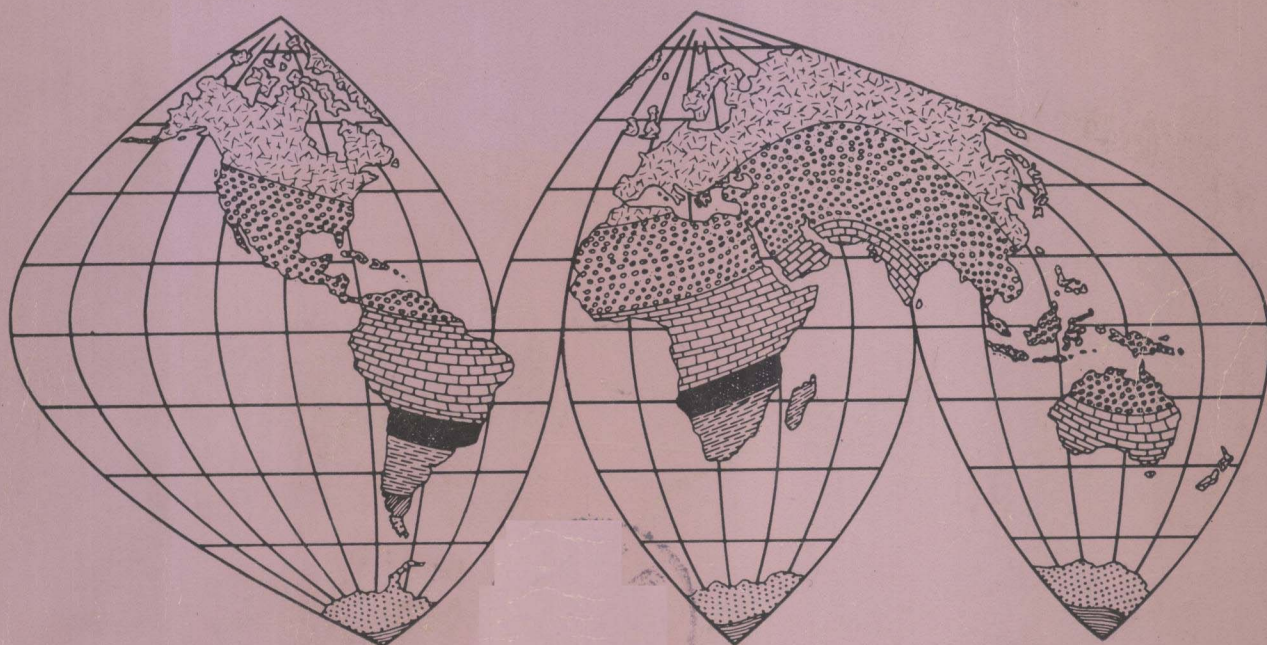


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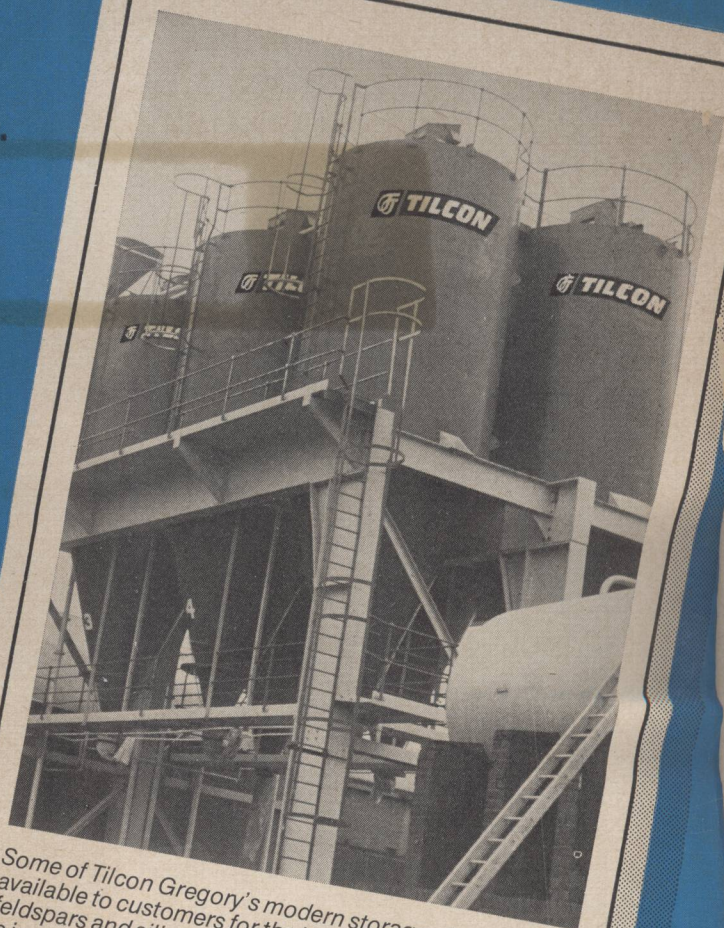
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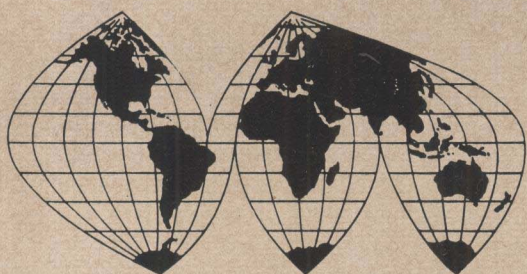
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An 'Industrial Minerals' Consumer Survey

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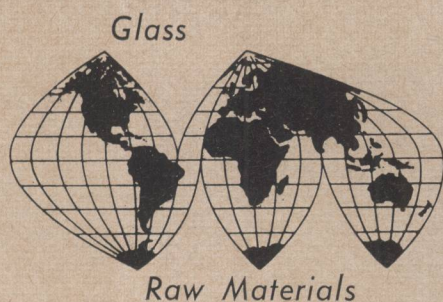
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Introduction

ABSTRACT

Glass, once described as 'a liquid that has become too cold to freeze', has a number of mechanical, thermal, optical, chemical, and electrical properties which makes it a highly practical and versatile material. The only commercial *primary* glass-forming compound is silica (SiO_2), although non-commercial examples include boric oxide, phosphorus pentoxide, and arsenic oxide; *intermediates*, such as lead oxide, titania, and alumina, will not form a glass independently but will partake in the process with a primary glass-former; and *modifiers*, for example lime, soda, and potash, affect or 'modify' the system and the final glass product. Glass manufacture requires four basic stages—*melting* the batch of raw materials; *refining* to a homogeneous mix; *working* to the desired shape; and *annealing* to relieve internal stresses. The major raw materials used are: silica; soda ash; limestone and dolomite; sodium sulphate; potash; feldspar, nepheline syenite, and other alumina additions; boron compounds; lead oxide, barium and strontium; lithia; fluorspar and cryolite; and a multiplicity of miscellaneous compounds. Soda-lime-silica, however, are the components for over 90% of the glass melted.

A definition of glass

IT MIGHT seem a little unnecessary to define glass since it is hardly the place of IM to tell everyone that glass is the material from which windows, bottles, jars, light bulbs, and a whole host of other products are made. As this article is attempting to introduce the role of raw materials in glass manufacture a chemical definition might seem appropriate. The number of glass types and the consequent range of materials used in their manufacture make a chemical definition hopelessly inadequate, however, and to have any absolute meaning, glass must be defined in physical terms. This in itself is an understatement since glass defines a precise physical state. Though it is hard and rigid, glass is not a solid in the strictest sense of the word. It is, in fact, a super-cooled liquid—a substance that is in the liquid state far below its theoretical freezing point.

To understand this concept one must look at the physical behaviour of a 'normal' inorganic substance with respect to temperature. At a high temperature this substance will be in the liquid state. As the temperature is lowered the viscosity increases i.e. the liquid flows less easily. At a certain point—known as the freezing (or melting) point—a physical change takes place whereby the random arrangement of molecules of a liquid is transformed into the ordered crystalline structure of a solid, and the substance is now hard and rigid. Glass does not behave in this way, however, since normally it does not 'freeze'. At a very high temperature 'molten' glass behaves in a similar way to any other molten substance and as the temperature is lowered the viscosity increases. Instead of crystallising at some point, the glass just continues to get more and more viscous until it is for practical purposes as rigid as any other solid.

