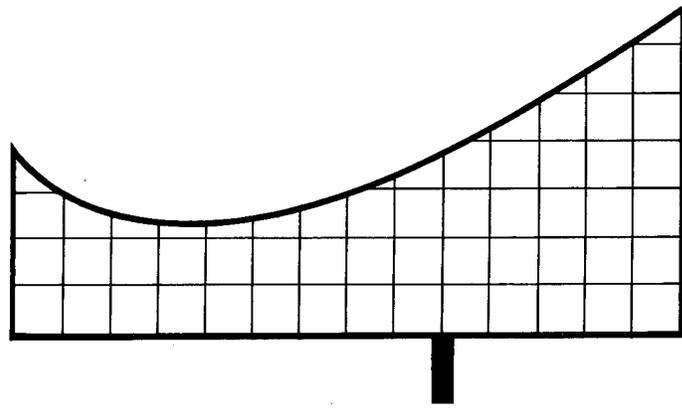


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plastics technical service

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PLASTICS TECHNICAL EVALUATION CENTER  
PICATINNY ARSENAL, DOVER, N. J.

# DESIGN ENGINEERING WITH DOW PLASTICS



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# DOW *Plastiatics*

DOW'S CLINICAL APPROACH TO HEALTHY PLASTICS APPLICATION

## STUDIES OF GAS PERMEABILITY GIVE VALUABLE DATA ON MOLDING AND PACKAGING MATERIALS

Plastic barrier films often must have a specific resistance, or lack thereof, to gas and vapor passage, such as in the packaging of aerosols, carbonated beverages, and foods. Data on gas permeability, provided by Dow Plastiatics studies, will be of value to plastics engineers and designers in the selection of proper barrier materials for use under known environmental conditions.

In the process of permeation—involving solution of the gas in the barrier material, diffusion through the barrier, and escape as a gas from the opposite side—permeability (rate of gas passage through a barrier of unit thickness) is a function of the diffusion rate and solubility of the gas in the barrier. Variables which affect permeability include temperature of the system, composition of the barrier, and size, shape and configuration of both the barrier molecules and gas molecules.

The general equation for gas transmission through a barrier is:

$$R = \frac{\bar{P} A \Delta p}{d}$$

where R = Maximum allowable gas transmission

$\bar{P}$  = Coefficient of gas transmission

A = Transmission area

$\Delta p$  = Pressure differential across barrier

d = Thickness of barrier

This equation may be used to specify or evaluate the degree of resistance to gas passage obtained from a plastic material. However,  $\bar{P}$  of the material must be measured experimentally. For example,  $\bar{P}$  data for Saran Wrap\* 7 and for Dow Polyethylene 610M are plotted on the basis of

$$\frac{\text{cc} - \text{mil}}{100 \text{ in.}^2 - 24 \text{ hrs.} - \text{atm.}}$$

in Figure 2.

Different sets of units are found in existing literature on permeability, and Figure 1 provides conversion factors for reducing the various units to common values.

Continuing Plastiatics studies by Dow Plastics Technical Service Engineers are constantly developing new data on gas permeability of Dow packaging and molding material. For further information on these studies, write THE DOW CHEMICAL COMPANY, Midland, Michigan, Plastics Sales Department 1800FT4.

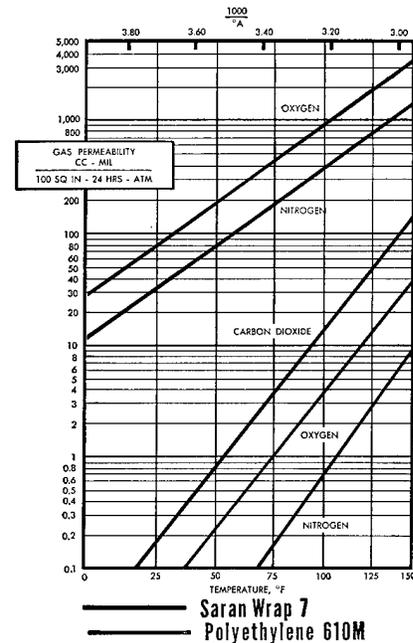


Fig. 2 Coefficients of Gas Transmission of Saran Wrap 7 and Polyethylene 610M, for various gases and temperatures.

### AMERICA'S FIRST FAMILY OF THERMOPLASTICS

- Styron® ●
  - Zerlon\* ●
  - Ethocel® ●
  - Tyril® ●
  - Polyethylene ●
  - PVC Resins ●
  - Pelaspas® ●
  - Saran ●
- \*Trademark

Fig. 1 Conversion factors for reducing permeability units to common values.

TO OBTAIN	MULTIPLY					
	$\frac{\text{cc-mm}}{\text{m}^2\text{-sec-cm Hg}}$	$\frac{\text{cc-mm}}{\text{m}^2\text{-sec-atm}}$	$\frac{\text{cc-mm}}{\text{m}^2\text{-24 hr-atm}}$	$\frac{\text{cc-mil}}{100 \text{ in}^2\text{-24 hr-atm}}$	$\frac{\text{cc-mil}}{\text{m}^2\text{-24 hr-atm}}$	$\frac{\text{cu in-mil}}{100 \text{ in}^2\text{-24 hr-atm}}$
$\frac{\text{cc-mm}}{\text{m}^2\text{-sec-cm Hg}}$	1.0	$1.32 \times 10^{-2}$	$1.52 \times 10^{-7}$	$6.00 \times 10^{-6}$	$3.87 \times 10^{-9}$	$0.98 \times 10^{-6}$
$\frac{\text{cc-mm}}{\text{m}^2\text{-sec-atm}}$	76.0	1.0	$1.16 \times 10^{-5}$	$4.56 \times 10^{-6}$	$2.94 \times 10^{-7}$	$7.47 \times 10^{-5}$
$\frac{\text{cc-mm}}{\text{m}^2\text{-24 hr-atm}}$	$6.57 \times 10^6$	$8.64 \times 10^4$	1.0	0.39	$2.54 \times 10^{-2}$	6.45
$\frac{\text{cc-mil}}{100 \text{ in}^2\text{-24 hr-atm}}$	$1.67 \times 10^7$	$2.19 \times 10^5$	2.54	1.0	$6.45 \times 10^{-2}$	16.4
$\frac{\text{cc-mil}}{\text{m}^2\text{-24 hr-atm}}$	$2.58 \times 10^8$	$3.40 \times 10^6$	39.4	15.5	1.0	$2.54 \times 10^2$
$\frac{\text{cu in-mil}}{100 \text{ in}^2\text{-24 hr-atm}}$	$1.02 \times 10^6$	$1.34 \times 10^4$	0.16	$6.10 \times 10^{-2}$	$3.94 \times 10^{-3}$	1.0

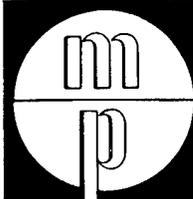
See "The Dow Hour of Great Mysteries" on NBC-TV

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**GAS TRANSMISSION**  
**BY**  
**PLASTICS FILMS**

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# Gas transmission by plastics films

By W. E. Brown<sup>†</sup> and W. J. Sauber<sup>†</sup>

Apparatus that provides simplicity, sensitivity, speed, flexibility, and automation is described for the determination of rate of gas transmission by plastics films. For these reasons, it is considered to be a practical, useful instrument for the packager and the material supplier in day-to-day measurement of gas transmission without sacrificing the requirements of a good research and development tool. Data for typical gas transmission rates of plastics films are presented.

The transmission<sup>1</sup> of gases by plastics is particularly important in food packaging; the choice of plastic will affect the shelf life of the product directly. For example, extremely low oxygen permeability is desirable in packages for nuts, processed meats, and other fatty or oily foods to prevent oxidation and rancid taste. Conversely, high permeability plastics are needed in packages for vegetables that must breathe to maintain their freshness. Similarly, fresh meats need plenty of oxygen to keep their bright red color.

Gas transmission was studied as early as 1866 by Graham. His work

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<sup>†</sup>Plastics Technical Service, The Dow Chemical Co.

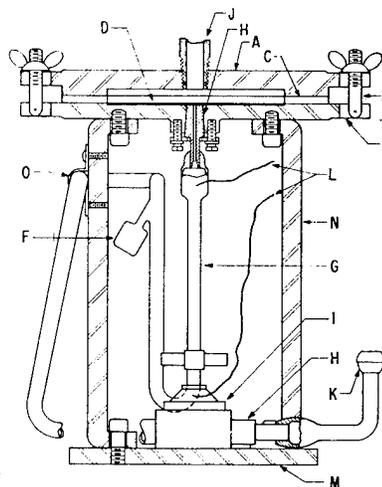
<sup>1</sup>There are many references which quote "gas permeability rates, P," in a multiplicity of units. P is almost universally related to unit thickness. This is not always true of gas transmission rates and is not a recommended procedure in ASTM D 1434-56T. Otherwise, gas transmission rate is equivalent to gas permeability.

<sup>2</sup>Nonetheless, two interesting analytical methods have been recently treated in the literature and deserve mention here. Landrock and Proctor (7) approximated conditions prevailing in and around packages with a refined mixed-gas analysis method. Kirshenbaum and Streng (6) studied permeability of elastomers with radioactive carbon (C-14).

dealing with the transfer of gases through rubber, shows that gas transmission is hardly a new problem. However, gas barrier materials available in Graham's time were far more permeable to gases than the present-day highly impermeable films such as saran, polyethylene terephthalate, saran-coated cellophanes, and others. Thus, the problem of measurement is more difficult now than before.

There are several ways of measuring the gas transmission rates of today's plastic molding materials and fabricated products: 1) thermal conductivity; 2) refractive index; 3) mass spectrometry; 4) gas analysis by chemical means; and 5) pressure-volume-temperature (PVT). For various reasons, mostly cost, all the foregoing methods, except the pressure-volume-temperature type, are impractical for day-to-day usage. As a result, the measurement of pressure, volume, and temperature of the transmitted gas has become the most popular procedure.<sup>2</sup> Even within

the PVT type of determination, there are several modifications which are described below. Each of these has its special advantages or design features. Some of the earlier work with



**FIG. 1:** Cross-sectional view of gas transmission apparatus. A—upper plate; B—lower plate; C—rubber gasket; D—porous filter paper with film to be tested over the paper; E—swivel bolts; F—mercury storage reservoir; G—calibrated portion of instrument; H—Kovar connection between steel and glass; I—Demi-G valve; J—freon tight tubing carrying gas to the film to be tested; K—vacuum pump attachment; L—lead wires to Brown recorder; M—base plate; N—stainless steel supporting legs; and O—the glass supporting clip.

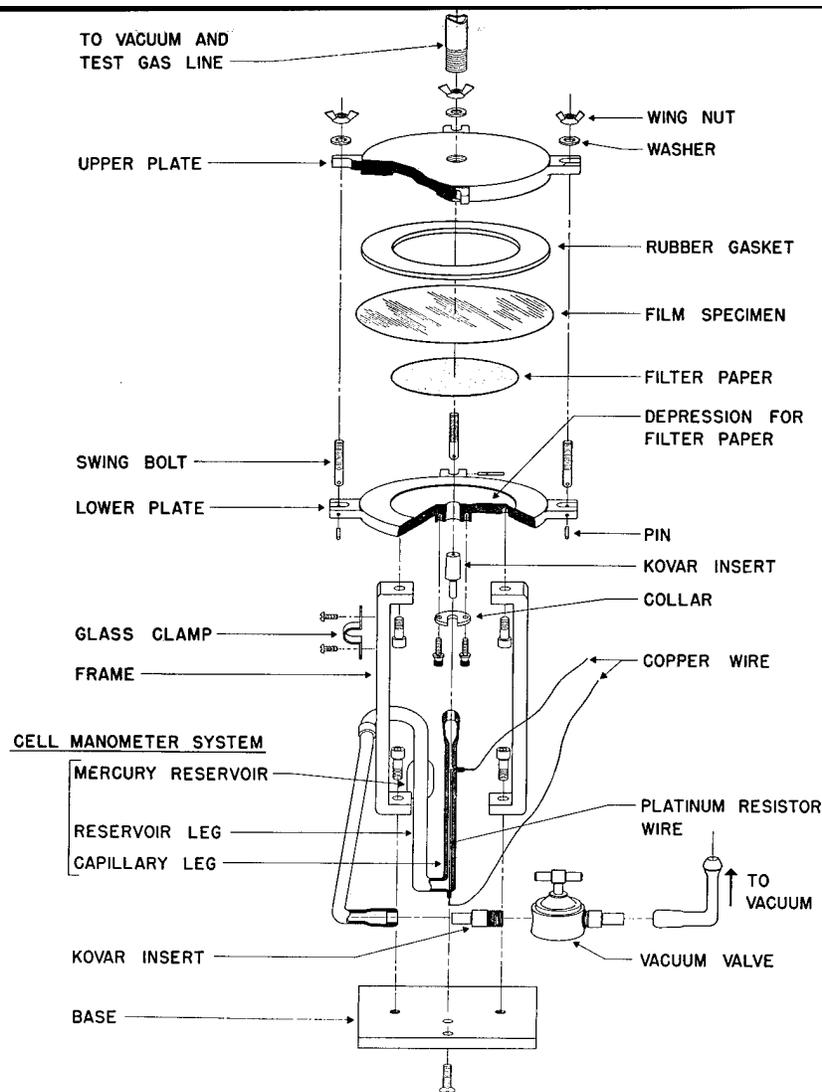


FIG. 2: Exploded view showing detailed construction of the cell.

synthetic polymeric films was reported by Elder (4).<sup>3</sup> He described a manometric system, subsequently called the General Foods cell, in which the test gas was continuously passed over the sample. The sample was supported over a glass manometer having a mercury-capillary center-tube.

In 1944, Shuman (12) described the same apparatus in greater detail claiming greater sensitivity and capability of measuring very low permeability constants.

Todd (15) pointed out that the method of Elder and Shuman permitted a decrease in pressure differential across the film from the start to the finish of the test, thereby resulting in a progressively lower transmission rate. Todd simply reversed the flow of gas in the manometer system. The gas was contained ahead of a column of liquid in a glass capillary. In

<sup>3</sup>Numbers in parentheses link to references at end of article, p. 116.

addition, the transmitted gas was collected on the opposite side of the film in a large, initially-evacuated chamber.

Cartwright (3) produced a cell that was said to be six times more sensitive than previous instruments. He indicated that the movement of the liquid column in the Todd apparatus was affected by small changes in temperature and barometric pressure. Cartwright's cell was similar in principle to that of Elder and Shuman, consisting of glass components with ground-glass joints carefully fitted and lubricated.

Sarge (10) extended the sensitivity of a manometer-type cell down to a range suitable for measuring gas transmission rates of extremely slow-transmitting polymers such as saran. This device also was similar in principle to the Elder-Shuman cell, but had the additional advantage of greater sensitivity at low transmission

rates and greater structural durability.

Brubaker and Kammermeyer (1, 2) developed a rugged apparatus which they claimed to be insensitive to leaks and independent of precise regulation of gas flow. These authors showed that rapid measurements could be made of helium and hydrogen transmission through a series of selected polymeric films. Park (9) designed a semimicro unit on similar principles.

More recently, Stannett, Szwarc, and co-workers (5, 13, 17) published several papers on the permeability and diffusion rates of a variety of gases and vapors through a variety of films and coated papers. Their technique leads to basic, absolute data by virtue of the design of the equipment and the method of operation. Essentially, it is a pressure-volume-temperature method in which gas is introduced at relatively high pressures on one side of the film and allowed to permeate to an evacuated, large-volume, low-

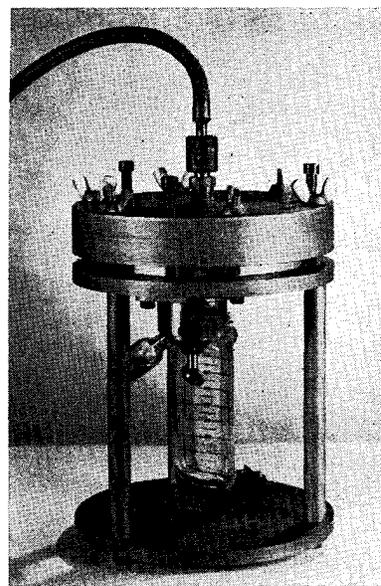
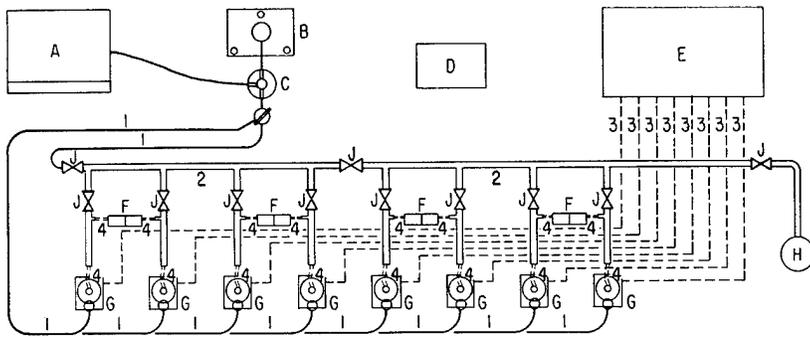
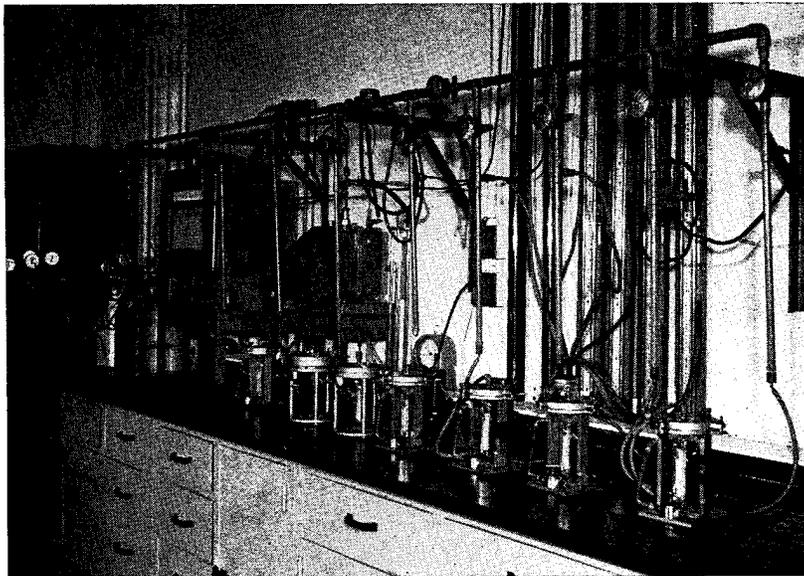


FIG. 3: This is the presently-used Dow gas transmission cell. It differs slightly in design from the one shown in the cross-sectional (Fig. 1) and exploded (Fig. 2) views in that the upper plate has been modified so that an O-ring gasket could be used to isolate the specimen from the atmosphere. In addition, the position of the vacuum valve has been changed to keep spillage of mercury into the mechanism to a minimum.



**FIG. 4:** Schematic view of an 8-cell multiple automatic gas transmission unit. Very little attention is required as soon as the determination is started and simultaneous determinations can be made on a variety of specimen-gas combinations. **A**—Welch duo seal vacuum pump; **B**—Du Brovin vacuum gage—to measure vacuum in cell; **C**—trap; **D**—barometer; **E**—Brown 8-point automatic recorder; **F**—mercury manometers—to measure pressure on gas side of membrane; **G**—gas transmission cells; **H**—gas cylinders; **J**—special freon tight valves; **1**—single solid lines indicate rubber tubing; **2**—double lines indicate copper tubing; **3**—dotted lines indicate electrical wiring; **4**—double dotted lines indicate freon tight tubing.



**FIG. 5:** The multiple automatic unit described in Fig. 4.

pressure, measuring system on the other side of the film. Volatile components which may be emitted from the film are condensed to prevent interference with calculation of the true gas transmission rate. The relatively long time required for a determination and the relatively high cost per cell makes this method less desirable for industrial service although it has great value in research.

#### Description of apparatus

Essentially, features of many of the above described PVT cells have been borrowed, combined, and further modified to produce a unit that: 1) provides an accurate measure of the transmission rate of films, sheets, and molded speci-

mens; 2) permits determinations of extremely low to extremely high transmission rates; 3) incorporates automatic recording to make the unit essentially self-operating; 4) provides for rapid determinations regardless of transmission rate; 5) provides a rugged design suitable for the industrial laboratory; 6) requires no highly specialized operating skills; and 7) allows adaptation to a multi-cell system.

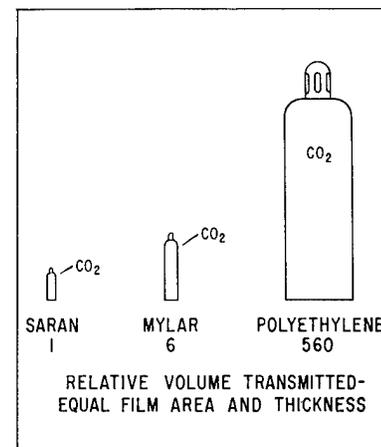
Such an instrument has been designed and adopted by the American Society for Testing Materials Committee D-20 as the preferred method of ASTM D 1434-56T "Tentative Method of Test for Gas Transmission Rate of Plastic Sheet-ing." A cross-sectional view, an exploded view, and a photograph

of the cell are shown in Fig. 1, p. 107; Fig. 2, p. 110; and Fig. 3, p. 110, respectively.

