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Symposium on the Development of the Plastics
Fabrication Industry in Latin America

Bogotá, Colombia, 20 November - 1 December 1972

POLYSULFONE - SEVEN YEARS IN THE MARKETPLACE [1]

by

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SUMMARY

POLYSULFONE - SEVEN YEARS IN THE MARKETPLACE[1/]

by

F.W. Wurtsell
Union Carbide Corporation
New York, USA

Polysulfone is produced by reacting bisphenol-A with dichlorodiphenyl sulfone in a solvent medium. The resulting polymer is a thermoplastic that is characterised by its excellent thermal stability, high heat distortion temperature and flame resistance.

Highlight physical and mechanical properties that have led to the acceptance of polysulfone are presented, along with a listing of approvals for applicable government and industrial standards. Fabricating conditions are briefly reviewed.

Commercial facilities for producing polysulfone were dedicated in the fall of 1965. One of the early uses for polysulfone was in injection molded integrated circuit carriers where its heat resistance, stable electrical properties and dimensional stability minimised damage and handling during the critical burn-in and testing operations. Other uses in the electrical-electronic market area include both extruded and cast capacitor dielectric films, TV parts and miniature phonograph arm connectors.

Automotive ignition and steering column lock switches have also been produced by Delco-Remy Division of General Motors from glass reinforced polysulfone. The reinforced grade was selected to provide greater insurance against costly call-backs and to meet high performance requirements of a new anti-theft switch.

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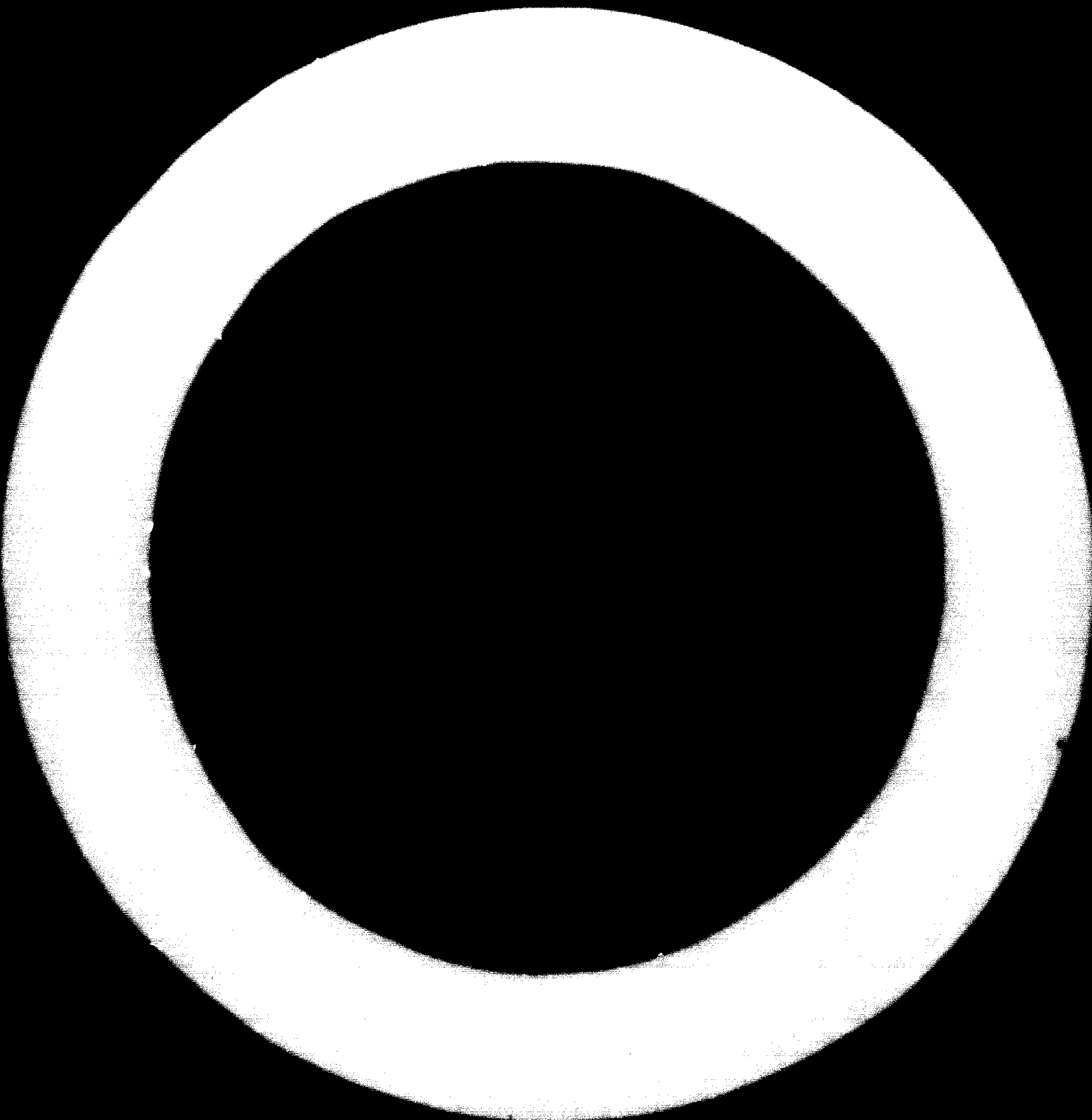

The appliance industry has found polysulfone to be well suited for use as a stainless steel or glass replacement in coffeemakers and juice dispensers. Polysulfone is used as the inner protective liner in a thermos pitcher. Since polysulfone is not stained by coffee oils or food products the impeccable original appearance of a percolator is retained in service. No special scouring or cleaning agents are needed.

A special grade of polysulfone is also employed as a thermostat insulator in the Hoover hair dryer.

Resistance to alkaline cleaners and detergents required to remove milk scum from milking machine parts led Alfa-Laval to specify clear polysulfone in their milking machine parts.

Finally the performance record of polysulfone indicates that it will come close to filling the developing need for a material that will withstand the extreme temperatures required for containers in the mass feeding market. A revolution in mass food preparation is now underway wherein food is prepared in central kitchens, dispensed into dishes (each holding an individual portion) flash frozen delivered in refrigerated vans and then reheated at point of use in either microwave or convection ovens. Polysulfone can operate between -150°F and 400°F, and dishes thermoformed from thin sheet perform as attractive serving dishes as well as economically suitable packages.

