complications leading to neocortical atrophy, often of considerable magnitude. The individuals are markedly retarded, often palsied, epileptic, and in a few instances even comatose. (iv) Increased intrauterine pressure in the monkey during prolonged labor leads to fetal and postpartum depression, in connection with which cerebral cortical injury occurs in the absence of typical asphyxial lesions. (v) The relationship of cerebral hemorrhages to mental retardation is not clear, but their presence at autopsy probably signifies trauma during birth, or is an agonal artifact associated with death after postpartum depression. (vi) Finally, kernicterus, a condition in which bile pigment escapes into the brain tissues from the blood when the bilirubin level is high and when there is, in combination with it, some depressing factor such as asphyxia, has been produced in the newborn monkey. It, too, is associated with mental retardation.

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Chemical Strengthening of Glass

After more than 70 years of research, glasses can now be made strong enough to be bent sharply.

Joseph S. Olcott

Glass is one of the oldest engineering materials known to mankind. Samples exist today which archeologists date back to many thousands of years before the birth of Christ. Through the years glass has been particularly noted for its transparency, refractoriness, and chemical durability. Unfortunately, because of its fragility, the use of glass has been limited wherever even modest forces might be applied to it. During the past few years, however, steps have been taken by glass scientists to reduce the vulnerability of glass to fracture.

Prince Rupert Drops

It seems strange that even though man has known for many centuries that glass can be strong, very little has been done until recently to make strong, useful articles.

Specimens of glass, now known as Prince Rupert drops, were reported in the mid-17th century as being extremely strong. These were named after Prince Rupert of Bavaria, who presented them to his uncle, King James I of England, in the early 17th century. A Prince Rupert drop is made by allowing a drop of molten glass to be quenched in a cold water bath. The glass generally assumes a teardrop configuration with a long, curled tail (Fig. 1). The thick part of the drop is so strong that it can be hit very hard with a hammer and still remain intact, and it is even said to withstand scratching by diamond. However, if the tail of the drop is flexed sufficiently to cause it to break, the great internal stresses are released suddenly with such violence that the glass shatters, frequently with a loud report, and the whole drop disintegrates into a fine powder. Figure 2 shows the powder that was produced when the Prince Rupert drop in Fig. 1 was broken in this manner. Samuel Pepys commented on these drops in his diary (13 January 1662): "Mr. Peter did show us the experiment of the chymicall glasses, which break all to dust by breaking off a little small end; which is a great mystery to me."

Indeed this must have been a great mystery to the 17th-century mind and although we understand the phenomenon of Prince Rupert drops today, we cannot, for a number of reasons, equal their strength in other forms of bulk glass.

Research by technologists who are attempting to increase the mechanical strength of glass has depended upon which end of the Prince Rupert drop they focused their attention. In the early days of glass manufacture, the main efforts were concentrated on the tail. People thought that the cataclysmic disintegration of glass was something to be carefully avoided. It was. Hence the art of annealing glass was developed.

Annealing is a process whereby the non-uniform stresses in a piece of glass are replaced by a controlled, very low stress level. It is accomplished by heating a formed object to a temperature where it can flow and relieve the internal stresses produced during formation. Then, by cooling it slowly and uniformly, the minimum amount of new strain is introduced. In a sense, one might say that annealing strengthens

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glass. Many glasses with high coefficients of thermal expansion would break spontaneously if they were not cooled in a controlled manner from their forming temperatures. Even those surviving the rapid, uncontrolled cooling would be extremely vulnerable to the slightest abrasion or chemical attack on an area near the surface which had residual tension. Such attack would initiate a crack that would propagate throughout the entire piece.

The foregoing discussion of annealing illustrates two very important properties of glass: (i) it is very strong in compression and extremely weak in tension and (ii) breaks originate at the surface.

