Hygrophotographic Studies on the Permeability to Water and Moisture* of Packaging Materials

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In earlier papers, one of us (J. S.)[1-3] described a new method of determining the permeability to water and moisture of packaging materials a hygrophotographic technique based on the use of a special photographic plate whose double silver and mercury salt layer is particularly sensitive to light and moisture.

The Hygrophotographic Technique

The first method of preparing hygrophotographic plates with conventional photographic materials is the following.

The silver bromide plate or film, after immersion in the developer solution (in the darkroom), is brought into daylight, fully developed, and summarily washed and fixed in a hyposulfite solution with the object of removing any trace of unreduced bromide. Next, after careful washing, it is dipped in a 3% solution of mercuric chloride in which it bleaches completely. Then, for removal of excess of mercuric chloride, it is immersed again for 20–25 min. in a basin filled with water (*not* in running water), and transferred to a solution of potassium iodide wherein the plate gradually turns a yellow color which, when uniform, is without trace of the white chloride or orange tint. This may be ascertained by examining the plate from the side of the backing. The plate is then removed from the bath, quickly rinsed in water, and put to dry.

The choice of concentration of the potassium iodide solution is a very important factor in successful results. We first established it at 0.5%, since the stronger concentrations brought about a total blackening of the hygrophotographic plates. However, from time to time we obtained the beginning of a superficial blackening of our plates even with this concentration, but it caused no in-

convenience as long as quantitative measurements and calibrations were not attempted. After applying the microdosage method of water with the aid of hygrophotographic plates, we once more took up the determination of the concentration the most favorable to adopt, and we arrived at the conclusion that it depends on the nature and brand of the plate used, varying thereby between 0.50 and 0.25%. As an example, we discovered that with the orthochromatic plates, without any coloring matter, and especially with "lactate" plates 9 × 12 cm., the optimal concentration of potassium iodide was 0.25%. The most dilute solutions are not of any use.

Our practice is to carry out this operation in two stages: After fixing and washing of the plates, they are put to dry and it is not until the next morning that all the plates are completely dry, whereupon they are put in the solution of mercuric chloride for bleaching.

The second method is the following.

An equimolecular mixture of colloidal silver and mercuric iodide is heated at 52–55°C. for about three hours, with stirring, in a 6% gelatin solution. The color of the solution gradually changes, becoming yellow. During this heating process the silver reduces the mercuric iodide while converting itself into iodide which, in the presence in the reduced mercury salt, gives the same double mercuro-silver iodide.

A mere pouring of the emulsion so prepared on glass plates or any other suitable support provides hygrophotographic plates identical with those made with conventional photographic silver bromide plates.

The double salt of mercury and silver thus obtained within the thickness of the emulsion in the course of these operations is highly stable and insoluble. It is sensitive to the action of light which causes a rapid change of color from yellow to a violet black. But its outstanding · feature, after

exposure, is its great sensitivity to water and atmospheric humidity which act in such a way as to revert it to its original yellow hue.

It is this new and valuable property, providing the recording of images and patterns under the combined action of light, in the first place, and that of humidity in the second place, which enabled us to achieve a practical method of investigation which J. Sivadjian has called hygrophotography.

An Application of the Hygrophotographic Method

One of the foremost applications of the hygrophotographic method is the study of the permeability to water and water vapor of plastic materials and other substances. This application consists of the following procedure.

The photographic plates, usually 9 × 12 cm., are blackened by exposure to daylight or an intense source of light, then placed in a desiccator under vacuum on P_2O_5, and conserved in a darkroom until the next morning so that the moisture inherent in the gelatin is removed.

Then, after a narrow strip 23 mm. in width is cut lengthwise for calibration, the remaining piece is divided in four portions, which may be numbered, and which are paired, with the sensitized sides outward, and wrapped in a plastic bag prepared as below.

Preparation of Plastic Bags by Heat Sealing

The plastic bags from polyethylene films are prepared by welding their three free sides by means of the pinpoint flame of a Bunsen burner, as follows.

The preparation is clipped between two metal bars, the edge protruding 2–3 mm., and is kept at a suitable height.

The flame is then moved slowly under the edge, which melts and, after cooling, makes an excellent and strong seal. When the two edges are so sealed, the two pieces of plates paired, as will be indicated below are put into the bag which is then sealed on the third edge.

The bag must be about 15 mm. longer than the plates, and when it is completely sealed vacuum is made in it by means of a hypodermic needle connected with a vacuum device. Then, without the bag's being removed from the vacuum device, it is resealed behind the needle, as near as possible to the plates.

The films of polyethylene (PE), polypropylene, and poly(ethylene terephthalate) may be sealed by flame, but the polyvinyl chloride (PVC), poly-

amide, and other halogenated films decompose upon contact with the flame. The PVC may be heated, however, by placing a metallic cloth between the sheet of plastic and the flame of a Bunsen burner, but it is much more practical and rapid to solder the polyvinyl chloride and other films of this kind with a heated pressing iron with which pressure is exercised on the plastic placed between the two thin foils of aluminum; this prevents the plastic from sticking to the iron.

To obtain a vacuum in the PVC and polyamide prepared bags in this way, which already contain the hygrophotographic plates, a wide soldered edge is made with the pressing iron at one end of each bag, care being taken to leave a narrow passage sufficiently long in the middle for a hypodermic needle to be slid. A vacuum is made by means of this needle connected with a vacuum device, and then, without the bag's being removed from the vacuum, the soldered part is terminated by the obstruction of the passage in front of the needle.