Polysulfone does not impart any taste to food products. Furthermore, it can be extruded and formed on exisitng forming lines provided provisions are made for additional heating of chill rolls molds and extruder. High capacity hopper dryers or high temperature molding rooms are needed to remove residual absorbed atmospheric moisture. Suggested conditions for processing polysulfone into dishware are listed, along with operating parameters for the finished dishes.

In the seven years since polysulfone became available on a commercial scale, it has grown from a thermoplastic selected mainly for its heat resistance to a material which brings many outstanding features in solving design problems. Because of its superior properties, it is replacing many other plastics in numerous applications. It is also recognized as an excellent replacement for various metals because of the ecological and economical advantages it offers.

Union Carbide developed and started commercial production of polysulfone* copolymer (referred to herein as "polysulfone") in late 1965, just seven years ago. This presentation will take you through the story of polysulfone from the beginning. It is an interesting story because it is an interesting product. We will have the opportunity to see how such a product progresses in the marketplace from its introduction to a position that can now be described as on the threshold of total commercial success.

Polysulfone is an unusual material. We often use the term "engineering thermoplastic" to describe it. This term designates those thermoplastics with premium properties, ones which are usually associated with thermosets. We are talking about, primarily, high heat resistance and excellent physical properties. An "engineering thermoplastic" delivers premium properties with the convenience and economy of injection molding and extrusion techniques. Polysulfone is the strongest, most heat resistant, most oxidation and flame resistant of all melt processable thermoplastics commercially available. The highlight properties of polysulfone are shown in the following slide. (Slide 1: Highlight Properties.)

Before we examine this exceptional thermoplastic and show how it is used in several commercial end-uses, let us look briefly at its chemistry. In an obvious over simplification, the patented process for producing polysulfone consists of a two-step condensation reaction between bisphenol -A and 4, 4' -dichlorodiphenyl sulfone. The reaction takes place in a solvent medium

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*Polysulfone copolymer is a proprietary product of Union Carbide Corporation sold under the trademark UDEL.

HIGHLIGHT PROPERTIES OF POLYSULFONE

TRANSPARENT

RIGID

TOUGH

SELF EXTINGUISHING

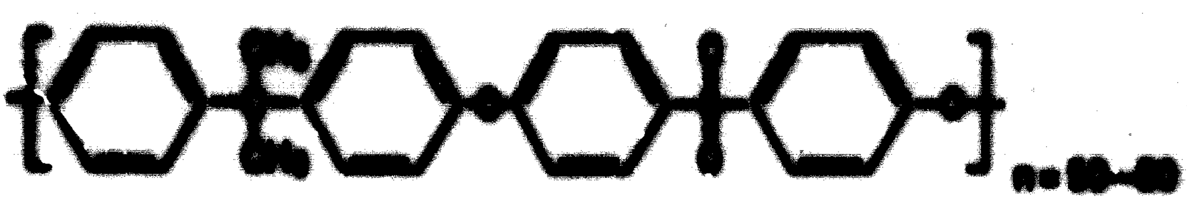
LOW CREEP

HIGH HEAT DISTORTION POINT

HIGH CONTINUOUS USE TEMPERATURE

Slide 1: Highlight Properties

(POLYSULFONE)



Slide 2: Polysulfone Structure

and is terminated when the desired molecular weight is attained. The polymer solution is then washed, filtered, concentrated and pelletized to produce the final product. The most popular grade in the industry is P-1700 which is suitable for both molding and sheet extrusion. (Slide 2: Polysulfone Structure.)

Usually speakers extol only the virtues of a product. Limitations are omitted or at best mentioned briefly. But we will depart from tradition and first mention polysulfone's limitations. The first of these is its cost. The base price of polysulfone in the U. S. is about one dollar per pound -- near the high end of the range for commercially available thermoplastics. Therefore polysulfone is often considered last, usually after lower cost plastics or other materials have been found wanting. However, polysulfone on a pound/volume basis costs 4.45 U. S. cents per cubic inch, which puts it just about even with zinc die-casting alloys and gives it a wide advantage over brass and stainless steel. As you will see later, many of polysulfone's applications result from replacing these metals, and economy turns out to be the reason for its selection after all.

There are two other limitations. Like most organic polymers, polysulfone is affected in varying degree by some classes of chemicals and solvents. It is softened by certain solvents, including ketones, esters, aromatic hydrocarbons and chlorinated hydrocarbons. The other problem is stress cracking and crazing. This effect can be largely offset by proper part design (by avoiding notches, sharp corners and other stress concentraters) and by minimizing fabricating stresses (through the use of heated molds at 149° - 169°C. [300° - 320°F.], large gates and runners, etc.). The addition of glass fibers at loadings of 10 percent and up serves to reinforce the molded piece and to minimize stress cracking and crazing problems. In most instances polysulfone will not present problems of this nature. It is resistant to most food chemicals and oils, fluorocarbons, acids, bases, detergent and soap solutions, organic fluxes and flux removers, kerosene, mineral spirits, heptane, naphtha, carbon tetrachloride, and methyl, ethyl and isopropyl alcohols.

One further caution. Polysulfone is not recommended for outdoor use. It degrades quite rapidly unless it is protected against attack from ultraviolet rays. Ordinary window glass screens out ultraviolet ray frequencies harmful to polysulfone, thus permitting it to be used indoors with little concern. So much for the negatives.