#### Operation of apparatus

Prior to admission of the test gas, evacuation to less than 0.2 mm. of mercury pressure on both the high and low pressure sides of the cell is completed. After the cell manometer system has been evacuated, mercury is dumped from the reservoir into the manometer legs. A relatively large volume of gas is admitted from the high pressure side of the cell to the specimen (which may be a film, sheet, or laminate) clamped between the upper and lower plates. The underside of the specimen is supported by filter paper to facilitate collection of the test gas. The specimen test area is defined by the upper and lower clamping plates, a gasket, and the filter paper. With a pressure differential existing across the specimen, gas will be transmitted. After passing through the specimen the gas is collected in the cell manometer system. As the pressure of the transmitted gas rises in the manometer, the mercury level in the capillary leg falls and the excess mercury spills into the reservoir, thus maintaining a constant head in the stationary leg. The pressure on the low pressure side increases from zero to some finite value.

It now remains only to measure the pressure rise in the manometer



**FIG. 6:** Gas transmission of films varies greatly. Gas transmission rates are depicted here as gas cylinders of a size required to hold the relative amounts of gas that were transmitted.

system as a function of time. A pressure-time curve may be obtained visually with the help of a cathetometer, or instrumentally with an autographic electrical resistance recorder.<sup>4</sup> The latter method is more convenient in operating the eight-cell system shown in Figs. 4 and 5. The pressure in the vacuum system and the pressures of the test gases are measured with a Du Brovin gage and 2-atmosphere manometers, respectively. Atmospheric pressure is measured with a recording barometer. The mercury height is plotted automatically with an eight-point recorder connected, as mentioned in footnote 4, to platinum resistance wires in each of the cell manometer systems.

A vacuum pump connected to each cell through appropriate piping is needed to evacuate the system above the specimen. The cell manometers may be evacuated individually through rubber tubing from the vacuum system to any one of the cells. Any of a number of gases may be admitted to the

<sup>4</sup>A fine platinum wire is inserted through the center of the capillary leg with exterior connections leading to a recorder. The mercury shorts out the resistance wire and, through falling, yields a resistance change proportional to the height of the mercury.

<sup>5</sup>The calibration for a given cell would normally be supplied by the manufacturer.

high pressure side of a cell. A different gas may be admitted to each cell or combination of cells.

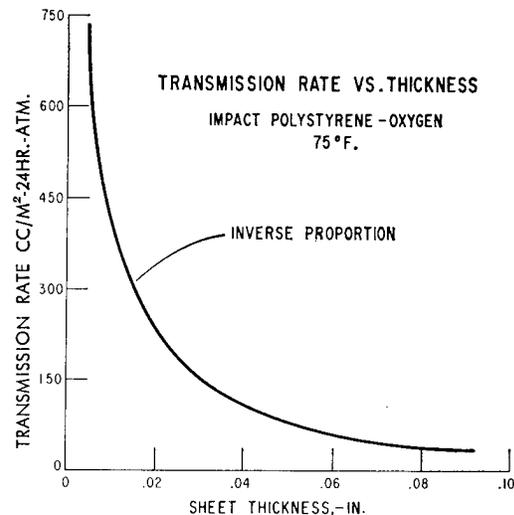
### Calculations

Gas transmission rate calculations involve simple multiplication and division of four quantities: 1) the cell constant; 2) the rate of change of the transmitted gas pressure (mercury height in the cell); 3) the gas conversion constant; and 4) the differential pressure across the film. (See p. 114 for complete derivation of equation used in the calculation of gas transmission rates.)

**Cell constant:** Most authors in the past have treated the calculation of gas transmission rates as the simple relationship,  $PV = nRT$ . In a determination of this nature, both the pressure of the transmitted gas and the volume that it occupies increase simultaneously but not at the same rate throughout the test. Therefore, these two variables must be treated in a differential equation. Based on the ideal gas law, a fairly simple derivation of the cell constant is:

$$\text{Cell constant} = \frac{2ah - a(h_L + h_B) - V_f}{A}$$

where  $a$  = area of capillary;  $h$



**FIG. 7:** Gas transmission rate is normally inversely proportional to specimen thickness. This rule may be used especially to compare films 1 to 5 mils thick, the range for many commercially available materials, and sheets whose thicknesses do not differ by a great amount.

= height of Hg in cell capillary leg;  $h_L$  = height of Hg in cell reservoir leg;  $h_B$  = height of capillary (cell manometer leg) from datum plane to B;  $V_f = V_{BC} + V_{CD}$  = total void volume from top of Hg cell capillary leg (B) to base of specimen; and  $A$  = area of transmission.

This constant is dependent only on the geometry of the cell, including film area, cell volume, and mercury height. It varies with the height of mercury in the manometer, but is linear with mercury height and thus can be shown as a straight line.<sup>5</sup>

**Rate of change of the transmitted gas pressure:** This rate corresponds to the change in height of mercury in the cell manometer with time which may be read visually in millimeters per hour or recorded autographically on a strip chart. In the latter case, the rate of change of pressure,  $dh/dt$ , is the recorder travel constant (or the rate at which the recorder pen moves with change in cell manometer height) times the rate of paper travel divided by the slope of the recorded curve.

**Gas conversion constant:** An appropriate gas constant depending upon the units desired to report gas transmission rate is used.  $T$  is normally reported as the absolute temperature in degrees Kelvin.

*Differential pressure across the*

**Table I:** Typical gas transmission rates of plastics films at 23° C. <sup>a, b</sup>

Plastic film	Gas transmission rates in cc./m. <sup>2</sup> -24 hr.-1 atm. <sup>c</sup>		
	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>
Cellulose acetate	350	1500	7800
Methylcellulose	1300	450	6800
Polyethylene			
0.917 density	2700		
0.950 density	1700		
0.960 density	1600	440	
Polyethylene terephthalate	50	8.4	240
Polystyrene	4500	640	11,000
Polyvinyl chloride, plasticized	190-3100	53-810	430-19,000
Polyvinyl chloride, rigid	120	20	320
Polyvinyltoluene	5700	1200	17,000
Rubber hydrochloride	390	62	1100
Saran	16	2.5	50
Styrene-acrylonitrile copolymer	900	120	2800

<sup>a</sup>Gas transmission rates depend especially upon composition of the film and, therefore, will vary with plasticizer type and content, molecular weight, molecular weight distribution, branching, and so forth. Thus, these rates must be considered only typical of a given film class.

<sup>b</sup>These rates were determined with dried gases. Moisture-sensitive films and those films that readily absorb water or water vapor usually exhibit gas transmission rates many times higher in the moist condition or in a moist gas atmosphere.

<sup>c</sup>Determined in accordance with ASTM method D 1434-56T; all films were 0.001-in. thick.

film: Our final consideration is the driving force of the gas. The differential pressure is simply the test gas pressure minus the cell pressure,  $P - P_t$ . As shown previously, the test gas pressure,  $P_t$ , is read conveniently from a manometer.

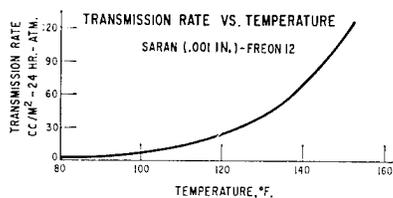


FIG. 8: As shown by this rectilinear plot, gas transmission rate of a film may vary with temperature.

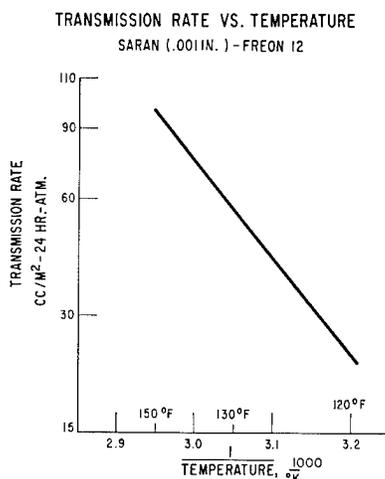


FIG. 9: The data in Fig. 8 have been plotted to produce a straight line. In regions where gases are perfect or nearly so, only 2 points are needed to determine the permeability rate over a wide range of temperatures. Three or four points are preferred, of course, to verify the slope, particularly as new materials are investigated.

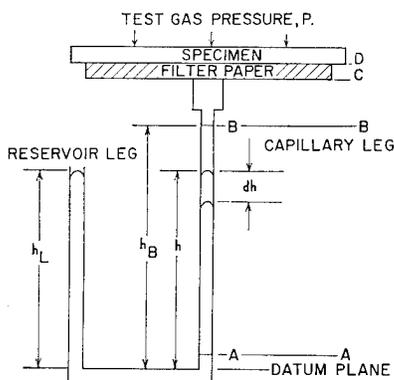


FIG. 10: Diagram of the system.

The internal cell pressure,  $P$ , is the height of mercury in the cell manometer.

### Review of gas transmission data

As mentioned previously, plastics are often chosen as packaging mediums primarily for their ability to permit or prohibit the transmission of certain gases. Various plastic-gas combinations show widely varying gas transmission rates (Table I, p. 113). Figure 6, p. 112, depicts the transmission rates of three films—saran, Mylar<sup>6</sup>, and polyethylene—as containers of a size required to hold the relative volumes of gas transmitted by specimens of equal area and thickness. Measurements of these extremes are possible with the previously described cell through varying the chart speed, the specimen test area, and the pressure of test gas applied on the film.<sup>7</sup>

Gas transmission rate is inversely proportional to specimen thickness as shown in the plot of oxygen transmission rate for various thicknesses of modified (impact grade) polystyrene sheet (Fig. 7). This general rule is especially helpful in comparing films up to 0.005 in. thick, the range for many commercially available materials.

Gas transmission rates vary significantly with temperature. As shown in the rectilinear plot (Fig.

<sup>6</sup>Du Pont brand of polyester film.  
<sup>7</sup>The cell may also be provided with inserts to change the void volume, and, therefore, the sensitivity.  
<sup>8</sup>Othmer and Frohlick (8) described a unique method of correlating and plotting permeability constants of gases through plastic membranes at various temperatures as  $\log \bar{P}$  versus a temperature scale derived from the vapor pressures of a reference liquid. The relationship:

$$\log \bar{P} = \left( \frac{E^* - \Delta H}{L} \right) \log p + C$$

where

- $\bar{P}$  = permeability constant,
- $E^*$  = energy of activation for diffusion,
- $\Delta H$  = heat of solution of the gas in the polymer membrane,
- $L$  = molar latent heat of reference liquid,
- $p$  = vapor pressure of reference liquid, and
- $C$  = a constant.

on which the method of plotting is based, yields a linear plot. Further treatment yields a nomogram in which a vast amount of data on various film-gas combinations can be plotted.

<sup>9</sup>It is much safer, of course, to verify such a relation with two or three additional points.

8, left), the transmission rate of saran increases rapidly with temperature of the transmitting gas. These same data plotted as the logarithm of the transmission rate against the inverse of the absolute temperature produce a characteristic straight line<sup>8</sup> (Fig. 9, left) derivable from the basic Arrhenius rate process relation:

$$\bar{P} = \bar{P}_0 e^{-E/RT}$$

$$\text{as } \log \bar{P} = \log \bar{P}_0 - \frac{E}{RT} \log e$$

For perfect gases only two points are needed to determine the transmission rate over a wide temperature range.<sup>9</sup> However, where the gas approaches its condensation point, the rate may unpredictably waver and even go up as lower temperatures are reached (13).

It has been shown that the gas volume transmitted through a film is directly proportional to the pressure across it; thus the rate, which accounts for pressure, remains the same. A sampling of data (Table II) shows that a constant rate is maintained for each gas (air, oxygen, or nitrogen) even though the pressure differential is varied. It is expected this will hold true only below those (high) pressures that cause distortion of the film.

Data from the literature (Table III, p. 116) were compared with those obtained with this cell. Good agreement was found when comparisons were made with data obtained by Stannett (14), Van Amerongen (16), and Brubaker and Kammermeyer (1, 2), which are believed to be among the most reliable published. Higher test temperatures no doubt account for the slightly higher rates reported by the latter authors.

### Derivation of equation

The symbols (see Fig. 10, left) used in the derivation of the equation for the calculation of gas transmission rates are as follows:

- $a$  = cross-sectional area of capillary AB, in square millimeters,
- $R$  = universal gas-constant,  $6.24 \times 10^7$  (cu. mm.  $\times$  mm.)/( $^\circ$  K.  $\times$  g.-mole)
- $T$  = absolute temperature, in degrees Kelvin,
- $n$  = quantity of gas transmitted, in moles,

**Table II:** Transmission rate independent of pressure differential. Data for 2-mil polystyrene film at 23° C.

Gas pressure differential	Transmission rate cc./m. <sup>2</sup> -24 hr.-atm.
Air	
1 atm.	450
2 atm.	450
Oxygen	
1/2 atm.	2320
1 atm.	2310
Nitrogen	
1 atm.	240
2 atm.	250

- t = time, in hours,  
 A = area of transmission, in square centimeters,  
 V<sub>CD</sub> = void volume of depression, in cubic millimeters,  
 V<sub>BC</sub> = volume from B to C, in cubic millimeters,  
 V<sub>f</sub> = V<sub>BC</sub> + V<sub>CD</sub>, in cubic millimeters,  
 V<sub>t</sub> = volume of transmitted gas, in cubic millimeters = V<sub>f</sub> + a(h<sub>B</sub>-h),  
 dP = -dh = differential pressure change of transmitted gas, in millimeters of mercury,  
 dV = -adh = differential volume change of transmitted gas, in cubic millimeters,  
 P = pressure of gas to be transmitted, in millimeters of mercury,  
 P<sub>t</sub> = h<sub>L</sub> - h = pressure of transmitted gas, in millimeters of mercury,  
 Pd = P - P<sub>t</sub> = driving force, in millimeters of mercury.

The number of moles of gas transmitted, n, may be determined from the ideal gas law (which is valid at the low pressure involved) as:

$$n = \frac{P_t V_t}{RT}$$

Or, for differential changes in P<sub>t</sub> and V<sub>t</sub>:

$$dn = \frac{P_t dV + V_t dP}{RT}$$

Substituting:

$$dn = \frac{-aP_t dh - V_t dh}{RT} = dh \left[ \frac{2ah - a(h_L + h_B) - V_f}{RT} \right]$$

Since the transmission rate is given by

$$\text{Rate} = \frac{dn}{dt}$$

and since the transmission rate must be reported per unit area, then A, the area of transmission, may be included here and the above equation for dn rewritten as:

$$\frac{dn}{dt} = \frac{dh}{dt} \left[ \frac{2ah - a(h_L + h_B) - V_f}{A} \right] \frac{1}{RT}$$

The expression in brackets is the cell constant.

The gas constant, R, and T are known at a given temperature. Thus, dn/dt reduces to dh/dt, which is determined experimentally, multiplied by two constants.

For determinations using a cathetometer: dh/dt = slope of the graph, where h is in millimeters and t is in hours.

For determinations using an electrical resistance recorder: dh/dt = (recorder travel constant × rate of paper travel)/(slope). The recorder travel constant and the rate of paper travel are determined by calibration in millimeters per inch and inches per hour,

respectively. Slope in this case is dimensionless.

Since the gas transmission rate is to be reported as cubic centimeters per square meter per 24 hr. per atmosphere at standard temperature and pressure °C., 1 atmosphere), dn/dt may be converted:

$$\begin{aligned} \text{Gas transmission rate} &= \frac{dn}{dt} \times \\ & \frac{(22,415 \text{ cu. cm.})}{(\text{mole})} \times \frac{10,000 \text{ sq. cm.}}{\text{sq. m.}} \\ & \times \frac{760 \text{ mm.}}{\text{atm. press.}} \times \frac{(24)}{(P - P_t)} \\ &= \frac{dn}{dt} \frac{4.08 \times 10^{12}}{(P - P_t)} \\ &= \frac{dh}{dt} (\text{cell constant}) \times \frac{4.08 \times 10^{12}}{(P - P_t)} \end{aligned}$$

### Acknowledgments

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**Table III:** Comparison of data

Film and gas	Gas transmission rate in cc./m. <sup>2</sup> -24 hr.-atm.	
	ASTM D 1434-56T Cell (23° C.)	Literature values (30° C.)
Saran		
Oxygen	16	13
Nitrogen	2.5	2.5
Mylar <sup>a</sup>		
Oxygen	50	57
Nitrogen	8.4	13

<sup>a</sup>Du Pont brand of polyester film.

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# DOW *Plastiatics*

DOW'S CLINICAL APPROACH TO HEALTHY PLASTICS APPLICATION

## CALCULATING CREEP AND STRESS RELAXATION FROM LONG-TERM DATA

For design engineers concerned with calculating the effects of stress and strain on plastics materials, particularly in designing for long-term applications, the Equations of State (Fig. 1) permit good approximations, to which, of course, will be added a reasonable safety factor.

Obviously, long-term strength data must be used in the equations, since short-term or elastic data do not correlate with long-term service. For example, in designing plastic lawnmower wheels, data obtained over a five-year period would normally be used because this period of time corresponds to a reasonable service life for this type of part. Below are examples of calculating stress, strain and the modulus of elasticity, using long-term data from Fig. 2. These are simple situations. Often shock, high temperatures or other environmental factors must also be taken into consideration.

**Example I:** A tensile stress of 1000 psi will be applied to a part made of Tyril 767. How much creep will occur during the first six months (4320 hours)? From Fig. 2, the Apparent Modulus at six months is 420,000 psi. Using Equation 2a (Tension):

$$E = \frac{S}{\epsilon} \text{ and } \epsilon = \frac{S}{E}. \text{ Then } \epsilon = \frac{1,000}{420,000} = 0.0024, \text{ or } 0.24\% \text{ elongation.}$$

**Example II:** Where a known strain is placed on a part, such as a bottle closure, calculate the remaining stress (resistance)

after one year. Assume the strain to be 0.42%. Apparent Modulus of Tyril 767 after one year is 380,000 psi.

$$S = E \epsilon = (380,000)(0.0042) = 1590 \text{ psi remaining.}$$

**Example III:** Creep is important in designing webbing and cloth from plastic monofilament. From Fig. 2, Apparent Modulus of Dow saran monofilament after 1½ years is 70,500 psi. Under a stress of 1000 psi, creep is then:

$$\epsilon = \frac{S}{E} = \frac{1000}{70,500} = 0.0142 \text{ in./inch, or } 1.42\% \text{ elongation.}$$

**Example IV:** In a hypothetical filter sump for a home water system, the filter must last five years, and operate at a maximum internal pressure of 75 psi. To insure a sufficient O-ring seal, total radial deformation of the sump must be less than 0.007 in., to prevent leakage. Tyril 767 has good long-term strength, ease of fabrication and low cost. Will it be satisfactory for this use? The design strength of Tyril 767 is 980 psi (from Fig. 2) over a period of five years (43,800 hours). From the following formula, solve for "P" (maximum allowable operating pressure).

$$P = \frac{S[r^2(b^2 - a^2)]}{a^2(b^2 + r^2)} = 120 \text{ psi.}$$

Where: a = Inner radius = 2.05 in.  
 b = Outer radius = 2.30 in.  
 r = Normal radius = 2.175 in.  
 v = Poisson's Ratio = 0.035  
 Δa = Change of inner radius, in.

S = (design) Hoop Stress, psi  
 P = (maximum allowable operating) Pressure, psi.

Thus, the maximum allowable operating pressure for Tyril 767 is well above the operational maximum encountered in the water system. To determine total radial change of the O-ring:

$$\Delta a = P \frac{a}{E} \left[ \frac{b^2 + a^2}{b^2 - a^2} - \nu \left( \frac{a^2}{b^2 - a^2} \right) - 1 \right] = 0.00225 \text{ inch.}$$

Not only is the five-year design strength of Tyril 767 adequate for this application, but it provides a safety factor of 1.6 for operating pressure, and of 3 for the O-ring seal.

Many long-term data of the type used in the examples above, are being developed by Dow Plastics Technical Service Engineers for use by plastics engineers and designers. Such continuing Plastiatics studies provide not only properties data, but also information on improved methods of design, molding and finishing of plastics. For more detailed information on these studies, write THE DOW CHEMICAL COMPANY, Midland, Michigan, Plastics Sales Dept. 1801CS7.

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### EQUATIONS OF STATE

I. To calculate simple stresses

(a) Stress in Tension; or in Compression  
 $S = \frac{P}{A}$  P = Applied load  
 A = Cross-sectional area of the part

(b) Stress in Flexure (rectangular beam)

(A) Simple support, center loading  
 $S = \frac{3PL}{2bd^2}$  P = Applied load  
 L = Distance between supports  
 b = Width of beam  
 d = Depth of beam

(B) Simple support, uniform loading  
 $S = \frac{3PLm}{4bd^2}$

(C) Cantilever beam, end loading  
 $S \text{ max.} = \frac{6PL}{bd^2}$  P = Applied load  
 L = Distance from load to support  
 b = Width of beam  
 d = Depth of beam

(D) Cantilever beam, uniform loading

$S \text{ max.} = \frac{8PL}{bd^2}$

2. To calculate modulus of elasticity in the above examples.

(a) Modulus in Tension; or in Compression  
 $E = \frac{S}{\epsilon}$  S = Stress  
 ε = Strain

(b) Modulus in flexure  
 (A) Simple support, center loading  
 $E = \frac{L^3m}{4bd^3}$  m = initial slope of flexure curve

(B) Simple support, uniform loading  
 $E = \frac{5L^3m}{32bd^3}$

(C) Cantilever beam, end loading  
 $E = \frac{4L^3m}{3bd^3}$

(D) Cantilever beam, uniform loading  
 $E = \frac{8L^3m}{2bd^3}$

FIG. 1

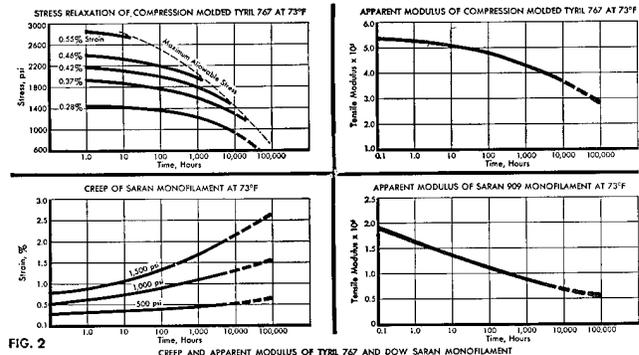


FIG. 2

# CALCULATING CREEP AND STRESS RELAXATION FROM LONG TERM DATA

There are many equations that have been and can be derived for the calculation of stresses and strains in bodies of various geometric shape. The modulus of elasticity of the material can also be derived from many of these same relationships. These equations assume (in most cases) that the body is elastic and obeys Hooke's Law. Also, they can only be applied with validity within the limit of proportionality of stress to strain. Properly used, these equations greatly facilitate the work of the designer and engineer who is dealing with the short time or elastic properties and can be successfully applied to design of plastic parts when stresses of short duration are anticipated.

