Water Vapor Permeability of Polyethylene and Other Plastic Materials

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Low-density polyethylene sheathing materials have water vapor permeabilities on the order of 10^{-8} *at 22°C. High-density polyethylenes have permeabilities about one-third to one-sixth that of the low-density polyethylene. Copolymers of polyethylene have higher permeabilities than the homopolymer. As an example, 15 percent ethyl acrylate comonomer increased the permeability by a factor of 10 over that of straight low-density polyethylene. The nonolefinic polymers tested have higher permeabilities. For example, polyurethane plug compound has a permeability more than 80 times higher than low-density polyethylene. Finally, it was found that the addition of carbon black decreases the water vapor permeability roughly in proportion to the amount of carbon black, and that the permeability of these materials increases with increasing porosity.*

To make these measurements, two types of laboratory apparatus have been constructed. The first of these makes the permeability measurement on a tubular sample of the material, and the other on films. Both methods used an electrolytic moisture monitor, which is commercially available, to make necessary determinations of water transfer rate through the plastic.

I. INTRODUCTION

The post war years have seen a phenomenal proliferation of plastic materials throughout industry, and the Bell System has been no exception. At least part of the reason for this widespread and ever increasing use is the attractive ease of fabrication of plastic materials and their relatively low cost. Their inertness to certain environmental factors and their chemical and physical stability also add to their value in a great number of applications, including environmental protection. Not only are these plastics used to enclose and isolate an entire apparatus or structure from its environment, they are also used as protective coatings and as seals such as O-rings in metal containers. One of the undesirable and detrimental factors in the environment is water, and consequently, a need developed for information on the water resistant characteristics of the many plastics in use. This water resistant characteristic is the *water vapor permeability* (WVP) of the material, and has been measured for several materials of interest. This paper discusses the need for the measurements, the method of making and correlating measurements, and the significance of the results.

Several problems have been documented involving moisture transfer rates in complicated, composite plastic materials. Water in small amounts, particularly in pulp insulated cable, has detrimental effects on the electrical characteristics of the core. Splicing an Alpeth cable into a paper insulated cable results in moisture accumulation in the latter cable, presumably as a result of moisture diffusion through the Alpeth sheath and subsequent migration into the paper core. Air fed into pulp cable through polyethylene air tubing also results in moisture accumulation in the pulp because of water transmission through the tubing walls.

Most of the design and investigational calculations made in regard to these problems were based on sparse data for more or less idealized systems. Unfortunately, for the materials of interest, there are no moisture transfer rate data available to the engineer. The studies described in this report were motivated by this paucity of data and it was planned to acquire such data for practically pertinent systems for the design engineer. Although the work is directed toward problems arising in the cable plant, the data and results of this study may be of use in other areas employing plastic materials.

In order to correlate and understand the effects of different parameters on permeation, it was necessary to include in the investigation measurements on systems far removed from practically applicable systems. For example, an investigation of the effect of carbon black loading on permeability must include measurements on natural (unloaded) polymers as well as actual sheathing materials which contain carbon black.

The reader will not be subjected to a long and detailed review and analysis of the previous literature in this field. There are two reasons for this; first, recent reviews[1,2] have been given of the literature on permeation processes in plastics. Secondly, the previous literature is principally concerned with purified materials and is not highly pertinent to the problems and information dealt with in this paper. Previous papers[1,3] have indicated that the permeabilities of polyethylenes to water vapor are quite low, on the order of 2×10^{-8} scc*/sec-cm-cm Hg. Also, the previous work has shown that permeability decreases with increasing polymer density.[3] In addition, it has been found that the permeability is an exponential function of reciprocal absolute temperature[3,4] and that the activation energy for permeation ranges from some 6 kilocalories to almost 10 kilocalories.[3,4]

Water vapor permeabilities of other materials have also been given in the literature. It is generally found that the permeabilities of materials such as nylon, cellophane, and other nonolefinic polymers are much higher than permeabilities of polyethylene.[1,2,4]

There is some disagreement[3,4] among previously published values of permeability of polyethylene, and this has been explained[3] in terms of differences in the samples of materials used, but all the previous work agrees on one point: The transport of water vapor through polyethylene obeys Fick's and Henry's laws. Fick's law relates mass transfer rate M to a concentration gradient and in finite difference form is

$$M = DA \frac{\Delta C}{\Delta X}, \tag{1}$$

where D is the diffusion coefficient, A is an area, and ΔC is a concentration difference across an increment in length, ΔX. Henry's law is

$$C = Sp, \tag{2}$$

where S is solubility and p is the vapor pressure of penetrant. If Henry's law and Fick's law are combined

$$M = DSA \frac{\Delta p}{\Delta X}. \tag{3}$$

Usually,

$$DS \equiv P, \tag{4}$$

the permeability.

These laws are used to correlate moisture diffusion rates by calculating P from the definition and data on transfer rates. These data must include, of course, M, Δp, ΔX. The principal experimental problem is measuring these factors on practically pertinent systems so that P can be calculated.

Essentially, the plastic sample separates two chambers, one of which

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* The term scc refers to cubic centimeter of vapor at standard temperature and pressure.

contains water at a known temperature. As this water permeates the sample, it is swept from the other chamber (with a carrier gas) and into a water measuring instrument. From the geometry of the sample, A and ΔX in (3) can be determined and from the water temperature, Δp can be obtained. The problem is in measuring M, the mass flow through the sample. The water measuring instrument must be capable of measuring very small amounts of water: for example, if a plastic tube is 10 cm long, 2.5 cm in diameter with a wall thickness of 2 mm, there will be only 5 μg of water per hour permeating through the wall. Previous workers have indicated the rather large amounts of water that can accumulate in some of the older cable designs but this is in terms of miles of cable and years of time. Obviously, for experimental facility we must use shorter lengths of cable and must be able to work on a much shorter time scale and this, in turn, forces one to work with very minute quantities of water. So there is no inconsistency in the larger amounts of water in the cable plant problems and minute amounts encountered in the laboratory experiments.

