• *Technical*

Permeability of Some Fat Products to Moisture[1]

WERNER LANDMANN,[2] N. V. LOVEGREN, and R. O. FEUGE,
Southern Regional Research Laboratory,[3] New Orleans, Louisiana

THE PERMEABILITY of confectionery fats to moisture should be a consideration when such fats are used in mixtures for enrobing or coating. Instances have been encountered in which chocolate and the chocolate type of candies have been returned to the manufacturer because the soft centers lost moisture, shrank, and cracked the coating. Soft centers coated with fat mixtures not containing chocolate or cocoa are, of course, subject to the same kind of deterioration. The acceptability of nuts and baked goods coated with fat mixtures undoubtedly is affected by the transfer of moisture to and from these products on storage at extremes of relative humidity.

Though the problem of moisture transfer has been encountered with confections coated with fat mixtures, practically no information relating to the problem can be found in the literature. This situation may result partly from the fact that, outside of the confectionery industry, fats are not regarded as coating materials and partly from a failure of technologists to realize that permeability might be controlled. Apparently the only published article concerned with the permeability of fats to moisture is a report by two of the present authors describing investigations carried out with acetostearin products (4). The effect of composition of the fat, film thickness, temperature, and vapor pressure on permeability was described.

The objective of the present investigation was to obtain information useful in developing improved confectionery fats and in obtaining the best possible performance from fat mixtures currently used in enrobing confections. In this work the permeability to water vapor, as influenced by temperature and vapor pressure, was measured for cocoa butter, completely hydrogenated cottonseed oil, mixtures of completely hydrogenated cottonseed oil with cottonseed oil, paraffin, chocolate liquor, and sweet milk chocolate.

Experimental

Materials. The cocoa butter was a sample of the commercial product produced by Hershey Chocolate Corporation and appeared to be typical in all respects. It had an iodine value of 38.0 and a melting point of 34.1°C. (93.4°F.). In the course of another investigation (3) its content of solids, calculated from dilatometric data on a sample tempered to the highest melting point, 34.1°C. (93.4°F.), was found to be as follows:

Temperature		Content of solids
°C.	*°F.*	*%*
0.0	32.0	99.4
5.0	41.0	98.1
10.0	50.0	95.9
15.0	59.0	93.2
20.0	68.0	89.2
25.0	77.0	83.3
30.0	86.0	63.9

The chocolate liquor was a typical product, obtained from a bakery supply company. Chocolate liquor is the term used in the confectionery trade for roasted and ground cocoa beans. The fat content of this product was about 54%.

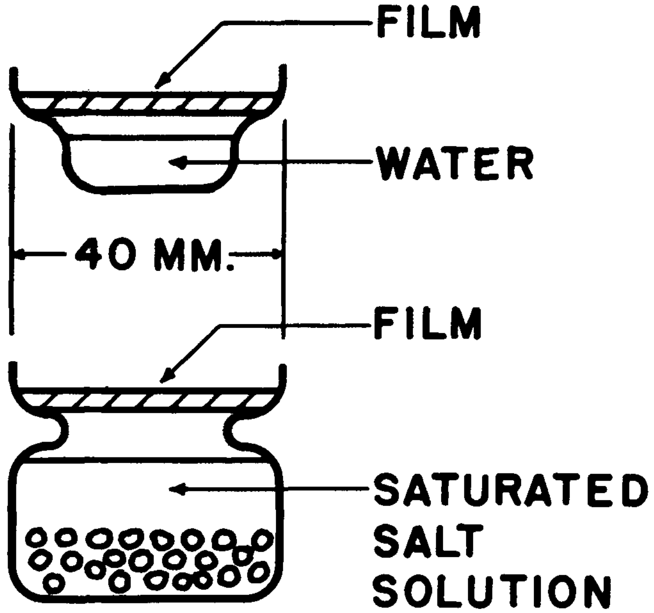

FIG. 1. Cups used in permeability measurements.