Glass has been described as 'a liquid that has become too cold to freeze', and the reason why it can be cooled to very far below its theoretical freezing point has to do with the strength of the inter-atomic bonds both within and between its fundamental molecules. In a so-called 'glass-forming material', these bonds are of

such a strength that viscosity increases exceptionally rapidly as it is cooled and the rearrangement of molecules necessary for crystallisation is prevented. The material retains the random structure of a liquid but in a network which is to all intents and purposes immobile, and it is this attribute that is directly or indirectly responsible for the unique properties of glass.

Properties of glass

Ask any non-technical man what properties of glass first spring to his mind and he will probably think of transparency, rigidity, and its ability to break easily. In technical terms these three characteristics relate to its optical, mechanical and thermal properties. The chief feature of its **mechanical** properties is that glass is strong in compression but weak in tension, and this is due to its crack sensitivity. Since glass is so rigid, a force that places the surface of glass in tension will be concentrated at the base of any small surface crack (a similar force applied to a flexible material is apportioned throughout the material as it bends). The random structure of glass means that there are no internal boundaries to halt the propagation of a crack, and therefore once a crack is initiated it spreads very rapidly indeed. Compression, on the other hand, tends to close up a crack thereby preventing any further propagation. The **thermal** properties of glass also have a bearing on its crack sensitivity. Since glass is a poor conductor of heat, any sudden change of temperature at the surface is transmitted very slowly to the interior. Expansion (or contraction) due to temperature change is responsible for the setting up of internal stresses which again may lead to crack propagation. The range of compositions of and types of glass means that a range of thermal and mechanical properties may be obtained and furthermore by various chemical and thermal process the defects (particularly crack sensitivity) may be minimised. A number of treatments have been devised to place the surface of glass in permanent compression.

Transparency and the other **optical** properties of

glass may also be explained in terms of the internal structure. The absence of internal boundaries inherent in glass (and liquids) means that light passing through it only encounters two optical boundaries i.e. the surfaces. Some light is lost through reflection at these boundaries but the greater part travels through unimpeded. A conventional solid made up of millions of individual grains will not allow the passage of light and is therefore opaque; the only crystalline solids that show transparency are single crystals. The fact that light travels at a different velocity in glass than it does in air gives rise to a number of other important optical properties including those of refraction and dispersion. These two properties of 'bending' light and separating light of different wavelengths are exploited in a wide range of optical instruments such as microscopes, telescopes, spectacles, and cameras, all of which use glass lenses or prisms. The wide range of compositions of glass allows much flexibility in directing optical properties and overcoming inherent properties such as chromatic aberration in lenses. Ideally a lens bends light to focus it at a single point, but since 'white' light is composed of a number of wavelengths (from red light to blue light), the different components are focused at separate points. A compound lens containing lenses of different chemical composition can be made to correct this defect. Not all glasses are transparent, of course, nor are they all colourless, and to achieve the many varieties of opaque and coloured glasses is once again a matter of changing the composition of the glass.

The two other main properties of glass to be considered are chemical and electrical. The **chemical** properties of glass are often taken for granted but it is amazing how many potentially corrosive liquids glass containers are expected to hold. Anyone who has felt the corrosive effects of cheap wine in his stomach cannot fail to be impressed by the bottle's ability to hold the liquid without protest. Most common glasses based on silica are resistant to water and the majority of acids, but are attacked by alkalis. Alkali-resistant glasses can be made by adjusting the composition. In fact it is probably fair to say that a glass can be manufactured to combat any particular corrosion problem (though this might be to the detriment of other properties). The other main problem of chemical stability concerns devitrification i.e. the glass may crystallise into a normal solid. As it happens, glass is most vulnerable to devitrification at temperatures just below that at which the component materials melt. At room temperatures the viscosity of the glass is too high to allow the internal rearrangement of molecules necessary to allow crystallisation.

So far as its **electrical** properties are concerned, glass is usually considered as an insulator since at room temperature it has a very high electrical resistance. This is not due to any inherent property, however, and glass can carry a current at high temperature. Common glasses contain metallic ions and it is the enormous viscosity at low temperature which prevents the flow of electricity through these ions. At high temperatures where the viscosity is low, glass may carry an appreciable current (in a similar way to an electrolyte dissolved in water.) It should be noted that this property is exploited in the electrical melting of glass-forming materials.

Chemical composition of glass

The compounds of about a third of the elements in the Periodic Table are used in glass at some time or another, but the number of materials used in bulk is small.

Furthermore, though it is theoretically possible to produce a 'glass network' from a large number of compounds (and even a single element such as sulphur) very few can be considered to be true glass-formers on practical grounds. When all such practical details as ease of formation, availability of raw materials, and stability of the finished glass are considered, one is left with just one truly commercial primary glass-forming compound—silicon dioxide (SiO_2) or, to give it its common name, silica. The other materials used in glass are not necessarily glass-formers on their own account and it is necessary to look briefly at the nature of the glass network to define the role of such materials. True *primary glass-formers* that will form a glass network in the pure form include silica, boric oxide, phosphorus pentoxide, tellurium dioxide, and arsenic oxide and sulphide. A number of other compounds such as alumina, lead oxide, titania and zinc oxide will not form a glass network on their own account but will partake in the network of a primary glass-former such as silica. These compounds are known as *intermediates*. A third category, known as *modifiers*, includes compounds such as lime, soda, and potash which are not bonded to the network but whose presence in the glass tends to 'open up' the network by reducing the number of network bonds. In this way the modifiers tend to reduce the viscosity of the glass as well as to confer beneficial chemical or optical properties when necessary.

Soda-lime-silica glass

On its own, silica is difficult to melt and work to shape because of the very high temperatures involved—its melting point is over $1,700^\circ\text{C}$. and working of silica glass cannot be carried out at temperatures much below this since its viscosity soon becomes too high. Pure silica glass displays some outstanding properties but for nearly all practical purposes these are not worth the enormous expense involved in its manufacture. Hence modifiers are used on economic grounds as well as for the various properties they confer. The two most common bulk additions to silica in glass are soda ash (sodium carbonate, Na_2CO_3) and limestone (calcium carbonate, CaCO_3). In the resultant glass the elements sodium and calcium are present as the oxides—soda and lime—and hence the name **soda-lime-silica** glass. These three components are the basis for over 90% of all glass melted. As well as lowering the temperature of initial formation of the glass, the presence of soda and lime lowers the viscosity sufficiently to allow working at temperatures as low as 600°C .

Minor ingredients

The most common composition of a soda-lime-silica glass is approximately 70% silica, 15% soda, and 5-10% lime, with the balance made up alumina, magnesia and other minor ingredients. These minor ingredients may be added intentionally or purely because of their presence in the main raw materials that introduce silica, soda, and lime to the glass. Neither alumina nor magnesia confers harmful properties on the finished glass, and in many cases both have a positively beneficial effect, adding chemical resistance and strength. Of the other minor ingredients used in soda-lime-silica glass special mention should be made of refining agents such as salt cake (sodium sulphate, Na_2SO_4). Like soda ash, salt cake finishes up in the final product in the form of soda but its role as a source of soda is secondary to its invaluable effect in preventing scum forming during the refining stage. A little carbon in the form of anthracite or coke is added with the salt cake to aid the reduction

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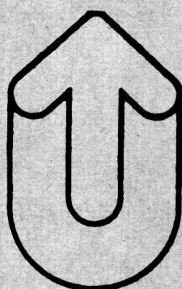
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of the sulphate radical. Lesser used refining agents include calcium sulphate (in the form of gypsum or anhydrite), arsenic oxide, antimony oxide, sodium nitrate, and 'Calumite' (a processed slag containing lime, alumina, and silica). Some glass manufacturers also favour small additions of fluxing agents such as boric oxide, lithia, or fluorspar to aid the melting process, but this is the exception rather than the rule.

