass in a bath of molten alkali. All the processes mentioned must be applied only to finished articles, for cutting the glass would release the inner tension and result in breakage.

#### Thermal durability

Thermal durability is the ability to resist sudden temperature variations. In glass, it is like the mechanical durability in being a matter of probability and depending on the same factors; however, it does depend on chemical composition insofar as this determines the thermal expansion coefficient of the glass. (See table 5.) Thermal durability is inversely proportional to the thermal expansion coefficient. Obviously, the greater the expansion or contraction for a given temperature change, the greater the stress introduced. The thermal durability of soda-lime glass ( $\alpha = 9 \times 10^{-6}$ ) is only about one third that of boro-silicate glass ( $3 \times 10^{-6}$ ), and fused silica ( $0.5 \times 10^{-6}$ ) is almost impossible to break by thermal shock alone.

### Glass-ceramics

Devitrification can be the bane of the glass technologist's life. A piece of cold refractory in the working-end of a glass furnace, to which the glass clings and devitrifies and from which it breaks away from time to time to give crystalline inclusions, perhaps in every article made, can cause havoc to the production figures because of the stresses set up around these inclusions and the resultant breakage. However, in recent years controlled devitrification of glass has been turned to excellent account in the creation of glass-ceramics.

Basically, the success of the glass-ceramics turns on two factors already referred to above. The first follows from the principle that if the scale of dimensions is made small enough, as in the case of glass fibre, a very high strength is obtained. Thus, if the material is sub-divided on a fine enough scale by fine-grained but uniform devitrification, not only will it stand up to the inherent stresses caused by differential thermal contractions of the different crystalline species, but also the practical strength of the composite may be much higher than that of the parent glass. The second factor is the extraordinary wide range of physical properties that can be tailored into these new materials.

It will be appreciated that so long as the physical properties of a material are a simple average of contributions from its component ions the possible range of properties is very restricted. That is the case with glass. In conventional ceramic materials, on the other hand, the range is much wider because the ions are arranged in the complex geometries of the component minerals; the properties are an average of the contributions of chemical compounds rather than of the individual ions. The range is limited only by the availability of natural minerals and one's ability to sinter a mixture of them into a compact whole more or less free of voids. In the case of glass-ceramics the mineral species are created in situ (they may actually be unknown in nature), and the problem of voids does not arise. As a consequence a very large range of properties is possible. For example, glass-ceramics can be made with a zero or even negative coefficient of thermal expansion so that their thermal shock resistance is almost infinite. And, because of the absence of voids, they can be made transparent if the optical properties of the crystallites are suitably chosen.

Glass-ceramics are melted and worked like conventional glasses. The trick of the new technology is to nucleate that type of crystal development that will produce the desired property. The nucleation may be done by ultraviolet light or by a nucleating agent such as  $\text{TiO}_2$ . The nucleation must be effective enough to over-ride the natural tendency for crystallization to proceed only from the surface; otherwise, a layered, non-random structure results. In this respect, a tendency for phase separation is actually advantageous. Not only does it give another parameter to help control the type of crystal obtained, but also the devitrification develops in the bulk of the glass from the myriad interfaces between phases. Often, therefore, the parent glass has two competing glass formers, such as  $\text{SiO}_2$  and  $\text{P}_2\text{O}_5$ .

A typical sequence of events in manufacture is first making the article by conventional means, cooling it to the nucleating temperature, which is usually well below the devitrification temperature, and holding it there for some time. The temperature chosen often corresponds to the incipient softening temperature, say  $600^\circ\text{C}$ . The temperature is then raised slowly enough for the crystals to grow large enough to give the article rigidity and finally held at say  $800^\circ\text{C}$  until the desired degree of crystallinity is obtained.

Although the broad principles of glass-ceramics technology are understood, its development is still largely empirical. Nevertheless, the potential scope of these new materials is so great that the technology is likely to grow and become as important as glass technology itself.

### III. RAW MATERIALS AND GLASS-BATCH ADDITIVES

#### Raw materials

The raw materials used to make glass must be chemically analysed to determine their oxide composition so that their proportions in the batch can be accurately calculated. The final glass must also be analysed to check on these calculations because some components may be lost by volatilization or carried away as dust by the flames. Every furnace has its own idiosyncrasies in that respect.

Soda-lime glasses usually contain magnesia ( $MgO$ ), alumina ( $Al_2O_3$ ) and a number of other oxides in small amounts that may be deliberately added or present as impurities in the available minerals. The suitability of local minerals for glass making turns largely on their freedom from contamination by iron. A glass containing 0.06%  $Fe_2O_3$  has an objectionable colour when seen against a white table-cloth. The colour can be masked by adding decolourizers to the batch to make glass table-ware containing that much iron salable. In window glass, a higher level of iron (0.1%  $Fe_2O_3$ ) can be tolerated because in service the edges of the glass are hidden and the colour is therefore less noticeable. Since silica sand is the largest component of the glass batch, its iron content should not exceed about 0.025%  $Fe_2O_3$  so as to allow scope for the limestone or dolomite, which frequently contain 0.1%, and for some inevitable iron contamination that may occur in the factory, particularly if a high proportion of scrap glass (cullet) is used. The problem of controlling colour requires daily attention because the colour depends not only on the raw materials but on the furnace atmosphere and flame settings.

The considerations mentioned above already constitute a formidable list for the conscientious glass technologist. It is clear that only some of the guiding principles can be given in a publication of this size. Most of the literature on glass making has been of an academic nature, making it difficult for the practical technologist to find and extract the information needed to solve immediate problems. The attempt made here to predigest the information for practical use has the usual disadvantages of trying to cut corners and should be approached with that in mind.

In dealing with common soda-lime glasses, the technologist never starts completely from scratch. Either such a glass is already in production or he is working to a text-book composition, so that new raw materials or batch

formulations are merely departures from a norm and, because of the additive relation, the physical properties of the final glass can be calculated as described in chapter II. The main question that arises is whether such a change will cause trouble in melting or working the glass. Conversely, the need may be to find some change in the batch that will alleviate a difficulty in melting or working.

The quality of the sand, about 60% of the batch, is the most important consideration. If it is contaminated with iron, a beneficiation treatment should be considered. The iron content largely determines how far other local materials can be used or whether an acceptable degree of colour can only be obtained by importing sand or using decolourizers. The quality must be reliably consistent or must be made so by pre-mixing, so that any calculation remains valid by the hour and by the day. That holds true, of course, for any of the raw materials used.

Minor additives such as de-colourizers and refining agents are best considered separately; the batch formulation is usually calculated on the basis of the main components to which a special mix is added to make day-to-day corrections. The proportion of special mix is often related to the proportion of cullet fed back into the furnace so that the proportion of cullet can be varied on a daily basis to keep from accumulating too much of it. Apart from serving in the interests of good house-keeping, large stocks of cullet should be avoided because they gather dirt and, being of uncertain age, may not correspond in composition to the glass currently being melted, thereby invalidating the batch calculation.

#### Glass sand

A first indication of the suitability of a local sand may be had by examination under a low-power microscope. The quartz grains, which are easily recognized, may themselves appear colourless, but there may be some dark grains among them. Often the quartz grains are partially cemented together by a yellowish material, a clay which contains much of the iron. The clay can usually be removed by scouring the grains against each other and washing. If that proves to be the case, there is a good prospect of beneficiating the sand by simple means, but if the quartz grains themselves are stained yellow, or if the dark grains are numerous, the prospects are

poor. The dark specks may be organic and burn away harmlessly, but often they are iron or titanium ores. Using sophisticated methods, it may be possible to eliminate them because of their greater density or their magnetic properties. An indication of the degree of the contamination can be obtained by supposing that the specks are 10%  $\text{Fe}_2\text{O}_3$ , so that if there are less than 1 for every 100 clear grains, the iron content of the sand is less than 0.1%. This rough test may indicate whether a thorough investigation of the quality of the sand is justified.

If the quartz grains are large, say greater than 0.6 mm in diameter, melting will be slow. In this case, it is usual to "scalp" the sand by sieving off the larger grains. If the grain size is too small (0.1 mm), there may be trouble with dusting both inside and outside the furnace. If the sand is washed, the tailings will often be carried away with the clay, but if the original sand does not have a fairly uniform grain size of about 0.5 mm, the yield of good sand may be poor because of large losses in sieving and washing.

The most effective parts of a beneficiation plant are usually the scourer and the classifier. Scouring usually consists of passing the sand, with water, through a battery of powerful impellers, the blades of which drive the slurry alternately upwards and downwards until it finds its way out at the exit. The solids content of the slurry should be high, 70-80%, so that the particles abrade each other. The slurry is then diluted so that it can be pumped (sometimes through more elaborate equipment of questionable value) to the classifier, where the sand and clay are separated by elutriation. This machine consists of an Archimedean screw operating in a cylindrical trough and flushed with water so that the clay and fine particles are floated away and the deposit of sand is driven to a higher level outlet, from which it falls to the draining pits. Ultrasonic sieves are available which can be very effective in separating the tailings from the clay particles.

One of the frustrating features of sand preparation is that at some stages it needs to be dry and at others, wet. The cost of drying is high, and dry sand creates dusting problems. When delivered from the quarry, it often contains stones or aggregates that must be removed to avoid damage to the process equipment. If the sand is stored under cover for a few days, it can usually be reduced in moisture content to allow sieving through a  $\frac{1}{2}$ " mesh



without further drying and then made into a slurry. The final sand will contain about 40% water, which may be reduced to about 15% in properly designed draining pits. This residual moisture would of course boil out in the melting furnace, but that would require fuel. Therefore, it is logical to remove it in advance, making it possible to base the batch calculation on dry sand without needing to know the moisture content. Full moisture removal also provides a free-flowing material well suited to mechanical handling but apt to give dusting and segregation problems, which are usually alleviated by adding moisture to the batch in the mixer. On the basis of the chemical analysis of the beneficiated sand, the glass technologist can judge to what extent he can use other local raw materials. For example, the alumina content may have been washed out of the sand, making it necessary to reintroduce about 2% alumina.

#### Sources of alkalis and alkaline earths

The second largest component of the batch, and the most expensive, is the source of alkali, usually soda ash (sodium carbonate). It is usually necessary to import it. Soda ash is specially prepared for the glass industry as free-flowing granules of high purity and presents no problems provided it is properly stored. The alkaline earths Ca and Mg are usually added as the carbonates, which decompose at red heat; the evolution of  $\text{CO}_2$  is regarded as advantageous in stirring the melt. The main reason for using the carbonates, however, is their low cost and excellent storage properties in the form of limestone. The inclusion of  $\text{MgO}$  is optional in bottle-glass formulations but essential in sheet glass because it helps solve the problem of devitrification in the sheet-glass process.

The grain shape and size of these materials is important. Even at its hottest, molten glass is about 1000 times more viscous than water and the amount of mixing that can occur during melting is small. The homogeneity of the final glass therefore depends greatly on the effectiveness of mixing in the cold and freedom from segregation thereafter. The effectiveness of mixing the raw materials, in turn, depends on their grain shape and size. If all the materials consisted of spherical grains of the same size, ordinary mechanical mixing would be quite effective since all grains would be treated alike. In that case, the ideal diameter of the grains would be about 0.5 mm,

which gives the best compromise between melting rate and dusting tendency for quartz sand. If the particles are unequal in size, the smaller ones will remain trapped there during melting, upsetting the local composition. If the grains are of uniform size but too large, there will be rich zones and depleted zones in the final melt.

In practice, because of different surface activity of different materials, there is an optimum duration for mixing. If it lasts longer, certain components may gather into balls so that their effective grain size becomes grossly excessive. The action is similar to the way rolling snowballs grow. For this reason a mixer that has a shearing action is to be preferred to one with a simple tumbling action.

The melting points of most of the individual oxide components are higher than practical glass-melting temperatures, so that the "melting" of glass at, say,  $1500^{\circ}\text{C}$  is actually a chemical reaction between the acidic and alkaline components rather than a physical melting and dissolution. (See table 7.) Pure  $\text{Al}_2\text{O}_3$ , being neither acid nor alkali, is difficult to "dissolve" in this sense. It is convenient to introduce it in the form of a mineral in which it is a constituent part of the structure e.g., feldspar  $(\text{K}_2\text{O}, \text{Na}_2\text{O})\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$ , which melts at  $1100^{\circ}\text{C}$ - $1200^{\circ}\text{C}$ .

The decomposition of carbonates takes place over a range of temperatures, and, although it is obvious that the sequence of events during melting is important, it is not possible to predefine the conditions. Such facts as these can be derived from table 7 or have been learned from experience: If  $\text{NaNO}_3$  (m.p.  $307^{\circ}\text{C}$ ) is the sole source of  $\text{Na}_2\text{O}$  in the batch, it may melt completely and drain out of the batch before the batch has reached a temperature high enough for reaction with the silica. The pressure of  $\text{CO}_2$  from  $\text{CaCO}_3$  reaches 1 atm at about  $950^{\circ}\text{C}$ , but it will dissolve in molten alkali carbonate at about  $800^{\circ}\text{C}$  and so be brought into close contact for reaction with quartz sand. If molten  $\text{Na}_2\text{SO}_4$  is reduced to the sulphite by addition of coal dust, it is even more reactive towards the quartz. It is because of such facts that it is advantageous to add the alkali in more than one form.

Small substitutions of  $\text{MgO}$  (m.p.  $2800^{\circ}\text{C}$ ) for  $\text{CaO}$  (m.p.  $2572^{\circ}\text{C}$ ) do not seem to make much difference in the melting rate. However, in experiments with a basic glass of 14%  $\text{Na}_2\text{O}$ , 12%  $\text{CaO}$  and 74%  $\text{SiO}_2$ , the replacement of 2 wt% units of  $\text{CaO}$  by  $\text{BaO}$  (m.p.  $1923^{\circ}\text{C}$ ) was found to be optimum as far as

Table 7. Melting and decomposition properties of compounds used in glass making

Compound	Melting point (°C)	Decomposition temperature (°C)	Decomposition product	Properties of product	
				Melting point (°C)	Decomposition temperature (°C)
SiO <sub>2</sub>	1725				
Li <sub>2</sub> CO <sub>3</sub>	618	...	Li <sub>2</sub> O	~1700	
Na <sub>2</sub> CO <sub>3</sub>	851	700-1000	Na <sub>2</sub> O	1275 <sup>a/</sup>	
NaNO <sub>3</sub>	307	380	Na <sub>2</sub> O <sub>2</sub>	460	657
Na <sub>2</sub> SO <sub>4</sub>	884				
K <sub>2</sub> CO <sub>3</sub>	891	...	K <sub>2</sub> O <sub>2</sub>	490	
MgCO <sub>3</sub>		~700	MgO	2800	
CaCO <sub>3</sub>		~800	CaO	2572	
BaCO <sub>3</sub>		1450	BaO	1923	
B <sub>2</sub> O <sub>3</sub>	490				
Al <sub>2</sub> O <sub>3</sub>	2050				
As <sub>2</sub> O <sub>3</sub>					
crystalline	193 <sup>a/</sup>				
amorphous	315 <sup>b/</sup>				

a/ Sublimes.

b/ With sublimation.

reduction of melting time was concerned. That amount reduced the melting time by 40%. If 0.2 of the Na<sub>2</sub>O content was supplied by Na<sub>2</sub>SO<sub>4</sub> instead of Na<sub>2</sub>CO<sub>3</sub>, a similar optimum gain was obtained, and the replacement of 1 wt% unit of SiO<sub>2</sub> by B<sub>2</sub>O<sub>3</sub> gave about half this gain.

The conversion of batch composition to the theoretical glass composition is most conveniently done in the manner set out in table 8. It is usual to start the calculation with the relative weights of raw materials in the batch,

Table 8. Example of the calculation of glass composition from batch composition

Batch composition					Glass composition		
Raw material	Relative weight	Oxide contribution			Oxide	Relative weight	Proportion of total (%)
		Oxide	Weight fraction in raw material	Relative weight in batch			
Sand	1 000	SiO <sub>2</sub>	0.997	997	SiO <sub>2</sub>	1 099	72.5
		Al <sub>2</sub> O <sub>3</sub>	0.003	3			
		Fe <sub>2</sub> O <sub>3</sub>	0.00025	0.25			
Soda ash	335	Na <sub>2</sub> O	0.580	194	Na <sub>2</sub> O	221	14.6
Salt cake	5	Na <sub>2</sub> O	0.430	2.2	B <sub>2</sub> O <sub>3</sub>	11	0.7
Borax	30	Na <sub>2</sub> O	0.163	4.9	Al <sub>2</sub> O <sub>3</sub>	30	2.0
		B <sub>2</sub> O <sub>3</sub>	0.365	11.0	CaO	90	5.9
Feldspar	150	SiO <sub>2</sub>	0.680	102	MgO	64	4.2
		Al <sub>2</sub> O <sub>3</sub>	0.180	27			
		Na <sub>2</sub> O	0.130	20			
		Fe <sub>2</sub> O <sub>3</sub>	0.001	0.2			
Dolomite	160	CaO	0.560	90	Fe <sub>2</sub> O <sub>3</sub>	0.6	0.04
		MgO	0.400	64			
		Fe <sub>2</sub> O <sub>3</sub>	0.001	0.2			
Total	1 680			1 516		100	

Note: The theoretical glass-to-batch ratio  $1516/1680 = 0.902$  takes into account only the loss of gas and water from the raw materials. In practice the weight fractions determined by chemical analysis (fourth column) are adjusted for each furnace to correct for volatilization losses and for losses by dust carried over by the flames into the flues. These additional losses usually amount to 5-10% in the aggregate and the practical glass-to-batch ratio (melted-weight factor) may lie between 0.80 and 0.85.

taking the weight of the sand to be 1000. Then the oxide contributions of each material are calculated from their weight fractions (as found by chemical analysis) in the material. (The values used in the table are assumed for the purpose of illustration.) Minor ingredients, such as colouring or refining agents, can be ignored in the first approximation.

Volatilization losses are also ignored in the example. They may, however, be significant. The following values have been quoted in the literature. They refer to percentage of the component, not of the glass, and in practice are found to vary from furnace to furnace, presumably depending on the extent to which the melting batch is exposed to the flames.

Na <sub>2</sub> O from soda ash (carbonate)	3.2
Na <sub>2</sub> O from salt cake (sulphate)	6.0
K <sub>2</sub> O	12.0
B <sub>2</sub> O <sub>3</sub>	15.0
ZnO	4.0

The reverse calculation, deriving the batch composition from the desired glass composition, can be done using reciprocal factors, starting with the most complex raw material and deducting the oxides supplied with it. However, for small departures it is often just as easy to work by trial and error in the forward direction.

