# CHAPTER 1

## INTRODUCTION TO SILICATE GLASS TECHNOLOGY

### 1.1 GLASS AND ANTIQUITY

GLASS is one of man's most useful and versatile materials. It is also one of the oldest. Obsidian, a glass formed by volcanic action, had widespread usage during the Stone Age because it was easily flaked to form sharp cutting edges for arrowheads, spearheads, knives and the like. Its use has been documented in East Africa as early as 150,000 years ago and it was used at least to the end of the Stone Age in the New World, about 1500 years ago. Indeed, obsidian has been known as the "Dating Stone" (1) because of the ease to which it lends itself in age determination. Wherever prehistoric peoples and volcanic glass occurred together in nature, humans made use of this natural product as a raw material for manufacture of tools. This has become evident from the widespread discovery of detritus, in the form of worked- fragments and shards, found in the vicinity of present- day deposits of eruptive rocks in many parts of the world.

Obsidian varies in appearance from nearly clear colorless to pinkish or even gray-green, brown, red, and black. Its usefulness as a tool- making material derives from the ease with which it furnishes the sharp edges required for cutting or scraping. Obsidian is readily flaked by percussion and pressure methods similar to those used for working flint. However, the edges produced are much sharper than any other material, except perhaps that of worked metals.

The obsidian dating method depends upon the fact that, while the glass originally formed contains about 0.1 to 0.3% water by weight, water from the atmosphere continues to slowly diffuse into the body of the glass over a long period of time. Obsidian itself is a complex silicate containing about twelve major components, including silica. Depth of penetration of the water is a measure of how long it has been since the surface of obsidian was created, or

when the stone was last chipped or cracked. If one removes an edge of glass from a given obsidian artifact and views it under magnification in polarized light, the edge that has been penetrated by water has a higher refractive index than that of the pristine glass. This allows one to observe an interface between the hydrated part and the non-hydrated part, seen in the microscope as a thin line. The uptake of water also changes the volume of the affected glass, and causes a mechanical strain which renders it visible as a bright band under polarized light due to an effect called strain- birefringence. The thickness of the rind may vary from 1.0 micron (0.00004 inches) to more than 50 microns. Dates have been established as far back as 200,000 years, and have been authenticated, in many cases, by radioactive Krypton/ Argon studies. It is thus clear that man (Homo Sapiens) has used natural glass from dates close to that of his origination.

Perhaps the earliest known **artificial** glass is the glaze found on stone beads of the Barbarian Age (12,000 B.C.). The oldest known articles made completely from glass have been dated to about 7000 B.C. There is a tale that glass manufacture was discovered in antiquity by sailors who were transporting large blocks of soda-ash to a distant port. They happened to land on a beach and used the blocks as a wind- screen for a bonfire. The heat of the fire caused the combination of sand and soda-ash to form a melt. This, when cooled, produced a hard product similar to obsidian. Thus, artificial glassmaking was born.

"Modern" glassmaking began in Egypt about 3500 years ago. This took the form of fibers, flattened plates, dishes and utensils, and bottles of varied shapes. Glass fibers were used as early as 1500 B.C. after the discovery that glass could be drawn into fine filaments from a melt. It was also discovered that additions of manganese, nickel, cobalt, copper, iron, and chromium could be used to produce "colored" glasses. In the Egyptian XVIIIth Dynasty, glassmakers created small vases for cosmetics by attaching either a small clay form or a bag filled with sand to a stick. Rotating this form in molten glass resulted in a small vase of the desired shape. Coarse fibers of colored glass were then heated and pressed into the external walls of the vessel to make decorative patterns. Similar decoration, using colored glass fibers, was used in the Rhineland of Middle Europe during the Roman Empire to make glass dishes, cups and bottles, i.e.- up until about 100 A.D.

However, the production of "flat" glass posed a seemingly insurmountable obstacle for nearly 2000 years. Somewhere around 200 A.D., the invention of the glass-blowing pipe in Syria permitted glassmakers to produce a forerunner of flat glass. Glass was blown into a large cylindrical shape, then cut and either "spun" or ironed flat before it hardened. The first colorless glass had been made about 100 years earlier by adding manganous oxide to the melt. Although attempts to manufacture acceptable flat glass went on for centuries, it was not until the 1600's that the first plate glass was produced in France by cutting and grinding. Until the late eighteenth century, flat glass was an expensive handmade luxury. Crown spinning, that is- formation of a blown bulb of hot glass which was cut and then spun to form a flat disc of glass, was the predominant method of making flat glass in this era. And it is only in recent times that man has learned how to make plate glass by a "float" method. This will be described in more detail below.

During the past 3000 years, man has learned how to make controlled melts of glass. Glass technology has advanced slowly, with more progress in the past 80 years than in all the preceding years that glassmaking had existed. This process began in the 1800's with the Industrial Revolution and the establishment of scientific research in Industry. Systematic studies of many thousands of compositions, the development of special manufacturing techniques, and the discovery of processes for attaining new and unusual properties, forms, and uses, have made glass an extremely versatile material. At present, about 700 different glass compositions are in use which have been fabricated into tens of thousands of different articles for varied uses.

Noteworthy among these modern developments are:

1. Air tempering to improve strength (some standard- temper products are strong enough to withstand severe abuse such as use as a hammer to drive nails).

2. Chemical tempering has produced glasses with strengths of more than 100,000 psi. in tensile strength.

3. Photosensitive glasses which reversibly darken and fade in response to light intensity exposure.

4. Glass-ceramics, which are partly crystalline bodies formed by additives which cause crystals to grow in the final glass product.

5. The development of continuous melting and high-speed automatic forming of high quality glass articles such as bottles, jars, electric light bulbs, window panes, and the like, in millions of tons.

6. Development of extensive knowledge of glass composition ranges, and the chemical-physical properties which determine whether specific compositions can be melted to form a useful glassy state.

7. Preparation of glass by a "sol-gel" method. This method consists of precipitating a silicic- acid as a gelatinous composite, drying the gel, and then consolidating the dried mass into a solid glass by heating. The advantage lies in the use of much lower temperatures to achieve glass articles of complex composition. We will describe this method in more detail later on in this Chapter.

Nevertheless, most of the prior-known glasses are silicate- based. That is, the main ingredient is sand (which is silicon dioxide, $SiO_2$ , containing small amounts of impurities). When other glass-formers such as phosphate, $PO_4^{3-}$, have been used, the glass products obtained were found to be extremely unstable to hydrolysis by boiling water. Indeed, because of perceived commercial advantages, Schott Glaswerke of Jena, Germany spent many years of research during the early 1900's attempting to obtain stable phosphate based glasses. There are many chemical and structural reasons why phosphate- based glasses are not easily obtained in a stable state. Notwithstanding, they **can** be prepared so that their stability to boiling water exceeds that of many of the silicate-based glasses. This is the subject of this manuscript. Indeed, the method to be described involves a completely new approach to non- silicate glass-making. We will describe the unique "rules" required for preparing such glasses, which contrast diametrically to those developed over many thousands of years for silicate-based glasses.

But, as we shall see, the main reason that Schott Glaswerke did not succeed is that they used the known glass-technology, based on rules developed for silicate glasses, to attempt to force the phosphate molecules to conform to

preconceived ideas of glass-preparation. We will describe the correct approach, based on the peculiarities of the $PO_4$ - tetrahedron, which utilizes the tendency of the tetrahedra to form long chains of polymeric molecules of specific coordination.

But first, let us examine the structure of glasses and then summarize silicate-glass technology so as to be able to compare the newest polymerization technology with that already developed for silicate glasses over a period of many thousands of years.

## 1.2 THE GLASSY OR VITREOUS STATE

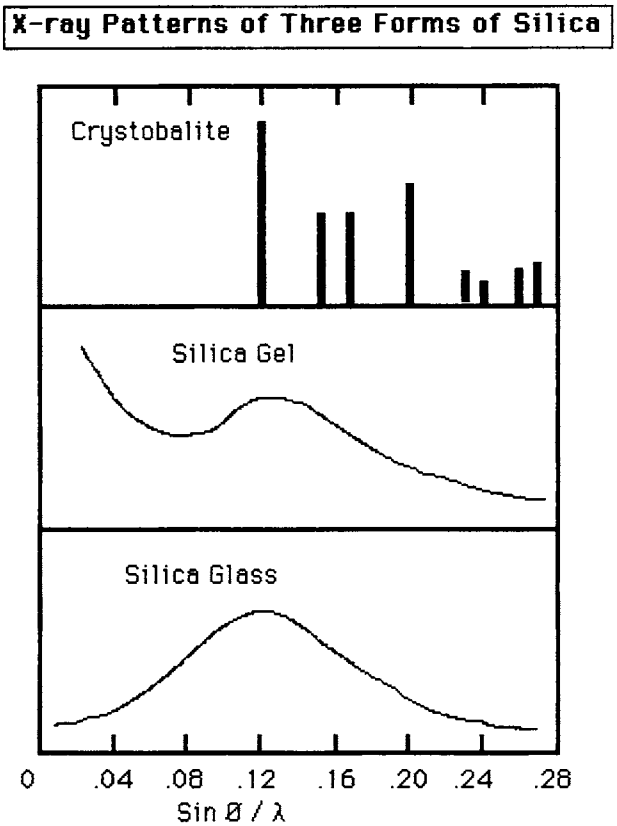
Glass is a non-crystalline solid. That is, it does not consist of an ordered arrangement of its constituent cations and anions. The American Society for Testing and Materials (2) defines glass as "an inorganic product of fusion which has cooled to a rigid condition without crystallizing". It has also been defined as "an inorganic substance analogous to a rigid liquid".

If one obtains an x-ray analysis of glass, the resulting diffraction pattern consists of a broad featureless band, in contrast to a crystal of the same composition. For example, sodium silicate is soluble and can be dissolved to form a solution. If one then adds acid and precipitates a silicic-acid, i.e.- $H_2SiO_4$ or $SiO_2 \cdot x\,H_2O$, and separates it from the solution (note that the sodium ion is lost), a silica- gel is first obtained, containing considerable water. Heating causes a loss of some of the water. Further heating causes the gel to crystallize in one of several forms of silica such as crystobalite.

If the crystalline phase is then melted and cooled more rapidly, a glassy phase results. As shown in Figure 1.2.1., given on the next page, the x-ray patterns of these three forms of silica have very specific, but differing, features.

Note that crystobalite shows specific diffraction lines indicating a crystalline structure, while the diffraction pattern of the other two forms exhibits only a broad featureless band. Yet, all three have identical chemical compositions, i.e.- $SiO_2$.

Figure 1.2.1.-




For many years, the structure of glass remained a mystery. In 1932, Zachariasen (3) proposed that atoms in silicate glass form an extended three-dimensional network which, although lacking the symmetry usually found in a crystalline structure, has an energy content comparable to that of the crystal. This means that the coordination numbers are approximately equal in both phases. Using these concepts, Zachariasen proposed a set of "rules" regarding the vitreous state. These are concisely stated in the following:

1.2.2.- Zachariasen's Theorems Relating to the Amorphous State

a. Each oxygen atom must be linked to no more than two cations.

b. The number of oxygen atoms around any one cation must be small, i.e. - three to four.

c. The oxygen polyhedra must share corners, not faces or edges, in order to form a three-dimensional network.

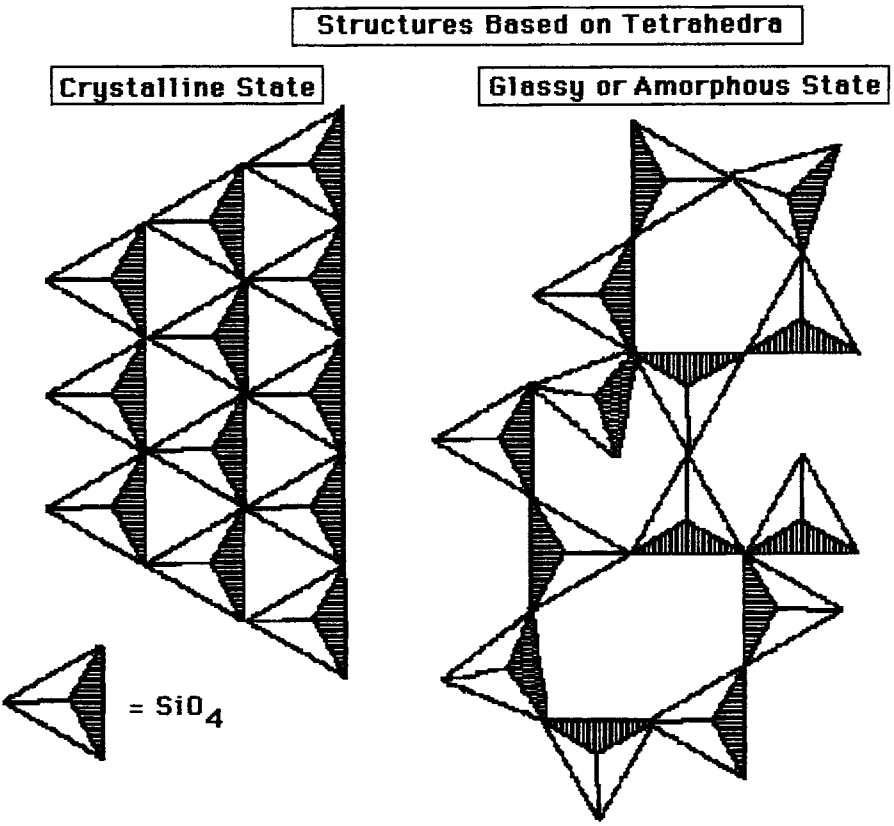
d. At least 3 corners of each polyhedra must be shared.

Zachariasen was aware that the $SiO_4$ - tetrahedron was the structural basis for silicate- glasses, but attempted to expand his concepts to include all possible types of glass compositions. Work by Warren (4) and others supported Zachariasen's concepts. Based on the $SiO_4$ - tetrahedron, it was obvious that the network would have to be three dimensional. From a Fourier analysis of the diffraction pattern of simple glasses composed of either: $SiO_2$, $B_2O_3$, or sodium silicates, **radial distribution curves** were obtained which showed the distribution of neighboring atoms about each atom in the glass. It was the combination of this work and that of Zachariasen which led to the **random network theory** for the structure of glass. Additionally, early workers postulated that glass-structure might well consist of "building blocks" which, when joined in a random configuration, represented the structure of glass. These represented "short-range order", but not "long-range order" in the amorphous solid.

The following diagram, given as Figure 1.2.3. on the next page, shows a representation, in two dimensions, of the differences between crystalline and amorphous silica, the latter a simple glass. Keep in mind that in a tetrahedron, each $Si^{4+}$ atom is surrounded by four (4) $O^{=}$ atoms.

It should be apparent in this diagram that both structures are three-dimensional with the next layer of tetrahedra attached to the top apex (oxygen atom) of the tetrahedral arrangement of atoms comprising the structures. Thus, considerable differences in structure exist between crystalline and amorphous phases, even though they may have identical chemical compositions.

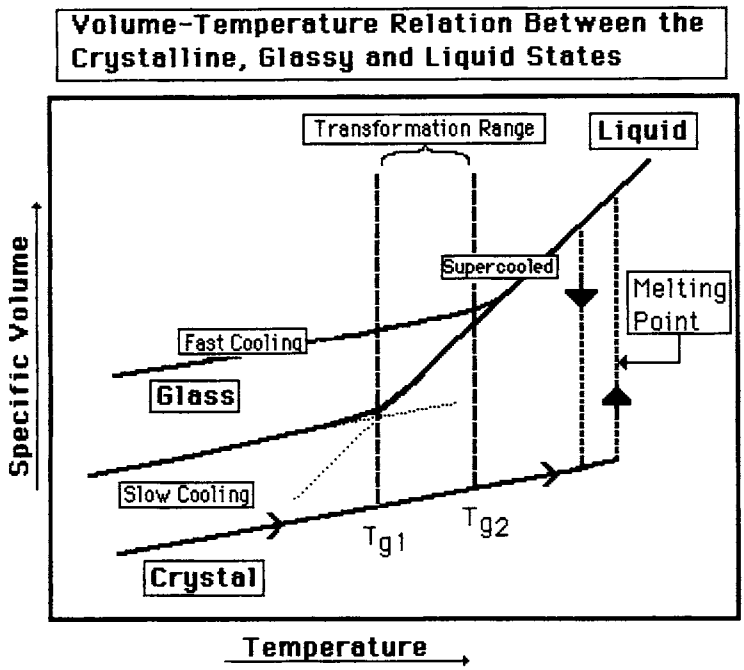
Figure 1.2.3.-




The conspicuous difference to be noted is that the volume occupied by the same number of tetrahedra is greater for the amorphous state as compared to the crystalline state. Indeed, such a volume-temperature relationship had long been known, where the amorphous state occupies a larger specific volume than the crystalline state.

This is illustrated in the following diagram, given as Figure 1.2.4. on the next page. In this Figure is shown the volume-temperature relation when a solid transforms into a liquid, and then cools to an amorphous solid. It is easy to see that a definitive change in volume occurs, as the nature of the phase changes.

Figure 1.2.4.-

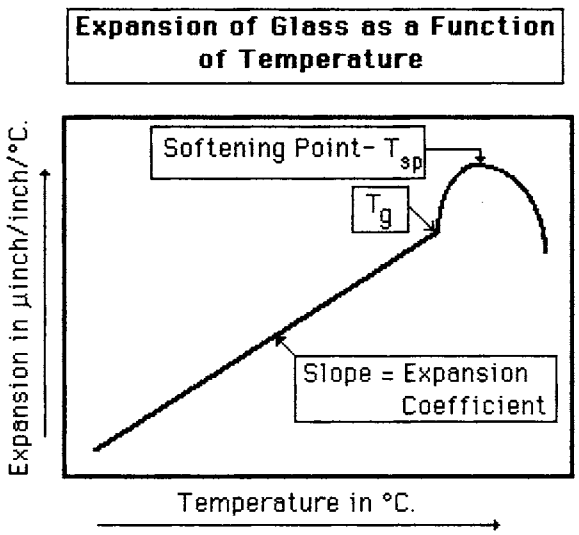



Glass is not a supercooled liquid. This is apparent in the above diagram where it is evident that a crystal, heated to its melting point, forms a liquid of greater volume. When this liquid is cooled, it will either recrystallize to form an ordered solid of decreased volume, or it may form an amorphous solid, particularly if the composition is comprised of so-called "glass-formers". In the latter case, the liquid becomes supercooled until it reaches a certain temperature, generally called the transformation point (or temperature), $T_g$, where a "glassy-state" is formed. This is seen in the above diagram as the "break-point" point in the cooling curve. For the amorphous state, this behavior is related to the absence of crystal nuclei and/or a melt viscosity too high to allow significant crystal- nuclei formation rates. Thus, a **transformation range** exists, which would not be present if glass were merely a supercooled liquid.

It was originally thought that the break in slope of the cooling curve given above (transformation range) was due to a kinetic factor. The structural configuration frozen-in at this temperature would then persist approximately

unchanged at all lower temperatures. If one measures the change in expansion of the glassy state **below the transition temperature**, one finds that it is a linear function of temperature, as shown in the following Figure:

Figure 1.2.5.-

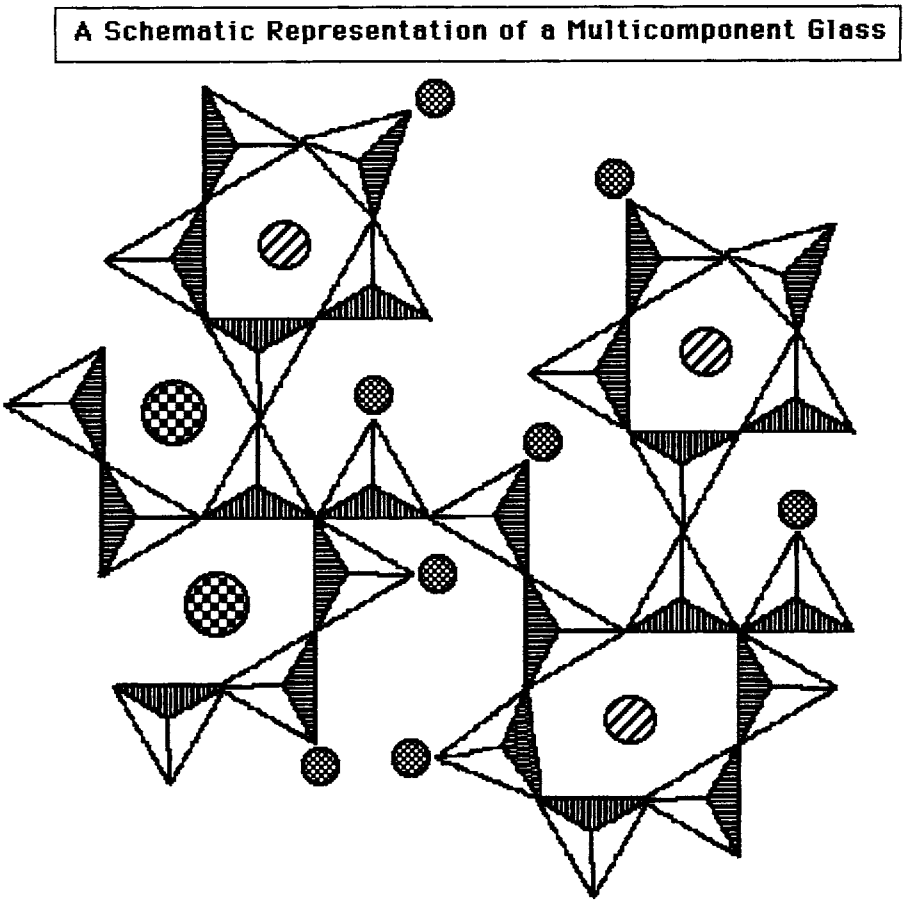



For most solids, expansion is usually linear. However, for glass, the expansion is linear up to the glass transformation point, $T_g$. Then an anomalous expansion occurs, corresponding to the transformation range given above in Figure 1.2.4., i.e.- $[T_{g_2} - T_{g_1}]$, which includes the softening point,$T_{sp}$.

