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FOOD COATINGS

Permeability of Acetostearin Products to Water Vapor

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The acetostearins are modified fats capable of being formed into waxlike films which are potentially useful as protective coatings. For this use they should be relatively impermeable to moisture. In the present investigation the permeability of such films was investigated using a modification of the standard cup method. Measurements were made at various temperatures and relative humidities using films of different compositions and thicknesses. From these data permeability constants were calculated. The permeability constants for these fat films were not independent of the thickness of the film or the concentration of water vapor. The results obtained were compared with those found in the literature for various plastic films. The permeability of acetostearin films to water vapor is less than that of cellulose acetate and slightly greater than the permeability of nylon, ethylcellulose, and polystyrene. Cellophane and paraffin wax have significantly smaller permeabilities.

ACETOSTEARIN PRODUCTS consisting essentially of di- and triglycerides containing one and two acetyl groups, respectively, solidify to unique waxlike solids (3). This unusual physical property has been shown to be associated with the alpha polymorphic form of the fats (7, 12). Spontaneous transformation to the nonwaxy form does not occur readily unless the product is a single compound of high purity. At room temperature and below, technical grade products will remain in the waxy form for several years.

The physical properties of the acetostearin products made them potentially valuable as protective coating materials. They are being evaluated for use as protective coatings for processed meats like frankfurters and for dressed meats that are to be stored at low temperatures, and as coatings for cheese, fruits, nuts, candy, and other food products.

Commercial utilization involving food products must await proof of edibility,

which should be furnished by tests now under way. Other types of information are desirable as an aid to commercial utilization—detailed chemical and physical data on the products.

In the present investigation the permeability of a number of acetostearin products to water vapor was investigated in order to obtain an indication of the performance of these compounds as protective films against moisture transfer.

A survey of the literature on the permeability of various types of films to water vapor reveals that measurements have been made on a wide variety of polymeric materials, including polystyrene, polyvinyl chloride, cellulose acetate, nylon, rubber, glue, gelatin, hardened shellac, and polymerized linseed oil. The permeability of paraffin wax has also been determined by a number of investigators. However, it appears that no measurements have been made on films of fat or fatlike materials.

Materials and Methods

Materials Two series of acetostearin products were prepared and examined. Series A was made from a technical grade monostearin derived from almost completely hydrogenated cottonseed oil (iodine value, 1). The method of preparation and purification was such that this technical grade monostearin contained about 60% of monoglycerides, 35% of diglycerides, 5% of triglycerides, and no free glycerol (2).

The other series of acetostearin products, series B, was made from a commercial, molecularly distilled monostearin (Myverol 18:05) derived from triple-pressed stearic acid having an average molecular weight of 270.9. The distilled monostearin had an actual monoester content of 91.5%, a hydroxyl value of 332.7, an iodine value of 1, and a free glycerol content of about 1%.

Both monostearins were converted

Table I. Products Used in Permeability Determinations

Product	Monostearin Used in Preparation	(CH ₃ CO) ₂ O per OH ^a	Melting Range ^b , ° C.	Mono-glyceride Content, %	Hydroxyl Value
A-1	Technical grade from hydrogenated cottonseed oil	0.5	44.5-46.8	10.5	107.0
A-2	Technical grade from hydrogenated cottonseed oil	1.0	30.0-39.8	2.5	49.4
A-3	Technical grade from hydrogenated cottonseed oil	2.0	32.4-35.6	0.2	27.7
B-1	Distilled product from triple-pressed stearic acid	0.5	35.0-41.0	14.2	136.1
B-2	Distilled product from triple-pressed stearic acid	0.75	32.8-37.2	5.0	95.5
B-3	Distilled product from triple-pressed stearic acid	1.0	25.3-35.0	2.4	73.1
1-Aceto-3-stearin	Pure 1-monostearin	...	49.0-49.3	0.0	142.0
1,2-Diaceto-3-stearin	Pure 1-monostearin	...	48.4-49.0	0.0	0.0
Hydrogenated peanut oil	30.0-37.5
Low-oil paraffin	49.1-52.2

^a Ratios are moles of acetic anhydride per OH equivalent used in preparation of aceto-stearins.