Glass articles break when they have even small amounts of tensile stress at their surfaces, whereas they can withstand extremely large compressive surface stresses when there are compensating interior tensile stresses. A. A. Griffith (*1*) has presented a hypothesis that explains the origin of glass fracture at surfaces. He postulated the existence of minute, narrow flaws, or scratches, often submicroscopic in size, which tend to act as stress-concentration centers that cause the glass to crack when it is subjected to tension.

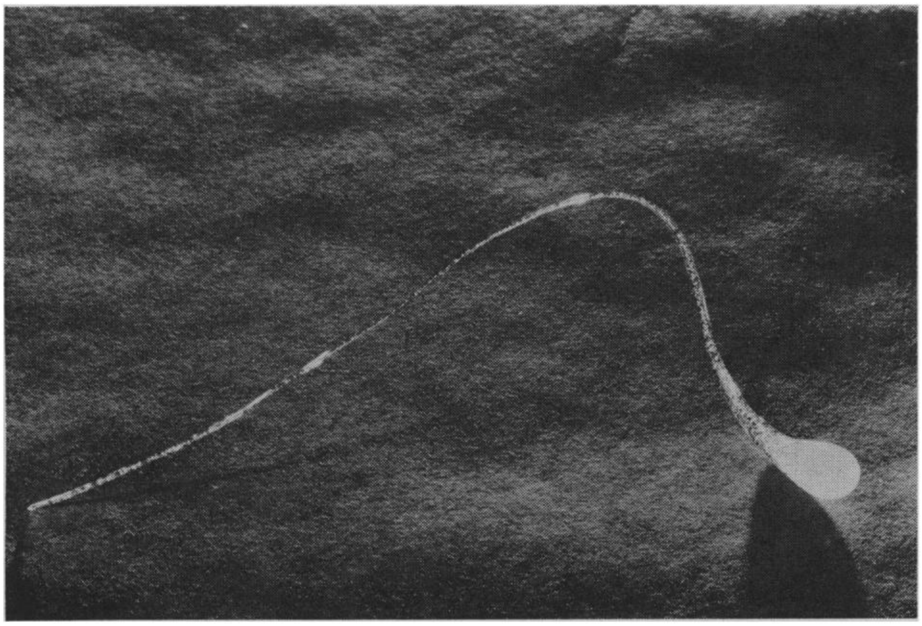


Fig. 1. Prince Rupert drop.

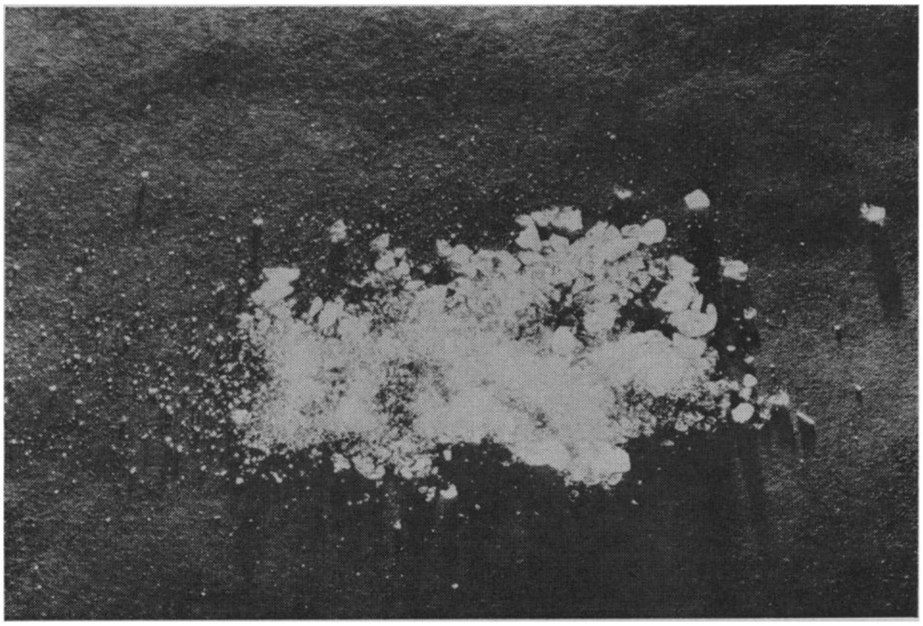


Fig. 2. Fragments of broken Prince Rupert drop.