It is this type of data (and others) which support the present concept of the amorphous state, but not that of the supercooled liquid. The work of Warren (1942) and other authors, who used x-ray diffraction to study the structure of glass, strengthened Zachariasen's concepts of a three dimensional, amorphous network.

An idealized multicomponent glassy structure is shown in the following diagram, given as Figure 1.2.6. on the next page, wherein several cations are illustrated in the diagram:

Figure 1.2.6.-




This structure is quite similar in concept to that already given in Figure 1.2.2. for silica, except that the structure is modified by the presence of several cations, each having its own degree of coordination. Note that three different cations are depicted in this two-dimensional representation of a multicomponent glass based on tetrahedra. Each cation has its own distinctive coordination in the glassy structure.

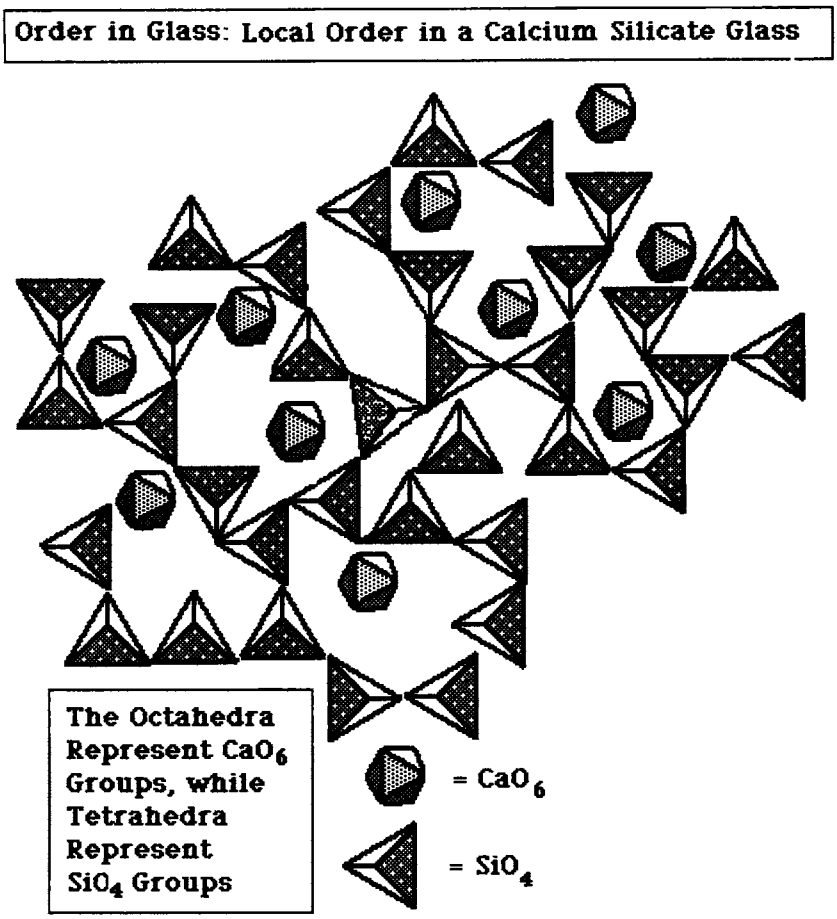
Diffraction patterns of glass have a very diffuse nature, and are similar to those obtained from liquids. Originally, it was thought that the diffuse nature of the x- ray patterns might due to very small crystals. However, there is no small

angle scattering from glass. To confirm this, examine the curves of Figure 1.2.1. again. Note the small-angle scattering present in silica gel, which has been shown to be due to the existence of discrete particles of some 10-100 Å in size, with gaps or voids between them. The absence of such scattering in the x-ray pattern for glass is perhaps the most persuasive experimental fact concerning this phenomenon and indicates that the bonding must be **essentially continuous**. It must therefore be concluded that glass is not a supercooled liquid. Because the position of the main diffraction bands of glass and gel in Figure 1.2.2. are comparable to that of the principle diffraction line for crystobalite, the conclusion can be drawn that the interatomic distances are about equal for all three materials. From a Fourier analysis of such diffraction patterns, radial distribution curves can be obtained which show the distribution of neighboring atoms about each atom. It is the combination of this work and that of Zachariasen which led to the ***random network theory*** for the structure of glasses.

The most recent work on glass structure has strengthened this concept. Although glasses typically display short-range order among nearest atomic neighbors, no observations had been made where longer range order was discerned. Using a special method of neutron-diffraction, Gaskell et al (5) observed the first evidence for medium structural order in an oxide glass. Their study of the distribution of calcium ions in a simple calcium silicate glass revealed that the immediate vicinity of a cation- that is, that encompassing its first few neighbors- looks very similar to the environment of a crystal. Thus, the cations shown in Figure 1.2.6. as an example of a multi-component glass do not have a readily apparent arrangement, and the major structural arrangement appears to be that of the silicate tetrahedra which comprise the amorphous structure. However, the work of Gaskell et al was the first to reveal that the cations **do** have an intermediate-range order.

This is seen in the following diagram, shown as Figure 1.2.7 on the next page. Here, we have shown but ten (10) octahedra, i.e.- $CaO_6$ - comprised of the $Ca^{2+}$ cation surrounded by six (6) oxygens, derived from the surrounding tetrahedra, arranged in a pattern having a medium range of order. The coordinate-covalent bonds of the Ca-O pairs arise from the "lone-pair" electrons always associated with the oxide-atom.

Figure 1.2.7.-



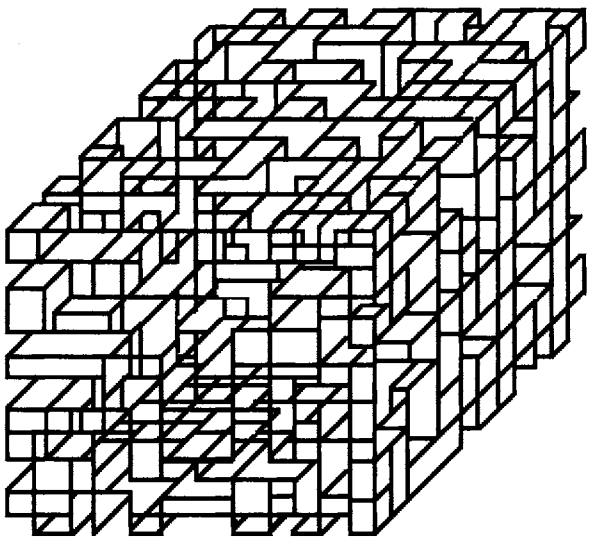

Thus the cations apparently impose an "order" on the tetrahedra, even though the overall structure is amorphous in nature.

However, it is easily seen, in the above Figure, that the amorphous structure comprised by the silica-tetrahedra is the major contributor to the overall vitreous structure. Thus, there is a "block" arrangement of the tetrahedra which form a short-range order along with an arrangement of cations having a medium-range order. This sequence comprises the overall vitreous structure. Such a structure would have a three-dimensional form where the basic structure is formed from tetrahedra. Additionally, cations having a medium-

range order would be present, but would be buried within the block-structure. Such an arrangement is illustrated in the following Figure:

Figure 1.2.8.-

**Three-Dimensional Arrangement of Tetrahedra in an Amorphous Structure**



Herein is shown an arrangement of tetrahedra with short-range order, but not with long range order. It should thus be evident from this discussion that the structure of glass does have a degree of order, but not a completely arranged order of atoms like a crystalline material.

## **1.3.** GLASS FORMERS AND GLASS COMPOSITIONS

On the basis of his rules, Zachariasen divided the simple oxides into those which should form glasses, and those that were structure modifiers. These are shown in Table 1.1. Both the oxides and the structural units are given, along with the oxygen- metal single bond strength. This general correlation was first made by Sun in 1947 (6) who suggested that glass forming capability was dependent upon the central bonding strength of the structural unit, as shown in the following Table:

TABLE 1.1

Glass Formers and Structural Modifiers

**Glass Formers**

| GLASS FORMERS | COORDINATION UNIT | VALENCE OF CATION | STRUCTURAL UNIT | SINGLE BOND ENERGY (KCAL/MOL) |
|---|---|---|---|---|
| $B_2O_3$ | $BO_2^-$ | +3 | TRIANGULAR | 119 |
| $SiO_2$ | $SiO_4^{4-}$ | +4 | TETRAHEDRAL | 106 |
| $GeO_2$ | $GeO_4^{4-}$ | +4 | TETRAHEDRAL | 108 |
| $Al_2O_3$ | $AlO_2^-$ | +3 | TRIANGULAR | 101 |
| $P_2O_5$ | $PO_4^{3-}$ | +5 | TETRAHEDRAL | 111 |
| $V_2O_5$ | $VO_4^{3-}$ | +5 | TETRAHEDRAL | 112 |
| $As_2O_5$ | $AsO_4^{3-}$ | +5 | TETRAHEDRAL | 87 |
| $Sb_2O_5$ | $SbO_4^{3-}$ | +5 | TETRAHEDRAL | 85 |

**GLASS MODIFIERS**

| | | | COORDINATION IN GLASS | |
|---|---|---|---|---|
| $B_2O_3$ | B- 0 | + 3 | 4 | 89 |
| $TiO_2$ | Ti - O | +4 | 6 | 73 |
| Zn | Zn - O | +2 | 2 | 72 |
| | | | 4 | 36 |
| Pb | Pb - O | +2 | 2 | 73 |
| | | +4 | 6 | 39 |
| Al | Al - O | +3 | 6 | 67 |

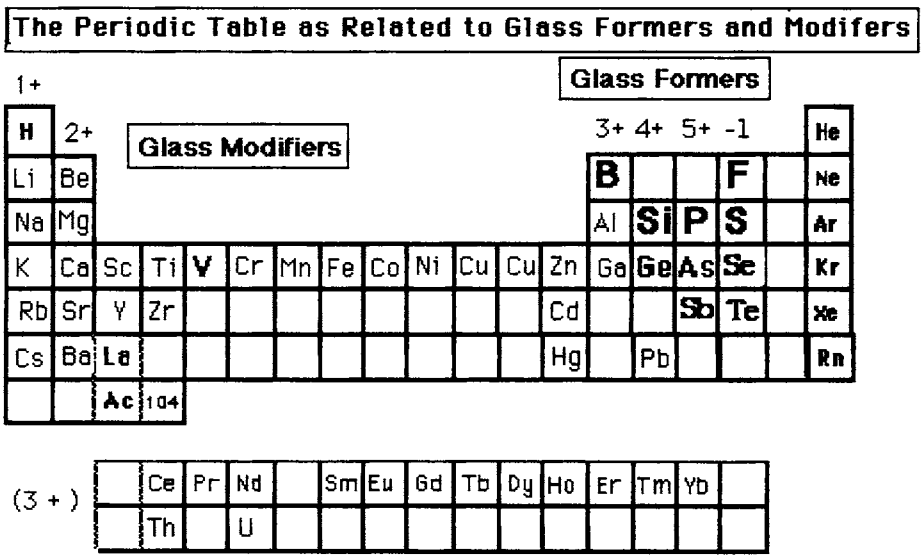
TABLE 1.1(Continued)

| Glass Formers and Structural Modifiers | | | | SINGLE |
|---|---|---|---|---|
| GLASS FORMERS | NETWORK MODIFIERS | VALENCE OF CATION | COORDINATION IN GLASS | BOND ENERGY |
| Zr | Zr - O | + 4 | 8 | 61 |
| La | La - O | + 3 | 7 | 58 |
| Y | Y - O | +3 | 8 | 64 |
| Ga | Ga - O | + 3 | 6 | 45 |
| Mg | Mg - O | + 2 | 6 | 37 |
| Ca | Ca - O | + 2 | 8 | 32 |
| Sr | Sr - O | + 2 | 8 | 32 |
| Ba | Ba - O | + 2 | 8 | 33 |
| Cd | Cd - O | + 2 | 2 | 60 |
| | | | 4 | 30 |
| | | | 6 | 20 |
| Li | Li - O | + 1 | 4 | 36 |
| Na | Na - O | + 1 | 6 | 20 |
| K | K - O | + 1 | 9 | 13 |
| Rb | Rb - O | + 1 | 10 | 12 |
| Cs | Cs - O | + 1 | 12 | 10 |

Bond strengths of glass formers are all above 80 Kcal/mole. All of these form **covalently** bonded anions to which the network modifiers are **ionically**

bonded in the glassy network. It is, perhaps, easier to visualize the relationship of glass-formers to each other, and to glass- modifiers, by considering the following Figure:

Figure 1.3.1.-




In this Figure, the glass-formers are given in the larger bold type, while the glass modifiers are given in normal type. It is easy to see that those elements generally regarded as anionic , i.e.- those which form anions easily, are those which are usually classified as glass-formers. Those elements which are cationic in nature are those which are glass (structure) modifiers.

Thus, glass-formers include: borates, silicates, germanates, phosphates, sulfates, and to a much lesser extent, arsenates and antimonates, as well as sulfides, and fluorides. Note also that vanadates are included as major glass-formers. The glass network- modifiers include: alkali metal cations, alkaline earths, and many of the transition metal cations (of varied valencies), plus the lanthanides, in some cases.

Sometimes in glass parlance, network modifiers are further divided into stabilizers and fluxes, according to the functions for which they are added to make commercial melts. For example, fluxes are added to lower melting and

working temperatures of silicate glasses by decreasing viscosities, e.g.- $Na_2O$ , $K_2O$ and $B_2O_3$ . Stabilizers are added to improve chemical durability and/or to prevent crystallization, e.g.- CaO, MgO, and $Al_2O_3$.

In general, the following oxides are added to a specific glass formulation to achieve the following results:

**Alkali Oxides**, e.g.- $Na_2O$ and $K_2O$: added as fluxes to reduce high viscosities of glass melts.

**Alkaline earth oxides**, e.g.- CaO and BaO: added to produce glasses resistant to water and acid leaching, i.e.- high chemical durability

**Boric oxide** : added to increase durability and stability of glass products

**Aluminum oxides**: added to increase "hardening of glass", i.e.- resistance to devitrification and improved durability.

Glass-network structures tend to be covalent. The Si-O, Ge-O, P-O, B-O, As-O and Sb-O bonds, according to Pauling's rules, are all 50% covalent, or greater. Modifiers are used to alter glassy properties, including refractive index , electrical conductivity and expansion coefficients. An intermediate, although not capable of forming a glass by itself, can enter into a glass-forming position and/or in a modifying position.

Notwithstanding, it should be obvious that the network structure which each glass former is capable of assuming is defined by the following:

1.3.2.- Network Dimensionality ≡ Coordination of Structural Unit - 1

Thus, only those anionic structural units having a coordination number of four **can form a three-dimensional network.**

The following table illustrates this aspect:

TABLE 1.2.

Dimensional Networks Formed by the Various Glass - Formers

| GLASS FORMER | STRUCTURAL UNIT | COORDINATION OF UNIT | | TYPE OF DIMENSIONALITY |
|---|---|---|---|---|
| | | Cation | Space | |
| $B_2O_3$ | $BO_2^-$ | 3 | 2 | Chains |
| | $BO_3^{3-}$ | 4 | 3 | Network |
| $SiO_2$ | $SiO_4^{4-}$ | 4 | 3 | Network |
| $GeO_2$ | $GeO_4^{4-}$ | 4 | 3 | Network |
| $Al_2O_3$ | $AlO_2^-$ | 3 | 2 | Chains |
| $P_2O_5$ | $PO_4^{3-}$ | 3 | 2 | Chains |
| $V_2O_5$ | $VO_4^{3-}$ | 3 | 2 | Chains |
| $As_2O_5$ | $AsO_4^{3-}$ | 4 | 3 | Network |
| $Sb_2O_5$ | $SbO_4^{3-}$ | 4 | 3 | Network |

Note that many non-silicate glasses form chains (two - dimensional) as the primary configuration. Of those which do form three-dimensional networks, only $SiO_4^{4-}$ and $GeO_4^{4-}$ have bond strengths sufficient to form glasses possessing high three- dimensional stability, with the desired properties of chemical durability and other properties of commercial interest. $SiO_2$ is by far the most important glass-forming system (because germanium is too expensive). Thus, most commercial glass melts are based on silicate compositions. A number of commercial formulas have arisen, and are being modified continuously in the Industry.

Table 1.3. gives some approximate compositions of commercial silicate-based glasses. The principle usage, and % by weight are given for the major components used to make the melts:

TABLE 1.3.

APPROXIMATE COMPOSITIONS OF COMMERCIAL GLASSES

| Glass* | | Percent by Weight | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Code | Usage | $SiO_2$ | $Al_2O_3$ | $B_2O_3$ | $Na_2O$ | $K_2O$ | MgO | CaO | PbO | Other |
| 0010 | lamp tubes | 63 | 1 | | 7 | 7 | | 22 | | |
| 0080 | lamp bulbs | 73 | 1 | | 17 | | 4 | 5 | 29 | |
| 0120 | sealing | 56 | 2 | | 4 | 9 | | | 29 | 0.8 As |
| 0281 | housewares | | 73 | 2 | 1 | 15 | .3 | 4 | 6 | .2As |
| 1720 | sealing | 61 | 17 | 5 | 1 | | 7 | 9 | | |
| 2475 | neon signs | 67 | | | 10 | 7 | | | | 12 ZnO |
| 6720 | general | 60 | 10 | 1 | 9 | 2 | | 5 | | 9 ZnO |
| 7250 | seal beam lamps | 78 | 2 | 15 | 5 | | | | | |
| 7740 | pyrex™ labware | 80 | 2.3 | 13 | 4 | | | .5 | | 2 BaO<br>.2 F/Cl |
| 8039 | ophthalmic flint | 35 | 2 | | 7 | | | 51 | | 4 $TiO_2$<br>1 $ZrO_2$ |
| 9741 | UV transmit | 67 | 6 | 24 | 2 | .1 | | .5 | | 1.1 F |
| OC-T | insulation | 59 | 4.5 | 3.5 | 11 | .5 | 6 | 16 | | |
| OC-C | acid-resist | 65 | 4.5 | 5.5 | 8 | .5 | 3 | 14 | | 8 $TiO_2$<br>4 $ZrO_2$ |
| LOF | window | 73 | 1 | | 13 | .1 | 3.8 | 8.6 | | .1$Fe_2O_3$ |
| PKT | windshield | 73 | 1 | | 14 | | 4 | 8.6 | | .1$Fe_2O_3$<br>.3$SO_2$ |

* refers to Corning Glass Works code numbers; OC = Owens Corning; LOF= Libby, Owens & Ford; PKT= Pilkington Bros. Ltd.

All of the above formulations are approximate but illustrate the diversity of formulations that are available. As stated, some 700 different glass compositions are in usage today, variations among which are designed to take advantage of some physical property such as expansion coefficient for a specific commercial application.

The following describes some of the various **general** classes of commercial glasses usually manufactured:

1.3.3.- Classes of Silicate-Based Glasses Usually Manufactured

1. Fused Silica
2. Alkali Silicates
3. Soda-Lime Glasses
4. Aluminosilicates
5. Borosilicate Glasses
6. Lead Glasses

These will be discussed in more detail below, after we survey the manufacturing methods used for producing silicate-based glasses.

## **1.4.** THE MANUFACTURE OF SILICATE-BASED GLASSES

The general steps in manufacture of glass (here we use the term "glass" to mean silicate-based glass) are:

1.4.1.- Steps in the Manufacture of Glass

a. Weigh out components (glass sand; soda ash; limestone; feldspar; and other components)

b. Mix with cullet (cullet is broken glass of the same composition)

c. Melt mixture

d. Allow to "fine" and become homogeneous

The raw materials generally used for manufacture of silicate-based glasses are given in the following Table:

TABLE 1- 4

SOME RAW MATERIALS USED IN GLASS MANUFACTURE

| Oxide Required | Materials Used |
|---|---|
| $SiO_2$ | glass sand, feldspar, petalite, nephaline syenite, lead silicate |
| $Al_2O_3$ | feldspar, petalite, nephaline syenite, calcined alumina, hydrated alumina |
| $B_2O_3$ | boric acid, borax |
| $Li_2O$ | lepidolite, petalite, spodumene, $Li_2CO_3$ |
| $K_2O$ | feldspars, pearl ash, potassium carbonate |
| $Na_2O$ | soda ash, feldspars, nephaline syenite |
| MgO | dolomite, calcined magnesite ($MgCO_3$) |
| CaO | limestones |
| PbO | litharge(PbO), lead silicates |
| BaO | barium carbonate |
| ZnO | zinc oxide |

Note that several minerals are specified. These are defined as:

**Nephaline syenite** = 54% albite ($Na_2O$ - $Al_2O_3$ -$6SiO_2$ ), 24% microcline ($K_2O$ - $Al_2O_3$ -$6SiO_2$ ), 22% nephalite ($3Na_2O$ -4 $Al_2O_3$ - $K_2O$ -$9SiO_2$).

**Feldspar** consists of three main types: microcline , albite and anorthite (CaO-$Al_2O_3$ - $2SiO_2$ ). The effects of addition of feldspar to commercial glass batches

may be summarized as follows: 1. increased resistance to scratching; 2. increased resistance to breaking during bending; 3. increased resistance to breakage due to impact; 4. improved thermal endurance of the glass; 5. improved chemical durability; 6. decreased tendency of glass to devitrify.

**Petalite =** ($Li_2O$ - $Al_2O_3$ -$8SiO_2$)

**Lead silicate** = PbO- $SiO_2$

**Borax** = ($Na_2O$ - $2B_2O_3$ - $10H_2O$)

**Lepidolite** = (LiF-KF - $Al_2O_3$ - $3SiO_2$ )

**Spodumene** = ($Li_2O$ - $Al_2O_3$ - $4SiO_2$ )

**Dolomite** = $CaMg(CO_3)$

Note that most of these materials are complex silicates, which break down under heating to form to form specific oxides required in a given formulation.