The next step is to immerse the plates, thus wrapped, in a receptacle filled with water and placed in the dark, if the experiments are carried out at room temperature, or to put them in a jar filled with water, in a water bath heated at a fixed and properly selected temperature. The preparation may be either immersed in hot water or kept at a certain height above it. The jar opening is closed with suitable plate fitted with a thermometer.

The discoloration time should be noted. When the discoloration of the plates is judged sufficient, the preparations are withdrawn from their receptacles, the plates are taken out of their plastic envelopes, and the degree of the discoloration is measured by comparison with the calibrated strip.

Calibration of Plates and Determination of Humidity

To assess exactly the moisture permeability of plastics, we compared the discoloration obtained in the manner described with a densitometric scale of six rates of discoloration designated according to gradually reduced quantities of water.

A circular recess, 0.748 in. in diameter (19.4 mm.) and 0.472 in. deep (12 mm.) is bored out of a Perspex (plexiglas) block 0.748 in. (19 mm.) thick, 5.511 in. (140 mm.) long, and 1.968 in. (50 mm.) wide. A little farther on, six much smaller cavities, 0.356 in. (9 mm.) in diameter and 0.472 in. (12 mm.) deep, are also made. These cavities are filled with pure water at equal levels, in our arrangement

0.157 in. (4 mm.) from the top of the Perspex block.

To calibrate the hygrophotographic plate by means of this arrangement, we proceeded as follows.

We cut lengthwise, as described above, a narrow strip 0.905 in. (23 mm.) wide from the 9 × 12 cm. plate, then we cut off a small square from one of the ends of the strip and, taking another square piece of the same size (cut from an unserviceable hygrophotographic plate), we applied them one against the other (on the gelatin side), whereupon we weighed them in a microbalance, the two pieces being joined by a clip provided with a ring for suspension to one scale of the balance. Likewise, a counterweight, consisting of two identical pieces (unserviceable) were set on the other balance scale. Equilibrium was restored by adding the balance weights required.

The piece of plate to be calibrated, thus weighed, was then placed above the larger cavity of the Perspexblock, whose diameter and hence area, were known. The plate was held firmly in position by weights set on it for 12 min., care should be taken to protect it against too strong a light and to cover it, if need be, with black paper. The time mentioned above may vary within broad limits according to room temperature. We found that, at an average of 72°F. (22–23°C.), the "exposure" required 12–18 min., the time during which moisture absorption by the plate, as a function of time, retains its linear aspect.

Thereupon a circular discolored area showed up on the plate, which was promptly removed from the block; the gelatin surface of the plate to be calibrated was covered at once by the gelatin surface of the other piece and joined by means of the clip. Both were weighed anew. The difference between the two weighings is the quantity of water absorbed and fixed by the hygrophotographic plate. The outer plate prevents the loss in weight of the plate to be calibrated through evaporation of its moisture at the time of the second weighing, the moisture so lost being absorbed by the outer plate. Since the area of the discolored surface and the quantity of water absorbed by it is known, the quantity of water fixed per unit area is readily determined.

The remaining part of the narrow strip was then set on the Perspex portion that included the six identical cavities, filled with pure water up to the above-mentioned level. Five of these cavities had been previously blocked off with a very thin, adequately rigid, transparent, and impervious plastic sheet. This strip of hygrophotographic plate was also pressed against the Perspex block by means of a suitable weight, the sensitized surface of the plate thus being in contact with the vapor given off by the sixth cavity. The pressure was held for 2 min. exactly. Then the pressure was reduced and, without moving the plate, the next cavity was uncovered by removing the plastic material. For this to be correctly done, a piece of paper is stuck underneath the transparent block; on this paper are equidistant black lines showing the points up to which the plastic sheet can be removed for fully uncovering one cavity without uncovering the next one at the same time.

After two more minutes, the remaining cavities were uncovered in sequence every 2 min. until eventually, a number of rounded spots exhibited a range of steadily weaker discolorations due to the effects of water vapor on the plate and according to the area during the periods of 12, 10, 8, 6, 4, and 2 min. for the six cavities. At one end one rounded area showed the greatest discoloration, and at the other end was that which showed the least discoloration. This narrow strip was then removed and, before being joined to the calibrated piece, was covered with the gelatin surface of another unserviceable strip of the same size, during a time equal to that needed for the weighing.

Under these conditions, and provided that the requirements mentioned are duly met, maximum discoloration of this densitometric scale is found to be identical with that of the calibrated piece, since exposure of both discolored portions are identical (12 min.). With the achievement of this identity, the quantity of vapor absorbed by the portion of hygrophotographic plate set above the small cavity for 12 min. shows that the plate has fixed, per unit of surface, a quantity of water equal to that fixed by the large circular reference area used for calibrating. It should be mentioned, however, that identical discolorations may also be derived from another portion of the densitometric scale.

As soon as the experiment is over, the various fragments of the 9 × 12 cm. plate, comprising the recorded densitometric scale, are joined together. Thereupon, they are photographed on standard silver bromide paper or, better still, on a transparency for densitometric measurements. The prints are made by the contact process, the hygrophotographic plate serving as negative.