The sweet milk chocolate, coating type, was a product manufactured by the Nestlé Company. The product had the following composition:

	%
Sugar	49.7
Nonfat milk solids	9.0
Milk fat	3.8
Chocolate liquor	10.4
Total cocoa fat	32.6

The cottonseed oil, obtained from the Wesson Oil and Snowdrift Company, was a refined, bleached, and deodorized product. It had an iodine value of 109.7.

The hydrogenated cottonseed oil was prepared in the laboratory by hydrogenating the cottonseed oil mentioned above to an iodine value of 1.0.

The low-oil paraffin was an "edible" grade used commercially in the coating of cheese. It had a melting range of 50–53°C.

Procedures. Permeability determinations were made by the well-known cup method, many modifications of which have been described by other investigators. The cups employed in the current investigation were made of borosilicate glass and were of the shapes and sizes shown in Figure 1. Cups of the smaller type were used when water was to be placed inside the cups to obtain a relative humidity of 100% on the wet side of the film. Cups of the larger type were

---

[1] Presented at the 32nd Fall Meeting of the American Oil Chemists' Society, Chicago, Ill., October 20–22, 1958.

[2] Fellow, National Confectioners' Association.

[3] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

used when saturated salt solutions were employed to maintain constant relative humidities below 100%.

In preparing films of the fat products, each product generally was heated to a temperature just below the point of complete melting, the point of complete melting of the fatty component in the case of the chocolate liquor and the sweet milk chocolate. The partially melted mixture was poured between two plates of aluminum, which previously had been covered with aluminum foil, and spaced with the aid of spacing bars to obtain the desired thickness of film. To convert the components of cocoa butter to their highest melting polymorphic forms, films of the cocoa butter and cocoa butter-containing products were tempered for one week at room temperature, 27–28°C. (80.6–82.4°F.).

To obtain films of untempered cocoa butter with a low melting point, the cocoa butter was heated to 60°C. (140.0°F.) and poured in the molds; the latter were chilled quickly with the aid of brass blocks chilled to −18°C. (0°F.). The quickly chilled films were never allowed to come to a temperature above 5°C. (41.0°F.).

The thickness of all films was carefully measured with a micrometer after the films had been cut into disks to fit the permeability cups. Generally the films were sealed in the cups with the aid of a small amount of melted fat of the type of which the film was composed. The exceptions were films of the low-melting cocoa butter, paraffin, and hydrogenated cottonseed oil; the first two were sealed to the cups with the aid of a hot wire while the last was sealed with melted paraffin.

The vapor pressures on both sides of the films were kept constant by putting water or a salt solution inside the cups and storing them in a desiccator with a salt solution or Drierite, a specially prepared anhydrous calcium sulfate used as a drying agent (Table I). Changes in the weights of the cups with time were recorded. Permeability constants were calculated from these data after equilibrium conditions were reached, that is, after the change in weight per unit of time remained constant.

Permeability Constant. To facilitate the comparison of permeability under various conditions, permeability constants were calculated by using an equation based on Fick's linear diffusion law and Henry's solubility law. Fick's law, derived by analogy to the laws of heat transfer, states that the quantity of material diffusing per unit time is proportional to the area and to the concentration gradient in the direction of diffusion. Henry's solubility law, which was used to express the concentration of the water vapor in terms of its pressure, states that the partial pressure of the solute is proportional to its concentration in the solution. Barrer (1) and other investigators have derived the equation for calculating the permeability constant and have shown that the permeability constant is the product of the diffusion constant and the solubility coefficient. In the present investigation the permeability constant, P, is defined by this form of the equation

$$P = (W)\,(x)/(A)\ \ (t)\,(p),$$

where W is the weight of the moisture, in grams, diffusing through a film of thickness x, in centimeters, and area A, in square centimeters, during the time t, in seconds, when the pressure difference p, is measured in millimeters of mercury.

TABLE I

Temperature and Humidity Conditions Used in Permeability Measurements

Humidifying agent	Temperature	Relative humidity	Vapor pressure
	°C.	*%*	*mm. Hg*
Drierite	......	0.0	0.0
CH_3COOK [a]	26.7	22.5	5.9
K_2CO_3 [a]	26.7	43.7	11.5
$NaCl$ [a]	26.7	75.4	19.8
	3.0	76.0	4.3
H_2O	26.7	100.0	26.3
	3.0	100.0	5.7

[a] Saturated solutions as per International Critical Tables (2).