#### Glass-batch additives

##### Additives to prevent devitrification

In making an article by pressing or blowing glass in a mould, there is seldom any major problem with devitrification because the glass is chilled rapidly through the devitrification range by contact with the mould. In the case of drawn glass for sheet or tubing, there is no abrupt chilling and the process depends critically on maintaining temperatures suitable for the glass to adopt the required shape unassisted by a shaping tool.

For each glass composition there is a critical temperature, known as the liquidus temperature, above which the melt is a stable liquid but below which crystalline phases start to form. At the liquidus temperature, the liquid and crystalline phases are in equilibrium; crystals will neither grow nor dissolve. For a glass of composition 16% Na<sub>2</sub>O, 12% CaO and 72% SiO<sub>2</sub> this

temperature is  $1010^{\circ}\text{C}$  and the maximum rate of growth takes place at a somewhat lower temperature,  $955^{\circ}\text{C}$ . Growth usually starts from the surface and proceeds inwards at about 1 mm/h. Below  $955^{\circ}\text{C}$ , the increasing tendency for crystal growth is offset by the decreasing mobility of the ions. Of course, the viscosity is also increasing rapidly as the temperature is lowered; but this does not affect the rate of crystal growth, which requires a certain ordering of the ions that is not directly related to the viscosity as such. Nevertheless, the mobility of ions decreases rapidly with temperature and one would therefore expect the rate of devitrification to decrease rapidly with decrease in liquidus temperature.

A small addition of almost any soluble oxide different from the three main ones,  $\text{SiO}_2$ ,  $\text{CaO}$  and  $\text{Na}_2\text{O}$ , should reduce the tendency to devitrify because it must increase the difficulty of marshalling ions into the crystal lattice; that is, it should lower the liquidus temperature. If too much is added a new crystal species with a relatively greater growth rate may arise.

The partial substitution of  $\text{MgO}$  for  $\text{CaO}$  in a soda-lime glass is of great practical importance and illustrates the point. In a parent glass of composition 16%  $\text{Na}_2\text{O}$ , 10%  $\text{CaO}$  and 74%  $\text{SiO}_2$ , two different crystals, cristobalite ( $\text{SiO}_2$ ) and devitrite ( $\text{Na}_2\text{O}\cdot 3\text{CaO}\cdot 6\text{SiO}_2$ ), grow at the temperature of maximum growth rate. As the calcium is replaced devitrification is suppressed, but eventually new  $\text{MgO}$ -containing crystals appear in the manner shown in table 9. The figures suggest that the amount of devitrification could be reduced to about 20% if  $\text{CaO}$  and  $\text{MgO}$  are used in the ratio of about 6 to 4, provided the working characteristics of the glass are not adversely affected. As it happens, the mineral called dolomite ( $\text{CaO}\cdot\text{MgO}\cdot 2\text{CO}_2$ ) has  $\text{CaO}$  and  $\text{MgO}$  in the ratio 5.82/4.17. The rock called dolomite, formed in nature from solutions rich in both calcium and magnesium carbonates, is rich in the mineral dolomite and is uniform in composition over large areas. A much more common dolomite-containing rock is dolomitic limestone, a limestone that has become enriched in  $\text{MgO}$  as a result of ion exchange with magnesium solutions percolating through it. This rock has a much more variable  $\text{CaO}/\text{MgO}$  ratio.

Table 9. Effect of substitution of MgO for CaO in a glass of composition 16% Na<sub>2</sub>O, 10% [x MgO, (1-x) CaO], 27.1% SiO<sub>2</sub>

X (%)	Liquidus temperature (°C)	Temperature of maximum growth rate (°C)	Growth rate (mm/h)	Crystal species
0	1000	910	0.095	Cristobalite (SiO <sub>2</sub> )
	970	910	0.31	Devitrite (Na <sub>2</sub> O·3CaO·6SiO <sub>2</sub> )
2	995	895	0.02	Cristobalite
	950	895	0.11	Devitrite
4	970	860	0.01	Cristobalite
	925	860	0.06	Devitrite
6	920	850	0.008	Cristobalite
	880	850	0.005	Na <sub>2</sub> O·2MgO·6SiO <sub>2</sub>
8	950	860	0.018	Na <sub>2</sub> O·2MgO·6SiO <sub>2</sub>
	970	910	0.008	Diopside (CaO·MgO·2SiO <sub>2</sub> )
10	1100	910	0.05	Na <sub>2</sub> O·2MgO·6SiO <sub>2</sub>

The effect on viscosity of, say, a 4% replacement can be judged by the figures in table 6 by imagining that 4% CaO is first replaced by 4% SiO<sub>2</sub> and then this silica replaced by 4% MgO. This would require the temperature corresponding to log  $\eta = 2$  to be increased by  $4(20-9) = 44^\circ$ , so that melting would be more difficult.

The addition of  $\text{Al}_2\text{O}_3$  to the batch (which is approximately the same as substituting it for silica) has similar effects. The maximum benefit occurs at about 2% addition. This lowers the liquidus by about  $40^\circ\text{C}$  (corresponding approximately to 4% substitution by  $\text{MgO}$  in table 9) but requires an increase in melting temperature of about  $25^\circ\text{C}$  and in working temperature of about  $19^\circ\text{C}$ .

Although the aim is always to produce a homogeneous glass of calculated composition, in practice there may be considerable variation from the calculated composition because of solution of refractories, for example, and particularly from differential volatilization of constituents. The exposed hot surface is most likely to be deficient in  $\text{Na}_2\text{O}$ . It is instructive to take a typical soda-lime composition, such as 16%  $\text{Na}_2\text{O}$ , 10%  $\text{CaO}$ , 74%  $\text{SiO}_2$ , and follow the liquidus temperature as the  $\text{Na}_2\text{O}$  is progressively extracted:

$\text{Na}_2\text{O}$ content, %	16	14	12	10	8	6	4
Liquidus temperature, $^\circ\text{C}$	1000	1120	1240	1400	1470	1520	1580

It is clear that if the surface, depleted of alkali by volatilization, is not compensated by diffusion from within, it will devitrify even at a melting temperature of  $1500^\circ\text{C}$ . This is the reason for the formation of scum in the melting furnace referred to in the next chapter. Devitrification also occurs in the flame working of simple soda-lime glasses, which usually develop a mat surface when worked in this way. The strong yellow colouration of the flame indicates the presence of sodium vapour in it; an early trick of the trade was to melt common salt onto the surface to restore its polish.

### Fining agents

The time taken to dissolve all the raw materials, the batch-free time, is only a small part of the total time required to free the glass of bubbles (the fining time) and to make it homogeneous (the refining time). (The term "refining" is often used for both the latter processes and fining agents added to expedite the removal of bubbles are sometimes called refining agents.)

The processes involved in fining are not fully understood, but a rough idea of them (and of the bubble problem, in general) can be obtained by considering the interaction between gas and glass. Glass is a composite of oxides in which the metal and oxygen ions are in almost exact stoichiometric



proportions; however, slight variations can occur, and these are of importance in certain properties, such as colour, which depend on the presence of trace admixtures. Thus, one speaks of oxidized and reduced glasses although only small differences in oxygen potential are involved. These differences are often brought about by the furnace atmosphere above the molten glass. The molten glass adjusts itself to this atmosphere, and the content of dissolved gases reflects the partial pressures of the gases in the furnace atmosphere. The total volume of dissolved gases at standard pressure and temperature (STP) is about equal to the volume of the glass, but of course the proportion by weight is very small, about 5 parts in 10 000. In some respects the dissolved gas behaves as if chemically combined, in others as if it were merely physically absorbed. If the glass contains an oxide like  $As_2O_3$ , which readily takes up oxygen to convert to  $As_2O_5$ , it may take up about 20 times the normal oxygen content.

If molten glass is placed in a vacuum chamber it usually foams up to about six times its former volume. That suggests, first, that there is no great difficulty in nucleating bubbles (as there is in the case of super-heated water, which "bumps" and "hammers"), and, second, that it takes time for the dissolved gas to diffuse to the surface, where it could escape without having to form new bubbles. Diffusion time is proportional to the square of the distance: it takes 100 times longer to travel 1 cm than to travel 1 mm. Therefore, gas will escape more readily into a nearby bubble than into a more distant but larger surface. It also follows that, although on the average the gas in the glass is in equilibrium with the gas in the furnace atmosphere, there will be local and rapid departures from the average in the vicinity of each gas bubble in the glass.

It is known that the solubility of gas in glass decreases with increasing temperature. The diffusion rate, on the other hand, increases rapidly with temperature. Naturally, both the solubility and the diffusion rate differ for different gases. The small hydrogen molecule can permeate glass easily at intermediate temperatures, particularly if the channels through the network are not blocked by modifier ions, but the large  $CO_2$  molecules appear to have a very low diffusion rate. Of course, the diffusing gas may also react with either the ions in the glass lattice or other diffusing species. As mentioned above, oxygen may be taken up by  $As_2O_3$  and chemically combined as  $As_2O_5$ . Hydrogen

may be oxidized to water or carbon monoxide may be oxidized to carbon dioxide, and these larger molecules may become physically trapped because they cannot readily diffuse. That is often a practical difficulty in melting glass under reducing conditions. A glass refined under an atmosphere containing hydrogen and carbon monoxide contains a certain amount of these gases after equilibrium is reached. If the glass is now brought under an oxidizing atmosphere in the working end or fore-hearth of the melting unit, the gases, as they diffuse out, will be met by oxygen diffusing in, and bubbles of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  may form just beneath the surface. The phenomenon is known as "re-boil" and can be very persistent because the refining stage is over and the bubbles are too small to have enough buoyancy to float them to the surface. Similarly, in the case of an oxidizing atmosphere, specks of carbon building up on the burner tip may become detached and fall onto the oxidized glass. The carbon monoxide that forms diffuses into the glass and is further oxidized to  $\text{CO}_2$ , which is precipitated as fine bubbles that mar the product.

Aside from large amounts of air and moisture, significant amounts of  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{O}_2$  and other gases are given off during the melting of the raw materials, mostly in large bubbles, which rise quickly, float and burst at the surface of the melt. The small bubbles are less buoyant and take much longer to rise. The situation is illustrated in table 10, which gives the time taken by bubbles of various diameters to rise 20 cm to the surface of the melt at various viscosities. The corresponding temperatures indicated are those for a typical soda-lime glass.

There are only two possibilities for bubble elimination: they either float to the surface and escape, or the gas in them dissolves in the glass. The figures in table 10 show that any bubble less than 1 mm in diameter would take more than three hours to rise from the bottom of a tank 1 m deep even at the highest temperature. Since convection currents in the tank move approximately that fast, one might say that any smaller velocity is not significant and any bubbles smaller than 1 mm must be removed by other means.

The disappearance of bubbles by dissolution depends on the solubility of the contained gas, its concentration in the glass surrounding the bubble, and the pressure of the gas within the bubble. Because of surface tension acting over the curved surface of the bubble, the gas pressure inside is higher than the hydrostatic pressure outside; the calculated excess pressure is given in the last column of table 10.

Table 10. Time for bubbles of various diameters to rise 20 cm to the top of a typical glass melt at different temperatures (Minutes)

Bubble diameter (cm)	Temperature (°C)					Excess pressure (atm)
	1542	1451	1373	1305	1245	
	log $\eta$ = 2.2 $n$ = 158.5	log $\eta$ = 2.4 $n$ = 251.2	log $\eta$ = 2.6 $n$ = 398.1	log $\eta$ = 2.8 $n$ = 631.0	log $\eta$ = 3.0 $n$ = 1000	
1.0	0.4	0.6	0.9	1.5	2.4	0.0012
0.5	1.5	2.5	3.3	6.2	9.8	0.0024
0.1	38.9	61.5	97.3	154.3	244.7	0.0113
0.05	155.2	245.8	389.7	617.5	978.7	0.0239
0.01	388.3	615.4	975.3	1545.9	2449.9	0.1134

Table 11. Experiment demonstrating the differential solution of small bubbles in glass a/

Elapsed time (min)	Observed diameter of four bubbles labeled a, b, c, d (0.25 mm)				Remarks
	a	b	c	d	
0	3	4	5		Separation 3-4 mm
25		4	6		Bubble a dissolved
45		3	7		
50		2	6	20	Approach of large bubble d
55		1	3	20	
60				20	Bubbles b and c dissolve, leaving only the large bubble d.

a/ Based on a microscopic examination of a borosilicate glass at 1300°C.

These excess pressures are not large enough to increase significantly the overall concentration of dissolved gas, but they are of great importance locally, that is, within distances small enough for diffusion to be rapid. To be in equilibrium, a small bubble would have to be surrounded by a higher concentra-

tion of dissolved gas than a larger bubble, but if the bubbles are close to each other, diffusion will level out the concentration gradient with the result that the small bubble will tend to dissolve and the large one grow. The reality of this situation is illustrated by the experiment recorded in table 11, in which three bubbles separated by 3-4 mm and later a fourth, larger one were observed under the microscope. The glass was a borosilicate at a temperature of about 1300°C. It will be seen that, even separated by distances 10 times greater than their diameters, the smaller bubbles are absorbed by the larger ones.

It is clear that if this differential solubility could be exploited one would have a means of expediting the fining of glass, for, at one and the same time, the small bubbles of negligible buoyancy are dissolved while the larger ones are made more buoyant. One way of doing this would be to saturate the glass with a gas that diffuses readily. In oxidized glasses, oxygen is the obvious choice; the common practice is to add oxides of arsenic or antimony with enough nitrate to oxidize them to the higher oxides  $As_2O_5$  or  $Sb_2O_5$ , which are also soluble in the glass. These oxides tend to retain their excess oxygen until the highest melting temperature and then give it up when it is most needed. Too much would cause foaming and there is little advantage of adding more than 1 lb per 1000 lb of sand in the batch. If the cullet content of the batch is high, it is well to remember that the arsenic oxide it contains requires reoxidation by addition of nitrate. The soda added as nitrate should be sufficient to oxidize all the  $As_2O_3$ .

Another possible way of expediting fining would be to cause bubbles to coalesce. In fining with arsenic coalescence is apparently extremely rare. It was observed only once in the writer's experiments. Bubbles may cling together for a long time if they have the same diameter until eventually the balance topples and one grows at the expense of the other. When sulphate is added to the batch, however, the situation completely changes and coalescence becomes the rule. Apparently this is a surface tension effect, the sulphate acting as a foam-breaker. Since the effect requires actual contact it can hardly be of importance in the later stages of fining when the "seed" (fine bubbles) are well dispersed.

#### Colouring and decolourizing agents

Small amounts of coloured oxides may be added to the batch to colour the glass. Some oxides, such as cobalt oxide, give extremely intense colours and

are therefore used in extremely small quantities. For example, only one part per million (ppm) of cobalt oxide will give a pale blue glass.

The actual colour produced by a colourant depends on the environment of the particular colouring ion in the glass and particularly on the oxygen potential of the glass. Many colours are therefore sensitive to the furnace atmosphere. Some of the commonly used colourants and the colours they produce in different atmospheres are listed in table 12.

More often the glass technologist is concerned with trying to remove an unwanted colour, e.g., green from the unavoidable inclusion of some iron oxide in his raw materials. There are two courses open to him. He can melt under oxidizing conditions so that the iron gives a less objectionable, pale yellow-green colour, or he can mask the residual colour by deliberately adding colourants (now called decolourizing agents) of a complementary shade, just as the laundryman may add blue to change a yellow-whiteness into a more acceptable blue-whiteness. In the case of glass, considerable skill is required. Not only is there the problem of keeping in step with variations in the iron content of the raw materials, but also the quantitative and qualitative problem of contending with variations in melting conditions, for a more reducing furnace atmosphere will change the basic shade towards blue-green and at the same time intensify the colour. In a continuous melting furnace it takes four or five days for a change in batch composition to become 50% effective and another four or five days to reach the 75% mark. There is real danger therefore, in taking emergency measures to correct a sudden development of, say, a green colour in what is supposed to be colourless glass and ending up with a pink glass because the conditions which caused the green corrected themselves before the batch change took effect.

The yellow-green shade of oxidised iron requires a complementary violet colour to mask it. If the glass is a potash-lime glass rather than the much more common soda-lime glass, nickel oxide can be used; unfortunately, the violet colour does not develop in soda-lime glasses. Neodymium is an excellent decolouriser but too expensive for use in most glasses. Manganese dioxide can be used in pot-melted glass, but then the glass becomes susceptible to solarisation, i.e., the development of a purple colour under prolonged exposure to sunlight. The most common practice is to use selenium (pink) combined with cobalt oxide (blue). Although these chemicals are expensive, both have such colouring power that very small quantities can be used.

Table 12. Colours given by common colourants used in glass making

Colourant	Melting conditions	
	Oxidizing	Reducing
Cobalt oxide	Violet-blue	Violet-blue
Chromic oxide	Yellow-green	Emerald-green
Iron oxide	Yellow-green	Blue-green
Manganese dioxide	Amethyst to purple	None
Neodymium oxide	Violet	Violet
Nickel oxide	Violet (in potash glasses) Brown (in soda glasses)	
Selenium	Fugitive	Pink
Se-CdS	None	Ruby (after reheating)
Sulphur	None	Yellow to amber
Uranium	Yellow with fluorescent green	Fluorecent green

Table 13. Approximate selenium requirements for decolourizing glaes as a function of its arsenic and iron content (Parts per million (ppm) in the batch)

Fe <sub>2</sub> O <sub>3</sub> content of the glass (%)	As <sub>2</sub> O <sub>3</sub> content of the batch (%)			
	0.00	0.05	0.10	0.25
0.01	1.9	5.0	6.9	16.9
0.02	3.8	9.4	13.7	32.5
0.03	5.6	13.1	20.6	50.0
0.04	7.5	17.5	30.6	67.4
0.05	11.2	25.0	41.2	89.8
0.06	16.9	36.2	60.0	125.0
0.07	28.7	63.0	100.0	

There is a basic conflict in requirements here. Table 12 shows that high-cost selenium is fugitive under oxidizing conditions and yet oxidizing conditions are necessary to avoid the blue-green iron colouration. If one depended only on the furnace atmosphere to strike the right balance the colour rendering would be variable. Some stabilizer is wanted and, as discussed in connexion with fining,  $As_2O_3$  acts as an oxygen buffer and is very effective in stabilizing the colour, although this means that much of the selenium is lost. Table 13 gives some indication of the quantities of selenium usually found necessary in glasses of given iron and arsenic content. Bearing in mind that arsenic is required to function also as a fining agent it seems that about 0.05%  $As_2O_3$  in the batch will provide a good compromise. If much more arsenic is used, it is necessary to take into account that the colour shade is perceptibly influenced by annealing.