Apart from the constituents mentioned so far, it is probably true to say that any other additives to a soda-lime-silica glass batch are made either to counter the effects of impurity present in other raw materials or to give special effects such as coloured and opaque glass. An example of the former is the use of a selenium-cobalt oxide mixture to decolourise the green tint that iron oxide impurity gives to glass. Colouring agents include selenium (pink), cobalt oxide (blue and, in conjunction with other compounds, green), nickel oxide (blue to brown), iron oxides (green, yellow, blue, brown), and iron sulphide (amber). The principal opacifying agents are fluorspar, cryolite (sodium aluminium fluoride), and zinc oxide.

Other commercial glass types

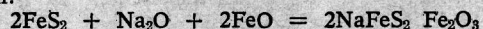
After soda-lime-silica glass, the most important commercial glass types are lead-alkali-silica, borosilicate, and aluminosilicate glass. **Lead-alkali-silica** glass, as its name would suggest, consists primarily of lead oxide, silica, and an alkaline modifier which may be soda, potash, or both. The lead oxide content varies from 20% to as high as 80% in certain circumstances. When used to make tableware it is often known as 'crystal' glass and, in fact, the so-called 'flint' glasses produced by the optical industry are lead-alkali-silica glass. The primary constituents of **borosilicate** glass are silica (60-80%) and boric oxide (10-25%) with smaller quantities of alumina, soda, and barium oxide (occasionally). **Aluminosilicate** glass contains silica (10-60%), alumina (20-40%), and lime (5-50%). Between the last two there exists an intermediate range of glasses known as **aluminoborosilicates**, and the two groups are often considered as one. These glasses display outstanding properties of low thermal expansion and high chemical resistance. In general the borosilicates possess the better thermal characteristics and the aluminosilicates the better chemical resistance. They are used for laboratory glass ware, industrial piping, domestic ovenware (such as *Pyrex*), etc. Lithia is also a frequent constituent of these glasses, both for its fluxing properties and for the thermal properties it lends to the finished glass.

Other glasses

Apart from the glass systems mentioned above there are a number of other glass types which, though small in terms of tonnage output, are of more than academic interest. Many of them have been developed for special optical or electrical properties required by the nuclear power, space research, and electronics industries. Not all of them contain silica so that other primary glass-formers such as boric oxide, phosphorus pentoxide, vanadium pentoxide, and tellurium dioxide assume the role of parent glass-former. The raw materials required for such glasses are strictly beyond the bounds of industrial minerals, however, and their relevance to this survey are therefore minimal.

The desirable qualities of a good amber glass—an attractive amber coloration, a minimum of seed and blistering, and a good colour stability—are achieved by the use of a variety of additives, the sulphur content of which combines with the iron content in the sand or other materials to produce the amber coloration. Elemental sulphur as an

additive is inefficient as up to 90% of the sulphur is burnt away, leaving only a small proportion of the original input to be effective in the coloration process, and sulphate may give rise to certain technical problems during production, as it has first to be converted into sulphide, during which process SO_2 is released, which can give rise to reboil bubbles in the glass. Moreover, there arises a further formation of bubbles when the sulphides react with the remaining unconverted sulphates, thus prolonging the time required for refining and causing excessive seed and blistering in the finished glass. The experience over a number of years of Continental European amber glass producers has proved that certain advantages are obtained by the use of a single additive containing both the sulphur and the iron necessary (as a pure iron sulphide), which gives rise to the following reaction:



This reaction releases only a minimal amount of oxygen and therefore only a limited number of bubbles, hence reducing the risk of imperfect production due to blistering. The amount of iron sulphide additive used depends on the Fe and S content of the other raw material inputs, and there is a strict colour intensity correlation between the pure iron sulphide additive and the carbon reducing agent.

Glass manufacture

There are four basic stages common to the manufacture of all glass products: **melting** of the raw materials; **refining** to achieve homogeneity of the molten glass; **working** to form the glass into the desired shape; and **annealing** to relieve internal stresses developed during the working stage. Other treatments such as toughening or decorating may be regarded as additional stages for specific types of glass. The melting process begins with a chemical reaction between the various raw materials at temperatures well below the individual melting points of the materials. To assist melting, the raw materials are thoroughly mixed before entering the furnace and waste glass of the same type, known as cullet, is also added. Cullet melts before any of the separate constituents and therefore speeds melting quite considerably. In soda-lime-silica glass the reactions take place in the 600-900 deg. C. range, releasing carbon dioxide and other gases which form bubbles in the rather sticky mess that is the partially-formed glass. To remove these bubbles and to ensure that the reactions are complete the temperature of the batch is raised to about 1,500 deg. C. or 1,600 deg. C.—the refining stage. The refining agents such as sodium sulphate (which are added to the original batch) become most active in their role of aiding the release of bubbles and preventing the formation of a scum on the surface of the molten glass. At the end of refining the glass should be truly homogeneous but it is too thin and watery for working. The melt is therefore cooled to about 1,000 deg. C. to obtain the required viscosity for working to begin.

Furnaces

The melting process was traditionally carried out in pots, or large crucibles, with up to twenty pots heated in one furnace. Pots are still used when glass of a specific composition is required in limited quantities—such as for optical, coloured, or artistic glassware—but all large scale production of glass is carried out in tank furnaces, in which one chamber serves to hold the glass as well as restricting and retaining the heat. These tank furnaces may be periodic or continuous. The periodic type, often known as a 'day tank', is generally used for producing glass in batches of between 5 and 10 tons. Accepted practice is for melting and refining to take place at night, to be followed by working during the day, so that the furnace is ready for charging again the next



A skilled glassworker fabricating the coils of a heat exchanger made in borosilicate glass. This particular item forms part of a consignment of glass plant, made by the Process Plant Division of James A. Jobling & Co. Ltd. of the UK, for use in precious metal refining. In addition to its heat-resisting properties, the borosilicate glass must stand up to a corrosive environment involving the use of caustic soda and strong hydrochloric acid

night—hence the name ‘day tank’. Although day tanks can produce larger tonnages more economically than pots, for really large scale glass production one must use continuous tank furnaces. Virtually all bulk glass manufacturers today use continuous tanks where raw materials are fed in at one end and molten glass is removed from the other end at the same rate.

Most tank furnaces in current use are oil or gas-fired and are of the regenerative type, i.e., the heat from the hot waste gases is employed in heating the air used to burn the fuel. This system is particularly suitable for large mass production processes where the continuous recycling of heat allows great savings in fuel costs. If such a furnace is subjected to a stoppage every few days, however, the economic benefits are lost in the time and expense consumed in restarting the operation. Glass manufacturers who wish to combine the economic advantages of continuous melting with flexibility of composition (requiring a stoppage every time a change is made) therefore use another type of furnace known as a unit melter. These are also oil or gas-fired tank furnaces but are smaller and simpler than the regenerative type. They make optimum use of fuel by heating from the refining end of the furnace and causing a heat flow counter to the flow of the batch.

In recent years electrical resistance heating has found favour in certain applications. Some oil and gas-fired furnaces employ resistance heating to boost the melting rate and achieve greater control of flow currents in the melt. All-electric furnaces are used when a particularly clean melt is required since then there is no possibility of picking up impurities from furnace gases.

The working stage—glass-forming

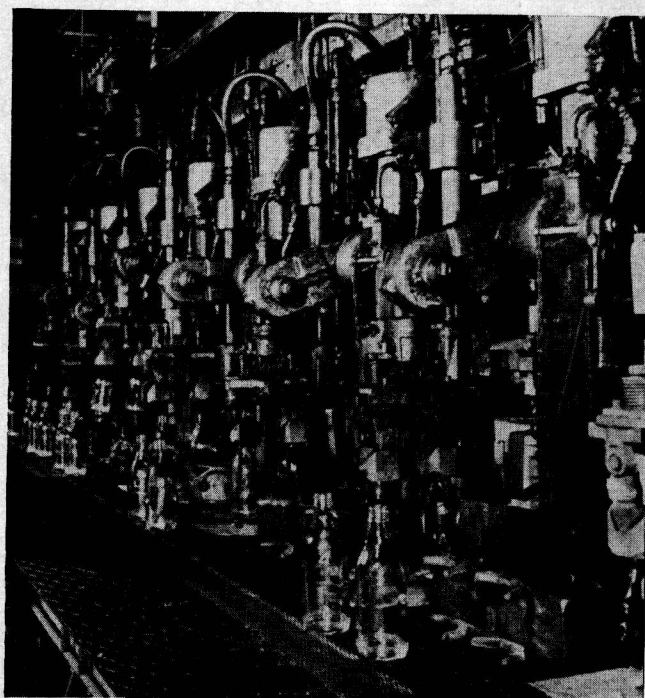
The two largest tonnage areas of glass manufacture are containers (bottles) and flat glass (windows) respectively, and over 75% of all glass melted is consumed in their manufacture. The remainder is consumed within the

broad areas of glass fibre; domestic (including fancy goods and ovenware); scientific and industrial (tubes, rods, beakers, thermometers, etc.); and optical and special glasses. These areas and the principal glass-forming processes are discussed in the following sections.