Physical Tempering

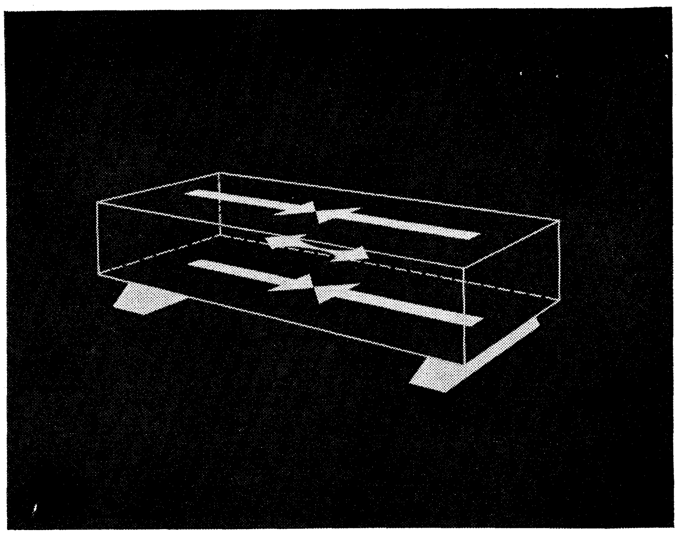
Since the discovery of annealing, the first major step in reducing the hazards of surface flaws has been the development of a process known as physical tempering. During the 1930's this process came into being as a large-scale commercial method of strengthening glass. Briefly, physical tempering is a modification of the quenching process that is used in making Prince Rupert drops, but the quenching is not nearly as drastic. Whereas Prince Rupert drops are quenched all the way from the molten state, in physical tempering, the already formed glass article is heated to some temperature just below its softening point and then quenched, usually in air, molten salt, or oil. The softening point of glass is that temperature at which its viscosity is low enough for it to deform under its own weight. For most glasses this corresponds to a viscosity just below 10^8 poises.

During the rapid quench of physical tempering, the exterior of a piece of glass cools rapidly and becomes hard, while the interior cools more slowly and continues to contract after the exterior has become rigid. This interior contraction pulls on the exterior surface putting it into compression, while the interior develops compensating tension.

Figure 3 schematically represents this condition by arrows converging on the surface, indicating compression, and other arrows diverging in the interior, indicating tension.

In essence then, a structural gradient is established from the surface inward, with glass in a low-density form on the exterior and a high-density form in the interior. The ability of glass to form this structural gradient is a direct consequence of its high viscosity. During the rapid cooling process of the exterior, the atoms do not have a chance to flow to a state closer to equilibrium because the rate of flow is slow compared to the rate of quench.

In order to break a piece of glass in such a stressed condition, not only must the inherent breaking stress of the piece be exceeded, but the residual surface compression must be overcome. This idea is shown in Figs. 3, 4, and 5. Figure 3 represents the stress configuration in a tempered piece of glass mounted on knife edges. As the load is applied (indicated by the vertical arrows) the tension layer moves toward the bottom of the piece and compression



