NEW DEVELOPMENTS IN GLASS CONTAINERS*

By WILLIAM R. PRINDLE

Continental Can Company, Inc., Hazel-Atlas Glass Division, Wheeling, W. Va.

GLASS IS AN interesting material to work with and to talk about because it has many unusual, even unique, characteristics. Glass is an ancient material (it has been called the first synthetic material) yet the composition of commercial glasses today are not vastly different from those used by the old Egyptians, Syrians and Romans. While you might interpret this as laziness and lack of imagination on the part of the glass industry, it is really the result of economics and the laws of physical chemistry. The raw materials that were used by the Phoenicians are still the cheapest and best to use. The same proportions of the raw materials still melt readily to form a viscous liquid that resists crystallization as it cools.

The properties of glass are also rather unique. It is completely isotropic: its structure imparts no directional effects to its physical properties. The refractive index, the electrical conductivity, the strength, the thermal expansion and thermal conductivity are the same in all directions in the glass regardless of how the glass is manipulated or shaped.

Glasses conduct electricity freely at high temperatures, yet are so completely nonconducting at room temperature as to be used in making insulators. Glasses exhibit tremendous changes in viscosity with temperature; the viscosity of glass at 500°C. may be 1,000,000,000,000 times as great as it is at 1300°C.

Glass has no melting point or freezing point but exhibits a continuous change in all properties from room temperature up to very high temperatures. Glass fibers have been tested with breaking strengths of one million pounds per square inch, or much stronger than the strongest steels.

Needless to say, the properties of glass have aroused the curiosity of chemists and physicists and a considerable amount of fundamental research has been carried out on glass, particularly in recent years. This research has been carried out in government laboratories, at universities, at research institutes and by industry. Hazel-Atlas, Corning Glass Works,

* Presented at the December 13, 1956, Meeting, New York City.

Owens-Illinois, Bell Telephone Laboratories, Pittsburgh Plate Glass and General Electric are some of the companies that have contributed. Glass is a fine material in many ways; it is inexpensive, odorless, tasteless, resistant to corrosion, impermeable to vapors, transparent and is capable of being formed in many shapes, etc., but it has the one disadvantage of not being as strong in service as we would like it to be. As a result much of the recent research on glass has been on strength. Just this last August the American Association for the Advancement of Science sponsored a one week Gordon Research Conference on glass strength to disseminate the latest ideas and to generate new ones.

This concern about strength may sound strange in view of the comment above that strengths of one million pounds per square inch have been achieved. The extremely high strengths, however, have been achieved in the laboratory under special, carefully controlled conditions. In practical use the strength of glass is more of the order of 10,000 lb. per sq. in.

The reason for the discrepancy between the high strength values obtained in the laboratory and the lower values observed in practice lies in the fact that glass is susceptible to stress concentration. Engineers call this "notch sensitivity." Glass is inherently very strong, but it may be seriously weakened by surface flaws, such as chips, pits, scratches and abrasions. These abrasions are the points where glass starts to break. Just as a notch cut in the edge of a piece of cloth before tearing it in two enables one to start the tear more easily, the scratches on glass act as notches that make it easier to break. Because glass does not flow plastically like most metals do, the stress at the head of a surface crack may build up to a very high value under load and cause the glass to fracture. There are various ways of dealing with these surface defects. One solution is to remove surface damage by fire polishing in which an intense flame played on the surface of the glass softens the glass and heals the flaws. Another method of flaw removal utilizes a hydrofluoric acid polishing solution to round off the defects so that they are no longer serious stress concentrations. Neither of these methods has been used commercially because they are complicated and expensive.

Another solution was to protect the surface. As a result, the idea of coatings to protect the glass from damage has been developed in the last few years. Glass is very strong as manufactured and has a surface that is very nearly free of scratches. Therefore, if one could keep the surface from being damaged and avoid the formation of stress concentrations the original strength of the container could be preserved. Coatings act like lubricants so that objects which might scratch the surface slide over it without digging in.

Many materials have been tried as bottle coatings, but they must meet three criteria to be generally useful and acceptable:

(1) They must provide a lubricity to the glass surface that protects it from damage.
(2) They must be nontoxic.
(3) They must accept a label applied with conventional adhesives.

The first type of surface coating to be used was a thin film of sodium sulfate. This was produced on the ware by admitting sulfur dioxide gas to the annealing lehr. The sulfur dioxide combined with the sodium in the surface layers of the glass to produce sodium sulfate. The coating was visible as a white or grayish "bloom" on the ware and provided a slick, greasy, lubricating film. The extraction of sodium from the surface leaves a tough skin on the glass that resists abrasion to a certain extent. Sulfur coating is still used extensively on beer bottles, but has never been used to any extent on glass containers for other purposes.