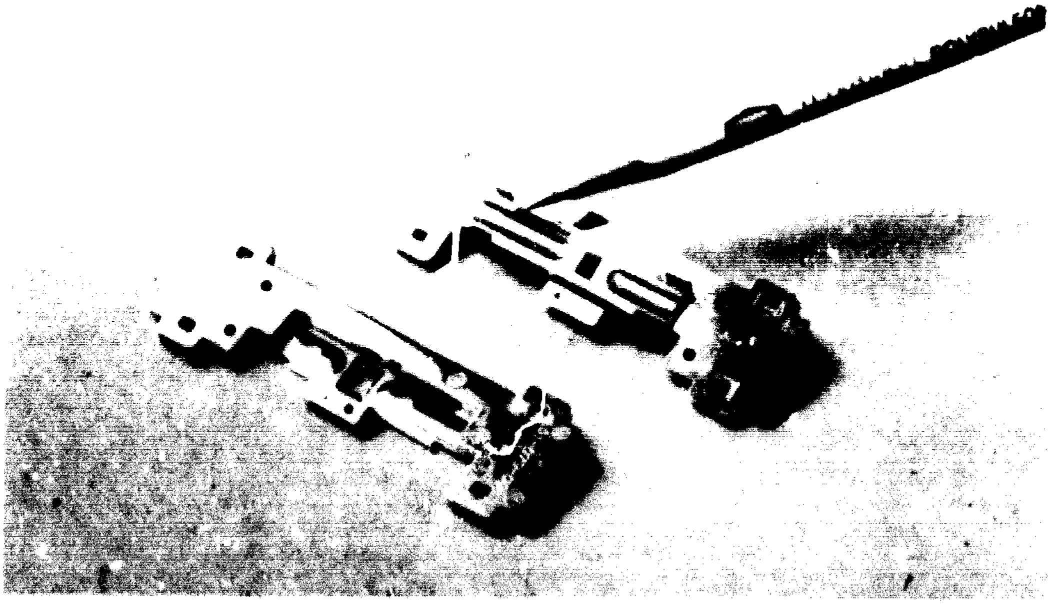
Polysulfone's most celebrated property is its exceptional thermal stability. Its heat distortion temperature is 174°C. (345°F.). Underwriters' Laboratories lists polysulfone for continuous use at 150°C. (302°F.), and depending on the grade, also rates it SE-0, which means self-extinguishing almost at once. When burning, it does not drip and emits little smoke. Incidentally, polysulfone has low heat transmission; it makes a useful lamp-shade, for instance.

Most early applications for polysulfone were considered because of its heat resistance. Usually it was some piece of hardware, often electrical or electronic and normally small and intricate. Examples include connectors and switch housings where miniaturization required precision molding and excellent dimensional stability. Another typical application was integrated circuit carriers. These small and intricate parts protect the delicate leads and hold integrated circuits during testing and "burn-in" operations where test temperatures range from -100° to 150°C. (-148° to 302°F.). (Slide 3: Integrated Circuit Carriers.) The carriers were originally made of diallyl phthalate, but this material required transfer molding. Polysulfone provided a way to reduce fabrication costs. It was the only thermoplastic that met the stringent requirements of this application, which also included excellent dielectric properties.

Polysulfone's heat resistance can also be measured in terms of thermal endurance. Under long-term aging, some properties actually improve. For instance, after two year's continuous exposure at 149°C. (300°F.), tensile strength at yield increases from 10,200 to 13,000 psi. Modulus of elasticity and heat distortion temperature also rise appreciably, while electrical properties remain constant.

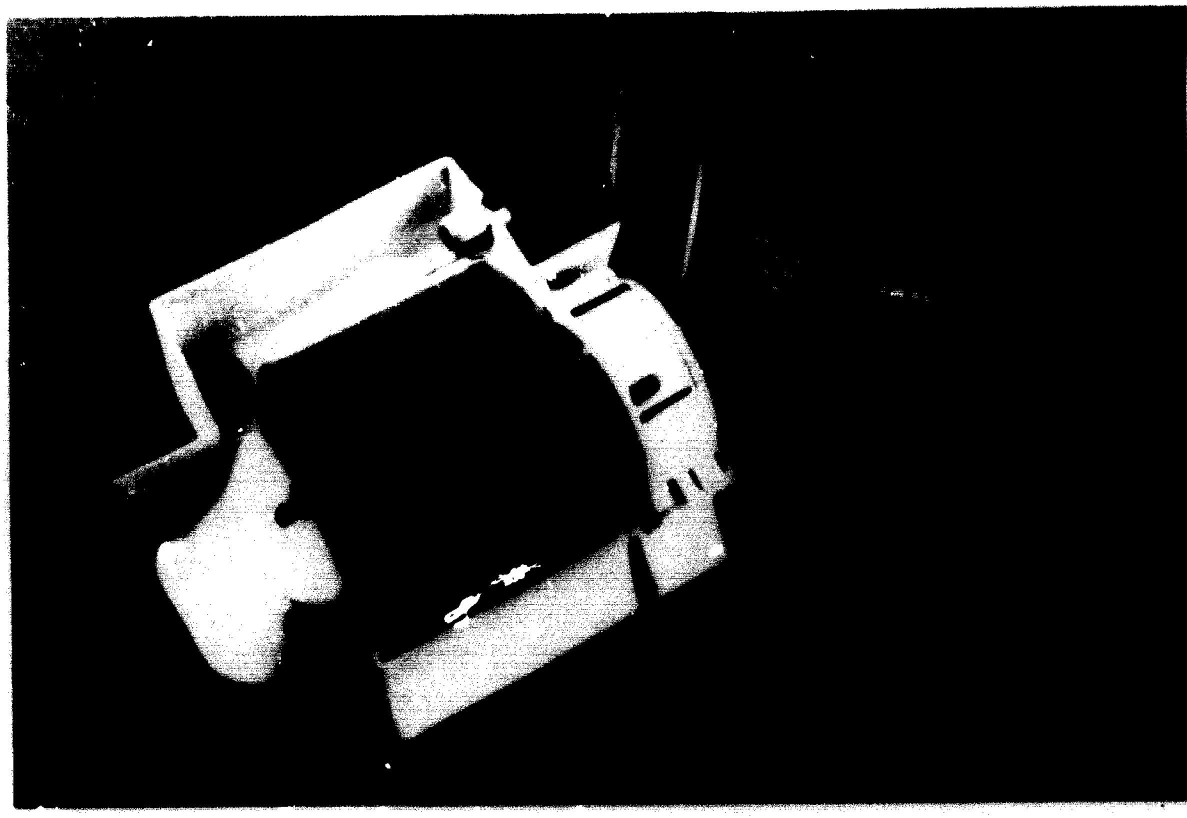
It was heat resistance that helped get polysulfone into its first big consumer application -- electric coffeemakers. (Slide 4: Clear Coffeemaker.) This coffeemaker has a clear polysulfone body. The term "clear" is used although polysulfone resins in their natural state produce transparent moldings which are light amber in color. Polymers of water-white transparency have not yet been successfully produced.

The coffeemaker application also capitalizes on polysulfone's resistance to boiling water and to staining -- normally a severe problem in brewing coffee. Unlike such plastic dishware materials as urea and melamine, polysulfone presents no staining or cleaning problems. It is unaffected in applications such as this home furnace humidifier (Slide 5: Home Humidifier), where it is alternately exposed to wet and dry conditions under varying temperatures.



