POLYETHYLENE AS A PACKAGING MATERIAL

By ROBERT H. MARRIOTT, D.Sc., F.R.I.C.*

INTRODUCTION

THE PLASTIC made by polymerising ethylene and known generally as polyethylene is a very useful material from the point of view of the cosmetic industry. Interest lies notably in the fact that it requires no plasticiser and maintains its flexibility remarkably well over a wide range of temperatures. The fact that no plasticiser is required eliminates the dangers that so often arise when other plastic materials are employed. Very often a plastic which has to be plasticised rapidly deteriorates owing to the migration of the plasticiser, although rubber chloride, which is known under the trademark "Pliofilm," can also deteriorate, i.e., become brittle, even though no plasticiser is normally employed.

Another advantage of polyethylene is that it is readily heat-sealable and, indeed, the temperature of sealing need not be higher than 100° C. The melting point of polyethylene is of the order of 110 to 115° C. and it is quite easy to fuse the polyethylene to produce a seal which can be far stronger than the film itself. Its relatively low fusion point enables polyethylene to be employed for making bottles, which are blown in a way similar to that used in manufacturing glass containers. Polyethylene bottles possess a characteristic flexibility which enables them to be employed for packaging liquid cosmetic preparations, the user merely squeezing the bottle to eject the required quantity for use. They have considerable attractiveness as well as a good life, since the flexibility of the plastic is well maintained, and unless certain materials, notably of a polar character, are in long contact, embrittlement does not occur. Other desirable features of polyethylene are its relatively low specific gravity (·92) and the fact that it is perfectly resistant to moulds and other micro-organisms.

Although polyethylene is impervious to water, it does allow water vapour to diffuse through it. Within the ordinary range of temperatures, it is not seriously acted on by oils, although even at ordinary temperatures it will absorb 3 to 5 per cent of its weight of mineral oil. It will also absorb, or allow to be dissolved within it, essential oils, and reduce the intensity of odour of the preparation with which it is in contact,

---

* Technical Director,
County Perfumery Co., Ltd., London.

but in this respect it is superior to polyvinyl chloride. On the other hand, it is sensitive to oils when the temperature is somewhat elevated and certainly at temperatures above 60° C. it is liable to disintegrate when in contact with the white oil normally employed in cosmetic manufacture. This has the effect that, with an oil-containing emulsion, especially if the emulsion be of the reverse type, i.e., water dispersed in the oil, the outer surface of the polyethylene container becomes greasy and, indeed, if the temperatures be even warm, staining of an outer paper wrapping can occur. If the emulsion, however, is of the obverse type, i.e., oil in water, this danger is considerably lessened, especially if the outer phase contains surface-active materials which induce the surface of the polyethylene to be preferentially wetted by water.

The important point to remember, however, in the case of polyethylene, is the fact that although the rate of diffusion of water vapour through the film is by no means high, it is permeable to gases such as nitrogen, oxygen, hydrogen and carbon dioxide. In respect of its water vapour permeability, polyethylene is more porous than rubber hydrochloride although less permeable than polyvinyl chloride.

EXPERIMENTAL

Experiments have been carried out to determine the suitability of polyethylene for holding reverse emulsions such as hair cream. It was found that when the product was held in a sealed tube of the material, swelling of the sac occurred. Investigation showed that this swelling was due to the inward diffusion of air which replaced the water vapour which diffused outwards. A sealed package containing a water-in-oil emulsion and freely exposed to the ordinary laboratory atmosphere commences immediately to swell although the rate is very slow. After the lapse of 3 or 4 weeks, evidence of swelling is quite easy to discern by visual examination and handling the package. The precise extent of the swelling can easily be determined, however, by measuring the displacement in water of the package after various intervals of time. It was found by storing packages at various temperatures, e.g., 37°, 50° and 60° C., the rate of swelling increased with increase of temperature, and at 60° C. the distension was so great after 4 weeks that bursting of the pack was prone to occur. The time taken to reach the point when bursting was imminent varied inversely as the temperature of storage. The amount of distension, as measured, was not due in any way to the expansion of the air within the sac by change of temperature, since all the determinations were carried out by immersing the sac in cold water. An analysis was carried out on the gas content in the sacs. The values found were virtually identical with those of the ordinary atmosphere. The swelling, therefore, was presumably brought about by the diffusion of air into the sealed sac.

Experiments were then carried out in which polyethylene sacs were filled with water, with air-free water and with oil, and the loss in weight and volume changes were determined after storage at various temperatures. It was found that the volume increase was the same when ordinary water was employed as when air-free water was used ; the presence of air within the closed sac does not arise from air dissolved in the water. On the other hand, oil caused no swelling even at a temperature of 60° C. Since the premise was that the swelling was due to migration of air and bearing in mind that carbon dioxide, as so often with other plastic materials, diffuses at a rate contrary to the normal rate of diffusion as laid down by Graham, sacs were filled with filtered lime water and stored under various conditions. It was observed that the extent of swelling was similar to that when water alone was used but it was noted that the internal surface of the polyethylene became covered with a white deposit which was subsequently identified as calcium carbonate. It was also noted that the loss in weight was a direct function of the increase in volume and was greater the higher the temperature. A further interesting observation was made that if a sac was completely filled with air-free distilled water and stored, a bubble of air soon made its appearance.