It seems logical to suppose that the amount of cobalt oxide used should be directly related to the  $Fe_2O_3$  content and the amount of selenium not made fugitive by the arsenic. In practice, the iron content is seldom analyzed; it is inferred from the colouration, and the cobalt oxide added is about 0.5 ppm.

If colour develops in a clear glass because of a reduction of oxygen potential, it is possible, in theory, to correct it by increases in amount of complementary colouring agents added; but every such increase reduces the over-all transmission of the glass, giving it a grey dullness. Obviously it is better to remedy the cause than to try and cover it up by masking it. The technologist will therefore attempt to assign causes and remedy them before modifying a well established batch composition. The colour shade and the speed with which it develops are indicative; a rapid development of a blue-green shade is probably due to flame impingement, for example. Is tramp iron being properly removed by the magnetic separator? Is the batch or cullet contaminated with carbonaceous dirt that is tending to reduce it? Is the furnace atmosphere properly controlled with at least 2% excess air? Is carbon building up on the burner tips and deflecting the flames, or is misalignment causing the flames to touch the glass? If he is satisfied with the answers to those questions, the technologist's next question is, "Is there sufficient nitrate to oxidize the arsenic?" If nitrate alone will put things right, there is no problem; but if more arsenic is needed, the selenium will probably also have to be increased, in accordance with the figures in table 13.

Instrumentation is of little help in gauging these slight colour variations. Colour comparisons are often made by observing the colour through 15-cm long rods drawn from the furnace each day and retaining those which form a range of colours for future comparisons. It is useful to remember that it usually takes a 10% change in colouring agent to give a perceptible change in colouration.



#### IV. GLASS MELTING

The melting of glass is not simply a matter of reaching a melting temperature. The process takes time and most of the fuel used is expended in maintaining the temperature during the process. The melting efficiency is largely determined by the ability to complete the process in the shortest possible time so that the cost of fuel is minimized.

The thermodynamic heat content of the finished glass is only about 0.017 kWh/kg greater than that of the raw materials. When this is compared with the 0.45 kWh/kg or so required to heat the glass to a temperature suitable for working, it is obvious that it matters little whether raw materials or cullet is used as the starting material. Four times as much energy, about 2 kWh/kg, is needed to maintain the furnace temperature during melting. This energy is of course expended by the hour rather than according to through-put and is largely a fixed cost for as long as the furnace is in operation. Actually, the variable fraction of the fuel input is rather greater than the 20% that the figures above suggest because when the load on the furnace increases, not only must additional fuel be used to maintain the temperature, but also the temperature itself needs to be increased to offset the shorter time available for the melting process.

Furnaces identical in design and set at the same control temperature often have significantly different performances. One reason, frequently overlooked, is that although in the ideal case (no heat losses) the heat input is related only to the temperature at which the glass is withdrawn from the furnace and not to any higher temperature it may have reached, in reality the melting rate depends strongly on these higher temperatures and their distribution in the furnace. Because of heat losses, the local heat input corresponding to the difference in temperature between the hot and the withdrawal temperature is not wholly recovered within the furnace chamber. Nevertheless, the principle remains: the distribution of the heat input is as important as its actual magnitude.

#### Furnaces

In fuel-fired furnaces, a large amount of heat is required to heat the vast quantities of air necessary to burn the fuel. About 10 ft<sup>3</sup> of air are necessary for every 1000 Btu heat content of the fuel. If the heat required

to heat the air is carried away by the waste gases discharged to the stack at  $1450^{\circ}\text{C}$ , the loss would be 475 Btu, reducing the effective calorific value of the fuel to 525 Btu. The usual practice is therefore to preheat the air, using the hot waste gases to do so. In the regenerative furnace the waste gases are passed through a large chamber of loosely packed refractory bricks, which act as a heat store; meanwhile the combustion air is drawn through a similar regenerator chamber which, in a previous cycle, was made hot in this way. Approximately every 30 min the roles of the two chambers are interchanged.

In this system, the combustion air is usually preheated to about  $930^{\circ}\text{C}$ , and 83% of the calorific value of the fuel is realized. Its disadvantages are that the furnace must be equipped with two sets of burners and a complex valve system that enables switching the flame, air and waste gases. The switching must be carried out quickly and effectively (usually automatically) because any disturbance to the melting conditions must be avoided. The regenerator chambers often occupy more space than the furnace itself.

The recuperative furnace employs a simpler system of heat recovery. The hot waste gases and the combustion air pass through parallel channels in a refractory or metal heat exchanger (recuperator) and no switching is involved. On the other hand, the conditions are very exacting, since hot gases and cold air are passing in close proximity in an intricate structure and a leakage of one into the other can cause the system to fail. For this reason a preheating to more than  $700^{\circ}\text{C}$  is seldom achieved, so that the effective utilization of the calorific value of the fuel is about 75%.

For large furnaces, the greater capital expenditure of the regenerative system is usually justified by the additional savings; hence it is more common than the recuperative system.

In fuel-fired continuous furnaces there is also a problem in that the flame must have sufficient volume and length for combustion to be complete before it is drawn into the flues. In a large furnace this can be accomplished across the tank and the temperature distribution adjusted by control of four or five burners. Therefore, large furnaces are usually cross-fired. For small furnaces cross-firing would require many small burners (see unit-melters below), and such furnaces are usually end-fired, the flame being projected up the tank length and the gases being conducted in U-turn back to the end from which they entered to be drawn off into the recuperator or regenerator.

The required temperature distribution can also be obtained by differential insulation. Obviously, insulation must be used with caution because its reactivity with the molten glass and furnace gases increases rapidly with interface temperature, which is largely determined by the degree of external insulation. The following table gives the relative heat losses of two 90-t/d regenerative furnaces, one a typical tank furnace built in 1955 and the other a similar furnace built 20 years later.

	<u>1955</u>	<u>1975</u>
Melting glass and delivery at working temperature	19.1	19.1
Tank walls and bottom	<u>16.9</u>	<u>9.01</u>
	36.0	28.1
Stack	18.3	18.3
Crown	9.8	3.04
Breast walls	2.8	1.68
Port neck	<u>2.7</u>	<u>1.26</u>
Subtotal	33.6	24.3
Regenerator system	13.3	6.10
Cooling water and air	8.4	8.40
Unaccounted for	<u>8.7</u>	<u>6.38</u>
Subtotal	<u>30.4</u>	<u>20.88</u>
Total	100.0	73.3

The 27% lower loss of the newer furnace was due to the use of heavier insulation, which was made possible by the use of the superior refractory materials available in 1975. The specific energy consumption of the two furnaces was 2.42 kWh/kg and 1.77 kWh/kg.

The design of a furnace is not dictated by its thermal efficiency alone. If frequent colour changes are required, for example, it is important to make the change in the shortest time possible. A change is usually made by draining, flushing out with the new cullet and refilling with the new batch. Besides the time taken and the fuel used in the interval, a large amount of cullet is formed if the holding capacity of the tank is large. The problem is solved in part by the unit melter, a low-capacity, low-cost furnace designed to supply

a single glass-forming machine. Here, adaptability is more important than fuel economy. The unit melter consists of long, narrow channels along which the glass progresses through its various stages of melting. It is cross-fired by many small burners, but the burnt gases are drawn back to the end of the furnace so that it has some of the features of an end-fired furnace. The unit melter has proved so popular that sizes much larger than envisaged by the original design concept are now made, and sometimes recuperators are fitted as a concession to fuel economy.

Even more versatile than the unit melters are the all-electric furnaces, which, in contrast, have a very high thermal efficiency. They have the disadvantage of using an expensive fuel, electricity. Here the heat is produced within the glass itself by ohmic losses; thermal losses are minimal. The glass is actually melted from within rather than from the surface. Of course, the glass must be in a container and heat will be lost through the container walls; but, as can be seen from the figures combining to give the first subtotal under 1975 in the table above, an efficiency of at least  $19.1/28.1$ , or 68%, should be attainable. In practice, efficiencies between 60% and 80% have been achieved because higher glass temperatures are possible and the tank can be much smaller than in conventional furnaces.

A common practice is to seek the best of both worlds by placing electrodes in a conventional oil-fired furnace and boosting the output with additional electrical heat. So-called "mixed melters" have been introduced. These use oil to provide the holding heat and meet the heat losses and electricity to actually melt the glass.

As has been mentioned above, the performance of any glass-melting furnace depends very much on the skill of those controlling it and upon the standard of quality of the glass produced. The expected performance of the different melting technologies for container glass given in the following table will nevertheless provide a first guide for comparison. The expressions give the total daily (24-h) energy consumption in kilowatt-hours as a function of the design capacity C (tons per day) and the amount drawn T (tons per day). In each expression, the first two terms (in parentheses) represent the fixed, and the third term the variable, consumption rates.

Oil-fired furnaces

Regenerator	(14 654 + 14070) + 1612T
Recuperator	(17 100 + 885.80) + 1783T
Unit melter	(15 322 + 720.60) + 2363T

Mixed

Oil recuperator (17 100 + 1445.9C) + 500T with 50% electrical boost	
Mixed melter	(17 100 + 40.72C) + 600T

Electric

All-electric	(1143.8 + 171.8C) + 460T
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When the fuel cost is considered, one finds that for large furnaces the regenerative type is the most economical, but for smaller furnaces there is a wider choice which may be determined by other considerations. Of course, fuels other than oil can be used - coffee beans have been used in Mexico, and furnaces are sometimes equipped with dual systems so that, for example, a switch from natural gas to fuel oil can be made at short notice to meet supply difficulties. The exceptional performance of all-electric furnaces is usually offset by the high cost of electrical energy. In effect, the thermal inefficiency is shifted out of the glass factory back to the power station and still has to be paid for.

Melting

Good melting practice, that is, making the most of the furnace in use, turns on two broad principles. The obvious and most important one is that good glass, once formed, must not become contaminated by incompletely melted glass. The second has already been mentioned: A local high temperature, and therefore a rapid melting rate, need not cost additional fuel, provided the heat excess associated with the local high temperature is subsequently usefully employed.

It is clear that the first principle can be met by heating the batch of raw materials uniformly so that every part of it goes through each stage at the same time and any intermingling does not hold up the process. This is practiced in pot melting and in day-tanks that work on a cycle. A batch large

enough to meet a day's requirements is placed cold in the hot pot or day-tank, heated until melted, and worked. The pot, which may be covered, is in a furnace that runs continuously, whereas in the day-tank the glass bath is itself the furnace and is usually directly heated by flames applied above the glass. When the glass level becomes too low to permit further hand-gathering, the cycle is repeated. Obviously, such a process is not suited to the production of glass by automatic machines; however, it has its place in the production of high-priced articles made by hand.

The unit melter provides another means of meeting the first principle. The batch is introduced continuously at one end of a long channel and goes through the various melting stages as it passes along to the working end. Some success in meeting the second principle is achieved by drawing some of the excess heat from the hottest section back over earlier, cooler sections, using the hot gases to carry it.

The situation in a conventional tank furnace is not nearly so well defined. The melting chamber, which may be only 50% longer than it is wide, communicates with the working end, a much smaller chamber, by means of a "throat" or opening at the bottom of the "bridge-wall" that separates the two chambers. It might be thought that this low throat serves to separate the melted and unmelted glass; in fact, the skimming action of the bridge above is effective in excluding only the most buoyant contaminations, and partially melted glass reaching the bridge-wall will almost certainly be drawn down by the viscosity of the glass and so reach the working end. The real function of the bridge-wall is to act as a temperature barrier, so that the glass at the working end is at a temperature low enough for working. Some other means must be found for ensuring that the glass in the region of the bridge-wall is already fully melted and refined. Although a mechanical barrier is impracticable, a thermal barrier can be created by establishing an excess-temperature zone across the tank, two thirds of the way down the length of the melting chamber. Superheating of the glass at this point causes it to rise, and on reaching the surface it flows both forwards to the bridge-wall and backwards to the back wall, pushing back any unmelted material floating on the surface. Besides preventing contamination by unmelted batch in this way, the excess heat assists in the melting of the batch. When the superheated glass is cooled by this action, it sinks to the bottom, only to be drawn again into the excess-temperature zone to repeat its beneficial action.

Meanwhile, the forward flowing stream of superheated glass is rapidly refined because of its excess temperature and sinks when cooled by contact with the bridge-wall. These convection currents involve much more bulk movement than that caused by the withdrawal of glass from the furnace, so that most of the glass flowing down the bridge-wall flows back across the bottom to rise in the hot zone and repeat its refining action.

With good furnace control, therefore, the first principle is obeyed, and, since at least half the excess heat is carried back to the melting batch, the second principle is also. It is clear, however, that the thermal barrier requires a strict maintenance of temperatures, for if the hot zone moves about or fades, a pocket of unmelted glass may pass through and become entrained in the forward roll of glass, and glass quality will suffer. In controlling the situation it is not sufficient to rely on the temperature records; the surface of the melting glass itself should be frequently examined. It should show a clear lake of glass extending back from the bridge-wall to a line of scum about half way down the tank. This line is the forward edge of the melting batch. There may also be a thin line of scum along the bridge-wall; this is usually silica formed because of the loss of volatiles from the superheated glass. The scum should not increase in amount, because it is continuously being washed back into solution by the superheated glass.

Well-positioned sight holes that are comfortable to use are an important aid to control; sometimes closed-circuit television is used.

#### Bubblers

Sometimes a submerged weir and bubblers are placed across the tank to help stabilize the thermal barrier. Bubblers are simple devices by which air bubbles about 6 in. diameter are fed through pipes in the bottom of the tank and allowed to float to the surface, where they burst. There is a common misconception that the rising bubbles drag the glass upward, as solid bodies would, but that is not true; there can be no shearing action at a gas-glass interface. Upward motion occurs because the mean density of a column of glass containing bubbles is lower than that of a neighbouring column that does not. The glass in the column therefore tends to float. Since the displacement of glass where the bubble is first formed may cause erosion of the bottom refractories, the pipes should be installed some distance above the bottom. The air has to be pulsed or metered because the pressure necessary to start a bubble forming against surface tension would blow a bubble of indefinite size if maintained.

### Air pollution

It was mentioned in connexion with batch formulation (chapter III) that it is necessary to allow for the volatilization losses of some of the constituents during melting. In some cases the loss exceeds 10%. Much of the volatilized material condenses in the regenerators and flues and is a nuisance, but part of it escapes to pollute the atmosphere. In the case of common soda-lime glasses, the main pollutant is sodium sulphate, but in the case of lead glasses or fluoride opals, the pollutants are much more serious and may require expensive equipment to scrub or otherwise remove them from the waste gases.

The major source of the volatiles in a conventional furnace is the large area of melting glass exposed to the flames in the melting chamber. In an all-electric furnace, in which the surface of the melt is covered by a blanket of cold batch, the volatiles are trapped in situ, and the loss of fluorine, for example, is typically reduced from about 30% to 2½%. The all-electric furnace is therefore preferred for continuous melting of such glasses. In pot-melting for hand production the pot is closed during melting and the problem does not arise.

It is instructive to attempt to account for all the inputs to a glass furnace as a means of determining what is lost to the atmosphere. For example, an oil-fired furnace may be melting 50 t of glass per day with an oil consumption of 10 t. If the oil has a sulphur content of 5%, it means that 0.5 t of sulphur must be going somewhere. If it passes to the atmosphere as 1.5 t of sulphuric acid, that could hardly be regarded as a neighbourly act. In fact, much of the sulphur reacts with the soda vapours in the furnace to form about 2 t of sodium sulphate, much of which will condense in the flues, regenerators etc. The loss of expensive soda from the glass composition (a cost of about \$90 per day in this case) is therefore not wholly wasteful if oil of high sulphur content is being used, for it is compensated by the beneficial neutralization of a more objectionable pollutant.

Usually, the more elaborate the heat-recovery system is (i.e., the lower the exit temperature) the less is the amount of pollutants discharged at the chimney but the greater is the need for regular cleaning of the system. The capital and maintenance costs of operating waste-heat boilers etc. has tended to militate against these energy-saving devices. However, in view of the increasing awareness of the evils of pollution, it is wise to bias a decision based on economic factors in the direction that favours reduced pollution.



## V. GLASS FORMING

As thick as syrup, as soft as butter, as hard as iron; these are all similes that can be applied to glass depending on its temperature. Yet it is never ductile or plastic in the sense that many materials are, that is, flow cannot be induced by force alone. If, because of its temperature, glass has fluidity, it will respond to force in a predictable way, but if it has no fluidity it will respond by breaking. The shaping of glass is therefore always a question of temperature combined with force and constraint, and, since while glass is being worked it is usually varying rapidly in temperature, and thus extremely rapidly in fluidity, the working process must be adjusted accordingly.

On the other hand, many forming processes not applicable to other materials are possible with glass because of its very nature. It can be blown into thin-walled shapes or drawn into sheets, tubing or fibres, natural cooling and the consequent increase in viscosity providing an inherent control of the process. These two processes, blowing and drawing, together with simple pressing, have made glass the universal material it is today.

### Gathering and feeding

One of the problems in working glass is that of transferring the required amount of melt to the place where it will be worked. As with syrup, if a spoon is used, so much sticks to the spoon that metering is hopelessly inaccurate. In a drawing process, the problem can be solved by drawing the shape continuously from the melt and subdividing into the required lengths when it is cold. In casting, as in making plate glass, the whole crucible containing the glass can be tilted to pour the glass out onto the casting table or the glass may be allowed to overflow continuously into rolling machines. But in the direct production of individual articles, there still is a problem.

For hand production, a gathering iron, rather than a spoon, is used. It is a long iron rod with a ball (often of clay) fixed to its end. By dipping and rotating this ball in the molten glass, the right amount of glass can be gathered, transferred to the work station, and allowed to pour off, the stream of glass being severed when the quantity is right. The process requires skill and judgement by both the gatherer and the shearer.

If the glass is to be mouth-blown in a mould, the gathering iron is a hollow pipe and the excess glass is blown out as a bulbous extension of the article, thin enough to be cracked off the iron. The trimming of the article is left to a later process. Even in semi-automatic production, this rather unsatisfactory way of gathering is retained and only the moulding operation itself is automated.