^b Temperature range over which sample melted, as determined by capillary tube method (1/3° C./min. rate of temperature rise).

into acetostearin products by acetylating them with various proportions of acetic anhydride for 1 hour at 110° C. and then removing the acetic acid and unreacted acetic anhydride (3,4). The products were further purified by bleaching with neutral, activated clay and then mild deodorization or steam distillation at low pressure. The finished products were analyzed for melting range, mono-glyceride content (5), and hydroxyl value. The latter was determined according to the acetylation method of West *et al.* (13), modified by using 1 part of acetic anhydride to 3 parts of pyridine.

Pure samples of 1-aceto-3-stearin and 1,2-diaceto-3-stearin were prepared by acetylating 1-monostearin (12) and purifying the reaction products by fractional crystallization from solvents. The melting points and some other properties of the compounds were determined and found to correspond to previously determined values for the pure compounds (7, 12).

The low-oil paraffin used in the tests was a commercial grade obtained from a chemical supply house.

Peanut oil was hydrogenated in the laboratory to an iodine value of 62.5 and had a shorteninglike consistency.

The individual compounds on which permeability determinations were made are listed in Table I together with some of their properties. Not listed are a hydrogenated cottonseed oil of iodine value 1 and a commercially obtained beeswax, which were added in a minor

proportion to the samples of product used in a few of the tests.

Measuring Procedures

Permeability measurements were made by the well-known cup method, many modifications of which have been used by previous investigators. In the present experiments the two types of cups represented in Figure 1 were used, both made of borosilicate glass. Cup A was used in most of the tests. Cup B was used only when the amount of moisture passing through the film under test was expected to be relatively large.

The product whose permeability was to be measured was melted and poured into a shallow dish containing mercury heated to just above the melting point of the product. The mercury and product were allowed to cool to room tem-

perature, and the solidified film was removed. A circular portion was cut from this film and fitted into the cup as shown in Figure 1, an electrically heated wire and some additional product being used to seal the edge of the film to the shoulder of the cup. At the conclusion of the test the film was removed from the cup and the area actually exposed to the absorbent was measured.

In most of the experiments Drierite, a specially prepared anhydrous calcium sulfate used as a drying agent, was placed inside the cup just before the film was sealed in place. In a few experiments distilled water was placed in the cup.

During the actual permeability measurements, the sealed cup was stored in a closed jar in which the atmosphere was maintained at a constant temperature and relative humidity. The humidity was kept constant by placing either distilled water or a saturated solution of one of several salts (see Table II) in the bottom of the jar.

Periodically the cup was removed from storage for a brief time and its change in weight determined. With absorbent in the cup the rate at which the weight of the cup changed was initially rapid, but after 3 to 6 days it decreased to a constant value. Permeability constants were determined on the basis of this constant or equilibrium value.

For measurement of water absorption, acetostearin films were prepared in the following manner. Acetostearin products A-1, B-1, and B-3 were dried by stripping the melted samples with hydrogen while they were under a partial vacuum. Sufficient amounts of the stripped samples to form films approximately 2 mm. thick were poured into Petri dishes and allowed to solidify. In the case of product B-3 a dish containing a film approximately 6 mm. thick was also prepared. All samples were aged in a desiccator over Drierite for 1 week to allow for any rapid polymorphic changes and then placed in an atmosphere having a relative humidity of 75.2% and a temperature of 21.1° C. The gain in weight of the films *vs.* time was recorded.

Table II. Temperature and Humidity Conditions Used in Permeability Measurements

Source of Constant Humidity ^a	Temp., ° C.	Relative Humidity, %	Vapor Pressure, Mm. Hg
Satd. soln. of MgCl ₂ ·6H ₂ O	21.1	32.85	6.17
	27.0	32.52	8.70
	21.1	75.24	14.13
NaCl	27.0	75.14	20.09
	21.1	97.12	18.24
K ₂ SO ₄	27.0	96.91	25.91
	0.0	100	4.58
Distilled water	25.0	100	23.76
	27.0	100	26.74

^a From International Critical Tables (6).