Results and Discussion

Film Thickness. From Table II, in which permeability data for all of the fat products are recorded, it is evident that the permeability constant for cocoa butter increased as the film thickness increased. For film thicknesses between 1.59 and 2.92 mm. the permeability constants ranged between 31.0×10^{-12} and 81.6×10^{-12}. While the smallest constant was not found for the thinnest film, probably because of minor variations in the molding and tempering of the films, the trend nevertheless is clear. The actual amount of moisture transferred, on the other hand, appeared to be practically independent of film thickness over the range shown. The practical significance of these data appears to be that loss of moisture from a piece of candy coated with a fat mixture cannot be retarded by a moderate increase in the thickness of the coating.

The dependency of the permeability constant on film thickness indicates that the diffusion does not obey Fick's law, a situation usually encountered in the passage of vapors through membranes. In an earlier investigation (4) the permeability constant for an acetostearin product to water vapor also was found to be dependent on film thickness. While Fick's law does not hold, the permeability constant is still a measure of permeability under a given set of conditions and a valuable index.

Aging and Tempering. Polymorphic changes in a film of a fat product greatly affect its permeability. A comparison of the data (Table II) reveals that the quickly chilled cocoa butter, the components of which were practically completely solid and were in lower melting polymorphic forms, had a permeability constant of 310×10^{-12} to 580×10^{-12}. The same cocoa butter tested under similar conditions, except that it had been heat-treated to convert its components to the highest melting forms, had a permeability constant of 33.3×10^{-12} to 37.2×10^{-12}. In this instance tempering produced an approximately 15-fold difference in permeability. The exact difference in permeability could not be determined because some polymorphic changes occur in cocoa butter even at 3°C. The data obtained are qualitatively in accord with data obtained previously (4) for 1,2-diaceto-3-stearin. With the latter compound it was found that the permeability constant of a quickly solidified film decreased over a 12-day period from 121×10^{-12} to less than 1×10^{-12} when the film was stored at 21.1°C. and the relative humidity on one side of the film was kept at 0% while that on the other was kept at 75.2%. Extensive polymorphic changes occurred in the 1,2-diaceto-3-stearin during this period of storage.

The transformation of a fat to a higher-melting

TABLE II

Permeability of the Fat Products to Water Vapor

Product	Temperature [a]	Vapor pressure gradient	Film thickness	Moisture transferred	Permeability constant x 10^{12}
	°C.	*mm. Hg*	*mm.*	*mg./hr./sq. cm.*	
Cocoa butter	3.0	5.7–0	1.57	0.00437	33.3
		5.7–0	1.58	0.00486	37.2
	26.7	11.5–0	1.58	0.00384	14.8
		19.8–0	1.60	0.00261	5.8
		19.8–0	1.60	0.00295	6.6
		26.3–0	1.59	0.0216	35.7
		26.3–0	1.63	0.0180	31.0
		26.3–0	1.96	0.0177	36.7
		26.3–0	2.14	0.0269	60.5
		26.3–0	2.16	0.0163	36.7
		26.3–0	2.91	0.0257	78.7
		26.3–0	2.92	0.0263	81.6
Cocoa butter, components in lower-melting polymorphic forms	3.0	5.7–0	1.54	0.0416	310
		4.3–0	1.51	0.0417	410
		4.3–0	1.52	0.0588	580
Hydrogenated cottonseed oil	3.0	5.7–0	1.59	0.000152	1.19
		5.7–0	1.56	0.000309	2.35
	26.7	19.8–5.9	1.55	0.000444	1.37
		19.8–5.9	1.58	0.000410	1.27
		26.3–0	1.52	0.000775	1.23
		26.3–0	1.60	0.000816	1.38
Hydrogenated cottonseed oil, 80%, cottonseed oil, 20%	26.7	26.3–0	1.57	0.00808	13.4
Hydrogenated cottonseed oil, 60%, cottonseed oil, 40%	26.7	26.3–0	1.57	0.302	500
		26.3–0	1.55	0.208	340
Chocolate liquor	26.7	11.5–0	1.71	0.00194	8.0
		19.8–0	1.70	0.00382	9.1
		19.8–0	1.69	0.00560	13.3
		26.3–0	1.63	0.323	556
		26.3–0	1.61	0.309	526
Sweet milk chocolate, coating type	26.7	19.8–5.9	1.78	0.00403	14.3
		19.8–5.9	1.75	0.00429	15.0
		26.3–0	2.08	0.492	1080
		26.3–0	1.73	0.649	1190
Paraffin	26.7	26.3–0	0.8	0.0000	0.0