The most important classes of glasses currently manufactured are summarized in the following:

1.4.2.- Types of Glasses Manufactured

Silica-glass: This is the familiar "quartz" glass (or "fused- silica" glass) which is used extensively in microelectronics as a substrate for IC's. It has excellent ultraviolet transmission capabilities to about 1850 Å, a low coefficient of expansion and is highly resistant to chemical attack by water or other chemicals. It also finds use in optics and as crucibles for solid state work.

Alkali Silicate Glasses: Pure silica glass has a very high melting temperature. The addition of alkalis reduces the high viscosity inherent in pure-silica glasses and brings glass manufacture into the range of industrially accessible temperatures and usable refractories. It does so by the formation the breaking of Si-O bonds, and the formation of Si-O-

Na linkages. The limit of glass formation is about 1.0 $M_2O$ : 1.0 $SiO_2$ . Alkali silicate glasses are usually soluble and sodium silicate glasses form the basis of the soluble silicate industry. They have usage as adhesives, cleaners, cements, defloculents and to some extent as protective coatings.

Soda-Lime Glasses: Soda-lime glass is by far the most often used glass composition because it is cheap and easy to manufacture. If soda, i.e.- $Na_2O$, is added, it "breaks" Si - O bonds and "softens" the glass. When "lime" is also added, i.e.- $CaCO_3$ , it "stabilizes" the glass with respect to cost, chemical durability, and ease of manufacture. The optimum glass usually consists of: 72% silica, 15% soda, about 10% lime and magnesia, 2% alumina, and 1% miscellaneous oxides. This composition comprises by far the most numerous "melts" made in the Glass Industry. Soda - lime glass is used for windows, containers and lamp envelopes. It accounts for about 90% of all tonnage manufactured.

Borosilicate Glasses: Boric oxide enters the silica network as a structural modifier while lowering the viscosity of the melt.. Consequently, it is regarded as a flux. The result is the typical borosilicate glass, which is represented by "Pyrex™", as originally developed by Corning Glass Works. Pyrex glass is used to make laboratory glassware because of its excellent thermal resistance, a property not found in other types of glasses. However, too much boric oxide causes either a phase separation to occur, or the chemical durability to suffer.

Aluminosilicate Glasses: When alumina is added to a soda-lime melt, it assumes a tetrahedral coordination, healing the Si-O bonds broken by the addition of alkali. It also improves the chemical durability and resistance to devitrification. However, a solubility limit exists for the most part. Currently, it has proved useful in strengthening glass compositions, typically by an ion-exchange process. Such glasses show much higher strengths than comparable low-alumina containing glasses. Alkaline earth aluminosilicate glasses have high temperature resistance and good dielectric properties, and are used for cook-ware, fiber glass and glass-ceramics.

Lead Glasses: Lead oxide is a good flux for glass melts and yields glasses with high refractive indices, high density, and a low softening point. Commercially, The addition of PbO produces a "softening" effect and yields glasses with high refractive index and density. Lead glasses are used for radiation-shielding windows, optical glasses, lead-crystal art ware, and low-melting solder glasses.

Colored Glasses: Certain minor constituents are added to glass melts for the purpose of adding color, or other spectral properties, to the finished product. These additives include:

1. Red Glasses - colloidal Au or Cu

2. Pink Glasses - manganese plus cerium oxide

3. Orange Glasses - cadmium sulfide

4. Amber Glasses - iron oxides

5. Yellow Glasses - uranium oxides

6. Green Glasses - chromium oxides, ferric oxide, copper oxides

7. Blue Glasses - cobalt oxides, copper oxide

8. Violet Glasses - nickel oxides

9. Gray Glasses - nickel plus cobalt oxides

10. Black Glasses - manganese plus chromium oxides

11. Ultraviolet Absorption Glasses - cerium oxide, titanium oxide, vanadium oxides

12. Infrared Absorption Glasses - iron or copper oxides

13. Specialty Uses :

Decolorization of Glasses - add manganous oxide

Opacified Glasses - add calcium fluoride, zinc sulfide

Fluorescent Glasses - add $Ln^{3+}$ ions, $Mn^{2+}$ , $U^{3+}$ , $Cu^{-}$ , $Tl^{+}$, $Sn^{2+}$, or $Pb^{2+}$ .

Radiation Protection - add cerium oxide

14. Fining Uses - add sulfate, fluoride, chloride, bromide, iodide, antimony oxide, or arsenic oxides.

Note that nearly any color can be achieved in a finished glass article. Some colors, particularly the yellow-green color obtained from iron oxides (present as an impurity in the minerals used to make the glass melt), are deliberately masked by the addition of small amounts of MnO or a selenide which introduces a balancing absorption in the blue and the green portion of the spectrum.

The following diagram, given as Figure 1.4.3. on the next page, shows steps required to manufacture glass. These include:

a. Batch Mixing

b. Melting

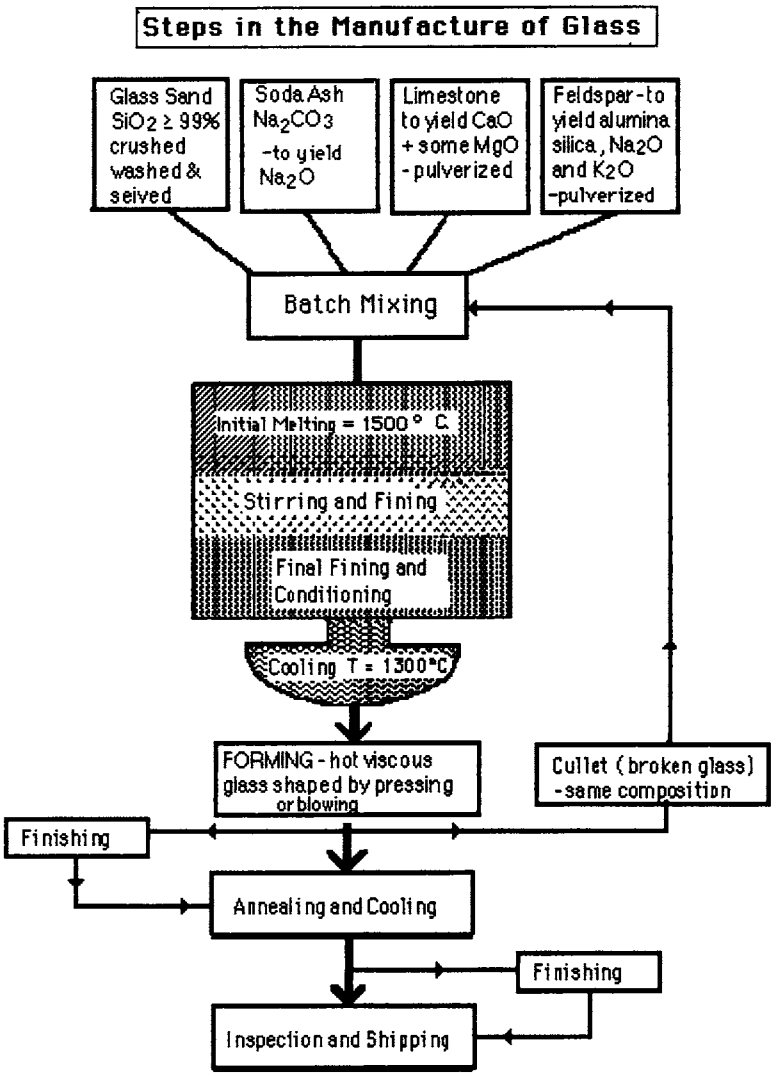
c. Stirring, fining and conditioning

d. Forming

e. Annealing and cooling

The most important step is that of melting and fining, followed by that of forming and then annealing. It should be clear that silicate glass manufacture has evolved from the use of sand, with specifically chosen oxides added to

Figure 1.4.3.-




achieve certain effects in the final glass composition. These oxides are commonly added as complex silicates, which break down during melting to provide the final composition of the glass.

Because such silicates have a rather high melting point, it is customary to add "cullet", which is broken glass, to the front-end of the furnace. The glass has a

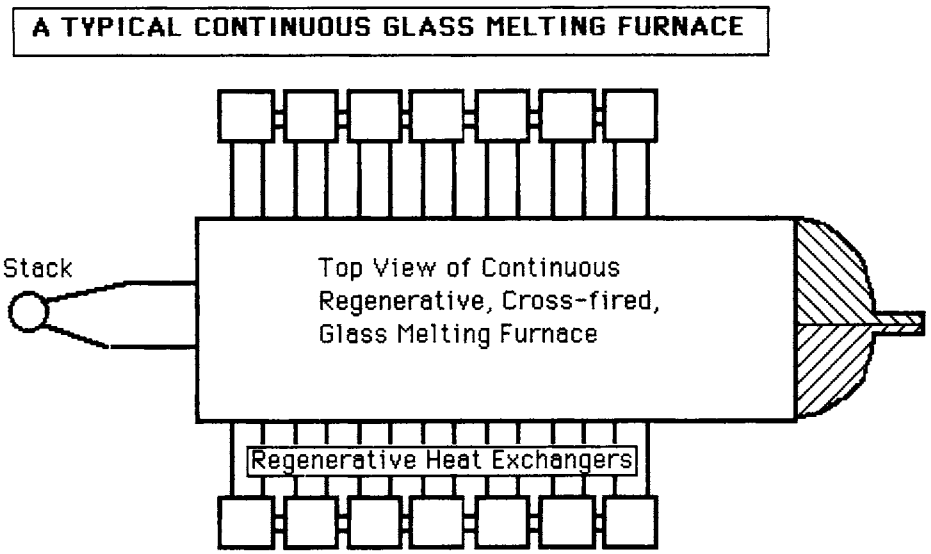
much lower softening and melting point, and serves to form a liquid phase which causes the silicate additives and sand to melt faster, with less heat required.

Glass furnaces are charged automatically or manually, and continuously or intermittently. Most glass is melted in a continuous tank, whose holding capacity may be as high as 1400 tons. Outputs of 300 tons per day are common. The glass-melting furnace itself is lined with a refractory material such as mullite, which is an aluminum silicate. The refractory must be capable of withstanding dissolution in molten glass. Most materials are soluble therein, and the part which dissolves must not be deleterious to the finished glass batch. Fortunately, once the surface of the refractory is exposed to molten glass, the rate of dissolution decreases radically. Natural gas and oil are the primary fuels used. However, since the molten glass batch is usually electrically conductive, it can be heated by the passage of an electric current. Electric heating is used in Europe, and in the U.S., electric heating is used as a booster in some cases.

Once a melt is obtained, the fining operation proceeds. Fining is the process where bubbles, obtained from melting of the raw materials, are caused to dissipate. In some cases, special compounds are added, while in other cases, air or nitrogen is blown in to cause the small bubbles to subside. If a continuous furnace is used, fining continues as the glass batch proceeds down the furnace. Figure 1.4.4., given on the next page, shows a top view of a typical continuous furnace used for processing glass.

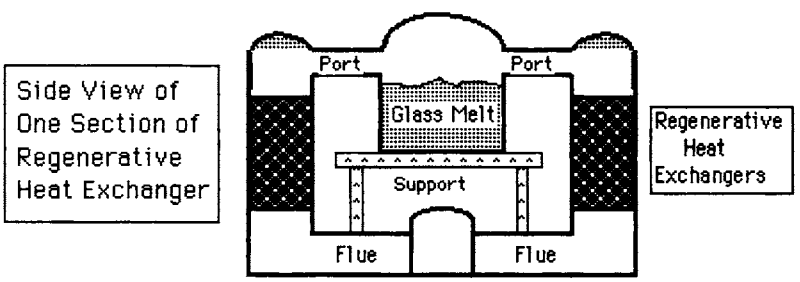
In this case, the furnace is cross-fired, i.e.- heated from both sides, and is constructed with seven (7) regenerative heat exchangers to recover heat from the flue gas before it passes to the stack. They are usually operated in pairs, one chamber being heated by passage of flue gas from combustion while the other is being preheated.

Figure 1.4.4.-



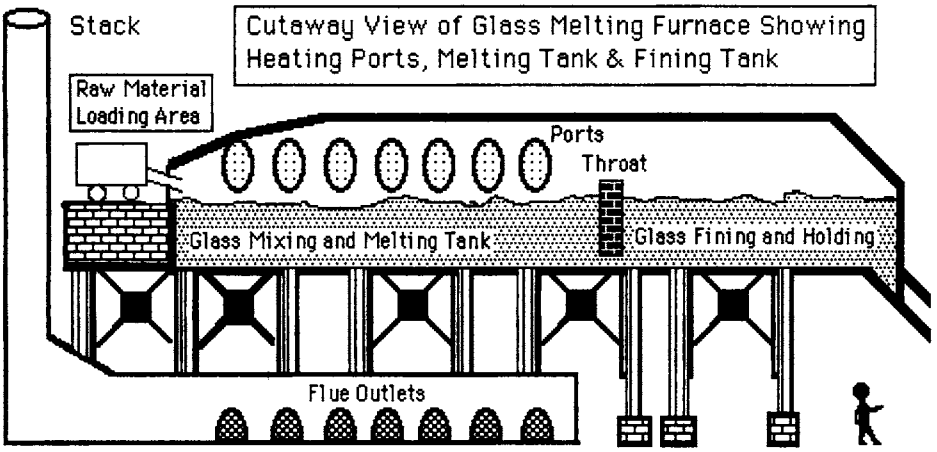

Each regenerative heat exchanger is connected to the other. In a typical operation, the flow of air, combustion gases and flue gases is reversed about every 30 minutes. The melting and mixing tank is the one usually heated, while the fining and holding tanks are usually heated by convection. A cross-section of a typical regenerative heat exchanger is given as follows:

Figure 1.4.5.-




In Figure 1.4.6., given on the next page, is shown a cutaway of the same continuous furnace which shows the total lengthwise cross-section:

Figure 1.4.6.-




Here, we have shown the glass tank divided into two parts by a throat. By common consent, the area of molten glass is arbitrarily divided into the melting zone, the fining zone and the working zone. No actual demarcation exists in these areas, except as temperature differences exist. In the melting zone, the lumps of batch float in a mass of foam produced by their own melting and the mass of boiling glass about and below them. The foaming is most violent about half way through the melting zone, where the temperatures are highest. Further on, the temperature is maintained at a level high enough to reduce the viscosity of the molten mass so that foam bubbles burst easily and rapidly. Thus, a foam-line is established beyond which no foam is apparent. Here begins the fining zone where the glass is quiescent and any small bubbles present have an opportunity to rise to the surface and burst. Since no heat is introduced into the furnace within the fining zone, radiation is used to maintain the temperature during fining. It is here that "fining agents" are introduced to aid in removing small bubbles and other inhomogeneities such as unmelted particles. Typical fining agents used are:

1.4.7.- TYPICAL FINING AGENTS USED IN THE GLASS INDUSTRY

1. Agents which give off oxygen gas

| | | | |
|---|---|---|---|
| nitrates | peroxides | chlorates | perchlorates |
| ceric oxide | manganese dioxide | $As_2O_3$ & $Sb_2O_3$ | |

2. Agents which give off $SO_2$ gas

sulfates sulfites

3. Agents which depend upon evaporation from melt

Halides (NaCl, KCl, etc.) ammonium salts ($NH_4$ Cl , etc.)

These agents are added to the melt at the fining section of the tank, usually on a continuous basis. Fining agents introduce gas bubbles which cause existing bubbles to grow larger in the melt, thereby increasing their rate of destruction. *Artificial bubbling* is also used to increase fining rates during the final stages of the melt processing before usage.

Gas evolution during melting and convection- currents resulting from differences in temperature within the tank are tremendous aids to homogenization of the melt. But, uncontrolled lengthwise waves can sweep gaseous inclusions, foam and scum, and "stones" (unmelted particles) into the area of glass removal from the furnace. We have shown a throat within the furnace shown in 1.4.5. whose function is to prevent this.

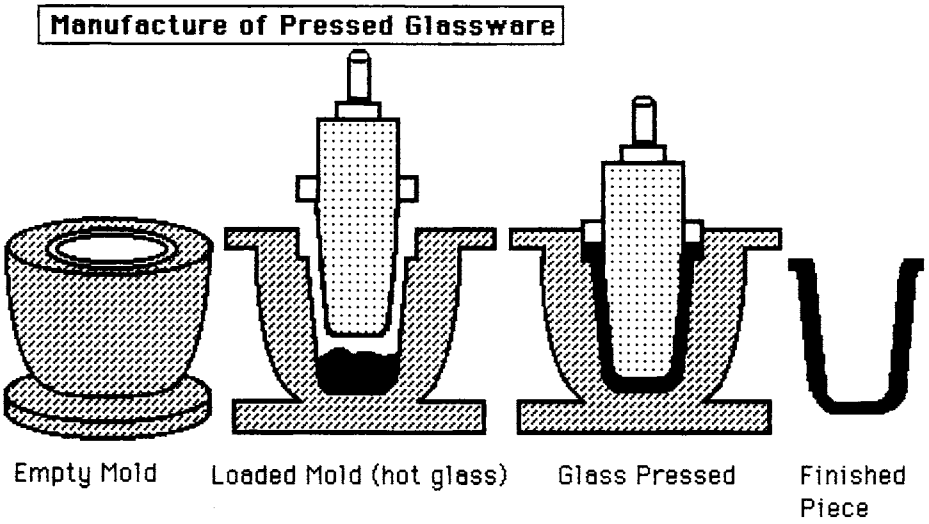
## **1.5.** FORMING AND FINISHING OPERATIONS

Glass is used to make over 10,000 different articles. Many, such as light bulbs, are made on high speed forming lines, where the individual articles move at 40 miles per hour. Glass may be rolled between heavy iron rollers to form patterned glass. Glass may also be cast, drawn or pressed.

Forming operations include:

1.5.1.- **Pressing**: an operation where glassware is formed by pressing hot glass between a mold and a plunger.

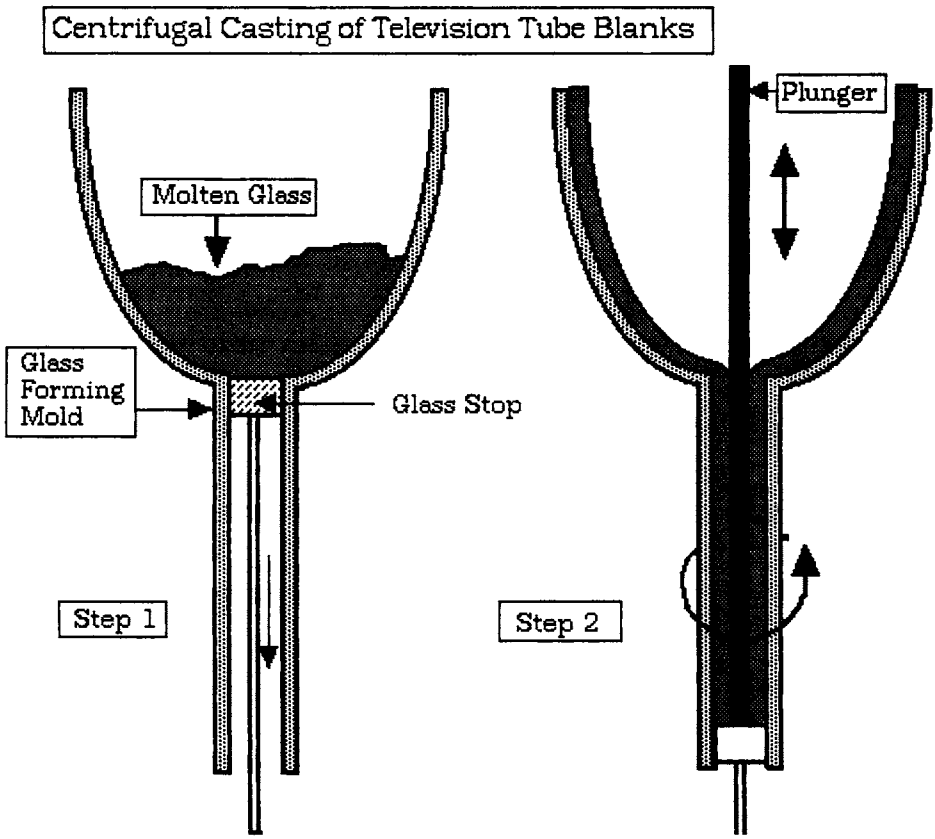
This is illustrated in the diagram given on the next page, viz.-




Care must be taken not to introduce undue strain in the finished piece since the amount of residual strain is usually proportional to its size and thickness. Most finished pieces are small in size. Following the pressing operation, the glass piece must then be annealed thoroughly. Other variations include the use of a split mold and a so-called "font-mold" for making solid pieces of glass. Glass articles made by this method are usually those of the "cut-glass" variety, where an artisan uses a grinding wheel to cut designs into the surface of the glass. Lead - crystal is made by this method.

