

Glass Engineering Handbook

Third Edition

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Charles H. Greene was head of the Department of Glass Technology at Alfred University when he wrote Chapters 7 to 9 for the second edition of *Glass Engineering Handbook*. His Chapters 8 and 9 have been updated for this edition, and Chapter 7 has been completely rewritten because of the many changes in glass melting technology in recent years.

George B. Hares, a senior research associate with Corning Glass Works, has developed many new glass compositions, most of them for optical glasses. His service with Corning dates back 31 years.

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Foreword

Glass is one of the most important materials serving humanity. Its transparent properties, along with its strength and durability, make it ideally suited for a vast array of products that require light transmission as a major function. The inert properties of glass have made it useful for the storage and serving of food and beverages, and it has found wide use in the scientific laboratories of the world because of its high chemical durability.

Although glass has been known to human beings for thousands of years, it was not until the turn of the century that this material received serious study by scientists and engineers. Since that time our knowledge of glass and its derivatives has grown exponentially. From a few simple base glasses, we can now count over 75 000 different glass and glass ceramic formulations.

As new and unique properties of glass were discovered, new highly versatile and efficient melting and forming processes were developed, and a great variety of new and improved products found wide acceptance in the marketplace.

Glass products and components have found their way into almost every major industry—transportation, construction, packaging, lighting, food preparation and serving, optical and ophthalmic products, consumer electronics—and, more recently, into telecommunications, with the advent of optical waveguides.

With so many diverse uses of glass and glass ceramics, scientists and engineers in almost every field are in need of specific information about the different properties and manufacturing methods of glass in order to make proper use of this modern engineering material. This book gives the reader a good general introduction to the modern scientific field of glass applications engineering.

David E. Leibson

Preface

The purpose of this book is the same as that of the second edition: "to provide information and data essential for the engineering and technical application of glass in various fields of use." The need for coordinated information of this kind is even greater now than when the second edition was published. Glass has become even more versatile, and new glasses have proliferated, many of them highly specialized and some of them unique. The limited number of applications cited demonstrates the principles and methods described. These apply to many other applications, as well as to applications not known at this time.

The sections on flat glass and fiberglass have been completely rewritten because of the many changes within these product areas since the second edition was published.

Both SI and U.S. Customary units are used throughout the book, except in some areas where the metric system is used exclusively. The SI system of units is explained in Appendix C.

ACKNOWLEDGMENTS. Since this book deals with so many engineering and scientific disciplines, many specialists have contributed to it, some by writing complete chapters or sections, and some by reviewing parts of the manuscript. The review process produced many revisions and some welcome additions. Besides the nine contributors, whose names are listed with the chapters they wrote, six others rewrote parts of chapters to include knowledge gained since the second edition of this book was published.

Henry E. Hagy reviewed Chapters 4 and 5 and made important additions to each chapter to reflect new knowledge acquired in the field of glass rheology.

John A. Bonk, Raymond E. Muth, and Bruce R. Simson wrote additional parts of Chapter 16 to include the latest developments in electric lamps.

William H. Dorman and John P. Hoxie both reviewed Chapter 17 and added new material in the field of illumination.

In addition, 29 others gave generously of their time and knowledge. The list includes James W. Alpha, James J. Attaya, William L. Babcock, Raymond R. Barber, Willis H. Barney, William J. Buffington, Kenneth A. Burket, Henry S. Craumer, Donald H. De Clerck, John F. Dockum, Jr., Carmén A. Esposito, Robert W. Gress, Suresh T. Gulati, Les C. Gunderson, Lawrence P. Galanter, Herbert L. Hoover, Ken C. Kao, Peter C. Knott, Edward K. Lofberg, Robert M. Maurer, Wendy L. McAfoose, Robert M. McMarlin, R. Harry Miles, Jr., Herbert A. Odle, Herbert E. Rauscher, Robert C. Reese, Joseph M. Sheeche, Peter J. Venuto, and Richmond W. Wilson.

And there are others who, possibly unknowingly, have aided the production of this edition by informal comments and observations. Whether the contribution involved a complete chapter or a paragraph, the interchange of ideas that took place is a stimulating and vital part of the task of revising an edition such as this one. Many thanks to all of them.