Since the hand gathering process is awkward, wasteful (30% or more of the glass gathered is returned to the cullet bin), and clearly unsuitable for automatic production, two automatic gathering methods have been developed. In the first, applicable to blown ware, a hollow metal cup of the right size and shape is placed open and downwards on the surface of the glass and a vacuum is applied. Normally, this cup also plays a part in the preliminary shaping of the article and is called a parison mould as distinguished from the blow-mould used to form the final shape. The parison mould, filled by suction, is then used to transfer the glass. If the shape to be blown is symmetrical, it is evident that the temperature distribution in the gathered glass must also be symmetrical. One of the problems associated with this method of gathering is that insertion of a cold mould into the melt leaves a chilled region that interferes with the next gather. The system is therefore complicated by the need to rotate the pot containing the glass or to stir it so that each successive suction cup is placed in fresh glass.

The second automatic gathering method is much more widely used. A narrow channel extension, the forehearth, communicates with the working end of the furnace, allowing glass to flow to a "feeder", a device for delivering measured portions ("gobs") of glass, at the other end. The function of the forehearth is to adjust the temperature of the glass to suit the feeder; it has both a cooling and a heating section. Sometimes it is equipped with stirrers to improve homogeneity, and also coloured glasses can be added at this point so that coloured articles can be made from the feeder while the furnace itself is melting colourless glass.

The feeder consists basically of an orifice at the bottom of the channel and a refractory plunger that pushes glass through it, somewhat on the principle of a syringe. Thus, instead of flowing out in a steady stream, the glass comes out in pulses and is sheared off to form gobs that are then fed to the forming machine. The reciprocating plunger is usually cam driven so that its

motion can be designed and synchronized with the automatic shear blades to control the shape of the gob. The weight of the gob is determined coarsely by the size of exchangeable orifice rings and the temperature and finely by the plunger movement. Usually, the plunger is surrounded by a slowly rotating sleeve or suspended cylinder that helps to make the temperature of the glass symmetrical and that can be dropped down to the bottom of the channel to cut off the glass supply while orifice rings or plungers are being replaced.

There are many advantages to this system. It can feed automatic presses as well as blowing machines; the gob weight can be adjusted without stopping the run; and the long forehearth means that the machines are sufficiently clear of the furnace to make operation and maintenance simpler and cooler. A further advantage is that orifice plates with two, or even three, holes can be fitted so that multiple gobs can be delivered if the size of the article is small enough to allow the machine to carry moulds with multiple cavities.

#### Pressing and glass-forming faults

Even the simplest pressing operation employs moulds. A mould consists of the following parts: the plug, or plunger; the body; and the ring. The plug determines the inside shape of the article, the body the outside shape, and the ring the shape of the upper rim. The main function of the ring is actually to provide a closely fitting sliding surface through which the plug is guided and which therefore allows the plug to be pressed home without glass being able to escape.

A gather or gob of molten glass large enough for the finished article is placed in the body. To do that easily, the body must be moved with respect to the plug. Thus, whether they are accomplished automatically or by hand, the movements are straightforward: the movement of the body to an exact location and the vertical movement of the plug while the body is stationary in that location. Usually, the ring is carried on a spring-loaded cage mounted on the plug so that it can be positioned on the body before the plug completes its downward stroke. Likewise, on the upward stroke, the ring serves to hold the glass pressing in the body while the plug is drawn out of contact with the glass. Often, the body also has a loose central section, a "jumper", which by upward movement can lift the pressing clear of the body when the pressing is cool enough to hold its shape. If the shape of the pressing is such that it cannot be drawn from a one-piece body, the body is constructed of two or more parts hinged together.

As has been said, successful pressing cannot be done by brute force alone. The changing temperatures of the glass must be taken into account. Consider in detail the sequence of events. The hot gob, at perhaps  $1100^{\circ}\text{C}$ , drops into the mould, which may be operating at an average temperature of about  $450^{\circ}\text{C}$ . At first contact the interface temperature may be about  $650^{\circ}\text{C}$ - $700^{\circ}\text{C}$ , i.e. it is biased by the metal, which has a higher thermal conductivity than glass. If the interface temperature is much higher, that is, if the mould temperature is too high, the glass will wet the metal and will either adhere to it, stripping off any oxide film, or replicate the details of the crystalline structure of the metal. In either case, the finished article will appear dull over the affected areas. If the mould is too cold, and the interface temperature is below the setting temperature of the glass, the process will take place at virtually zero pressure, so that the glass will be crudely shaped by the mould surface and will have a mottled or orange-peel appearance. There is therefore a rather small critical range of mould temperatures at which the glass can be pressed into intimate contact with the metal surface without actually wetting it.

Somewhat similar considerations govern the occurrence of "wave-mark", "ripple" or "settle", names applied to the series of rippling contours that may surround the contact area of the gob as it lies in the mould. These are caused by the gathered glass flowing out so slowly that the curved periphery, chilled by the proximity of the metal, is overtaken by the hotter glass behind which in turn becomes chilled and is overtaken, and so on. The undulations so formed will only be pressed out subsequently if the chilling has not been too severe.

When the plug starts to press the glass into the mould, the glass is forced to flow too rapidly for wave-mark to form. However, if the glass has a volatile component, the fresh glass squeezed out from the centre of the gob may exude vapour, which condenses on the cold metal in advance of the flowing glass and accumulates there, so that after a while a "halo", or ring of dull glass, may develop where the glass (or the metal) reacts with the condensate.

If, because of the shape of the mould or the shape of the gob laid in it, the glass flows on two fronts that later reunite, the junction will often show as what might be taken for a surface crack. Since the glass laps over on itself the fault is often called a "lap-mark". A "shear-mark" is another fault and is often associated with a lap-mark. It is formed if the chilling introduced by the shears has not been restored by the bulk heat of the glass before pressing.

Finally, if the mould is too cold, the surface skin of the molten glass may be solidified and thermally shocked to the extent that this skin cracks, while the bulk of the glass is fluid enough to be pressed to shape. If the gob itself has become too cold, these "crizzles" may develop throughout the bulk of the glass. If there is some yield of the mould parts under pressure (due, for example, to an ill-fitting ring) a similar set of fine cracks may develop called "pressure crizzles". Often the ring, which has least contact with hot glass and therefore tends to run cold, is the offending member, and the ware may be rejected for rim cracks or crizzles.

These possible faults have been described to illustrate the points where trouble may arise in forming glass. They are not confined to the pressing operation but may turn up in many different situations. A familiarity with them is essential in trouble-shooting.

The mould has more functions than simply defining the shape of the article; it has the function, for example, of removing sufficient heat from the molten glass to set it. Its temperature, and its temperature distribution are therefore critically important. The mean temperature of the mould depends on the rate of working, the rate at which the heat it gains from the glass is lost to the air or press table, and upon its heat capacity, thermal properties and external shape. The temperature distribution depends mainly on the external shape; and a well-designed external shape can help significantly in eliminating many of the faults referred to above.

Another method of pressing is the "font" mould, which is particularly useful when small, intricate solid shapes are required. This is closely similar to the injection moulding of plastics, except that the pressure mechanism is part of the moulding equipment. The mould consists of a simple press mould of the type described above, except that the body has holes (fonts) through which the glass is squeezed into one or many cavities of the required shape. The body is designed in two or more parts to allow access to the pressings, which are broken loose at the font, the break-off points being finished in a later process.

### Blowing

Soap bubbles, as every child knows, can be blown into accurately spherical shape with walls so thin that interference colours appear.

Virtually no skill is required. The surface tension acting freely on the mobile liquid enforces the spherical shape by making the liquid occupy the smallest area which will contain the volume of enclosed air, the soap adding the property that when the film gets too thin locally the surface tension increases there, drawing back more liquid to strengthen it and so give the liquid bubble stability.

In the blowing of bubbles of glass, the surface tension can only partially achieve the same ends because the glass is not sufficiently fluid to be re-distributed by it; however, since thin sections cool and stiffen more quickly than thick ones, there is a mechanism similar to the function of the soap which tends to make the final thickness more or less uniform. The initially thicker sections balloon out until they too become thin and stiff. The final shape depends on the thickness distribution in the gather of glass just prior to blowing. The making of "free-blown" articles (i.e., without a mould) is therefore a matter requiring great skill and much of the craftsman's time is spent in "marvering", placing the gathered glass and working it by rolling it on a smooth table (once made of marble) into a preliminary shape that can be blown to the shape of the vessel required. Even if a mould is to be used in the final blowing, skilled preparation is necessary. Indeed, in the fully automatic production of blown ware this preliminary shaping is a vital part of the process, although it too is done by moulding (in a parison mould, as described above).

In the days of handmade bottles the shaping of the rim of the bottle was the final stage, and even though in the modern bottle, whether made by automatic or semi-automatic means, the rim is actually the first part to receive its final shape, this part of the container is still known as the "finish". The top of a bottle or jar usually has a complex shape with re-entrants (screw threads or reinforcing rims) and is best formed when the glass is hottest by a process that is essentially a pressing process, although it may be done by air pressure. Once formed, the finish provides a means of gripping the semi-molten glass during transfer from one operation to another. It is therefore the first part of the parison to be shaped and the part of the parison mould in which it is made is carried forward to the blow-mould, taking the parison with it.

The shape of the parison mould is very important since this shape and the chilling caused by contact with the parison mould determine the way in which the glass will expand in the final blow-mould and therefore determine the wall-thickness distribution of the bottle.

When the glass is gathered by the suction process, the suction cup is itself the parison mould and the shaping of the finish is done by vacuum. The final shape is formed in a blow-mould by blowing air through the finish. These are examples of a suction-blow process. In a blow-blow process, a gob is placed in an inverted parison mould and the glass forced down to form the finish by air blown from above. The parison is turned over while being transferred to the blow-mould. It is particularly suited to narrow-necked bottles. For wide-mouthed jars, a press-blow system is used. The parison is formed either inverted or erect by mechanical pressure.

A fully automatic bottle-making machine is a complex piece of equipment involving about a dozen precisely timed mechanical movements for each bottle every 12 seconds. That rate of bottle making, five per minute, is not fast enough for the process to be economic. The output is therefore multiplied by making bottles in overlapping sequence, with a corresponding increase in mechanical complexity. In some bottle machines the mechanical parts are mounted on rotating tables (either one or two, with transfer of the parison between them). Others have sections, each of which is an independent bottle machine, that are fed with gobs in sequence by a distributing chute. This type has many advantages; dissimilar bottles can be made at the same time, provided the weights and production speeds are identical and one section can be made idle for maintenance without stopping production completely. The machines can be operated on both the blow-blow and the press-blow systems.

With such complex machines, a considerable amount of time is needed to find the machine settings most suited to a particular bottle. Although moulds are preheated, their working temperature is not established until the settings are made final. It therefore takes some hours before the machine is producing good bottles at say, 90% yield. It may take some days before the costs incurred in the trial period are recovered. It is therefore necessary to stipulate minimum orders of 100 000-150 000 bottles if fully automatic production is to be justified.

Blown ware made in hot moulds shows evidence of the seam where the blow-mould halves join. Where this is undesirable (in tumblers, for example) the article may be made on a "paste-mould" machine, which employs cold blow-moulds lined with a porous paste (usually of powdered cork) kept wet by spray or immersion. The heat of the glass generates steam at the mould surface, and

it is against this cushion of steam that the glass is blown. Either the glass or the mould is rotated during blowing. Since there is no friction between the steam cushion and the glass, there will be relative rotary motion between the mould and the glass, resulting in obliteration of the seam. Holes drilled in the mould allow the steam to escape.

The general mechanical arrangement of most paste-mould machines is not dissimilar to that of a hot-mould press-blow machine, although the part of the parison corresponding to the finish is cracked or cut off and discarded in these seamless products. There is therefore no reason that this rejected part should be accurately moulded. In some machines the gob is crudely shaped into a thick disc, which is laid on a thin metal plate having an orifice somewhat smaller than the disc. The disc starts to sag through the orifice, and a blowing head bears down on it to blow the glass into a paste-mould underneath. The orifice plate, with its sharp inner edge, causes the glass to break away both above and below the plate so that it is stripped clean for the next cycle. The high speed ribbon machine, used for making electric light bulbs, is of this general type, except that the glass flows continuously from the furnace, passing through a pair of rollers that shape the stream of glass into a ribbon with evenly spaced, thick discs along its length. These discs are made to coincide with a line of orifice plates mounted on a continuous chain. The paste moulds and the blowing heads are likewise carried on continuous chains so that the operation is continuous and the movement linear rather than circular. Production rates may be as high as 250 pieces per minute.

The complexity of glass-forming machines and the severity of the conditions under which they work, especially with regard to temperature variation and abrasive debris from glass breakage, makes regular maintenance critically important. However, each machine represents such a large part of the output of the factory that unproductive time is extremely costly. It is most important therefore that maintenance should be done as far as possible while the machines are working. If that is not possible it should be done during the enforced idle times when moulds or feeder parts must be changed. Maintenance planning calls for close liaison with quality-control personnel to ensure timely receipt of information on what needs to be done and for careful production planning to ensure that maintenance and mould-change crews are available at the proper time so that they can accomplish their tasks as expeditiously as possible.



### Drawing tubing and sheet glass

The importance of the preliminary shape, the parison, in the case of blown glass was stressed above. In drawing glass, the preliminary shaping is in fact the only positive shaping that is done. The final dimensions are determined by the extent to which the glass is drawn in one direction and by which it consequently contracts in directions perpendicular to the draw. The reshaping is terminated when the cooling glass becomes too stiff to be further distorted.

If a thick-walled, hollow cylinder is formed and drawn out, the ratio of bore diameter to wall thickness will remain the same, but since the volume of glass is not changed, the cross-sectional area itself will be reduced in inverse proportion to the extension of the length. Since the loss of heat, and with it the loss of ductility, depends on time, the amount of extension depends on the drawing rate. One can therefore draw tubing down to any size by varying the rate of draw. The ratio of bore diameter to wall thickness, however, is determined by the preliminary shape.

Of course, if production is to be continuous the preliminary shaping must be done in a continuous way. In the Danner machine it is done by wrapping a stream of molten glass around a rotating mandrel, set at a small angle to the horizontal, and drawing the glass off at the free end, where it has flowed down to cylindrical form. The preliminary shape is determined in part by the mandrel diameter and the thickness to which the glass is built up, as well as by the pressure of air blown through the mandrel. The flow of glass to the mandrel is usually controlled in a similar way to that for a gobbing feeder, except that the plunger is stationary and acts as a regulating valve.

In the Vello process, the preliminary shape is created by flowing the glass through a ring between refractory parts, the glass flowing vertically downwards but drawn into the horizontal while it is still soft enough to bend. In some machines the glass flows over a circular wiper through a central hole. In others the glass is drawn upwards from an onion-shaped pre-form in a circular bowl with a central cone, and air is blown through the apex. Large-diameter tubing (18 cm) can be made in this way.

Rod, i.e., "tubing of zero bore", can of course be made on any of the machines mentioned above by cutting off the central supply of air; indeed, rod can be made directly from a feeder orifice. An extreme case of making rod is the manufacture of fibreglass. One problem in making fine glass fibres is drawing at a sufficient rate to get down to size. Another is the problem of handling the great length of fibre so drawn and yet producing economic weights. A single gram of glass may yield 4-5 miles of filament.

Different methods are employed to make glass fibre depending on whether the product is to be in continuous, uniform filaments for textiles or plastic reinforcement or whether shorter pieces are wanted to make open mats for thermal or sound insulation. The fibres may be drawn from the ends of rods slowly fed into flames and drawn down by engagement with a rotating drum or from molten glass in a platinum trough having about 35 nipples through which the glass is drawn and the fibres attenuated by a blast of steam or air, or they may be expelled centrifugally from the rim of a disc rotating at high-speed. Often a combination of these means is used.

In making circular tubing, rod or fibre, surface tension forces are no problem, since they are counteracted in the direction of draw and are symmetric across the section. In drawing sheet glass, however, the process has to be designed to overcome the tendency for the section to "waist" and become circular under surface tension forces. In the Fourcault process, the preliminary shape is formed by pressing a long refractory boat with a slot along its length (the débiteuse) into the surface of the molten glass up vertically through asbestos covered rollers, the lateral contraction being prevented by rotating knurls, which chill the edges of the glass and so maintain the width of the sheet. The process is started using a metal "bait", to which the glass at the slot of the débiteuse adheres, threading it up through the rollers in the drawing tower until the rollers grip the following glass. Cooling of the sheet has to be exactly controlled so that it sets properly and is neither too hot to be marred by the drawing rollers nor too cold to be broken by them. While passing up the tower, it must be annealed sufficiently to facilitate the cutting off operation at the top of the tower and ensure a high yield of rectangular sheets. If the continuous sheet is not adequately annealed, a crack may develop down through the tower, interrupting the process and necessitating a repetition of the tedious baiting procedure to re-establish the draw. The edges, thickened by the knurls, are also cracked off.

The Fourcault process is easier to control than the more modern variants of it because one is drawing from a pre-determined shape, the débiteuse slot. For this reason, the process is the one usually recommended where a sheet glass industry is starting for the first time. The variants dispense with the débiteuse (which has to be replaced every two months or so), the preliminary shape being determined by the sheet itself, by temperature control and by the knurls. The rate of draw is then faster and the surface free of the vertical lines that can arise from any roughness in the débiteuse. In one machine the glass is actually bent over a roller into a horizontal plane while still soft so that annealing and crack-off can be performed more conveniently.

#### Rolled and plate glass

As with any other liquid, if molten glass is poured onto a table which it does not wet, it will flow out in all directions until the surface tension acting over the curved edges counter-balances the hydrostatic pressure or "head". For a given glass, the final thickness is always the same; it is about 6 mm in the case of soda-lime glasses. Except near the boundaries, the surface is perfectly flat. Of course, if the glass is cooled too fast as it flows, the process will be arrested and the thickness will be greater and non-uniform.

A cast-iron table cannot be run at molten glass temperatures without the glass wetting it. It therefore becomes necessary in casting flat glass on such a table to run the table at a lower temperature and expedite the flowing and levelling by passing a roller over the surface. Thus, both the top and the bottom of the glass layer are chilled by metal contact, and both surfaces suffer from the defects mentioned above in connexion with the flow of glass in a press mould. After annealing, the surfaces must be ground and polished if full transparency is to be achieved. The finished product is known as plate glass.