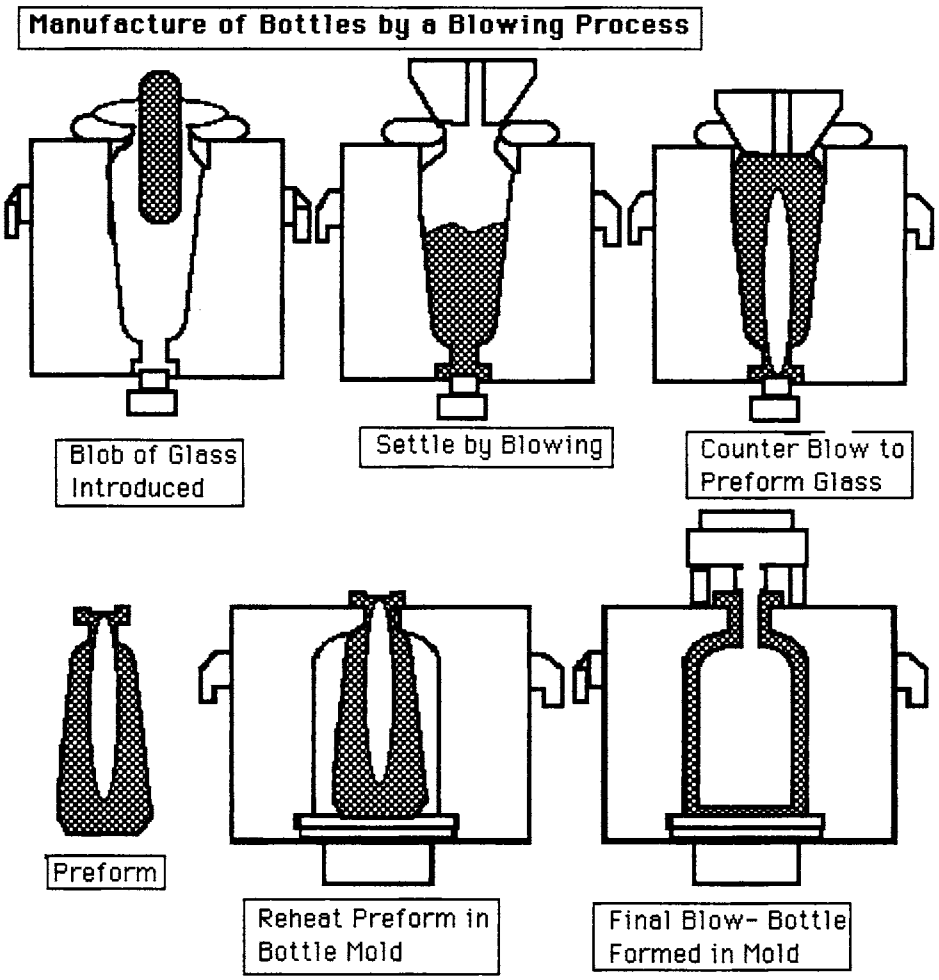
1.5.2.- **Casting**: hot glass is poured into a mold and allowed to cool. Then it is annealed (sometimes in place). It is this method which is used to make large solid articles of glass. Television tube blanks are made by a centrifugal casting method where the hot glass is cast within the hollow mold, which is then spun to make the hot malleable glass conform to its outer surface. Such an apparatus is given in the following diagram, given on the next page.

In this case, hot glass is introduced into a spinning mold (Step 1). The centrifugal force causes the molten glass to climb up the sides of the mold, while a plunger pushes the glass-stop to the bottom of the spinning mold, thereby forming the neck of the television tube blank (Step 2).




1.5.3.- **Rolling**: flat glass of all kinds is made by rolling. In a batch process, glass is poured from a pot onto a large iron table and rolled to desired thickness by a heavy iron roller. In another process, the hot glass is passed through a set of heavy, water-cooled, rollers to form a continuous sheet of predetermined dimensions. This sheet is then cut to desired size for usage thereof. Prior to the development of "float-glass", these sheets had to be ground and polished, if they were to be used as window panes, and/or plate glass. Patterned and wired glass is also formed by this method.

1.5.4.- **Blowing**: this operation refers to the use of gas pressure (usually air) to form a shape in a mold. The glass container industry is based on this operation. A typical operation to form a bottle includes the following steps, as shown on the next page.




Note that the preform is reheated for the final blow. When a hot "blob" of glass is introduced into the mold, it settles to the bottom under air pressure. Additional air pressure introduced from the bottom of the mold causes the hot glass to conform to the outline of the mold, as shown in the third part of the diagram. The "preform", as it is called, is then introduced into a bottle mold, reheated and then caused to conform to the desired bottle shape by a "final blow". The final step is annealing (see below). Millions of bottles and containers are made by this method every year.

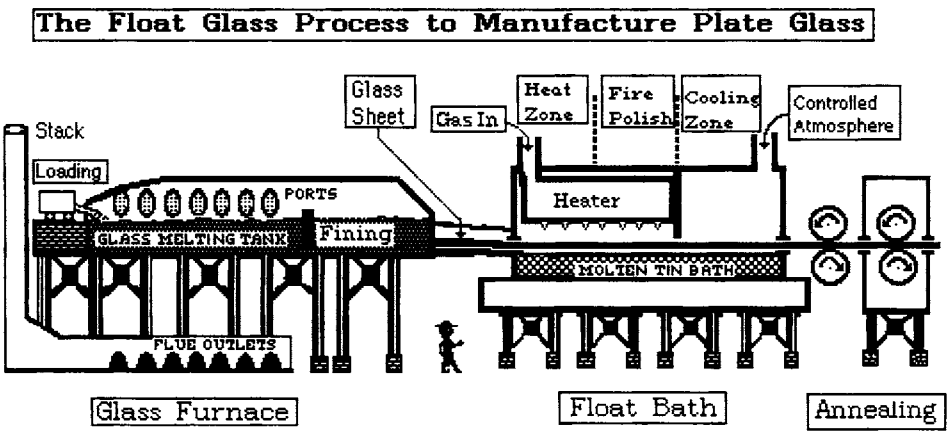
When glassware made by a blowing process exits the molding stages, they enter a "lehr" where they are annealed. Because the surface of the glass containers is not completely smooth, they tend to rub against each other and microscopic cracks are induced in the glass-surfaces. Breakage can be severe. In the past, when glass containers were heavy and line speeds slow, there was little need to prevent such microcracks. However, present day demands for lightweight glass containers have mandated the use of "hot-end" coatings immediately after forming.

The coating materials most often used are tin-oxide based, derived from tin tetrachloride and/or butyltin trichloride. Application protects the pristine glass surface from reaction with moisture, and controls microcracking of the glass surface as well. Another benefit is reduction of breakage during the lehring operation.

In most modern glass container manufacturing facilities, bottles and containers have become increasingly lighter in weight and speeds in the lehr and customer's filling lines have accelerated enormously. This has dictated the use of a "cold-end" coating as well. Basically, the reason glass is cold-end coated is to further protect and lubricate the glassware so that it can be moved smoothly with high speed handling equipment, without damage to the glass surfaces. Thus, a massed group of bottles on the lehr is moved into single lines for inspection and then on through packaging. When the containers reach the customer's plant, the glass is unpacked, cleaned, filled, labeled and repacked. Glass to glass contact occurs during all of these processes and efforts to minimize surface damage is mandatory. Although glass is theoretically a very strong material, resistance to scratching must be achieved so as to keep the inherent strength of the containers high. Cold-end coatings most often used include oleic acid and water-based polyethylene emulsions. The former is easily removed by washing, whereas the latter is not.

1.5.5.- **Float Glass**: This process was originally developed by Pilkington Bros., Ltd. in England in the late 1950's. Essentially, it involves casting molten glass upon a molten bed of tin-metal to form a sheet of glass in a continuous manner. The atmosphere in the float zone is inert to prevent the tin from oxidizing. This process totally eliminates any grinding and polishing

operations, and is used worldwide to manufacture plate glass, including mirrors. The following diagram illustrates the process used:




In this case, the output of the glass furnace is fed as a flat sheet into the float-bath, where it is reheated, fire-polished and and cooled, all in an inert atmosphere to prevent the melted tin from oxidizing. Additionally, various coatings can be applied to the plate glass.

1.5.6.- **Drawing**: tubing of all sorts, cane or glass-rod, and sheet are made in a continuous operation. The operation can be vertical or horizontal. The three major methods of drawing tubing use the Danner, Vello or Updraw machines. All are basically the same: hot glass flows around a ceramic cone or mandrel and is carried along asbestos-covered rollers. Air blowing through the mandrel maintains the glass as a continuous tube. This is then cut into manageable lengths before usage.

1.5.7.- **Fiber Forming**: this process makes fibers for textiles, and electrical, thermal, and acoustical insulation. In one process, molten glass is forced under pressure through platinum orifices, with steam jets set at right angles to the flow, in order to form fibrous-glass wool. In another, glass is remelted, and forced through a mandrel with small holes, to form continuous filaments which are wound to form a glass fiber for weaving thereof. A more specific description of this process, and the products made, will be given below.

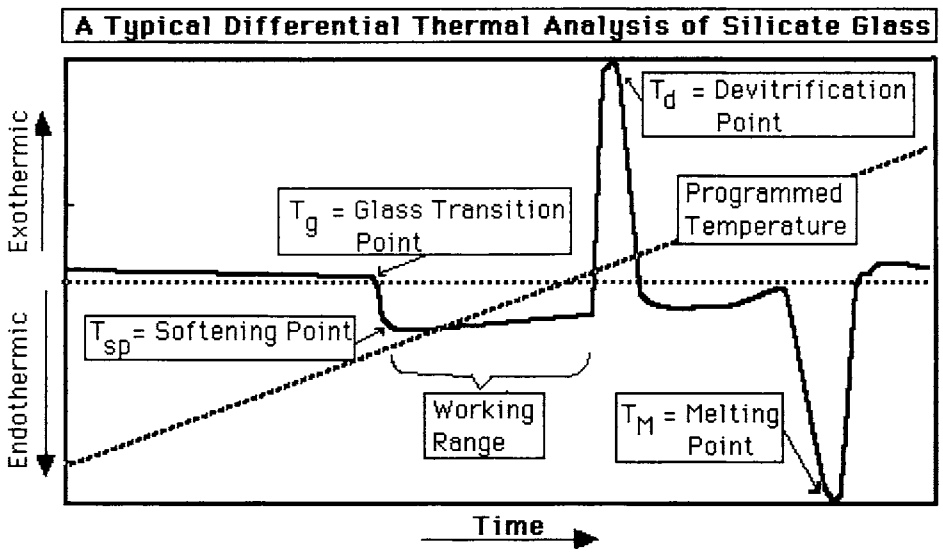
## 1.6. THERMAL PROCESSING AND PROPERTIES OF SILICATE GLASSES

The glassy state possesses several interesting properties in regard to its manipulation by thermal means. Many of these properties are inherent, while others can be induced. The following describes some of these induced properties, including that of glass- ceramics. In that case, controlled recrystallization is used to make various glass-ceramics which have qualities not available in "ordinary" glass.

### 1.6.1.- Glass Points and Devitrification

All glasses are unstable to one or more crystalline compounds and will recrystallize, given the proper thermal treatment. This process is called devitrification. Such behavior is familiar to most glass manufacturers and is usually prevented by adjustment of the starting glass- formulation.

When glass is heated from room temperature, it undergoes several thermal changes. The easiest way to show this is to examine the DTA-thermogram of a typical silicate glass, as shown in the following, viz-




In the above diagram, the abscissa is time where the temperature is programmed in a linear manner, i.e.- $\partial T/\partial t$ = a constant. When the glass is

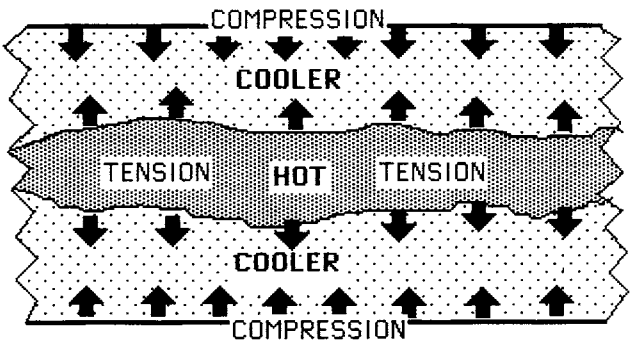
heated (usually as a powder for differential thermal analysis, i.e.- DTA), the first thermal anomaly reached is $T_g$, the glass transition point. Since DTA is essentially a plot of differences in heat capacity, this first point appears as a discontinuity. At the bottom of the discontinuity is the softening point, $T_{sp}$. The next point is an **exothermic** peak which is the devitrification temperature, i.e.- the glass undergoes a transformation from the amorphous to the crystalline state with evolution of heat. When these crystals are further heated, they melt at $T_M$. These thermal changes are reversible, and the glassy state again results when the melt is cooled properly. The temperatures between the bottom of the discontinuity, i.e.- $T_{sp}$ and the point of incipient devitrification is called the "working range" of the glass. There, the viscosity of the glass is low enough so that forming operations can be carried out.

1.6.2.- Annealing

Although we have mentioned this operation, we have not described it in detail. When a glass article is made, either by casting, pressing or blowing, and allowed to cool, it will develop internal strain within the glass walls. This strain results because it is the outer surface of the glass where heat escapes, while the inner part remains hotter. Thus, a heat differential is set up where the outer part of the glass article cools and contracts faster than the inner part, as shown in the following illustration:

DEPICTION OF WHY STRAIN RESULTS IN A HOT GLASS LAYER

NOTE: THE OUTSIDE OF THE GLASS LAYER COOLS FASTER THAN INSIDE. THEREFORE, THE INSIDE, BEING HOT, DEFORMS UNDER TENSION, FROM THE COMPRESSIVE FORCES AT THE OUTSIDE AND AN INTERNAL STRAIN REMAINS WHEN THE GLASS LAYER IS COMPLETELY COOL.




Internal strain is universal in glass because of the amorphous structure put into place as the glass cools below its glass- transition- point. If the strain is not relieved, the solid glass will, at some point, explode violently. It is

therefore necessary to "anneal" the glass. There is a temperature at which strain- introduction is maximum, called the "strain-point". To anneal the glass, one heats it slightly above the strain-point temperature, at the so-called "annealing" (strain-relief) temperature. When both external and internal temperatures of the glass become even, the external temperature is reduced slowly through the strain-point, so that a "strain-free" glass article results.

Examples of these so-called "glass-points" are listed for several varieties of silicate glasses, as given in the following table:

TABLE 1-5

Glass Points for Some Silicate Glasses in °C.

(refer to Table 1-3 for compositions)

| Glass | Strain Point | Annealing Point | Softening Point | Working Point |
|---|---|---|---|---|
| 0010 | 392 | 492 | 626 | 983 |
| 0080 | 473 | 514 | 696 | 1005 |
| 0120 | 395 | 435 | 630 | 985 |
| 0281 | 491 | 532 | 714 | 1024 |
| 1720 | 667 | 712 | 915 | 1202 |
| 6720 | 505 | 540 | 780 | 1023 |
| 7250 | 436 | 480 | 712 | 1128 |
| 7740 | 510 | 560 | 821 | 1252 |
| 8039 | 440 | 475 | 617 | 866 |
| 9741 | 408 | 450 | 705 | 1161 |
| LOF | 486 | 525 | 700 | 985 |
| PKT | 522 | 551 | 734 | 1047 |

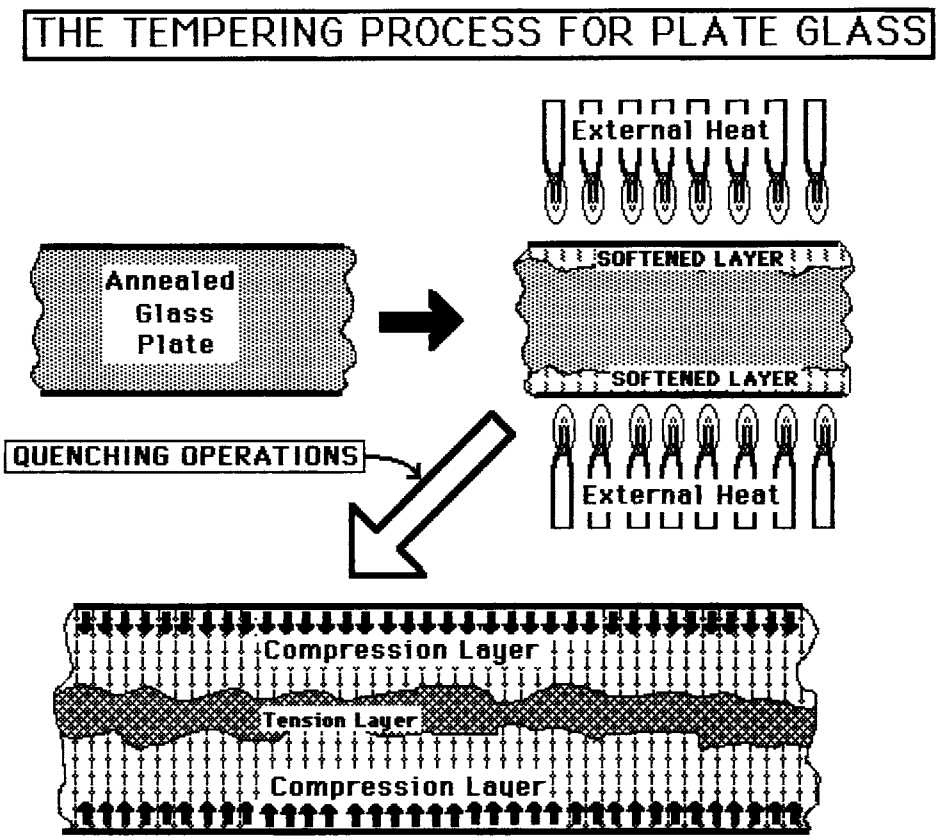
The "glass-numbers" refer to the varieties already described in Table 1- 3. To properly anneal a glass article, it is necessary to hold the article at the annealing temperature for the time required until the internal temperature matches the external temperature, which in turn depends upon the thickness of the glass article.. Cooling slowly (usually no more than 1-2 °C/minute) through the strain point then produces a strain-free glass object. Note that neither the glass transition point, nor the softening point, is ever exceeded. Details on how the temperature cycle is calculated so as to produce strain-free glass will be given in the following Chapter.

1.6.3.- Tempering

Tempering is achieved by by rapid cooling of the surface of the glass from temperatures near to the softening point. The result is a high compressive stress on the surface, as illustrated in the following diagram given on the next page.

Several advantages accrue, notably that of strength which can range up to 50,000 psi. Another advantage is that the breaking pattern can be controlled. The tempering process requires meticulous control of time and temperature of heating. The glass is heated in electric or gas-fired ovens to a temperature near to its softening point. It is then quickly removed and **quenched** by air-blasts or by immersion in a bath of oil, or in fused inorganic salt baths. Properly performed, there is no perceptible difference in appearance between annealed and tempered glass plate. However, It is quite difficult to temper flat glass plate less than about 1/8 inch thick.

Even though tempered glass is very strong, it is possible to break it by excessive stress. If the stress system is unbalanced, as by disruption of the surface even at a single, isolated point, or flaw, the whole piece ruptures into small, interlocking, blunt-edged fragments. These fragments become smaller, on the average, the greater the strain energy released. That is, the greater the original degree of temper, the greater is the energy released. An effort is often made to obtain maximum strength without exceeding an amount of tension called the "dicing limit". At the dicing limit, the glass, when broken, breaks, or "dices" into pieces roughly 1/4 inch square, **if the tempered glass plate has been properly manufactured.**




The largest usage for tempered glass plates is that of windshields for automobiles. In this case, the thermal tempering is accomplished in a hot bath, composed of either oils, fused salts or blasts of hot air.

Still another method for preparing tempered glass is that of "chemical-strengthening". In this method, one places the glass article to be tempered in a molten salt bath. For example, the ion, $K^+$, will exchange with $Na^+$ ion in a sodium aluminosilicate glass at 500 °C. to produce strengths in excess of 100,000 psi. Sometimes the lithium ion, $Li^+$, is used as well. The volume increase (or decrease) required to accommodate larger or smaller ions in the surface is restrained by the interior glass structure. This exchange, which affects only a thin surface layer, permits compressive strengths much higher than previously possible. Removal of the exchanged ions on the surface can be

effected by the use of sulfur dioxide, or by heating. This results in a low-expansion glass surface.

Considering the low density of glass (about 2.50 gm./$cm^2$) these strengths are especially advantageous, since chemically-tempered glass compares quite close to those of commercially available materials. The following Table is a summary of the measured strength to weight ratio of several types of glass:

TABLE 1-6

Strength to Weight Ratios for Glass and Other Materials in $lb/in^2$ per $lb/in^3$

| Glass forms | | Other Materials | |
|---|---|---|---|
| Abraded glass | $2 \times 10^4$ | Tin metal | $1 \times 10^4$ |
| Pressed glass | $5 \times 10^4$ | | |
| Blown glass | $9 \times 10^4$ | Wrought iron | $1.5 \times 10^5$ |
| Tempered glass | $3 \times 10^5$ | | |
| Glass ceramics | $4 \times 10^5$ | | |
| Ion-exchanged glass | $9 \times 10^5$ | Stainless steel | $8 \times 10^5$ |
| Glass fibers in plastics | $4 \times 10^6$ | Carbon steel wire | $1.5 \times 10^6$ |
| Drawn glass fibers | $6 \times 10^6$ | SiC whiskers | $2 \times 10^7$ |

It is easily seen that glass forms produced by the various methods compare very favorably with other high strength materials.

1.6.4.- Thermal Shock Resistance of Glass

The application of heat to glass results in a stress caused by expansion of the glass at the point of heating. Actually, this is a type of birefringence which is reversible. There are upper limits of temperature usage for glass articles,

determined by stresses set up by temperature differences across the glass. If a glass plate is completely restrained, the tensile strength on the cool side is given by:

$$\sigma = E \alpha \Delta T / 2(1- \nu)$$

where $\Delta T$ is the temperature difference across the glass, $\alpha$ is the expansion coefficient, E is Young's modulus, and $\nu$ is Poisson's ratio. The maximum thermal shock resistance of glass-ceramics is about 480 °C., which is much higher than most glasses which range from about 100 - 300 °C.