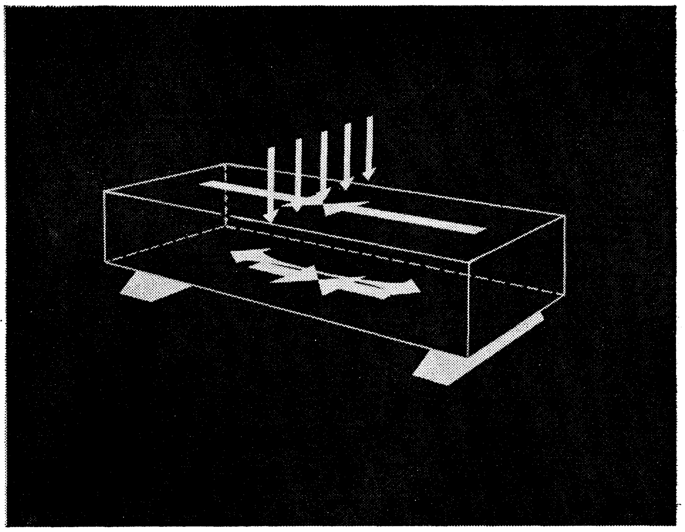


Fig. 3 (left). Diagrammatic representation of stress in physically tempered glass. Fig. 4 (right). Diagrammatic representation of the stress configuration of a glass specimen under load.

is reduced at the bottom surface, as shown in Fig. 4.

Finally, we have only tension on the bottom and compression on the top, and, as the load is increased, the tensile strength of the bottom is exceeded and the piece ruptures, as illustrated in Fig. 5. Thus the origin of breakage always appears on the surface which is subjected to tension.

Chemically Strengthened Glass

During the last few years, scientists at the Corning Glass Works have been working on chemical methods to generate the same sort of stress configuration that is shown in Fig. 3. This work has succeeded to such an extent that late last year the company was able to announce what it calls the Chemcor process. This process actually represents many different chemical techniques whereby the exterior of glass articles can be placed in compression. Each process requires its own special glass compositions in order to maximize the benefit of the process. The unifying idea in all these Chemcor processes is that, after treatment, the surface glass is chemically different from the interior glass. Indeed, more than a structural gradient is produced.

Chemical strengthening is not a new discovery. Attempts go back more than 70 years. In 1891 Otto Schott (*2*) succeeded in making Jena boiler gauge glasses by overlaying a high-expansion glass with a low-expansion one. He inserted an iron rod into a pot of molten high-expansion glass and gathered a lump of this on the iron. He then removed the iron from the furnace and after it had cooled slightly he inserted it into a second pot of molten low-expansion glass and gathered a layer of this glass on top of the first. Then, when he drew the compound glass out into a rod, the high-expansion glass on the interior, on cooling, pulled on the low-expansion exterior, which did not tend to contract as much. Thus, the exterior was placed in compression in the same way as was done by physical tempering. Compensating tension was, of course, produced in the interior. This imaginative experiment has pointed the way for many of the succeeding methods that have been used to strengthen glass by chemical means.

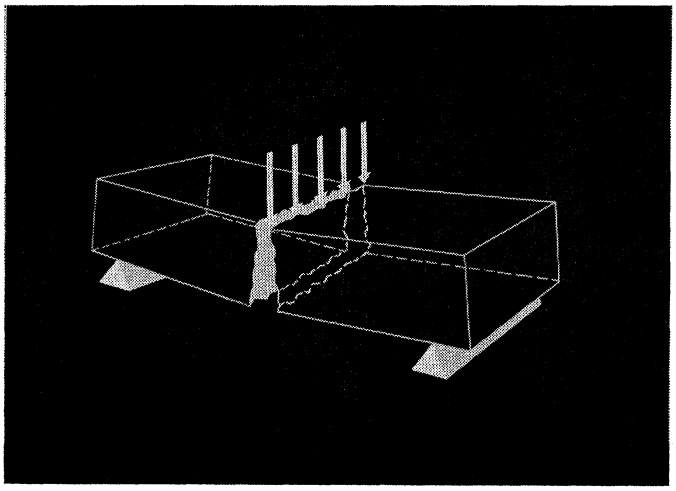
As another illustration, it has been well known for many years that glassmakers seem to get a stronger product from the soda-lime glasses (*3*) when they place sulfur in their lehrs (annealing ovens).