If, instead of a table, a second roller is used on the under-side of the glass, a better surface texture can be obtained because temperature control of the roller is much easier. The process can then be made continuous by overflowing the furnace output through a pair of water-cooled rollers at a rate sufficient to shape the glass and yet leave it flexible enough to be flattened before annealing. If the rollers are embossed or patterned, that pattern is carried to the glass; in this way, a wide range of patterns can be made for windows for which perfect transparency is not wanted. If a continuous roll

of wire mesh is fed into the melt so that it enters the rollers with the glass overflow, the product is flat glass with wire embedded in it. If such glass is broken in service, the wire serves to hold the fragments together, a safety feature that makes it the preferred choice for skylights, doors, factory windows etc.

All the rolled products mentioned above are made as continuous strips and cut to customer's orders at the end of the production line. If polished plate glass is to be made, the grinding and polishing may also be done on the continuous strip as integral operations of the production line, which in this case may extend as far as 400 m, the plate progressing slowly between grinding and polishing heads. However, this last process is being rapidly superseded by the float-glass process.

The float-glass process is really a return to first principles made possible by the discovery that the casting table can be replaced by a bath of molten metal that will not stick to the molten glass even though it is hot enough not to chill it. The surface in contact with the liquid metal has the same final quality as the free upper surface. The metal used is tin, which is protected from oxidization by a reducing atmosphere in the chamber above the bath. In fact, rollers are still used, but their function is to distribute the molten glass without significantly chilling it. The glass flows from these rollers onto the bath, across which it floats, acquires its final thickness, then proceeds through the normal annealing tunnel. Glass thinner than the natural limit can be produced by drawing out the edges of the plate with knurls as in sheet-glass manufacture. The optical quality of the product is almost as good as that of polished plate glass and it has superior strength.

A special kind of float glass for controlling solar heat gain in buildings can be made by a simple electrolytic process. While the semi-molten glass is floating on the tin in the bath chamber, a pool of molten alloy is floated on the upper surface of the glass and a dc voltage is applied between the pool above and the tin below, driving metallic colouring ions into the surface and staining the glass without affecting its transparency.

## VI. SECONDARY GLASS-WORKING PROCESSES

Any after-working of glass that involves temperatures above about  $450^{\circ}\text{C}$  usually requires re-annealing; therefore, if possible, such after-working is done while the glass is still hot, i.e., before the first annealing, so that the time-consuming annealing process need not be repeated. Usually, the high-temperature processes involve surface tension as an inherent means of reshaping part of the glass without touching it with tools so as to leave the product clean and unmarked.

### Fire-polishing and flame-cutting

The effect of surface tension is always to reduce surface area, so that any asperities of the surface tend to smooth out. It is a surface effect only and only the surface of the glass need be fluid. That means that if only the surface of a product of complex shape is heated, the product can be fire-polished without losing shape.

A pressed tumbler, for example, tends to be rough on the inside of the rim because in the pressing operation there is relative movement between the plug and the ring at that point. This roughness can be removed before annealing in a fire-finish machine, which passes the pressing through a tunnel of flame on a rotating pedestal. The design of fire-finish machines is not always well conceived. The object is to provide surface heating with only enough body heat to prevent cooling and cracking, and not enough to cause warping or squatting of the ware. Because of the transparency of the glass, radiant heat penetrates deep into the bulk of the glass, yielding unwanted body heat. But it is the convected heat from the flame that causes the surface to heat, and the design must allow this heat to reach the region to be polished. The function of the tunnel walls should therefore be to provide a general ambient temperature of about  $700^{\circ}\text{C}$ , exclude draughts and confine the flames, not to be a source of radiant heat.

If a glass rod or fibre is fed into a flame, the end melts and gathers up into a nearly spherical bead because of surface tension. As the feed-in continues the bead increases in size until the surface tension, acting around the circumference of the fibre, can no longer support the accumulated weight. Then the fibre waists and the bead drops off. The tail left on the fibre

immediately gathers up to start forming a bead again. In the same way, if a narrow circumferential band of a cylinder of glass supported at the top is intensely heated, the lower part, being too heavy to be supported by surface tension, will fall away, severing the glass at that point. The lower edge of the suspended part will immediately gather up to form a reinforcing bead of perfect smoothness. Serviceable tumblers, for example, can be made by initially blowing the shape with an extension that is later cut off in this way.

The thickness of the bead is obviously determined by the amount of glass made molten, i.e., by the thickness of the glass and the width of the flame. It tends to be a desirable pear shape unless the glass is very thin, in which case the bead is more circular and has a dirt-collecting re-entrant at its stem. For the finest tumblers, therefore, the glass is usually annealed, the surplus cracked or cut off and the asperities removed by delicately applying only sufficient flame to smooth the glass without its gathering into a bead.

#### Annealing

Common glasses can break under thermal stresses caused by temperature differences exceeding about  $50^{\circ}\text{C}$ . A glass blowing or pressing coming straight from the mould may be exposed to much greater temperature differences. It does not break because the glass is soft enough to yield, but if the glass is allowed to set in the presence of such differences, a corresponding stress will remain in it when it finally reaches temperature uniformity at room temperature. To avoid breakage from the stress, the glass must be annealed.

Annealing consists of two stages. In the first, the temperature is allowed to become uniform by holding the glass at a temperature high enough for the stresses which develop to be relieved and yet not so high that the softened glass sags under its own weight. After the glass is stress-free and at uniform temperature, it is cooled slowly enough to ensure that temperature differences do not develop again. The cooling rate can be increased when the glass is cool enough ( $450^{\circ}\text{C}$ ) to yield again to thermal stresses; these will eventually disappear when the temperature differences that cause them vanish after the object has reached room temperature.

The higher the holding temperature, the shorter the time taken to relieve the stresses in the first stage, but if it is too high the initial cooling rate must be so slow that the over-all annealing time is unacceptably long.

At the other extreme, if a low holding temperature is chosen, it takes a long time to get the glass free of stress but the cooling stage can be shorter. The shortest annealing time corresponds to some intermediate course, and the actual time depends on the thickness of the glass and the degree of perfection of annealing required. As mentioned in chapter II, the physical properties of glass change with time at annealing temperatures, making it necessary to be guided by empirical rules to optimize the process. For optical glass, good annealing is essential and may last for days or even months if the piece is large, but for common glass articles the whole cycle can be completed in less than three hours, the ware being carried on a continuous belt down a tunnel, or lehr, of controlled temperature profile. For most sheet and container glass the critical temperatures are the annealing point ( $545^{\circ}\text{C}$ ) and the strain point ( $510^{\circ}\text{C}$ ). Typical annealing schedules are based on holding the glass at  $5^{\circ}$  above the annealing point for a time that depends on thickness and cooling at a rate that also depends on thickness until the glass is about  $10^{\circ}$  below the strain point. The cooling rate can then be increased about 20% with each further drop of  $10^{\circ}$ . Table 14 gives examples of annealing schedules of this type.

Table 14. Typical annealing schedules for sheet and container glass

Glass thickness (mm)	Holding time at $550^{\circ}\text{C}$ (min)	Initial cooling rate ( $^{\circ}\text{C}/\text{min}$ )
3	4	4.2
5	10	1.8
10	20	0.5

#### Cutting by scribing and cracking

The glazier's ability to split glass precisely along a line scratched on it with a diamond point or steel wheel is an acquired knack that is not easy to analyse and explain. The nature of the scratched line, or scribe line, is important. The stresses on the glass under a diamond point or steel wheel scribing tool are immense, even if only finger pressure is used on the tool. If they are narrowly localized, i.e., if the point or wheel is sharp enough, they cause the glass to flow without cracking (for approximately the same reason that fine fibres resist breakage). The glass is furrowed and the greatest displacement is at the bottom of the furrow. It is the distortion remaining after the point has passed which best guides a subsequent crack.

If the point is too blunt or if it is pressed so heavily that its broader sides bear on the glass, the glass tends to "shell out" on either side of the scribe line. The result is a band of weakness that obviously has some tendency to guide a crack; however, each shell has its own minute fracture system, which may direct the crack away from the scribe line. The best scribe line is therefore one that is made by a single stroke at a pressure just insufficient to cause sideward flaking. With a diamond, the angle at which the point is held is critical; with a wheel cutter, less skill is required.

The crack is easily started by a rap on the reverse side. The situation is that a huge flaw is supposed to be guided by a relatively minor one, the narrow line of permanent strain due to the distortion caused by the diamond. The stress at the tip of the crack, however, is not permanent: it is an intensification of any temporary stress applied externally to the glass. If the applied stress is not symmetrical about the scribe line the crack is likely to be diverted. But a symmetrical stress applied at the start of the crack may not remain symmetrical as the crack progresses and changes the geometry of the workpiece. Another skill of the glazier enters here: he has the knack of applying a stress that will remain symmetrical throughout the development of the crack.

In repetitive production, it is usually possible to scribe and crack off mechanically. Often, in the case of cylindrical articles, the crack development can be done by thermal stress, and this so accurately that only a short scratch mark is necessary to initiate the crack; the scratch need not circumscribe the cylinder.

#### Grinding and polishing

As with the glazier's diamond when incorrectly angled, the rubbing of any hard abrasive on glass causes scratching and sideways flaking. If scratches are made in random directions, the surface will be uniformly ground away. For a given abrasive, the amount of damage is roughly proportional to the size of the abrasive particles: 100-mesh carborundum gives a surface roughness about twice as great as 200-mesh carborundum, glass is removed about twice as fast, and the resulting scratches are about twice as deep. If the grinding is to be followed by polishing, it therefore saves time to do the grinding in stages using ever finer particles, grinding at each stage



down to the depth of the scratches left from the previous stage. Then, only scratches corresponding to, say, 600-mesh carborundum remain to be polished out. In practice, progressively softer materials - corundum, garnet or fine sand - that scratch less deeply are usually used.

If an obscured surface is wanted the process can be stopped when the required texture attained. Alternatively, the glass may be blasted with sand (subject to health regulations) or other airborne abrasive. The normal grinding operation is done wet, the water serving to distribute the particles, keep the glass cool and wash the debris away.

The nature of polishing, an art practised even before glass was discovered, is difficult to explain in macroscopic terms. One theory is that the heat generated at the interface between the glass and the polishing tool is sufficient to melt the glass and that the action is therefore equivalent to flame polishing. Rouge (ferric oxide  $\text{Fe}_2\text{O}_3$ ) or sometimes ceric oxide  $\text{Ce}_2\text{O}_3$  is usually used in a cream-like slurry with a felt or pitch tool. It is certainly true that polishing is most rapid when the tool is on the point of drying out and the frictional work is greatest, but a supposed temperature greater than  $600^\circ\text{C}$  is hardly consistent with the fact that water is still in intimate contact with the surface. The paradox is resolved when it is realized that the shearing action of the fine particles of the polishing powder imparts sufficient translational energy to the individual surface ions of the glass for them to be as free to move in the direction of the shear as if they had the average random kinetic energy corresponding to a high temperature.

Whatever the theory, it is quite easy, with a polishing tool and rouge slurry, to transfer glass from the crests to the troughs of asperities and thereby polish the glass. Asperities as deep as 0.02 mm can be polished out completely and all defects rendered invisible. It is these invisible defects that prevent ground-and-polished glass from being as strong as fire-polished glass.

Quite a different method of polishing is acid polishing, in which the surface is dissolved away in a solution of hydrofluoric acid. If the action is followed under the microscope, it is found that dissolution starts from nuclei on the surface and continues from each nucleus on a spherical front, so that the surface has a microscopic stipple with a texture that depends on the

density of nuclei and length of attack. These variables can be so well controlled by temperature and admixture of sulphuric acid that a range of textures from a satin finish to a full polish, little short of that obtained mechanically, can be produced. Acid polishing is widely used in the production of cut crystal glass but is seldom acceptable for optical purposes. The surface, so long as it remains intact, is stronger than that obtained by mechanical polishing. The robustness of "pearl" (inside-frosted) electric light bulbs owes much to this acid fortifying process, and the inaccessibility of the inside surface means that its strength is retained indefinitely.

### Reshaping

The primary forming of glass, particularly of tubing, is often only a first stage in the production of the finished article. Sometimes the article is complex, as in the case of certain laboratory apparatus, and requires additional forming stages, but more often a simple reshaping or joining of two parts is all that is involved. Only when very large quantities are required (light bulbs, radio valves, Dewar flasks) is the manufacture fully mechanized; even then such machines usually merely copy the actions of hand fabrication. Some actions involve such drastic reshaping that the glass, or parts of it, must be brought back to the original working temperature. Others require only simple bending, e.g., curved wind-screens for cars, and temperatures of  $700^{\circ}$ - $800^{\circ}$ C are sufficient for the glass to respond to the bending forces in reasonable time. The production of a double curvature requires a higher temperature. Even higher temperatures (about  $1200^{\circ}$ C) are needed to make a satisfactory seal between two pieces, for to achieve a smooth transition from one part to the other in the finished article the glass must be fluid enough to respond to surface tension forces. Obviously, the two pieces cannot be heated higher than the point at which they would lose their shape; the heat must be localized. Flame heating is the usual solution. For pieces small enough to be held in the hands, the operation is performed with a blow-lamp by skilled lamp-workers.

The lamp-workers are probably the most skilled workers in the industry. They must have perfect co-ordination in the movements of both hands; know exactly when to blow, when to allow surface tension to do the work and whether to allow the heat to penetrate or disperse; and remember instinctively how hot all parts of the piece are, lest they either deform or develop a strain great enough to start a fracture at some point remote from the part being worked.

Condensers and other laboratory ware have counterparts in industrial processes that are too heavy to be manipulated by hand. Glass-working lathes replace the hands and contoured burners replace the simple blow-lamp. Since much of the heat generated by these burners is wasted, they are sometimes replaced by an electrical method of heating that works in this way: two small, diametrically opposed hydrogen flames directed through copper nozzles impinge on the tube to be heated or joined. The hydrogen flames have enough direct heating effect to make a circumferential band of the rotating glass hot enough to conduct electricity, and a high voltage applied between the nozzles creates an arc through the ionized hydrogen flames and a current through the glass that develops ohmic heating deep within the glass itself.

If it is necessary to make a seal between glass components without heat damage to close-by components, the problem can be met by using solder glass, a very soft glass that is compatible with the main parts in thermal expansion and which may be crushed and applied as a paste to the surfaces to be joined. It becomes a mobile liquid at  $550^{\circ}$ - $600^{\circ}$ C and flows into the joint to make the seal. Solder glass may be formulated as a glass-ceramic (chapter II) so that once fired it can withstand a higher temperature than the firing temperature. This technique is particularly useful, for example, in fusing the conical backs to the screens of television picture tubes, where it avoids the problem of heating the rectangular joint uniformly on a lathe.

There are other products for which crushed glass is a secondary starting point. Carefully graded particles of crushed, chemically resistant borosilicate glass are placed in moulds and heated to  $800^{\circ}$ C until the grains seal together to form the porous sintered-glass discs used for chemical filtration. Similarly, crushed glass with a combustible plastic binder can be pressed cold in a suitable mould and then fired like a ceramic. The forms pre-cast in this way are of precise dimensions and precisely match the parent glass in physical properties. They can become part of a complex structure of the parent glass or serve as insulating beads in electronic components.

Crushed glass can also be used to make a rigid glass foam with cellular structure. Glass grains are mixed with a gasifying agent, such as carbon dust, and heated in a crude mould to a temperature at which the glass flows and the gases are generated. The final product is a rigid material more than

90% of whose volume consists of void - enclosed bubbles that cannot trap moisture. The crude blocks are easily cut and shaped by saw and rasp to the form required and serve as excellent insulation, particularly at low temperatures, where condensation could spoil the performance of permeable insulating materials.

#### Toughening

The unpredictable strength behaviour of glass in service and the dangerous fragments into which it breaks are serious limitations to its use. Although test samples may show strengths of 5000-6000 psi, a design strength of only 1000 psi may be used to give a margin of safety for strength reductions due to scratching and bruising. This margin is a contingency factor against abuse rather than a true safety factor in the sense used by engineers.

The process of toughening glass supplies a double-edged weapon to overcome these disadvantages. By prestressing the glass thermally or chemically, so that all exposed surfaces are placed under a permanent compression, the glass is immunized against any superficial damage that does not penetrate the compression zone. This increases the service strength by a factor of from three to five. Of course, there has to be a counterbalancing tensile stress in the body of the glass, but it happens that this proves to be an advantage. When it is exposed by penetration of the surface damage it breaks into many tiny cubical fragments whose edges are much less sharp than those of the razor-like pieces into which annealed glass often breaks. For this reason, toughened glass is classified as a "safety" glass. Successful thermal toughening of glass depends on achieving a symmetrical strain pattern across the section. For a flat plate this is usually parabolic in form with a maximum compression on both surfaces equal in value to twice the tension induced in the central fibres. The protective skin then has a thickness of about one sixth of the thickness of the plate.

It was mentioned in connexion with annealing that the residual stress in the glass was high if the holding temperature was high and the subsequent cooling rapid. Thermal toughening exploits this situation to the full. The holding temperature is made as high as the glass will stand without sagging and the cooling rate made as rapid as the glass will stand without breaking under the temporary chilling stress. In fact the sagging temperature is slightly exceeded and the ware usually shows signs of distortion or tong marks. The high

temperature is necessary to ensure that a parabolic temperature distribution, and consequently a parabolic strain pattern, is set up before the glass becomes rigid, somewhere between the annealing point and the strain point. If that is done, all parts of the glass will pass through the critical temperature at the same cooling rate and all parts will have the same physical properties. If it is not done, glass at different depths will have different cooling rates and, as was mentioned in chapter II, the physical properties will differ over the thickness. In the former case, when the glass finally becomes uniform in temperature, the frozen-in temperature differences give a strain pattern that is an exact replica of the temperature distribution. In the latter case, the strain pattern is distorted.

The rapid cooling is usually done by jets of air carefully deployed to give uniformity of chilling and allow spent air to escape. Liquid baths of molten salts or oils are also sometimes used. They give a somewhat different strain pattern because of the different heat-transfer process and can give a better final product if the article has abrupt changes of thickness.

Because of its rapid cooling from high temperature, toughened glass retains some high-temperature character and has a strain point about  $100^{\circ}\text{C}$  lower than that of annealed glass. Its highest service temperature is therefore correspondingly lower.

There are also chemical means of producing a skin of compression on the glass and so toughening it. The chemical constitution of the surface layers can be changed either by substituting one alkali for another or by producing a glass-ceramic type of conversion in the surface layers. If a soda-lime glass plate is immersed in a molten salt with a high concentration of some other alkali ion there is a tendency for ion exchange to take place, a tendency which is quite strong near the strain point of the glass. When cooled to room temperature the surface layers are put under stress according to the differences in thermal expansion brought about by the ion exchange. It is therefore a question of freezing-in expansion differences rather than temperature differences as in thermal toughening. Very high surface compression can be developed and therefore very high strength, but the protective skin is thinner and less effective against severe scratching. The pattern of stress across the section is of course far from parabolic.