Slide 3:
Integrated Circuit Carriers

Slide 4:
Clear Coffeemaker



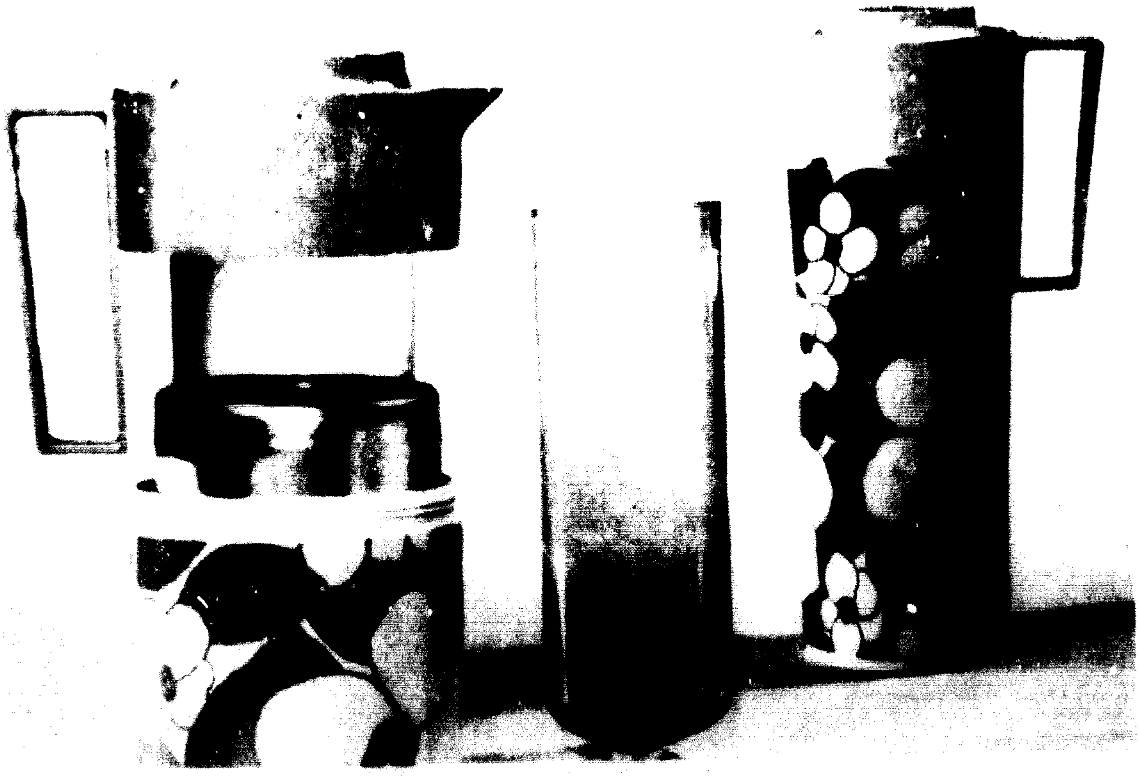
Slide 5: Home Humidifier

At room temperature it can be used in a water environment under a continuously applied stress of up to 3,000 psi and at intermittent stresses of 3,500 psi. As the temperature increases, the maximum recommended working stress decreases.

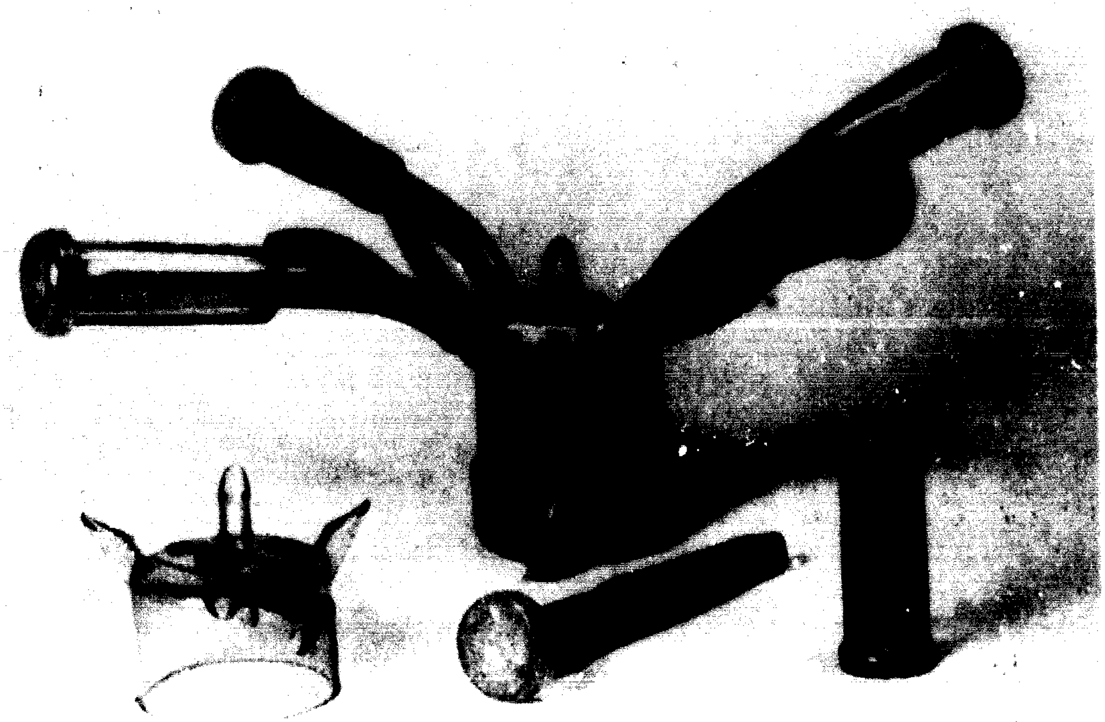
Other applications that require resistance to staining include reservoirs for hot and cold beverage dispensers, and as introduced earlier this year, the first plastic liner for a thermos container. Here is an injection molded part that brought about an entirely new design (Slide 6: Beverage Thermos Pitcher) -- a one quart thermos pitcher for hot or cold beverages. The inner shield of polysulfone protects the glass vacuum filler from the impact of metal stirrer or ice cubes.

The foregoing applications have no doubt indicated to you that polysulfone is approved for food use. That is correct. In the U. S., the use of polysulfone in repeated contact with food has been sanctioned by the Food & Drug Administration; for contact with potable water by the National Sanitation Foundation; and for use in milking equipment by the Dairy and Food Industries Association. Polysulfone does not impart any taste or odor to foods.