Many of the applications for plastics today involve long term loading, or stressing, of the parts rather than short term loading. The design and engineering of parts for long term applications cannot realistically be based on short term data because plastics, like all other materials, are subject to a phenomenon under stresses of long duration known as "creep", "cold flow" or "stress relaxation". This means that if the material is free to act under stress its dimensions will gradually change resulting in creep or cold flow. On the other hand, if the part is originally and deliberately deformed to some predetermined shape and then restrained in that position so that total deformation will neither increase nor decrease, then a second phenomenon known as stress relaxation takes place. In this case, the initial stress built up in the piece as it tries to resist being deformed gradually decreases and if left in that position long enough would theoretically decrease to zero. If then removed from the deforming force, the part would retain completely the shape into which it had been forced.

Actually the two phenomena of creep and stress relaxation are very closely related, and the end result is identical in that permanent deformation of the part occurs. Because of their close relationship, a knowledge of the creep behavior of a plastic will enable one to accurately calculate the amount of stress relaxation that would occur in those applications where the part is initially deformed and then restrained in that position. The reverse is also true.

Various applications for plastics make use of materials in such a way that they are subject to either creep, stress relaxation, or a combination of both. The type of material, the temperature, the magnitude of the applied

load, and the length of time the part is under stress will determine the rate and extent of creep and stress relaxation. A knowledge of the rate and extent to which materials will creep or relax is necessary to be able to predict and design for the expected performance of the material.

When long term strength data on materials are available (stress relaxation and/or creep) these same equations can be used by the designer and the engineer to obtain a good approximation of how much creep or stress relaxation will take place in a given period of time. The long term creep or stress relaxation data must be substituted for the usual short term elastic data in the equations. For example, if lawnmower wheels or motor housings are to be designed, data obtained over a five year period should be used. If, on the other hand, a rocket or missile component is to be made of plastic, then the stresses will be applied for a very short period of time and the short term data should be used.

Several examples of some of the simpler forms of equations used to calculate stress, strain, and the modulus of elasticity are:

## 1. Equations for calculating simple stresses.

(a) Stress in tension.

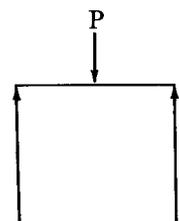
$$S = \frac{P}{A} \quad \begin{array}{l} P = \text{Applied load} \\ A = \text{Cross-sectional area of the part} \end{array}$$

(b) Stresses in compression.

Same as for tension.

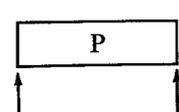
(c) Stress in flexure (rectangular beam).

(1) Simply supported, center loaded beam.



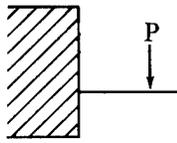
$$S = 3/2 \frac{PL}{bd^2} \quad \begin{array}{l} P = \text{Applied load} \\ L = \text{Distance} \\ \text{between} \\ \text{supports} \\ b = \text{Beam width} \\ d = \text{Beam depth} \end{array}$$

(2) Simply supported, uniformly loaded beam.



$$S = 3/4 \frac{PL}{bd^2}$$

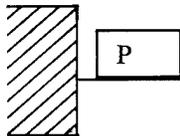
(3) Cantilever beam, end loaded.



$$S_{\max.} = \frac{6 PL}{bd^2}$$

$P$  = Applied load  
 $L$  = Distance from load to support  
 $b$  = Beam width  
 $d$  = Beam depth

(4) Cantilever beam, uniformly loaded.



$$S_{\max.} = \frac{3 PL}{bd^2}$$

2. Equations for calculating modulus of elasticity in the preceding examples.

(a) Modulus in tension.

$$E = \frac{S}{\epsilon}$$

$S$  = Stress  
 $\epsilon$  = Strain

(b) Modulus in compression.

Same as (a).

(c) Modulus in flexure.

(1) Simply supported, center loaded beam.

$$E = \frac{L^3 m}{4 bd^3}$$

$m$  = Initial slope of flexure curve

(2) Simply supported beam, uniform load.

$$E = \frac{5}{32} \frac{L^3 m}{bd^3}$$

(3) Cantilever beam, end loaded.

$$E = \frac{4 L^3 m}{bd^3}$$

(4) Cantilever beam, uniform load.

$$E = \frac{3}{2} \frac{L^3 m}{bd^3}$$

Using these equations of state and the long term data such as that given in Figures I, II, III, IV, and V, the creep or stress relaxation occurring in a plastic part held under stress can be calculated. The following examples and problems demonstrate the application of long term

data. The long term data used in these examples were obtained on Tyril® 767, Styron® 475, and Dow saran monofilament.

#### EXAMPLE 1

From the expression of modulus of elasticity in tension and the curve of "apparent modulus" vs. time, the creep or stress relaxation can be calculated if a limit can be determined for one or the other. Let's assume that for Tyril 767 the tensile stress to be applied is 1,000 psi, and we want to know how much creep will occur in a part during the first six months (4,320 hrs.). From Figure II the apparent modulus at six months is 420,000 psi.

$$\text{Equation 2(a)} \quad E = \frac{S}{\epsilon} \quad \text{and} \quad \epsilon = \frac{S}{E}$$

$$\epsilon = \frac{1,000}{420,000} = 0.0024 \text{ inches/inch or } 0.24\% \text{ elongation}$$

#### EXAMPLE 2

If, on the other hand, the application is such that a known deformation is to be imposed on the part (example: plastic closure for a bottle) then the amount of stress (resistance) still remaining in the part after a given time may be desired. Assuming the strain to be imposed will be 0.42%, the stress still remaining after one year is found as follows: (apparent modulus @ 1 year = 380,000 psi)

$$\text{Equation 2(a)} \quad S = E \epsilon = (380,000) (0.0042) = \underline{\underline{1600 \text{ psi}}}$$

#### PROBLEM NO. 1

Plastic monofilament is quite commonly used to manufacture the webbing or straps used in making office, home and lawn furniture. The filaments are usually circular in cross section with a diameter of about 10 mils and are highly oriented. In an ordinary chair, there will be five straps across the seat and five straps parallel to the seat for supporting the weight of the person sitting in the chair.

Designers, of course, wish to use the most economical material and this is dependent on the following factors:

1. Cost per pound of base resin.
2. Density of base resin.
3. Fabrication and weaving costs.
4. The design strength of the material.

Once the correct material has been chosen, the designer must then determine the number of strands to

be used in each of the straps. This he can determine from the design strength of the material and the size of the monofilament to be used.

In this hypothetical problem, the designer has two satisfactory materials to choose from and he must decide which is more economical and how many strands will be required in each web or strap. His design is to be based on a five year expected service life and the webbing must not develop a permanent sag greater than one inch at the center during the five year period. The design will also assume ambient temperatures of 75 to 80° F., and the size of the chair seat is to be 19 by 19 inches.

The following data on the two materials have been supplied to the designer:

	<i>Material A</i>	<i>Material B</i>
1. Design strength, psi . . . .	See Figure 3	
2. Safety factor . . . . .	— 2 —	
3. Specific gravity . . . . .	0.995	1.12
4. Cost per pound of base resin . . . . .	\$0.54	\$0.42
5. Fabrication cost . . . . .	— equal —	
6. Weaving cost . . . . .	— equal —	

**SOLUTION**

As previously stated, the chair is to be designed such that the load as a person sits in the chair will be uniformly distributed over ten straps. The maximum load to be encountered is assumed to be 300 pounds and with a safety factor of two, the working load then becomes 600 pounds and each strap must then support 60 pounds. The straps are fastened at each end, and the load can be assumed to be uniformly distributed. From the Fifth Edition of Mark's Handbook for Mechanical Engineers, Page 1362, the horizontal load can be calculated from the equation:

$$H = \frac{W_1 S^2}{8h}$$

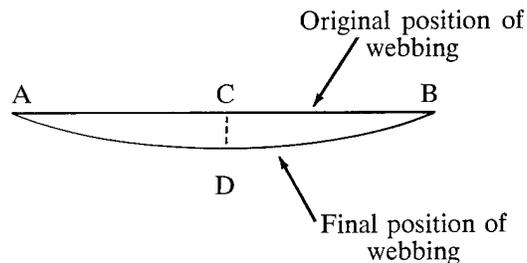
$$H = \frac{60 \left(\frac{19}{12}\right)^2}{8 \left(\frac{1}{12}\right)} = 226$$

Where:  
 H = Horizontal load, lbs.  
 W<sub>1</sub> = Total load carried by each strap, lbs.  
 S = Span, ft.  
 h = Vertical deflection, ft.

It is assumed also that the chair will be occupied approximately 6 hours per day or one and one-quarter years over a period of five years.

The first step in the solution to the problem is to determine how much creep can be permitted to take place in the straps before the design limit of the one inch permanent deflection at the center of the seat is reached. The sag or permanent deformation taking place in the webbing can be treated as a segment of the

arc of a circle and the strain or creep taking place in the monofilaments is calculated in the following manner:



CROSS-SECTION OF CHAIR SEAT

AB = Original length of webbing = 19 inches.

CD = Maximum allowable permanent deflection (5 Yrs.) = 1 inch.

ADB = Final length of webbing and is the arc of a circle subtended by chord AB.

$$\text{Then } ADB = \frac{\pi r \theta}{180}$$

Where: r = Radius of the circle =  $\frac{1}{2} \frac{AC^2 + CD^2}{CD}$

θ = Angle included by the radii connecting points

$$A \text{ and } B = \text{Arcsin } \frac{AB}{r}$$

$$ADB = \frac{\pi \left( \frac{1}{2} \frac{AC^2 + CD^2}{CD} \right) \left( \text{Arcsin } \frac{AB}{\frac{1}{2} \frac{AC^2 + CD^2}{CD}} \right)}{180}$$

$$= \frac{(3.14) \left[ \frac{1}{2} \frac{(9.5)^2 + (1)^2}{1} \right] \left[ \text{Arcsin } \frac{19}{\frac{1}{2} \frac{(9.5)^2 + (1)^2}{1}} \right]}{180}$$

$$= 19.6 \text{ inches}$$

$$\text{Strain (creep)} = \frac{\text{Change in length}}{\text{Original length}} = \frac{0.6}{19} = 0.032 \frac{\text{in.}}{\text{in.}}$$

Next it is necessary to calculate the limiting stress for each of the two materials. Since plastics will undergo permanent deformation in the form of creep when a load is applied, the limiting stress must be calculated from creep data obtained in a series of experiments on these two materials. For convenience to the designer, these data from numerous experiments are represented by a curve of apparent modulus versus time. The simple relationship, apparent modulus, psi, equal to stress, psi divided by strain, in./in., is used to calculate the limiting stress when the allowable creep is known. This is done as follows:

From Figure III the apparent moduli for the two materials is obtained.

	<i>Material A</i>	<i>Material B</i>
Apparent modulus, psi (initial)	$2.42 \times 10^5$	$1.85 \times 10^5$
Apparent modulus, psi (1¼ years)	$1.45 \times 10^5$	$0.88 \times 10^5$

Design stress for Material A  
 $S_D = (E_2) (\epsilon_1 + \epsilon_2)$

Where:

$S_D$  = Design stress

$E_2$  = Apparent modulus (1¼ yrs.) =  $1.45 \times 10^5$  psi  
 = Total strain on the webbing =  $\epsilon_1 + \epsilon_2$

$\epsilon_1$  = Initial elastic strain =  $\frac{S_D}{E_1}$

$\epsilon_2$  = Permanent deformation (creep) =  $0.032 \frac{\text{inch}}{\text{inch}}$

$E_1$  = Apparent modulus (initial) =  $2.42 \times 10^5$  psi

$S_D = (E_2) \left( \frac{S_D}{E_1} + \epsilon_2 \right)$

$= 1.45 \times 10^5 \left( \frac{S_D}{2.42 \times 10^5} + 0.032 \right)$

$= 0.6 S_D + 4640$

$0.4 S_D = 4640$

$S_D = \underline{11,600}$  psi

Design stress for Material B

$S_D = (0.88 \times 10^5) \left( \frac{S_D}{1.85 \times 10^5} + 0.032 \right)$

$= \underline{5,350}$  psi

The designer is now in a position to determine which of the two materials is more economical. Since the fabrication and weaving costs for the two materials are essentially the same, the only factors remaining to be considered are the cost per pound, the specific gravity and the design strength. For purposes of comparison, these factors can be related in an equation to obtain the cost index for each material.

Cost Index =  $\frac{(\text{Resin cost/pound}) (\text{Specific Gravity})}{\text{Design Strength}}$

Cost Index (Material A) =  $\frac{(0.54) (0.995)}{11,600} = 0.0032$

Cost Index (Material B) =  $\frac{(0.42) (1.12)}{5,350} = 0.0057$

From these results, it can be concluded that Material

A is the more economical choice by a factor of almost two to one. The remaining problem which the designer must answer is to determine how many strands each web or strap must contain in order to support the anticipated loads.

No. of strands required per strap =  $\frac{A_{\text{total}}}{A_1} = \frac{P}{S_D/A_1}$

Where:

$A_{\text{total}}$  = Total cross section of material required.

$A_1$  = Cross sectional area of one monofilament.

$P$  = Load applied at the end of each strap = 226 lbs.

$S_D$  = Design stress.

Strands/strap =  $\frac{P/S_D}{A_1} = \frac{P/S_D}{\pi r^2}$   
 $= \frac{226/11,600}{3.14 (0.005)^2} = 27$

Twenty-seven monofilaments in a webbing would be rather narrow so the designer can either reduce the size of each monofilament to gain a larger total number, and hence a wider strap or he can specify additional strands to be added even though they are not necessary.

#### PROBLEM NO. 2

A filter sump must be designed for use in a home water system. The filter must have a life expectancy of five years and operate at a maximum pressure of 75 psi internal pressure. The design also dictates that, to insure a sufficient O-ring seal, the total circumferential deformation of the sump cannot exceed a change in radius of 0.007 in. If this amount of creep is exceeded, the sump will leak.

#### SOLUTION

The filter sump is a thick-wall cylinder, the limiting stress would be the hoop stress, and the following equations would apply for calculating fiber stress and change in radius:

$S = \text{Hoop Stress} = P \frac{a^2 (b^2 + r^2)}{r^2 (b^2 - a^2)}$

$\Delta a = P \frac{a}{E} \left[ \frac{b^2 + a^2}{b^2 - a^2} - \nu \left( \frac{a^2}{b^2 - a^2} - 1 \right) \right]$

Where:

- a = Inner radius = 2.05 in.  $\Delta a$  = Change of inner radius, in.
- b = Outer radius = 2.30 in.
- r = Nominal radius = 2.175 in.
- v = Poisson's Ratio = 0.305
- S = Hoop stress, psi
- P = Internal pressure, psi

The material proposed for this application, because of its good long term strength (Figure I and II), ease of fabrication, and low cost was Tyril 767. The design strength in a creep application such as this, obtained from an extrapolation of the stress relaxation curve (Figure I), is 980 psi. The maximum allowable operating pressure can then be calculated from the equation:

$$S = P \frac{a^2 (b^2 + r^2)}{r^2 (b^2 - a^2)}$$

Solving for P: 
$$P = \frac{S [r^2 (b^2 - a^2)]}{a^2 (b^2 + r^2)}$$

$$= \frac{980 [4.73 (1.09)]}{4.2 (10.02)} = \underline{\underline{120}} \text{ psi}$$

The maximum allowable pressure found here is well above the operational requirements. The designer must then determine if the change in radius due to internal pressure is within the design limitations to insure that the O-ring will maintain an adequate seal.

$$\Delta a = P \frac{a}{E} \left[ \frac{b^2 + a^2}{b^2 - a^2} - v \left( \frac{a^2}{b^2 - a^2} - 1 \right) \right]$$

$$= \frac{75 (2.05)}{5.23 \times 10^5} \left[ \frac{9.49}{1.09} - 0.305 \left( \frac{4.2}{1.09} - 1 \right) \right]$$

$$= 0.00225 \text{ in.}$$

The five year design strength of Tyril 767, therefore, affords a safety factor of 1.6 for the operating pressure and three for the O-ring seal. It is possible that a slight decrease in wall section thickness could be considered for economic reasons. However, the designer will probably want to maintain a safety factor of 1.5 against contingencies.

### PROBLEM NO. 3

An engineer has designed an adjustable television receiver antenna which is to be mounted on the back of a portable television set. The antenna mounting well houses a spring which is compressed and inserted between the antenna rod and a spring washer. The spring washer rests against a ledge on the inside of the mounting well.

The spring is compressed 9/16" and exerts a force of 40 lbs. on the spring washer. The cross sectional

area of the mounting well wall supporting the spring washer is 0.230 square inches.

A high impact polystyrene is being considered for this application and the designer must know whether the part will last ten years under the present design loading or if the material will creep enough to allow the antenna rod to become loose in the socket making it unserviceable. The spring must maintain a force of 35 lbs. on the base of the antenna rod to keep it operable.

### SOLUTION

The antenna housing will be mounted on the back of the cabinet where the temperature will be approximately 100° F. while the set is in operation. Since viscoelastic materials stress relax and creep at a faster rate at elevated temperatures, the designer uses a safety factor of 2.0 to compensate for the time when the set is turned on.

The stress on the well wall is:

$$S = \frac{P (S_f)}{A}$$

- Where: P = Load, lbs. = 40 lbs.
- S<sub>f</sub> = Safety factor = 2.0.
- A = Cross sectional area = 0.230 in.<sup>2</sup>
- Stress =  $\frac{40 (2)}{.230} = 350$  psi.

The apparent modulus and stress relaxation data, extrapolated to ten years, for Styron 475 are shown in Figures IV and V respectively. The stress remaining in the well wall after ten years is calculated as follows:

$$\epsilon = \frac{S_0}{E_0}$$

$$S_{10} = (\epsilon) (E_{10})$$

- Where: S<sub>0</sub> = Initial stress = 350 psi
- E<sub>0</sub> = Modulus of elasticity = 3.8 x 10<sup>5</sup> psi
- S<sub>10</sub> = Stress remaining @ 10 years
- E<sub>10</sub> = 10 years apparent modulus = 1.4 x 10<sup>5</sup> psi (Figure IV)
- ε = Strain.

By calculation:

$$\epsilon = \frac{350}{3.8 \times 10^5} = 0.00092 \text{ inches/inch}$$

$$= 0.092\% \text{ strain}$$

The remaining stress is:

$$S_{10} = (0.00092) (1.4 \times 10^5 \text{ psi}) = 130 \text{ psi}$$

The ten years design stress of Styron 475 is 220 psi (Figure V) which is high enough over the 130 psi remaining stress to give an additional degree of safety.

To determine whether the part will creep enough to allow the antenna rod to become loose the designer must assume the load to be constant, thereby imposing a constant stress of 350 psi. The following formulas apply:

$$\epsilon_{10} = \frac{S_0}{E_{10}}$$

$$P_{10} = L_{10} (K)$$

Where:

- $\epsilon_{10}$  = Creep @ 10 years
- $S_0$  = Initial stress = 350 psi
- $E_{10}$  = Apparent modulus @ 10 years  
=  $1.40 \times 10^5$  psi
- $P_{10}$  = Spring force @ 10 years
- $L_0$  = Original amount spring is compressed = 0.5625 inches

$$L_{10} = L_0 - \epsilon_{10} = \text{Amount spring is compressed after creep}$$

$K$  = Spring constant (71.2 lbs./inch)

By calculation:

$$\text{Creep} = \epsilon_{10} = \frac{350}{1.4 \times 10^5} = 0.0025$$

$$L_{10} = .5625 - .0025 = 0.56$$

Therefore, the spring force is:

$$P_{10} = L_{10} (K) = (0.56) (71.2) = 39.8 \text{ lbs.}$$

The amount of creep occurring in ten years, at this stress level is insignificant. The part in its present design will perform satisfactorily when made of Styron 475.

These examples and problems have been relatively simple situations. Many applications also involve temperatures and environments other than those shown here and some may involve "shock" or rapid stressing of the part. The effect of such additional factors should be taken into consideration.