Table III. Permeability at 25° C. and a Difference of 100% in Relative Humidity^a

Product	Film Thickness, Mm.	Moisture Transferred, Mg./Hr./Sq. Cm.	Permeability Constant $\times 10^{-12}$
A-1	1.31	0.0194	29.6
	2.61	0.0154	46.5
A-2	2.07	0.0244	58.6
	2.61	0.0174	52.7
A-3	0.30 ^b	0.1170	40.7
	1.09	0.0489	61.8
	1.14	0.0280	37.0
	1.36	0.0206	32.5
	1.45 ^b	0.0269	45.4
	1.95	0.0199	45.0
	2.03	0.0300	70.5
	2.20	0.0242	61.8
	3.43	0.0120	47.7
	3.60	0.0132	55.1
B-1	0.54 ^b	0.0854	53.0
	1.38	0.0631	101
	1.77	0.0535	110
	1.81 ^b	0.0532	112
	2.29	0.0510	135
	2.55	0.0476	141
	2.80	0.0501	163
	4.24	0.0349	172
B-2	1.65	0.0526	101
	2.65	0.0460	141
B-3	2.73	0.0625	198
B-1 plus 10% beeswax	1.80	0.0195	40.7
B-1 plus 10% hydrog. cottonseed oil ^c	1.83	0.0302	64.0
B-1 plus hydrog. peanut oil ^d	1.70	0.0648	128
B-1 plus 10% paraffin	2.11	0.0516	126
Hydrog. peanut oil ^d	3.39	0.0131	51.4
Paraffin	0.66	...	0.3

^a Film sealed over cup containing Drierite and stored in air saturated with moisture.

^b Filter paper placed under film for support.

^c Iodine value of 1.

^d Iodine value of 62.5.

Permeability Constant

In order to facilitate the comparison of permeability under various conditions, permeability constants were calculated on the basis of Fick's linear diffusion law and Henry's solubility law, assuming that under equilibrium conditions the diffusion constant times the solubility constant equals the permeability constant. In the present investigation the permeability constant, *P*, is defined by the equation

$$P = \frac{(w)(x)}{(A)(t)(p)}$$

where *w* is the weight of water, 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 vapor pressure difference, *p*, is measured in millimeters of mercury.

Results and Discussions

Permeability of 1-Aceto-3-stearin and 1,2-Diaceto-3-stearin. Films of 1-aceto-3-stearin and 1,2-diaceto-3-stearin having thicknesses of 1.71 and 1.77 mm., respectively, were sealed over cups containing Drierite and the cups were stored at 21.1° C. in an atmosphere having a

relative humidity of 75.2%. The initial rate of water absorption corresponded to an apparent permeability constant of 137×10^{-12} for 1-aceto-3-stearin and 121×10^{-12} for 1,2-diaceto-3-stearin. The actual constant, which could not be determined at this stage, was much smaller. After 6 days, equilibrium con-