The protective coatings most commonly used on glass containers today are edible waxes of the stearate or glycol type. The two used most extensively are polyethylene glycol ("Carbowax" manufactured by the Carbide and Carbon Chemical Co.) and polyoxyethylene monostearate ("Myrj.-52 S" manufactured by the Atlas Powder Co.). These materials are applied by dissolving in water and spraying the solution on the containers as they emerge from the lehr. The wax coating is extremely thin, less than one thousandth of an inch, but even though the film cannot be seen it successfully lubricates the surface so that it is protected from abrasion. These materials are nontoxic and cause no difficulty in the application of labels with any of the usual adhesives.

The wax materials are soluble in water so that some of the coating is washed off if there is a washing operation in the filling line. Some silicone coatings have developed that are not soluble in water and provide more lasting coatings. These coatings work on exactly the same principle as the sulfur and wax coatings, i.e., by surface lubrication. The degree of protection provided is approximately the same as that given by the other materials. The silicones are sprayed on at the annealing lehr in the same fashion that the waxes are applied. The Food and Drug Administration does not object to the use of some silicones, but there are still some that have not been cleared for use as coatings for food containers. Many conventional adhesives will not adhere to some of the silicone treated glass surfaces. Special adhesives can be used to keep the labels from falling off, but these adhesives do not work well in all types of labeling equipment.

Two of the newer silicones that show great promise are Dow Corning's 4141 and Union Carbide's 520. The D. C. 4141 affords very good surface protection, but is not easy to label and has not yet been cleared by the F.D.A. The U.C.C. 520 affords good protection, has been cleared by the F.D.A. and labels fairly well although the coating is somewhat less permanent than most silicones. Silicones are also occasionally mentioned as

coatings for the inside surfaces of bottles for the purpose of helping drain out all of the contents. This will work for very fluid, watery products such as penicillin solutions, but will not work for products of heavier consistency, such as sirups, hand creams and catsup.

The most recent product to appear as a protective coating for bottles is a low molecular weight polyethylene plastic. This provides a nontoxic film which protects the glass fairly well (though not as well as some of the silicones) and which takes labels reasonably well (although not as well as the waxes do). The effectiveness of the coating in protecting the glass surface from dangerous abrasion can be tested by subjecting the coated containers to a standardized abrasion followed by impact or pressure testing. The controlled abrasion can be applied by passing a sample of two dozen coated containers through a rolling trough that simulates both rolling abrasion and filling line impacts. The containers are then tested with an instrument applying a controlled impact to determine their impact strength. The results are compared to the results of a similar test run on a control group of uncoated containers to see what degree of protection the coating provided.

We were not satisfied with the state of knowledge on the strength of glass, so we started a research group at Mellon Institute in Pittsburgh to study specifically the weakening effect of abrasions on glass. This group has developed an entirely new method for testing glass strength based upon the rupture of circular glass discs by hydrostatic pressure. The disc is not clamped at the edges but is free to deflect symmetrically under the hydrostatic load until it breaks. The strength can then be calculated by means of a rather complicated mathematical expression. The advantage of this new method lies in its ability to give accurate values of the actual breaking stress at any specific location on the specimen. Now, for the first time it will be possible to find the exact effect of a given type of surface damage. When this type of information is collected it is then possible to develop treatments to prevent the most serious types of surface damage.

The flat surface, which simulates the side of a bottle, enables us to use ellipticity of reflected light, electron microscopy, multiple beam interferometry, infrared reflection, gas absorption and other techniques to study the surface and the changes taking place in the surface before fracture occurs. One technique currently in use involves the introduction of metal atoms into the surface of the glass to locate the position of cracks. Such research tools enable this group to study the effectiveness of various surface treatments under carefully controlled conditions. In addition to the strength research, we are carrying out investigations on the physical chemistry of glass with particular emphasis on the solubility of gases in glass. It has been found for example, that water vapor is soluble in glass and that it changes the physical properties of the glass. These changes

in turn influence the melting of the glass, the removal of seeds and bubbles and the forming of the glass.

In this work, which is being carried on at Massachusetts Institute of Technology and more recently also at Pennsylvania State University, we see a study which began as purely fundamental research, but which now has definite practical application. This new information should aid in the more efficient production of better glass containers.

Along other lines, such as glass color, research has not been as productive and practical considerations have limited the advances. New colors are always being sought in glasses, but the glass technologist must use inorganic oxides and metals as colorants. The high temperatures of the glass melting process rule out the wide variety of vivid colors produced by organic dyes. Also, many of the colorants are rather expensive, such as the gold used in producing certain ruby glasses, or presently unobtainable, such as the uranium used in producing a striking yellow green. Other colorants are so weak that they must be used in very large quantities and the result is a change in the working properties of the glass that makes it impossible to form the glass by machine. However, with the advent of the plastic coated bottle, brilliant colors of practically any hue may be incorporated in the plastic covering that is placed over the glass bottle. This system was developed by the Wheaton Plastics Co., and Hazel-Atlas is now a licensee for the process. In this plastic coating operation the bottles are heated and dipped by machine into a bath of hot polyvinyl chloride plastisol. The bottles are then removed and cured to develop a smooth coating that is approximately one millimeter thick.