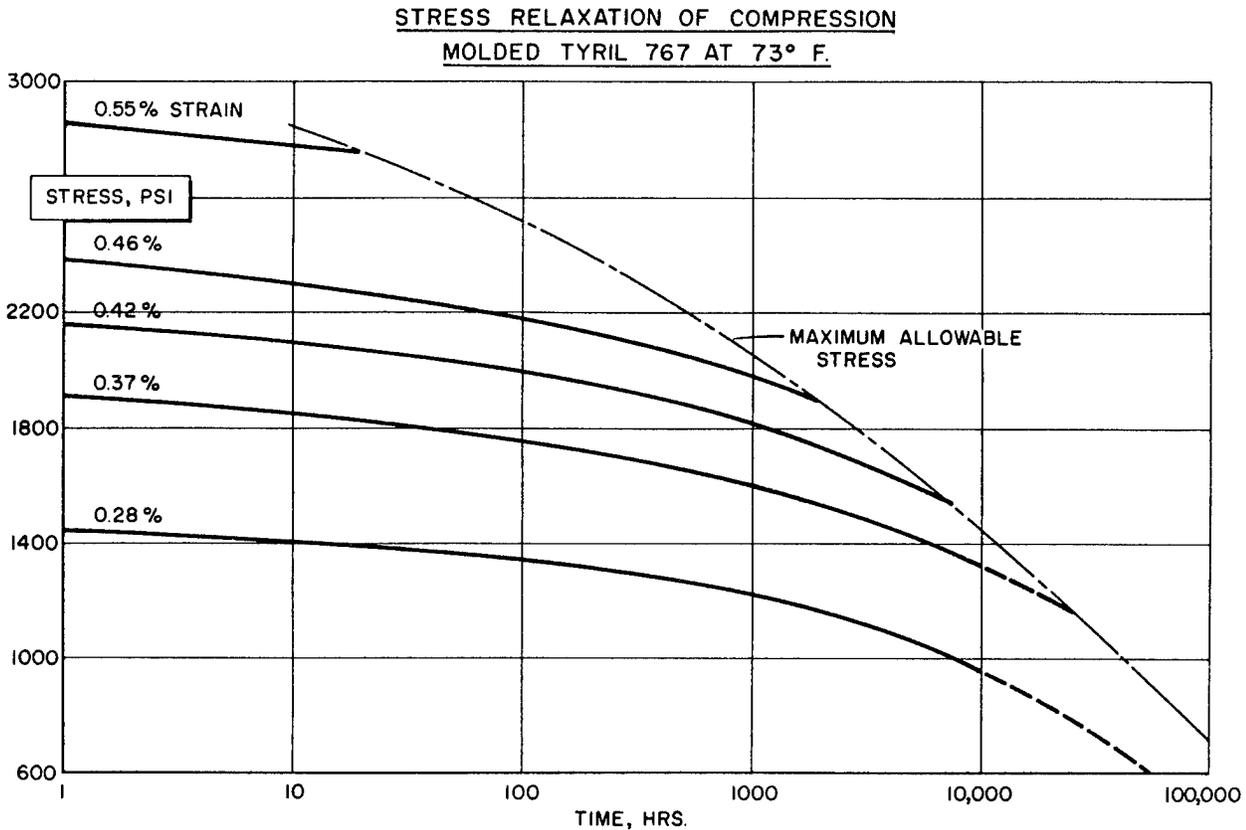


Figure 1

APPARENT MODULUS OF COMPRESSION  
MOLDED TYRIL 767 AT 73° F.

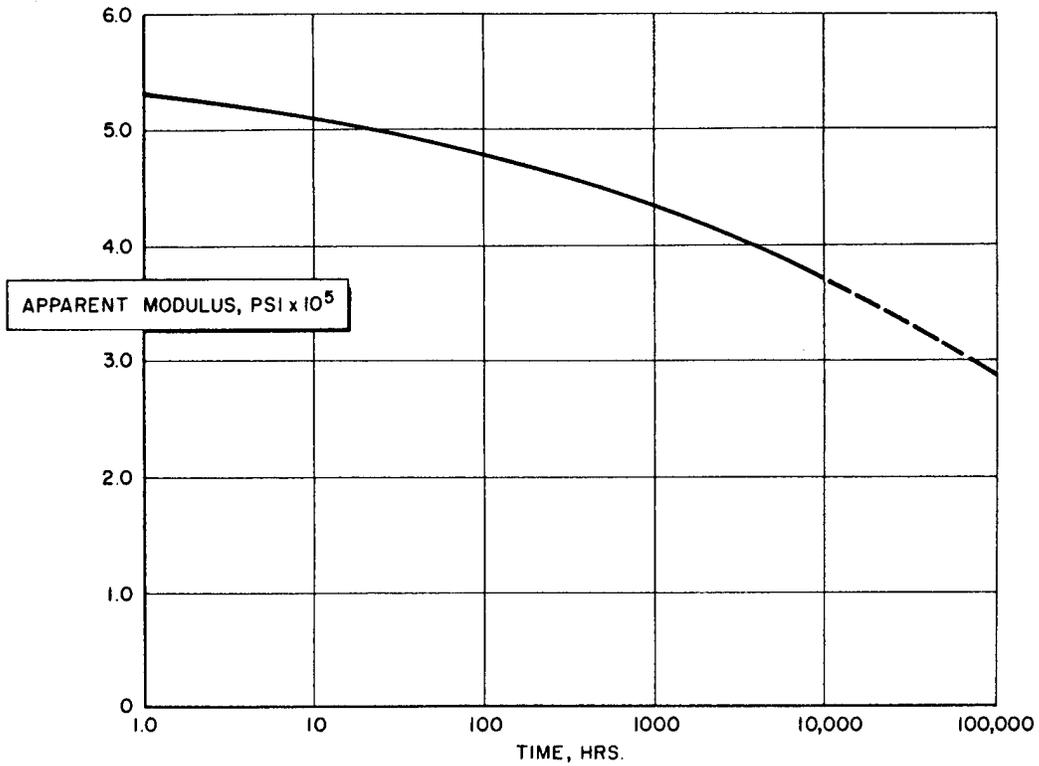


Figure II

APPARENT MODULUS VS TIME  
(FROM CREEP DATA)

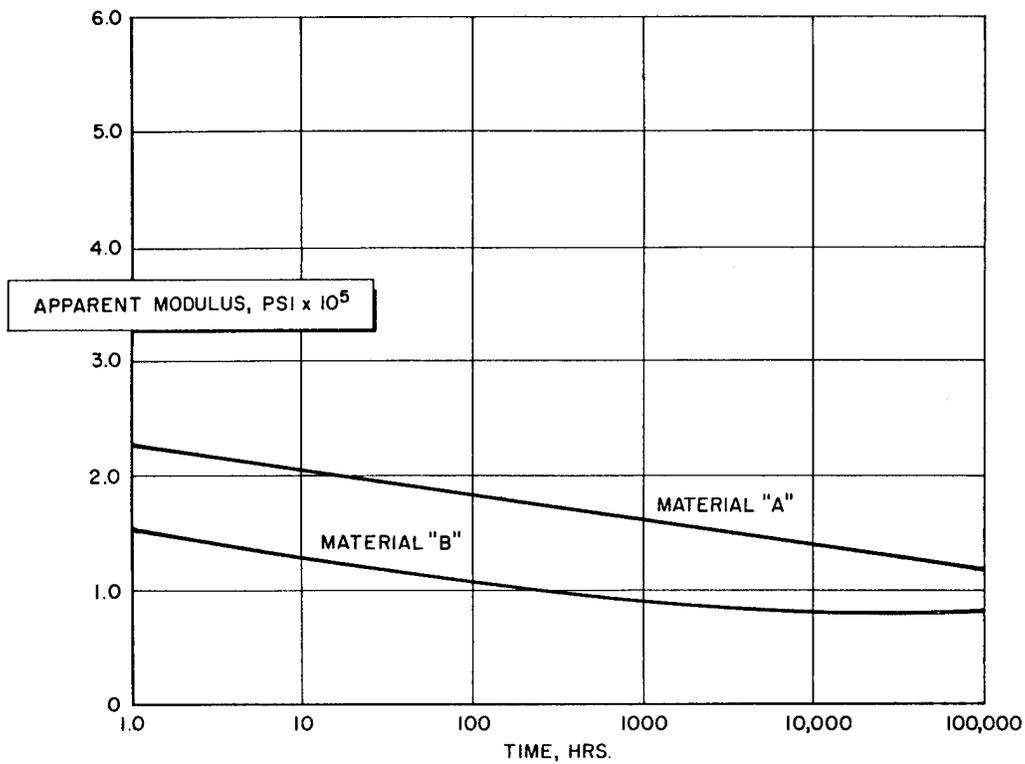


Figure III

APPARENT MODULUS COMPRESSION MOLDED  
STYRON 475 AT 73° F.

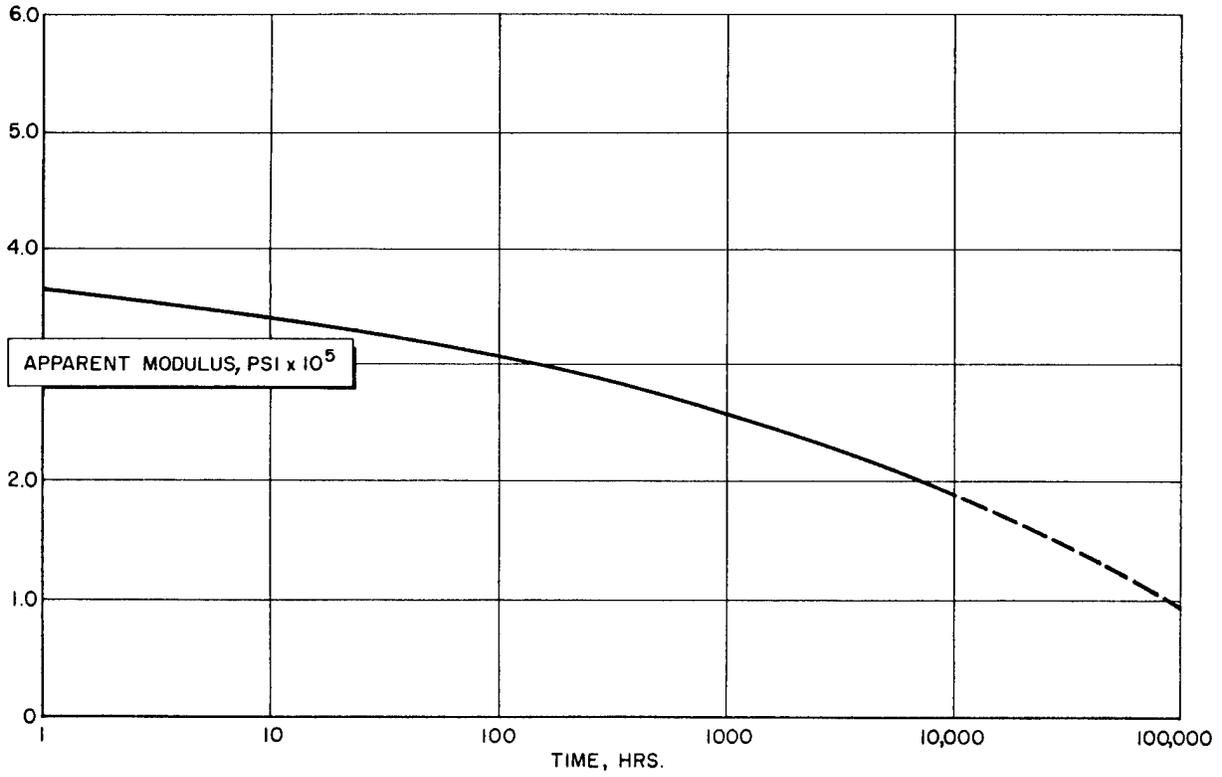


Figure IV

STRESS-RELAXATION COMPRESSION MOLDED  
STYRON 475 AT 73° F.

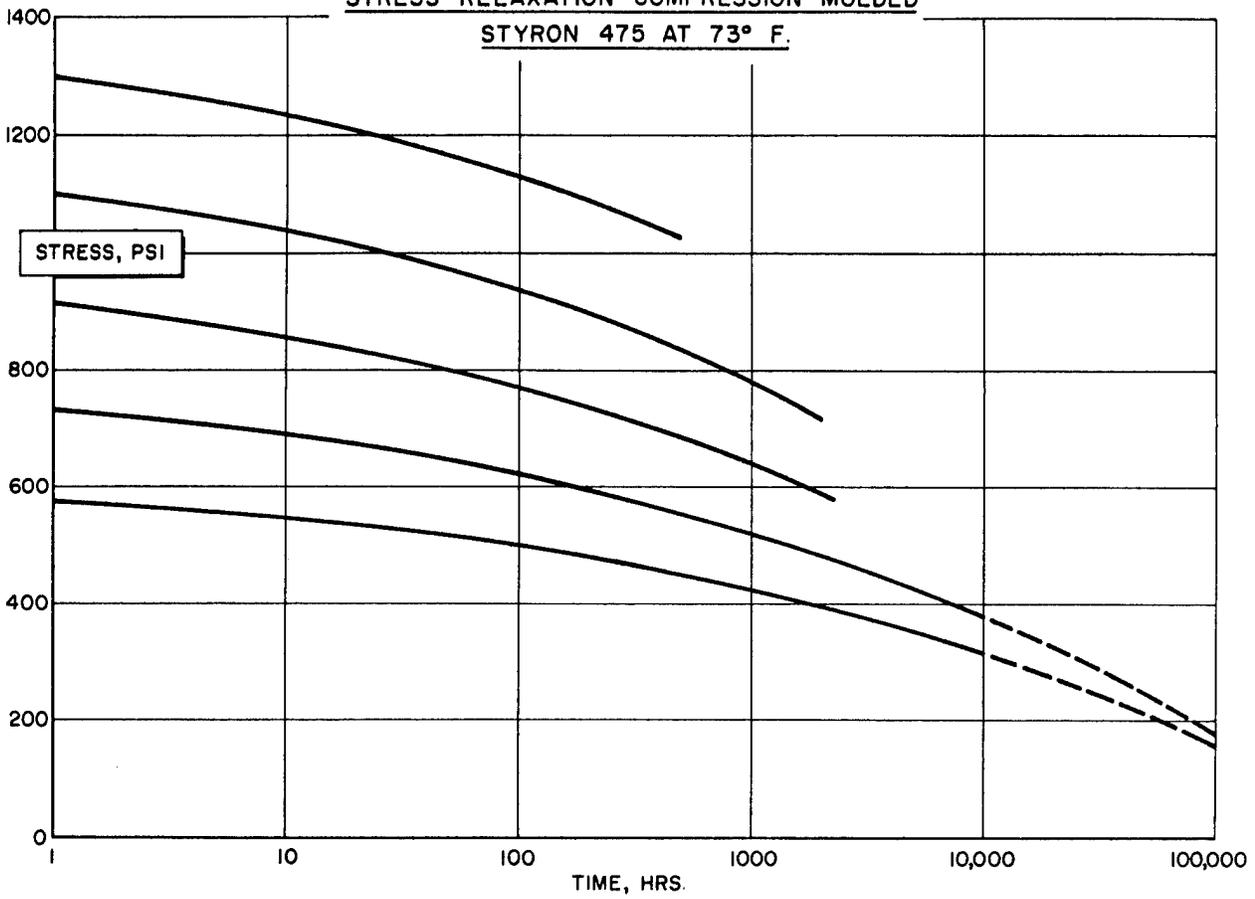


Figure V

# Dow *Plastiatics*

DOW'S CLINICAL APPROACH TO HEALTHY PLASTICS APPLICATION

## ACCURATE STRAIN GAGE ANALYSIS OF PLASTICS REQUIRES VISCOELASTIC DATA

Strain gages are becoming increasingly important analytical tools for plastics engineers and designers. However, in using them to evaluate the behavior of plastics under conditions of stress and strain, designers have found that accurate interpretation of strain gage readings is possible only if the readings are related to other factors—notably, time, temperature and environment.

Because standard strain gages (both bonded wire and metal foil types) detect strain by changing electrical conductivity when bent or distorted in any manner, careful mounting on the test part is essential to accurate readings. Once secured to the surface of the test part, however, a gage will measure any strain imposed on the part, directly in micro-inches per inch of strain.

Plastics materials are viscoelastic and their moduli of elasticity are generally quite low compared with wood, metals, ceramics, etc. Because of this, strength characteristics are largely dependent on time, temperature, and the environmental conditions. Since variations in these three factors will affect strain gage readings, the relationships between the factors *must be known* for accurate interpretation. To assist designers, Dow Plastics Technical Service Engineers have developed much data on Dow plastics. An example of their use in stress analysis follows, taking data from Fig. 1.

A hypothetical part for a creep application will be made from Tyril® 767; an application which will subject the part to a constant load (P), producing an initial strain ( $\epsilon_1$ ) on the part. The imposed strain can be measured with a strain gage, then stress calculated using:

$$S_1 = \epsilon_1 E_1$$

where:  $S_1$  = Initial stress, psi

$\epsilon_1$  = Initial strain in micro-inches/inch (from the strain gage)

$E_1$  = Apparent modulus, psi, at 0.1 hr. (Fig. 2)

If  $\epsilon_1 = 2800$  micro-inches/inch =  $2800 \times 10^{-6}$   
 $E_1 = 5.35 \times 10^5$

Then  $S_1 = \epsilon_1 E_1 = 2800 \times 10^{-6}$  in./in.  $\times 5.35 \times 10^5 = 1500$  psi.

The amount of creep for any given time can then be determined using:

$$\epsilon_c = \epsilon_2 - \epsilon_1$$

where:  $\epsilon_1$  = Initial strain reading

$\epsilon_2$  = Strain reading at time "t"

$\epsilon_c$  = Amount of creep

Let  $\epsilon_1 = 2800$  micro-inches/inch

$\epsilon_2 = 3200$  micro-inches/inch

Then  $\epsilon_c = (3200 - 2800)$  micro-inches/inch =  $400 \times 10^{-6} = 0.0004$  inch/inch, the creep occurring at time "t".

One application of a strain gage to a plastics design problem is shown in Fig. 2. A freezer flip lid was studied to determine cause of breakage, the magnitude of stresses at failure, and at what period in the life of the part stresses were being imposed. Strain gages were bonded to critical areas of the flip lid,

and measurements made of strain developed during assembly and actual service on the freezer. It was found that failure cracks (see Fig. 2) occurred because the mechanical and thermal applied stresses exceeded the design strength of the material. Further, the gages revealed that the stresses originated during both assembly and in service. The primary source of stress was discovered to be a rigid bond between metal and expanded plastic insulation. This prevented the plastic frame from acting independently, restricting its movement instead. The solution to the problem was self-evident, once the strain gages revealed the mode of stress development.

A few other applications of strain gages to plastics design and engineering problems are: measurement of coefficient of thermal expansion; measurement of Poisson's Ratio; elongation in test specimens; and stress analysis of bottle closures, home water filters, refrigerator parts, automotive parts, etc.

This study of strain gage applications is one of the continuing series of studies undertaken to assist plastics designers and engineers in the most effective selection and use of plastics materials. For information, and for data on Dow plastics materials, write THE DOW CHEMICAL COMPANY, Midland, Michigan, Plastics Sales Department 1802DU8.

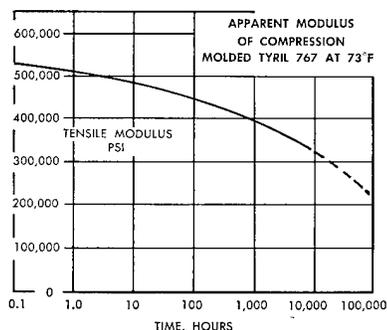


Fig. 1. Long-term data on Apparent Modulus of Tyril 767, for use in strain gage analysis.

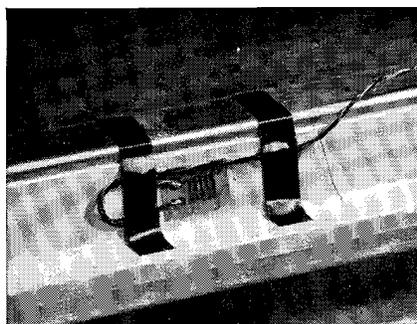


Fig. 2. Strain gage analysis of freezer lid reveals source of stress which caused failure.

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- Tyril® • Saran

# STRAIN GAGES AND THEIR USE ON PLASTICS

Strain gages have been by far the most important single tool available to the stress analyst. Many of our outstanding industrial achievements (satellites, rockets, economical air travel service and a host of products old and new) would not now be reality if it were not for strain gages. Yet despite the complexity of the tasks they perform, they are amazingly simple in construction and use.

The two most common gages are the bonded wire and the metal foil (less than 1/10,000 inch thickness) gage usually carried on either a paper or plastic backing. Both types are formed into a grid pattern (Figure 1) and have the characteristic that when bent, pulled, pushed, or in any way distorted the ability to conduct an electric current changes. This change in conductivity can be measured with sensitive electrical instruments and related to the amount the gage has been deformed. If this grid pattern can then be attached to some object and that object be deformed by any means, the gage will also be deformed and the electrical measurements made will indicate how much deformation took place in the part. In this manner, they can be used to accurately measure any force that causes or can be made to cause movement in a body.

Strain gages have been widely used for years in the metals industry and indeed the airplane, as we know it today, carrying thousands of passengers for millions of miles each day safely and at an economical rate, would not be possible without the strain gage. Until now they have found little use in the plastics industry, but with the rapidly increasing use of plastics in industrial applications (automotive, refrigeration, furniture, housewares, etc.) their use is becoming increasingly important to the designer.