Materials which at room temperature are highly water repellent, such as plastics, rubber, and the
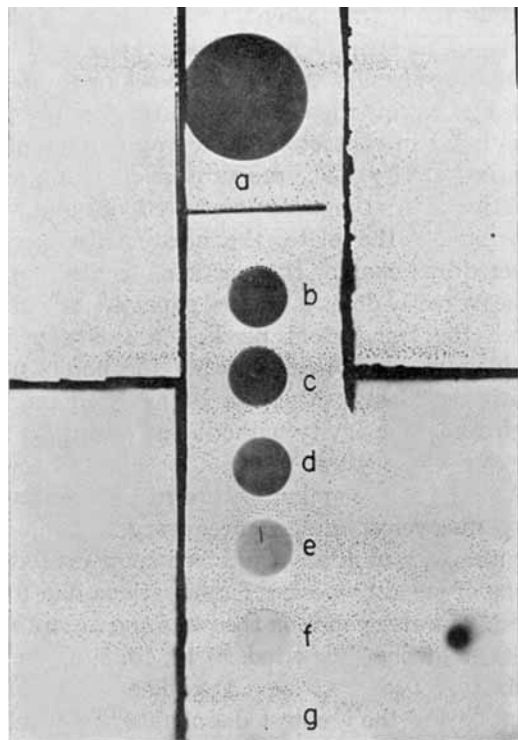
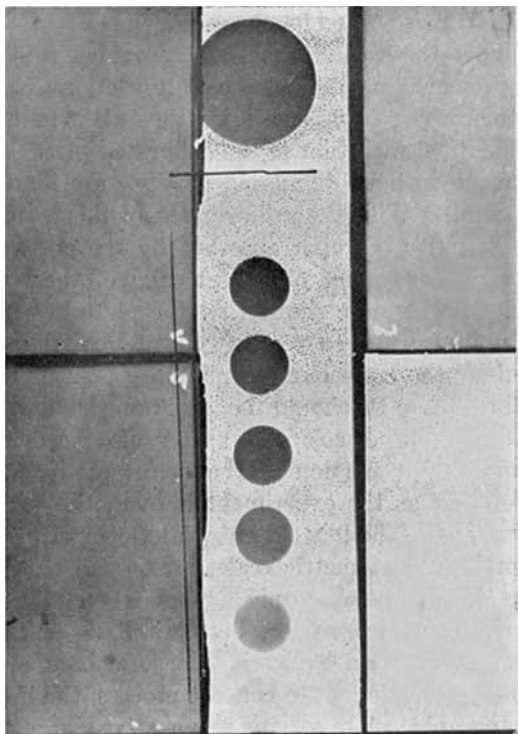Fig. 1. Hygrophotographic recording of the permeability test carried out with a 20 μ polyethylene sheet.

Fig. 2. Hygrophotographic recording; 50 μ polyethylene sheet after 254 hrs. in water at room temperature.

like, require 24 hrs. to several days to bring about discoloration.

The above procedure does not allow comparison of the discoloration obtained with the reference discs because the disc discoloration is likely to increase. In this case, the calibrated narrow strip must be kept in the desiccator as usual or, better still, another procedure must be used.

After calibration, the various pieces of the plate are joined together and a print is made on a transparency, the time required for this and the time required for a fully extended development being duly noted. A second print is then made with the same exposure, taking care this time to mask the fragments intended for permeability tests with black paper, leaving only the densitometric scale uncovered. This plate is put aside after being wrapped in black paper. The whole 9 × 12 cm. plate is reconstituted a second time, once the permeability tests are over, and photographed on the half-exposed plate previously put aside, the exposure of the previously masked portion being this time exactly the same while the narrow band of the densitometric scale is conversely masked.

This plate is then fully developed for the same length of time as the first reference plate. Under such conditions, the two images of the densitometric scale are identical.

Merely as an example, the results obtained with a 20 μ polyethylene sheet at room temperature are shown.

The densitometric scale is in the middle of Figures 1 and 2. In Figure 2, the reference densitometric value a, obtained by means of a known quantity of
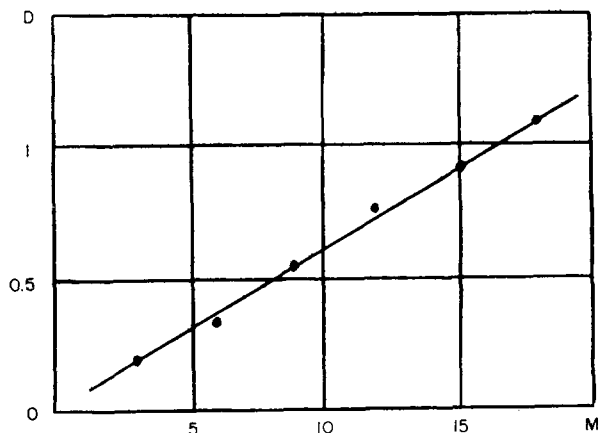

Fig. 3. Plot: every division shows the quantity of water absorbed per minute and per surface area equating unity: M, time in minutes; D, $\log I/I_0$.

water, is identical with b, corresponding to maximum discoloration in the decremental scale.

Since the diameter of this reference area, which is pure yellow in the hygrophotographic plate and black in the positive (a in Fig. 2) is 19.4 mm., its area is 295.5 mm.[2] and, as the quantity of water absorbed by the surface is 3690 μg., the quantity of water fixed is therefore 12.49 μg./mm.[2]. The same applies, of course, to b and, as absorption of water vapor by gelatin conforms to a linear law within limits of the period of time and temperature selected (18 min. at an average of 22–23°C.,
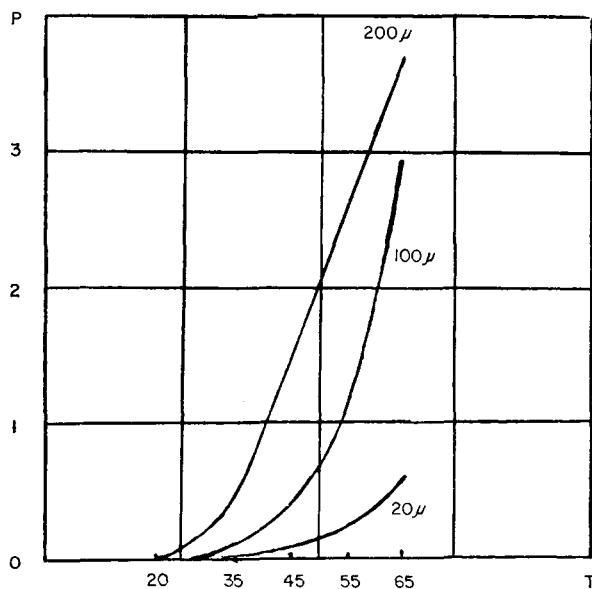

Fig. 4. Augmentation of the permeability of Manolene films according to elevation of temperature: T, temperature, °C.; P, permeability, mm.[2]/hr./mm.

in this case), the quantities of water fixed per unit of surface in the other portions of the densitometric scale can be readily determined, these portions being exposed during 15, 12, 9, 6, and 3 min., respectively.