II. DESCRIPTION OF EXPERIMENTAL APPARATUS

Moll[2] has described some of the more widely used techniques of measurement of permeability. Most of these methods were not directly applicable to water permeation in the materials of practical engineering interest. One such earlier method uses a thermistor (to detect water) which can become fouled from plasticizers and other volatile additives in sheathing material. The "cup method" is usually used on materials with higher permeabilities. Moreover, both methods are more suited to very thin samples—less than 5 mils and sometimes as low as 1 mil.[4] At these thicknesses, surface imperfections (holes, pits, etc.) can account for a large part of the water transferred across the film. For these reasons, it was felt desirable to construct a new apparatus based on an electrolytic water measuring technique which has proved reliable.[5]

An instrument capable of making the necessary water measurements is available commercially (Consolidated Electrodynamics Corporation). This "moisture monitor" operates as follows: A glass cell is coated with phosphorus pentoxide which is a tenacious absorbent for water. The coat of phosphorus pentoxide is interspersed with platinum electrodes and a carrier gas sweeps the moisture from the test sample and into the cell. As the water is absorbed by the phosphorus pentoxide it is electrolyzed to hydrogen and oxygen and the current necessary for electrolysis is directly related to the amount of water so that the detector is calibrated essentially by the definition of electrical current. The precision of measurement depends on the precision of a microammeter. The detector also has the advantage of being specific for water: other materials (such as antioxidants and light oils) which diffuse through the plastic or out of it do not interfere with the water measurement.

Several factors are involved in deciding on size and form the sample should have. Considerations of accuracy determine the size of the sample; the larger the sample area the greater the rate of water penetration which, in turn, permits more accurate measurement.

The apparatus should be capable of making measurements on tubular samples such as cable sheath and air tubing, for example, but certain test materials are not available in quantities sufficient to extrude tubes and certain others (e.g., polyurethane) cannot be extruded easily so that it was necessary to make measurements on films of these materials. Obviously, two different methods must be used—one for tubes and one for films.

III. TUBULAR APPARATUS

Briefly, the tube apparatus (Fig. 1) consists of one or more tubes of plastic material submerged in a tank of water and connected at one end to the "moisture monitor." Dry carrier gas is forced through the tube to sweep out water which has permeated the tube wall. The rate at which moisture is registered on the moisture monitor gives M in μg/sec and from this and the geometry of the tube P is calculated.

3.1 *Carrier Gas Supply*

The water is swept out of the plastic tube and into the moisture monitor with an inert carrier gas and it is imperative, for accuracy, to have the carrier gas enter the tube dry as possible. The carrier gas used has a water content of approximately three parts per million which is in the order of the water content of the gas in the tube. Thus, it is necessary to remove even this small amount. This operation is accomplished with an electrolytic drier cell as shown in the upper left of Fig. 1. The "wet" carrier gas from the supply cylinder is passed through the cell and the water is absorbed on the phosphorous pentoxide and electrolyzed. This gives a carrier gas *free* of moisture.

3.2 *End Seals*

The ends of the plastic tubes are sealed into the apparatus with "Swagelok" fittings. These fittings were originally designed for metal

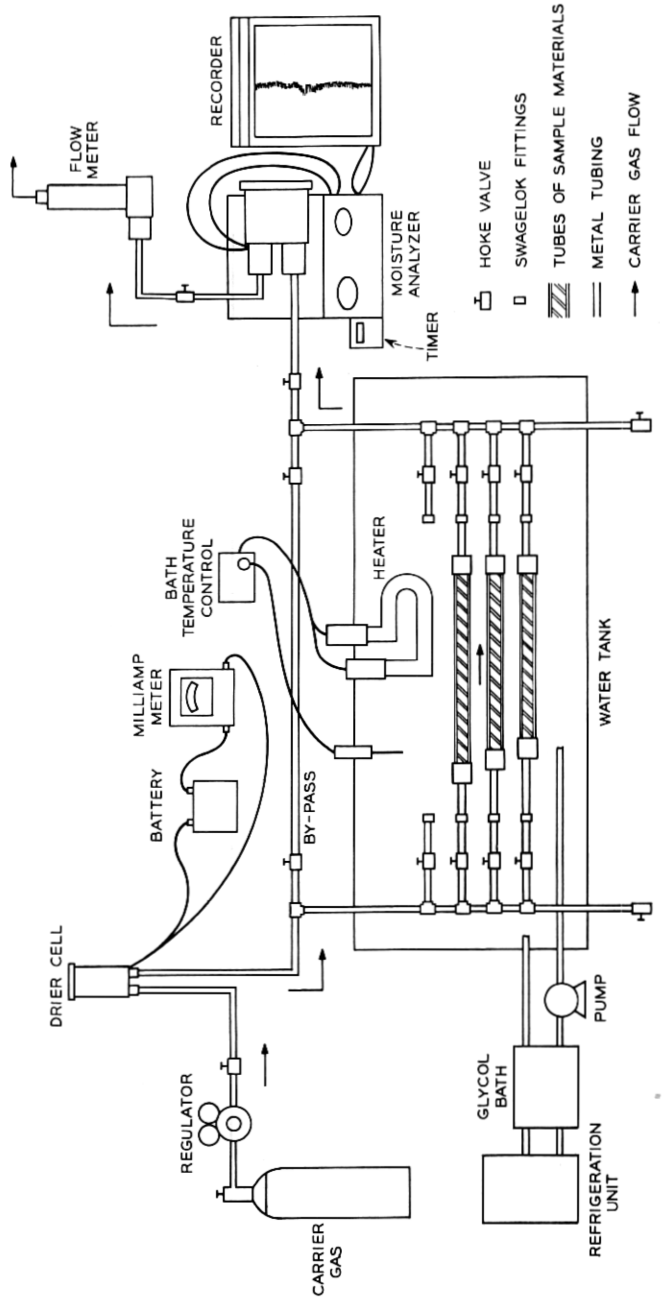

Fig. 1 — Moisture permeability apparatus for tubular samples.

tubing but they were adapted to plastic tubing by inserting a supporting element inside the tubing. These end seals were thoroughly tested and proved very effective as discussed below.

The seal consists of an anvil and chuck and two swaged ferrules supported by an insert inside the plastic tube. When the anvil and chuck are tightened together, the ferrules deform inward against the tubing which is supported by the insert. The ferrules also make a tight metal-to-metal seal against the chuck and anvil, respectively, so there is no path for vapor leakage through the fittings.

3.3 *Fittings and Other Equipment*

Stainless steel tubing is used in parts of the apparatus which could contain water to minimize sorption of water on the tubing walls. In other parts of the apparatus which contain only dry gas, copper tubing is used because it is much easier to fabricate.

The outlet from the moisture monitor is connected to a flow meter to insure that the carrier gas is not flowing so rapidly as to "flood" the electrolytic cell and permit water to escape electrolysis.