Strain gages which can be applied to plastics come in a great variety of sizes and shapes with gage lengths from 1/64 inch on up to many inches in length. Gages to meet almost every requirement are readily available to the designer at a very nominal cost and where a gage of special size, shape, or type may be needed they can generally be custom made by the gage manufacturer.

With proper adhesives and techniques, strain gages can be applied directly to the surface of many plastics and will faithfully reproduce for the engineer any movement taking place within that particular part of the surface of the plastic directly beneath the gage. To make use of the data obtained, however, certain precautions must be taken and certain other data must be available. Plastics are not highly elastic materials and their moduli of elasticity are quite low compared with those of

woods, metals, ceramics, etc. Because they are not highly elastic, their strength characteristics are largely dependent on time, temperature and the environment to which they are exposed. Therefore, to accurately interpret the strain gage readings made on plastics these relationships must be known for that plastic. Fortunately The Dow Chemical Company has obtained much of these data making possible the correct interpretation of strain gage readings made on parts molded from Dow Plastics.

Because plastics have low moduli of elasticity, the addition of a thin metallic membrane and adhesive used to mount the strain gage undoubtedly affects the properties and the behavior of the part. The extent of this effect must also be determined and accounted for before correct interpretation of strain gage readings can be made.

Care must at all times be exerted in the use of strain gages to be certain that in applying them the chemical and physical structure of the plastic is not altered, that the effect of the addition of the gage on strength is accounted for and that data on the stress-strain behavior of the plastic as a function of time, temperature and environment be available so that correct interpretation can be placed upon the observed results.

## CALCULATING STRESS AND STRAIN FROM STRAIN GAGE READING

Determining the load applied to refrigerator components from strain gage measurements.

Strain gages can be bonded to many plastics using an epoxy resin adhesive. A simpler, more efficient method, however, is to use a pressure sensitive cyano-acrylate adhesive (Eastman 910M) if temperatures higher than 125° F. are not to be encountered. With this adhesive a gage can be installed, wired, checked and ready for use by a skilled operator in just five minutes.

The effects of static or slowly changing stresses can be recorded using a very sensitive potentiometer or strain indicator connected to the strain gage. Dynamic or rapidly changing stress can be observed with an oscilloscope and camera.

In one application of this very versatile instrument, a freezer door liner was studied through its manufacture, assembly, and simulated service to determine what was causing breakage, what the magnitude of the stresses at failure were and at what point in the history of the part the stresses were being imposed.

Strain gages were bonded to various critical areas of the component and measurements made of the strain in the parts through the assembly line. The parts were then put through simulated service tests. (Simulated service temperatures as low as  $-20^{\circ}\text{F}$  were used.)

It was found that failure was occurring in the parts because of the application of purely mechanical stresses which exceeded the design strength of the material. These stresses were originating both in the process of assembly and during service or use of the part. It was also determined at just what point the load or stress was being applied to the part and the magnitude of that stress.

From this study it was concluded that the primary reason the stresses were arising was because the plastic was rigidly bonded to a metal component which did not allow the plastic to act independently but rather restricted the movement of the plastic. When the problem had been thoroughly analyzed in this manner, the solution to the problem became self-evident. This same technique can be applied to almost any plastic component and much can be learned about expected performance and improvements in design.

#### EXAMPLES

When the time dependent behavior of the plastic is known and the designer or engineer has determined whether the application is a stress relaxation or a creep application, a complete and accurate analysis of the stress in the part can be made. The following examples illustrate how strain gages and long term data are used to calculate the stresses in plastic parts in stress relaxation and creep applications.

The time dependent behavior of Dow Tyril® 767, the plastic selected for these examples, is shown in Figure I. In a creep application the part is subjected to a constant load,  $P$ , which will initially strain the part,  $\epsilon_1$ . The amount of strain imposed on the part will be indicated by the strain gage. Since the time required to apply the load is relatively short, the initial stress can be calculated using:

$$S_1 = \epsilon_1 E_1$$

Where:

$S_1$  = Initial stress, psi

$\epsilon_1$  = Initial strain measured by strain gage, micro-inches per inch.

$E_1$  = Apparent modulus, psi, at 0.1 hours (Fig. 1)

Let

$\epsilon_1 = 2800$  micro-inches/inch  $= 2800 \times 10^{-6}$  in./in.

$E_1 = 5.50 \times 10^5$  psi

Then, by calculation,

$S_1 = \epsilon_1 E_1 = 2800 \times 10^{-6}$  in./in.  $\times 5.50 \times 10^5$

$S_1 = 1540$  psi

Under constant loading the part will experience creep. The amount of creep for any given period of time can be determined by subtracting the initial strain gage reading from the strain reading at a given time, as follows:

$$\epsilon_c = \epsilon_2 - \epsilon_1$$

$\epsilon_1$  = Initial strain reading

$\epsilon_2$  = Strain reading at time "t"

$\epsilon_c$  = Amount of creep

Let

$\epsilon_1 = 2800$  micro-inches/inch

$\epsilon_2 = 3200$  micro-inches/inch

Then

$\epsilon_c = (3200-2800)$  micro-inches/inch

$\epsilon_c = 400 \times 10^{-6} = .0004$  inch/inch

This will be the amount of creep taking place in time, "t".

In a stress relaxation application, the part is strained or deformed a certain amount and this strain remains constant. The initial stress would be calculated the same as in the creep application. However, the stresses remaining in the part and the amount of permanent deformation that occurs in the part can be determined only from a knowledge of the long term behavior of the plastic. Assume the initial conditions to be the same as before.

$S_1$  = Initial stress = 1540 psi

$E_1$  = Initial apparent modulus =  $5.50 \times 10^5$  psi

$\epsilon_1$  = Initial strain = 2800 micro-inches/inch

For this hypothetical test problem the duration of the test is 5,000 hours. The problem is to determine how much permanent deformation has taken place in the part and the stress remaining in the part at the end of the test. From Figure I the apparent modulus of Tyril 767 at 5,000 hours is found to be  $3.95 \times 10^5$  psi. The stress remaining in the part is then calculated by:

$$S_r = \epsilon_1 E_t$$

Where:

$S_r$  = Stress remaining

$E_t$  = Apparent modulus at time, "t" (5000 hours)

$\epsilon_1$  = Initial strain

By calculation:

$S_r = (3.95 \times 10^5) (2800 \times 10^{-6})$

$S_r = 1105$  psi, the stress remaining in the part after 5000 hours

The strain or deformation imposed on the part is initially elastic and recoverable. As time goes by, part of this elastic strain becomes permanent deformation and is no longer recoverable. The amount of permanent

deformation can be calculated but it can also be determined experimentally with strain gages. At the end of the test program, the permanent deformation can be calculated from the equation:

$$\epsilon_1 = \epsilon_2 + \epsilon_3$$

Where:  $\epsilon_2$  = Elastic strain  
 $\epsilon_3$  = Permanent deformation

Also— 
$$\epsilon_2 = \frac{S_f}{E_1}$$

By calculation:

$$\epsilon_2 = \frac{1105}{5.50 \times 10^5} = 2.01 \times 10^{-3}$$

$$\epsilon_2 = 2010 \times 10^{-6} \text{ inches/inch of strain}$$

Therefore, the permanent deformation would be:

$$\epsilon_3 = \epsilon_1 - \epsilon_2$$

$$\epsilon = (2800 - 2010) \times 10^{-6}$$

$$\epsilon_3 = 790 \times 10^{-6} \text{ inches/inch}$$

When the part with a strain gage attached is released from its strained position at some time, "t", (5000 hours) the final strain gage reading will not be zero but will reflect the amount of permanent deformation. In this case the final reading should be 790 micro-inches/inch of strain, the same as that obtained above by calculation.

## APPLICATIONS WHERE STRAIN GAGES HAVE BEEN USED ON PLASTICS

1. Measurement of coefficient of thermal expansion, Photo No. 1
2. Measurement of Poisson's Ratio, Photo No. 1
3. Elongation in test specimens, Photo No. 1
4. Stress analysis of:
  - a. Bottle closures Photo No. 2
  - b. Home water filters Photo No. 3
  - c. Refrigeration parts Photo Nos. 4 & 5
  - d. Automotive parts Photo No. 6

## REFERENCES ON STRAIN ANALYSIS

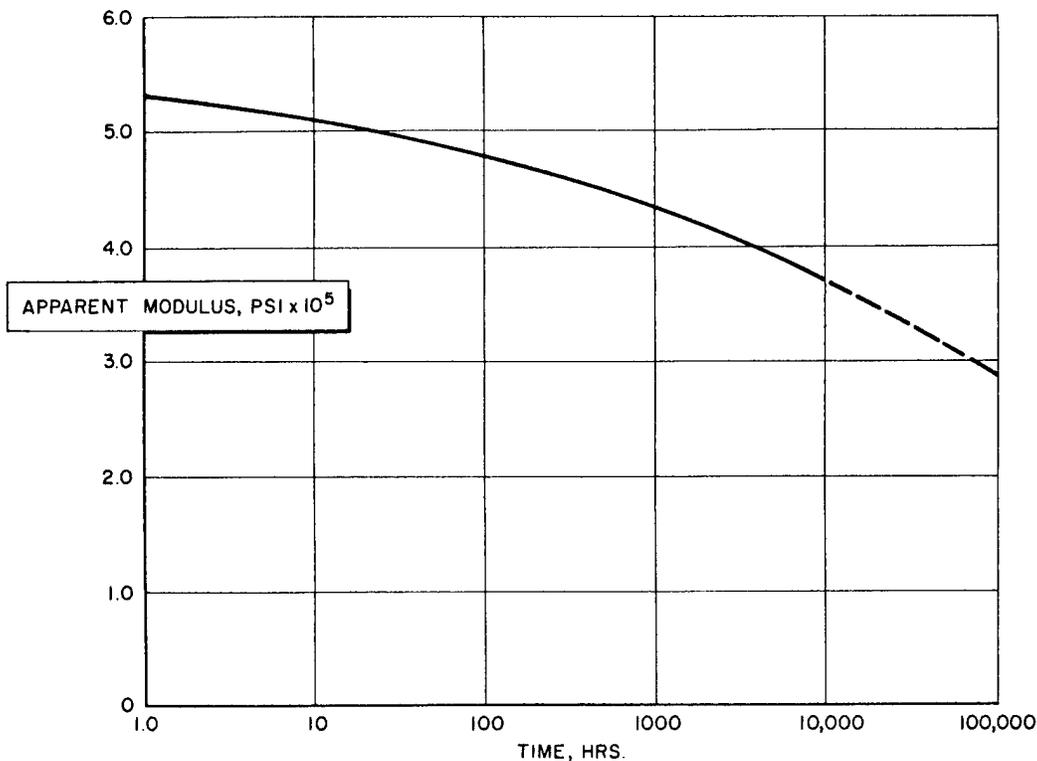
Stress Gage Readings, Stein Engineering Services Publication

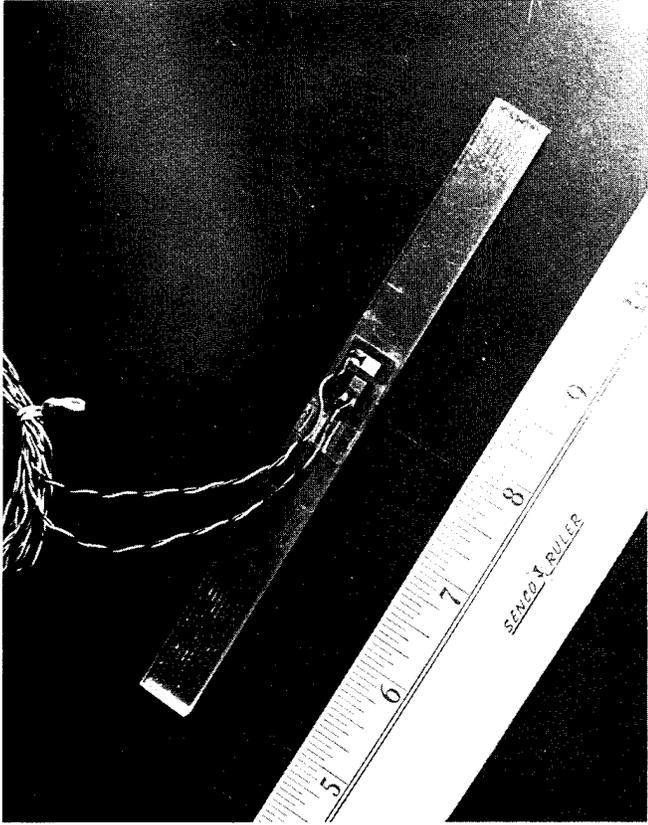
Testing Topics, Baldwin-Lima-Hamilton

Proceedings, American Society for Experimental Stress Analysis

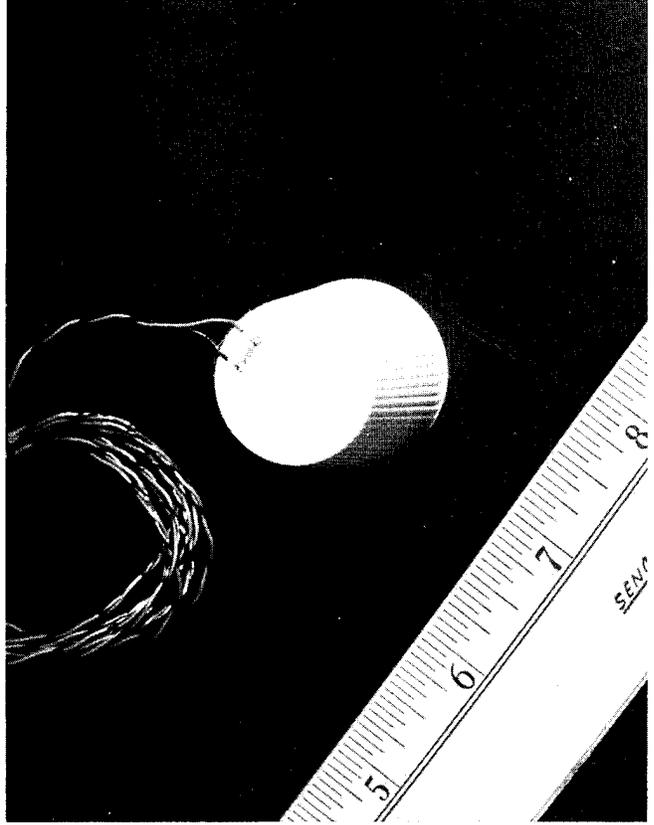
Figure 1

### APPARENT MODULUS OF COMPRESSION MOLDED TYRIL 767 AT 73° F.

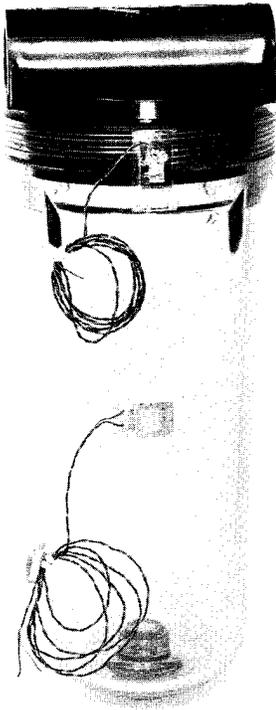




MEASUREMENT OF PROPERTIES



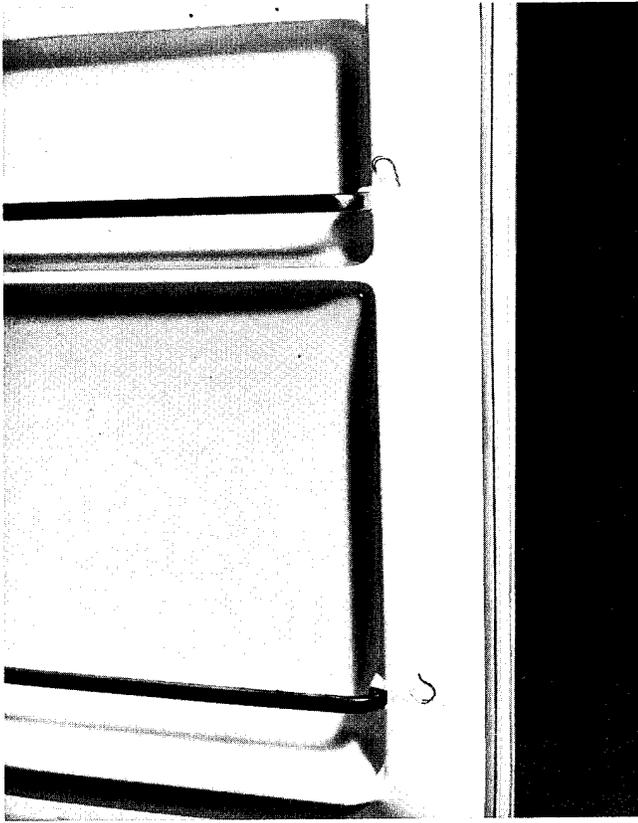
BOTTLE CLOSURE



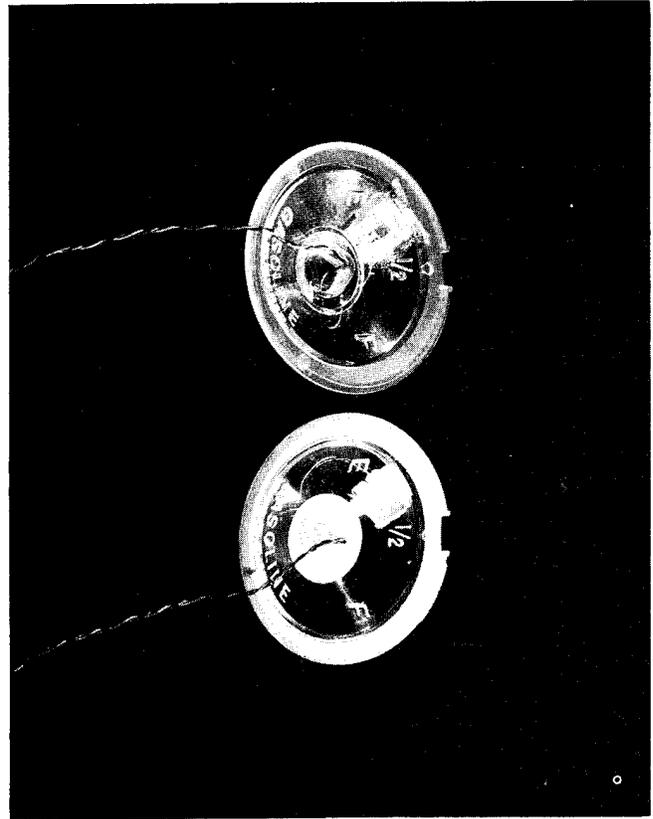
HOME WATER FILTER



REFRIGERATOR FREEZER LID



REFRIGERATOR INNER DOOR LINER



MEASUREMENT OF AUTOMOTIVE PARTS

# DOW *Plastiatics*

DOW'S CLINICAL APPROACH TO HEALTHY PLASTICS APPLICATION

## TEMPERATURE AND PHYSICAL STRUCTURE DICTATE PLASTICS' WATER VAPOR TRANSMISSION

As with gas permeability, water vapor transmission rate (WVTR) through a plastic barrier is determined by several factors. The most important of these are temperature and composition of the barrier. When the plastic is partially crystalline, the degree of crystallinity also has an important influence on this property.

Water vapor permeability is a function of the diffusion rate and solubility of water vapor in the barrier material. Water vapor apparently permeates by dissolving into the plastic at the incoming surface, establishing a concentration gradient for further penetration. Under the influence of this gradient, the dissolved water vapor diffuses through the plastic superficially in accordance with Fick's Law of diffusion. At the outgoing surface, the penetrant evaporates. Diffusion within the plastic is considered to be the rate-determining factor.

In the case of water molecules diffusing through a hydrophobic polymer, only small concentrations of water will prevail within the polymer. It is expected that Henry's Law will be obeyed and,

since the polymer is swollen negligibly by the absorbed water, the diffusion coefficient in Fick's Law should be independent of concentration. In such an ideal system, the permeability coefficient characterizes the transport of water vapor through the polymer. By definition, the permeability coefficient is equal to the product of the solubility coefficient and the diffusion coefficient.

$P = DS$ , where:

P = Permeability Coefficient

D = Diffusion Coefficient

S = Solubility Coefficient

An increase in temperature increases the water vapor permeability. Also, the transmission rate varies exponentially with the reciprocal of the absolute temperature ( $\log \bar{p}$  vs.  $\frac{1}{T}$ ). The linear relationship holds between 35° and 97° C.

Permeability is directly affected by the molecular structure of the plastic barrier. For example, with partially crystalline polymers such as polyethylene, water vapor transmission is believed to occur almost entirely through the amor-

phous phase, with little or no transmission through the crystalline phase. Therefore, the amount of penetrant absorbed appears to be in direct proportion to the amorphous material present in the polymer.

One explanation of the negligible degree of vapor permeation through the crystalline phase of the polymer is that there is no free volume to accommodate the water molecule.