George W. McLellan

About the Editors

George W. McLellan, currently a consultant, has had extensive experience in laboratory work, research and development, and training program development—all with Corning Glass Works in Corning, New York. Mr. McLellan received his B.A. in physics from the University of Maine and attended graduate school at Rensselaer Polytechnic Institute.

The late E. B. Shand was a consultant and research staff engineer with Corning Glass Works.

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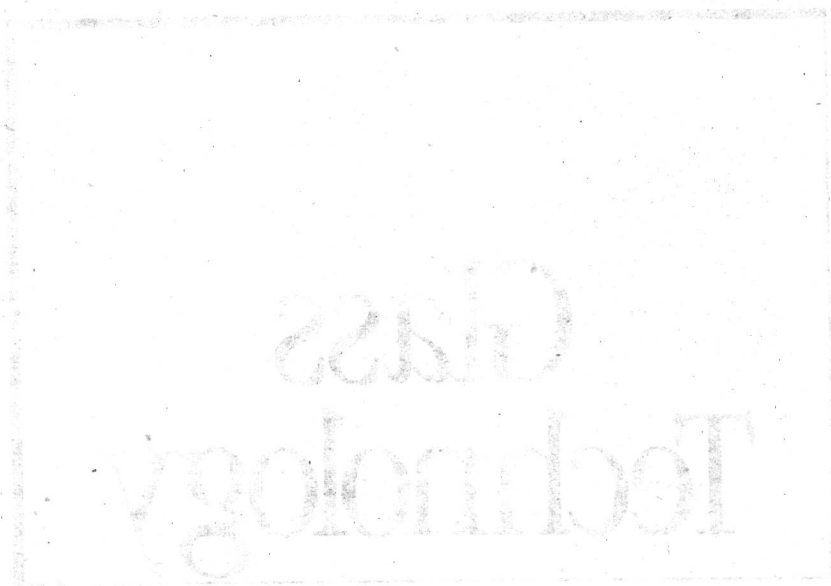
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section 1

Glass Technology

Index



Composition and Constitution

by George B. Hares

NATURE OF GLASS

Common commercial glasses are hard, brittle, usually transparent materials. They are products of the fusing or melting of crystalline materials at elevated temperatures to produce liquids which have subsequently been cooled to rigid condition without crystallization. Their chemical composition is largely inorganic, with silica (SiO_2) being the most important constituent.

It is possible, though, to cool certain organic materials and some metals from the molten condition without crystallization, and thus to produce materials that can be correctly termed *glasses*. However, this book will deal only with glasses that are inorganic and nonmetallic.

From an engineering standpoint what distinguishes glass from other inorganic materials is the absence of a definite melting-point temperature. When a glass is heated, it will gradually deform or slump, eventually forming a viscous liquid.

To better understand the nature of this viscous liquid, consider what happens to the volume occupied by any arbitrary mass of glass as it cools from the molten state to room temperature. Like most materials glass contracts on cooling. However, for glass the contraction is a combination of two effects. One is the ordinary contraction of any definite structural arrangement such as occurs with most crystalline substances. The second contraction effect in glass is due to a rearrangement of the structure itself on cooling. These two contractions are represented graphically in Fig. 1-1.

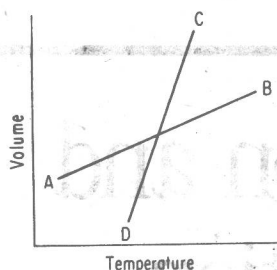


Fig. 1-1 Contractions in a glass as it cools from the molten state. Line *AB* is normal thermal contraction. Line *CD* represents thermal contraction caused by structural readjustment.

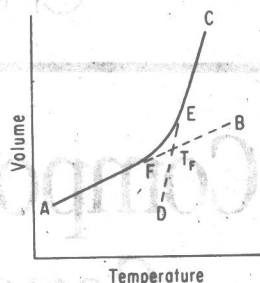


Fig. 1-2 Contractions in a glass as its viscosity increases with cooling. Below point *E* the glass is essentially rigid and structural adjustment stops, leaving only normal thermal contraction.