Containers

The container industry today is typified by automatic bottlemaking machines churning out milk bottles by the thousand. At first sight this type of production appears far removed from its origins in glassblowing. Glassblowing in its simplest form may be represented as a blowpipe with a bubble of hot glass at one end and a gentleman with inflated cheeks at the other. Very soon after its initial discovery 2,000 years ago, however, mass production methods evolved as Egyptian and Roman glassmakers began blowing glass into moulds to produce vessels of a standard shape. The modern bottlemaking processes of today still employ this basic technique except that compressed air equipment has replaced human lungs and automatic handling equipment of a highly sophisticated nature has been added. Although handblowing has not died as an art it is generally restricted to artistic glass and fine tableware.

Today's automatic processes are essentially two-stage operations—first a blank must be prepared and secondly this blank is blown into a mould for the final shaping. The earliest variant of this operation—known as the suction process—prepares the blank by sucking up molten glass from the furnace into a small mould. This blank is then transferred to a larger mould where it is blown to its final shape. Although this method is still employed in some glassworks, it has been largely superseded by the so-called gob-feeder process. In this case a measured ‘gob’ of molten glass is dropped into a mould where it is roughly shaped by blowing or pressing. It is then transferred to a larger mould to be blown to its final shape. The shaped containers then travel by automatic conveyor for annealing.



An automatic bottlemaking machine in operation. The bottles are blown to their final shape in a mould and deposited on to the conveyor. This particular machine is capable of producing more than 9,000 containers per hour. (Photo by courtesy of United Glass Ltd.)

Pressed glass

Pressed glass is essentially an offshoot of the container glass industry: instead of glass being blown into a mould, the hot glass is pressed into a mould by means of a plunger. It is a useful method for producing simple shapes such as bowls, dishes, and tumblers. For many years pressed glass was considered the poor relation of the industry since very little skill was required in producing pressed ware at a time when containers and flat glass were still craft industries. The increase in mechanisation throughout the industry has allowed pressed glass to become an accepted part of modern production, however, and some pressed glass products, such as television tubes, are highly sophisticated.

Flat glass

The prime requirements for high quality flat glass are uniform thickness (to prevent optical distortion), smooth surfaces (to allow the optimum passage of light), and the ability to produce it in large sizes. Until recently there was no completely acceptable method of satisfying all three requirements in the same sheet of glass. Flat glass produced in previous centuries—notably crown glass, broad glass, and cast plate—each had its own characteristic drawbacks. Crown glass, which was formed by the manipulation of molten glass in air, had smooth 'fired' surfaces but was of uneven thickness and its development was also hampered by size limitations. Cast plate was made by casting molten glass on to a flat metal table and flattening it with a roller. It could be made to even thickness and with a large surface area but the surfaces of the glass were dulled by contact with the metal table and roller. These surface defects could be removed to a large degree by grinding and polishing but this was a laborious and costly exercise. Broad glass was made by blowing a cylinder, cutting along its length and rolling it flat but here again the contact with metal left a dulled surface, if not as pronounced as in cast plate.

Drawn and rolled glass

In the early part of this century two techniques were evolved to produce flat glass in a continuous process. Neither of them was entirely successful in solving all three of the requirements mentioned above but they were, and still are, important methods for economically producing flat glass on a large scale. In the first method—known as the flat-drawn process—a continuous sheet of glass is drawn upwards from the melt by a series of asbestos-covered rollers enclosed in a vertical annealing kiln. The width of the sheet is maintained either by drawing the glass through a slit or by employing side rollers at the point where the sheet emerges from the melt. The temperature of the sheet is carefully controlled so that the glass is 'solidified' before reaching the first set of non-chilling asbestos rollers. In this way the smooth 'fired' appearance of the glass is preserved. Drawn sheet is not free from distortion, however, since very small differences in cooling rate and composition are sufficient to give rise to uneven thickness. It is therefore used in windows where a small amount of distortion is acceptable, e.g., domestic buildings, greenhouses, and factories.

The second method is essentially an extension of the cast plate technique mentioned earlier but, instead of casting molten glass on to a table, a continuous flow of molten glass from a tank furnace is fed between a pair

of rollers and travels horizontally on more rollers into an annealing kiln. Unlike the previous method the first pair of rollers actually shapes the glass, and the surfaces are therefore dulled by the contact. Such glass is suitable for applications where clear vision is not important e.g. factory windows, patterned glass partitions, and in wired glass. When clear vision is important, however, rolled glass needs the additional treatment of grinding and polishing. This treatment has already been termed laborious and costly and, despite the invention of large-scale mechanised techniques, these labels still apply. Furthermore the manufacturer of polished plate glass is faced with a waste problem with his ground glass and spent grinding and polishing media.

The float-glass process

These problems were solved satisfactorily only with the inception of the float-glass process, which first appeared in its commercial form in 1959. In this process, a continuous ribbon of glass moves out of the melting furnace and floats along the surface of a bath of molten tin. The ribbon is held at a high enough temperature for a long enough time for the irregularities to melt out and for the surfaces to become flat and parallel. Since the upper surface is in contact with the air and the lower surface with the perfectly flat surface of a liquid, the smooth fired surfaces are retained. The glass is cooled down while still on the molten tin until the surfaces are hard enough for it to be taken out of the bath without rollers marking the bottom surface. The natural forces within the float bath determine glass thickness at about 6mm. but techniques have been developed to produce a range of thicknesses from 2.5mm. to 25mm. Another major innovation to the process allows surface modification to be carried out during manufacture. Metallic ions such as copper can be made to replace metallic ions in the glass by creating an electric current between the molten tin and an electrode placed above the glass. This treatment, by the so-called electro-float process, yields glasses that reduce glare and reduce heat transmission.

Glass fibre

Glass fibre can be used for one of two main functions—insulation (of heat, sound, or electricity) and reinforcement (of plastic). The different requirements for each end usage dictate different methods of production. Glass fibre insulation is required in the form of a wool. This is most commonly achieved by pouring molten glass into a rapidly spinning dish whose circumference is punctuated by hundreds of small holes. The fibres that are forced out of the holes by centrifugal force are sprayed with a binder and are blown into a random distribution to form a matted wool. After further treatment the fibres are cut into a flexible mat or a rigid board. Fibreglass reinforcement is made by a continuous filament procedure whereby up to 500 or more individual filaments are drawn from tiny orifices. A binder is applied and the filaments are then combined into a single strand on a high-speed winder.

Tubes, rods, and light bulbs

Nearly all tube is manufactured in the mechanical drawing method in which molten glass flows from the tank on to a slowly revolving core or mandrel. A steady flow of air through an aperture in the mandrel fills the glass and the resultant tube is drawn off in a continuous process. Rods are produced in a similar way using a solid mandrel and no air. Electric light bulbs are produced by passing a ribbon of glass under a line of moving

'blow-heads' or nozzles. Air from the 'blow-heads' blows the glass into a corresponding line of 'blow-moulds' below the ribbon. When the final bulb shape has been blown the moulds open and the bulbs are automatically cracked off and carried away on a conveyor.

Annealing

In all the glass-forming processes described above, the glass product has been subject to uneven rates of cooling at some time during its formation. Contact with moulds, rolls, and other handling equipment cools the surface of the glass but leaves the interior at a comparatively high temperature. This sets up internal stresses within the glass which render the product fragile. These stresses are relieved by annealing, i.e., reheating the glass to a temperature sufficient to allow the internal flow of glass to remove the stresses. This temperature is typically around 500°C or 600°C for soda-lime-silica glasses. The products are then cooled slowly to room temperature to prevent the development of new stresses. This whole operation is carried out in an annealing kiln—or 'lehr'. For continuous production processes the lehrs take the form of a tunnel, through which the glass products proceed by conveyor. A temperature gradient is maintained through the length of the tunnel so that the emerging products are sufficiently cool to be handled at room temperature.