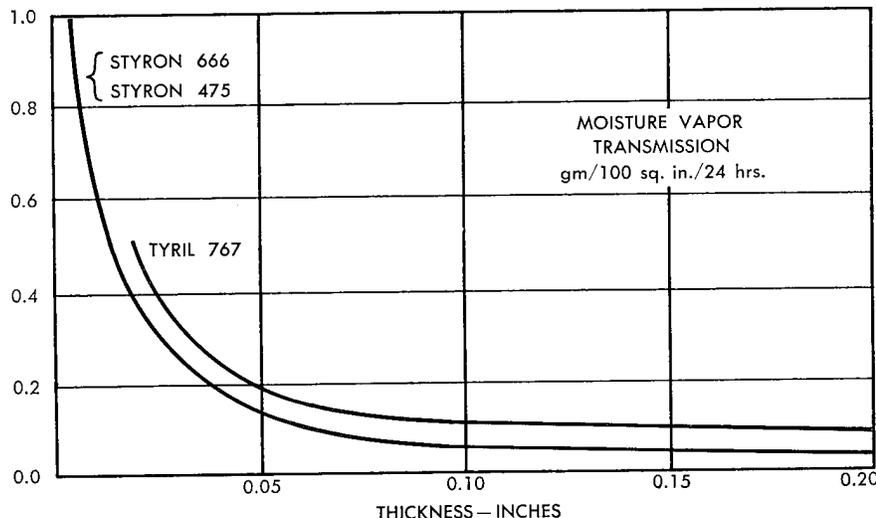
In the case of most plastic materials, the water vapor transmission rate is treated as an activated rate process, with the assumption that the water molecules diffuse as holes are formed in the polymer due to segmental motion of the polymer chains. However, in the case of polystyrene it is generally assumed that moisture transport proceeds along submicroscopic cracks or channels, not by the usual mechanism which apparently holds for most other materials. As with all plastic materials having low water absorption, the WVTR for polystyrene is not sensitive to the humidity at which the tests are made.

This study on water vapor permeability is one of a continuing series of Plastiatics Studies being made by Dow Plastic Technical Service Engineers. For detailed information on this study, and on others covering every area of interest to plastics designers and engineers, write THE DOW CHEMICAL COMPANY, Midland, Michigan, Plastics Sales Department 1803CS9.

CURVES OF WVTR VS. BARRIER THICKNESS FOR THREE DOW PLASTICS.

ASTM METHOD E 96-53T PROCEDURE E

TEMPERATURE 100°F RELATIVE HUMIDITY: 0% IN DISH, 95% OUTSIDE DISH



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# WATER VAPOR PERMEABILITY OF PLASTIC POLYMERS

Water vapor permeability of plastic polymers is a function of the diffusion rate and solubility of water vapor in the barrier. Water vapor is generally considered to permeate the plastic by dissolving into the plastic at the incoming surface and thereby establishing a concentration gradient for the penetrant within the plastic. By virtue of this gradient, the penetrant diffuses through the plastic superficially in accordance with Fick's law of diffusion. Upon reaching the other surface the penetrant evaporates from the plastic.

In the case of water molecules diffusing through a hydrophobic polymer, only small concentrations of water will prevail within the polymer at these low concentrations. It is expected that Henry's law will be obeyed and since the polymer is swollen only negligibly by the absorbed water, the diffusion coefficient in Fick's law should be independent of concentration. In such an ideal system the permeability coefficient, which by definition is the product of the solubility coefficient and the diffusion coefficient, characterizes the transport of water vapor through the polymer. (1) (2)

Therefore:  $\bar{P} = DS$

Where:  $\bar{P}$  = Permeability coefficient  
D = Diffusion coefficient  
S = Solubility coefficient

Several variables affect the water transmission rate including temperature, composition of barrier and degree of crystallinity.

An increase in temperature increases the water vapor permeability. The transmission rate varies exponentially with the reciprocal of the absolute temperature ( $\log \bar{p}$  vs  $\frac{1}{T}$ ) This linear relationship holds between 35 and 97° C. The data shown in Figure I illustrates the effect of temperature on the water vapor transmission rate of Saran Wrap.

The amount of penetrant absorbed appears to be directly proportional to the amount of amorphous material present in the polymer. It appears then that to obtain a good water vapor barrier, the polymer must have a high degree of crystallinity.

In the case of polystyrene it appears that moisture transport proceeds along submicroscopic cracks or

channels and not by the usual mechanism which holds for other polymers. (3)

Water vapor transmission tests are conducted according to the method described in ASTM E96-53T, "Test for Measuring Water Vapor Transmission of Materials in Sheet Form". Copies of this procedure may be obtained by writing directly to ASTM headquarters at 916 Race Street, Philadelphia 3, Pennsylvania. Briefly, the test consists of waxing the specimen under test to a dish which contains either desiccant or water, depending upon the procedure used. A template of known area is then placed on the test specimen and the exposed sample is coated with wax so that only the template area will be allowed to transmit water vapor. After waxing, the template is removed and the initial test assembly weight is obtained. The assembly is then placed in a humidity chamber operating at appropriate test conditions (usually 100°F. and 95-100% RH). Weight checks are made daily until a constant rate of weight gain is obtained. The weight gain per unit time is then calculated and converted into a transmission rate in gms/24 hours/100 inches squared.

Table I shows water vapor transmission rates for Dow plastics. Test procedures in this table represent normally expected service conditions. These conditions range from those experienced when an aqueous solution is stored at average humidity to when a deliquescent product is stored at high humidity.

For practical purposes, WVT rates at normal container thicknesses (20 - 80 mil) can be estimated by regarding WVT rates as inversely proportional to thickness. A more exact relationship for a number of Dow plastics is shown in the WVT vs. thickness curves of Figures II, III, and IV.

Table II contains factors for converting to various WVT units.

## References

1. "The Permeation of Water Vapor Through Polyethylene", Klute, C. N. and Franklin, P. J., October, 1958, Pages 161-162, Journal of Polymer Science.
2. P. E. Rouse 69, 1068, (1947), Journal of the American Chemical Society.
3. Styrene — Its Polymers, Copolymers and Derivatives, Boundy, R. H. and Boyer, R. F., Reinhold Publishing Company, New York, New York, 485, (1952).
4. "Conversion Table for Various WVT Units", Page 1024, ASTM Standards on Plastics, September, 1958.

TABLE I  
WATER VAPOR TRANSMISSION RATES OF DOW PLASTICS MATERIALS (ASTM E 96-53T)  
MATERIALS TESTED AT THICKNESS OF 0.020"

	Procedure B, 75° F 100% RH Inside 50% RH Outside	Procedure C, 75° F 0% RH Inside 50% RH Outside	Procedure E, 100° F 0% RH Inside 100% RH Outside
	gms/24 hrs - 100 in. <sup>2</sup>	gms/24 hrs - 100 in. <sup>2</sup>	gms/24 hrs - 100 in. <sup>2</sup>
Ethocel®			Up to 6.5
Polyethylene (Types I, II, III)	Less than 0.01	Less than 0.01	Less than 0.01
Styron® 440	0.10-0.11	0.08-0.10	0.22
Styron 475	0.10-0.11	0.08-0.10	0.30-0.40
Styron 480	0.10-0.11	0.08-0.10	0.30-0.40
Styron 666	0.10-0.11	0.08-0.10	0.40
Styron 683	0.10-0.11	0.08-0.10	
Styron 689	0.10-0.11	0.08-0.10	0.40
Styron 700	0.10-0.11	0.08-0.10	0.25
Tyrlil® 767	0.16	0.12	0.44
Zerlon® 150		0.08	0.33

TRANSMISSION RATES OF DOW PLASTIC FILMS — ASTM E 96-53T, PROCEDURE E

Material	WVT Rate, Gms/24 hrs/100 in. <sup>2</sup>		
	Thickness, in. 0.001	Thickness, in. 0.0015	Thickness, in. 0.002
Trycite® Film	7.6	5.8	4.0
Saran Film	0.21	0.13	0.10

TABLE II  
CONVERSION FACTOR FOR VARIOUS WVT UNITS<sup>a</sup>

To obtain	Procedure	Multiply			
		g	g	grains	Perms <sup>a</sup>
		24 hr sq m by	24 hr 100 sq in by	hr sq ft by	
$\frac{g}{24 \text{ hr sq m}}$	A and B, 73.4 F	1	15.5	16.7	6.94
	C and D, 90 F	1	15.5	16.7	11.9
	E, 100 F	1	15.5	16.7	29.1
$\frac{g}{24 \text{ hr } 100 \text{ sq in}}$	A and B, 73.4 F	0.0645	1	1.08	0.448
	C and D, 90 F	0.0645	1	1.08	0.767
	E, 100 F	0.0645	1	1.08	1.88
$\frac{g}{\text{hr sq ft}}$	A and B, 73.4 F	0.0597	0.926	1	0.415
	C and D, 90 F	0.0597	0.926	1	0.710
	E, 100 F	0.0597	0.926	1	1.74
Perms <sup>a</sup>	A and B	0.144	2.23	2.41	1
	C and D	0.0841	1.30	1.41	1
	E	0.0343	0.532	0.575	1

<sup>a</sup> The conversions to perms are based on the following vapor pressure differentials:

Procedure	In. Hg.
A and B	0.415
C and D	0.710
E	1.740

Data obtained by one procedure cannot be reliably compared with data obtained by another procedure.

Figure II  
 WATER VAPOR TRANSMISSION VS  
 THICKNESS OF SARAN WRAP  
 No's. 1 THRU 19

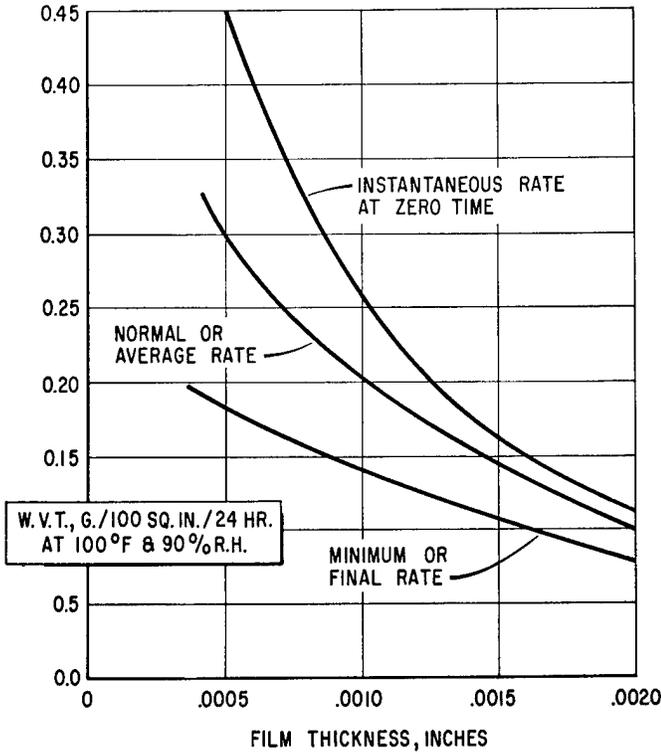


Figure I  
 WATER VAPOR TRANSMISSION VS  
 TEMPERATURE OF SARAN WRAP  
 No's. 20 THRU 39

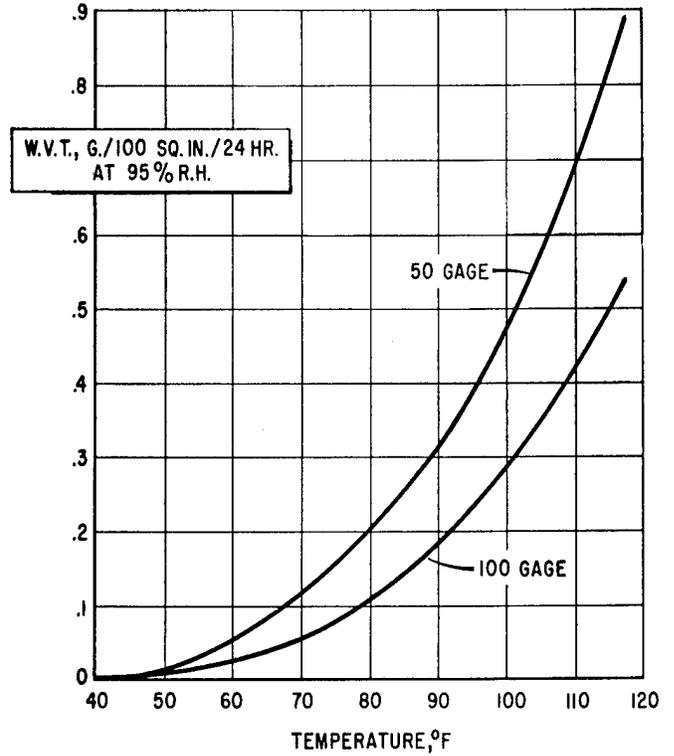


Figure IV  
 MOISTURE VAPOR TRANSMISSION  
 VERSUS THICKNESS

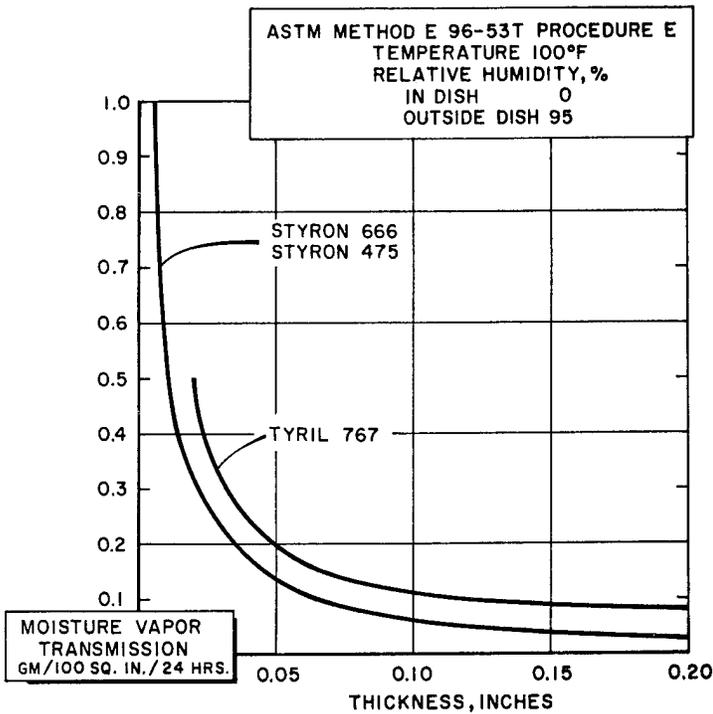
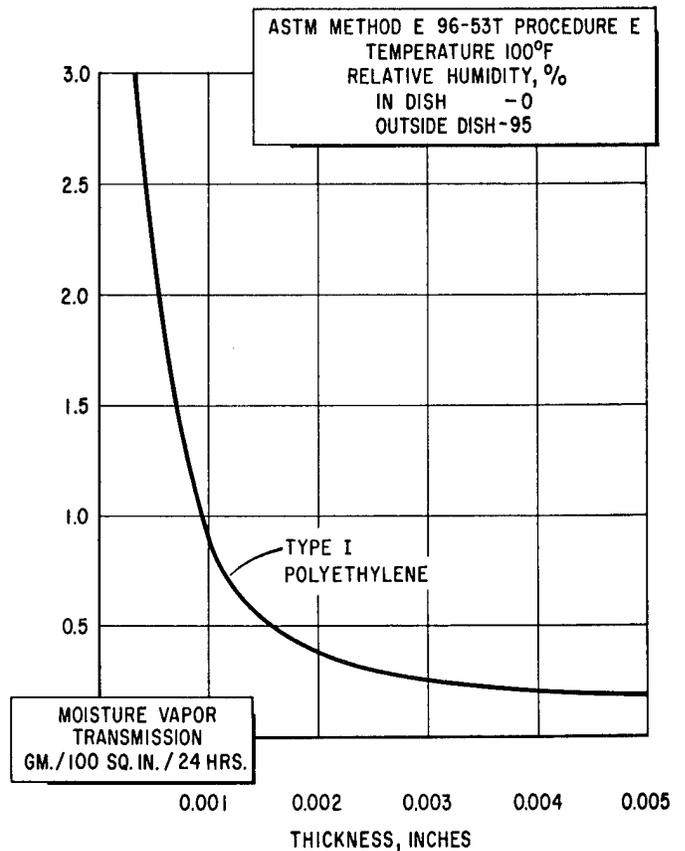


Figure III  
 MOISTURE VAPOR TRANSMISSION  
 VERSUS THICKNESS





# Dow *Plastiatics*

DOW'S CLINICAL APPROACH TO HEALTHY PLASTICS APPLICATION

## ACCELERATED AGING TESTS HELP EVALUATE PLASTICS' WEATHERABILITY

The weatherability of plastics materials is most accurately determined by exterior exposure testing. However, accelerated (machine) aging is often valuable for initial screening, and usually a correlation of results between outdoor and indoor testing can be established.

In selecting plastic materials for engineering use, major considerations are maintenance of adequate strength and acceptable appearance. Both properties are degraded during weathering, a complex process involving interactions of sunlight, air, humidity, wind, rain and heat. Since the full effects of variable climates cannot yet be duplicated in the laboratory, outdoor testing is carried out at stations where extreme weather conditions are the rule. Fig. 1 shows the relative effects of outdoor exposure on three different Dow polyethylene formulations.

Accelerated aging (or weathering) test equipment is designed to accelerate the rate of aging—that is, to produce the same effects as the normal aging process in considerably less than normal time. Two widely-used devices are the "Fadeometer" and "Weatherometer." The Weatherometer uses a carbon arc with intermittent water spray; the Fadeometer an arc only.

An S-1 sunlamp is also valuable for conducting laboratory aging tests. Fig. 2 shows relative severity of accelerated aging equipment. Initial evaluation of

Dow plastics is first made in the Fadeometer. Materials which retain good strength and appearance after 2000 hours in the machine are considered suitable for further testing outdoors.

In evaluating Zerlon® 150, a new Dow plastic, exposures were made in the Fadeometer, in Florida and Arizona. Changes in luminous transmission were plotted at varying time intervals for each exposure station. It was found that 1600-1800 hours in the machine produce the same effect on luminous transmission as one year of weathering at the outdoor stations. Similar relationships were found for certain other properties—such as impact strength—but without an across-the-board correlation. Although such relationships are close approximations, weathering data are still required.

It is possible to predict weatherability in areas having different climates by using a measure of langley units (actinic radiation of one gram calorie per cm<sup>2</sup>). Exposures are first conducted in a selected area and property losses established as a function of the number of langleys (amount of incident light energy). Then, on a basis of pre-set requirements for residual strength and appearance, service life of the plastics material in other areas can be predicted by determining relative langley ratings for those areas.

Most plastics have good aging characteristics for indoor use. The two most

significant factors in degradation are heat and light. For heat, the most important consideration is a safe continuous operating temperature. The effects of light are more varied, with the rate of degradation increasing as ultraviolet energy content rises. Neither incandescent nor fluorescent light degrades plastics appreciably under ordinary conditions, but even filtered sunlight contains relatively damaging UV levels, depending on severity of the climate.

Germicidal ultraviolet lamps commonly used in appliances can be harmful to component plastic parts. UV radiation is relatively intense, and the extent of damage encountered will depend on type, size and location of the bulb, and also the type of plastic chosen. Studies on property retention and light stability should be conducted with prototype parts prior to settling on a final material and finished design for full scale appliance production.

Dow Plastics Technical Service Engineers work with designers and plastics engineers, assisting in materials selection and providing information on design, molding and finishing of plastic parts. Also available are detailed data from continuing Plastiatics Studies on weathering and aging of plastics materials. For these data, and for information on Dow plastics, write THE DOW CHEMICAL COMPANY, Midland, Michigan, Plastics Sales Dept. 1804EX10.

FIG. 1 RELATIVE EFFECT OF OUTDOOR EXPOSURE ON POLYETHYLENE FORMULATIONS

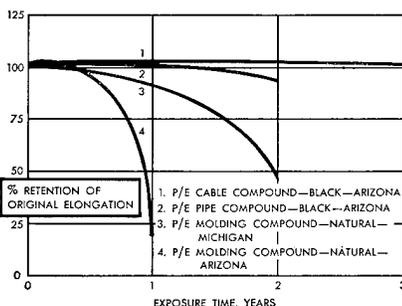
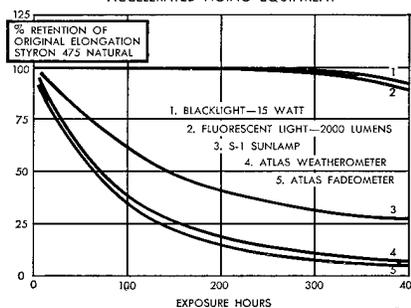


FIG. 2 RELATIVE SEVERITY OF ACCELERATED AGING EQUIPMENT



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# PERMANENCE PROPERTIES OF DOW PLASTICS

## ACCELERATED AGING

### SCOPE

Laboratory aging tests can and do serve a useful purpose in determining overall durability of plastics and other products. These tests perform a dual service in that many materials can be evaluated on a comparative basis at the same time under specifically chosen environments. In addition, predictions on indoor aging and outdoor weathering are possible if a material of known behavior is included in the test program.

Accelerated aging tests are intended to provide quick answers by establishing general trends rather than absolute modes of behavior. The speeding up of results can be accomplished in two ways. One method is by continuous operation rather than waiting for the intermittent effects of direct outdoor exposure. For example, rain is an occasional occurrence. Sunlight varies in intensity and in duration according to location and season of the year. Natural freezing and thawing occur only during the winter months in northerly areas. However, all of these occurrences can be rather closely duplicated in an orderly prearranged manner through the use of specialized equipment.

Another method of acceleration is to increase the severity of exposure conditions above that are usually encountered during normal usage. Of the two methods there is much to commend continuous operation. There is no assurance that large increases in the intensity of various forces of degradation, such as ultraviolet energy, temperature and moisture will increase the rate of deterioration accordingly. Instead there is a good chance that material breakdown will occur at a vastly increased rate. Under these conditions accelerated aging tests may be expected to produce distorted results.