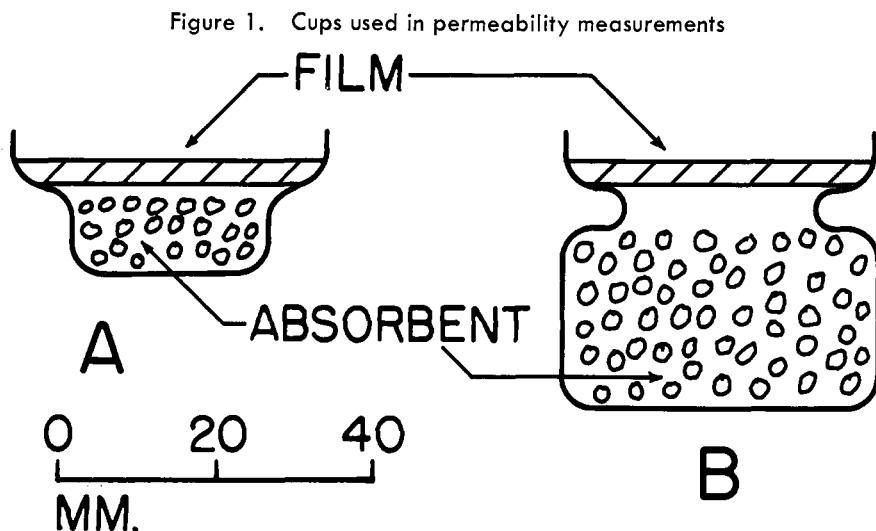
ditions were attained for the film of 1-aceto-3-stearin, and its permeability constant was found to be 25×10^{-12} . During this same period polymorphic changes occurred in the 1,2-diaceto-3-stearin—the film lost its original translucency and plasticity and became white and opaque (12). On the sixth day the permeability constant was 6×10^{-12} , and after 12 days it had decreased to less than 1×10^{-12} .

A second experiment with a film of 1-aceto-3-stearin measuring 1.71 mm. in thickness was conducted at a temperature of 27.0° C. and a relative humidity of 75.1%. Under these conditions the permeability constant was found to be 28.5×10^{-12} . The 1,2-diaceto-3-stearin was not tested at 27.0° C. because at this temperature its rate of transformation from the waxy alpha to the nonwaxy beta form would have been even greater than at 21.1° C.

Effect of Composition. The permeabilities of the various acetostearin products, hydrogenated peanut oil, and paraffin wax were determined at room temperature (25° C.) with a relative humidity of 100% on the outside of the permeability cup and 0% on the inside. Various film thicknesses were used and some mixtures of products were tested. The results obtained are recorded in Table III.

An inspection of the calculated permeability constants (Table III) reveals that they varied from 29.6×10^{-12} to 198×10^{-12} . The experiments were conducted at room temperature, which fluctuated by a few degrees, but only a small proportion of the variation in permeability constants can be attributed to this factor. Undoubtedly the constants were affected by differences in film thickness and the composition of the acetostearin products. This is to be expected in view of the mechanisms involved in the transfer of moisture through films (8-17).

As a class, the acetostearin products



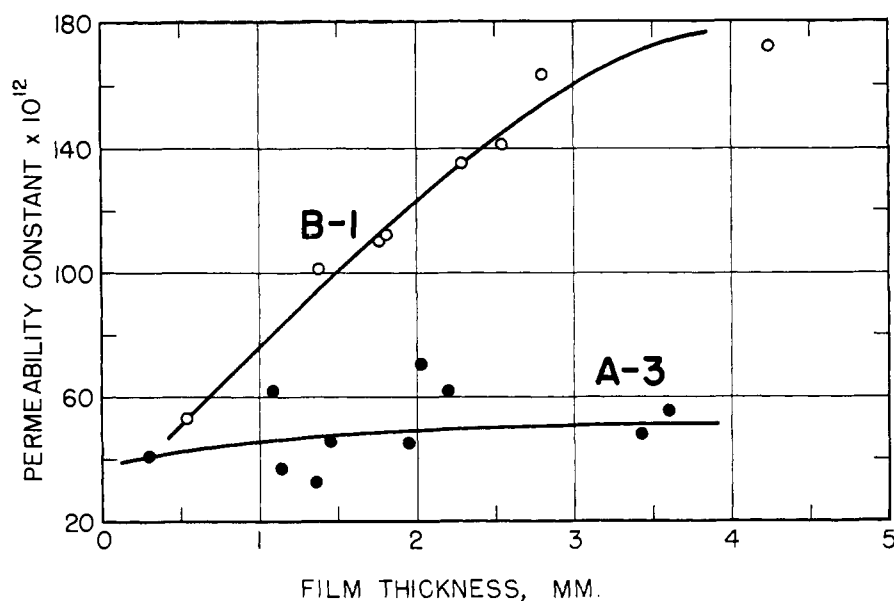


Figure 2. Relation of film thickness to permeability constants for acetostearin products A-3 and B-1