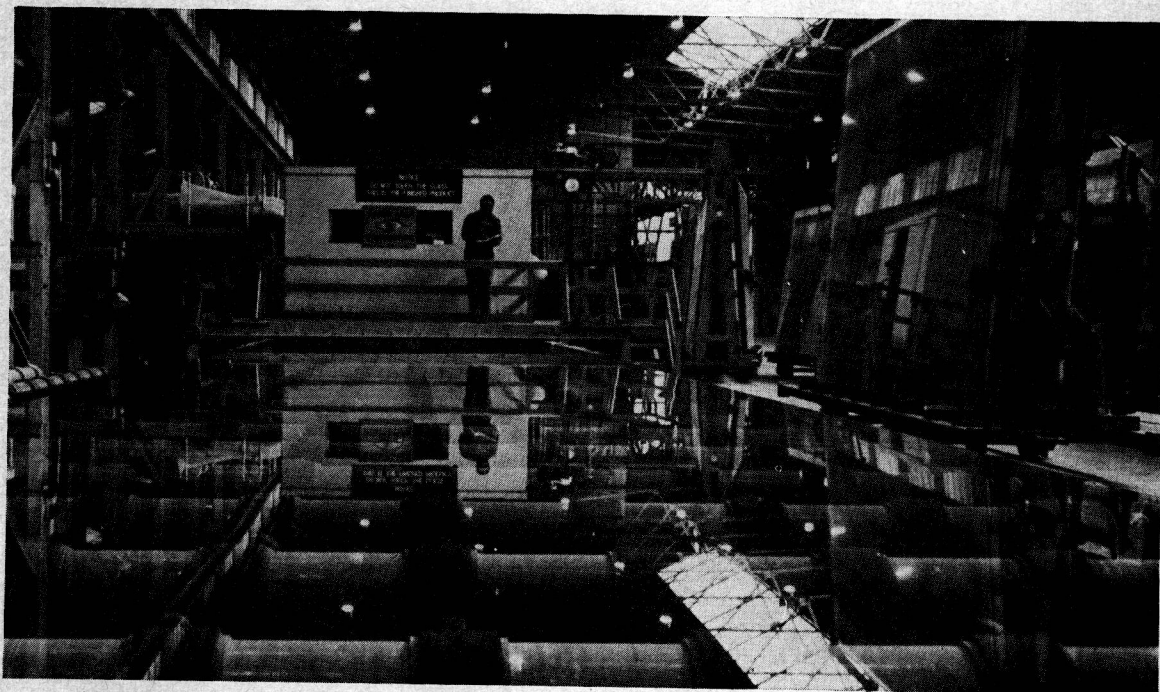
Raw materials

The earlier section on the chemical composition of glass dealt with the reasons for making a particular raw material addition on theoretical grounds, i.e., whether it acts as a glass-former or modifier, etc. The suitability of a particular raw material must also depend on a number of practical considerations, however, many of which are common to all batch materials. In most cases the most important of these practical considerations concern cost and availability; purity and consistency of chemical composition; and grain size and other physical characteristics. On cost and availability grounds it must be remembered that common glass is a low-cost, high-bulk product that will not stand the use of costly raw materials used in bulk. A glass manufacturer will use a natural mineral rather than a manufactured chemical, and a by-product material rather than a natural mineral if it will give him the required properties at a lower cost.

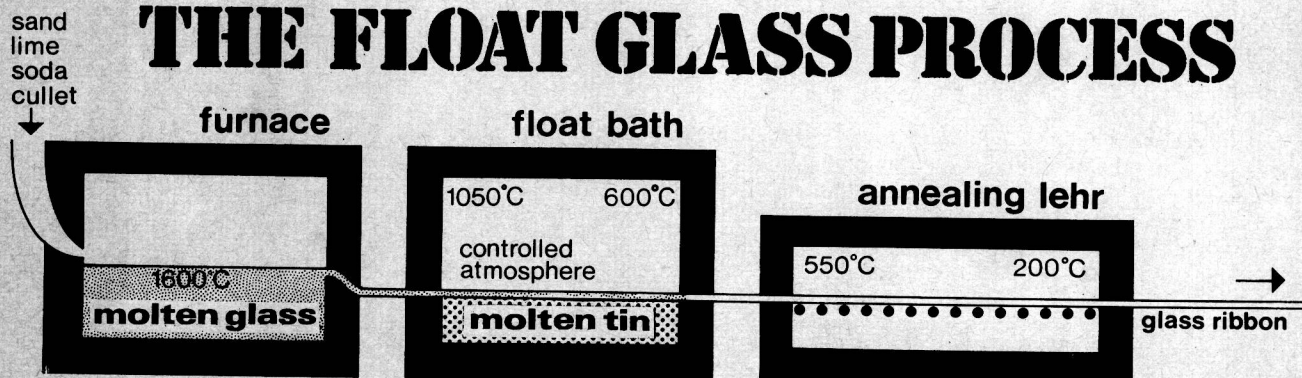
Purity and consistency

The nature of the glassmaking process is such that any material added to the raw material batch will leave one of its compounds (usually the oxide) in the finished glass. There is no slagging stage to remove impurities

Part of Pilkington Brothers' float glass production line in the UK. The process is now licensed to a great number of glass producers all over the world.



THE FLOAT GLASS PROCESS



from the melt as, for instance, in steel manufacture. Therefore the utmost importance is attached to the quality of raw materials to prevent undesirable impurities from entering the finished glass. Iron and chromium are probably the two most troublesome impurities encountered. Ferric oxide (Fe_2O_3) gives a green coloration, and if the content is above an acceptable level the glass manufacturer must resort to the use of expensive decolorising agents (or change his raw material). Chromic oxide (Cr_2O_3) also colours the melt but is most destructive in the form of chromite (FeCr_2O_4), which is insoluble in the glass melt and remains as black particles in the finished glass. Other important impurities include titania and zirconia. As would be expected, the maximum acceptable quantities of these impurities decreases as the quality of the glass increases, and where an iron content of about 0.1% may be acceptable in ordinary flat glass, it must be below 0.001% in many optical glasses.

On this subject of impurity, it should be pointed out that for bulk production of glass the consistency of the impurity content is probably more important than the absolute value. As long as the glass manufacturer knows how much iron oxide he is adding to the melt he can adjust the process accordingly. What he fears most is the sudden increase of impurity which will manifest itself in marked colouring of the finished glass. Naturally the large-scale, continuous processes for producing glass have made consistency a prime requirement, regarding not only chemical composition but also grain size. It is easier to form a uniform finished glass by starting with uniform raw materials than by trying to achieve homogeneity during the refining stage. Uniformity of grain size allows better mixing of the raw materials in the batch which, in turn, leads to more even melting in the glass tank. Coarse grains, which take longer to melt, may create areas of different viscosity and may even survive the melt to leave small crystalline imperfections in the finished glass. Conversely, grains that are too fine will find their way to the top of the batch where they may remain unaffected by the mixing of the rest of the melt.

Other properties of the raw materials that must be taken into consideration include behaviour during storage, e.g., hygroscopic materials must be kept free from moisture; and effect on furnace refractories (substances which readily attack refractories are avoided, if possible).

Summary of raw materials

The following section is a brief summary of the major raw materials used in glass manufacture and list some of the more common minor additives. It will be noticed that, although most of the materials end up as oxides in the finished glass, the actual additions are usually in the form of carbonates, sulphates, nitrates, or more complex compounds. This is not only for reasons of cost and availability (many of the additions are in their most common natural mineral form) but also for reasons of chemical reactivity in the glass-forming process.