### TEST APPARATUS

In selecting laboratory test equipment to determine permanence properties, consideration should be given to the material being tested and the intended application. Equipment is available today which can provide freezing and thawing conditions, water immersion and exposure to high humidity, thermal shock and ultraviolet light. In many instances there is a combination of two or more of these factors depending upon the effects that are desired. It is also possible to make adjustments in intensity when the need arises. Variation may be required because all materials are not degraded at the same rate and conditions encountered in service are seldom constant. Therefore, in many laboratories it is quite common to see Fadeometer, Weatherometer,

S-1 sun lamp, and other test equipment used both individually and collectively.

### CORRELATION OF DATA

There is one other benefit possible from accelerated aging tests. Frequently close correlation can be established between a test apparatus and outdoor climatic conditions. Usually the association is rather specific and involves only certain materials and perhaps one or two properties, but this can be entirely satisfactory. Such a situation was discovered for luminous transmission of Zerlon® 150, a new Dow plastic copolymer. Fadeometer exposures of 1600 to 1800 hours duration provided the same changes in optical properties as one year of direct weathering in Arizona. Formulation changes to effect improved durability were then made in record time.

## INDOOR AGING

### SCOPE

Most plastics exhibit good aging behavior during indoor usage. Heat and light, the two most significant factors in degradation, are usually encountered at a low intensity level and cause only minor changes in durability. In reference to heat and its effects, the important consideration is a safe continuous operating temperature. There can be a considerable difference in behavior during short or long term usage at the same temperature level. The effects of light are more varied and therefore warrant a more thorough discussion.

### LIGHT SOURCES

Indoor lighting requirements are furnished by infiltration of natural sunlight and by artificial means such as fluorescent or incandescent lamps. Quite often there is a combination of the two sources. Incandescent light is usually not harmful to plastics because no appreciable amount of ultraviolet energy is emitted. Fluorescent light, however, does have somewhat more ultraviolet energy and can affect some plastics adversely. The amount of degradation encountered would depend upon distance from the light source. For example, Styron® Verelite, a light stabilized polystyrene intended for fluorescent light diffuser panels, shows different rates of discoloration depending upon clearance space.

### SUNLIGHT

Direct natural sunlight even though filtered of a high percentage of its ultraviolet energy during transmission through window glass is a source of degradation to plastics. The extent to which damage will occur is

dependent upon climate severity and the material involved. Continuous exposure in a southerly direction in an area such as Arizona would be a harsh test. For less severe exposures as with indirect sunlight and/or northerly climatic conditions, indoor aging is a slow process and need not be a matter of much concern.

TABLE I  
LONG TERM FLUORESCENT EXPOSURE OF  
STYRON VERELITE (CLEAR) TO  
STANDARD COOL WHITE 40 WATT LAMP

Distance of Sample from Lamp, Inches	Yellowing Factor Versus Time*			
	12 months	24 months	36 months	48 months
1/2	0.9	1.4	4.5	11.0
1	0.3	0.9	2.0	6.0
1 1/2	0.0	0.3	1.7	4.5
3	0.0	0.0	0.6	1.7

$$*Y.F. = \frac{(T_{420B} - T_{420E}) - (T_{680B} - T_{680E})}{T_{560B}} \times 100$$

T = % light transmission, B = blank, E = exposed

1. The Society of The Plastics Industry and the Illuminating Engineering Society define objectionable discoloration in polystyrene as a yellowing factor in excess of 15.
2. By way of comparison general purpose polystyrene (Styron® 666) discolors at a rate at least three times as fast as the Styron Verelites.

#### DARK STORAGE

The same general pattern of good permanence is even more applicable to dark storage. Most plastic products can be expected to remain virtually unchanged in the absence of high heat and bright light. For example, Styrofoam® boards removed from the ceiling of a cold storage room cycled between +40° F and -40° F exhibited original values for thermal conductivity and compressive strength after 8 1/2 years of service.

#### U. V. — OZONE LAMPS

Recently there has been widespread interest in ozone-generating ultraviolet lamps for dehumidifiers, clothes driers, refrigerators, etc. The primary purpose here is the achievement of a germicidal effect. Radiation of this type would have an adverse effect on component thermoplastic parts used in such equipment. The amount of degradation would depend upon the type and size of these bulbs and also their location. Color changes and reductions in strength that would occur

might not be tolerable for long term use, and it would be advisable to conduct preliminary investigations to determine specific effects before full scale production of parts is scheduled.

## OUTDOOR WEATHERING

### SCOPE

Direct outdoor weathering is a complex process involving interactions of light, heat and humidity. For a complete study of weatherability it would be necessary to study the effects of all the various climates. However, for practical purposes it is adequate to confine testing to those localities where product use is anticipated or where extreme weather conditions are encountered.

### CLIMATE — TEST SITE

In the United States there are two commonly used exposure testing areas: Florida, a marine subtropical climate, and Arizona, a semidesert with high temperatures, little rain and intense ultraviolet radiation. Dow plastics are also exposure tested in Michigan where sunlight is less intense but temperatures are non-uniformly cyclic and often very low or very high.

### PROCEDURES

Due to seasonal and geographical weather variations there is good reason to impose as much uniformity on other test conditions as possible. Such factors as exposure direction, angle of repose, backing material, and method of placement have significant effects and are therefore standardized in most exposure studies. Furthermore, weather is so highly variable in some areas that exposure results for short periods of time, that is less than one year, may have very little value in estimating what might happen over longer periods of time.

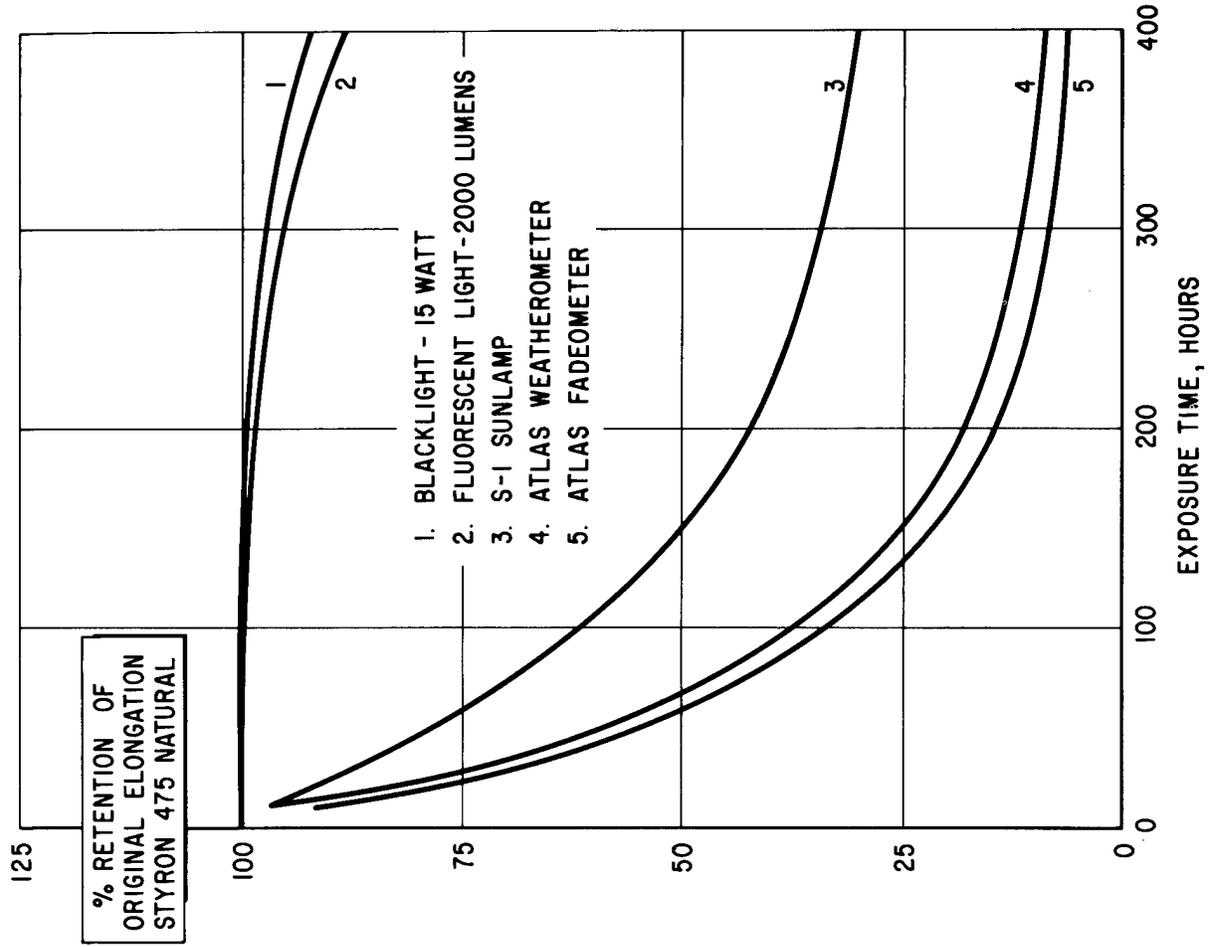
### EVALUATION OF DATA

Weathered samples are evaluated for permanence properties after careful observations of visual appearance, determination of residual strength, or some other specific measurement related to the application. The extent to which original properties are maintained is the basis for ratings and subsequent recommendations for product use. Due to the wide range of outdoor permanence exhibited by plastic materials, consideration should be given the variables. These are:

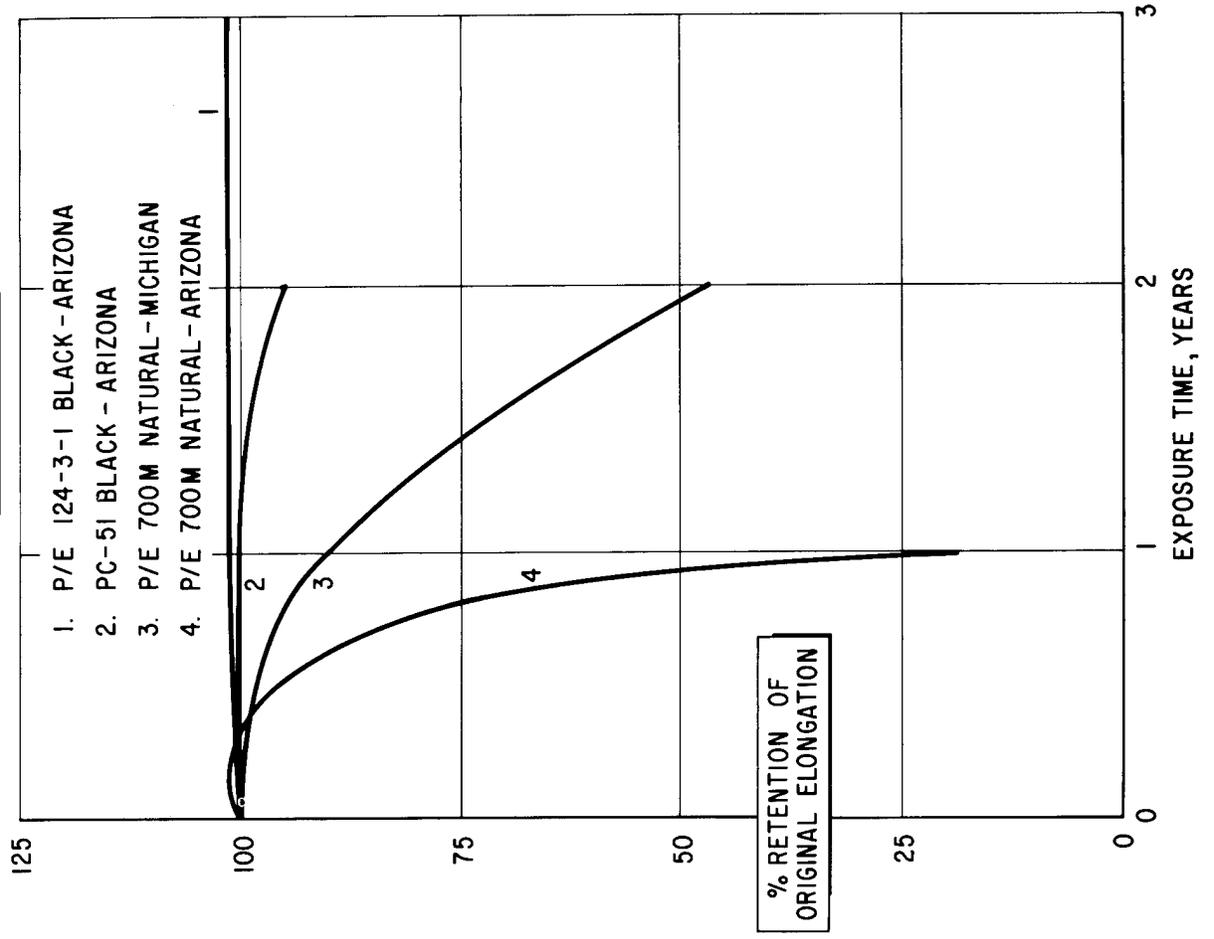
- 1) Requirements of the intended application.
- 2) Climatic conditions in areas of intended use.
- 3) Expected use life.

Careful review of the above factors is necessary because only the most durable of plastics can be safely recommended for continuous outdoor use.

### Relative Severity of Accelerated Aging Equipment



### Polyethylene



# *Plastiatics*

DOW'S CLINICAL APPROACH TO HEALTHY PLASTICS APPLICATION

## IMPACT ENERGY DATA GUIDES SELECTION OF PROTECTIVE PACKAGING MATERIALS

Today's packaging applications are unlimited, ranging from heavy industrial parts to fragile instruments. Though protective requirements may vary from product to product — including protection against heat, cold, water, dehydration—the one common to most packages is impact protection.

Regardless of the source of impact, or how the impact load is delivered, package contents must be cushioned in such a way that acceleration or deceleration at the moment of impact is kept below certain limits, depending on the contents' fragility. In evaluating packaging materials such as the Dow foam materials, Ethafoam\*, Styrofoam®, and Pelaspan®, several related factors must be considered:

- 1—thickness of cushioning material
- 2—conformance to the shape of the object
- 3—velocity of the impact blow
- 4—force of the impact blow
- 5—temperature
- 6—amount of energy absorbed by the cushioning material
- 7—resiliency (springback) of the cushioning material

A camera or optical instrument, for example, would require far greater protection against impact than an electric motor. But precisely how much protection? To help packaging engineers answer this question, Dow Plastics Technical Service Engineers have developed extensive data on the dynamic cushioning properties of Dow foam materials.

The curves in Fig. 1 show the relationships between peak deceleration in "g's" (multiples of acceleration due to gravity) and static stress in psi, for 2-inch thick Ethafoam from varying drop heights.

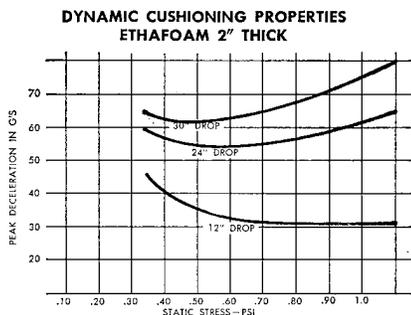
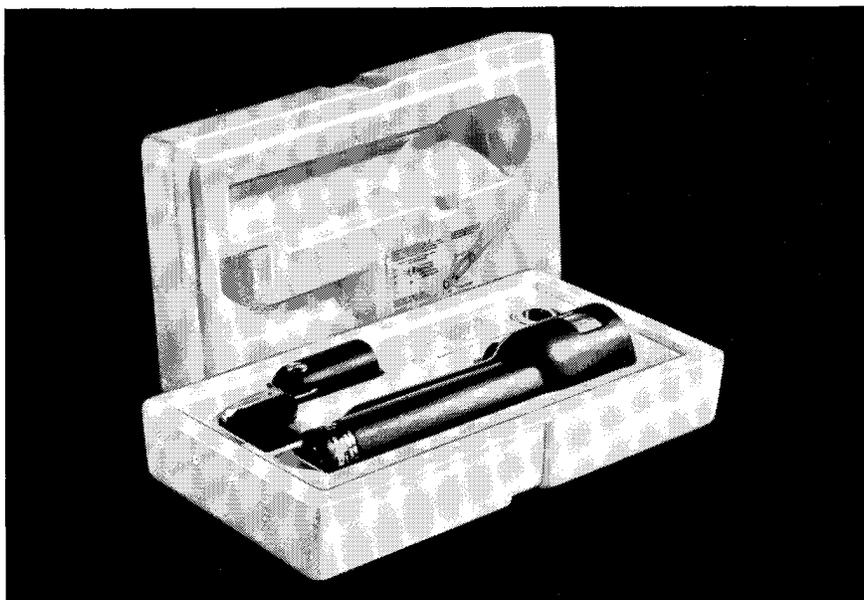


Fig. 1. Cushioning properties are plotted for varying drop heights.



Molded Pelaspan plastic package gives delicate microphone positive impact protection.

The equipment on which these studies were made is shown in Fig. 2. A loading head, mounted on a vertical guide, is dropped from a predetermined height onto a sample of the cushioning material under test. Attached to the loading head is an accelerometer which measures impact deceleration in "g's." Accelerometer output is recorded on the oscilloscope.

In this test, the weight and surface area of the loading head in contact with the test sample determine the amount of static stress exerted on the sample. By continually increasing the weight on the loading head, deceleration in "g's" vs. static stress in psi can be plotted. Once an initial evaluation has been made (factors 1 through 7, in column 1),

data from the dynamic cushion tests can be used to select the packaging material which provides the proper degree of resilience, rigidity and energy absorption. The data will also be of value in package design, and in determining the optimum thickness of the foam material to be used.

Data from these and other continuing Plastiatics Studies are available to packaging engineers and designers. These studies provide information not only on packaging, but on plastics properties, and on improved methods of design, molding and finishing of plastics. For information, write THE DOW CHEMICAL COMPANY, Midland, Michigan, Plastics Sales Dept. 1805FT11. \*Trademark

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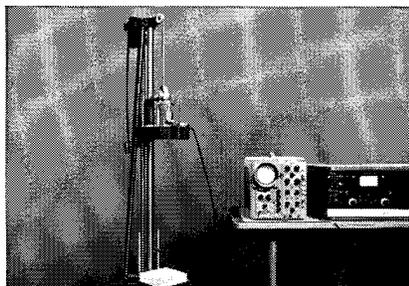


Fig. 2. Dynamic cushion testing equipment for evaluating packaging materials.

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# THE PROBLEMS OF PROTECTIVE PACKAGING

## INTRODUCTION

Package protection usually means protection from damage due to impacts, although it may also include protection from damage due to temperature, air, water and other contaminants. A packaging material should protect against as many damaging effects as possible.

Today there is a wide choice of packaging materials available. Prominent and among the newest are plastic foams. They offer excellent protection from damage, particularly damage due to impacts. These foams combine impact resistance with light weight (as little as  $\frac{1}{2}$  pound per cubic foot), and they are easily molded into desired shapes. Their versatility make them readily adaptable to most packaging jobs.

The problem of evaluating any packaging material is complicated. Impact resistance of a packaging material varies not only with drop height and load per square inch but also between samples, with a change in sample size, and with a change in impact velocity. Packaging materials vary greatly in the amount of permanent compression they attain from impacts. In addition, successive impacts usually result in a decreased ability of the packaging material to absorb shocks. All of these factors make evaluation of packaging materials very difficult. ASTM has developed a test method for flexible foams which solves some of the testing problems. The work covered in this report was in accordance with the ASTM method of evaluating impact resistance of flexible foams, and a modification of the method was used for rigid foams.

## TESTING PLASTIC FOAMS FOR IMPACT RESISTANCE

Cushioning properties of foams are evaluated in accordance with ASTM Test Method D1596-59T by use of an impact tester. This test method specifies that three random samples be impacted five times and the results of the last four be averaged. The selected sample size, thickness, and drop height are fixed for the test while the variable is the platen weight or load on the specimen. These evaluations are made by dropping a platen of known weight from a given height onto a foam sample. The drop height may be any figure, however, 18 inches and 30 inches are quite common. If the sample thickness decreases 10% during the test, it is discarded and a new sample selected. The foam sample should be square to conform to ASTM specifications. Details of specimen preparation and testing can be found in the ASTM Manual.

To obtain impact data, an accelerometer is mounted on the platen and its output signal is recorded on an oscilloscope. A typical equipment setup is shown in Fig. 1. This setup also uses a preamplifier to intensify the signal from the accelerometer before it is fed to the oscilloscope. The oscilloscope used here is a Hughes Model 104E which has a memory circuit that enables the operator to hold a trace as shown in Fig. 2. Without this memory circuit it would be difficult for the operator to accurately record the impact readings because of the speed at which they occur. If an ordinary oscilloscope is to be used for this work, a polaroid camera is the most convenient device for recording the impact trace.

A curve of cushioning properties is obtained by plotting maximum deceleration versus static stress on the foam sample. Maximum deceleration is read as the peak of the curve shown in Fig 2. Static stress is obtained by dividing the sample area by the platen weight. Varying the static stress on the foam sample gives a continuous curve which shows the deceleration from each static stress loading of the sample. This enables the packaging engineer to select an optimum thickness, size and type of foam for a given application from a set of such impact curves.

## TEST RESULTS

Fig. 4 shows the test results for Ethafoam, a light weight, flexible polyethylene foam. In this test, samples eight inches square were subjected to impact. The oscilloscope in Fig. 1 shows a typical trace for Ethafoam. Thicker samples reduce the peak deceleration as shown in Fig. 4 by absorbing the energy of the impact over a longer period of time, therefore, the thicker samples in this example have oscilloscope traces which are lower and broader.