1.6.5.- Glass Ceramics and Nucleation Processes

Glass- ceramics are made by heterogeneous nucleation and crystal growth processes in which more than 50% of the glass is converted to a fine-grained crystal. This process was discovered by Stookey (14) and is made possible by the addition of a nucleating agent such as NaF. Subsequent thermal processing, also called "ceramming", serves to cause the major crystal phases of the glass to grow. Other nucleating agents that have been used include: metal colloids, $TiO_2$ and titanates, chromic oxide, $P_2O_5$ , $ZrO_2$ , ZnS , plus various fluorides. Obtaining such fine-grained fully dense ceramic materials is based on the fact that one can cause the glass to fully nucleate and recrystallize. Such a process allows the fabrication of a new class of materials having unique and useful properties not found in glass alone.

Glass - ceramics are used as:

- Cook-ware where the utensil can be directly heated on a hot surface without breaking due to thermal stress.

- Low expansion printed- circuit boards
- Stove-tops for cooking where the heating elements are placed beneath the glass-ceramic surface.

- Table ware which will not break when hot food is placed in or on the dishes.

Sales of smooth cook-top stoves has become big business where fully 48% of stove- appliances sold in 1990 were of this variety, that is- incorporating a glass-ceramic surface. Such electric or gas appliances use a resistive coil heating element, or a radiant element such as a halogen lamp of the same wattage, on the back side of the surface. The overall cleanability and visual impact of the smooth- top stove has made it a leading design for the 1990's, and was made possible by the advent of glass-ceramics.

### 1.6.6.- Opacification

Still another thermal nucleation process is used in the Glass Industry. Opal glasses are translucent, that is - they are partially transparent due to multiple internal scattering processes. Opacification is obtained by selectively precipitating crystals, having a refractive index differing from that of the glass matrix, within the glass structure. The amount of opacification is determined by the difference in refractive index between the glass and the crystals, as well as the number and size of the crystals. This allows the manufacturer to control opacification by reheating techniques. Opal dinnerware is obtained by the addition of zinc sulfide or calcium fluoride to the melt to form a second phase of small crystals.

### 1.6.7.- Colloidal Colors

The development of colloidal colors in glass also depends upon controlled nucleation and growth of small metallic crystals in glass. Gold, silver and copper are most often used. Such crystals have selective absorption and reflection properties, and impart a unique "color" to the glass article. The metal to be precipitated is dissolved in the glass melt in conjunction with a reducing agent such as SnO or $Sb_2O_3$. After melting, the glass is rapidly cooled in a temperature region where the nucleation rate is high. It is then reheated to a temperature where crystal growth of the metal crystals is high. This technique allows the size and number of crystals, and therefore the color, to be controlled. Gold imparts a flaming red color and produces a deep red crystalware.

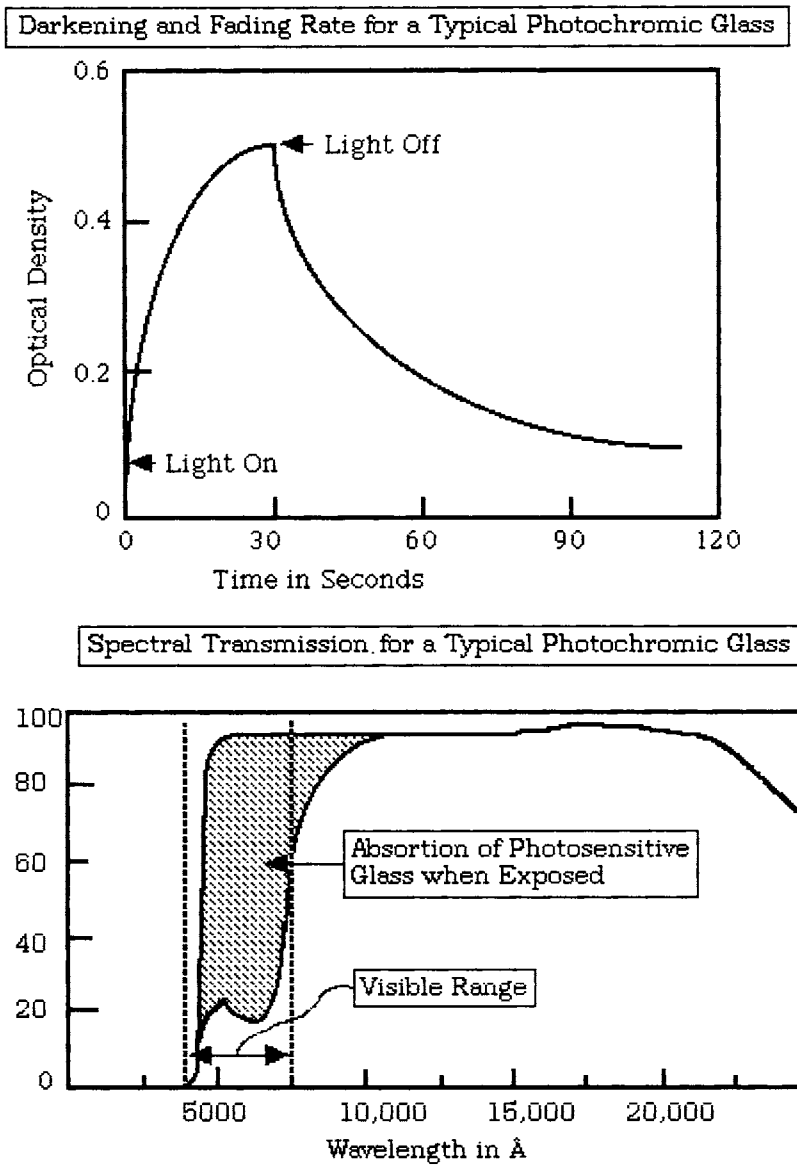
1.6.8.- Photosensitive Glasses

The reduction step required in the formation of colloidal colors is the basis for preparation of photosensitive glasses. If an optical sensitizer such as $Ce^{3+}$ is substituted for SnO or $Sb_2O_3$ in the glass formulation, colorless glasses can be made that are photosensitive. Exposure to ultraviolet radiation results in absorption by the $Ce^{3+}$ ion and the subsequent reduction of $Au^{3+}$ ions to form nuclei. These nuclei grow to colloidal size upon reheating. If a photographic negative is used during the exposure, a three-dimensional image can be formed in the glass. In a like manner, metallic nuclei can be used to induce heterogeneous nucleation of a crystalline phase in the glass itself. Photosensitive opal glass products, called FOTO-LITE™, are made by precipitation of NaF on Ag.

The use of lithium silicate glass makes possible a type of glass which can be "chemical machined". In this process, a heterogeneous crystalline phase, $Li_2SiO_3$, can be formed, which is much more soluble in 10% HF. Once the glass is exposed to ultraviolet and the crystal phase dissolved, the glass is again exposed to ultraviolet and then reheated to produce a hard, nonporous, strong ceramic. This is called FOTOCERAM™. Both are trademarks of Corning Glass Works, Elmira NY.

Another photosensitive glass was reported in 1964 (15). In this case, the clear glass changes to a uniform gray color when exposed to either ultraviolet or visible light. Such glass has found use as "sunglasses" and are sold widely. Crystallites of silver halide, about 50 Å in diameter and separated by about 500 Å, are the active centers. The analogy to a photographic film is quite clear, except that the nucleated centers are not allowed to grow in size (as they do when the photographic film is "developed"), but remain the same size while entrapped within the glassy structure. Thus, the photochromism is reversible, that is- the glass darkens and fades in response to the amount of light present.

The following diagrams illustrate both the rate at which such photochromism occurs, and the wavelengths affected:




Note that it takes about 30 seconds for the darkening effect to become maximum. As long as the light intensity remains the same, the absorption, due to photochromic centers, remains. When the light intensity dims, the absorption decreases. The transmission curve given above shows the

wavelengths affected. These include most of the visible range, making the glass almost ideal for use as reversible sunglasses.

It is also possible to use other halides such as gold, but they have not found such widespread usage as the silver halide used for the sunglasses trade.

The above discussion has centered on devitrification and properties associated with control of nucleation. It is clear that a large variety of glasses can be made having specific properties much superior to those of non-nucleated glass. Let us now examine some of the inherent properties of glass.

## **1.7.** INHERENT PROPERTIES OF GLASS

These properties are those which appear as a result of the indigenous structure of glass itself, as a usable medium for forming articles of commerce. Let us first examine the strength of glass.

### 1.7.1. - Strength of Glass

The *inherent strength* of pristine glass has been estimated to be about 4,000,000 psi. The practical strength of glass is, however, much lower. Glass itself can be considered to be a perfectly elastic material. No matter how much stress is applied, so long as the stress is not sufficient to cause fracture, the glass will return to its original shape when the stress is removed. Nevertheless, nearly all glass products, including plate glass, break under stresses less than 1% of the inherent strength. This tremendous discrepancy is believed to be due to the presence on the glass surface of a multitude of imperfections ranging from submicroscopic fissures to scuffs and scratches visible to the naked eye. Some are introduced due to manufacturing processes, while others may be due to subsequent handling. Several separate systems of flaws may be present in a single piece of glass, the total number being as many as several thousand per square inch, and most of them will be invisible. Since flaws are randomly distributed, it is a matter of chance whether a major or minor flaw happens to fall within a zone of maximum stress, and the observed breaking stress will vary accordingly. In any case, **each flaw acts as a stress concentrator** and a deep, narrow crack with

sharp apices may cause a local increase of over 1000:1. Thus, the actual stress at the apex of such a flaw may be 1,000,000 psi or more.

Glass always fails in tension or from a tension component set up by the applied load. The failure nearly always occurs at a flaw. For example, a normal glass plate may have an inherent breaking strength of 15,000 psi. Abrading the surface lowers this to about 8000 psi, while tempering raises this value to a practical limit of about 35,000 psi. It has been said that ***"we measure not the strength of glass, but the weakness of the surface".*** In the case of tempered glass plate, the increased strength most certainly is due in part to the initial softening of the surface wherein part of, if not most of, the surface flaws are eliminated before the quenching operation is begun. Yet, if abrasion (or scratches) of the tempered glass plate occurs subsequently, the glass plate can be subject to failure. Since glass is brittle, completely lacking the plasticity of metals, it is unable to relieve high local stress *except* by forming new surfaces. This leads to propagation of the original flaw or fault, and occurs almost instantaneously. It is therefore obvious that stress concentrators- holes, grooves, notches and the like should be absent whenever possible, particularly in the case of tempered glass plates.

One other factor needs to be mentioned, that of the effect of moisture. If the glass has been subjected to high moisture over a long period of time, even if it has been in storage, its surface will develop submicroscopic fissures which may become the cause of failure.

1.7.2.- Chemical Durability

All silicate glasses are subject to hydrolysis losses in water, more so in boiling water. They are also subject to loss in hot (100 °C.) hydrochloric acid, and even greater losses in hot (100 °C.) NaOH. These losses are related to the diffusivity of the cations from the interior of the amorphous structure, vis:

Relative Ratio of Diffusivity = $M^{+} >> M^{2+} > M^{3+}$

Water also dissolves the surface layer of silicate-tetrahedra slowly, Hot HCl less so and hot NaOH even more. These losses have been tabulated and compared. Although the losses have usually been rated as A, B, C, etc. or

1,2,3, we will find it more useful to use the actual weight losses experienced in terms of:

$$mg/cm^2/hr. \text{ or } gm/cm^2 / hr$$

where $cm^2$ is the actual exposed surface of the glass to water or other liquids. In general, silicate glasses are resistant to corrosion by oxidizing and reducing liquids and chemicals, including hydrocarbons, amines, mercaptans, oils and fats, and metal salt solutions. A certain amount of dissolution occurs in strong acids, strong bases and boiling water. HF is particularly corrosive because it forms fluorosilicic acid, which is soluble in water. However, silicate glasses can be made which are water- soluble, acid- soluble or base- soluble, depending upon the intended end- usage.

1.7.3. - Dielectric Strength

Glass is often used as a substrate for electronic applications because of its high dielectric strength. If a voltage is applied to a glass form, no electrical conduction will be noted. As the voltage is increased, a slight increase in conduction will be observed, up to the point where the applied voltage gradient exceeds that of the inherent dielectric strength of the glass. Since conduction of electrons is carried mainly by monovalent ions such as $Na^+$ within the glassy structure, it is easy to see that dielectric strength can be tailored to its end- usage.

Moisture and other products will deposit on the surface of glass. The result is a decreased surface resistivity. Most glasses have a surface resistivity of about $10^7$ to about $10^{16}$ $ohm/cm^2$ , depending upon the relative humidity.

1.7.4.- Hardness of Glass

The hardness of glass is intermediate between apatite (5 on the Mohs scale) and quartz (7 on the Mohs scale). Thus, it is easily scratched by most metals and many minerals including sapphire and diamond.

1.7.5.- Coefficient of Friction

The static coefficient of friction is very nearly one (1.0) on fresh formed surfaces of glass. After several hours of exposure to air, moisture or other contaminants, the result is a much decreased coefficient. Values as low as 0.15 are observed. It is for this reason that freshly formed glass surfaces are routinely overcoated to prevent "microcracks and chips" from forming on the surface of glass articles by rubbing, while the articles are being manufactured. Materials used include tin oxide, oils and waxes and sometimes antimony oxide.

1.7.6- Elasticity

Glass is in general almost perfectly elastic. No plastic flow has been observed even at rather high pressures. The Young's modulus (E) for most silicate glasses lies between about 7 and 13 x $10^6$ psi. The addition of $Ca^{2+}$ or $Be^{2+}$ ions to a glass formulation has produced compositions with Young's modulus of up to 20 million psi. Knowing Poisson's ratio, v, and E allows one to calculate other elastic properties via the following:

| | | Typical Values |
|---|---|---|
| Modulus of Rigidity: | $G = E/\{2(1+ v)\}$ | $4.1 \times 10^6$ psi |
| Bulk Modulus : | $K = E/\{3(1- 2v)\}$ | $6 \times 10^6$ psi |
| Compressibility: | $C = 1/K$ | $1.7 \times 10^{-7}$ $psi^{-1}$ |

However, these parameters are not used very often, except for applications where dimensional stability is a must.

## 1.8. SILICATE GLASS PRODUCTS CURRENTLY BEING MANUFACTURED

A number of novel uses for glass products have evolved over the past 100 years, due to new properties of glass discovered and particularly to the new methods of manufacture that have evolved during the past few years. For example, the so-called "sol-gel" method of preparing silicate glass involves the

precipitation of a gelatinous medium, which is then carefully dried and then consolidated to form the desired article of glass, with a much lower expenditure of energy.

1.8.1.- Fibers of Glass

Though glassmakers have known since ancient times that small fibers of glass could be drawn out as fine filaments, the enormous number of applications for glass fibers was not realized until early in this century. In general, there are four major uses for glass fibers at the moment, namely:

1. Fiberglass textiles

2. Tangled mats for thermal insulation

3. Mixtures with other structural materials to provide extra strength

4. Use as fiber-optics.

**FIBER - GLASS TEXTILES**

In the early 18th century, glass makers made fine fibers by drawing a thread from a heat- softened glass rod onto a spinning wheel. As a novelty, Carlo Reva of Venice wove some of this "spun-glass" into a sample of cloth. In 1713, René Reaumur submitted Reva's glass cloth to the Paris Academy of Science for inspection. An entire garment was made from woven glass and given to a Spanish princess, but the fiber was too coarse to allow the garment to be folded.

In 1908, G. von Pazsiczky developed a method for drawing several glass fibers from holes in the bottom of a refractory glass-melting chamber. In 1911, E. Pick received a patent for his technique of using centrifugal force to draw fibers through tiny holes in a rotating drum. And, during the First World War, Germany used similar methods to make fiber-glass as a substitute for asbestos insulation. By 1920, W. Schuller had found a new way to make fiberglass out of glass rods, drawing strands from a hundred such rods which had been gas or

electrically heated, then winding the strands onto a single drum. The strands were small enough, and elastic enough, to allow glass cloth to be woven. In the 1930's, the Owens-Illinois Glass Company and the Corning Glass Works combined their separate fiber-glass facilities to form Owens-Corning Fiberglass. Workers there developed mass production methods that allowed industrialization of fiber-glass to proceed during the period of 1936-1950.

To draw out a continuous single glass filament, such as for making glass yarn or optical fibers, molten glass is fed through precious-metal spinnerets having very accurate holes in their ends. About 400 such spinnerets is used in any single machine, and thin glass fibers are drawn off at a rate of several miles per minute. One piece of feed-glass about 1.9 cm. in diameter, and a meter long, produces about 156 kilometers of filament. After being drawn, the glass is usually coated with organic resins to prevent further degradation while being processed further, to form glass cloth by weaving and the products manufactured from glass cloth, including drapes for the home. Other products can include yarns, cords, braids, cloths and tapes. Although glass cloth itself is colorless, the organic resins used for coating can be dyed or pigmented. Glass fibers are very strong, but have little ductility. The thinner the fiber, the more it can bend without breaking. Fibers made from specific types of glass are used for particular applications. Low alkali lime-alumina borosilicate fibers, which have excellent dielectric and weathering properties, are used for general and electrical textiles and for reinforcing plastics, papers, rubbers and gypsum. Inexpensive soda-lime fiberglass is used for air and liquid filters. Soda-lime borosilicate fibers, with their high acid resistance, are used for corrosion protection and as mats for storage-battery retainers, as well as acid filter cloths and anode bags. The excellent weathering properties of lime-free soda borosilicate glass fibers makes them ideal for high efficiency filter papers and for light weight thermal and acoustical insulation material. Finally, high-lead silicate fiberglass, with its special x-ray opacity, is used for surgical pad strands and for x-ray protection aprons.

**FIBERGLASS INSULATION**

On the other hand, production of glass insulation demands a dense cluster of many short, fine fibers of glass. A completely different process has come into

usage. In 1929, the Hager brothers and F. Rosengarth of Britain succeeded in developing a new process for making glass wool. In this process, a stream of molten glass falls on a fire-clay disk with radial serrations. By rotating this refractory disc about a vertical axis, short thin glass fibers are thrown off tangentially, along with some large blobs of glass. Both Cie de St. Gobain of France, and Owens-Corning improved on this process, this time replacing the ceramic disc with a metal spinner pierced with thousands of holes. The vertical cylinder spins, drawing out a fiber through each hole via centrifugal force. The fibers are deflected downward, and further attenuated by a "blowing" ring. The fibers are then bonded with an organic resin, collected on a conveyor belt, and then subjected to another blower that tangles the glass fibers into a random mat.

Fibers formed by this production method range from 6 to 12 μm. in diameter and have an excellent degree of uniformity. The natural density of glass wool made this way is about 24 kg./$m^3$ and can be used at temperatures up to about 500 °C. Each strand of fiberglass, though thinner than a human hair, is still a glass rod, and so retains the properties of glass. In general, fiberglass is heat-resistant and non-combustible, making it a good substitute for asbestos. It does not rot or decay, nor does it absorb moisture. It does not conduct electricity and is resistant to ordinary weathering. Fiberglass insulation has excellent thermal properties and can be used, in conjunction with appropriate resins to construct "fiberglass" forms and shapes.

**COMPOSITE FIBERGLASS MATERIALS**

Until the 1940's, the combined cost of the resin and the fiberglass precluded major industrial development of composite materials. In 1947, it was found that the reinforcing fibers need not be so fine, and that coarser materials could be made more cheaply. This opened up new techniques such as the diamond-pattern mat and swirled-mat fabrics and plastics. What is done is to place shorter glass fibers in a patterned mat which is then used to form the final object. For example, fiberglass mats are laid down on a given form, say a boat-hull, and alternated with coats of thermosetting resin. A great number of manufactured items are sold today, including large tanks for underground burial at gasoline stations. The latter have evolved because of the resistance of

fiberglass to corrosion by gasoline aliphatic hydrocarbon fractions, and the ease of manufacture of such tanks.

In 1951, I.A. Rubinsky in the United states investigated the use of fiberglass as reinforcement for concrete, but found that fiberglass would not replace steel because of its low modulus of elasticity. However, in 1957, work in Russia determined that if the fibers were protected against the alkali in the cement, its use in the Construction Industry was quite feasible. The quality of commercially available fiberglass has improved dramatically in recent years, making fiber-glass-reinforced concrete an important building material. Such materials are now in general usage throughout the world.

**FIBER OPTICS**

A new and major usage of glass fibers has come about since 1970 in the field of information transmission. Nowadays, nearly all of the new telephone lines being installed consist of optical-fiber cables. If one forms a glass fiber, and surrounds it with a material having a refractive index **less** than that of the glass, one obtains an optical fiber capable of conducting **all** of the light which enters it.

However, there is a limit to the angle to which the light is admitted, which in turn depends upon the refractive index of the glass. Actually, this "acceptance angle" is the Brewster angle, $\Theta$ , beyond which point all of the incident radiation is reflected. The so-called "acceptance angle" is actually:

$$\theta = 1/2\,(180 - 2\Theta)$$

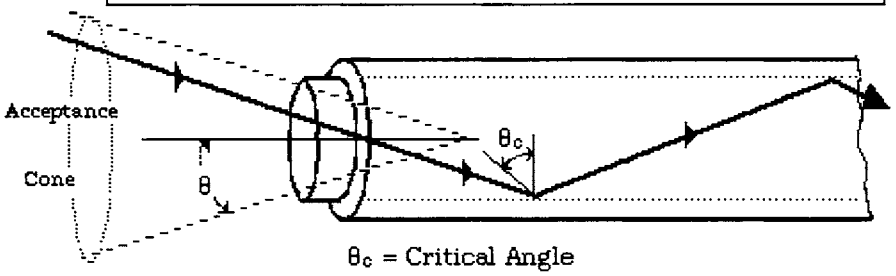
and the amount of light that will actually enter the optical fiber is:

$$NA = n_1 \sin \theta = [n_1^2 - n_2^2]^{1/2}$$

where NA is the numerical aperture, $n_1$ is the refractive index of the glass fiber, and $n_2$ is the refractive index of the material used to coat (or "clad") the fiber. This only occurs when: $n_1 > n_2$ .