[a] The temperature of 26.7°C. (80.0°F.) was the average room temperature. Maximum variation from this average was 1.5°C. (2.7°F.). (3°C. = 37.4°F.).

polymorphic form might be expected to be accompanied by a decrease in permeability. Such a transformation produces denser and better ordered crystals, making it more difficult for the molecules of water vapor to slip through the crystal structure. If it were possible to reduce the atomic distances in fat crystals to those found in metals, perfect barriers to moisture would be obtained.

The data recorded in Table II were obtained after diffusion had reached equilibrium conditions. With films containing hydrogenated cottonseed oil, equilibrium was reached after two or three days; and thereafter the rate of water transfer was quite constant, indicating that no polymorphic transformations or other changes occurred on the aging of these films. However with films containing cocoa butter an unexpected behavior was encountered in tests at room temperature. After a film of cocoa butter was tempered at room temperature for several days and then installed in a permeability cup, the rate of vapor transfer increased continuously over a period of two to three weeks. In one typical run the following data were obtained for a film 2.91 mm. thick:

Time	Permeability constant x 10^{12}
days	
3	6.0
7	11.5
10	18.5
12	27.0
14	37.2
17	54.6
19	71.6

The reason for this observed change in permeability is not known. It may be associated with crystal growth during aging. Because the cocoa butter contained about 20% of liquid component at room temperature, 26.7°C. (80.0°F.), the minute crystals obtained on the original solidification could have been dissolved slowly in the liquid component and redeposited as larger crystals. This possibility is supported by the fact that in all of the tests made with cocoa butter at 3°C. (37.4°F.), at which temperature practically no liquid component existed, equilibrium was reached in a day or two.

Composition. On considering the mechanics of vapor transfer, it might be expected that the percentage of liquid oil in a film of fat is an important factor. This is confirmed by the data for the highly hydrogenated cottonseed oil and its mixtures with cottonseed oil. The permeability constant for the highly hydrogenated cottonseed oil, which contained no liquid component at room temperature, was about 1.3×10^{-12}. This constant increased to 13.4×10^{-12} for a mixture containing 20% liquid oil and to 340×10^{-12} to 500×10^{-12} for one containing 40% liquid oil.

Concerning the effect of nonfat components, a comparison of the data for cocoa butter, chocolate liquor, and sweet milk chocolate, at room temperature, comparable film thickness, and vapor pressures corresponding to less than 100% relative humidity, reveals that the presence of sugar, proteins, etc., had no marked effect on permeability. The permeability constants ranged from about 5.8×10^{-12} to 15.0×10^{-12}.

Temperature. The permeability constant for the highly hydrogenated cottonseed oil was practically unaffected by reducing the temperature from 26.7°C. (80.0°F.) to 3°C. (37.4°F.) though the amount of moisture transferred through each square centimeter of area was, of course, greatly reduced because of the reduction in vapor pressure. The films of cocoa butter behaved in a similar manner, but an explanation for their behavior is undoubtedly different from that for the highly hydrogenated cottonseed oil. On reducing the temperature of the cocoa butter, the approximately 20% of liquid component solidified, which might be expected to decrease the permeability. However the 20% of liquid component probably solidified in the relatively permeable, low-melting forms. Furthermore shrinkage accompanying the solidification may have created a structure which was porous to some extent.

Theoretically the permeability constant for permanent gases varies exponentially with temperature, a relationship first pointed out by Barrer (1); at ordinary temperatures the permeability constant should approximately double for a rise of 10°C. (18°F.). While many systems involving vapors behave according to this rule, the limited data given in Table II indicate that systems of fats and water vapor do not behave in this manner.