Douglas and Isard (*4*) later showed that the use of sulfur resulted in the formation of sulfur dioxide, which promoted an ion-exchange reaction in which sodium ions from the glass were replaced by hydrogen ions from water in the atmosphere of the lehr. Then, as the samples continued to be heated, the surface dehydrated, leaving a silica-rich surface. It is well known to glass technologists that glasses richer in silica have lower coefficients of expansion, in general, than those deficient in silica. Therefore, as these samples cooled from elevated temperatures, the glass with the lower expansion coefficient was overlying the glass with the higher coefficient, and high strength was produced in the same way that Schott produced it, though in a less direct manner.

In 1957 Hood and Stookey showed that other ion-exchange reactions could produce similar conditions (*5*). They exchanged lithium ions from molten salt baths for sodium ions in the surface of glasses at temperatures where the glasses could flow to accommodate the lithium ions. Lithium ions diffused into the glass and exchanged with the sodium ions that were originally present. After a while, a lithium glass was present on the outside of the specimen and a sodium glass on the inside. It is also commonly known that this type of alkali substitution, in which a smaller alkali metal ion replaces a larger one, results in glass with a lower coefficient of expansion, and, when the sample is removed from the bath, the exterior tends to shrink less than the interior, and thus the favorable stress profile is produced.

In 1959, Sil'vestrovich and Boguslavskii (*6*) described a method of strengthening glass by quenching hot glass into silicone oils. They claimed they produced compression on the surface, not only by tempering, but also by decomposing the oil and leaving a residual low-expansioin silica glass layer on the surface of the piece. The chemical part of the strengthening they accomplished was again due to the difference between interior and exterior coefficients of expansion.

Last year Kistler described how he had replaced sodium ions on the sur-



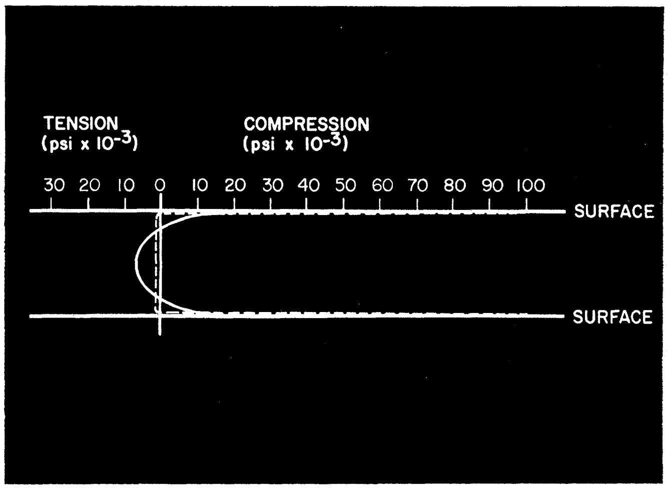


Fig. 5 (left). Rupture of a glass specimen from the surface in tension. Fig. 6 (right). Comparative stress profiles of physically tempered and chemically strengthened glass.

face of glass by larger potassium ions from molten potassium nitrate salt baths (*7*). In his experiments the exchanges were conducted below the so-called "transformation" range of the glass. In this temperature range the viscosity of the glass is so high that stresses induced in it because of the exchanged ions could not be relieved by flow during the time period in which exchange occurred. Therefore, because of the interdiffusion of potassium and sodium ions, potassium ions occupied positions in the surface of the glass formerly occupied by the much smaller sodium ions. This led to "crowding" of the surface and thus to rather high surface compressive stresses. Kistler calculated a maximum compressive stress for his experiments of 124,000 pounds per square inch in the surface of Leitz cover glasses.