Dividing 12.49 by the longest exposure (18 min.) gives the quantity of water absorbed per square millimeter of area per minute, i.e., 0.69 μg./mm.[2]/min.

In Figure 3 the exposures of the various portions of the densitometric scale are shown as abscissas, while ordinates show the densities of the blackening expressed by the logarithm of the ratio between the strength of the incident and transmitted light I/I_0. The density equating unity is that which will let through one tenth of the incident light strength,

A linear plotting is thus obtained, every division of which shows the quantity of water absorbed every minute per surface area equating unity; in the present instance, 0.69 μg. Since the blackening due to the moisture percolating through the sheet of the plastic material, after remaining 87 hrs. and 15 min. (87.25 hrs.) in the water, is identical with that of g in Figure 2, obtained after a 3-min. exposure, the blackening corresponds to an absorption of $3 \times 0.69 = 2.07$ μg. of water square millimeter. Since this quantity of water is absorbed by the hygrophotographic plate after remaining 87.25 hrs. in the water at normal temperature, this represents a permeability P of 0.023 μg./mm.[2]/hr. Figure 2 also revealed a defect on the plastic material which, in a certain spot, let through much more moisture than on the remainder of the surface.

Figure 1 shows a test made with a 50 μ polyethylene sheet which had stayed 254 hrs. in the water at normal temperature.

Irradiation

We have tested samples of irradiated polyethylene of two different origins. The first were polyethylenes, containing no additive, that had been irradiated by electrons. We had obtained them irradiated from General Electric Company.

The second were polyethylenes of low pression, called Manolene, which had been irradiated by [60]Co γ-rays for 193 hrs. 45 min., under 80,000 r/hr. Therefore they had received a dose of 1.55×10 r. One part had been irradiated by free air and had lost its flexibility, having become extremely fragile and brittle, crumbling into pieces at the slightest touch. We had tried to render it flexible once again by annealing, but even after total fusion it conserved its fragility while solidifying. On the other hand, the films irradiated in the vacuum under 10^{-3} mm./Hg had kept their flexibility and were easily handled.

Gravimetric Methods

Gravimetric studies were made at an ordinary temperature and by the classic cup method; experiments at more elevated temperatures were carried out with the aid of plastic bags prepared as we have described. These bags, which had been half filled with water, were weighed before and after the heating at a determined temperature during 7–8 hrs.

Experimental Results

TABLE I
Action of Temperature on Permeability[a] of Polyethylene
(Manolene, hygrophotographic method, Figure 4)

μg./mm./mm.^{2}/ hr. 10^{-3}	Temp., °C.				
	20	35	45	55	65
20	1.58	30.4	122.8	229.6	574.0
50	3.04	170.0	278.0		1825.0
100	3.60	132.0	358.0	1190.0	2940.0
200	5.25	476.0	1860.0	2620.0	3680.0
100 (transparent)	11.40			1280.0	2310.0

[a] $P = \mu$g./mm./mm.^{2}/hr. $\times$ 10^{-3}.

TABLE II
Action of Temperature on Permeability[a] of Polyethylene
(Irrathene)

	Film thickness, μ	Temp., °C.	
		55	65
Irradiated	254	3060.0	6310.0
Unirradiated	254	3560.0	6310.0
Irradiated	127	2550.0	4300.0
Unirradiated	127	1620.0	3590.0

[a] $P = \mu$g./mm./mm.^{2}/hr. $\times$ 10^{-3}.

TABLE III
Action of Temperature on Permeability[a] of Polyvinyl
Chloride
(Hygrophotographic method, Figure 5)

Film thick- ness, μ	Plasticizer content, %	Temp., °C.			
		35	45	55	65
32		81.5	598.0	940	4890
40	14	274.0	626.0	4490	5110
50	20	385.0	1509.0	1624	3310
120	30	674.0	2895.0	4315	9330

[a] $P = \mu$g./mm./mm.^{2}/hr. $\times$ 10^{-3}.

Discussion of Results

According to Klute and Franklin,[4] in the steady state the permeability of the polyethylene does not vary much with thickness. In accord with these authors, we have found in our experiments with polyethylenes of the same origin—for example, Manolene—that while the water vapor permeability was a little more the same for films having thicknesses of 20, 50, and 100 μ, the films of 200 μ have a higher permeability.

This result is due, according to us, to the structure of these films conditioned by their methods of obtention. Obtaining these very thin films im-

TABLE IV
Permeability[a] of Plastic Films of Different Natures and Thicknesses, Measured at Room Temperature by Hygrophotography and by Gravimetry

	Film thickness, μ	Hygrophoto.	Grav.
Polyethylene	25	6.48	4.85
	45	8.80	5.14
	70	—	4.69
	150	11.20	
Polyamide	100	28.40	26.40
	160	6.00	16.60
Poly(ethylene tereph- thalate)	15	18.00	16.50
	30	7.50	12.48
PVC (Lucolene)	30	3.66	
	70	7.78	
PVC	32	24.60	27.30
PVC plast.	95	65.40	65.80
Manolene	20	1.58	1.90
	50	3.04	3.45

[a] $P = \mu$g./mm./mm.^{2}/hr. $\times$ 10^{-3}.