made from the technical grade monoglycerides derived from cottonseed oil are more impermeable than the products made from the commercial, molecularly distilled monostearin. The technical grade monoglycerides contained about 5% of triglycerides and 35% of diglycerides of stearic and palmitic acids, and in the conversion to acetostearins diglycerides were acetylated and the triglycerides left unchanged. On the other hand, the molecularly distilled monostearin contained practically no di- and triglycerides of long-chain fatty acids. It could be argued that in the solid state the "impurities" present in the acetostearins derived from the technical grade monoglycerides are more impermeable than are mono- and diaceto-containing stearins, but the experiments made with 1-aceto-3-stearin and 1,2-diaceto-3-stearin disprove this. The latter compounds were found to be more impermeable than the acetostearin products of series B. The higher permeabilities for the products of series B might be caused by differences in crystal packing or the presence of liquid components at the test temperature. A sizable proportion of 1,2-diaceto-3-palmitin, having a melting point of 22.4°C., probably was present in the product of series B, because the average molecular weight of the long-chain fatty acids combined in the products was 270.9.

It might be expected that the hydroxyl value of acetostearin products would have a large influence on their permeability, but this is not borne out by the data in Tables I and III. Hydroxyl value appears to have little effect when films of equal thicknesses are compared. A possible explanation is the fact that all of the hydroxyl groups, with the exception of half of those in the monogly-

cerides which may be present, are located at the inner or number two position of the glyceride molecules. In this position their polar or hydrophylic properties might not contribute significantly to the properties of the film. The suggested explanation is strengthened by the established fact that the surface activity of diglycerides is less than 1/100 that of the corresponding monoglycerides.

Effect of Film Thickness. An examination of the curves in which are plots of some of the data in Table III (Figure 2) indicates that film thickness had a significant effect on the permeability constant where products of series B were concerned, but the effect was not significant for products of series A. Stated somewhat differently, the rate of moisture transmittance through acetostearin films of series A tended to be inversely proportional to the film thickness,

but for acetostearin films of series B a doubling of the film thickness reduced the moisture transmittance rate to a value greater than one half of the original. The reason for this fact is discussed below.

Effect of Added Compounds. From the data in Table III it is indicated that the permeability of product B-1 could be decreased greatly by adding 10% of either beeswax or highly hydrogenated cottonseed oil. Similar amounts of paraffin wax or partially hydrogenated peanut oil had practically no effect, even though the partially hydrogenated peanut oil itself possessed a fairly low permeability and that of wax was very low.

Effect of Temperature. Films of products A-1, A-2, and B-1 were tested at various temperatures and vapor pressures to establish the effect of these variables on the rate of moisture transmittances through the acetostearin products. In most of the tests, films of the products were sealed over permeability cups containing Drierite, and the cups were stored at various temperatures and vapor pressures. In the remaining tests, distilled water was sealed into the cups, which were then stored as usual. The results of these tests are summarized in Table IV.

In making the tests it was impracticable to hold the vapor pressure constant while varying the temperature. Therefore, the effect of varying the temperature must be established by comparing permeability constants obtained at approximately equal vapor pressure gradients, the latter including both vapor pressure difference and level. Under such a comparison the effect of temperature appears to be fairly small and erratic. For example, when the vapor pressure difference was in the range of 4 to 9 mm. of mercury and the dry sides of the films were at a vapor pressure of 0, the permeability constant for products A-1 and A-2 increased somewhat with increasing temperature; however, at vapor pres-

Table IV. Variation of Permeability Constant with Temperature and Vapor Pressure Gradient