3.4 *Temperature Control*

Temperature affects permeability and the temperature of the water must be controlled accurately. This is accomplished with a large, constant temperature heat sink consisting of a glycol bath cooled continuously with a refrigerator. The water is circulated continuously (two gallons per minute) from the sample tank through coils in the cold glycol bath and then back into the tank. This gives a large heat sink and effectively isolates the sample tank temperature from room temperature variations. The temperature of the water is regulated by heating with a temperature controller. Temperature variations can be kept below 0.1°C at 30°C or above. The water in the tank is stirred to keep a uniform temperature throughout. A ten gallon per minute pump, located outside the tank, pumps water from the tank and directly back to the tank through a tube with holes. This effectively stirs and distributes the water and keeps it at a uniform temperature.

3.5 *Measurements*

To calculate P from the measurements on tubes, (4) must be put in cylindrical coordinates. This form of the equation has been given previously[6]

$$P = \frac{M \ln (D_o/D_i)}{2\pi(p_o - p_i)L} ,$$

where L is the sample tube length and D_i and D_o are inside and outside tube diameters. p_i and p_o are water vapor pressures inside and outside the tube. Because the dry carrier gas sweeps water from inside the tube, p_i is small and can be neglected in comparison to p_o.

The inside and outside diameter required care in measurement because the calculated values of P are sensitive to errors in D_o and D_i of the tube samples. These diameters were measured accurately in the case of clear plastic by means of water displacement. A measured length of the sample tube L (usually one meter) was filled with an accurately measured volume V of distilled water. Obviously,

$$V = \frac{\pi D_i^2 L}{4},$$

or

$$D_i = \sqrt{4V/\pi L}.$$

D_i can be calculated from the volume of water V, contained in the length of tube, L. The thickness of the tube wall was measured by encapsulating a short segment of tube in epoxy resin and polishing the mount down until the tube cross section was exposed. The wall thickness was then measured with a stage micrometer. D_o can be obtained from D_i and the wall thickness. The outside diameters of opaque tubes are measured by inserting a sample tube (sealed at one end) into a graduated glass column and measuring the volume ΔV, of water displaced by a given tube length, L. The outside diameter, D_o can then be calculated from

$$D_o = \sqrt{4\Delta V/\pi L}.$$

The inside diameter, $D_i = D_o - 2 \times$ wall thickness.

3.6 *Preliminary Measurements and Tests of Apparatus*

Initial measurements were made to prove the feasibility of the apparatus. It was necessary to check the seals at each end of the tubes to assure that they were watertight. This was done as follows: The permeability was measured for samples of different lengths (67.95 cm, 113.64 cm, and 154.31 cm) of the same material. If the end seals are secure, there should be no difference in permeability for these three samples because P is a property of the plastic and should not depend on the experiment. Fig. 2 gives the results of this test and the good agreement in P for three samples indicates the integrity of the end seals. These tests were made on low density ($\rho = 0.917$) polyethylene tubing supplied by Hydrawlik, Inc., Roselle, New Jersey.

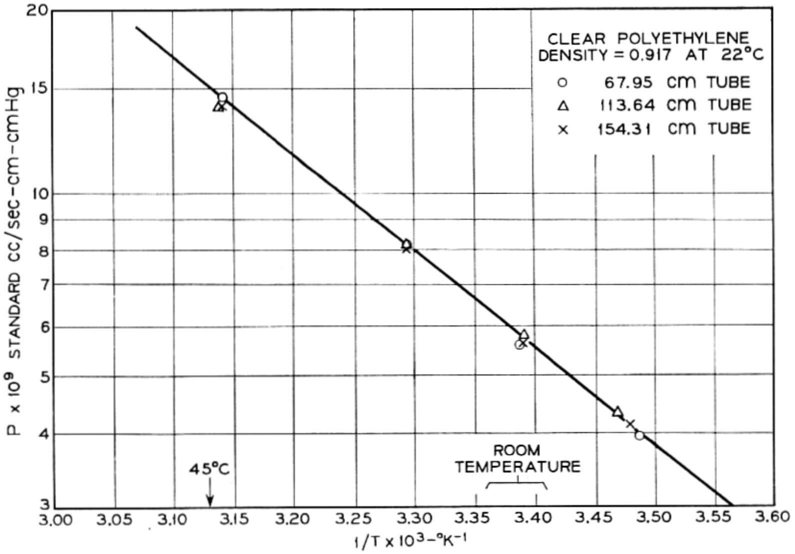

Fig. 2 — Permeability as a function of temperature for various lengths of sample.

IV. FILM APPARATUS

The film apparatus (Fig. 3) consists essentially of two aluminum discs; one on each side of the circular test film. The two discs are identical so that it is necessary to describe only one of them. Two cavities are machined in each disc: one of these is covered with an aluminum plate to form a reservoir for temperature controlled water; the other cavity is adjacent to the test film when the apparatus is assembled. The test film is clamped between the two discs with 6 bolts (see Fig. 3). Water, which is to permeate the test film, is put in the cavity immediately below the film; electrolytically dried N_2 is passed over the film to expel the permeated water. The "wet" gas is then run through the moisture monitor and the rate of water permeation is measured. From this permeation rate, and the thickness and the diameter of the film, the permeability can be calculated.

The diameter of the film exposed to moisture transfer is 5.75 inches. Several considerations influence this dimension of the cell. The first is precision of measurement of water vapor permeation rate. If the diameter of the film is too small, the rate at which water permeates the film will be low and the moisture monitor will be unable to measure accurately the permeation rate. On the other hand, if the diameter of the cell is large (greater than 8 or 10 inches), it becomes difficult to

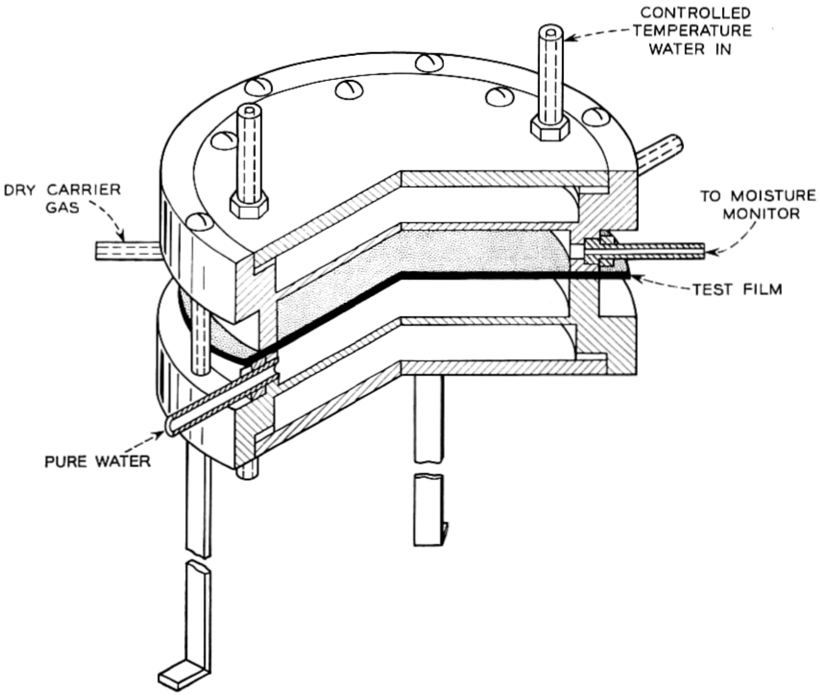

Fig. 3 — Cut-away view of film cell.