TABLE V
Permeability of Irradiated and Unirradiated Manolenes
(Figures. 6 and 7)

Film thick- ness, μ		Temp., °C.			
		35	45	55	65
20	Unirr.		41.7	89.0	238.7
	Irr.		28.7	99.3	224.5
50	Unirr.		31.4	99.0	
	Irr.		23.0	164.6	542.0
100	Unirr.	33.9	118.0	241.0	714.0
	Irr.	28.5	148.0	246.0	862.0

poses on the latter, during the calendering or the extrusion-blowing, conditions which provide in films molecular orientations so much more important as the films are thinner.

Always, according to Klute and Franklin, we find in the literature on the permeability of conventional polyethylene of weak density, values which vary according to the authors, that is to say, according to the origin of the films: from the simple to the quintuple, from 0.074 to 0.0015 g.1mm./m.^{2}/day/cm. Hg. According to Slone and Reinhart,[5] who worked with the cup method, these values varied from 0.08 to 0.04 g.1mm./m.^{2}/day/cm. Hg.

By converting these values to those adopted in our own calculations, that is to say, to μg./mm./mm.^{2}/hr., we obtain values which vary also in the same interval, that is to say, from 6.48 to 11.20 for three polyethylenes of different thicknesses and
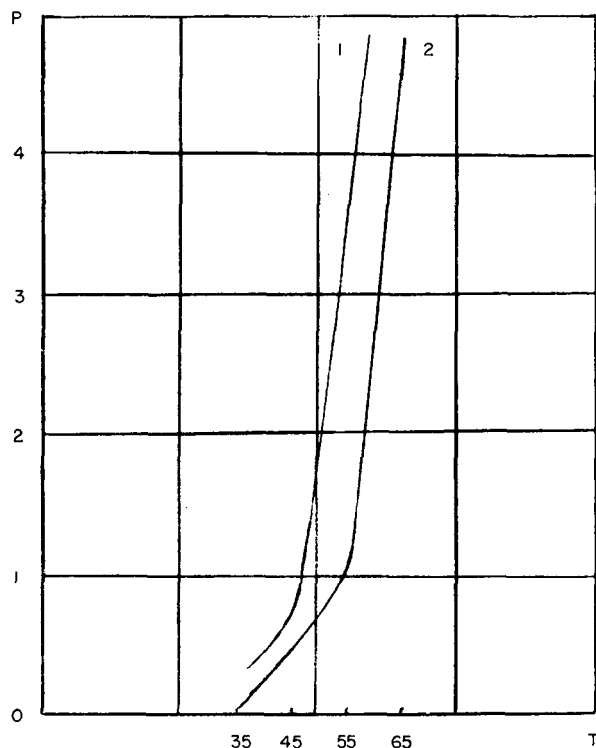
Fig. 5. Augmentation of the permeability of PVC films according to rise in temperature: T, temperature, °C.; P, permeability, mm.²/hr./mm. (1) PVC 40 μ; (2) PVC 32 μ.

ture according to an exponential law. This relation, formulated by Van't Hoff and Arrhenius, states that when the temperature rises by 10°C. the velocity of most chemical processes increases two to three times:

$$k_{t+10}/k_t = Q_{10} = 2\text{-}3$$

Besides its action upon the kinetic energy of the molecules of water vapor, temperature can act upon the permeability by modifying the physical properties of the plastic film and, as Table I shows, the law of Van't Hoff is sufficiently verified in the case of polyethylenes for the temperature range of 35 to 65°C. and, in consequence, the permeability of polyethylenic films increase from 2 to 3 times for each temperature elevation of 10°C.

In the PVC series, we have delt with plastic films very different one from the other in thickness and in content of plasticizers. It is exceedingly difficult to formulate a well-defined law on the modification of the permeability according to temperature. Figure 5 shows, however, the general aspect of this modification. The law of Q_{10} is not strictly verified; the augmentation is at times much more considerable, especially between 45 and 55°C., than
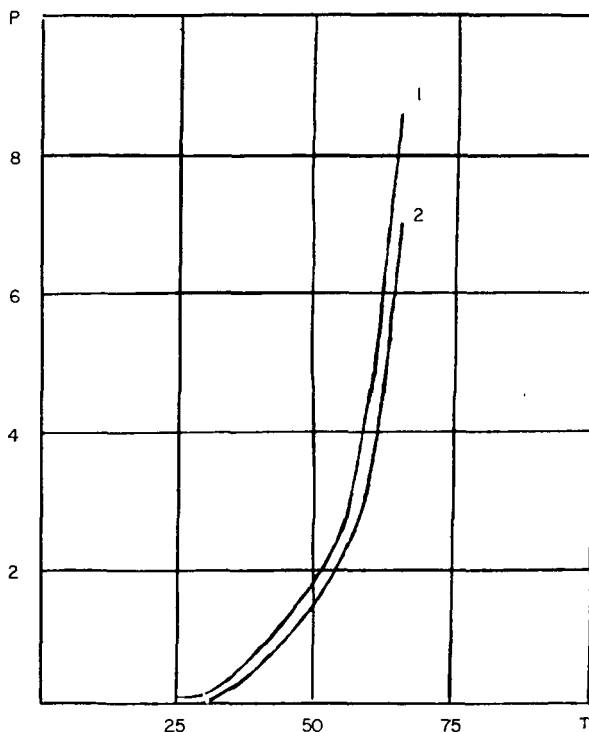
origins, while they vary only a little for three Manolenes of the same origin and thicknesses of 20, 50, and 100 μ (permeability, respectively: 1.58, 3.04, and 3.60).