Temp., ° C.	Vapor Pressure Gradient, Mm. Hg	Vapor Pressure Difference, Mm. Hg	Permeability Constant $\times 10^{12}$ for Acetostearin Product ^a		
			A-1	A-2	B-1
0	4.58-0	4.58	...	27.7	188
	4.58-0	4.58	...	31.1 ^b	168 ^b
21.1	18.78-14.13	4.65	140.4	...	410
	6.17-0	6.17	18.3	38.6	44.7
	18.78-6.17	12.61	79.1	84.2	237
	14.13-0	14.13	33.5	48.1	73.1
	18.24-0	18.24	59.4	57.0	133
27.0	26.74-20.09	6.65	144	...	434
	8.70-0	8.70	27.0	40.8	52.9
	26.74-8.70	18.04	80.8	...	234
	20.09-0	20.09	40.3	53.3	85.8
	25.91-0	25.91	59.5	57.4	142

^a Film thicknesses ranged between 1.71 and 1.80 mm.

^b Film aged for 13 days at 25°C. before permeability tests were begun.

sure differences of 18 to 21 mm., the dry side again being at a vapor pressure of 0 mm., the trend was reversed.

In the discussion permeability constants are compared. If a comparison is made of the rate at which water vapor is transmitted at a given relative humidity, it will be found that in nearly all instances the rate increases with temperature. The reason is, of course, that at a constant relative humidity the vapor pressure increases with temperature.

The effect of temperature on films of acetostearin products is somewhat at variance with that generally found for polymeric substances commonly used as film-forming materials. In general, increasing the temperature increases the permeability constant of polymeric substances and often a 10° increase doubles the value of the constant (7, 10).

Effect of Vapor Pressure and Moisture Absorption. From the data in Table IV it is evident that the permeability constants for films of acetostearin products are affected greatly by the vapor pressure differences across the films and the vapor pressures at the surfaces of the films. For example, maintaining one side of a film of product B-1 at a vapor pressure of 0 mm. of mercury while increasing the vapor pressure on the other side from 6.17 to 18.24 increased the permeability constant from 44.7 to 133. When the vapor pressure on both sides of the film was raised to a high value (18.78 and 14.13), the permeability constant increased still further to 410.

This behavior has been encountered by other investigators working with other substances (70, 77) and is said to be related to the adsorption of water by the film. The diffusing molecule of water passes into the film by being adsorbed on an active spot on the internal surface of the film. The molecule of water vibrates in this position until it acquires sufficient energy to evaporate. It then passes on to the next active spot, and the process is