make films of uniform thickness. Moreover, large diameter discs are difficult to machine accurately and hard to handle in assembling the cell. The choice of diameter is a compromise between these factors. Consideration of the sensitivity of the moisture monitor and the other factors noted above indicated a 5 to 6-inch diameter film would be optimum. A film of this diameter can be pressed to the necessary uniformity and a cell of this diameter would not be difficult to machine or handle in the laboratory.

The films were made by compression molding and their thickness was measured in two ways. First, the thickness was measured at several points with a micrometer and averaged. In the second method, a circle, $6\frac{1}{2}$ inches in diameter, was cut from the test film and weighed on an analytical balance. The density of this material was then measured with use of density gradient columns. The volume of this circular sample would then be given by the weight, w, of the $6\frac{1}{2}$-inch circle divided by the density, ρ, of the material

$$\mathrm{Vol} = \frac{w}{\rho},$$

and this volume would also be given by the relation

$$\mathrm{Vol} = \frac{\pi}{4} D^2 t$$

(where D is diameter of the circle and t its thickness) so that by combining these two equations and eliminating volume the thickness of the sample can be calculated. In one case, the first method (micrometer) gave an average thickness of 11.9 mils, and the second method a thickness of 11.85 mils. This agreement indicates that the micrometer measurements, which are uncomplicated and much more convenient, would be as reliable and accurate as necessary.

4.1 *Tests of Film Apparatus*

Tests were made to determine the effect of film thickness on measured permeability. If the films are extremely thin, say 1 mil or so, surface imperfections such as pits could contribute substantially to the total moisture transfer rate through the film. These tests were carried out with two materials—a sample of low-density polyethylene (10- and 12-mil films) and a sample of high density polyethylene (7- and 13-mil films). The comparison of the two film thicknesses for each material respectively is shown in Fig. 4 and indicates that the permeability is not dependent on film thickness in the range of film thicknesses (9 to 12 mils) used in these experiments.

4.2 *Additional Tests of Apparatus—Comparison of Films and Tubes*

In Fig. 5 the measured permeability for tubes of the polyethylene materials are compared with the data obtained on films. The permeability of the polyethylene films is about 4 percent lower than for tubes of the same material, while the permeability of the PE-Butyl copolymer film is about 10 to 12 percent lower than that for the tube of this material. These differences are probably due to the differences in processing since the tubes were extruded and essentially quenched, while the films were compression molded and cooled more slowly (about 5°C per minute). The slower cooling anneals the films and they become more highly ordered. Because the permeability of the highly ordered regions is less than the amorphous portion, the permeability of the entire film would be less.

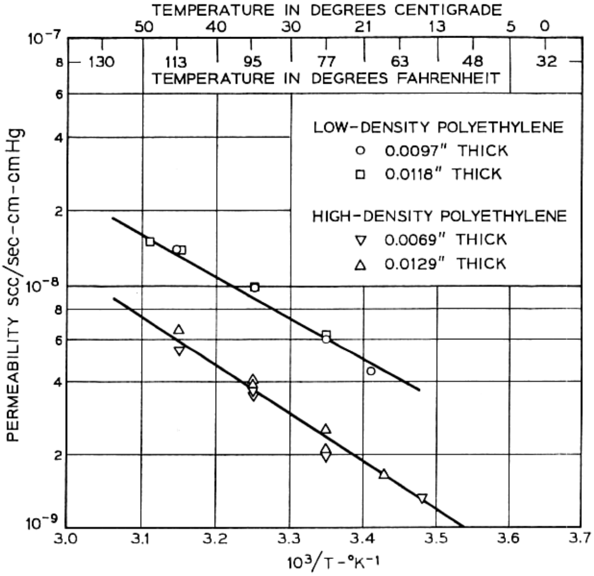

Fig. 4 — Measured permeability is not a function of film thickness.

V. RESULTS AND DISCUSSION

5.1 *A Few Words About Organization*

The discussion will be divided into two categories: the effects of chemical composition and of physical parameters. This is an historical classification rather than a logical one. In this study it was first desirable to measure WVP's of cable sheathing materials, both those in use and proposed. These were all basically polyethylenes but some contained varying contents of comonomers, *viz.* vinyl acetate, ethyl acrylate, and acrylic acid. Polymers of other chemical types (polyester, polyvinyl chloride, *et al.*) are also of interest because they, as sealing and plugging materials, help bear the brunt of nature's attack on the outside plant segment of the Bell System.

As a consequence of this work, it was found that physical parameters such as porosity and other heterogeneities influence WVP and will be discussed last.

5.2 *Effect of Chemical Nature*

Fig. 6 contains the WVP's of representative samples of polyolefins to give an overall picture of these materials and to orient the reader. The point to be noticed in Fig. 6 is the greater WVP's of low-density polyethylene materials compared to those of high density. The ratio of WVP's of high- and low-density polyethylene ranges from $\frac{1}{3}$ to $\frac{1}{6}$.

The water vapor permeability of low-density polyethylene has been reported earlier[4,6] as 2×10^{-8}, whereas the values found here for 0.92 density polyethylene were on the order of 10^{-8}. This difference is most probably due to the differences in the types of polyethylene used and the differences in the thickness of the film samples used. In the previous measurements, the sample films were on the order of 1 to 2 mils so that surface irregularities such as pits could contribute substantially to the overall moisture transfer rate across the film. In the present measurements, the sample films were on the order of 10 to 12 mils thick, and at these thicknesses surface irregularities, if they are present, would not contribute substantially to the moisture transfer rate.