Silica

As should now be apparent, silica is the most important raw material used by the glass industry and it constitutes by far the largest tonnage commodity. In nature it occurs on a large scale and some deposits are exceedingly pure—over 99% silica. Such deposits are rare when compared with the overall abundance of silica minerals, however, and glassmakers are dependent on a relatively small number of sources. Reserves of glass-grade silica sand have been

increased substantially by using modern beneficiation techniques on less pure sand. Hence there is no immediate threat to supplies of the qualities used in common soda-lime-silica glasses. Suitable qualities for optical and special glasses are in tighter supply, however, and deposits such as those in Belgium and the Netherlands, and in West Virginia and Pennsylvania in the USA, where sand with a silica content greater than 99.5% is produced, are highly prized.

Constituent in finished glass: SiO_2 .

Soda ash

The second largest tonnage commodity used in glass is soda ash, or sodium carbonate (Na_2CO_3). It may be obtained from naturally occurring brines such as trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) and natron ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) or by a chemical process in which salt, limestone, and ammonia are reacted (the Solvay process). The choice between the natural and synthetic varieties is primarily one of availability, and consumption patterns vary accordingly. In the United States, where deposits of both trona and natron occur, the glass industry consumes both natural and synthetic sodium carbonate in roughly equal proportions. In Europe, where there are no natural brine deposits of commercial significance, glass manufacturers rely solely on the synthetic variety.

Constituent in glass: Na_2O .

Limestone and dolomite

Together limestone (CaCO_3) and dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) form the third largest raw commodity used in glass. The two minerals are considered together because either of them may be used as the source of lime in soda-lime-silica glasses. The choice between the two depends partly on availability and partly on the desired magnesia content of the finished glass. The presence of magnesia in small quantities assists the melting rate as well as increasing the chemical resistance of the finished glass. Therefore limestone and dolomite are often added together to the batch in the correct ratio to give the desired lime and magnesia contents to the finished glass. Occasionally caustic-calined magnesia is added in with lime as an alternative source of magnesia. Deposits of acceptable quality for container and flat glass manufacture are of fairly widespread occurrence, but higher purity grades for more specialised glasses are less common. Notable among the latter are Derbyshire limestone from the UK, and Spanish and Norwegian dolomites.

Constituents in glass: $\text{CaO} + \text{MgO}$.

Salt cake (sodium sulphate)

Like soda ash, salt cake is a source of soda in soda-lime-silica glasses, but this property is only secondary to its role as a refining agent. Its effect is to prevent the formation of scum on the surface of the melt during the refining stage. The actual quantity required varies with the composition of the glass but is most dependent on the lime content. In high-lime glasses the salt cake content may be as high as one-fifth of the total soda in the batch. A small quantity of carbon in the form of anthracite or coke is added to any batch containing sodium sulphate to act as a reducing agent. Without carbon, sodium carbonate would not decompose under normal furnace operating conditions. Like soda ash, salt cake may also be obtained from natural brines or as a chemical by-product either from viscose rayon (*Cellophane*) production or from hydrochloric acid produced from salt and sulphuric acid. The choice of natural or synthetic is governed by availability, and the only bulk consumers of natural sodium sulphate are producing countries such as the USA, Canada, and Mexico. Elsewhere it is more normal to use by-product material.

Constituent in glass: Na_2O .

Potash

Potash (K_2O) is added to some glasses to replace or supplement soda. It has a similar effect to soda but makes a more viscous glass and is more corrosive to furnace re-

fractories. It is therefore not used on the same scale as soda and the principal uses of potash glasses are in decorative and illuminating glassware. In many cases lead oxide is added to it to lower the viscosity, thereby making the glass more workable. The normal forms of addition are potassium carbonate or nitrate produced from naturally occurring potassium chloride deposits, which are fairly widespread. Small quantities of potash (and soda) may also be introduced into glass in the form of feldspar or nepheline syenite.

Constituent in glass: K_2O .

Feldspar, nepheline syenite and other alumina additions

Both feldspar and nepheline syenite are sources of alumina in glass. Alumina is a minor constituent of soda-lime-silica glass, particularly containers, where it is said to assist melting and working and to impart properties of strength, toughness, and durability to the finished glass. It is also a minor constituent of many borosilicate glasses and a major constituent in aluminosilicate glasses. In broad terms, both feldspar and nepheline syenite are minerals containing mixtures of sodium aluminium silicate and potassium aluminium silicate and, as such, add not only alumina but also silica, potash, and soda to the glass melt. Feldspar is one of the most abundant of all minerals but some of the best glassmaking grades are produced in the USA, Norway, and Finland. Nepheline syenite is rarer and production of glassmaking qualities is restricted to Canada and Norway. Some glass manufacturers use a specially-prepared blast furnace slag containing lime, silica, alumina, and magnesia as an alternative source of alumina. The most widely known from is the *Calumite* brand produced in the USA and under licence in the UK and elsewhere. For more specialised glass, purer alumina forms such as calcined alumina and alumina hydrate ($Al(OH)_3$) are sometimes used. These chemically manufactured compounds are produced by many primary aluminium producers.

Constituents in glass: Al_2O_3 + (as applicable) SiO_2 , Na_2O , K_2O .

Borax and other boron compounds

Boric oxide (B_2O_3) is a minor constituent of soda-lime-silica glasses used in containers, tableware, and fibreglass, and is a major constituent of borosilicate glass. The actual addition may be made in a number of different ways—borax (hydrated sodium borate, $Na_2B_4O_7 \cdot 10H_2O$) is available in mineral form (rasorite) or as a chemically prepared compound; anhydrous or fused borax ($Na_2B_4O_7$) and boric acid (H_3BO_3) are both chemically manufactured; and the mineral colemanite (hydrated calcium borate, $Ca_2B_6O_{11} \cdot 5H_2O$) is also used. Anhydrous borax is probably the preferred form of addition to soda-lime-silica glasses since it is free from the frothing associated with hydrated forms of borax; less of it is required and it leads to faster melting rates. The use of colemanite has increased in recent years, notably in glass batches for producing glass fibre. Boric acids finds favour in the production of borosilicate glasses, where it provides pure boric oxide unaccompanied by other compounds. Boron minerals are produced in the USA, Turkey, and South America; they are used in the mineral form or form the basis for boron compound production by specialist chemical manufacturers.

Constituent in glass: B_2O_3 + (as applicable) Na_2O , CaO .

Lead oxide

Lead oxide is a primary constituent of lead-alkali-silica glasses used in domestic glassware (which is then known as crystal glass) and in optical and illuminating glasses (then known as flint glass). The lead addition may be made either as litharge (lead monoxide, PbO) or red lead (Pb_3O_4), but red lead is the preferred form because litharge is susceptible to reduction to metallic lead in the glass melt.

Both metallic lead and lead compounds are derived from the mineral galena (PbS), which is mined in the USA, Mexico, Australia, Canada, Germany, and elsewhere.

Constituent in glass: PbO .

Barium and strontium

Barium oxide (BaO) has been used from time to time as an alternative to lead oxide in crystal glass where it has similar (though not so effective) properties of adding density and brilliance to the finished glass. The one exception to this rule was in pressed glass where barium-containing glasses gave a more brilliant finish than lead. Its application in pressed glass has been furthered by television—not through publicity on this medium but as a major component of television tubes, which are pressed glass products. The presence of barium oxide in the glass screen shields the viewer from radiation which would otherwise be emitted. Strontium oxide was also found to have this property and was found to be more effective than barium oxide in colour television tubes. Barium oxide lost ground to strontium oxide in this respect, but the modern practice is to use a combination of the two. The two elements are usually added as carbonates, which are manufactured from the naturally-occurring sulphate minerals—barytes (barium sulphate) and celestite (strontium sulphate).

Constituents in glass: BaO and SrO .

Lithia

Lithia (Li_2O) is a minor constituent in many of the more specialised commercial glasses such as heat-resisting borosilicate and aluminosilicate glasses, opal glasses, and in television tube glass. Its powerful fluxing action is valuable in these low-alkali glasses, which are otherwise difficult to melt. The manufactured product, lithium carbonate, is used in certain cases but it is more normal to add lithia in one of its natural mineral forms. The three most important minerals—petalite, lepidolite, and spodumene—are all basically forms of lithium aluminium silicate, although lepidolite also contains combined potassium and fluorine. The principal source of these minerals are the USA, Rhodesia, South-West Africa and Brazil.

Constituents in glass: Li_2O + (as applicable) Al_2O_3 , Si_2O_5 , K_2O , F .