Vapor Pressure. The permeability of the highly hydrogenated cottonseed oil at 26.7°C. (80.0°F.) does not appear to be affected by the changes in vapor pressure shown in Table II though possibly the accuracy of the method employed and the low values found for this material were such that moderate changes would not be detected. The data obtained for cocoa butter at 26.7°C. (80.0°F.) and a film thickness of about 1.6 mm. definitely show that the permeability constant was reduced by reducing the pressure gradient across the film.

The effects of changes in vapor pressure were very large for the chocolate liquor and sweet milk chocolate. When the vapor pressure difference across the films was increased to 26.3 mm. at 26.7°C. (80.0°F.), a difference in relative humidity of 100%, the permeability constant for the chocolate liquor increased to about 540×10^{-12} and that for the sweet milk chocolate to about 1130×10^{-12}. These large permeability constants cannot be attributed to the behavior of the fat component of the films; rather they must be attributed to the nonfat components, the protein, milk solids, sugar, etc. At 100% relative humidity these components absorbed enough moisture to destroy the structure of the film.

Summary

Films of cocoa butter, highly hydrogenated cottonseed oil, mixtures of highly hydrogenated cottonseed oil and cottonseed oil, chocolate liquor, and sweet milk chocolate were prepared; and their permeability to water vapor was determined by the cup method. The permeability constant was calculated in terms of grams of water diffusing through a centimeter cube in one second under a vapor pressure gradient of one millimeter of mercury across the cube.

Under the test conditions employed, the permeability constant for cocoa butter at room temperature was found to vary from 5.8×10^{-12} to 81.6×10^{-12}. The permeability constants for the highly hydrogenated cottonseed oil and the cocoa butter, under comparable conditions at room temperature, was found to be approximately 1.3×10^{-12} and 33×10^{-12}, respectively.

From data obtained with cocoa butter it was concluded that the permeability constant increased with moderate increases in film thickness.

Polymorphism was found to have a large effect on permeability, an approximately 15-fold difference was found between quickly chilled and tempered films of cocoa butter at 3°C. (37.4°F.).

The percentage of liquid component in the fat was found to have a large effect on permeability. The increasing of the percentage of liquid cottonseed oil in highly hydrogenated cottonseed oil from 0 to 40% increased the permeability constant from 1.3×10^{-12} to about 420×10^{-12}.

The permeability of chocolate liquor and sweet milk chocolate at room temperature was increased greatly when the relative humidity on the wet side of the films was increased to 100%. The nonfat components absorbed enough moisture to impair the structure of the film.

REFERENCES

1. Barrer, R. M., "Diffusion in and Through Solids," London, Cambridge University Press, 1941.
2. International Critical Tables, vol. 1, p. 67–68, New York, McGraw-Hill Book Company, 1926.
3. Landmann, Werner, Feuge, R. O., and Lovegren, N. V., J. Am. Oil Chemists' Soc., in press.
4. Lovegren, N. V., and Feuge, R. O., J. Agr. Food Chem., 2, 558–563 (1954).

[Received December 18, 1958]

A New Development in Vegetable Oil Refining Equipment

HERBERT R. KAISER and COLLIN M. DOYLE,[1] Podbielniak Inc., Chicago, Illinois

A NEW DEVELOPMENT in vegetable oil refining equipment has made possible similar advancements in process technology. This device is a rotating contactor, and its application for refining all types of vegetable, fish, and animal oils by any of the processes in common use will be described in this paper. Data obtained from pilot and commercial plant operations on a number of oils show obvious advantages in simplifying the process flow sheet and reducing the number of units to a maximum of two for any size of refining plant.

It has been pointed out previously (1) that separation of gum and soapstock from oils did not depend solely on high centrifugal force as obtained in centrifuges; rather coalescing surface and residence time play equally important roles. Moreover a combination of these factors and relatively lower separating force in the contactor accomplishes the same and, in most instances, superior results.

---

[1] Present address: 632 North Dearborn street, Chicago, Ill.