When used to replace stainless steel and glass parts in milking machines, polysulfone shows no loss in toughness or strength after 500 hours exposure to a two per cent detergent solution at 60°C. (140°F.) and 1,500 psi stress. It will not craze or crack when treated with cleaning and sterilization solvents. One new type of milker, designed to minimize bovine discomfort, employed polysulfone simply because it was lightweight. (Slide 7: Milking Machine.) It



Slide 6: Beverage Thermos Pitcher



Slide 7: Milking Machine

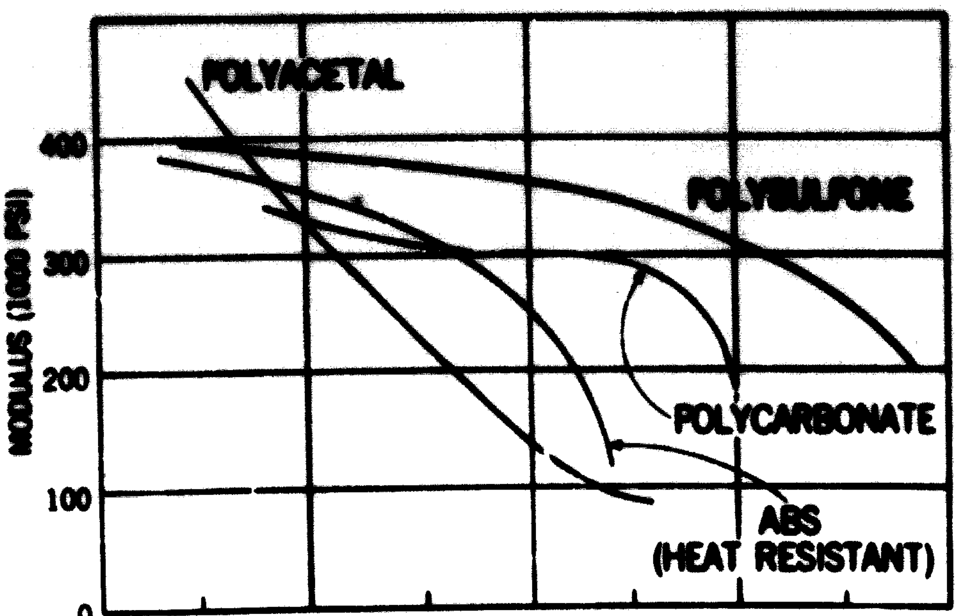
does the job stainless steel does in other milking machines but could not do in this new design because steel is too heavy.

The next major property area of polysulfone is strength. An interesting example of how ESB Company combined the strength and moldability of polysulfone is their new portable zinc-air battery designed for rapid recharging by replacement of the individual cells. (Slide 8: Battery Cells.) Each cell comprises two ribbed halves and an anode closure, all molded of polysulfone. The three parts are solvent-welded together. The battery, consisting of twenty cells inside a fiberglass case, withstands 26 four-foot drops without springing a leak. The application also requires resistance to the electrolyte, which is 31 per cent potassium hydroxide. Here again is an example of a product which simply could not have been manufactured without the existence of a really strong thermoplastic -- at least not at a reasonable cost.

Polysulfone has a tensile strength at yield of 10,200 psi. It also has a high modulus of elasticity in both flexure and in tension. Compared to other high performance plastics, only polyacetal has a higher flexural modulus. The following slide shows how the modulus of polysulfone compares with polyacetal, polycarbonate and heat resistant ABS plastics as the temperature increases. (Slide 9: Graph -- Flexural Modulus vs. Temperature.)

The notched Izod impact strength of polysulfone is approximately 1.3 foot-pounds per inch over a wide temperature range for thicknesses from 1/8 to 1/2 inch. In the unnotched Izod impact test, polysulfone will bend but will not break. The practical impact resistance of molded polysulfone is good as long as proper part design practices are followed. For example, generous radius of curvature should be used in support ribs and bosses, and abrupt

Slide 8:
Battery Cells



FLEXURAL MODULUS VS. TEMPERATURE

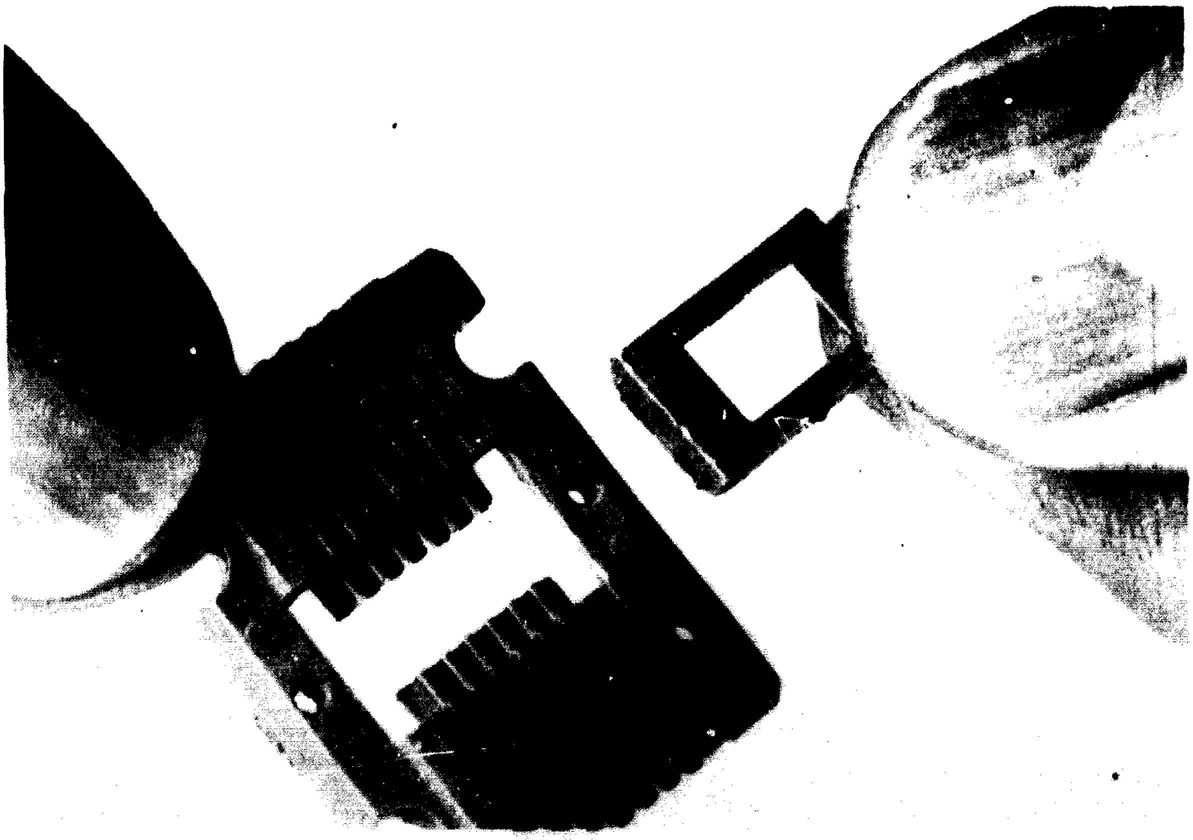
Slide 9:
Graph - Flexural Modulus vs. Temperatur

changes in part cross-section should be avoid[illegible]. Not[illegible] in a part design act as severe centers of stress [illegible] should be avoided wherever possible.