The WVP's of cable sheathing materials (shown in Fig. 7) were of the order of 10^{-8} scc/sec-cm-cm Hg. The homopolymers, in general, have lower WVP's than either copolymers or materials containing low molecular weight additives. This greater WVP is probably due to several factors. Copolymers and additives, even in small amounts, can affect molecular and morphological factors such as branching in the polymer chain, molecular weight, and crystallinity among others. Because all these factors influence permeability, it is not surprising

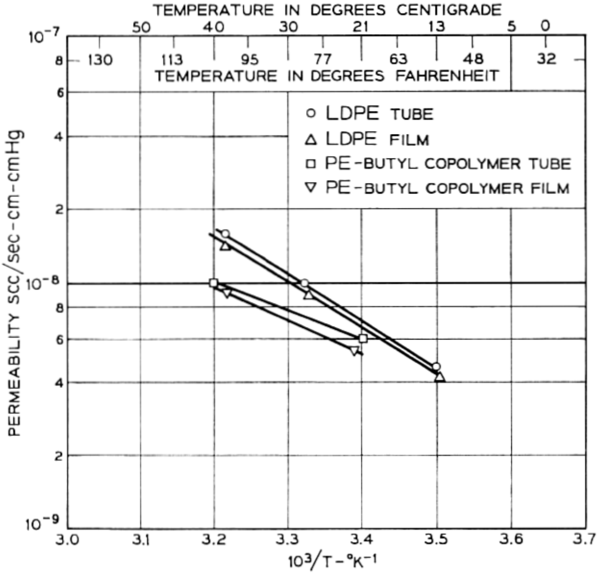

Fig. 5 — Permeabilities of films are slightly lower than tubes.

that copolymers and other additives should cause an increase.

The WVP of polypropylene is intermediate to that of high- and low-density polyethylenes (Fig. 8). This is of interest for two reasons, one of them of practical interest, the other academic. In the first place, polypropylene and low-density polyethylene compete for use in some protective applications. If other factors are equal, advantage should be taken of this lower permeability of polypropylene.

A second point of interest in the findings of polypropylene permeability concerns the effect of density. In the case of polyethylenes, increasing the density decreases the permeability. However, this obviously does not hold true for polyolefins as a class because polypropylene has a density of 0.91 and yet has a lower permeability than low-density (0.92) polyethylene. The lower permeability of polypropylene can be attributed in part to its high crystallinity (about 80 percent). Crystalline regions are much less permeable[3,4] than the noncrystalline regions, hence, the material as a whole has a lower permeability. Moreover, it would be expected that the intermolecular friction would be higher in the case of polypropylene which would, in turn, decrease the diffusion rates through the amorphous regions of the polymer.

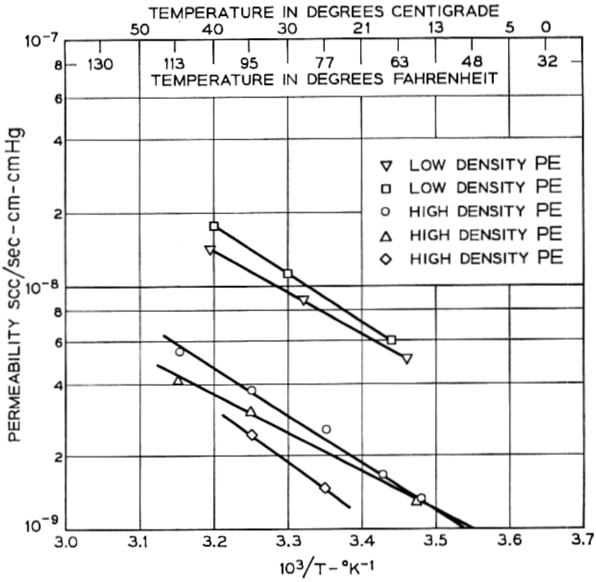

Fig. 6 — Comparison of high-density with low-density polyethylene.

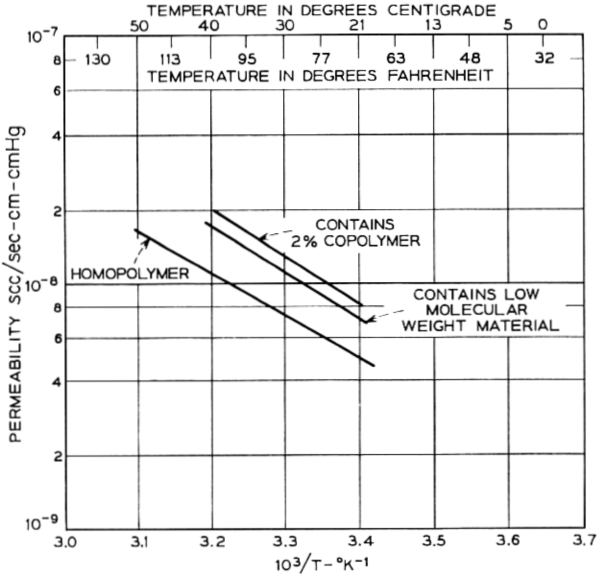

Fig. 7 — Typical cable sheathing materials.

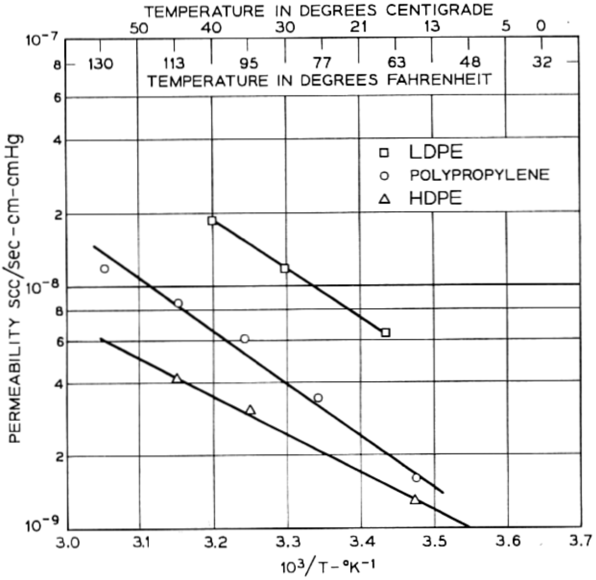

Fig. 8 — Comparison of polypropylene with typical high- and low-density polyethylenes.