The same principle employed by Kistler was applied by Jack and Winterburn (*8*). By heating samples of vitreous silica for limited periods of time in atmospheres having a high partial pressure of water, they were able to get diffusion of the water into the glass. When the temperature of this diffusion was below the strain point of the vitreous silica—in other words, below the temperature at which the glass could readily orient itself to accommodate the presence of the bulky water, the same sort of compressive stresses described by Kistler were induced in the silica surface. Also, by dehydrating the surface of vitreous silica above the strain point, they were able to produce even lower expansion silica surfaces on the vitreous silica. As with Otto Schott's method, when the sample was cooled from the dehydration temperature, toughening compressive stresses were produced on the glass surface.

Last summer at the 6th International Glass Congress, in Washington, D.C., my co-workers and I (*9*) presented a paper describing two somewhat different methods of strengthening glass. In the first, a glass-ceramic layer, containing a β-eucryptite solid solution phase, grows in spontaneously from the surface of some lithia-alumina-silica glasses at elevated temperatures. Because of the very close index of refraction match between the glass and glass-ceramic phases and because of the small size of the β-eucryptite crystals and their small degree of anisotropy, the surface layer is translucent and in some samples very high specular transmission can be obtained.

Beta-eucryptite is an extremely unusual mineral in that it shrinks when heated and expands when cooled. Thus, when these glasses were cooled from the temperatures where their surface layers were formed, the surfaces tended to expand and the interior glass shrank, producing extremely high surface compression. Moduli of rupture up to 80,000 pounds per square inch were measured. Experimental cups of this glass were dropped from the top of our nine-story building in Corning, New York, onto ¼-inch steel boiler plate without any breakage of the glass.

The second method is a combination of the Hood-Stookey idea and the β-eucryptite surface crystallization. Hood and Stookey had reported that in some compositions they formed β-spodumene, another low expansion lithium aluminosilicate, on the surface of some glasses when they subjected them to lithium for sodium ion exchange. A very similar process was followed in this new method. Titanium was added to the batch of some soda-alumina-silica glasses. It was known that at elevated temperatures titania would nucleate β-eucryptite precipitation in lithia-alumina-silica glasses. Stookey and Maurer (*10*) had shown that transparent glass ceramics could be formed by this method. Thus, when the new glasses were immersed in molten lithium sulfate, lithium ions interchanged with sodium ions in the glass and the surface layer became a lithium glass. The presence of titania caused a β-eucryptite solid solution to be precipitated. Even higher strengths were achieved in this system than those obtained by spontaneous surface nucleation. Sometimes moduli of rupture as high as 100,000 pounds per square inch were achieved on abraded samples. For comparison, modulus of rupture in annealed glass would be about 7000 pounds per square inch in the same test, and in physically tempered glass, about three to six times that value, depending upon several factors.

When discussing the strength of bulk glass, it is important to state the condition of the surface at the time of the test. We abrade the surface of the glass rather heavily in order to normalize the glass surfaces and reduce the randomness of the so-called Griffith flaws. Thus, if one does not abrade a series of glass samples, a high average strength will be obtained, but a very high degree of dispersion among the individual samples will be observed also.

By abrading the samples in a standard manner the average value is lower but the dispersion is decreased markedly. Abrasion also closely approximates the condition of glass after prolonged service. The reason strength values obtained by the ion-exchange method are higher than those obtained by spontaneous surface nucleation is that soda-alumina-silica glasses, the substrate for the ion-exchange process, have higher coefficients of expansion than comparable lithia-alumina-silica glasses, and the strength achieved is proportional to the difference between the coefficients of expansion of the interior and the exterior.

At present, the only chemically strengthened glass sold commercially is a line of dinnerware called Centura, which is marketed by the Corning Glass Works. This dinnerware is strengthened in a manner very similar to the overlay used by Schott in 1891. A low-expansion glass is fired onto a high-expansion glass-ceramic substrate at an elevated temperature. As the piece cools, the favorable profile develops. In this case, since the substrate is opaque, the composite is of course opaque. The modulus of rupture of this material is 35,000 to 40,000 pounds per square inch when made into bars. With the same principle, other glazed, glass-ceramics have produced much higher strengths.