Polysulfone's strength can be increased by the addition of 10 to 40 per cent glass fibers. In addition to improving the solvent resistance, substantial increases in both tensile and flexural moduli result. Glass-filled polysulfone parts are being used in automotive applications where impact or under-the-hood conditions warrant the higher values. For example, glass-filled polysulfone is being used for the one-piece molded housing of the ignition switch now used on all General Motors' cars.

Polysulfone can be electroplated using techniques somewhat more involved than those for ABS and other plastics. Plating improves the surface hardness of polysulfone parts. This has been demonstrated recently in two demanding applications -- an aperture plate for a film projector by Technicolor and a computer print wheel for I/O Devices Company. (Slide 10: Aperture Plate.) Tolerances are close for the aperture plate, which must hold its exact dimensions even when subjected to the heat of the projector lamp, 100°C. (212°F.). The required wear resistance was provided by the metal plating; 400 hours contact is the minimum requirement. (Slide 11: Print Wheel.) The impact print wheel, used for high-speed computer printing, has 96 raised characters on its surface. These wheels operate at 30 to 50 characters per second and have logged over 10 million impressions per character without breakdown.

Polysulfone has outstanding dimensional stability. Parts have been



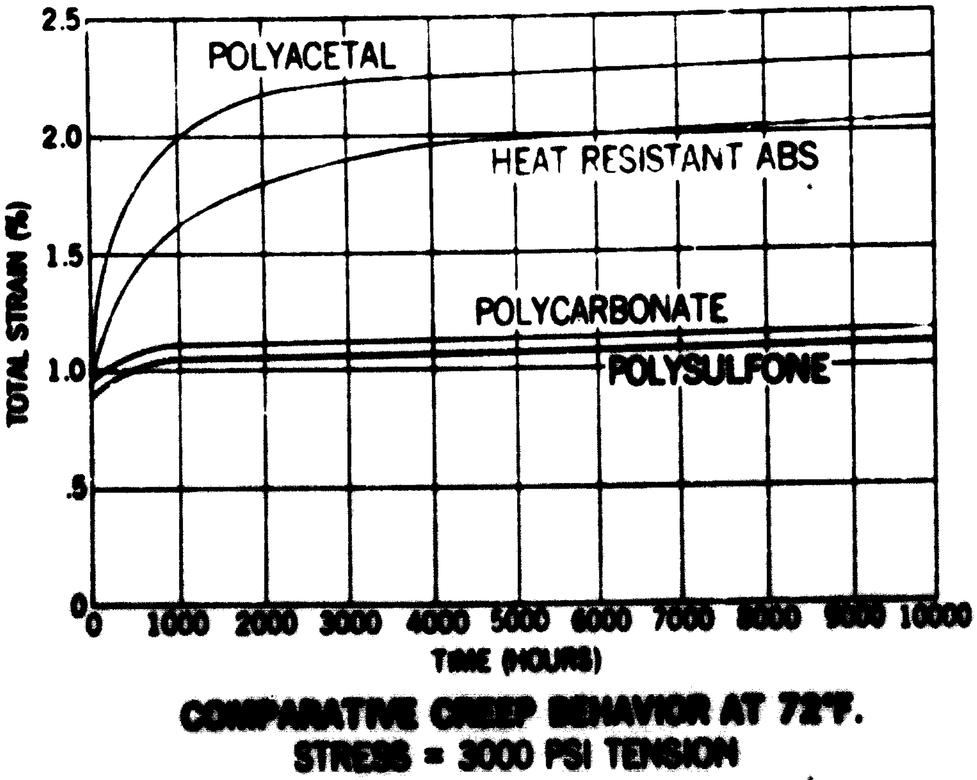
Slide 10:
Aperture Plate

Slide 11:
Print Wheel

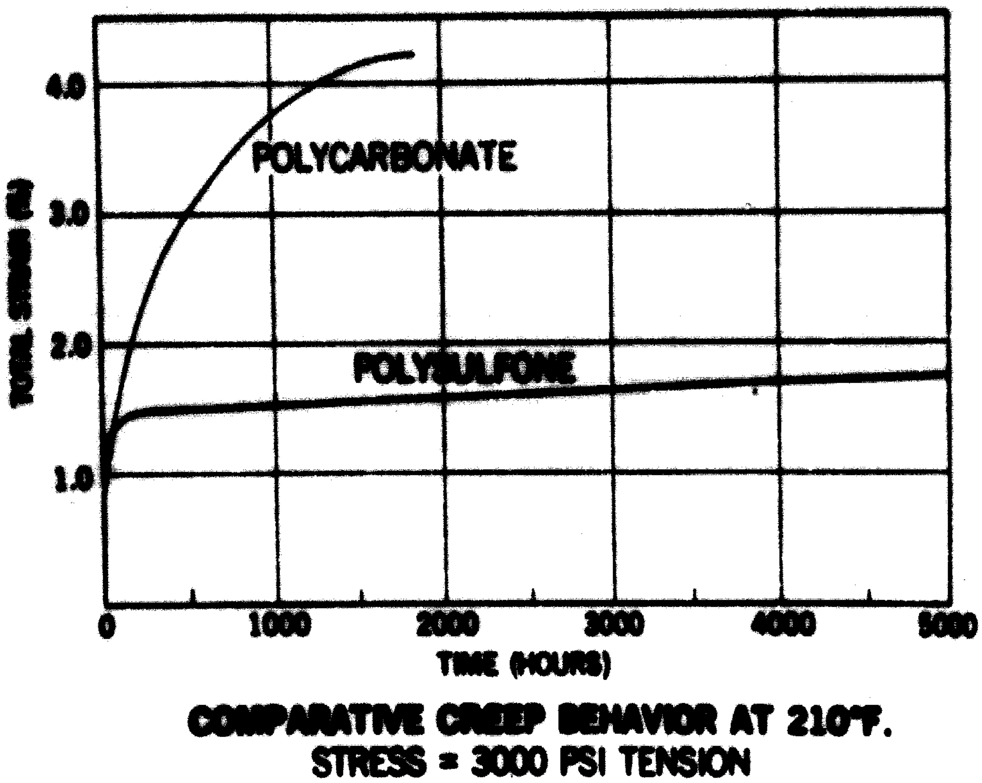
molded to tolerances as low as two thousandths of an inch. This is possible in part because polysulfone's mold shrinkage is very low and completely predictable. In addition, polysulfone has the lowest creep of any thermoplastic. (Slide 12: Comparative Creep at 22°C. [72°F.].) Comparing polysulfone with other high performance plastics again, one sees that at room temperature polysulfone and polycarbonate are quite close in creep. (Slide 13: Comparative Creep at 99°C. [210°F.].) However, at a temperature of 99°C. (210°F.), again with 3,000 psi stress, polysulfone is superior. It still demonstrates nearly linear behavior. It should be noted that, because of this low creep, any stresses introduced during molding are permanently locked in, sometimes reducing resistance to stress cracking. This problem can be eliminated by annealing which provides several benefits -- major improvement in chemical resistance, and improved strength and resistance to severe thermal cycling. Annealing can be done by immersion in mineral oil or glycerine at 166°C. (330°F.) for one to five minutes, depending on the thickness of the parts. Air annealing at the same temperature requires two to four hours.