Another surface treatment, often adopted to make bottles more robust in service, provides an additional surface skin designed to minimize surface damage instead of strengthening the glass itself to resist such damage. A "cold-end" strengthening treatment, i.e., one applied at the cold end of the annealinglehr, may consist of spraying or vaporizing an organic film onto the glass. The film lubricates any subsequent glass-to-glass contact of the bottles, which can cause damage by scuffing. The 'hot-end' titanizing treatment is generally more effective in this respect, probably because the tin oxide film formed on the surface in this process is rigid and, being of lower thermal expansion, is put under compression and therefore contributes to the strength. In both cases, the films are chemically bonded to the glass, that is to say the silicon-oxygen bonds of the glass continue into the film, in the first case because the organic film is a silicone, and in the second because the tin oxide bond Sn-O is compatible with the Si-O bond of the glass. In both cases, the films are too thin to be visible.

#### Decorating

In the comparatively quiescent period of 2000 years between the discovery of the glass blow-pipe and the development of modern technology at the start of this century, artistic embellishments of immense variety were practiced. It is a sobering thought to reflect that, actually, man is no more intelligent now than he was 2000 years ago. Only the accumulated knowledge and technological environment have changed. Many of the modern developments unconnected with decoration are in fact adaptations of ancient recipes and practices designed for artistic merit. For example, the titanizing process just mentioned above might be said to be based on the fact, well known to the ancients, that glass could be given an iridescence with permanent rainbow colours by exposing it when hot to the vapour of tin chloride. So it is that decoration is not so much a matter of development as one of choosing those techniques which are most compatible with modern ideas of mass production. Here we shall consider only one of the techniques.

Many of the decorations applied to pottery look insipid when applied to transparent glass; they need an opaque backing to give a satisfactory contrast. On glass, the colours must be thick and strong. They must also mature to a glaze at a temperature low enough to avoid risk of glass deformation, and,

being thick, they should when fired have an expansion compatible with that of glass. Since the composition of common glasses is already the result of the optimization of raw material cost, ease of melting and serviceability, it follows that some departure from the optimum must be made if the goal is to produce an intensely coloured glass that will glaze at a temperature at which the base glass is virtually rigid. Since the decoration is such a small part of the substance of the article, cost is not a serious consideration and sometimes even precious metals such as gold or platinum can be used without raising costs unduly. Chemical durability, on the other hand, particularly if low firing temperatures are used, is almost always significantly worse than that of the base glass, which may outlive its decoration.

The printing technique which is best able to apply an adequate thickness of colour is the silk-screen process, usually direct but sometimes via a transfer paper later applied to the glass. In this process a paint slurry is applied through a fine screen of dark nylon or stainless steel with its holes blocked or left open to form a stencil as the pattern requires. The screen is pressed into contact with the glass by a squeegee, which also serves to drive the paint through the stencil. When the pressure is released the screen strips free leaving the pattern as a series of dots, which fuse together when the article is fired.

If more than one colour is required, a succession of precisely registered stencil applications must be made. If a bottle is to have an applied colour label (ACL), it is formed with a small dimple at some convenient point so that registering can be done automatically by reference to this point. To avoid waiting for the paint to dry between colours, it is now usual to employ a wax as the paint medium and to use heated screens. The wax then solidifies on the cold bottle and can immediately be over-painted with the next colour without smudging.

The ware is usually fired in a continuous decorating Lehr, the latter part of which is exactly the same as an annealing Lehr and has the same function. On the front there is an extension to heat the bottles from cold, first to a temperature of about 400°C to burn out the paint medium, and then briefly to about 580°C to fuse the enamel. Failure to burn out the organic medium completely in the first step leads to a situation corresponding to the production of foam glass mentioned above, i.e., to a discoloured bubble structure.

Failure to reach maturing temperature gives a poor lustre, and the chemical durability is reduced because of the larger surface area of the rough finish.

The preparation and blending of the ceramic paints for this process is a highly specialized art and is normally left to the paint suppliers. The silk screens, however, are prepared in the glass factory. Photographic methods are used almost exclusively. The screen is varnished over with a polyvinyl alcohol or gelatine preparation sensitized by dichromate and placed under ultraviolet light in contact with a photographic positive. The exposed areas of the varnish - areas where the positive is light or clear - become insoluble in hot water. The areas that are not exposed - the dark areas in the positive - will remain soluble. When the screen is washed in water, the areas that are required to pass the paint are washed clear of the blocking varnish.

Some manufacturers blend their own ceramic paints if they require a great diversity of colour, as in the cosmetics industry. There is also a growing tendency to use organic paints for the less exacting applications. These can be baked at a much lower temperature (about 180°C), allowing organic dyes and non-precious metallic finishes in an almost infinite range of colours to be used.



## VII. QUALITY CONTROL AND TROUBLE SHOOTING

The quality of glass as glass is not the over-riding concern of most users of glass articles. The buyer of bottles, for example, is concerned that the bottles should hold the correct quantity of liquid; that the cork, cap or closure bought from a different supplier should be a good fit; and that the height, diameter and strength of the bottles should be compatible with the operating requirements of his filling machines (which may need to work effeciently at rates as high as 500 bottles per minute). After all, it is the buyer who has to deal with the ultimate consumer and who has certain legal responsibilities to that consumer in regard to weight or volume of contents and robustness in handling.

The bottle maker, for his part, knows that the accuracy of the moulds in which the bottles are blown is only a small part of his problem. He is dealing with a material of construction that, unlike metal, cannot be made to conform invariably to a mould. The volume also depends on the gob weight, which is subject to variations, and on whatever deformations the bottle may undergo when released from the mould. The wall-thickness, too, depends on the gob weight, and its distribution is variable. Even if the bottles are being made at the modes. rate of about 80 per minute, it would require an army of inspectors with calipers to check the critical dimensions of every single bottle. It is true that automatic and electronic machines can be devised to carry out most of these measurements at extremely high speeds, but that does not solve the problem of the cost of inspection; instead of paying the salaries of an army of inspectors, one makes a large capital investment in machines and then must employ highly qualified personnel to set them up and maintain them.

Of course the price paid by the buyer must cover all the costs involved: the cost of making the bottle, the cost of rejects and the cost of inspection. It is therefore in his interest, first, to make sure that the dimensional accuracy he calls for is not more exacting than he really needs, and second, to agree to some less expensive method of checking these dimensions. Obviously, if only a fraction of the bottles is selected for measurement the cost of inspection will be reduced proportionately. But what assurance is there that this sample really represents the whole consignment? And what are the chances that, once the consignment is accepted, there may be some bottles so much oversize that they will break on the filling machine or cause damage to it? The statistical method of quality control provides answers to such questions.

Statistical control

The term "average" used in everyday speech is actually a strictly defined statistical term. To say that on the average 1.8 goals are scored in every football match is statistically meaningful, even though there is no way that a fraction of a goal can be scored in a real match. The use of the term implies that the actual measurements one has in mind are scattered, or distributed, in some specific way about the value called the average. One of the terms used to specify the distribution is the term "standard deviation". It is defined in such a way that it, too, like the average, can be calculated. Statisticians have found that, provided the variations are due to random causes, the distribution can be adequately described if just these two values, the average and the standard deviation, are known.

Putting it more precisely, if the frequency of occurrence of a particular measured value in a group of measurements that vary because of random causes is plotted against the measured value, the resulting distribution curve will be the so-called normal, or Gaussian, curve. It is a bell-shaped curve, symmetrical about a certain value, the average ( $A$ ). Its shape is rather like the italic letter  $f$  and its own mirror image joined together at the top. The horizontal distance from the point where the cross-bar of one of the  $f$ s crosses the vertical stroke of the letter to  $A$  is equal to the standard deviation ( $SD$ ). If the  $SD$  is large, the curve is broad; if the  $SD$  is small, the curve is narrow. But what is interesting is that the shape of the curve is fully defined by the  $SD$ : from the  $SD$  one can calculate the probability that any particular value will turn up in the group of measurements. Thus one must expect that 16% of all values will lie below  $A - SD$  (and 16% above  $A + SD$ ), 2.3% below  $A - 2SD$ , and 0.13% below  $A - 3SD$ , provided the variations are indeed due to random causes.

Statistics, of course, goes much further; but for our purposes this first step will suffice. Indeed, for many purposes one need only apply the principle in a crude way. Suppose, for example, that the density of the glass from the furnace is accurately measured every day and the values obtained are plotted as dots against a time scale. If the variations are due to random causes, a series of dots will develop in the course of time and these dots will be scattered about some central value, with no pronounced trend upwards or

downwards. By eye, one can draw a line through the points which seems to represent the average value  $A$ . One can also draw lines above and below  $A$  between which about 68% of the dots are included, leaving about 16% above the top line and 16% below the bottom line. These lines then correspond to  $A + SD$  and  $A - SD$ . By doubling and trebling the spacing one can also draw lines corresponding to  $A \pm 2SD$  and  $A \pm 3SD$ . The resulting diagram is called the control chart. As long as the daily dots continue to fall mostly between the 1SD lines, occasionally between the 2SD lines and rarely outside them, the process is in control and nothing need be done about it. If, however, the dots drift consistently off the centre, it is a signal that some non-random feature has been introduced, and steps must be taken to diagnose and rectify the trouble. In this example, the drift may be due to a consistent error in weighing, a change in composition of raw material or excessive loss of volatiles during melting. If the dots become more (or less) scattered, it is a sign that some new random factor has crept in (or vanished); the weighing machines may have become erratic and require maintenance, for example.

Control charts are extremely useful but are not an end in themselves: they do not actually control anything. They merely provide information on which action can logically be based. Incidentally, complete notes on action taken should be entered on the chart.

Inexpensive electronic pocket computers that can perform statistical calculations quickly have become readily available. With them, calculations can be done on the factory floor, meeting the vital need to determine quickly the significance of some recorded variation so that immediate remedial action can be taken or, just as important, so that needless adjustments to machine settings in a vain attempt to correct what is only a random variation can be avoided.

The drafting of a statistically based quality specification is often rather arbitrary and consequently not the best that can be devised in everybody's interest. Because the normal curve never actually reaches zero at its extremities there is always a theoretical possibility of passing an article that should ideally be rejected. In practice, the actual distribution, although near enough to a normal one to allow the simple mathematics to be applied, does not have infinite tails. In bottle making, for example, a certain amount of automatic rejection occurs: the bottle machine is incapable of making bottles with extreme deviations from the average without breaking them.

The specification should have two aims: it should make the probability of a troublesome bottle reaching the filling machine acceptably small, and it should minimize the size of the sample necessary to give this assurance. For example, a bottler finds from past experience that, on the average, he has lost 5 out of every 1000 bottles through breakage on the filling machines. He is therefore unlikely to be dissatisfied if 1 out of every 1000 bottles delivered to him are potential breakers. Having this goal (specification) in mind, knowing the standard deviation and using tables of the normal curve of errors, the bottle manufacturer can determine the tolerance to which he must work if he is only going to test say, 10% of the consignment which is to contain no more than one defective bottle in a thousand. The smaller the fraction tested, the tighter must his tolerance be.

#### Feedback

The function of a quality control department is not simply quality observation or quality selection; it is just what it implies: control. The vital need is that those in a position to control quality on the production line are informed immediately by the department when a trend in quality, good or bad, becomes apparent. There is a delay of about three hours while articles are being annealed and cooled to room temperature. With modern high-speed machines, that may mean that an entire lot of perhaps 15 000 articles risks rejection. The gob weight, at least, should be determined and spot checks on quality made before the glass goes into the lehr.

The onus is on the quality control personnel to bring any discrepancy directly, even if informally, to the notice of whoever they believe can rectify it, since they are the first to have the information. Formal reports and records are secondary. Quality control personnel must therefore learn to recognize a fault for what it is and establish a relationship with all levels of the production staff so that their activities are accepted as a service and not as fault-finding (in the sense of complaining). Quality control is therefore a staff function supervised by the glass technologist and not directly by the production manager. Usually the sorters do form part of the production team because often they also pack the ware. In this case, the quality control personnel are like referees: they maintain the comparison standards to which the sorters work.

The quality control department is backed by the laboratory, the chief concern of which is quality control in depth. Frequent analyses of the raw materials, for both consistency and content, must be made and the moisture content of stored materials determined to ensure that the batch calculation is valid. Simple checks, e.g., on the acid-soluble fraction of the mixed batch, indicate whether the weighing and mixing operations are satisfactory. At one time the composition of the melted glass was determined by chemical analysis. A complete analysis took about 5 days and was too slow to be an effective control. Rapid modern methods have brought chemical analysis back into its own as a direct measure of composition. However, inferences as to composition based on measurement of physical properties is still widely employed because of their rapidity. Since glass is sold on the basis of its properties rather than its composition, there is logic in this method of control.

Some physical measurements are so precise and easy to perform that they are an invaluable means of forestalling trouble. The density, for example, can be easily measured (or rather compared with a standard) to an accuracy of 1 part in 100 000, using tiny fragments. Not only can any trend in composition be discovered, but the homogeneity of the glass can be measured by testing many fragments from the same article. The density is compared with a standard by a sink-or-float method in which the fragments are placed in a dense liquid adjusted by admixture until the fragments just float at room temperature. On gentle heating the fragments start to sink at a temperature that depends on their density; the temperature scale can be calibrated as a density scale. This sensitive test will often detect signs of trouble long before it has grown to proportions which would necessitate rejection of the ware.

A qualitative test with a similar sensitivity involves examining a cross-section of the finished article in polarized light. A ring section is cut out of a bottle, for example, with an abrasive wheel or by scratching and cracking off with a hot wire. The section is immersed in a liquid of matching refractive index, the rough fractured surfaces disappear, and if placed between crossed polaroid films, inhomogeneous glass shows up as light and dark bands. The test can be made crudely quantitative by assigning numbers to a graded series of inhomogeneous samples.

The quality control personnel on the factory floor are in the first line of defence against glass-making troubles. When problems outside their competence

to solve arise, more experienced technologists or laboratory experts may be called in. Often the problem is associated with breakage of glass. Fracture diagnosis by such experts is an important step toward solution.

#### Fracture diagnosis

Provided all the fragments of a broken glass article are available for examination, it is almost always possible to find the point from which the fracture originated. The state of stress existing when the cracks were formed is also revealed so that the reason for failure can be determined.

There are three generalizations that make fracture diagnosis relatively easy. First, the strength behaviour of glass is such that the possibility of glass failing instantaneously from more than one point is so small at normal stresses as to be negligible; only at extremely high stress does this possibility become significant. Second, since glass is amorphous on a sub-microscopic scale, any features which develop on a crack surface can only be due to the stresses existing in the glass at the moment when the crack was created at that point. Third, the velocity of crack propagation is limited to a value about one third the velocity of sound in the glass. The stress at the crack tip is extremely great when this limit is reached.

Taking the last point first, it will be appreciated that the stress at the tip of a crack depends on the length of the crack, because all the stress originally supported by the glass across the line of the crack before fracture must be concentrated at the tip after fracture; behind the tip, the glass is separated by the crack and is free of stress. A crack therefore tends to accelerate as it lengthens. Since the ultimate velocity is limited, however, but the stress intensification because of increasing length is not, a stage is reached where the first generalization breaks down. Multiple fracture is then possible, and the crack forks into three or more branches. This forking gives a pattern to the breakage which is characteristic of the type of stresses prevailing at the moment of fracture, and the distance travelled before forking occurs is an inverse measure of the magnitude of the stress under which failure occurred.

Suppose, for example, that a cylindrical bottle is weakened by a deep scratch on its side and is then subjected to internal pressure sufficient to

burst it. The internal pressure has the effect of trying to split the bottle from end to end. The scratch intensifies the stress locally but may not lie exactly parallel to the axis. The first crack therefore develops from the scratch, both upwards and downwards, and tends to direct itself along the axis as soon as it extends beyond the influence of the misaligned scratch, but soon the stress at both tips becomes so great that the crack forks at top and bottom to form, as it were, arrowheads pointing back to the origin. The origin will lie about midway between them and may be recognized as a cusp where the initial realignment took place. Primary forking may be followed by secondary forking, but some of the subsidiary branches may stop abruptly when the pressure is released. The fracture pattern may also be complex because of the shape of the bottle.

As a second example, suppose that a similar bottle, without internal pressure, is struck on its side by a hammer blow. The induced stress is extremely high and localized. The cracks fork and fork again all within an area crushed by the follow-through of the hammer so that the general appearance is that of many radial cracks emerging from a single central star. Again the breakage becomes complex because of the shape of the bottle and interference of one crack with another as they meet around the bottle.

By reassembling the fragments of a broken bottle one can usually recognize the fracture pattern, identify the origin, and so determine the reason for failure. In both the examples, the breaking forces were externally applied. In the case of thermal breakages the situation is rather different because for every thermal stress there must be a counterbalancing stress elsewhere in the bottle and as a crack develops the whole distribution of stress changes throughout the bottle. The crack system therefore does conform initially to an imposed pattern but becomes meandering in response to the varying stress distribution. Forking may occur, but it is not likely to be symmetric about the fracture origin because the bottle shape is not symmetric about this point. Also, the crack velocity usually remains low because the cracking is releasing stress as it goes and this partially offsets the tendency for stress intensification at the crack tip. The fracture origin is seldom obvious and one must usually employ the second generalisation and study the features of the fractured surfaces.

The detailed markings on a fracture surface contain a wealth of information. A crack develops with a curved leading edge convex in the forward

direction. If for some reason it hesitates, it is almost certain that the stress distribution will have changed slightly in the interval, and when the crack resumes its growth it will do so in a slightly changed direction, leaving a trace of its hesitation as a curved mark indicating the direction it was travelling. If, because of the shape of the article or because of a torque applied to it during breakage, there is a tendency to twist the plane of the crack, fan-like marks are left, broadening out in the forward direction. These marks reflect the competing tendencies for the crack to remain in a plane and yet comply with the twist. The fan is again a direction indicator.

If the breakage was a noisy affair, sound waves travelled backwards and forwards in the glass during the growth of the crack and the developing crack will record these as a fine-scale rippling of the surface. These marks are best seen with a magnifying glass in light at grazing incidence and indicate the direction of crack propagation in the same sense as the hesitation marks mentioned above do.