What we are discussing is made evident by the following diagram:

The Front End of a Fiber Optic Showing the Angle of Acceptance, θ, and Total Internal Reflection of an Optic Ray




$\theta_c$ = Critical Angle

Here is shown the acceptance cone, the angle of acceptance, θ , and the total internal reflection of an optic ray of light. Note that θ is one-half of the angle which describes the cone. The angle of refraction in the cladding can be determined from Snell's Law, i.e.-

$$n_1 \sin \theta_1 = n_2 \sin \theta_2$$

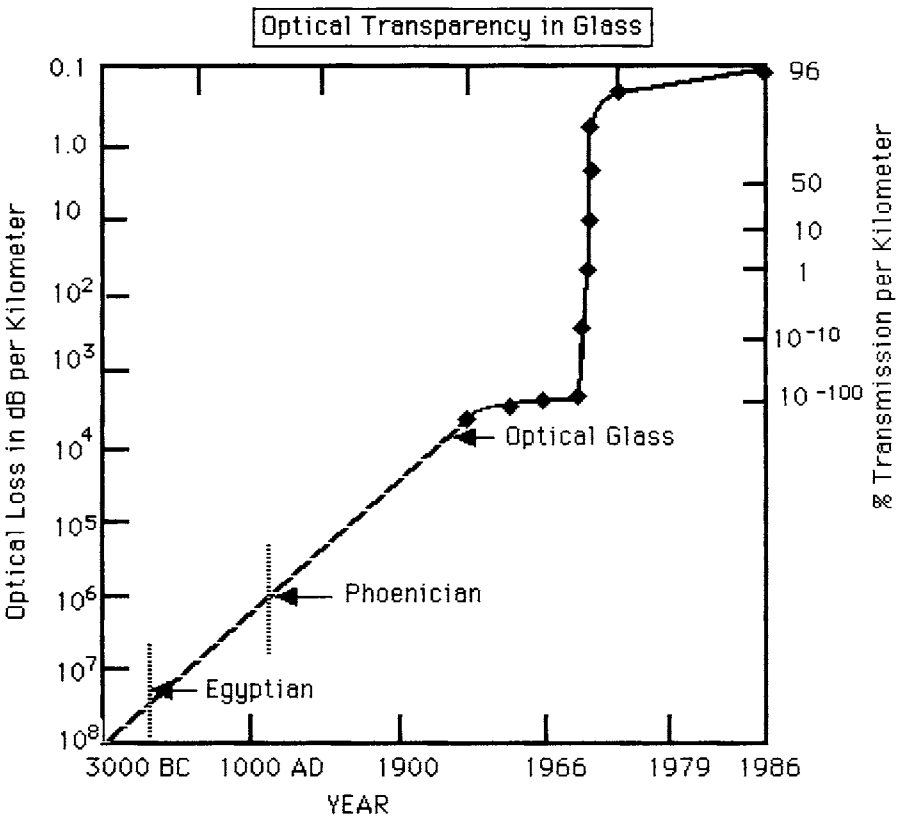
where $n_1$ is the refractive index of the core and $\theta_1$ is the acceptance angle of the core, etc. When $n_1$ is greater than $n_2$, a specific angle, called the critical angle, $\theta_c$ , can be determined, and is defined as:

$$\theta_c = \arcsin (n_2/n_1)$$

For example, the critical angle for light incident from a quartz medium having a refractive index of 1.46 and reflecting from a cladding surface having a refractive index of 1.33 is equal to 65.6 °. For incident angles less than this, propagating light does not refract into the cladding at all, but is totally reflected.

It is patent that as a light beam enters front end of a fiber, it propagates through a series of total internal reflections and emerges on the far end of the fiber. However, the reflectance at each reflection point is not exactly 100%, but some value less than this. Thus, an internal loss in the intensity of the light beam (or attenuation) occurs through any given optical fiber. Therefore, a major concern is the transparency of glass for this application. For short path lengths in glass, this poses little problem. However, for lengths greater than about 100 meters, the attenuation becomes serious. Scientists and

technicians have continually improved the transparency of silicate glass over the centuries until about 1966 when attenuation became important for optical fibers. Today, such fibers are some 100 orders of magnitude more transparent than they were in 1966. This is shown in the following diagram, viz-




In 1966 when the first work was being carried out on optical fibers, because the path lengths became lengthy, the method of measurement of attenuation of light was specified in terms of decibels, i.e.- dB, similar to that used for sound waves. This is actually an attenuation in steps of ten
where $10^1$ = 1.0 dB, $10^2$ = 2.0 dB, etc. Optical loss is then specified as dB/km. , as shown in the diagram. It is clear that the transparency of glass fibers has improved by at least 100 orders of magnitude since the first optical fibers were made.

The idea of transmitting light through a long narrow cylinder of glass originated as long ago as 1854 when British physicist John Tyndall demonstrated that light could be guided within a jet of water. The first quantitative experimental investigations of light communications were made in 1920, but it was not until the invention of the laser that an adequate light source became available.

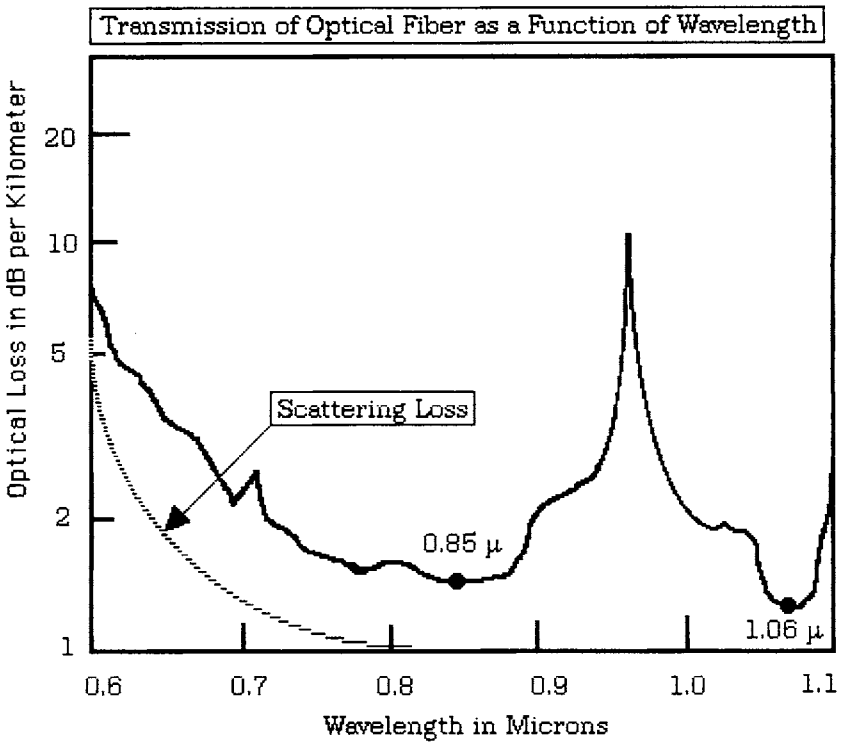
Today, the light source is usually infrared light from a semi-conductor laser. Flashing off and on millions of times per second, the laser sends bundles of light through the fibers, similar to the 0's and 1's of computer language. The greatest attraction of fiber optic systems is their carrying capacity, or bandwidth, as it is sometimes called. Bandwidth is the range of frequencies that a signal can be flashed on and off. In other words, the bandwidth is the number of pulses, in megabits or even gigabits per second, that the optical fiber can carry. With fiber optics, two or even three pulsed frequencies can be sent simultaneously. This is called "multiplexing". This increased bandwidth leads to high volume, high speed information transfer. The reason that semi-conductor lasers are used is two-fold:

1) they can be synchronized rather easily to existing audio sources.

2) they have wavelength emissions that correlate well to the glass core transmission.

A typical transmission of a silica fiber is shown in the following diagram, given on the next page.

Note that the loss reaches a low value at about 0.85 μ and 1.06 μ. The former corresponds to an output wavelength emitted by a GaAlAs laser, while the latter is that of a YAG:Nd laser. The large absorption peak at about 0.96 μ is due to $OH^-$ ions contained in the glass. A comparison of the measured transmission loss with the intrinsic scattering loss shows that the fiber adds very little excess loss between 0.5 and 0.7 μ. This is an indication of the purity of the glass and the perfection of the waveguide.




There are three (3) types of fibers currently being used. These are:

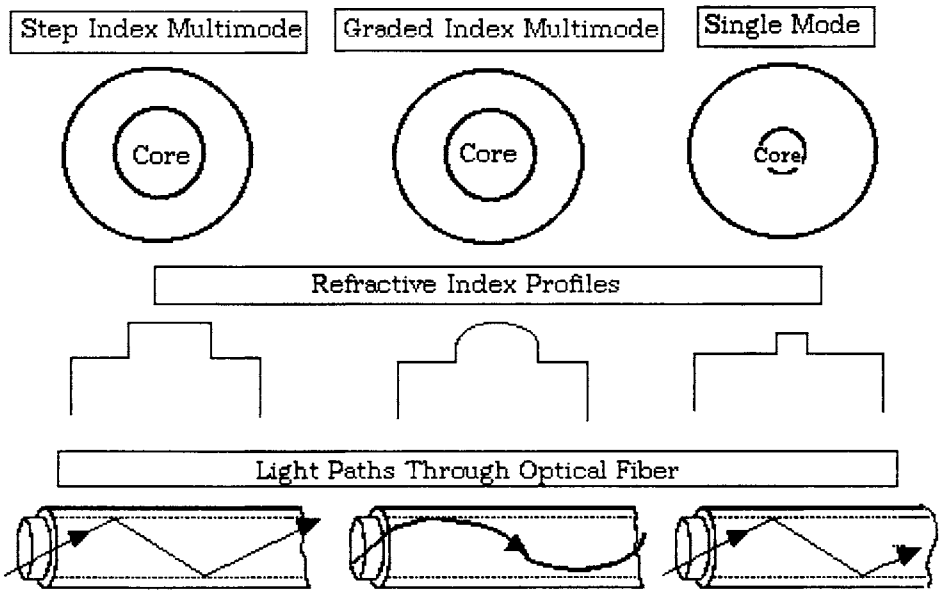
1) Step-index multimode.

2) Graded- index multimode

3) Single- mode fibers.

These are illustrated in the following diagram, as given on the next page.

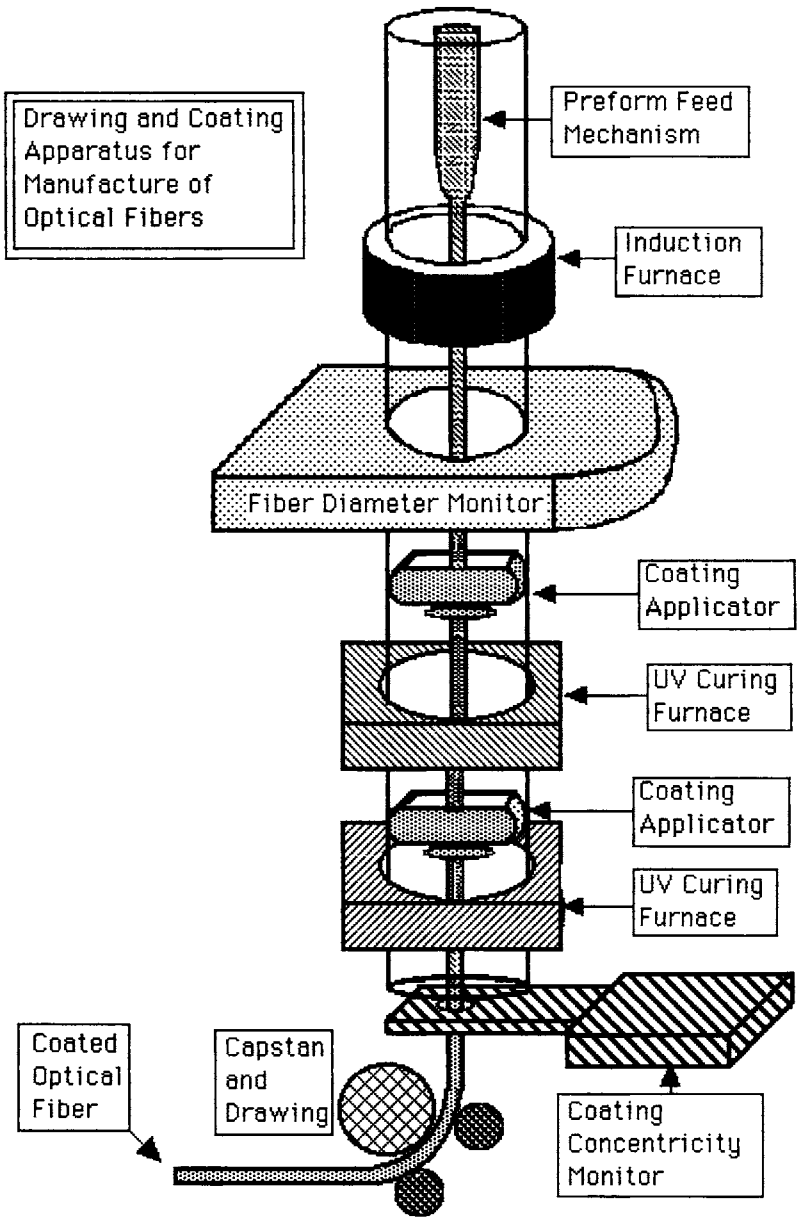
The major difference shown there is that the graded index fiber consists of a core in which the refractive index varies in a continuous manner, the middle of the core being of higher refractive index than the outer parts of the fiber. The method of manufacture is essentially the same as that described above for preparing "chemically-strengthened" tempered glass. The surface of the glass fiber is immersed in a molten salt bath where a smaller ion such as $Li^+$ is




introduced, causing a change in the refractive index as well. This results in a "graded-index" glass, where the inner part of the core has a higher index than the outer layers. In some cases, layers of glass having differing indexes are formed, and the whole is then softened so that the layers mix together. The step-index multimode fiber is the same as we described above where a cladding of lower refractive index is employed. As of 1991, the most common fiber used has been a pure silica ($SiO_2$), doped with $TiO_2$, $P_2O_5$ , or $Al_2O_3$ to increase the refractive index of the silica core.

As we stated, the outer cladding of a multi-mode fiber can be of a glass having an expansion coefficient close to that of the core. Alternatively, a coating can be placed on the core as it is being formed. The latter process has several advantages, the main one being that pristine surface of the fiber is immediately covered so that chemical interactions with impurities and moisture of the air are circumvented.

An apparatus designed to manufacture such glass optical fibers is shown in the following diagram, as given on the next page. Note that this apparatus can be used for both step-graded and graded index fibers as well.




Control of both the drawing processes and the coating has a profound effect on the quality of glass fibers used for optical communications. A process for coating fibers immediately after the forming process was described in 1980 (16) in which a low modulus polymer coating was used to protect the freshly

formed fiber surface from abrasion or other damage. Using a laser forward-scattering monitor, researchers were able to obtain fibers with diameters exhibiting standard deviations of < 0.25%. An in-line temperature controlled coating applicator, resembling a magnet-wire-coating applicator, and a coating concentricity monitor enabled a protective layer to be applied that could be cured quickly.

Since the fibers need to be protected as soon as they are formed, the types of coating materials, the techniques for applying them, and the curing methods are severely limited. As a practicality, any system that requires removal of solvents and/or reaction by-products will be too slow to permit commercial production of coated fibers. Additional restrictions are that the application of the coating must not damage the surface of the fiber, and the film must be solid by the time it reaches the capstan that guides the fiber onto spools or drums.

It is important that the modulus of the coating be low, because it must withstand stretching and bending after the fiber is coated. Many of the low-modulus thermoplastics are viscous, and they remain hot (and thus soft) too long for high- speed operations.

Among the low-modulus thermosetting plastics, urethane-acrylate and epoxy-acrylate polymers, cured by exposure to ultraviolet light, have been used successfully. Certain acrylics and silicones are also used.

Typical parameters of coating include:

1. Rate of draw = 5 to 10 meters per second

2. Low absorption of water = 0.3% in 21 days immersion

3. Tensile strength of coating = 500 psi.

4. Refractive index = 1.42

5. Glass transition = - 126 °C.

6. Ultimate elongation = 145%

7. Young's modulus (psi @ 2.5%) = 140 - 390 @ 125 °C; 360 - 1240 @ - 60 °C.

The glass transition temperature for these thermoplastics is the same as we have already described, i.e. the temperature at which the plastic coating changes from a soft elastomer to a hard glassy state.

Present uses of optical fibers include worldwide telecommunication cables, analytical instruments, military hardware, process controls and computer links.

1.8.2.- The Sol-Gel Process

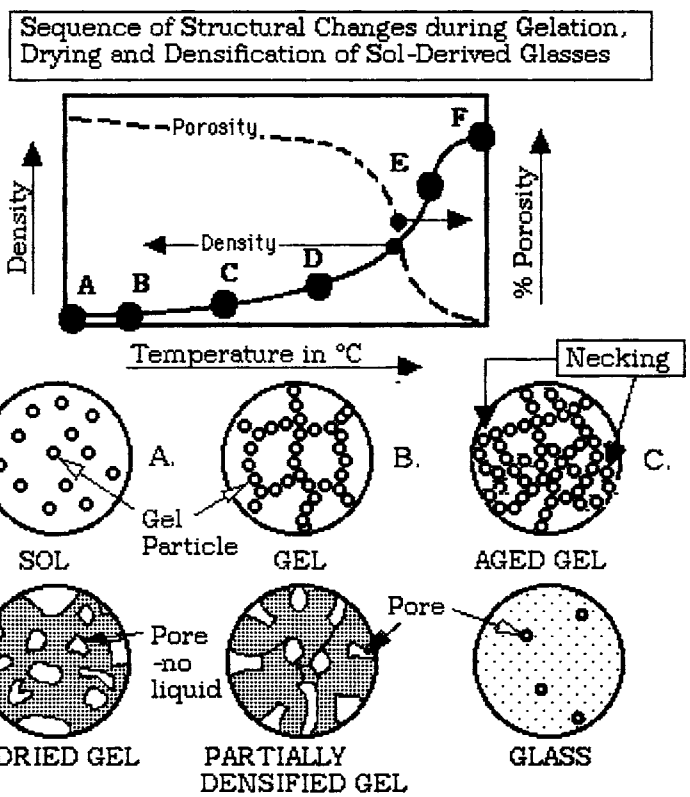
During the 4000 year history of silicate glass technology, materials that could be added to make glass were limited to salts , minerals and oxides. It is only in the past 40 years that a new method, called the "Sol-Gel Process", has evolved in which amorphous silicates and oxides can be prepared at room temperature via solution chemistry.

There are essentially two different kinds of sol-gel technology. The first, or "colloidal" method, involves the dispersion of colloidal particles to form a sol and then the destabilization of the sol to produce a gel (17). The second method involves the polymerization of organometallic compounds such as alkoxides to produce a gel with a continuous network (18). It is the latter that has received the most attention, although if one wishes to add metallic ions, including Na, Ca, Al and others, to a silicate sol, one must do so by concurrently forming a colloidal gel of hydroxides.

In the polymerization method, a solution of alkoxides of Si, Al, Ti, and other elements are hydrolyzed and condensation polymerization is caused to take place. For example, tetra-ethyl silicate is converted into a silica $[(SiO_2)_n]$ glass via a network of Si- 0 chains and rings. Such a reaction is illustrated as follows:

$$(RO)_4Si + 4\ H_2O \rightarrow 4\ EtOH + Si(OH)_4$$

where R is usually either Me, Et or Isoprop, i.e.: $CH_3$- , $C_2H_5$ - or $C_3H_7$ - . It is the silicic acid, i.e.- $Si(OH)_4$, which forms the base for polymerization. This reaction can be catalyzed by either acid or base. Thin films of the same material can also be made using a dip-coating process. As the polymerization takes place in solution, the monomer solution gradually thickens and becomes a gel. On drying, the gel slowly shrinks and, when dry, becomes a rigid, amorphous, porous mass called a xerogel. The rate at which the gel dries out and collapses on the substrate has a major effect on the porosity, which in turn affects the mechanical, optical and electronic properties of these amorphous oxide glasses. Controlling the porosity has definitive effect on the final properties of the glass so-produced. This is made more evident by the following diagram, where various stages in formation of a xerogel are shown:




The steps in preparing a gel- derived glass, as shown in the above diagram include:

A. Forming the Sol

B. Gel Formation

C. Aging the Gel

D. Drying the Gel

E. Densifiying the Gel

F. Glass Formation

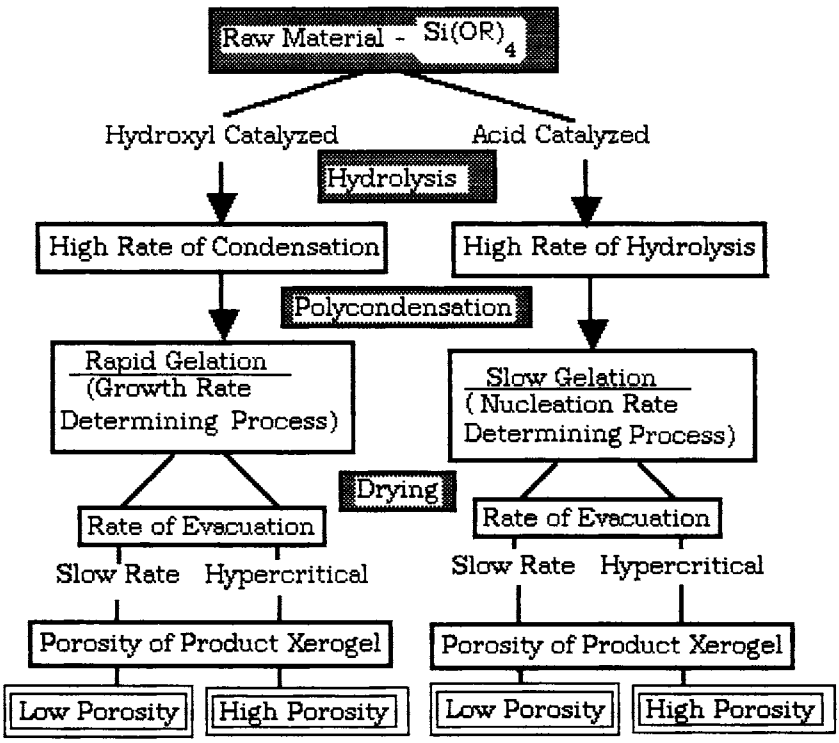
Note that a sol is first formed as individual particles which then coalesce to entrap water to form the gel. As the gel ages, it condenses and finally becomes dried to form a semi-solid (dried-gel). Upon further aging and drying , a partially densified gel results, which is the xerogel. Firing at an elevated temperature then produces the desired glass (but usually not without pores). Note that the porosity is influenced by a host of processing factors, including the aging conditions and the relative rates of condensation and drying. It is thus possible to systematically vary the pore sizes in xerogels from less than 0.4 nanometers to greater than 3.0 nanometers. Note that the Figure given above shows how each separate stage affects both the **density** and the **porosity** of the product xerogel.