The values that we have discovered in comparing the permeabilities of plastic films measured by the hygrophotographic and by the cup methods coincide as regards the films of weak thickness examined thus far.

In the group of PVC, as was expected, the thick Lucolene with 20% plasticizer had, at room temperature, a higher permeability (7.78) than the thin Lucolene with only 5% plasticizer (permeability 3.66). These results are shown in Table IV, which shows also that the PVC films, even those not plasticized, have a greater permeability than the polyethylene.

On the other hand, the temperature can act in two different ways on the permeability of plastic materials to water vapor.

The first way is by increasing the kinetic energy of the molecules of the water vapor; the number of collisions of these molecules on the surface of the film is thus increased. The number of these molecules varies rapidly with the absolute tempera-

Fig. 6. Permeability of an irradiated 50 μ Manolene film compared with that of unirradiated film: T, temperature, °C.; P, permeability, mm.²/hr./mm. 10^{-3} (1) Irradiated; (2) unirradiated.
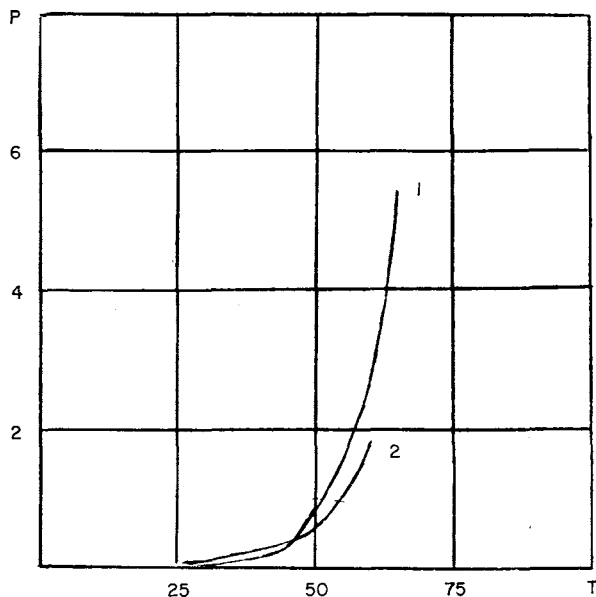
Fig. 7. Permeability of an irradiated 100 μ Manolene film compared with that of unirradiated film: T, temperature, °C., P, permeability, mm.²/hr./mm. 10^{-2} (*1*) Irradiated; (*2*) unirradiated.

this law indicates, whereas between 55 and 65°C. it seems to verify itself more clearly.

The role of the plasticizers is once more proven, since for the temperature of 35°, for example, when the percentage of the plasticizer augments from 0 to 30, the permeability constant augments from 81.5 to 674.0.

To study the action of irradiation, we have tested samples of irradiated polyethylene of two different origins. The first sample was a polyethylene (Irrathene) containing no additive, irradiated by electrons, and having thicknesses of 5 and 10 mils. The second was a polyethylene of low pressure (Manolene) with thicknesses of 20, 50, and 100 μ.
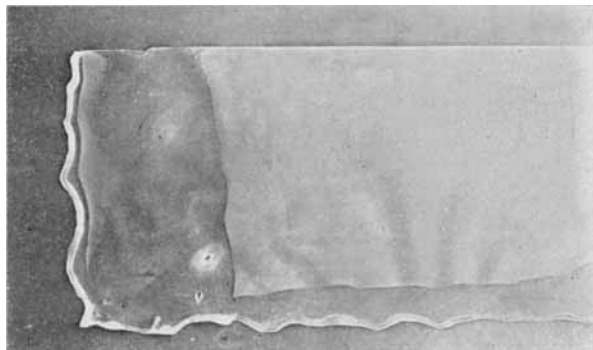

Fig. 8. A polyethylene (Manolene) bag made with an irradiated sample showing the melted parts which are more transparent (more black in the figure) than the remainder.
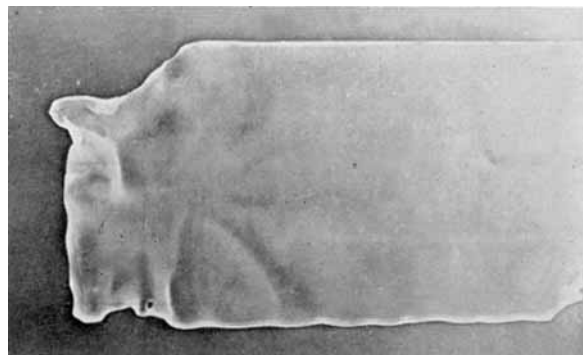

Fig. 9. Polyethylene (Manolene) bag made with an un-irradiated sheet.

The samples of Manolene had been irradiated by ^{60}Co γ-rays as we have described above.

With the samples irradiated in vacuum, we were able to prepare bags which we utilized for a comparative study of their permeability to water with that of the corresponding unirradiated polyethylenes.

In spite of their normal appearance, we noticed, however, a difference in behavior between the samples of Manolene irradiated and that unirradiated. Manolene in its normal state is not transparent, but translucent, with a milky aspect; after the fusion for soldering, the melted parts become once again milky in cooling (Fig. 8), whereas these parts in the irradiated Manolene conserve a certain transparency (Fig. 9).