Fluorspar and cryolite

Like lithia, fluorspar (CaF_2) is sometimes added in small quantities to soda-lime-silica glass where it acts as flux, but its most important effect is when used in larger quantities to produce opal glasses. Cryolite (Na_3AlF_6) has a broadly similar effect and is often used to supplement fluorspar in opal glass batches or, more rarely, to replace fluorspar as the principal opacifying agent. One of the most common opacifying additions is a mixture of fluorspar, cryolite, and feldspar. Both fluorspar and cryolite occur naturally but whereas fluorspar operations are in abundance, there is only one commercial source of natural cryolite—Greenland. Therefore much of the cryolite in use is synthetic material produced as an intermediate in aluminium metal production.

Miscellaneous

(i) Other refining agents

calcium sulphate (gypsum or anhydrite), sodium nitrate, antimony oxide, arsenic oxide, zinc oxide.

(ii) Other opacifiers

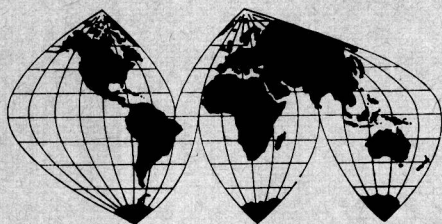
zinc oxide, titanium dioxide.

(iii) Colouring and decolourising agents

antimony oxide, arsenic oxide, cadmium sulphide, chromium oxide (also potassium dichromate), cobalt oxide, copper oxide, iron oxides, iron sulphide (pyrite), manganese dioxide, nickel oxide, rare earth oxides, selenium (in combination with cobalt oxide, this is the principal decolourising agent), sulphur, tin oxide.

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Glass



Raw Materials

Silica sand

ABSTRACT

Despite the abundance of silica in the earth's crust, commercial deposits of glass-grade material are relatively scarce. Specifications for glass-grade sand depends upon the type of glass being produced—broadly speaking is 99.5% SiO_2 (min.) and 0.008% Fe_2O_3 (max.) for optical glass; 99.5% SiO_2 and 0.013% Fe_2O_3 for colourless art and domestic glasses; and 98.5% SiO_2 and 0.030% Fe_2O_3 for colourless container and flat glassware. Additional chemical requirements include a content of less than 6 ppm chromium, 2 ppm cobalt, and 0.05% TiO_2 , and ideally the grain size should be 0.1-0.5mm. Large tonnages of glass-grade sand—either natural or processed—are produced in Belgium, the Netherlands, France, the UK, West Germany, Scandinavia, and Italy. Each of these producers is in turn a major consumer through the large domestic glass-manufacturing industry, although there is still a lively trade. The bulk (80 to 90%) of high quality sand production in North America is found in the states of West Virginia, Illinois, Pennsylvania, New Jersey, and Missouri, that is adjacent to the large industrial areas. Production elsewhere in the world is mainly for local consumption.

Silica, silicon oxide (SiO_2), and silica-bearing minerals—principally feldspar—constitute around 95% of the Earth's crust. The enormous predominance of silicates and aluminosilicates faithfully reflects the abundance of the major elemental constituents in the crust, namely oxygen (47%), silicon (28%), and alumina (8%). The silica group of minerals consist of three-dimensional lattices of SiO_4 tetrahedra with all four oxygens of each tetrahedra shared by an adjoining tetrahedra (see diagram). The various silicate types—for example, nesosilicates (such as olivine, garnet, and sillimanite minerals), phyllosilicates (mica, clay minerals, and talc), tectosilicates (quartz and feldspar), etc.—differ in the relationship between silicon-oxygen tetrahedra. The structures are often very complex and the differences so slight as to be only distinguishable by X-ray techniques. It is curious, however, that relatively few elements form specific silicate minerals—it is the multiplicity of silicate types that forms the variety. Silica itself occurs in nature in seven distinct mineralogical forms or SiO_2 polymorphs; quartz is by far the most common, with tridymite, cristobalite, opal, coesite, stishovite, and lechatelierite the other varieties.

The most common natural forms of silica are as follows:

Quartz may be found in nature as a hydrothermal deposit in veins and fissures, and often it is the host rock for a wide variety of mineral deposits. Large tonnages of quartz occur as **quartzite**, a metamorphosed detrital sedimentary rock in which the constituent grains—largely quartz—recrystallise and develop an interlocked mosaic texture. Impurities in the original rock are converted to equivalent metamorphic minerals such as wollastonite. Quartzite is exploited commercially for use in the production of silicon, ferrosilicon, refractories, etc. Very pure natural crystal quartz, produced almost exclusively in Brazil, is termed **piezoelectric quartz** and is highly prized for its electrical and optical properties.

Sandstones, the recemented product of weathered quartz, are mainly classified according to their quartz content—for example, protoquartzite (75-95% quartz) and orthoquartzite (over 95% quartz)—the other

material being impurities and cement. A particular variety of orthoquartzite is **ganister** which is an arenaceous seat earth found below coal seams, and has a characteristically high silica and low iron, alumina, and alkali content. **Sand and gravel**, the distinction between the two being merely particle size, is another material made up almost entirely of silica.

Silica sand is an assemblage of individual silica grains in the size range $\frac{1}{16}$ to 2mm. (that is mid-way between silt at $\frac{1}{256}$ to $\frac{1}{16}$ mm. and gravel at 2 to 4mm.). A sand can be formed in nature by the natural weathering of sandstone and quartzite, or synthetically by crushing a sandstone/quartzite or by a process of flotation whereby the various constituents in a pegmatite or a kaolin mixture are separated.

Cryptocrystalline forms a silica found in nature include **chalcedony** (subvarieties include carnelian, sard, chrysoprase, agate, and onyx); **flint**, a compact black silica (varieties include hornstone and chert); and **jasper**, an impure opaque mineral often red, brown, or yellow in colour. These forms trend with increasing water content to **opal**, an amorphous hydrous silica with the formulae $\text{SiO}_2 \cdot n\text{H}_2\text{O}$. Other cryptocrystalline hydrous forms of silica include **siliceous sinter** (deposited in hot, mineral-rich streams) and **diatomite** (deposits of tests and skeletons of siliceous organisms such as algae and diatoms).

Miscellaneous silica-rich materials include **tripoli**, a sedimentary rock probably formed by the weathering of siliceous limestones; **pumice**, a vesicular silicate of alumina; and **perlite**, a natural glass.

Silica consumption

Silica is utilised extensively in metallurgy (as a refractory, foundry sand, flux, and in the production of silicon and ferrosilicon); ceramics; abrasives; as a fracturing sand and filtration medium; as a construction material; and in the production of silica-based chemicals. However, the glass industry is by far the largest individual consumer of silica.

What constitutes a glass-grade sand? It is very difficult to give a specific answer to this question, since so

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much depends on factors such as individual glass-makers' preferences and the type of glass being made. The question can be answered in general terms, however, by outlining those characteristics of a silica sand that the glassmaker regards as most important. To do this it is worth summarising some of the points made in the introduction, which applied to all glass industry raw materials. These were that the primary considerations concern purity and grain size; that the most important undesirable impurity is iron (in the form

of ferric oxide, Fe_2O_3), followed by chromic oxide (Cr_2O_3) and heavy minerals (ilmenite, zircon, etc.); that the grain size should be uniform; and that, for large continuous glass-making processes, consistency—of both chemical composition and grain size—is probably more important than the actual values themselves.

Specifications and standards

In general terms, a particular glass-grade sand is defined by its silica and iron contents. The presence of iron in glass leads to a green colouration at small concentrations and to a definite shade of brown at higher concentrations. Other impurity contents and the granulometric analysis cannot be disregarded, of course, but are essentially secondary considerations. As far as granulometry is concerned, a size range of between 0.1mm. and 0.5mm. is the glass-makers' most common requirement. Most industrialised countries possess standards to define chemical and granulometric analyses necessary for the production of a particular type of glass. In many respects these standards follow rather than lead the practice in industry. This is not to belittle their usefulness, but is purely a feature of the way in which the glass industry operates. Different glass manufacturers will agree on the broad limits, but details are an individual matter between sand producer and glass manufacturer.