The characteristics of xerogels of a particular composition are related to factors that affect the rate of hydrolysis and polycondensation reactions. So far, pH, gelation temperature, aging time and temperature, and concentration and molar ratio of water to the metal alkoxide have been identified as the most important parameters. These factors are summarized in the following diagram, where R can be any alkyl group such as methyl or ethyl, as given on the next page.

These stages apply not only to tetraethyl silicates being hydrolyzed, but to metal alkoxides as well. In the diagram given on the next page, five (5) stages are shown.

These are:

1. Raw material stage (monomer)
2. Hydrolysis stage
3. Polycondensation stage (rate of gelation)
4. Drying stage (rate of removal of water from gel)
5. Xerogel stage (dried gel product)




In general, hydroxyl (base) catalysis produces a lower degree of porosity in the xerogel than the acid-catalyzed material. The pores of sol-gel glasses are significant not only for the physical attributes they confer, but for what they can contain. Dopants can be added to the alkoxide mixture undergoing hydrolysis and polymerization. The most recent advancement has been the addition of organic compounds which are contained within the disordered

channels and pores of the glass. Applications are foreseen in optics, electroöptics, sensors, catalysts, biosyntheses, and others (19).

It is well established (20) that the presence of acid $\{(H_3O)^+\}$ in the solution increases the rate of the hydrolysis reaction, whereas hydroxyl ($OH^-$) ions increase the polycondensation reactions. Depending upon the experimental conditions of solvent extraction, either powders, large grains or monoliths can be obtained.

## THE GELATION AND CONDENSATION PROCESSES

The alkoxides mostly employed include: $(RO)_4Si$, $(RO)_4Ti$, $(RO)_3B$, and $(RO)_4Al$, where R is usually Et- or Me-. Prassas and Hench (21) studied the gelation, condensation and xerogel-glass conversions of silica-based compositions, using infra-red techniques to determine rates of gelation and condensation. Whereas $(EtO)_4Si$ (tetraethyl silicate = TES) is rather insoluble in water, $(MeO)_4Si$ (tetramethyl silicate = TMS) reacts rapidly to form both $Si(OH)_4$ and MeOH. Therefore, methyl or ethyl alcohol is often used to increase solubility in water. If the chemical process is carefully controlled (pH, ratio of concentration of $(RO)_4Si$ to water, temperature, etc.), precipitation can be avoided and homogeneous gelation takes place.

As stated before, it is the $Si(OH)_4$ which acts as a base for the polymerization-condensation reactions taking place. The same is true for the products from the titanium-based, aluminum-based and boron-based alkoxides as well. It is also easy to see that the **ratio of water** to alkoxide present is the major factor which controls the gelation process. Too low a water/alkoxide ratio results in a sol. A correct proportion will result in a monolithic gel and xerogel. Note also that the water added can be pH-controlled so as to control the rate of gelation and polycondensation.

There is no incubation time for the polycondensation reaction. This takes place between a silanol (and/or titanol, etc.) and an alkoxide group. The molecular complexity is intricate and not thoroughly understood, primarily because it depends upon several factors, including that of the ratio of alcohol and water present, pH, temperature and total concentration of the alkoxides

present. Nevertheless, from the infra-red data observed (21), linear and cyclic polymers are known to result.

Crosslinking agents such as ethylene glycol have also been used concurrently to control the viscosity of the polymer solution. Such agents prevent premature hydrolysis of the alkoxides present. This also has the advantage of controlling the homogeneity of the gel so-produced. These agents react (22) with the alkoxides to form glycolate intermediates so as to control the stability and rheological properties of the gel being produced.

**DRYING THE GEL**

The gel consists of two phases, the network solid phase and the connected pores filled with liquid phase. Initially, the surface is covered with the liquid phase. As it drys, the liquid tends to impose a capillary force on the solid network (due to surface tension forces) and the solid surface is exposed. Because the network is compliant, the gel shrinks under capillary force as the liquid evaporates. The gel thus becomes stiffer because the solid network is becoming more tightly bound. When the gel is too stiff to contract under capillary force, shrinkage stops and the meniscus of the liquid phase in the bigger pores begin to recede into the interior of the gel. Note that the menisci of the bigger pores have a larger radius of curvature and hence a lower capillary force. Thus, the rate of evaporation is greater in large pores than in smaller ones. Additionally, liquid will flow back into smaller pores, if they are connected to the larger pores, because of the greater force of capillarity in the small ones. When the walls of the bigger pores are dry, the interior surface does not shrink further, even though the region around the smaller pores shrinks under surface tension. This causes a stress concentration at the bottom of the bigger pores. The bigger pores thus act as a microscopic flaw, and when the stress concentration is great enough, a macroscopic crack will develop. It is for these reasons that gels with different pore sizes are easily cracked during drying. Indeed, it has been shown (22) that only gel films with a thickness of less than 1.0 μ can be dried on a substrate without cracking.

Since the cracking of monoliths and films is caused by capillary forces imposed by both the liquid phase present, and the variation in pore sizes,

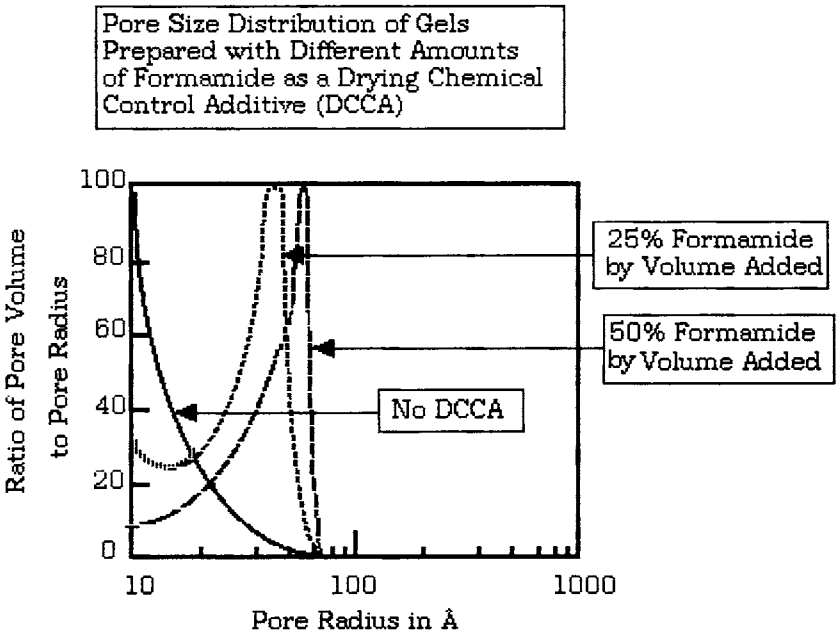
reduction of the surface tension of the liquid and formation of uniform pore sizes would be expected have a major effect upon the drying and aging of monolithic gels and xerogels. Two methods are currently being practised: 1) the use of drying control chemical additives (DCCA), and 2) hypercritical drying. By the use of these two techniques, it is possible to optimize gelation, aging and drying of gels to produce fully dried monolithic xerogels rapidly and routinely.

In hypercritical drying, the monoliths are dried by heating the gel under pressure to a point above the critical temperature and pressure of the solvent. Thus, no capillary force is present. The hypercritically formed xerogel has the same volume as the gel from which it was made. If it has been prepared carefully so that the pores are nearly the same size, the xerogel monolith can then be fired to form the glass article without fear of pores or cracking in the final glass product.

A surfactant acts to reduce the capillary force of the liquid phase so that its use will reduce the stress concentration in the solid phase during the drying stage. The same may be said when DCCA's are employed. Several kinds of chemicals have been used as a DCCA, including formamide and oxalic acid. Both of these produce more uniform pores than can be obtained otherwise, which helps to increase the permeability of the gel.

Both of these DCCA reagents can be used in either an acidic or basic medium. In a basic medium, formamide slows down the hydrolysis reaction by some five times (23). In contrast, formamide in an acidic medium results in a 3.5 times faster rate of hydrolysis. Additionally, its use leads to a larger pore distribution, but with a narrow distribution of sizes. Thus, the gel network has substantially larger necks, greater strength, and is more capable of resisting drying stresses.

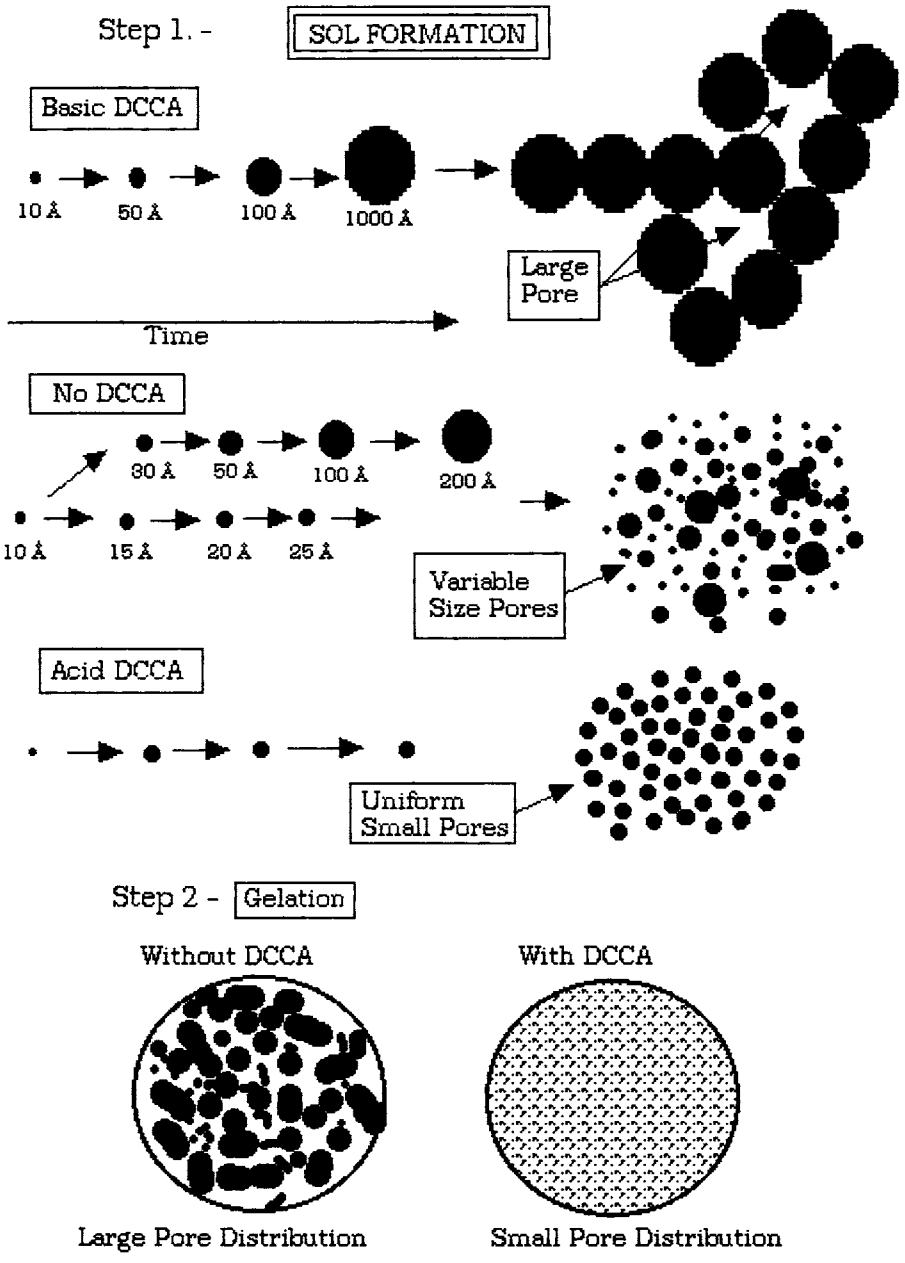
The following shows a representative pore distribution obtainable with formamide, viz-



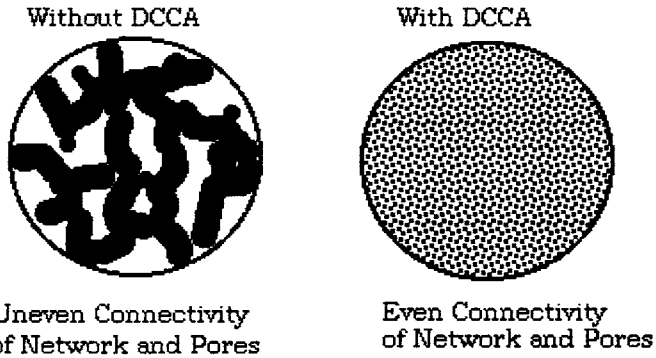

Use of oxalic acid as a DCCA also controls the size and shape of the pore distribution level. Either DCCA. i.e.- formamide or oxalic acid, greatly decreases the breadth of pore distribution which decreases the magnitude of capillary stresses during drying.

It is clear that the use of DCCA's in the sol-stage affects each of the succeeding stages. Addition of a basic DCCA such as formamide produces a large sol-gel network with uniformly larger pores. An acidic DCCA such as oxalic acid results in a somewhat smaller scale network after gelation, but also with a narrow distribution of pore sizes.

What we are addressing is illustrated in the following diagram, where the three stages of the gel formation are shown, viz-


Step 1. -
SOL FORMATION
Basic DCCA
10 Å
50 Å
100 Å
1000 Å
Large Pore
Time
No DCCA
30 Å
50 Å
100 Å
200 Å
10 Å
15 Å
20 Å
25 Å
Variable Size Pores
Acid DCCA
Uniform Small Pores
Step 2 - Gelation
Without DCCA
With DCCA
Large Pore Distribution
Small Pore Distribution

Step 3 - Aging of the Gel

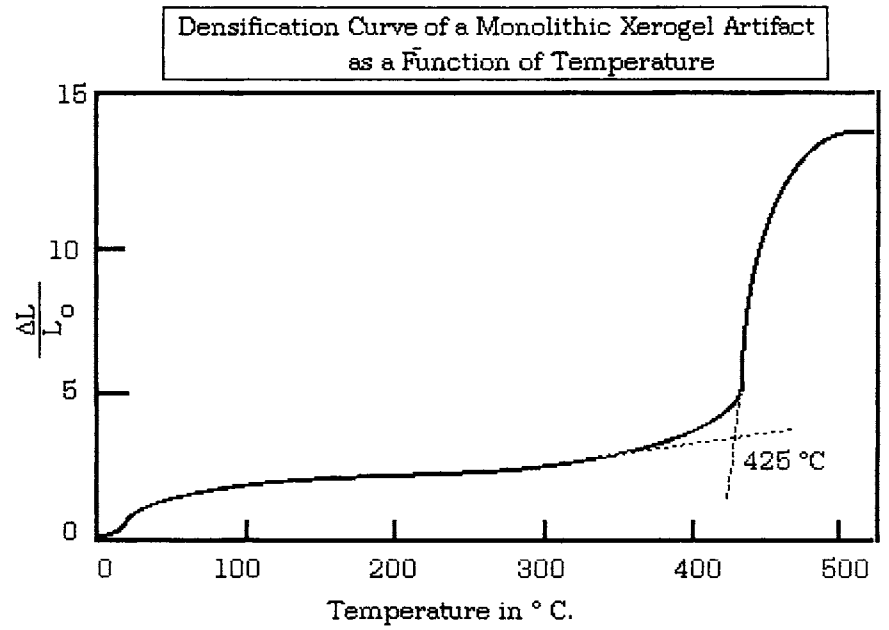


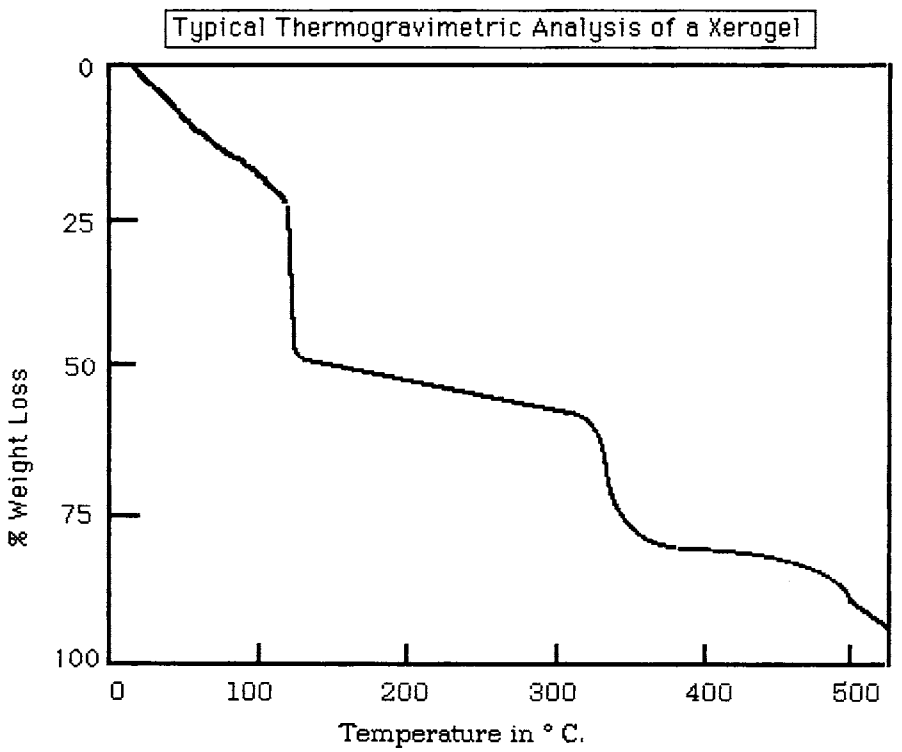

Thus, either basic or acidic DCCA's can minimize differential drying stresses by minimizing differential rates of evaporation and ensuring a uniform thickness of the solid network which must resist the drying stress.It should be clear, then, that the use of DCCA's in sol-gel technology represents a major achievement in glass science, and the ability to prepare monolithic glass articles.

**THE GEL TO GLASS CONVERSION**

Successful conversion of gel monoliths to glass depends upon knowledge of the phenomena that lead to densification, and the avoidance of crystallization. It has been shown (21) that there is a characteristic temperature at the beginning of densification, called $T_{bd}$ . Estimation of $T_{bd}$ can be made by dilatometric means. This is shown in the diagram given on the next page.

Note that $T_{bd}$ in this case is about 425 °C. Sintering to form glass appears to involve a viscous flow mechanism. An abrupt change in textural properties above $T_{bd}$ usually is observed. Thus, the original textural characteristics of a given xerogel has a major effect on its behavior during sintering. For example, xerogels with the same chemical composition, but with variations of 3- 25 times in their specific surface areas, exhibit marked differences in their sintering behavior. A xerogel with a low surface area of, say, 9.0 $M^2$/gm could not be densified to form an amorphous product. A xerogel with a high surface area of 355 $m^2$/gm densified easily (21). Thus, the firing process is strongly dependent on the xerogel microstructure, which is determined by conditions of gelation, aging and drying.


Densification Curve of a Monolithic Xerogel Artifact as a Function of Temperature
15
10
5
0
ΔL/L₀
425 °C
0
100
200
300
400
500
Temperature in ° C.


Typical Thermogravimetric Analysis of a Xerogel
0
25
50
75
100
% Weight Loss
0
100
200
300
400
500
Temperature in ° C.

Thermogravimetric analysis can also be applied to identify some of the processes taking place. A diagram illustating this aspect is also given on the previous page, and may be regarded as representative of the weight changes which occur.

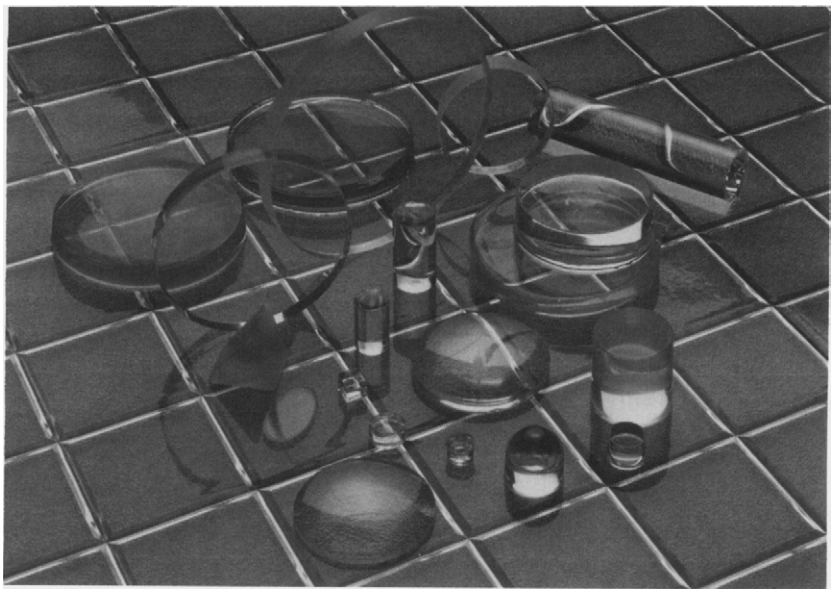
Up to about 150 °C, the xerogel continues to lose weight by evaporation of physically adsorbed water and solvent. At 150 °C., pyrolysis of the organic residues begins and continues to about 400 °C. From 400 - 600 °C., the tiny pores collapse and the article is densified. This continues up to about 800 °C, by a viscous flow sintering mechanism. In this range, the large pores collapse and a dense amorphous product results. The resulting product is identical to that made by conventional glassmaking processes.