*

The loss in weight and the increase in volume of polyethylene sacs containing a reverse emulsion were compared with bags made with polyvinyl chloride and "Pliofilm" (the "Pliofilm" being rubber chloride of American origin). The values obtained are given in Table I.

It will be seen that with sacs made of polyvinyl chloride there is a loss in weight but this is not accompanied by an increase but rather by a slight decrease in volume. In the case of "Pliofilm," there is again a loss in weight accentuated by an increase in temperature and a loss in volume. Comparative figures for the polyethylene sacs show that both the loss in weight and the increase in volume are, at ordinary temperatures, small. On the other hand, at 37° C. the loss in weight is significant and this is accompanied by a large increase in the volume. It should be remarked that the change in weight and the increase in volume of polyethylene sacs is a straight-line curve, at any rate up to the point when the sac is about to burst.

It should be remarked here that in all cases there was some evidence of oiliness on the outside of the sacs which was accentuated at 37° C. Of the three varieties of film, "Pliofilm" showed probably the least greasiness, polyvinyl chloride a slightly greater amount and polyethylene sufficient to bring about greasing of any absorbent material with which it came in contact.

The films used in the above experiments were ordinary commercial ones and were of varying thicknesses. For example, the "Pliofilm" was $2{\cdot}5 \times 10^{-3}$ in., the polyethylene

5×10^{-3} in. and the polyvinyl chloride 15×10^{-3} in. in thickness. Because of this variation, it is not possible to make too close a comparison between the different plastics, but the significance of the results lies in the fact that it is only the polyethylene sacs which show any increase in volume, i.e., diffusion of air into the sac.

TABLE I

Changes in Weight and Volume of Plastic Sacs containing Water-in-oil Emulsion when stored at various Temperatures

Type and thickness of film	Temp.	Weight after storage (weeks)					Volume after storage (weeks)				
		0	2	4	6	8	0	2	4	6	8
	°C	gm.	gm.	gm.	gm.	gm.	c.c.	c.c.	c.c.	c.c.	c.c.
P.V.C. 15×10^{-3} in.	20	94·2	93·8	93·0	92·4	91·4	100	100	100	100	99
		87·3	87·0	86·1	85·4	84·4	94	94	94	94	91
	37	100·6	97·0	94·5	92·7	90·9	109	110	110	105	105
		95·0	92·1	90·2	87·6	85·9	101	103	102	99	100
Pliofilm $2{\cdot}5 \times 10^{-3}$ in.	20	110·8	112·1	111·2	110·5	109·2	133	133	133	130	130
		121·5	120·9	119·0	119·0	117·9	137	137	137	137	137
		116·1	115·7	114·4	113·7	112·8	157	157	157	157	151
	37	125·2	122·9	120·5	117·9	114·2	153	153	150	150	147
		134·9	130·5	128·0	124·8	120·7	153	153	150	150	149
		121·8	116·9	114·5	111·2	107·2	135	135	133	133	129
Polyethylene 5×10^{-3} in.	20	75·0	75·2	74·3	73·7	74·0	82	80	88	82	82
		69·1	68·9	67·4	67·4	67·0	75	74	76	78	78
		63·6	63·4	62·0	61·6	62·8	72	70	72	74	74
	37	60·1	58·5	57·5	57·0	56·3	72	80	90	100	107
		78·6	78·0	76·5	76·0	74·2	85	94	105	110	113
		74·3	73·9	72·4	71·3	70·3	80	85	96	100	107

TABLE 2

The Effect of Thickness of the Polyethylene Film on the Rate of Loss in Weight of Sacs when Stored

Thickness $\times 10^{-3}$ in.	Rate of Loss in weight mg./m.^{2}/d.	
	18–25° C	37° C
2·0	3,600	— *
3·0	1,000	10,600
5·0	430	6,800

* In the case of the sac 2 × 10^{-3} in. thick stored at 37° C., bursting occurred after one week and the value for the rate of loss in weight could not be determined.

Experiments have been carried out in which polyethylene of two different thicknesses obtained from the U.S.A. have been compared with the English variety 5 × 10^{-3} in. thick. In each case, a sac of precisely the same dimensions was filled with a reverse emulsion and the figures shown in Table 2 obtained.

The rate of swelling of the different sacs was determined by storing them in a dry atmosphere, i.e., over calcium chloride, at 50° C., the change in volume being measured by displacement. The thinnest sac burst within 48 hours! The sac, 3 × 10^{-3} in. thick, showed an increase of volume of 50 c.c., whereas the thickest film, 5 × 10^{-3} in., showed a volume increase of 30 c.c. in 48 hours. It is quite clear from these experiments that if a polyethylene pack be envisaged, the thickness of the film should not be less than 5 × 10^{-3} in. and even then precautions should be taken with regard to storage. It would appear from the results given that the loss in weight and the swelling are not straight-line functions of the thickness, although the experiments are not by any means complete enough for the true relationship to be determined. The evidence, such as it is, suggests that the permeability of the film varies inversely as about the square of the thickness.