The Irrathene films, as we have said, were of two thicknesses, 5 and 10 mils (127 and 254 μ), and contained no additive or stabilizer of any kind. Some were irradiated, others not. We gave these films a great number of tests for permeability at room temperature and were not able to prove any difference between the irradiated and unirradiated films.

On the other hand, for the Manolenes irradiated by γ-rays, we verified an increase in permeability over that of the nonirradiated samples.

These results conform with those obtained by Chmutov and by Finkel,[6-8] who irradiated polyethylene films of 0.030 to 0.035 cm. thickness with a ^{11}Co source with radiation intensity of 46 to 299 r. The permeability of these samples was measured by means of water tagged with tritium.

According to the results of those authors, in a humid atmosphere and when the dose of the irradiation increases, the coefficient of the permeability and of the solubility increases whereas the coefficient of diffusion diminishes.

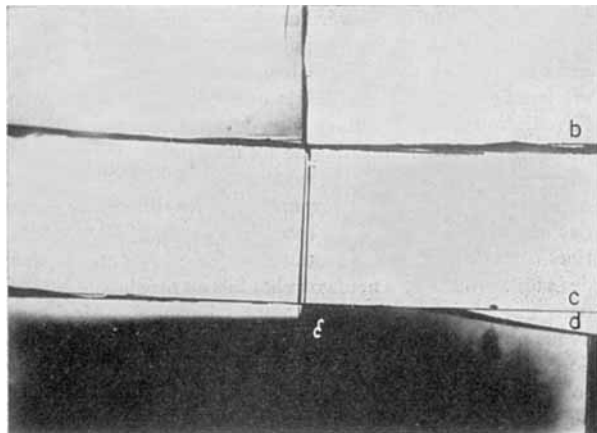For example, when the dose of irradiation is in-

Fig. 10. Hygrophotographic recording of the water sorption of polyethylenic films (Manolene), 200 μ: (a) new film, not heated; (b) film heated for 13 hr. at 65°C.; (c) control (the plates are placed in the oven without plastics).

creased six times, the coefficient of diffusion is three times weaker, the coefficient of permeability is almost ten times higher, and the coefficient of solubility twenty-five times higher.

The increase in the diffusion coefficient is attributed to a partial conversion of the film from a crystalline to an amorphous state and to an increase in the density of the polyethylene through crosslinkages. The steam solubility increased because of the formation of polar groups by irradiation, and the permeability increased because of the increased solubility.

During the experiments with the polyethylene films at the temperatures already cited, we noticed a discoloration of the hygrophotographic plates when our preparations had not yet been submitted to the action of the water vapor; we attributed this
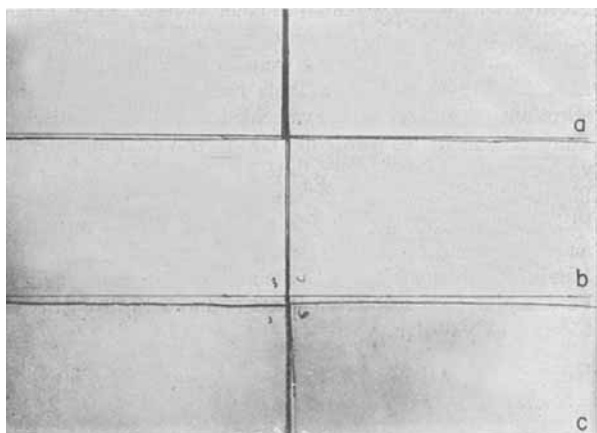
discoloration to the humidity retained at the surface of these films by adsorption. We made, in consequence, a series of systematic tests to determine the importance of this phenomenon of adsorption for the different kinds of plastic films, comparing the degree of discoloration of the hygrophotographic plates, enclosed in plastic bags new or previously heated in the oven at 65°C. during a specified time. In that way we compared the Manolene 200 μ to the Irrathene 254 μ and observed that, the thicker the films, the more humidity absorbed.

It was necessary to heat the 200 μ Manolene films for 13 hrs. at 65°C. in order to do away completely with the sorbed water (Fig. 10). We also noted that the 50 μ PVC with 20% plasticizer contained more adsorption water than the 40 μ PVC, with 14% plasticizer, and more than the 75 μ PVC without plasticizer (Fig. 11). It can be seen that the plasticizer and the thickness are determining factors in the adsorption of humidity by the plastic films, the plasticizer being more hygrophilic than the polymer. In any case, the polyethylene films adsorb a much more considerable quantity of water than do the PVC films. Likewise, the poly(ethylene terephthalate) contains more adsorption water than the polyamide.

According to Thomas,[9] the origin of the sorption sites of PVC is not so clear.

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Synopsis

The permeability to water and humidity of films of plastic materials of different natures and thicknesses was the object of much research achieved by many methods. However, these methods, while relatively simple, are very laborious, demand much time (for example, the gravimetric method), and are often imprecise. The hygrophotographic method is as simple as it is rapid. It requires a minimum of measuring

Fig. 11. Hygrophotographic recording of water sorption of the PVC films: (a) PVC 75 μ unplasticized; (b) PVC 40 μ, 14% plasticizer; (c) PVC 50 μ, 20% plasticizer.

instruments, or, in cases of urgency, no instruments at all. Special attention was given to the action on the permeability of certain factors such as presence of plasticizers, radioactive rays, temperature, and aging. It was demonstrated that while the presence of plasticizer increases the permeability to water, aging lowers it, precisely because of the departure of this plasticizer during the aging process. It was confirmed that in certain cases (e.g., polyethylene deprived of plasticizers) the law of Q_{10}, according to which in general the permeability of a good film approximately doubles for a 10°C. (18°F.) rise in temperature, is sufficiently verified and that in other cases (e.g., plasticized PVC) the experimental results deviate considerably from this simple law: the augmentation is at times much greater, especially between 45 and 55°C., than this law indicates, whereas between 55 and 65°C. the law obtains better. On the other hand, the action of the γ-rays is manifested by an increase, sufficiently visible, of the permeability when the polyethylenic film is irradiated in vacuum, but when irradiated in air the films become too brittle for handling. A series of systematic tests determined the importance of the phenomenon of sorption for the different kinds of plastic films; the degrees of discoloration of the hygrophotographic plates enclosed in plastic bags new or previously heated in an oven at 65°C. during a specified time were compared. It was observed that the thicker the film, the more humidity absorbed. The Manolene films, 200 μ in thickness, had to be heated for 13 hr. at 65°C. for the sorbed water to be completely evaporated.