Nevertheless, standards give an accurate guide to types of silica sand being used for a particular application. The British Standard Specification B.S. 2975:1958 is fairly typical. In brief, this states that optical glass requires the purest sand (minimum silica content 99.5%, maximum iron content 0.008%), colourless art and domestic glasses require the next purest grades (minimum silica content 99.5%, maximum iron content 0.013%), and at the lower end of the scale is sand for general colourless container and flat glassware (minimum silica content 98.5%, maximum iron content 0.030%). It should be noted that many flat, window glasses are actually green if viewed from an oblique angle but are, for practical purposes, regarded as colourless. An iron content of 0.1% may therefore be quite acceptable in a sand used for such glass. The minimum silica content may also be waived if the silica is partially replaced by a non-harmful (or even beneficial) impurity such as alumina.

Some general specifications for silica/quartz by end use [%]

End use	min SiO_2	max Al_2O_3	max Fe_2O_3	max CaO/MgO	Grain size	Remarks
Glass sand						
Optical	99.5	{ variable 0.1-0.5 }	0.008		{ 0.1-0.5mm. }	Must be less than 6 ppm chromium and 2 ppm cobalt. 0.01-0.05% TiO_2 . Grain size and purity constant.
Colourless domestic	99.5		0.013			
Container/flat	98.5		0.030			
Foundry sand	88-99	Extremely variable			20-200 mesh	Chemical composition variable; 98-99% SiO_2 now preferred. Sub-angular to rounded grains.
Silica flour	97-98	0.5	0.2		micron sizing	
Silicon carbide	99.5	0.06-0.25	0.1	absent	+100 mesh	No phosphorus allowed. 0.25% Al_2O_3 sand for black SiC, 0.1% for green SiC.
Silicon	98.0	0.4	0.2	0.2 each	>1 inch diameter	No phosphorus or arsenic allowed.
Ferrosilicon	96	0.4	0.2		>1 inch diameter	0.1% phosphorus maximum.
Silica brick (refractory)	96-98	0.1		low	-8 mesh	
Sodium silicate	99	0.25	0.03	0.05	20-100 mesh	Broadly the same specifications as glass-grade sand.
Silica flux	90	1.5	1.5	0.2	<5%—P inch	

The above figures are general indications only

West European sands: analysis of some high quality grades

	Belgium Sibelco Mas 1	Sibelco Heerlen	Holland Hanno 1st	Lieben B12	W. Germany WQD Haltern	France Siffraco Fontainebleau	United Kingdom Tilcon Loch Aline
SiO_2	99.75%	99.80%	99.87%	99.85%	99.67%	99.65%	99.73%
Fe_2O_3	0.011%	0.008-0.012%	0.01%	0.009%	0.0245%	0.02%	0.013%
Al_2O_3	0.1%	0.08%	0.04%	0.06%	0.13%	0.08%	0.057%
L.O.I.	0.12%	0.10%	0.104%	0.05%	0.13%	0.13%	0.04%

Sands for coloured glasses very rarely appear in standards since a great deal of leeway is allowed as far as iron content is concerned (and iron is usually the colouring medium anyway). Obviously there must be some sort of limit depending on the degree of colour required, but consistency is usually the main consideration. As an approximate rule it may be said that the iron content of a sand for green glass should not exceed 0.3%, but for amber and brown glass the sand may have an iron content as high as 1.0%.

Specifications for seven high-grade sands produced in Europe are given in the table below, and some general specifications (for the glass and other industries) are tabulated for comparison.

Consumption in glass—the 70% silica average

Accurate figures for the consumption of silica sand by the glass industries of each country are generally unobtainable. The simple and oft-used 'production + imports — exports' formula for estimating consumption is impractical in this case since—with the exception of France—no country breaks down silica sand production and trade into 'glass-grade sand' and 'sand for other uses'. There is one useful technique for obtaining an apparent consumption figure, however, and this is based on the fact that the vast bulk of glass produced today has a silica content of about 70%. An approximate value for the consumption of silica sand in glassmaking can therefore be obtained by calculating 70% of a country's total glass production. The table below records glass production totals of some Western European countries, and the apparent consumption figures derived from them using the 70% silica average*.

Production and trade

Some sand deposits—such as those in southern Holland and at Fontainebleau in France—are pure enough in their natural state for the production of colourless glass. Other deposits—notably in Belgium, West Germany, and France—require only the most elementary washing and screening procedures to give the required qualities. Other countries, such as the UK, are less fortunate, however, and although large deposits of silica sand exist there, extensive beneficiation is required to reduce impurities to an acceptable level. Furthermore, sands undergoing this purification treatment must be able to compete with naturally pure sands on price grounds, and this can only be achieved through the economies of operating on a large-scale. An outside observer who witnesses the sophisticated scrubbing, leaching, and flotation procedures of a modern British sand operation cannot fail to be amazed at the amount of time, money, and effort spent in preparing a product that sells for little over £2 per ton, ex-quarry. Apart from the beneficiation of impure sand, modern mineral

Glass production in the EEC ('000 metric tons)			
	1973	1974	1975
West Germany			
Plate and mirror glass	938.6	786.1	776.5
Window glass	399.8	312.0	216.5
Cast glass	168.4	137.1	120.1
Mirror glass	206.6	209.2	349.6
Container glass	3,004.0	3,223.4	2,940.7
Total	4,716	4,667	4,402
France			
Plate and mirror glass	678.5	662.1	515.8
Window glass	226.8	261.2	185.8
Cast glass	98.6	93.8	73.3
Mirror glass	347.0	300.0	251.6
Container glass	2,464.6	2,773.0	2,629.1
Total	3,816	4,090	3,656
United Kingdom			
Flat Glass	654	621	539
Glass containers	2,040	1,918	1,825
Domestic glass	107	110	110
Glass fibre	65	70	88
Other products	198	194	194
Total production	3,064	2,913	2,756
Exports	329	381	277
Imports	218	166	279
Italy			
Plate and mirror glass	598.3	638.1	512.5
Window glass	320.5	299.9	162.6
Cast glass	140.0	132.9	77.7
Mirror glass	137.8	205.3	272.2
Container glass	1,528.4	1,670.8	1,289.4
Total	2,724	2,804	2,314
Belgium			
Plate & mirror glass	929.9	830.7	—
Window glass	471.1*	421.0*	—
Cast glass	98.0*	82.0*	—
Mirror glass	361.0*	327.0*	—
Container glass	370.0*	418.0*	—
Total	2,230	2,078	—
Netherlands			
Plate and mirror glass	87.0*	82.5*	—
Window glass	87.0*	82.5*	—
Cast glass	—	—	—
Mirror glass	—	—	—
Container glass	449*	506*	—
Total	218	215	—
Denmark			
Total	204†	197†	183†
Sweden			
Total	393†	387†	376†
Portugal			
Total	264†	273†	—
Norway			
Total	160†	180†	200†

*Estimate made by Eurostat †Source: UK Glass Manufacturers Federation ‡Estimate based on production plus imports minus exports equals consumption. Source: Eurostat Quarterly Bulletin of Industrial Production, October 1976.

W. Europe—Glass production and apparent silica consumption ('000 tons)

		1972	
		Glass prod.	70% SiO ₂ Average
Spain	839	590
Sweden	350e	240
Austria	252	175
Portugal	221	154
Switzerland	199	140
Denmark	194	136
Norway	170e	120
Finland	155	108
Greece	99	69
Ireland	100e	70

*1971 figure e—estimate

W. Europe—Glass production and apparent silica sand consumption based on 70% silica average ('000 tons)

		1972		1973		1974		1975	
		Glass prod.	70% SiO ₂ Average	Glass prod.	70% SiO ₂ Average	Glass prod.	70% SiO ₂ Average	Glass prod.	70% SiO ₂ Average
W. Germany	3,790	2,650	4,716	3,301	4,667	3,267	4,402	3,081
France	2,950	2,050	3,816	2,671	4,090	2,863	3,656	2,559
UK	2,748	1,930	3,064	2,145	2,913	2,039	2,756	1,929
Belgium	1,252	880	2,230*	1,561*	2,078*	1,455*	—	—
Netherlands	491	345	218*	153*	215*	150*	—	—
Italy	2,277	1,590	2,724	1,907	2,804	1,963	2,314	1,620