Finally, the measurements of permeability of polypropylene bring home another point. In searching for materials for use in environmental protection, we would like to find an inexpensive material with an extremely low water vapor permeability, and if possible, we would like to say that this material is impermeable to water vapor. We must be brought up short in this search, however, in view of the findings in the case of polypropylene. Here is a material that is about 80 percent crystalline so that only 20 percent of the polypropylene contributes to moisture transfer, and even this 20 percent gives the polymer an overall permeability greater than some of the higher density polyethylenes. It is not likely that we could obtain a flexible usable olefinic material with any higher degree of crystallinity, and in this direction polypropylene represents a limit in lowering the water vapor permeability of materials by increasing crystallinity.

5.3 *Copolymers*

Interest in copolymers of olefins stems from two areas. In the first place, with even small percentages of copolymers such as vinyl acetate or ethyl acrylate the polymer is much more flexible and less susceptible to mechanical failure from stress. In the second application, these copolymers are used to compound semiconducting materials by loading them with up to 40 percent carbon black.

These copolymer materials have higher permeabilities than the straight polyethylene homopolymers. The permeabilities of the acrylic acid copolymers are shown in Fig. 9 as a function of acrylic acid copoly-

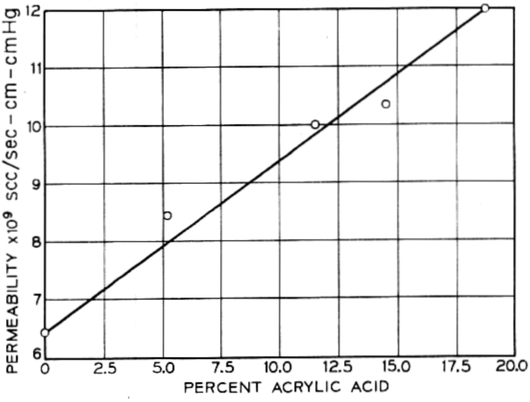

Fig. 9 — Increasing acrylic acid comonomer content increases the permeability of polyethylene.

mer content. These data indicate that the permeability increases with added acrylic acid in the polymer chain. The increase in permeability with the addition of these comonomers is due to morphological factors: the comonomer interrupts the regularity of the polymer chain and thereby reduces the *crystalline content* of the polymer and increases the amorphous content. The amorphous, disordered regions are more permeable; hence, the permeability of the material is increased. In the case of ethyl acetate copolymers, the permeability increased by almost a factor of ten with incorporation of 15 percent copolymer.

5.4 *Oxidized Polymers*

The oxidized materials were made by atmospheric oxidation of unstabilized homopolymer. After oxidation and before the film samples were made the materials were stabilized with Santonox.

The permeability of these materials (Fig. 10) indicates that the introduction of polar groups, such as carbonyl groups in this case, does not *necessarily* cause an *increase* in permeability. Other factors can play a part. Table I compares permeability, density, and carbonyl content of these three materials.

As the carbonyl content goes up the density also increases, and the permeability decreases. Winslow[7] has shown that this increase in density is due to an increase in molecular order in the polymer and because the more highly ordered regions are less permeable, the denser material would have the lower permeability. This reduction in permeability with increased carbonyl content is of interest in cable sheath-

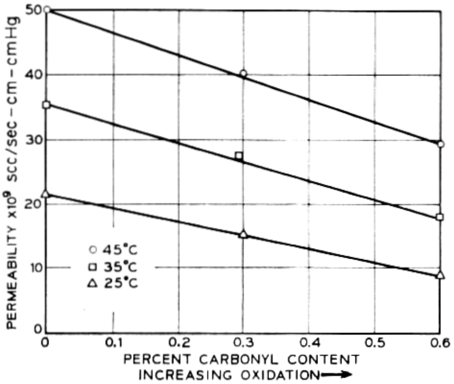

Fig. 10 — Increasing oxidation decreases permeability of polyethylene.

TABLE I—EFFECT OF OXIDATION ON DENSITY AND PERMEABILITY AT 25°C

Percent carbonyl	Density	Permeability
0	0.944	$2.20(10)^{-9}$
0.3	0.956	$1.57(10)^{-9}$
0.6	0.964	$0.82(10)^{-9}$

ing applications for obvious reasons and more materials of this type will be obtained to investigate this effect in more detail.

5.5 *Nonolefinic Polymers*

The results on polyester are compared with low density polyethylene in Fig. 11. The permeability of polyester films was reported[4] several years ago as $1.3(10)^{-8}$ at 25°C. The value measured with the present

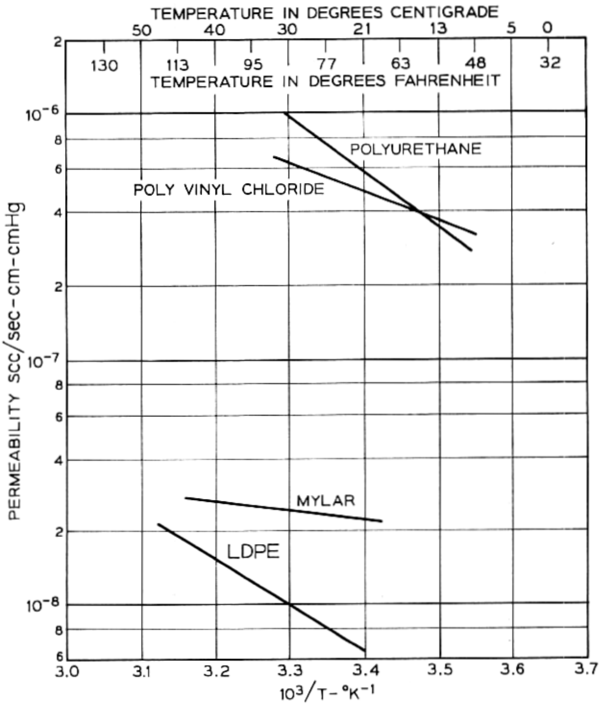

Fig. 11 — Comparison of nonolefinic polymers with a typical low-density polyethylene.

apparatus on polyester commercially available today was $2.3(10)^{-8}$ at 25°C. The older sample of polyester was unplasticized whereas that used in the present study was plasticized slightly and because of these differences a direct comparison is not entirely valid.

The permeabilities of plasticized poly(vinyl chloride) and polyurethane are also shown in Fig. 11; both are over an order of magnitude greater than typical low density polyethylene.