One of the difficulties encountered in the experiments, and which prevents accurate values, lies in the fact that polyethylene film, especially when made into "lay-flat tubing" is liable to have points of weakness which can develop into tiny pinholes and with an increase of internal pressure, some of the contents are expressed through the tiny holes. Under the polarising microscope, the incidence of striations can readily be seen and incipient points of weakness can easily be detected. Pin-holing is considerably less with the thicker films.

DISCUSSION

It would appear from the above results that polyethylene is an excellent membrane for demonstrating the principles of diffusion. The swelling of the sacs can be explained only on the basis that the total pressure of a gaseous mixture is equal to the sum of the partial pressures and if the external atmosphere be of a different composition from the gases inside, diffusion outwards and inwards will occur and result in a change in pressure due to the difference in diffusion rates of the components of the two gaseous mixtures. At the moment the filled bags or sacs are sealed, the internal pressure will be equal to the external pressure of the atmosphere. After a short time, some of the water molecules from the emulsion will have evaporated and the air inside the sac will become more or less saturated with water vapour. This will lead to a very slight increase in the volume of the bag which is accommodated by the flexible nature of the package. The total pressure inside the bag will still remain equal to the outside atmospheric pressure but it is now made up of two partial pressures, viz., one due to the air itself, i.e., oxygen, nitrogen, carbon dioxide and the other rare gases of the atmosphere, together with the partial pressure of the water vapour. In an average atmosphere in England, the partial pressure of the water vapour inside the sac will be greater than the partial pressure of the water vapour in the external atmosphere and the polyethylene being permeable to water vapour will permit it to diffuse outwards. This will lead to a fall in the vapour pressure and, as a consequence, a fall in the total pressure within the sac. This can be accommodated by diffusion of air into the sac. Simultaneously, the gases inside the sac will not be in equilibrium with the water and water will evaporate to give a high humidity, which then starts off the cycle again. The result is that there will be an increase in the volume of the air which will continue until an equilibrium is obtained or until the bursting point of the sac is reached.

The rate of distension will depend on the rate of vaporisation of water and, of course, on the vapour pressure produced. This will depend on the temperature in which the pack is stored. It is quite clear, however, that if the water-vapour pressure of the external atmosphere is equal to the internal vapour pressure, then no migration of water vapour will occur and the sac will not swell. On the other hand, if the sac is swollen so that the partial pressures of the oxygen, nitrogen, etc., are higher than their partial pressures in the external atmosphere, then a fall in volume will be observed. Such an effect can be shown by taking a sac containing a reverse emulsion which has distended almost to the bursting point and putting it into an atmosphere saturated with water. A slight fall in volume can in fact be determined in the course of a few weeks.

Polyethylene bottles can be used to demonstrate quite clearly the increase in pressure brought about by this physical process. To do this, the bottle should be half-filled with water and fitted with a stopper through which two tubes pass. One of the tubes should be connected to a mercury manometer, the other fitted with a stopcock so that the bottle can be opened or closed to the external atmosphere. The bottle should be placed in an incubator at 60° C. and left for about 16 hours in order to get thoroughly heated through and the air inside the bottle expanded. The stopcock is then closed and the pressure developing determined by the mercury manometer. In the case of a particular polyethylene bottle, it was found that after four days, the mercury had risen to a height of over 10 mm. It will be appreciated that even in this space of time the pressure developed was quite significant, in spite of the fact that the polyethylene bottle had a thickness of approximately 0·05 in.

SUMMARY

From the foregoing investigation it can be deduced that if a polyethylene sac be employed as a container for any preparation containing water, an internal pressure will develop at a rate depending on the thickness of the walls and the actual conditions under which it is stored. If the container is freely exposed to the air, then the rate of swelling will increase as the temperature rises. It will also increase with increased movement of the air and with increase in dryness of the external atmosphere. Thus, the ideal environment for storage is a cool, damp place free from draughts. In practice, however, the polyethylene package should be enclosed in an outer container which will protect it from variations in external humidity and temperature as well as from draughts. In England, it is sufficient if the polyethylene sacs of suitable thickness are packed in a rigid strawboard container. In warmer countries, especially those where the relative humidity is likely to be very low, further protection is necessary. Enclosing the sac in an outer one will give very good results, the double sac being, of course, packed in a good strawboard carton. Where the polyethylene is thick, as for example in the case of bottles, the use of a good quality carton will probably suffice to prevent any serious development of pressure.

* * *

The author wishes here to record that the work which forms the basis of this paper was carried out by Mr. J. H. Walker, B.A., B.Sc., in the laboratories of the County Perfumery Co., Ltd., Stanmore, Middlesex, England.