Thermoplastics processors should be aware of two major considerations when using polysulfone. (Slide 14: Molding of Polysulfone.) First, the resin must be dried thoroughly before processing, a requirement common to most engineering thermoplastics. And second, higher temperatures are naturally required for molding, extruding or thermoforming. However, no equipment modification is necessary.

Molding undried material will cause defects in the form of silver



Slide 12: Comparative Creep at 22°C (72°F)



Slide 13: Comparative Creep at 99°C (210°F)

MOLDING OF POLYSULFONE

PREDRYING NECESSARY

SCREW MACHINES PREFERRED

STOCK TEMPERATURE 625°F. - 750°F.

MOLD TEMPERATURE 200°F. - 320°F.

MAXIMUM PRESSURE

REGRIND CAN BE USED

Slide 14: Molding of Polysulfone

streaking, "splay" or splash marks on the surface of the molded parts. Extruded sheet or profiles will show surface streaks of bubbles. The physical properties of polysulfone are not degraded by fabricating "wet" material. Satisfactory parts can be produced from reground material provided it is properly dried before fabricating.

Moisture content should be reduced to less then 0.09 per cent to produce parts with a satisfactory finish. The optimum moisture content of 0.05 per cent should be attained whenever possible. Polysulfone pellets can absorb up to 0.3 per cent atmospheric moisture. Air temperatures in the range of 135° - 166°C. (275° - 330°F.) must be used to remove that moisture. These temperatures will not have any adverse effects upon the properties of the material. For low volumes of resin, oven drying can be used. Hopper drying is recommended for high volume molding lines and for extrusion. A dehumidifier will shorten drying time by 15-20 per cent. Here is a brief guide to drying times and temperatures: at 166°C. (330°F.), two hours are required; at 149°C. (300°F.), 2-1/2 hours; at 135°C. (275°F.), 3-1/2 hours.

Screw machines are preferred for injection molding. There are several reasons: heat history is reduced, cycles are faster and longer flow parts can be produced. Plunger machines have been used successfully, but they should be operated at about 50-60 per cent of capacity to avoid excessively long heating times.

Polysulfone, like polycarbonate, maintains a relatively constant viscosity with increasing shear rate. This low degree of shear sensitivity, meaning that molecular orientation during flow is low, results in molded parts with uniform physical properties that vary little with direction of flow. It also results in a minimum of die swelling.

Stock temperatures must be high -- between 343° - 399°C. (650° - 750° F.). The resin is stable at these temperatures provided that residence time is not excessive. The run should be started with a cylinder temperature of 316° - 329°C. (600° - 625°F.), then gradually raised until acceptable mold fill-out is obtained. Maximum injection pressure will usually be required. Speed can usually be set at maximum as well.

Required mold temperatures will vary from approximately 99°C. (210°F.) for simple parts of at least 75 to 100 mils thickness to 149° - 160°C. (300° - 320°F.) for complex parts of long flow or thin cross-section. Mold fill-out is achieved mainly by increasing stock temperature, not mold temperature.

Some general observations are in order about mold design for injection molding. The main consideration is that flow restriction in the sprues, runners, gates, and mold cavities should be minimized. Molds should be fabricated from tough, hard, rigidly supported steels to withstand the high injection pressure frequently used for polysulfone. Chrome plating will preserve the finish and prolong mold life. Sprues should be short and relativ[illegible]ick. Runners should be full round or trapezoidal and as short as possible. It is more important to deliver resin to the cavities while it is still hot and fluid than to try to keep the same runner length to each cavity. To minimize voids and sink marks, gates should be located so that resin flow is from thick to thin sections, and they should be relatively large. Multiple gates are recommended when molding large or long thin sections.

A shrinkage factor of 0.007 inches per inch should be used in designing molds. However, you are probably wondering about those applications where polysulfone will replace an existing plastic material. Can you use the same molds? We offer these general guidelines. Excellent results can be expected from molds designed for polycarbonate. Molds designed for ABS usually work well, but sometimes it is necessary to open gates and runners. Gate-runner design in molds for polyacetal is satisfactory, but shrinkage will be lower. Normally both the gate opening and runner system will require enlarging in molds designed for polypropylene and nylon.

Polysulfone is being extruded into sheet, thin capacitor film, pipe and other profiles, and wire insulation. Again, temperatures are high, ranging up to 410°C. (770°F.) for wire coatings and thin films. Standard machines that produce a melt processing temperature range of 302° - 357°C. (575° - 675°F.) are normally used. Low compression ratio screws work best; polyolefin screws should be avoided.

Any conventional thermoforming method can be used, such as straight vacuum, pressure, or plug assist. Sheet more than nine mils thick, or which has been stored at ambient conditions for 8-16 hours will normally require drying. To eliminate a separate drying step, the ideal method of operating is to integrate the thermoforming with the sheet extrusion process.