VI. EFFECT OF PHYSICAL PARAMETERS

One is not likely to find pure, homogeneous plastic materials used in the telephone plant. In addition to the deliberately added and necessary heterogeneities such as carbon black, these materials have inadvertent imperfections such as pores or solid particles. To give an example a cross-section of polyurethane cable plugging compound is shown in Fig. 12. The black areas represent pores formed in polymerization and indicate a porosity of up to 20 percent by volume although, superficially, the material usually appears to be homogeneous. Another example of porous material is the foamed polyethylene dielectric used in some coaxial cables.

6.1 *Porosity*

The effect of pores on permeability might not be straightforward: permeability involves both diffusion and solubility and although diffusion would be expected to increase with porosity, solubility decreases,

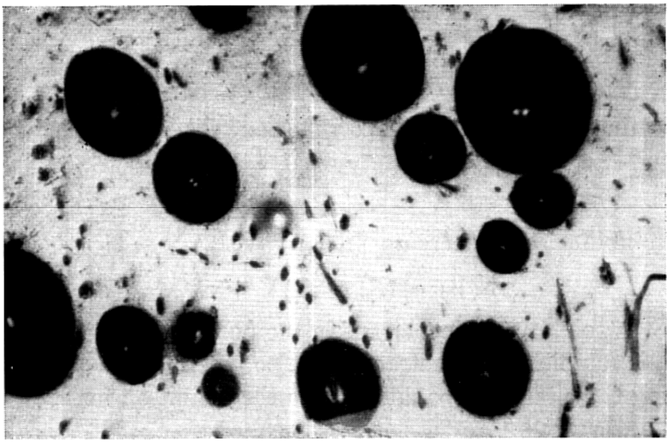

Fig. 12 — Photomicrograph (50×) showing pores in polyurethane.

because water is more soluble in the polymers of interest than in air or gas in the pore. First, the effect of pores on P will be calculated from a model for transport properties of heterogeneous, two-phase materials. These will then be compared with measurements of the effect with foamed silicone rubber.

If we can calculate the effect of pores on diffusion coefficient D and on solubility S, we can calculate the effect on P because

$$P(V) \equiv D(V)S(V) \tag{5}$$

where V is 'porosity' or volume fraction pores.

In calculating $D(V)$, use is made of models developed originally by Maxwell[8] in connection with the electrical transport properties of heterogeneous materials. With the analogies between Ohm's law and Fick's law, Maxwell's model can be used to calculate the diffusion coefficient of plastics containing small amounts of gas-filled cavities or pores. From Maxwell's work, the diffusion coefficient of a porous polymer is given by

$$D = \frac{D_p[D_a + 2D_p - 2V(D_p - D_a)]}{D_a + 2D_p + V(D_p - D_a)}, \tag{6}$$

where D_p and D_a are, respectively, the diffusion coefficients of the penetrant in polymer and in air (or the gas in the pore). It should be understood that the model from which (6) is derived ignores the interactions between adjacent pores so that for the case of porous plastics the value of D would be somewhat low. For polyethylene

$$D_p \cong 10^{-8} \text{ cm}^2/\text{sec} \tag{7}$$

and for air

$$D_a \cong 10^{-1} \text{ cm}^2/\text{sec}. \tag{8}$$

Neglecting D_p in comparison to D_a, Maxwell's relation reduces to

$$D(V) = \frac{D_p(1 + 2V)}{1 - V}. \tag{9}$$

The solubility $S(V)$ decreases linearly with V:

$$S(V) = (S_a - S_p)V + S_p, \tag{10}$$

where S_a is solubility of penetrant in the pore or in the gas within the pore; S_p is solubility of penetrant in the polymer.

Putting these last two equations into the definition for P

$$P(V) = [(S_a - S_p)V + S_p]\left[D_p \frac{1 + 2V}{1 - V}\right]. \tag{11}$$

For the case of silicone rubber foam $S_p \gg S_a$ and (11) becomes

$$P(V) = [(1 - V)S_p]\left[D_p \frac{(1 + 2V)}{(1 - V)}\right]. \tag{12}$$

The factors $(1-V)$ cancel so that P is proportional to V and a plot of $P(V)/D_pS_p$ *vs* V will have a slope of 2 and intercept $(V = 0)$ of unity. Such a plot is shown in Fig. 13 for foamed silicone rubber and as anticipated the measured WVP's are somewhat greater than those calculated from the model.

As Maxwell noted:[8]

> "When the distance between the [pores] is not great compared with their radii . . . other terms enter into the result, which we shall not now consider."

For the time being, we will follow his 70 year old cue and use the result in a qualitative manner only. Pore interaction in moderately and in highly foamed materials and its effect on diffusion is the subject of continuing research and will be reported on in a subsequent paper.

6.2 *Effect of Carbon Black*

Two magnitudes of carbon black content were investigated. Those used in cable sheath materials (about 2.5 percent by weight) and those higher contents (up to 40 percent) proposed for semiconducting sheathing materials. Fig. 14 shows some representative data for materials

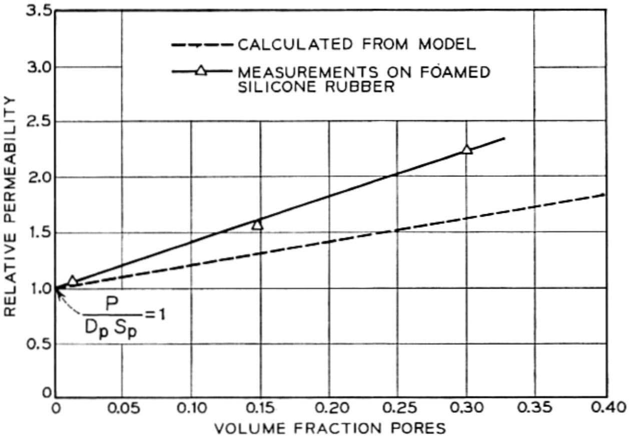

Fig. 13 — Measured foam WVP is higher than calculated.

containing about 2.5 percent carbon black compared with the natural materials. The carbon black at these contents lowered the permeability only slightly. Note also, that at these low percentages, the temperature dependence of the filled and unfilled material are essentially identical.

Materials highly loaded with carbon black also showed a linear decrease in permeability with increasing carbon black content. Fig. 15 gives some representative data. Qualitatively, this decrease in permeability with increasing carbon black content is not difficult to explain. The carbon black particles are most probably impermeable to moisture; hence, their presence in the polymer decreases the volume available to moisture diffusion. Again, we can use Maxwell's model discussed earlier to describe this decrease in permeability with increasing carbon black content. For the case of a polymer interspersed with *impermeable* particles, Maxwell's equation for the diffusion coefficient is given by

$$D = \frac{2D_p(1 - V_{cb})}{2 + V_{cb}}, \tag{13}$$

where D_p is the diffusion coefficient of water vapor in the polymer and V_{cb} is the volume fraction of carbon black.