The line *AB* represents the normal thermal contraction of a material with a fixed structural arrangement. This type of contraction is instantaneous and is reversible with any change in temperature. Line *CD*, on the other hand, indicates the thermal contraction due to the rearrangement of the atoms in the structure of the material. As drawn, it also is represented as an instantaneously reversible change with temperature.

The rates of atomic rearrangements in glass structures are dependent upon the viscosity of the glass. Since the viscosity increases rapidly on cooling, the time required for these rearrangements to take place will increase as the glass cools. At sufficiently low temperatures, depending on the cooling rate, the actual volume will be greater than that which would be observed if the glass were fluid enough for the structure to rearrange instantaneously.

As the glass continues to cool, the atomic rearrangement process becomes slower and slower until a temperature is reached where the viscosity of the glass becomes so high that no further change in the structural arrangement will occur for that particular cooling rate. Below this temperature the volume of the glass will contract at a rate fixed by the structure at that time. This is graphically represented in Fig. 1-2.

As the glass cools beyond point *E*, the increasing viscosity continually slows down the structural rearrangement process. At the temperature *F* no further structural changes occur and the contraction follows the normal contraction line *AB*.

The temperature region between points *E* and *F* is often called the *glass transition* or *transformation range*.

At room temperature the glass has a volume which is assumed to be characteristic of the equilibrium structure at some higher temperature called the *fictive temperature*. This temperature, T_f , is found at the intersection of lines *AB* and *CD* in Fig. 1-2. Again, the fictive temperature is a function of the cooling rate; the faster a piece of glass cools, the higher is the fictive temperature.

Other structure-sensitive glass properties are similarly affected by thermal history, including density (the reciprocal of specific volume), refractive index, and various electrical properties.

Thermodynamically, at low temperatures a crystalline form is generally more stable than an amorphous form of a material. Thus, when glasses are cooled from the molten state, they do pass through a temperature range where crystallization can occur. However, because of the high viscosity of most glasses and the consequent low mobility of the atoms, the process of crystallization is very sluggish. This sluggishness is an important factor in permitting glass manufacture without the occurrence, during cooling, of crystallization or devitrification. Devitrification can occur with some glass compositions, if the cooling rate is too slow or if the glass is reheated.

The highest temperature at which crystals can exist in glass is called the *liquidus* temperature. This temperature is dependent on the glass composition. For different glass compositions the viscosity at the liquidus temperature varies widely. Usually glasses which have a large change in viscosity with temperature (*short* glasses) have lower viscosities at the liquidus temperature than those with small changes of viscosity with temperature (*long* glasses).

The crystals which form in glass are seldom of the same stoichiometric chemical composition as the glass. Indeed, often more than one crystalline phase may appear. When this occurs, the different phases may have different liquidus temperatures.

In order to prevent crystal formation or devitrification, the viscosity at the liquidus temperature for a specific composition must be higher than the viscosity required for the desired forming process. Consequently, certain formulations which are commercially available in one form may not be available or feasible in a form which requires a higher viscosity for the forming process.

STRUCTURE AND COMPOSITION

Silicate glasses and minerals are not composed of discrete molecules but are three-dimensional connected networks. The basic structural unit of the silicate network is the silicon-oxygen tetrahedron in which a silicon atom is bonded to four larger oxygen atoms. The oxygen atoms are spatially arranged to form a tetrahedron.

The silica tetrahedra are linked at the corners by the sharing of one oxygen atom between two silicon atoms. All four oxygen atoms from one tetrahedron can be shared with four other tetrahedra to give a three-dimensional network. These shared oxygen atoms are called *bridging* oxygens. In pure silica glass or pure silica minerals, such as quartz, the ratio of silicon to oxygen is 1:2 and all oxygen atoms are bridging. Some atoms, such as sodium, when present in glass, are ionically bonded to oxygen. This disrupts the continuity of the network since some of the oxygen atoms are no longer shared between two tetrahedra,

but are bonded to only one silicon atom. This type of oxygen atom is called a *nonbridging* oxygen.

Appreciable amounts of most of the inorganic oxides can be incorporated into silicate glasses. Elements which can replace silicon are called *network formers*. Most mono- and divalent cations do not enter the network but form ionic bonds with nonbridging oxygen atoms and are called *network modifiers*. Certain small divalent ions, such as magnesium and zinc, may be either network formers or network modifiers, depending upon the nature and amounts of other constituents in the glass composition.