Comparative Stress Profiles

The difference between the stress profile in chemically strengthened and physically tempered glass should be understood. In Fig. 6 the stress profile of physically tempered ware is schematically shown by the solid curve. Compressional stresses are indicated on the right of the neutral axis, and tensile stresses on the left. This shows that the compressional stress at the surface is only 20,000 pounds per square inch and the profile is parabolic. For comparison, a schematic profile for chemically strengthened glasses is represented by the dashed curve. Up to 100,000 pounds per square inch surface compression have been produced in bulk glass. The shape of the profile is quite different. Figure 6 shows that the surface layer thickness is much less in chemically strengthened glasses. Because of this, smaller maximum tension can be obtained with chemically strengthened glasses and therefore violence of breakage, which is dependent upon the stored energy in the glass, can be quite low.

Another advantage of chemical strengthening over physical tempering is that chemical strengthening does not depend upon the thickness or shape of the sample. In physical tempering, a sharp temperature gradient must be produced during quenching. With thin ware, that is, less than 1/10 of an inch, this is extremely difficult to do. Also, it is very difficult to temper complex shapes such as those with sharp reentrant angles. Uniform quench, so important for success, is difficult to achieve. No such restrictions exist with chemical strengthening. As long as distortion, due to flow, is kept at a low level, even thin, intricate articles of glass can be strengthened by chemical means.

The flexibility of the new chemically strengthened glasses is a direct consequence of their higher strength. The moduli of elasticity of these glasses are no different from those of ordinary glasses. The difference is that with higher strengths, they can be bent to smaller radii of curvature than could ever be done with other glasses without the danger of fracture. The glass is still a brittle material. That is, it experiences no permanent deformation prior to rupture, as many metals do.

In our laboratory, we have made thin, chemically strengthened glass as strong as physically tempered plate, but with only one-fourth or one-fifth the thickness of plate glass. This can lead to rather large weight reduction where large amounts of glass are used in a structure. The optical quality of some chemically strengthened systems is as good as the finest optical glass made today.

The chemically strengthened glasses are distinctly different from annealed glass in one very important way. Once they have been strengthened, they can no longer be altered in any of the traditional finishing processes such as flameworking, cutting, and grinding. It is easy to see from the nature of these processes that altering the products after they have been strengthened will expose high tensile stressed areas of the interior to the surface and thus make them very susceptible to fracture. A sheet of chemically strengthened glass, .080 inch thick, has been bent over a radius of curvature of 50 inches. This type of test has been repeated mechanically many, many times in our laboratories with no failure of the articles. Sheets of glass have been twisted repeatedly thousands of times on torque machines. There is apparently no loss of strength due to repeated testing.

In conclusion, let me return to the Prince Rupert drop. By looking at the teardrop and not the tail, glass scientists have been able to produce bulk glass having more than ten times the strength of annealed glass. Chemical strengthening today has advanced us only part of the way toward the goal at which we are aiming. Glass fibers have been measured with moduli of rupture of greater than 2,000,000 pounds per square inch, which is believed to be close to the theoretical strength of glass. We are still trying to minimize the effect of Griffith flaws. Obviously, we are still more than a factor of 10 below the theoretical bulk strength of glass.

Work in this field is continuing in laboratories throughout the world and we would hope that progress will continue, and ultimately theoretical strength will be reached.

Summary

Although man has known for centuries that glass had potentially large mechanical capabilities, he had been content, until rather recently, to accept the fragility of bulk glass. Annealing, the first step in making glass a useful material, enabled him to make articles with strengths adequate for satisfactory service. Physical tempering provided the next big advance, permitting strengths more than three times those of annealed glass in simple shapes. Today, chemical strengthening is a real possibility for producing glass articles, regardless of design, more than three times the strength of physically tempered ware.

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