Indeed, it is now possible to produce 100 % pure silica that has been poured into molds of desired shapes and hardened, not ground down and polished as in conventional glass technology. As a result, optical parts can be molded to exacting dimensions.

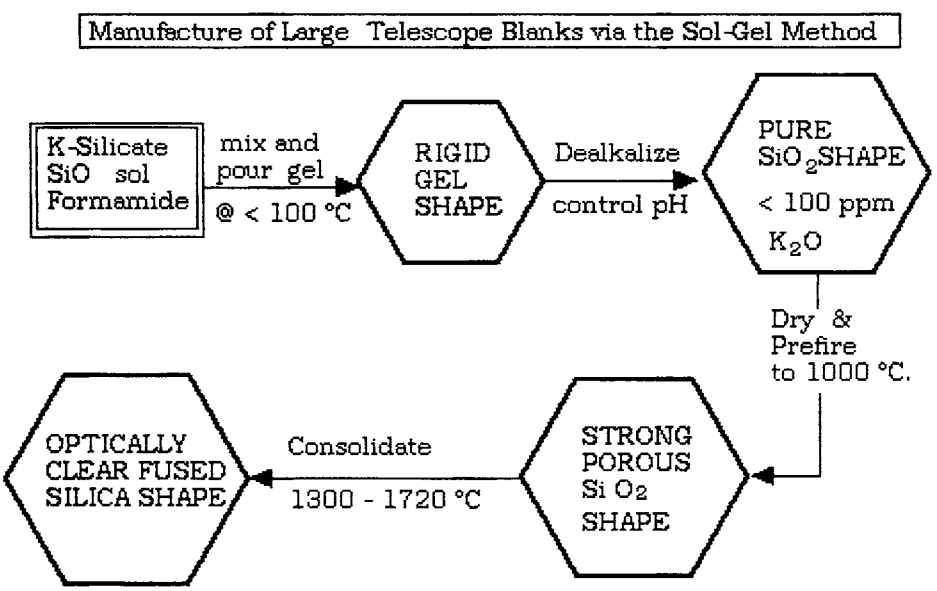
Geltech, Inc., located in Alachua, Florida 32615 uses proprietary sol-gel technology to custom-manufacture high-purity silica lenses and porous glass. As shown in the following photograph, given on the next page, they are available in various shapes and sizes, up to 40 mm. in diameter.

Also pictured are flanged lenses for easy positioning and alignment, as well as a porous silica glass which presents unique, fully interconnected and uniform porosity. this can be used as a single material, or as a basis for doping to create new composites. Lenses are available in any combination of plano, convex, and concave surfaces, including aspherical lenses, meniscus lenses and prisms.

Another commercial use of the sol-gel technology has been the preparation of lead-glass crystal (30% PbO). Aqueous $Pb(NO_3)_2$ solution is combined with potassium silicate (water-glass) solution to form a gel, which is then sintered @ 700 °C. , and then melted @ 1200 °C. A considerable savings in energy has resulted, in addition to a marked improvement in handling safety and product quality (24).



Still another use has resulted, that of manufacture of large mirror blanks for telescopes by the sol-gel technique. In this case, the glass composition required is that of fused silica or "ultra-low expansion" titanium silicate glass. The process steps (25) include:



In this process, each mirror segment is cast directly in the gel-form into its final configuration, and then processed to form the final structure. Physical properties of "gel-glass for reflective optics" was entirely equal to that of Code #7940 (Corning Glass Works, Elmira, NY) usually employed.

1.8.3.- Architectural Glass

By architectural glass, we mean panels of glass used in the construction of buildings and homes. The use of glass as windows to admit light dates back to Roman times, about 2500 years ago. Originally, man lived in caves and other natural structures. Later, rude dwellings were built from branches tied together and perhaps covered with mud. Or, they might be formed from animal-skins tied together over a framework of branches. The only inside light was from the hole at the top of the structure which allowed smoke from a fire to dissipate. More sophisticated structures began to appear near to the end of the New Stone Age, about 6000 years ago. At first, a window was merely an opening to provide light and air in a dwelling. Only crude shutters and lattices covered the first windows. Later, linen, oiled paper, and sometimes mica or gypsum were used for window panes, in addition to wooden shutters.

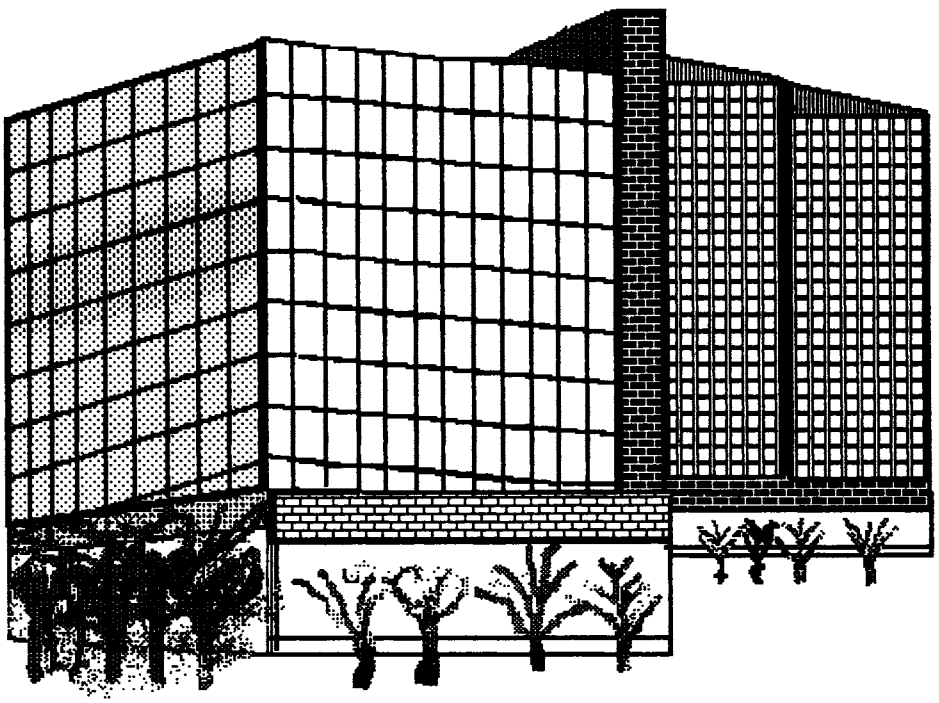
So-called "City-States" were established about 5000 years ago where people built complicated and fortified structures for mutual protection. Most walls were as much as 30 feet thick and were slanted from bottom to top to compensate for the poor strength of the sun-dried mud bricks used in their construction. Windows were an impossible luxury. Approximately 4000 years ago, the peoples of the Mediterranean area developed tombs and temples built of stone blocks. The great temples and pyramids, built about 3500 years ago, are fine examples of stone construction. However, windows were again an impossibility. In Egypt, houses were made largely of wood, sun-dried brick and mud plaster, with openings as windows. The hot climate dictated use of shutters, but not closure of the windows. Walls of buildings of the Babylonian and Assyrian era, constructed of clay and straw bricks, also had to be 30-40 feet thick in order to carry weight and not to crumble when wet. Long, narrow rooms were the rule and doors were narrow. Again, ventilation and internal lighting was accomplished by holes in the roof and torches hung on the walls. Windows were virtually unknown.

It was the use of bricks in Babylonian and Assyrian buildings that made possible the use of the arch and the vault. The Minoan culture on the island of Crete used the arch to support wall construction and the column to support the roof. Their buildings consisted of courts, surrounded by rows of columns, and had guarded gateways. Because of the warm climate, windows were not needed. The buildings were characterized by low, wide arches, thick walls, heavy roof supports and virtually no windows. This architecture was carried over into the Greek and Roman cultures, each of whom made contributions. Following the fall of Rome in 476 AD, Romanesque style buildings began to appear in Europe in the 900's, using the ribbed vault and pointed arch.

Houses then became more livable, with somewhat larger windows. However, very large windows were little used, except in the churches. In this case, a framework of light stone bars divided a large window into smaller areas so that colored or "stained" glass panes could be more easily supported. Usually, this took the form of tall narrow arched divisions below, with circles, cusps and other shapes cut into the stone filling the upper part of the window. When the great Gothic cathedrals of Europe were built in the Middle Ages, their beautiful stained-glass windows became famous. Because of the great difficulty in obtaining large flat pieces of stone, small panes were later fastened together by canes of lead metal to form a larger network. Such "windows" persist even today as "Stained-Glass". By the 1200's, small-paned glass windows began to be used and were common from the 1500's onward. In the present era, homes and buildings are planned so that windows will admit as much light as possible. Sometimes, walls of glass-blocks are used. Large picture-windows have become the norm. The disadvantage of having many large windows in a building or home is that they permit a great amount of heat to be lost during cold weather. This has led to "double-glazed" windows, that is, two glass panels set together, but separated by an air-space, in a single pane.

Today, in the 1990's, an ever increasing number of buildings, whether new or old ones requiring renovation, are being given an easy-care glass facade all around. The entire facade of the building is covered by sun-resistant glass sheets and color-matched parapets which are attached to the structural mass by means of a virtually invisible steel or aluminum support. Glass can also be adapted to other facade elements such as polished marble, granite, or other

decorative materials, producing buildings with a légère look and timeless elegance. Depending upon a building's function and construction, there are different facade systems available. Cold facades consist of glass sheets, normally toughened glass with rear ventilation, which are mounted at least 2 cm. away from the actual parapet. In the case of warm facades, the glass panes are fused onto a parapet without any air gap, by means of a heat insulating sheet and a steam barrier which faces inward. These elements form a wall and also protect the interior from climatic influences and heat. In waste air facades, the glazing consists of an external glass unit and another glass sheet attached from the inside at a distance of at least 15-20 cm. The volume between the panes is used to discharge waste air from the building and to heat a new supply of air. Another method is the "second-skin facade" where the facade is made primarily of sun-resistant insulating glass. Such a building can be seen in the following drawing wherein such glass panels are incorporated. Note that the entire external surface of the building surface is covered except for the columns.



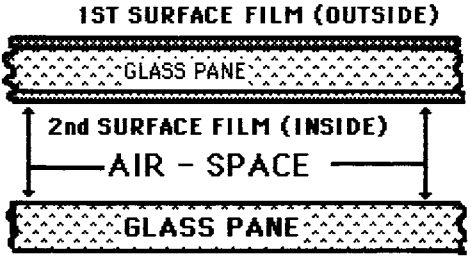
The glass surrounds the building like a secondary skin, also covering glazed parapet glass panes. Since the sun-resistant glass in front absorbs or reflects the sun's rays and the residual heat in the air gap is released to the glass in front of the facade, up to 80% of the insulating solar energy can be kept out, reducing the overall energy transmission (g-value) to 20%. This type of construction is primarily ideal for fully-air-conditioned buildings where sun protection is absolutely essential. It also can be assembled in front of existing facades of buildings, lending an entirely new appearance. By using colored or reflecting glass, the old facade is no longer visible but the view from the inside is not impaired.

Such construction has occurred in much of the United States and Europe because of the nature of so-called "solar-windows". There are two types of solar-windows, "passive" and "active". We shall address passive solar-windows first.

**Passive Solar-Windows**

In the early 1970's, costs of heating buildings were low, due primarily to the low price of heating oil. Since that time, costs have risen sharply, and impetus to reduce such costs have also greatly increased. Because of this, the numbers of solar-windows installed in buildings have risen dramatically. Such windows function to admit certain parts of the visible spectrum, while reflecting other parts, including the near infra-red part of the spectrum. In this way, heat **inside** the building is retained in winter. In summer, the heat of the Sun is reflected **outside**, thereby keeping the building cooler and reducing costs of air-conditioning. Although several glass manufacturers supply solar-windows, we will describe in detail those supplied by PPG Industries, Pittsburgh, Pa. which are marketed as SOLARCOOL BRONZE™ reflective windows. This name was chosen because of the reflective color one sees when the windows are in place. A wide range of reflective glass windows have become available for sun protection in a wide variety of colors, as described below.

The construction of such windows involves two plate glass panes, separated by an air-space. A layer of transition-metal oxides is applied to one surface of one of the glass panes, as shown in the following diagram:




The film can be on the outside of the glass pane or the inside. Usually, only one side is coated. Note that the window is "double-glazed" to ensure that heat losses do not occur when the window is installed in place on the building. The film functions to admit certain parts of the solar light spectrum and reflect others, so as to aid in climate control within the building.

The FILM is applied to the hot glass ribbon as it emerges from the "float-glass" furnace, using a pyrolytic method. This means that a mixture of the desired components is sprayed on the hot glass surface, where it pyrolyzes to form a uniform film. In this case, a mixture of transition-metal oxides is formed. This oxide film, once formed, is thermally stable and does not fade in bright sunlight, including Equatorial light-intensities. A typical chemical composition is:

**Chrome** - i.e.: $Cr_2 O_3$

**Cobalt oxides** - typically three valence states
i.e.: CoO, $Co_2O_3$ and $CoO_2$.

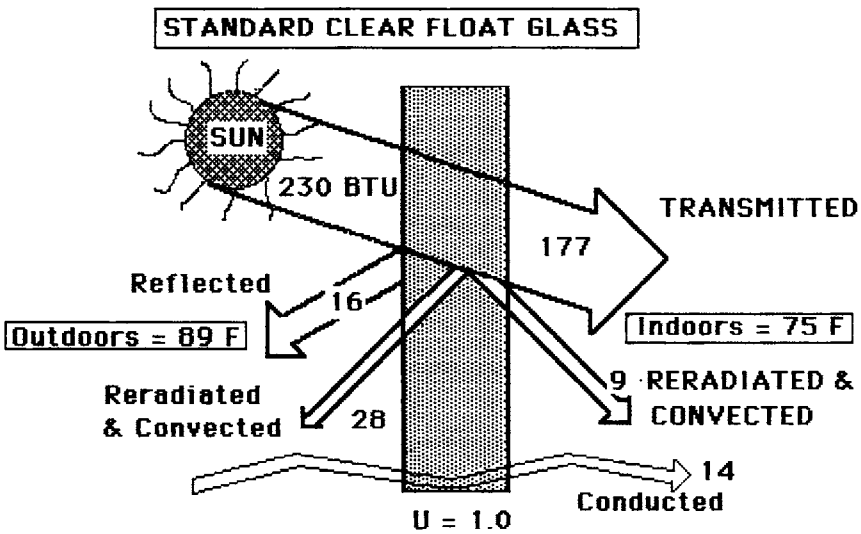
**Small amount of iron oxide (< 5%)**

The usual method involves spraying an ethanolic solution directly on the glass while it is still in the furnace. Such a solution can be easily controlled as to specific ratios of components and to total amount of components per unit volume. When sprayed on a hot glass surface, the ethanolate ignites and burns off, leaving a uniform dense layer of intimately mixed oxides as a film.

The Oxide-Film transmits only a part of the incident radiation from the Sun. The requirements for such a film are:

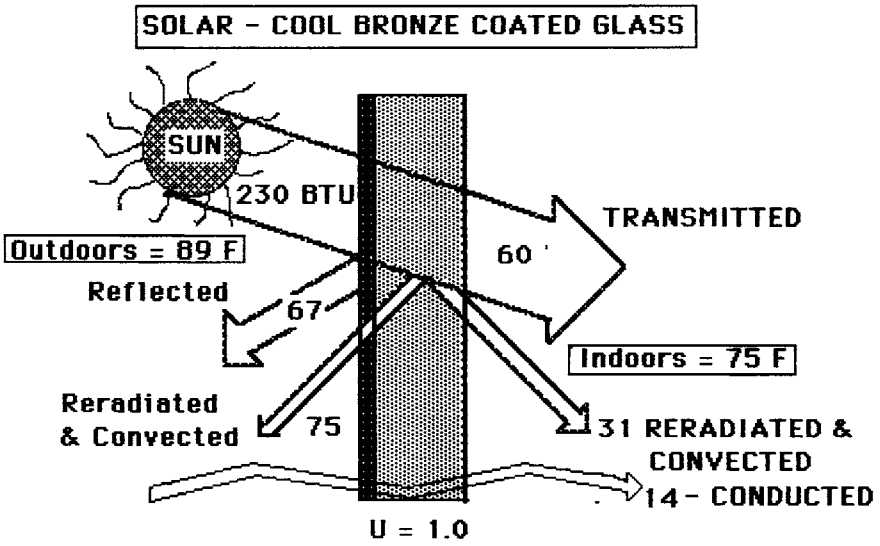
- Uniform within all parts of the FILM
- Of uniform transmission from pane to pane
- Contain no impurities not deliberately added
- Uncoated, and not overlaid by external Films or coatings.

The last requirement even applies to transparent coatings which may affect both the transmissive and reflective optical properties of the Oxide-Film. Even though such a film may be invisible to the naked eye, it could affect the operating characteristics of the SolarCool Film. The following diagram shows the reflective and transmissive properties of a plate glass window pane when installed in a building:




It is easy to see that about 77% of the Sun's energy is transmitted through the glass pane. A certain amount of energy is also reradiated and convected because of the reflective optical surfaces present.

The following diagram shows the reflective properties of SOLAR-COOL windows when installed in a building:




Note that only about 26% of the Sun's energy is transmitted by the Solar Bronze window (or about 1/3 as much as the uncoated glass). Additionally, 3.4 times as much of the internal energy of the building is reradiated and convected **inside the building** when Solar-Bronze windows are in place. The effect on costs of operating heating and air-conditioning equipment is significant, and in many cases, the installation of such windows is repaid within only a few years.

The Performance Data for 1/4" (6 mm.) glass panes are:

| | |
|---|---|
| Visible light transmittance | = 21% |
| Outdoor Visible Reflectance | = 35% |
| Indoor Visible Reflectance | = 14% |
| Shading Coefficient | = 0.43 |
| Relative Heat Gain | = 105 BTU/Hr./Sq. Ft. |
| Total Solar Energy Transmittance | = 26% |
| Total Solar Energy Reflectance | = 30% |

PPG applies quality-control procedures to all batches of Solar Cool Bronze glass. After installation, each window pane is expected to exhibit a uniform coating with no optical defects apparent. When viewed from the inside, each window is a uniform medium-grey as one views the sky line. From the outside, each window reflects as a mirror and has a dull bronze tint.

Several new reflective coatings have recently been introduced (26). These include Sky-Blue and Supersilver by The Glaverbel Group (Brussels, Belgium). The following Table gives some of the performance comparisons to be expected:

TABLE 1-7

Performance Comparisons of Some Reflective Glass Products

| 1/4" Tinted Glass | Visible Light Transmitt. | % Outdoor Reflectance | Total Solar Energy Trans. | Shading Coefficient |
|---|---|---|---|---|
| Azurlite Aquamarine | 72 | 7 | 38 | 0.61 |
| Solex Green | 76 | 7 | 46 | 0.69 |
| Solar Bronze | 52 | 6 | 43 | 0.71 |
| Solar Gray | 41 | 6 | 46 | 0.69 |
| Blue Tint | 57 | 6 | 48 | 0.70 |
| Stopray Silver | 43 | 47 | 27 | 0.65 |
| Stopray Neutral | 50 | 13 | 31 | 0.58 |
| Supersilver | 64 | 33 | 23 | 0.67 |
| Sky Blue | 35 | 19 | 23 | 0.60 |

Note the wide Variety of colors available and the dramatic improvements made in external reflectance of the glass panels.

**Active Solar Windows**

Most of these windows have remained in the research stage, but deserve mention here because of their potential usage in the near future.

One type of window can be classified as surface emissive, that is - surface emissivity can be controlled with applied voltage. The applied film consists of electrochromic materials formed by vacuum deposition of thin films. The absorptivity, emissivity and reflectance of such films can be changed reversibly by applying suitable voltage between two layers. Three versions have been tested in which tungsten oxide was used as the insertion layer, and lithium ions as the insertion medium to change optical properties. One example is a six-layered structure of:

polyethylene terephthalate/Al/$\alpha$-$Li_xWO_3$/liquid electrolyte/$\alpha$ -$Nb_2O_5$/$In_2O_3$

which can be switched from a state of high solar absorbtivity with high infrared emissivity to a state of low solar absorbtivity and low infrared emissivity. Another structure tested is:

glass/$In_2O_3$/$\alpha$-$Li_xWO_3$/liquid electrolyte/$\alpha$ -$Nb_2O_5$/$In_2O_3$

which can be switched from a state of low solar absorbtivity with low infrared emissivity to a state of low solar absorbtivity and high infrared emissivity. Still another combination is:

$As_2S_3$/$In_2O_3$/$\alpha$-$Li_xWO_3$/liquid electrolyte/$\alpha$ -$Nb_2O_5$/$In_2O_3$

which can be switched between thermally reflecting and thermally transmitting states. None of these "windows" have become commercial as yet.

Finally, a "switchable" glass panel has been constructed using nematic liquid crystals (27). At room temperature, the glass panel is translucent (like "frosted" glass). About one watt of electricity is required to make 1 $ft^2$ of glass completely transparent. When the power is off, the Liquid Crystal molecules are oriented in random fashion, giving a milky appearance. Application of power causes them to align to transmit light and the panel becomes clear.

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