There are therefore a number of direction signs to be found on the fracture surface of a broken glass article. If the edges of fragments are individually labelled with arrows according to these signs and the article pieced together, one will find that the whole crack system stems from one origin. The origin itself may be almost featureless if failure occurred under abnormally low stress, but then there usually is a small cusp because the initiating flaw is unlikely to have been precisely aligned with the maximum stress so that some realignment was necessary. Often, however, the region of the origin is quite distinctive and appears as a smooth mirror-like area surrounded by shell marks which are in fact hesitation marks focused at the origin. Microscopic examination will usually disclose some defect at this point. Since mating fragments must have corresponding markings, examining them provides confirmatory evidence.

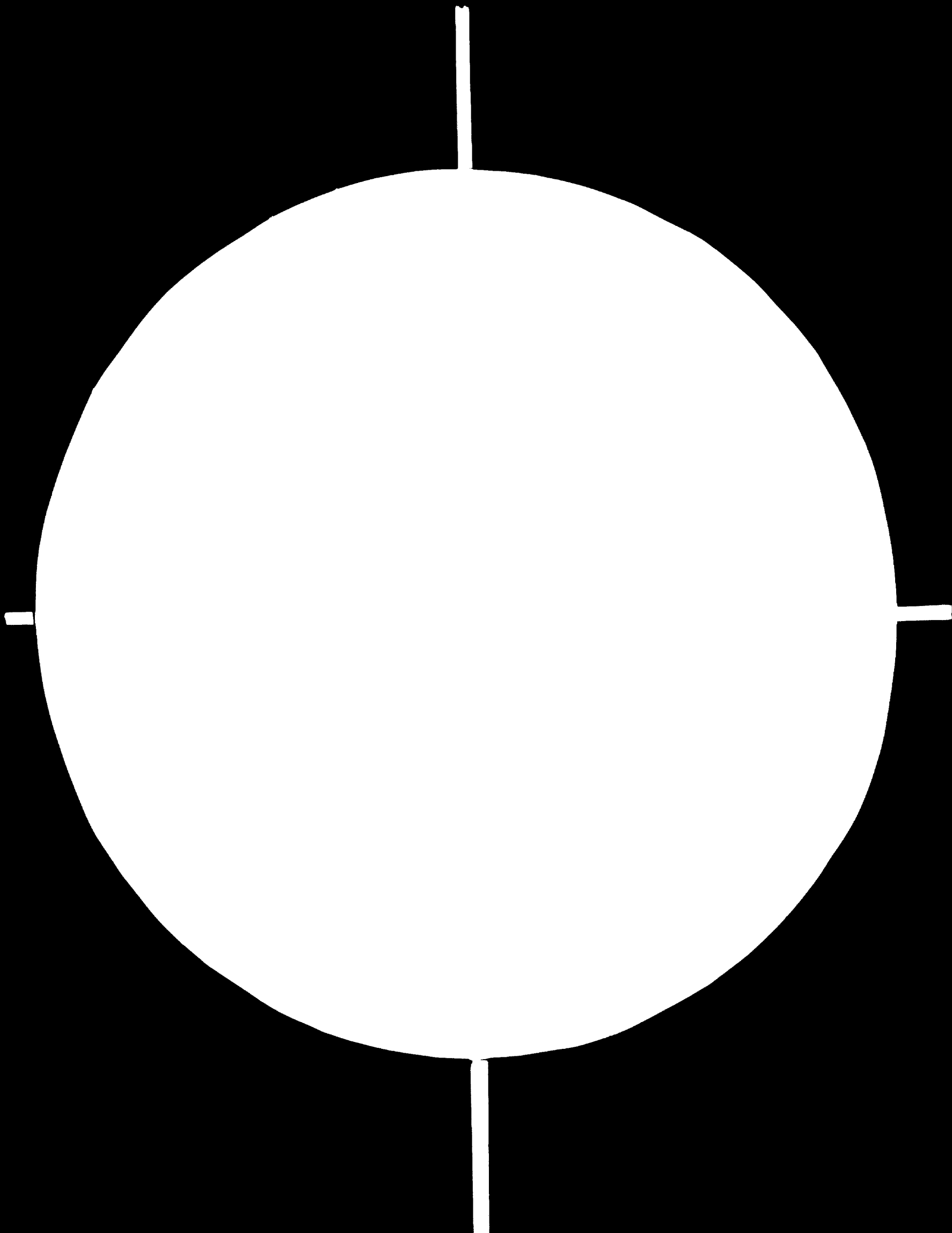
Sometimes the smooth mirror area of a fracture origin is bounded by a "grey" zone, an area that looks as if it has been slightly ground. Beyond this one may find a disrupted region from which sharp splinters have been thrown out. The grey zone is a sign that the local stress was very great and that there was a latent tendency to fork; indeed, the splinters are a consequence of forking. If the grey zone is close to the true origin, it means that the stress originally applied to the glass was very great, since the small size of



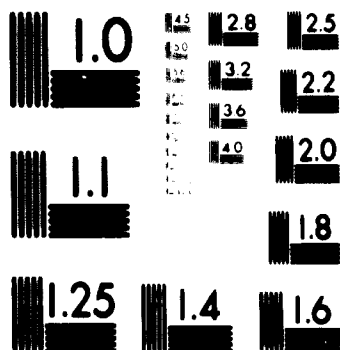
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MICROCOPY RESOLUTION TEST CHART  
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the mirror area indicates that the stress intensification cannot have been great. This is one source of information concerning the state of stress at the time of failure. Two others have already been mentioned: the fact that torsion tends to produce fan markings and, if severe, splinters, and the fact that elastic or sound waves are recorded by ripple marks of an intensity that reflects the amplitude of the waves.

Skill in fracture diagnosis is an invaluable weapon in trouble-shooting, but skill and confidence only come with experience, which must be acquired before trouble comes along. Fortunately, experimentation is easy and the study of fractures is fascinating.

### VIII. VIABILITY OF GLASS MAKING

Modern automatic glass making is a capital-intensive industry depending on a large output for its viability. However, even in the best regulated factories, a product rejection rate of about 10% is normal, so that it is obvious that a high degree of skill, experience and know-how is necessary for success; viability may be lost as easily from lack of these components, and the consequent inability to reach the projected output, as from an insufficient demand. A target of perhaps 60% yield in the first year, working up to 90% in the third year, is reasonable and will probably correspond to the time it takes to penetrate the market, but there will be a need for a considerable amount of working capital over this period.

Establishment of a glass-making industry is usually proposed in developing countries with a view to substituting for imports and in theory, therefore, the demand is known from import statistics. In practice, however, the degree of market penetration to be expected is unknown unless the industry is to be protected by tariff walls at least during the early stages of development. But that excludes the possibility of exporting as a means of expanding demand because the industry then seldom grows out of its early stages, and prices remain high and quality tends to remain low. Market trends over the three years of building and thereafter are very difficult to foresee; the establishment of the industry itself may have a significant effect on those trends. If the project is truly viable it is likely to realize potential markets because it makes glass locally available, but if it has only an apparent viability because of tariff walls, it may have the opposite effect, by driving bottle customers to alternative containers such as cans and plastics, for example.

The problem of skill and know-how is usually thought to be solved by putting the whole project out to turn-key tender. For a number of reasons, that involves a disproportionate capital cost and high production cost through the capital-dependent items, such as depreciation and interest. In addition, even with the best will in the world, the turn-key operator can do no more than offer training in well established factories abroad, where things seldom go wrong and the trainees acquire a false confidence quite unsuited to the teeth-ing problems they will meet in the very different environment of their own factory.

A more satisfactory solution is to invite foreign participation in the venture by glass manufacturers who will also provide know-how on a continuing basis. However, such participants are usually not disinterested and may exert influences that are not in the best interest of the local industry. Also, they will naturally tend to enforce a technology based on their home practices to make information transfer easier, but the technology may not be that best suited to the developing country, perhaps dooming the local industry indefinitely to a subservient role.

Where the market is large, the feasibility of a proposed glass-making operation can be judged relatively easily, and the study may be rather superficial. Devising a viable operation requires more study, but there is a degree of freedom of choice of the scale of operation. If, however, as is usually the case in developing countries, the market is limited, the study of feasibility is more difficult and requires at least the preliminary devising of a viable operation. Because of the importance of volume, and sometimes for reasons of political prestige, there is a tendency to make optimistic estimates of forward trends and even to include incompatible products, such as containers and sheet glass, to swell the volume. This inherently risky procedure has often been followed, encouraged it seems by the extraordinary fact that it is easier to borrow large sums of money than small.

An alternative, less glamorous, approach is to strive to set up a smaller but truly viable operation, discarding, if necessary, awkward sections of the market and if necessary adopting non-conventional technology in order to optimize the situation. Once a viable glass-making operation is established in a country, it can be used as a bridge-head from which to expand. Subsequent stages can be justified individually with much greater certainty and with domestic know-how to draw upon. The disadvantage of this approach is that much greater study is required in the planning stages. It is also necessary for the planners to follow through to eventual start-up because it is unlikely that a turn-key operator or a foreign participant would agree to the technology and processes laid down. A preliminary expense is involved whether or not the project finally goes ahead: the payments made to the consultant and the staff recruited to help with the details. The latter, as prospective management staff, will of course greatly benefit from the experience.

The per capita consumption figures given in chapter I suggest that the section of the industry most likely to be viable in a developing country is the manufacture of containers, which will therefore serve best to illustrate the three conceptional stages of a proposal:

(a) Pre-feasibility study with the purpose of determining whether a detailed study is warranted;

(b) Feasibility study to determine the best choice of product and technology, estimate the viability of the proposal, and establish the ground rules for going to tender;

(c) Preparation of tender documents. In the case of an invitation to turn-key tender, the intention is to specify and define technology and to stipulate the legal requirements only to the extent of ensuring that tenders are comparable, leaving the tenderer sufficient scope to recommend his own solutions to the task of producing the specified outputs. Where a turn-key operation is not envisaged, the technology must be worked out in sufficient detail that offers for the individual items of equipment or sections of the work can be solicited. This requires tentative production planning to optimize the utilization of equipment and labour.

Comparison of tenders and reappraisal of the project in the light of firm offers should not involve more than minor rethinking. However, it is probable that considerable economies in the capital cost can be made if the capabilities already existing in the country are exploited to the full, which may involve detailed guidance by the consultant.

#### Scale of operation

The size of the market and consequently the scale of the operation to be considered has more aspects than the important one mentioned, i.e., the effect of volume in absorbing fixed cost. If the volume requires several production lines, production can be planned to make the load on the furnace substantially constant and a furnace designed to this capacity will provide economical melting. On the other hand, if one forming machine will meet the whole of the demand, melting efficiency is going to be very low when a light-weight article is being made, and any breakdown will stop production altogether. Again, many of the capital items are required whatever the scale of operation is, and the cost of those which are scaled down in output is disproportionately high. In the same way, staff and labour requirements are relatively higher for small-scale operations. The size of individual orders is another important consideration; a production run on automatic machines must last long enough to absorb the setting-up time.

It seems therefore that attempts to scale down a conventional factory must reach an absolute limit corresponding to a one-furnace, two-machine installation. For both glass containers and sheet-glass production, this limit corresponds to an annual output of about 10 000 t, or 30 t/d. At rather optimistic per capita annual consumptions of 10 kg of glass containers and 2 kg of sheet-glass (see chapter I), such factories would require populations of 1 million and 5 million to support them.

If the market is considerably larger than that, a preliminary assessment can easily be made by the economist's usual methods. He can assume a conventional technology and so largely ignore technological details. If, however, the assessment shows only marginal viability, the basis of the calculation must be examined by a specialist because it does not necessarily follow that the technology used in industrialized countries is the one best suited to developing countries. After all, the glass-making industry grew from small beginnings, and even today some small bottle-works operate successfully in competition with their giant neighbours by paying careful attention to costs and to choice of product.

Little can be done in the case of sheet-glass manufacture, but for glass containers there is scope for breaking with convention and perhaps devising a viable operation where, at first sight, it would seem impossible. Assessment of viability then becomes complex: it involves optimizing the technology in conjunction with the spectrum of market demand.

#### Market spectrum, trend and penetration

Import statistics seldom give any details of the size, shape, and colour of containers or of the numbers in individual orders. This information, the market spectrum, is vital for automatic production; not only must orders smaller than the economic minimum be discounted but the total volume of each colour must be sufficient to justify perhaps a week's loss of production while the colour of the glass in the furnace is being changed.

Fortunately, a large part of the bottle imports is consigned to relatively few bottling firms, and this part of the spectrum is easily established. It usually happens that a country, hitherto without a domestic supplier, imports a wider variety of shapes and sizes than is necessary because they have had the whole world to choose from. The prospects of some degree of standardization must therefore be established, and the likely trend of future demand must be estimated.



The demand for miscellaneous small bottles and jars and for tumblers and tableware, which may prove to be compatible with the proposed factory, is much more difficult to quantify. Sales are usually through manufacturer's agents, and the spectrum and volume depend on their aggression as salesmen. The best ultimate policy to adopt in respect of this section of the market is probably to attempt to penetrate it on one's own ground rather than to duplicate it item by item, that is, to design products compatible with the equipment installed and win one's own way competitively on price. This should be borne in mind during the market survey.

The market survey is best conducted by interview rather than by posted questionnaire. An immediate assessment of the weight to be attached to an opinion or forecast can be made in a personal interview, whereas an impersonal questionnaire may be quite misleading. The success of the survey depends very much on the enthusiasm, or lack of it, for the proposed factory. The enthusiasts will see the possibility of cost savings through better deliveries and smaller inventories etc. and may be over-optimistic in their forecasts. The non-enthusiasts may feel that a local factory may force prices up through the imposition of customs duty.

In view of the importance of scale to the success of the enterprise, the accuracy of forecasting is of paramount importance. Unfortunately, it is most uncertain, and in such circumstances the uncertainty must be estimated. The opinions of the market survey provide one estimate. Study of past import trends, however erratic, give another. Trends of gross domestic product or per capita income provide others. In developing countries, the growth rate of glass consumption is often around 10%. That is important, since the project may take two years to implement and a further three years to mature. With such an estimate of growth rate, should the plant be designed to handle 160% of the present penetrable market, with the risk of tying up additional unproductive capital? Or should it be more modestly based, setting a limitation to the output no matter how the demand grows? These are complex questions, and knowledge of the highest and lowest forecast volume is necessary to answer them.

In the case of sheet glass the spectrum is not only the range of thickness required but also the qualities (grades) necessary to meet the market.

Greater freedom from visual defects, bubbles, cord, waviness etc. is required for mirror making and for laminated safety glass, for example. The superior qualities are obtained by selection rather than design, and unless the market spectrum matches the natural range of qualities produced, the disparity will cause overproduction of the inferior grades and underproduction of the superior grades.

Knowledge of the sizes of rectangles most commonly used is important since they must be cut economically from the strip of glass drawn from the machine. Obviously, the wider the drawn strip the greater the scope for economy of cutting. In some large flat-glass factories wide strips are drawn, customers' orders are analysed, and the cutting pattern worked out and set automatically by computer so as to maximize the saleable glass. In small factories, that is seldom feasible, and it is important that the drawn width (after trimming the edges) should be a multiple of the widths or lengths of popular sizes. In practice, cutting-room losses amount to about 30%.

#### Optimization of the technology

A native glass factory in a developing country has few advantages, and the most must be made of them in the competition from factories in industrialized countries, with their large markets, developed skills and know-how. The factory-gate cost of imported bottles is often 20% higher than the c.i.f. price because of port handling charges, breakages etc., but these same factors inflate the cost of imported capital equipment. A local supply of glass-making sand is usually regarded as a major asset, since sand constitutes about 70% of the raw material weight, but in fact it amounts to only about 10% of the raw material cost and, if it requires beneficiation, its final cost may be little different from that of imported sand.

The cost of labour, when efficiently used, is usually lower in developing countries. The scope for optimization depends very much on efficient labour utilization. Certainly, the use of two persons to do one person's work is particularly inefficient in the glass industry, where "too many cooks may spoil the broth". An appraisal must be made as to whether training can be effective and whether management can cope with possibly unco-operative attitudes before trying to cut operating costs by using more labour and less capital than would be usual in a conventional factory. On the crude basis that capital costs 30% to operate (10% each for depreciation, maintenance and interest), it

seems that up to \$10 000 can be spent on machinery to replace one person whose total cost, including training, is \$3000 per year. Of course, this argument only holds for those repetitive tasks which a machine can do, and if the machine works round the clock it replaces three or four workers. But if it is not fully employed, the worker, who can be put to any number of other tasks, is a much better investment.

The problem of replacing people with machines arises particularly at marginally viable scales of operation. Usually at the inception of a new industry, trade unions will accept the idea and problems will not arise if agreements are made in advance. A hand-gatherer, for example, can be switched to colour label application when not needed in his primary role.

The ability to maximize labour utilization opens up the possibility of maximizing capital utilization also and so allows the whole plant to be optimized. Consider, for example, the case where the demand for bottles is only enough to justify one bottle machine rather than the two needed to make a conventional factory viable. The spectrum of bottle sales is usually somewhat similar in most countries, the bulk of which is for standardized soft-drink and beer bottles and bottles for wines and spirits. Most of these bottles have weights ranging from 300 to 750 g with extremes of perhaps 50 and 1000 g. A four-section bottle machine would require glass to be melted at rates of 3.6-28 t/d to correspond to the extremes and a furnace designed to meet the maximum would be operating at only 13% capacity when making the smallest bottle. Apart from the poor melting efficiency the utilization of this large item of capital equipment would be very low. Suppose, however, that one excludes the extremes from the automatic machine. Then the furnace could be designed for 24 t/d for the 750-g bottle; for a 300-g bottle, requiring 14.4 t/d, the furnace would still be operating at 60% capacity.

Suppose, now, that facilities for gathering glass by hand are provided on the furnace, and that the extreme bottle sizes are made on semi-automatic machines when excess melting capacity allows. Then the utilization can be brought up to nearly 100% at all times, and the savings to be made are likely to offset the inherently lower productivity of semi-automatic production methods provided that the hand-shop teams can be gainfully employed when not needed on the furnace.

There are other departures from conventional practices that can help to make a small-scale operation viable. Electric melting is the most efficient way of melting glass but not extensively used in industrial countries because of the high cost of electric power and because their technology and know-how have been based on inexpensive fuels and large-scale melting. In fact, as can be derived from the data in chapter IV, there is a break-even point between electric and fuel-fired furnaces which favours electric melting at furnace capacities lower than 15-30 t/d, depending on relative fuel costs. For small-scale operations, electric melting may prove cheaper in both investment cost and running cost and much more versatile in allowing quick colour changes and the ability to match the power input to the glass required. Know-how must be learned in any case, but electrical engineers are easy to recruit.