It is hoped that these processing notes have made it clear that polysulfone can be successfully handled by an experienced thermoplastics processor. It is not necessary to make any investment in new equipment or modifications, with the possible exception of provision for drying.

In the course of reviewing the major properties of polysulfone, we have looked at a wide variety of applications. Many others could be mentioned, such as aircraft interior appointments that must be self-extinguishing and hair curlers which need dry heat resistance. Extruded products represent a small applications area at present, consisting mainly of specialty thin-walled wire insulation and extruded pipe for a laboratory animal's watering system.

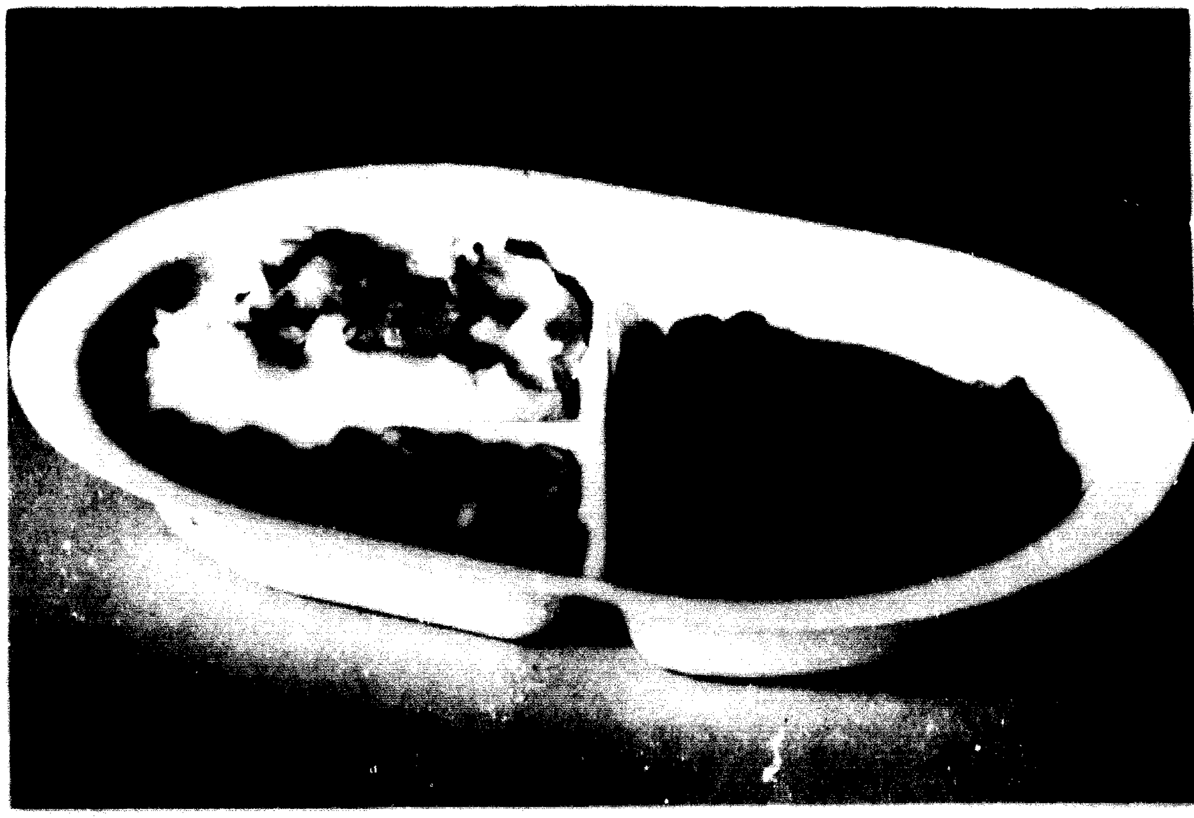
The many applications we have seen here bring us up to the present, wherein about half of these have been introduced within the past year. The future holds continued expansion in the appliance, automotive, electrical and other markets mentioned. But there are also some exciting new things on the horizon. One of these is still in the developmental stage. It is an application that has an enormous market potential: food trays. The food service industry has grown tremendously in the United States in recent years. Tens of millions of food containers will be used this year, serving individual meals on airlines and in hospitals and institutions. They are used in the growing food vending machine area and are also used for home consumption, as the variety of frozen dinners and individual gourmet food items continues to expand. Polysulfone is being made into a new container for this market, a single-use container that offers the ultimate in convenience. It is the one tray that can be used throughout the food handling cycle. That cycle consists of many operations. The food is loaded into the tray and the tray is sealed, frozen, shipped, reheated and finally served. Single-use trays made of polysulfone can be used for this entire cycle, without compromise. The trays will stand up to both freezing temperatures as low as -101°C. (-150°F.) and reconstitution temperatures. In conventional ovens they will withstand 204°C. (400°F.) and they can also be used in microwave ovens. The trays are heat-sealable using conventional techniques and sealing materials. In addition, the trays make attractive serving dishes as well.

(Slide 15: Food Tray.)

There are a host of food tray materials. Each has certain drawbacks. Many of them -- aluminum, some plastics -- cannot be used in microwave ovens. . . but polysulfone is transparent to microwaves. Paper and many plastic containers cannot be used in conventional ovens and most of these are not attractive for serving. Polysulfone, however, makes a handsome serving dish. It can be thermoformed into a wide variety of shapes and can be embossed and printed for special design characteristics. The color possibilities are endless, although a special China White is usually preferred. These trays are tough, too; in gauges as thin as nine mils they resist puncturing, wrinkling and crumpling.

The food tray shown was thermoformed from sheet stock in an aluminum mold on standard equipment. It can be handled with existing kitchen facilities. The user is buying convenience and in the case of institutional use, convenience means complete elimination of food transfer. By eliminating those operations labor costs are significantly reduced, which makes this new application so very attractive.

In the food trays we see most of polysulfone's major features: heat resistance, toughness, food contact approval, processability and excellent appearance, along with the bonus of its transparency to electrical high frequency microwaves. In the seven years since polysulfone has been commercially available it has developed from a material selected mainly for its extreme heat resistance to one which brings many features to bear in solving design problems. Because of its superior properties, it is replacing many other plastics in



Slide 15: Food Tray

numerous applications. It is also recognized as an excellent replacement for various metals because of the ecological and economical advantages it offers. We think the possibilities for polysulfone have only just begun.

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