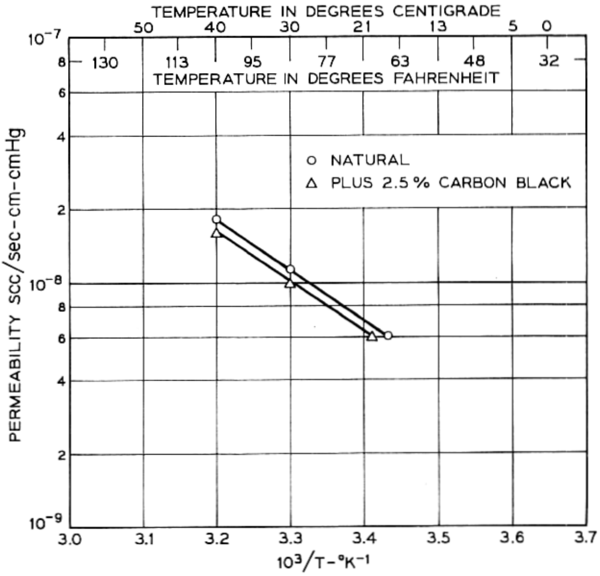

Fig. 14 — Effect of 2.5 percent carbon black.

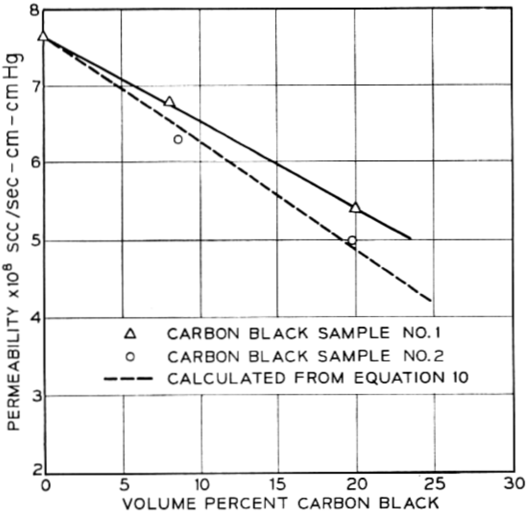

Fig. 15 — Effect of carbon black on permeability of poly (ethylene ethyl acrylate) copolymer.

The solubility of the loaded polymers decreases linearly with carbon black content

$$S(V_{cb}) = (1 - V_{cb})S_p. \tag{14}$$

Combining the equation for D and S with the definition of P gives

$$P(V_{cb}) = \frac{2D_pS_p(1 - V_{cb})^2}{2 + V_{cb}}. \tag{15}$$

This equation is shown as a dotted line in Fig. 15 and is slightly lower than the experimental values for WVP. In the equation for $S(V_{cb})$ above, it was assumed that the solubility of water on the carbon black was negligible, but as shown below there is some interaction and to be precise, we would be justified in assigning some contribution to $S(V_{cb})$ due to the carbon black. This would increase the calculated values of P to agree more closely with the data.

At higher carbon black contents (10 percent and above) the temperature dependence of filled and unfilled materials is markedly different. Fig. 16 gives an example of this behavior and shows that the activation energy for permeation, E_p, is decreased by carbon black. The decrease in E_p for the case of water sorption in polyethylene

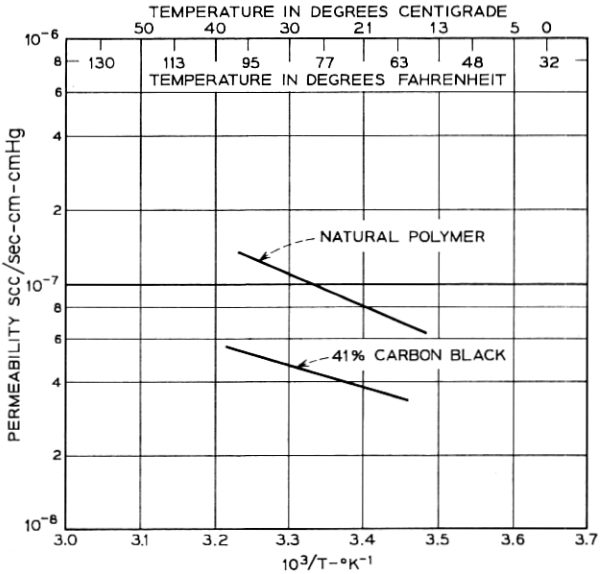

Fig. 16 — Effect of adding 41 percent carbon black to poly (ethylene ethyl acrylate) copolymer.

highly loaded with carbon black is not unexpected. For the water-polyethylene system,

$$D = D_o \exp(-E_D/RT), \tag{16}$$

$$S = S_o \exp(-\Delta H/RT), \tag{17}$$

and

$$P = P_o \exp(-E_p/RT), \tag{18}$$

where D_o, S_o, and P_o are constants; E_D and E_p are activation energies for diffusion and permeation, respectively, and ΔH is the heat of sorption. Substituting these equations into the definition of P (4) gives

$$P_o \exp(-E_p/RT) = D_o S_o \exp[-(E_D + \Delta H)/RT]. \tag{19}$$

From this

$$E_p = E_D + \Delta H. \tag{20}$$

For the case of water sorption on carbon black, ΔH is negative and increasing the carbon black to 41 percent gives a greater negative contribution and E_p is therefore decreased.

VII. SUMMARY

In general, the low-density polyethylene sheathing materials have permeabilities on the order of 10^{-8} scc/sec-cm-cm Hg at 22°C. High-density polyethylenes have permeabilities from 1/3 to 1/6 that of low-density polyethylene. The permeability of polypropylene is intermediate to high- and low-density polyethylenes. Copolymers of polyethylene (for example, vinyl acetate, ethyl acrylate, and acrylic acid) have higher permeabilities than the homopolymer; in one case 15 percent ethyl acrylate increased the permeability by a factor 10.

Nonolefinic polymers, in general, have higher permeabilities; for example, polyurethanes have permeabilities more than 80 times higher than low-density polyethylene.

Heterogeneities in the plastic such as carbon black and pores influence permeability. Addition of carbon black decreases the WVP roughly in proportion to the amount of carbon black. The permeability of these materials increases with increasing porosity.

VIII. ACKNOWLEDGMENT

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