Because of its network structure, attempts to express the chemical composition of a glass in terms of a unique chemical formula are meaningless. Still, a bookkeeping system of some type is needed to describe a glass composition in chemical terms. The usual method is to list the relative amounts of oxides derived from the raw materials used in a glass batch formulation, in spite of the fact that these oxides do not exist, per se, in the glass network. For manufacturing purposes the relative amounts are usually expressed in weight fractions or weight percents.

TYPES OF GLASSES

Vitreous Silica

This glass can be prepared by heating silica sand or quartz crystals to a temperature above the melting point of silica, 1725°C (3137°F). Because of the three-dimensional cross-linked nature of the network for both crystalline and vitreous silica, the melting process is very sluggish. The resulting glass is so viscous that any gas bubbles formed during the melting process do not free themselves readily from the molten glass.

A second technique for the manufacture of vitreous silica is a vapor deposition process. In this process silicon tetrachloride is reacted with oxygen at temperatures above 1500°C (2732°F). A finely divided particulate vitreous silica is formed, which can be consolidated by collecting the particles on a substrate kept at a temperature above 1800°C (3272°F).

In common parlance the vitreous silica obtained from melting quartz or sand is called fused quartz, while that from the vapor deposition process is called fused silica.

Vitreous silica has a very low thermal expansion coefficient and is ideal for space-vehicle windows, astronomical mirrors, and other applications where low thermal expansion is required for thermal shock resistance or dimensional stability.

Because of the extreme purity achievable by the vapor deposition process, vitreous silica, in the form of fibers, is used in optical waveguide communication systems.

Alkali Silicates.

In order to decrease the viscosity of molten glass from that of silica, it is necessary to add a *flux*, or network modifier. The alkali metal oxides are excellent fluxes. Since they are network modifiers, they *soften* the glass structure by generating nonbridging oxygens.

The alkali oxides are usually incorporated into the glass batch formulations as carbonates. At temperatures above 550°C (1022°F) the carbonates will react with silica to form a siliceous liquid (with the evolution of carbon dioxide) which, if the proportions of alkali carbonate and silica are proper, will form a glass on cooling. Even though these reactions take place below the melting point of silica, glass technologists refer to this process as melting.

The addition of alkali decreases the chemical resistance of the glass from that of vitreous silica. At high concentrations of alkali, the glass will be water-soluble, forming the basis of the soluble silicate industry. Soluble silicates, once known as *waterglass*, are usually sold as aqueous solutions and are used in adhesives, cleaners, and protective coatings.

Lime Glasses. To decrease the aqueous solubility of the alkali silicate glasses and yet maintain the ease of melting, stabilizing fluxes, in place of some of the alkali fluxes, are included in the batch formulation. The most commonly used stabilizing oxide is that of calcium, often in conjunction with magnesium oxide. These glasses are commonly called *soda-lime glasses*, and often simply *lime glasses*. They comprise, by far, the oldest and most widely used of the glass composition families. Soda-lime glass was used by the ancient Egyptians, while today most of the bottles, jars, windows, light bulbs, and fluorescent tubing are made of soda-lime glass.

The compositions of the majority of lime glasses fall within a narrow composition area. They usually contain between 8 and 12 weight percent lime (including magnesia) and from 12 to 17% alkali oxide (principally sodium oxide). Too much lime makes the glass prone to devitrification during the manufacturing process. Too little lime or too high an alkali content results in a composition with poor chemical durability. Usually, a small amount of alumina is included in the formulation to improve working characteristics and chemical durability.

Other alkaline-earth oxides may be substituted for lime or magnesia in compositions used for specialized products. For example, the glass faceplate of a color television bulb contains substantial amounts of barium oxide and strontium oxide to absorb x-rays produced during operation of a television set.

Lead Glasses. Lead oxide is usually a network modifier, but in some compositions can apparently act as a network former. Alkali-lead glasses have a long working range (small change in viscosity with decrease in temperature) and as such have been used for fine handcrafted tableware and artware for centuries.