Résumé

La perméabilité à l'eau et à l'humidité des films de matières plastiques de natures et d'épaisseurs différentes, a fait l'objet d'un très grand nombre de recherches, effectuées par des méthodes très variées. Mais ces méthodes, quand elles sont relativement simples, elles sont alors très laborieuses et demandent beaucoup de temps (méthode gravimétrique par exemple). Elles sont en outre peu précises. La méthode hygrophotographique a l'avantage d'être très simple et très rapide à la fois; elle n'exige qu'un minimum d'appareillage de mesure et même, dans des cas d'urgence, aucun appareillage du tout. Notre attention était surtout portée sur l'action d'un certain nombre de facteurs (présence de plastifiants, action des rayons radioactifs, de la température et du vieillissement) sur cette perméabilité. Nous avons pu ainsi démontrer que, tandis que la présence du plastifiant augmente la perméabilité à l'eau, le vieillissement la diminue, précisément à cause du départ de ce plastifiant au cours du processus du vieillissement. Quant à la température, nous avons confirmé dans certains cas, comme celui des polyéthylènes privés de plastifiants, que la loi de Q_{10}, d'après laquelle, én général, la perméabilité d'un bon film double d'une façon approximative pour une augmentation de la température de 10°, est assez bien vérifiée et que, dans d'autres cas (PVC plastifiés par exemple), les résultats expérimentaux s'écartent beaucoup de cette loi simple. L'augmentation est parfois bien plus considérable, en particulier entre 45 et 55° que ne l'indique la loi, alors que, entre 55 et

65° C, elle semble se vérifier davantage. D'autre part, l'action des rayons γ se manifeste par une augmentation assez nette de la température, lorsque le film polyéthylénique est irradié dans le vide. Mais quand nous avons effectué l'irradiation à l'air, les films sont devenus tellement friables qu'il nous a été impossible de les manipuler. Nous avons effectué en outre une étude systématique pour voir l'importance du phénomène d'adsorption pour les différentes sortes de feuilles de plastiques, en comparant le degré de décoloration des plaques hygrophotographiques enveloppées dans des sacs de plastiques neufs ou chauffés au préalable à 65° C dans une étuve pendant un temps déterminé. Ainsi nous avons pu constater qu'il était nécessaire de chauffer les films de Manolène 200 μ pendant 13 heures pour en chasser complètement l'humidité adsorbée, dont la quantité était d'autant plus importante que le film était plus épais.

Zusammenfassung

Die Permeabilität von Filmen aus Kunststoffen verschiedener Natur und Dicke gegen Wasser und Feuchtigkeit wurde schon viel untersucht. Die verwendeten Methoden erfordern jedoch bei relativer Einfachheit einen recht grossen Arbeits- und Zeitaufwand (z.B. die gravimetrische Methode) und sind oft ungenau. Die hygrophotographische Methode ist zugleich einfach und schnell. Sie erfordert ein Minimum an Messinstrumenten oder in dringenden Fällen überhaupt keine Instrumente. Spezielles Augenmerk wurde auf den Einfluss gewisser Faktoren, wie Weichmacher, radioaktive Strahlung, Temperatur und Alterung auf die Permeabilität gerichtet. Es wurde gezeigt, dass die Gegenwart eines Weichmachers die Permeabilität für Wasser erhöht und dass die Alterung sie, gerade wegen des Entweichens des Weichmachers während der Alterung, herabsetzt. In gewissen Fällen (z.B. Polyäthylen ohne Weichmacher) konnte das Q_{10}-Gesetz, nach welchem die Permeabilität eines guten Films sich für einen Temperaturanstieg von 10°C (18°F) im allgemeinen angenähert verdoppelt, genügend verifiziert werden; in anderen Fällen (z.B. weichgemachtes PVC) weichen die Versuchsergebnisse stark ab: manchmal ist die Zunahme viel grösser, als diesem Gesetz entsprechen würde, besonders zwischen 45 und 55°C, während zwischen 55 und 65°C das Gesetz besser erfüllt ist. Andererseits zeigt sich die Wirkung von γ-Strahlen bei Bestrahlung des Polyäthylenfilms im Vakuum in einer gut sichtbaren Erhöhung der Permeabilität, während bei Bestrahlung unter Luft der Film zu spröde zur weiteren Untersuchung wird. Eine Reihe systematischer Tests liess die Bedeutung des Sorptionsphänomens für die verschiedenen Arten plastischer Filme erkennen; es wurde der Grad der Verfärbung der in vorher im Ofen durch bestimmte Zeiten auf 65°C erhitzten Plastiksäckchen eingeschlossenen hygrophotographischen Platten verglichen. Es zeigte sich dass die Filme um so mehr Feuchtigkeit absorbierten, je dicker sie waren. Die Manolene-Filme von 200 μ Dicke mussten zur vollständigen Verdampfung des sorbierten Wassers durch 13 Stunden auf 65°C erhitzt werden.