This coating, besides providing any color desired, is pleasing to touch and provides protection of the glass against abrasion. The plastic coating also absorbs energy when struck and lessens the effect of impact blows. When the coating is used on aerosol containers, the coating provides a restraining skin that prevents flying fragments should breakage occur. A final possibility with the plastic coating is the incorporation of an ultraviolet absorbing compound in the coating to screen out the sun's actinic or chemically active rays.

The short wavelengths of the visible spectrum and the near ultraviolet are the spectral regions in which most of the chemically active radiation falls. This covers roughly a range of 250 millimicrons to 450 millimicrons. The changes that take place under actinic action are losses of potency of drugs, changes in color, odor and flavor. Any of these can cause considerable damage to a carefully prepared product. Amber glass will effectively screen out these actinic rays, but amber suffers from a lack of esthetic appeal.

Accordingly, there has been considerable interest in ultraviolet absorbing materials that would either be colorless or colored in a pleasing fashion.

As was mentioned above, ultraviolet absorbers can be incorporated in the polyvinyl chloride plastisol coatings applied in the Wheaton process. The absorbing materials most commonly used are beta methyl umbelliferone and some of the hydroxy methoxy benzophenones. These materials can also be incorporated in thin films of harder transparent polymers.

Ceramic color coatings can be applied by spraying and fired into the surface of the glass. These coatings stop ultraviolet radiation as well as provide a decorative film. They are cheaper to apply than dipped plastic coatings and yet provide an extremely wide range of colors. Cellophanes and lacquers will also provide a considerable degree of protection if they are the right color. Irradiation by high energy electrons or neutrons is a possible method of changing the color of glass. Small quantities of certain rare earth oxides can be incorporated in glasses which will cause the glass to develop unique colors after irradiation. If the bombardment or irradiation is properly masked on the glass surface, it would be possible to outline printing or trademarks and have the label for the product actually in the glass. While many plastics degrade after exposure to high energy radiation glass suffers no ill effects in its physical properties.

Recent engineering progress has led to many refinements in the forming of glass containers. Much of this progress has been in the field of heat transfer and temperature control. These advances have enabled containers to be manufactured with considerable reduction in weight. Extremely light weight containers, however, have been made only in a few cases where a large volume of production could be maintained without interruption.

Glass container design becomes particularly important when light weight containers are manufactured. With reduction in weight, it becomes particularly difficult to maintain uniform wall thickness in the containers. It is extremely important in these circumstances to avoid abrupt changes in the direction in the container surface. Sharp corners should always be avoided.

The thin walls of light weight containers are quite susceptible to breakage if they are abraded. Bottle coatings to prevent abrasions are really called for with most light weight containers.

Where glass containers for aerosols are involved, one does not want a light weight bottle. Glass aerosol packages should be reasonably thick (around $^1/_8$ inch thick) to give them strength and well designed to avoid breakage. If rounded corners are used ($^3/_{16}$ inch minimum radius), large panels avoided and the shoulder sloped gently up to the neck no problems should be encountered. It is to be remembered that a circular cross section is stronger than an oval cross section and both are substantially stronger than a rectangular cross section where internal pressures are involved.

Glass aerosols have excellent internal pressure strength if properly designed (over 600 lb. per sq. in.) but should always be plastic coated for safety. The plastic coating is very important in restraining the fragments if the container is broken. We also believe that the cold filling method is to be preferred in loading aerosols unless adequate purging is carried out with the pressure filling technique to remove entrapped air. Entrapped air is undesirable as it can increase the internal pressure considerably.

In conclusion I would say that fundamental research in physics and chemistry and progress in engineering and design are contributing new ideas to the glass industry at a greater rate than ever before.

Glass may be one of man's oldest structural materials but it is only now reaching a vigorous youth in research and development.

GAS CHROMATOGRAPHIC ANALYSIS OF AEROSOL PRODUCTS*

By M. J. Root and M. J. Maury

G. Barr & Company, Chicago 9, Ill.

Analyzing the volatile components of an *aerosol* product by conventional analytical means is extremely difficult and time consuming. We may determine the pressure or the specific gravity and arrive at a very crude analysis of the propellents present. A 1 per cent change in the composition of a mixture of equal parts of Freon® 12 (dichlorodifluoromethane) and Freon® 114 (tetrafluorodichloroethane) produces a pressure change of only $^3/_4$ lb. per square inch and a specific gravity change of 0.0015. Measuring these physical properties to within such increments is not readily accomplished. Fluorinated hydrocarbon mixtures have been commonly analyzed by both mass spectrometry and infrared spectrophotometry, but the presence of other volatile components makes even these costly methods of little value.

Determining quantitatively, for example, ethyl alcohol in the presence of trichloromonofluoromethane and dichlorodifluoromethane is extremely difficult. Although ethyl alcohol and trichloromonofluoromethane, which boil at temperatures of 176°F. and 74.7°F., respectively, can be readily separated by fractional distillation, the presence of dichlorodifluoromethane which boils at −21.6°F., introduces a complication. Not only must the distillation flask, column and receiver be kept under a very high pressure

* Presented at the December 13, 1956, Meeting, New York City.