The area under the trace is a function of the energy of impact. The most desirable way to absorb impact in packaging is through a gradual absorption while keeping the deceleration forces on the protected object at a minimum. The "y" axis on the oscilloscope shows this deceleration. Likewise, the slope of the trace is also an indication of the ability of the foam to absorb energy while minimizing shock.

The static stress on the foam is important in determining how well it will absorb a given shock. Stiff foams will absorb energy well under high static stresses but not low static stresses. Therefore, in selecting a foam for packaging, it's necessary to calculate the static stress to be encountered and then select a foam from

curves of impact absorption which give the best characteristics for that level of stress.

Rigid foams and semi-rigid foams present a different problem in evaluation. The ASTM test method was designed for flexible foams where the first impact is not recorded and the samples are used until they compress 10%. Rigid and semi-rigid foams often compress 10% or more on the first impact. In some applications, this is a desirable form of failure and it is necessary when evaluating these foams to use the first impact reading and then discard the sample if it compressed more than 10%.

Figs. 5, 6, 7 and 8 show the impact curves for Styrofoam® 22 and Pelaspan. Styrofoam® 22 is a rigid polystyrene foam with a density of 1.6 to 2.0 pounds per cubic foot. It is foamed as large planks and logs and cut into board stock for applications in packaging, buoyancy, insulation, etc. Pelaspan is also a polystyrene material, however, it is sold either unexpanded as beads or partially expanded in the shape of little spheres. Light weight foams used in packaging require the use of partially expanded beads (called prefoamed beads). These beads are further expanded by heat in the mold. The density of the molded foam is dependent upon the prefoamed bead density.

The density of the molded foam greatly affects its flexibility. As the density decreases to around 1 lb./cu. ft., flexibility increases. Flexibility is further increased when the foam is impacted. In these impact tests, 1 and 2 lb./cu. ft. density Pelaspan samples were used.

Fig. 3 shows an oscilloscope trace for Styrofoam. The flat, cut-off portion at the top of the curve is typical for rigid foams. The steep slope as the deceleration builds up rapidly is typical of a stiff inflexible cushioning material. This would be a very poor packaging material if the deceleration kept increasing at a rate indicated by the slope. However, at a certain point on the trace, the cell structure of the foam begins to collapse. These collapsing cells absorb energy very

effectively and flatten the deceleration curve. When most of the energy of impact has been absorbed, the deceleration returns to zero.

Figs. 5, 6 and 7 show the impact curve for rigid Styrofoam and 2 lb./cu. ft. density Pelaspan. These curves show the rigid foams are very good absorbers of impact, however, the number of impacts that can be absorbed is limited. When the cell structure is completely broken down, the foam is no longer an effective cushion. Increasing the foam thickness in a completely rigid foam has little effect on the deceleration curve; however it does increase the number of impacts that can be absorbed. Fig. 6 shows that Pelaspan has characteristics of both rigid and flexible foams. As the thickness of the cushion increases, the impact curve is lowered and the number of impacts that can be absorbed is increased.

Fig. 2 shows a typical trace for a semi-rigid foam of 1 lb./cu. ft. density Pelaspan. The trace has characteristics of the impact curves of both rigid and flexible foams. The upper portion of the trace is irregular, indicating cell destruction; however, flexible cushioning is also indicated by the general shape of the trace. As this sample was repeatedly impacted the shape of the trace changed to that similar to Ethafoam in Fig. 1. This occurs because the rigid cells are destroyed and only the flexible characteristics of the foam remain. During this process, the foam thickness decreased about 20%.

The original cushioning characteristics based upon the first impact are shown as the bottom curve in Fig. 8. The top curve in Fig. 8 shows the cushioning characteristics after the rigid cells have been partially destroyed and the foam becomes flexible. The area between the curves might be called the "area of cushioning". The maximum deceleration will always be between these two curves. All rigid and semi-rigid foams have an "area of cushioning", however, in most cases, the upper curve is beyond a reasonable range of deceleration. Therefore, if the package is subject to numerous destructive impacts, a flexible foam should be used.

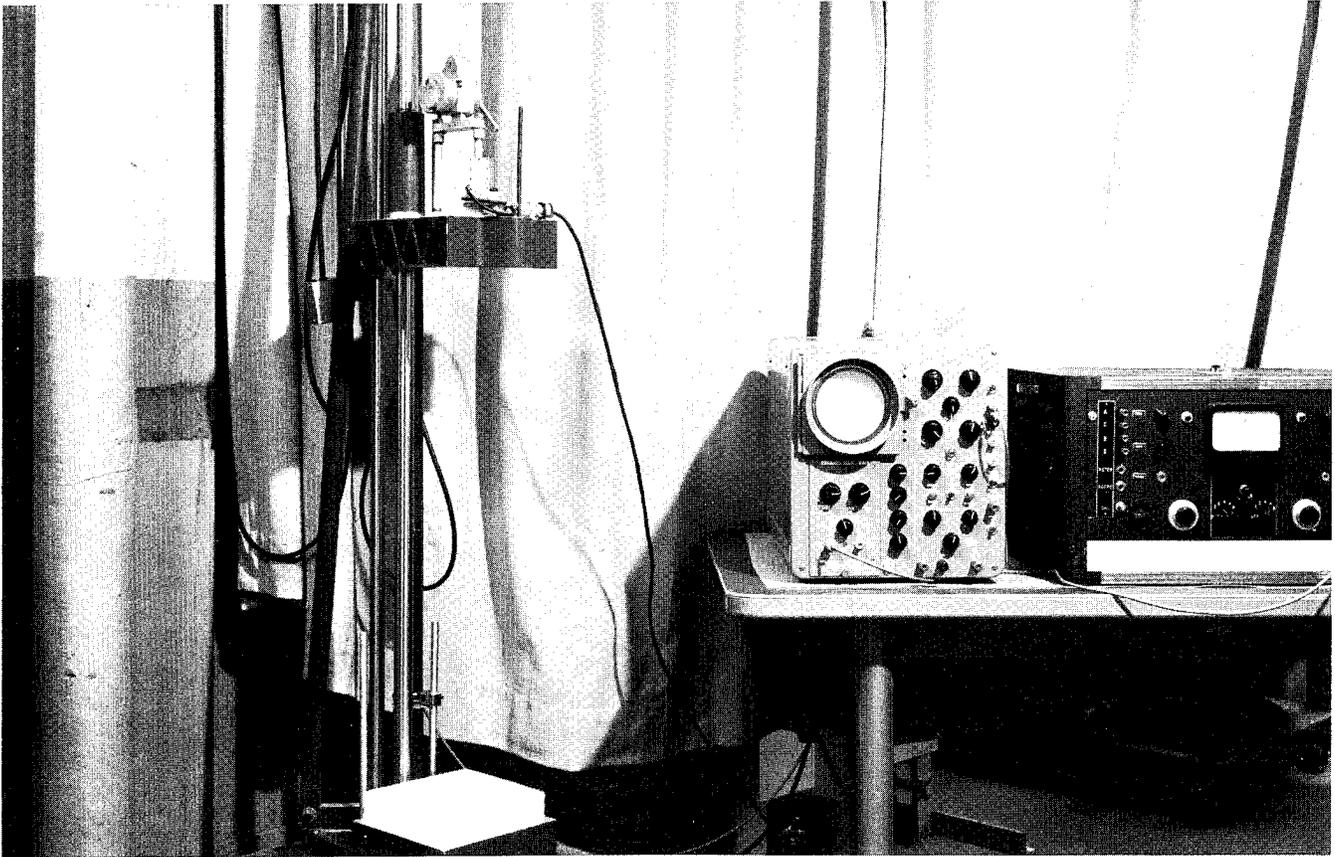


FIG. 1

Impact Testing Equipment for Evaluating Packaging Materials

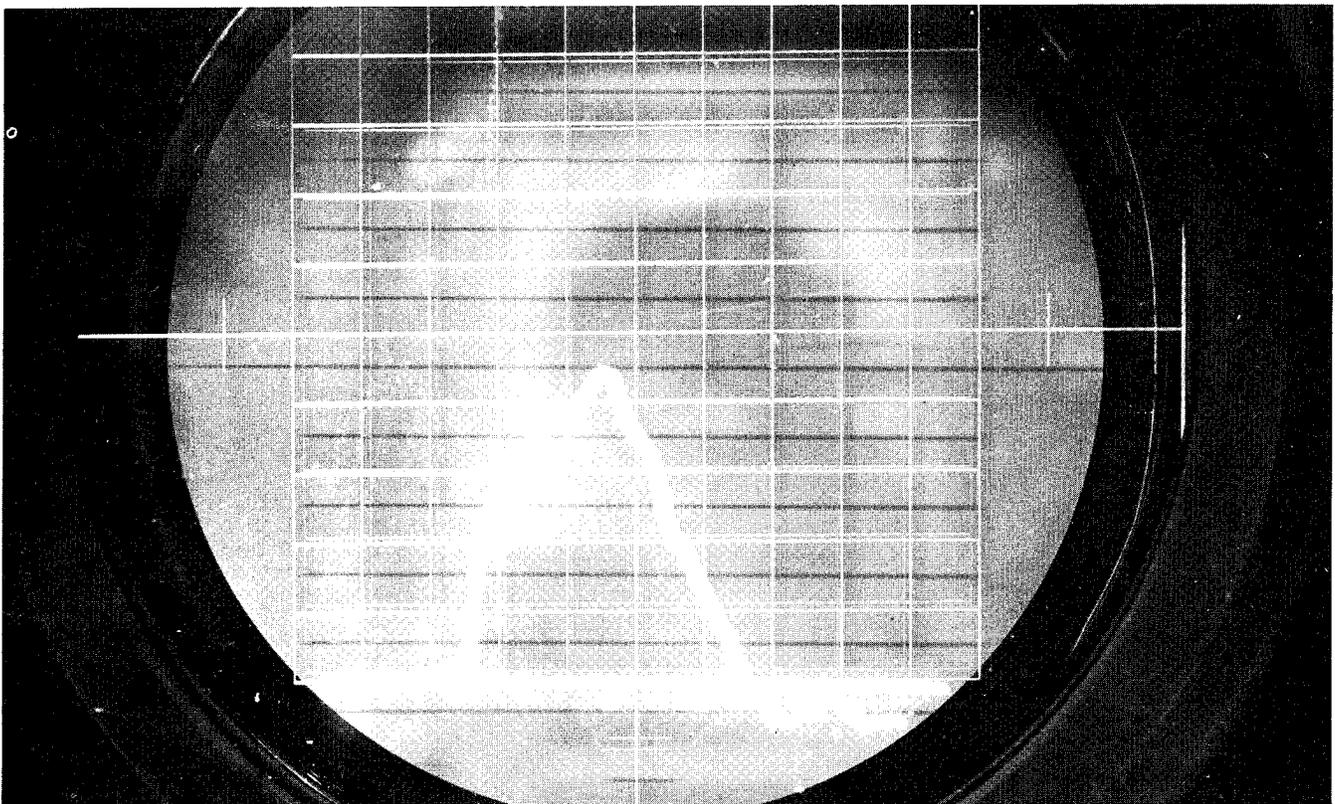


FIG. 2

Oscilloscope Trace Showing the Cushioning Characteristics for a Sample of Pelspan

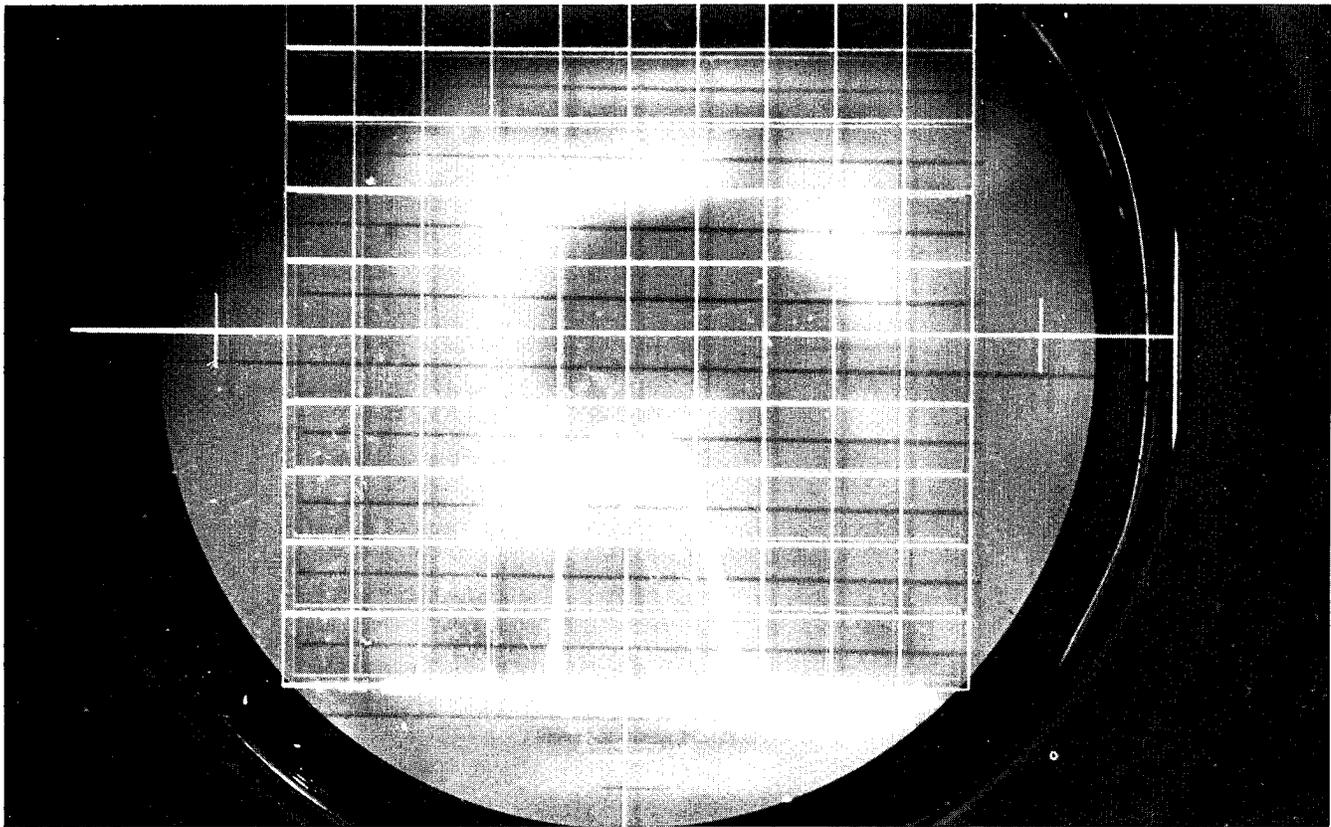


FIG. 3

Oscilloscope Trace Showing the Cushioning Characteristics for a Sample of Styrofoam

FIG. 4

DYNAMIC CUSHIONING  
PROPERTIES OF ETHAFOAM

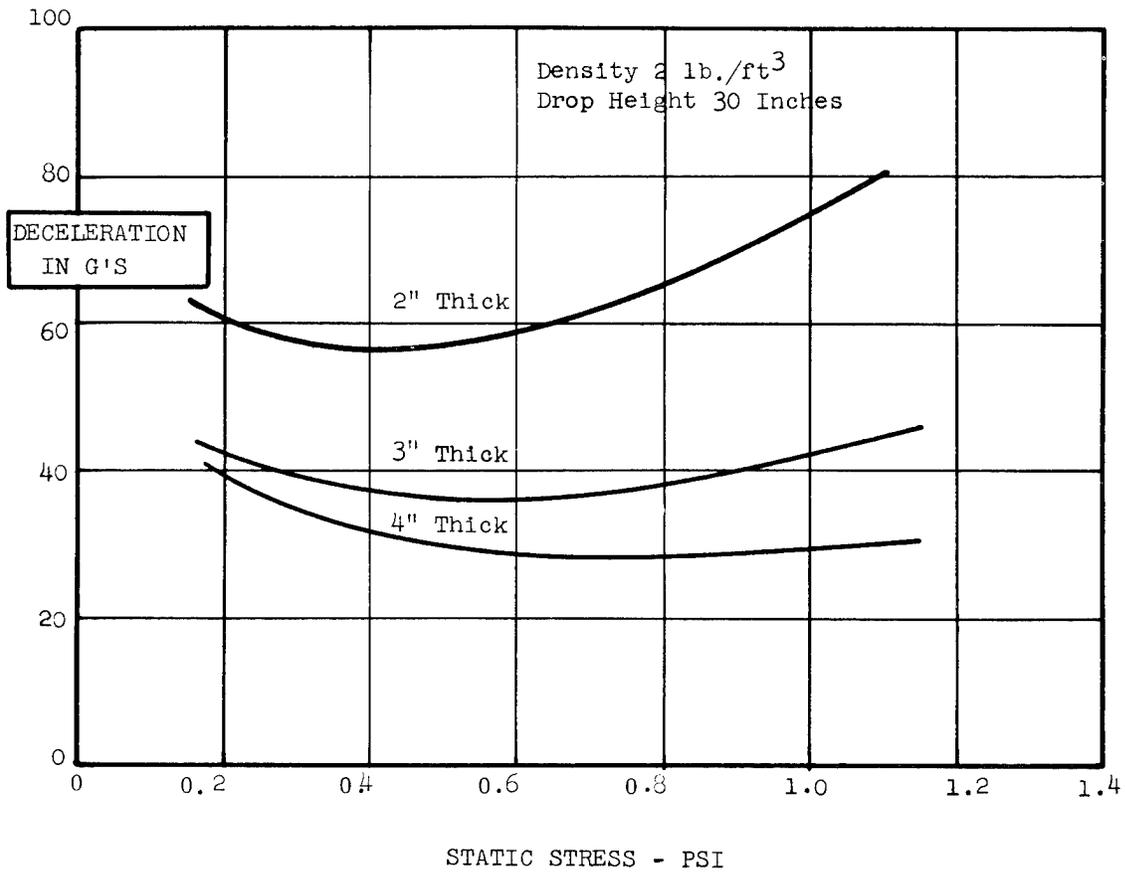


FIGURE 5

DYNAMIC CUSHIONING PROPERTIES OF STYROFOAM

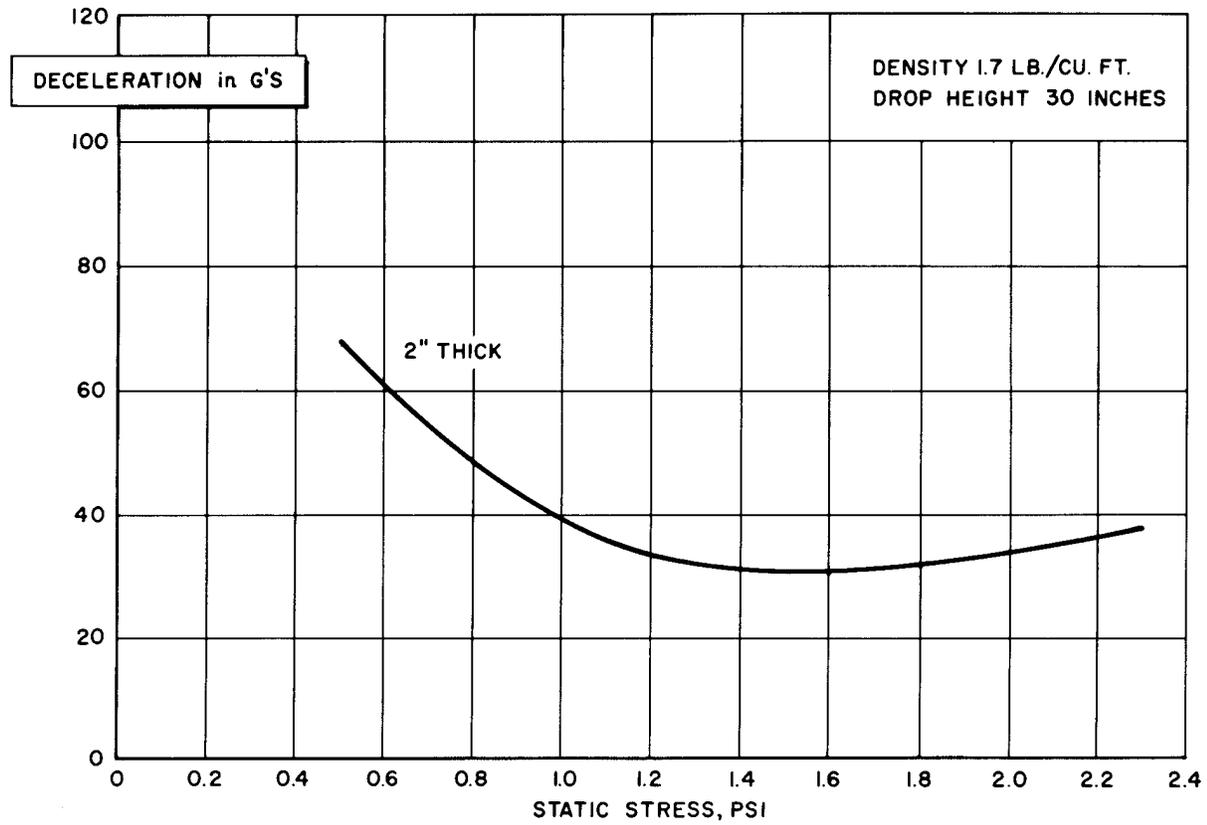


FIGURE 6

DYNAMIC CUSHIONING PROPERTIES OF PELASPAN 8