The choice between electric or fuel firing will usually turn on one's confidence in the forecast of future demand. An electric furnace is small, of shorter life, requires little in the way of special buildings and can therefore be designed to relatively short-term needs and enlarged as required. A conventional regenerative furnace, on the other hand, is a major structure requiring special buildings and is not easily enlarged except at the cost of a complete rebuilding. One is therefore forced to design to the long-term forecast of demand, under-run the facility in the short term, and carry the cost of unproductive capital in the interest of having a better ultimate melting cost.

It will be seen that the business of making a viable operation in a marginal situation is largely a question of cutting down the capital cost by maximum utilization. There is a tendency at the inception of a major project to spend money on things that are not absolutely essential in the belief that it may not be possible to find the money for them if they should be wanted later, or because the self-serving advice of some equipment supplier is blindly accepted. There have been many such "gold-plated" factories built in developing countries that can never be viable until the owners write down their capital to realistic values, write off accumulated losses, and recognize that the value of the plant is set by what it can produce and not by what it cost.

#### Staffing a small glass factory

It is well to remember that most of the advice given in textbooks on management and business management and administration has been evolved to cope

with the problems of large firms (usually engineering industries), where the ramifications make it difficult to see the broad picture. It is illogical merely to reproduce the textbook organization charts in miniature. For small-scale operations the staff can work inherently as a team without the same formalized job descriptions, defined lines of communication and departmentalization needed in large firms. It should have a structure like a football team, with broad areas of clearly understood responsibility, but with functions overlapping and interwoven as best suits the game at any moment of time. The size of the staff is then determined by the work-load and not by a need to include every type of specialist; a specialist can soon learn to cover adequately a field wider than his specialization.

In much the same way, administrative controls, budgetary controls or costing systems have been devised for large organizations and often have unrealistic aspects that are acceptable only because the large scale makes some arbitrary simplification necessary. When applied to small organizations these controls may only confuse the issues. Possibly their only value is as a means of presenting a monthly picture to some top policy-making body. Except at the policy-making level, however, the board has no control, and these systems are then no longer control systems but simply records of progress, irksome to operate and often detrimental to morale and to team-work.

In a small organization, the manager can see the broad picture easily, and any control system used should be designed to serve those who are actually in a position to control, so that they are the first persons, and not the last, to have performance data. The simpler the performance indicator, the better. Since so many of the costs are fixed costs and can be related to through-puts of departments as a function of time, there is seldom a problem in devising a performance figure that is both realistic and meaningful to the person in charge. The same figures can then be converted into a form more suitable for presentation to the policy-making body.

In developing countries, the problem of staffing is not so much one of finding academically trained personnel; they may lack practical experience and consequently have a tendency to try and make the organization fit the systems they have learned at school. What is wanted are managers who will do the opposite: study the needs of the organization and devise the system which best suits it, even if some of their academic training has to go unused.

## IX. COST PROFILES AND TRENDS IN THE GLASS CONTAINER INDUSTRY

It was mentioned in chapter I that the nominal price of bottles has been held remarkably constant since the days of hand production, despite a huge reduction in the real value of money. Unhappily, those days are over, for most possibilities for absorbing increased manufacturing cost have already been exploited. The fact that the industry was based largely on naturally occurring raw materials was a stabilizing factor, but now synthesized components, principally soda ash, dominate the manufacturing cost (it is about 70% of the total), which therefore follows world-wide inflation trends. The forming process is now almost wholly automated, and melting efficiency has been pushed nearer the ultimate by the introduction of refractories that allow better thermal insulation of the furnace, as was seen in chapter V.

Some idea of the way in which trends are likely to take place can be obtained by looking at the cost structure of a glass factory in different ways. Of course, the magnitudes and distribution of cost differ from one country to another and from one factory to another, but the relative values given in tables 15 and 16 are believed reasonable for a minimum bottle factory having one furnace serving two automatic machines and production lines. For 1976, the total capital cost might be of the order \$4 million, the average annual operating cost about \$200 per ton of glass produced (10 000-12 000 t/a), the total work force might number 100-120 and the total power required to operate the factory whether from electricity, gas or oil, about 7000 kW.

In table 15 the relative distribution of capital is shown together with that for power and labour because, to some extent, these are complementary and could represent alternative ways of accomplishing the same task. When labour rates increase at a greater rate than equipment costs there is naturally a tendency for automation to replace labour, but that is not the only driving force. Some years ago it was common to find archaic shovel and wheel-barrow methods used for batch mixing, because the high cost of a mechanical batch-house was not justifiable on a departmental basis by the labour that could be saved. However, with the development of improved quality-control methods it was found that the superior accuracy in weighing and uniformity of mixing of automatic plant paid for itself in improved quality of the ware. In large factories this operation is now usually full automatic and the furnace-minder himself activates it by pressing a button.

Table 15. Distribution of capital, total power and labour costs in a minimum glass factory  
(%)

Item	Capital	Total power	Labour
Buildings and civil works	17.50		
Sand and cullet treatment	3.60	4.24	2
Batch house	6.71	0.85	4
Furnace	13.43	59.19	4
Feeders	9.11	6.61	-
Forming machines	11.99	4.24	8
Annealing	7.19	9.11	4
Inspection and packing	0.48	-	18
Decorating	8.39	12.08	12
Workshop and maintenance	2.88	0.57	15
Laboratory	1.20	-	6
Electricity supply	4.80	-	5
Gas, oil and water services	6.71		
Compressor and vacuum	3.60	3.11	4
Transport and miscellaneous	2.40	-	8
Management and administration			<u>10</u>
Total	100	100	100

The table shows that both inspection and decoration (where returnable bottles are permanently labelled etc.) have a relatively high labour content. Both these activities can be largely automated, but the machines require so much maintenance that some of the labour displaced here may turn up as an increase in the next line of the table.

As an illustration of past trends, the industry as a whole in the United Kingdom of Great Britain and Northern Ireland succeeded in holding the labour cost at about 33% of total operating cost over 1968-1974 despite an increase in the average wage of 130%. This was achieved mostly by an increase in productivity (the reduction of staff was only 10%), no doubt due to increased mechanisation, and a doubling of the sales value of the output.

It is probable that the use of computers will increase in the sensitive operation of job control, where maintenance of shape and weight can improve the quality, yield and consistency of the product and shorten the unproductive setting-up time after a job change. It is probable also that automatic inspection will be directed to the input, or hot, end of the annealing Lehr, so that the feedback of information to the machine and feeder will be more immediate.

Table 16 gives the approximate distribution of operating cost. To determine the interest cost, it is assumed that the equity is 40% and the balance of the investment is borrowed at 9%. The need for a sufficient margin between selling value and operating cost is obvious but not simply to provide dividends for the equity holders. The loan must be repaid. There must be cash for operating capital to cover reserves of raw materials and products as yet unpaid for. Cash must be accumulated to meet the difference between replacement value and depreciation allowance and to provide for expansion or modernization.

Table 16. Approximate distribution of operating costs  
of a minimum glass factory  
(%)

Item	Fixed	Variable	Total
Raw materials <sup>a/</sup>	-	24.9	24.9
Other materials	-	3.4	3.4
Fuels	14.4	4.5	18.9
Electricity	2.0	-	2.0
Labour	12.6	2.0	14.6
Maintenance (excluding labour)	2.2	-	2.2
Transport	1.3	-	1.3
Depreciation	19.3	-	19.3
Loan interest	<u>13.4</u>	<u>-</u>	<u>13.4</u>
Total	65.2	34.8	100.0

a/ A developing country not well endowed with raw materials is assumed.

The greater the proportion of variable costs, the better is the ability to control and reduce costs at times of low demand, and a technology that permits this is preferred. In the example given only about one third is variable, but any competent accountant who has an accountancy system that suits the



factory would be able to disclose many items of fixed expenditure over which control could be exerted, so that the divisions made in the table are rather arbitrary. Nevertheless, the fact remains that much of the annual cost is predetermined by the original design of the factory, and particular consideration should be given at this stage of a new venture. Unfortunately, in developing countries, the customer is not sufficiently knowledgeable to resist the pressure of suppliers' salesmen and may be induced to accept elaborate equipment, excellent in its own way but unjustifiable for the planned scale of operation.

Sometimes it pays to shift an item of fixed cost into the variable column by hiring the service from outside the factory. Indeed, there has been a trend of this type in that furnaces are now usually rebuilt by outside contractors so that there is no need to employ permanent staff to perform this occasional but vital work.

An illustration of the influence of choice of technology is that electric furnaces and fuel-fired furnaces boosted by electricity have the advantage that the energy input can be more closely matched with the demand for glass. For an electric furnace the energy input is about halved (making for much more comfortable working conditions), but as this "fuel" is five times as costly as oil, the other advantages of melting by electricity have to be assessed. Freedom from atmospheric pollution is difficult to put a value on but is receiving more and more attention and in some countries may become mandatory particularly for fluoride or lead glasses. The ability to rebuild rapidly and to make colour changes quickly in the much smaller electric furnace may mean that the number of productive days per year is 10% higher; the fixed costs for the entire factory are therefore reduced to 90%, with a substantial economic advantage. Building costs are lower, and the load factor (the ratio of the average demand to the maximum demand for power at any one time), upon which the tariff is usually based, is much more favourable. Thus, the total outlay for power in the factory is reduced. The charges for electricity in many countries are determined by government policy; sometimes the industrial user is favoured, sometimes the domestic user. Even where there is no hydroelectric generation, the electricity authority's costs are not determined entirely by the cost of fuel, so that escalation of oil prices tends to reduce the differential between electricity and oil costs for glass melting. If the public supply is felt to

be too costly, one can consider the private generation of electricity, which can be done for about 3 cents/kWh (compared with about 0.62 cents/kWh for oil). That may be less than the rate charged by a public company because the cost of distribution, a high cost component in the public company's budget, is avoided.

There has been a trend to new methods of packing, to reduce the cost of the "other materials" item and reduce handling costs both in the factory and the customer's premises. The cost of getting the fragile product unbroken into the hands of the ultimate user is not negligible. The former practice of packing tableware in straw in returnable casks involved much labour at both ends of the journey, was untidy and was subject to health regulations. The higher cost of specially designed cartons can often be passed to the customer if there is an advantage to him. The cartons may also serve several purposes on the way: they may provide a convenient method of storage to the wholesaler, make an attractive display in the shop and simplify the wrapping for sale across the counter. For bottles and flat glass, the function of packaging is primarily to minimize breakage in handling, since these products are re-processed in some way before they reach the ultimate customer. Sometimes a bottler will supply his own cartons or crates and reuse them for delivery of his bottled product.

It seems that the effect of the label "Glass - handle with care!" is only to suggest to the handler that the package is designed to meet abuse; he therefore does not in fact handle the package with care. On the other hand, if it is obvious that care is required, it will be given. Thus, large fragile vessels of glass are usually safest when boxed in crates, which expose the nature of the contents. In the same way, pallets supporting perhaps 500 bottles, protected by nothing more than a heat-shrunk plastic sheet to bind them together, are treated with the care they obviously require. If the customer is within lorry distance of the factory, this "shrink-wrapping" method is the one usually preferred and is becoming increasingly popular.

A similar approach may be used in transporting flat glass by freight. Because of its nature, the product can be packed with high density, i.e., with a low ratio of packing material to product. Nevertheless, considerable savings in material can still be made by designing the package to give support and resistance to the actual forces likely to be encountered, rather than

using a case "built like a battleship". There are many new products, such as air-cushion plastic film, composition boards etc., which give scope to the designer and may ease the situation in a country where crating timber is in short supply.

Another trend has been the "light-weighting" of bottles. In general terms, the mechanical strength of a glass container is determined by the strength of its thinnest section; if strength is the only consideration, the thicker sections represent a waste of glass. There is, therefore, scope for reducing the weight of the product by closer control of its thickness distribution. Moreover, light-weight bottles are made faster on the forming machines, so that there are savings not only in raw materials and fuel but also on all fixed charges that accrue on a time basis. A disadvantage is that thin bottles superficially damaged in service are not suitable for reuse by the bottler, i.e. they are "single-trip" bottles. However, the huge growth of the super-market, where return of empties is rather impractical anyway, has created a need for attractive single-trip containers involving a minimum of wastage.

The thinner bottles are often made more robust by giving them an invisible coating of tin oxide or an organic film (or both) to minimize damage by scratching. When new, they are remarkably serviceable. The tin oxide is formed in situ as the bottles enter the annealing Lehr and seem to improve the intrinsic strength. The organic film, applied as the bottles cool in the final section of the Lehr, has the effect of lubricating any rubbing contact between bottles so that they scratch less easily.

The practice of using single-trip bottles in place of those which are used 30 to 40 times before being discarded, has naturally led to environmental problems in disposing of the waste. There have been many serious attempts made to return this waste as cullet to the glass factories for remelting. The difficulty is one of cost. As may be seen from table 16 the potential value of cullet, as a substitute for raw materials, is about 25% of the manufacturing cost and that therefore it might be said that a broken bottle is still worth (say) 20% of its purchase price. But that would be true only if the cullet could be returned to the furnace where it was first melted, uncontaminated and reduced to a free-flowing gravel. Recirculation of this kind is, of course, practiced within the factory itself. The cullet in this

case is usually clean, and the only additional cost is for crushing and handling. With each remelting there is usually some contamination by iron and some loss of volatiles, so that there is a progressive degradation in quality, which, however, is slight if the proportion of cullet is not high.

At a bottling plant, broken glass can usually be kept segregated by manufacturer and colour at little expense, but the additional cost of transport, removal of labels and separation of metal caps cannot be avoided. Cullet brought into the factory from outside is called "foreign" cullet and has to be used with circumspection because its composition may be different enough to upset the melting and forming processes.

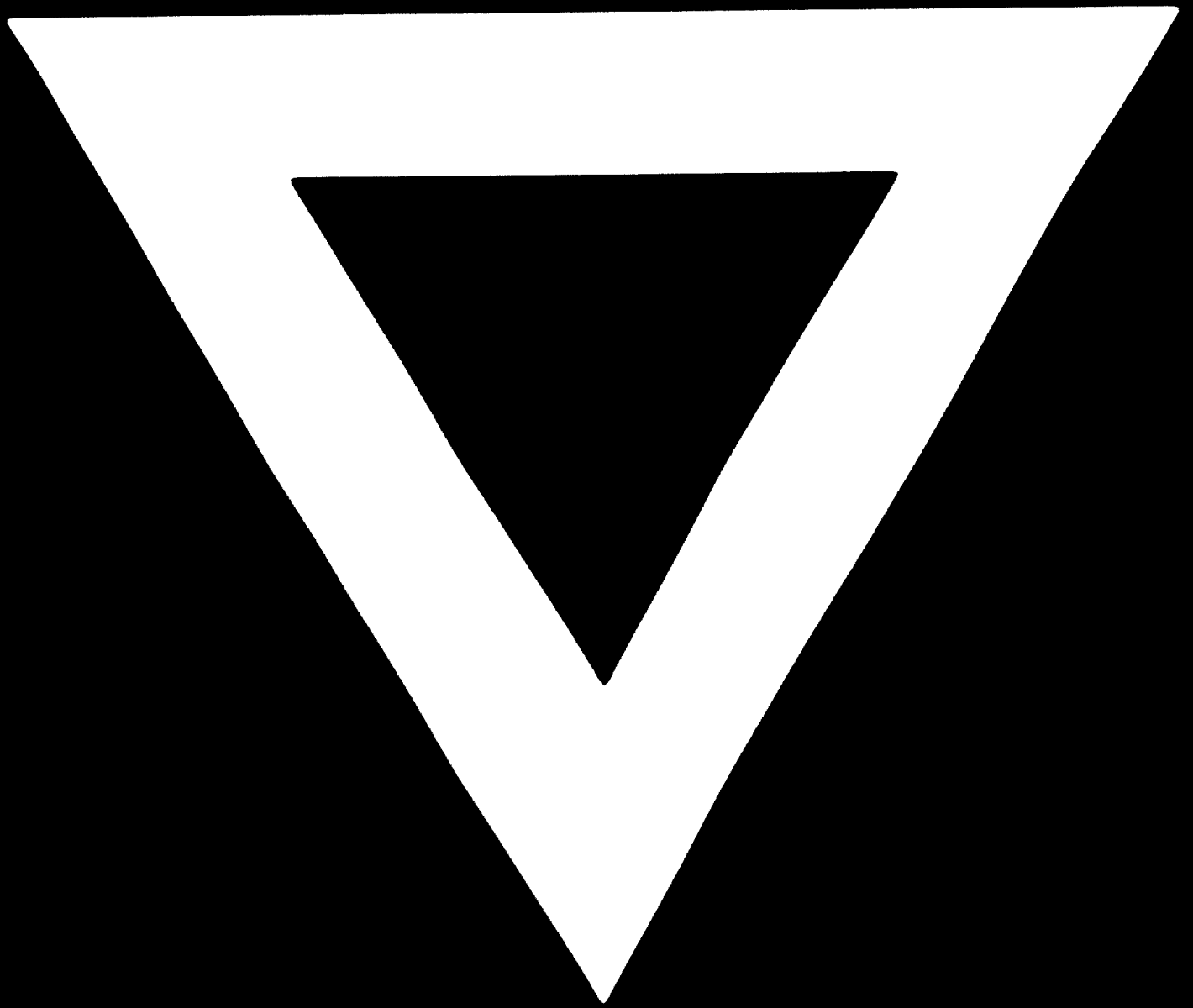
The real cost of recovering waste glass from individual households is prohibitive, although in some communities some of this cost is hidden because collection is done by unpaid volunteers. The task is comparable to that done by the postal services; at present postal rates it would cost less to use new bottles. The only practical solution would appear to be to use existing refuse collection schemes, challenging the operators to make it profitable. To judge from table 3, a city of 100 000 inhabitants would have to collect, wash and separate about 10 t of broken glass of various colours from perhaps 1000 t of general refuse. And, separation of colours is a major problem. Although cullet of mixed colour can be used for making glass-foam insulating blocks and pipe coverings or in making concrete and roads, it must be remembered that waste glass actually serves a useful purpose in the consolidation of refuse dumps and protecting them from erosion by wind and water. The discarded glass may look unsightly at first, but ultimately it breaks down to a "sand" not much different in nature from that from which it was made.



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