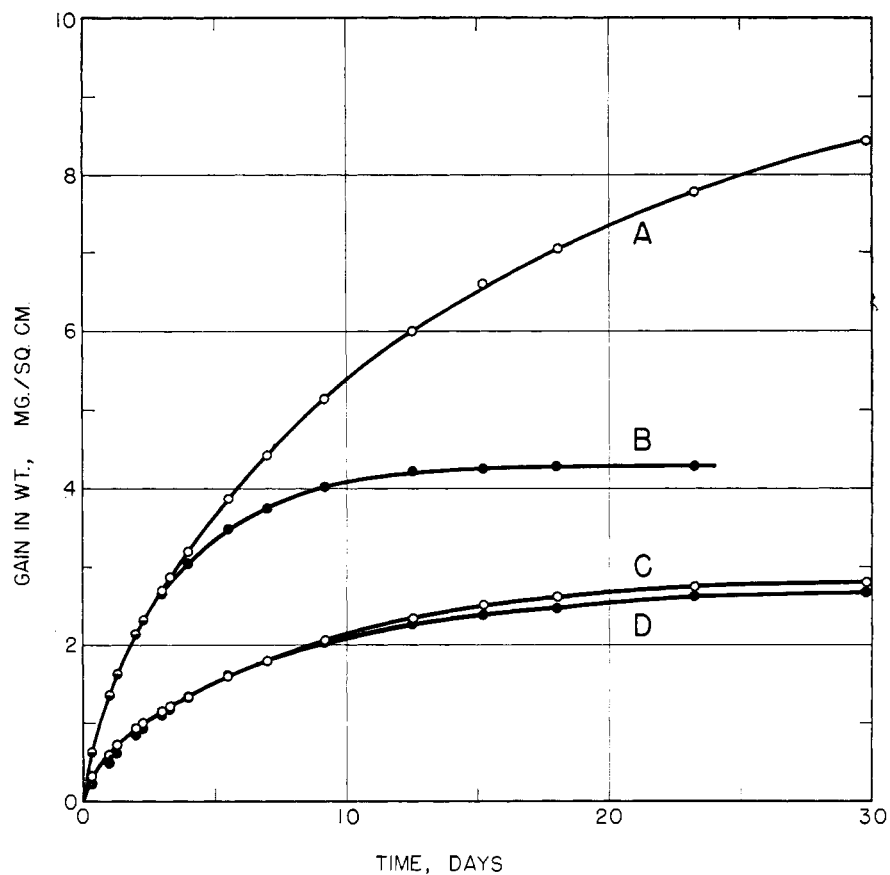


Figure 3. Absorption of water by films of acetostearin products at 21.1° C. and relative humidity of 75.2%

A. Film of product B-1 approximately 6 mm. thick and weighing 0.56 gram per square cm.
B, C, D. Films of products B-1, A-1, and B-3, all approximately 2 mm. thick and weighing 0.18 gram per square cm.

repeated until the molecule emerges on the other side of the film. When many molecules of water are diffusing, there is a significant weakening or even disruption of the intra- and intermolecular bonds originally in the film and the resistance to diffusion is lowered.

The mechanism of diffusion, which has just been described in rather simpli-

fied terms, also serves to explain the fact that doubling the thickness of a film of acetostearin product may not quite double its resistance to the passage of water. If one side of the film is kept at a vapor pressure of 0, then a relatively large part of the resistance of the film is located on this side. Increasing the thickness of the film will increase that portion which has a relatively smaller resistance.

The gain in weight of films of products A-1, B-1, and B-3 plotted against time is shown in Figure 3. The gains in weight or absorptions of moisture after 30 days for the films having a thickness of approximately 2 mm. were: A-1, 1.58%; B-1, 2.40%; and B-3, 1.54%. The film of product B-1 having a thickness of approximately 6 mm. had absorbed moisture to the extent of 1.49% of its weight. According to the shape of the curves, it required more than 10 days for the film having a thickness of approximately 2 mm. to come to equilibrium. In the permeability determinations, equilibrium was attained in a shorter period of time, possibly because the original films contained moisture. It is indicated from the curves and Table I that the more highly acetylated products absorb less moisture and that the products made

Table V. Permeability of Various Organic Compounds to Water Vapor

Product	Film Thickness, Mm.	Temp., ° C.	Vapor Pressure Gradient, Mm. Hg	Permeability Constant $\times 10^{12}$	References
Cellophane	0.035	25	20	0.38	(7)
Cellulose acetate	0.163	25.0	22.8-0.0	433	(17)
	0.156	25.0	22.8-0.0	450	(17)
	...	35	...	183	(10)
Ethylcellulose	0.505	25	20	41.1	(7)
Hydrocarbon wax	0.51	21.1	18.6-0.0	0.17	(17)
Nylon	...	35	...	28.1	(10)
Polyethylene	...	35	...	0.81	(10)
	...	25	...	0.52	(10)
	...	35	(10)
Polystyrene	0.54 to 2.09	21.1	18.0-0.0	11.1	(17)
	0.54 to 2.09	21.1	18.0-6.1	11.0	(17)
	...	35	...	8.7	(10)
Regenerated cellulose	...	35	...	111	(10)
Soft vulcanized rubber	0.354	25	7.66-0.0 to 23.6-0.0	18.4 to 21.4	(17)

from the technical grade monostearin absorb less moisture than do the products made from the purer or molecularly distilled monostearin.

Comparison of Permeability of Films of Acetostearin Products and Other Types of Coating Materials. There apparently are no data in the literature on the permeability of fats and fatlike products to moisture, but data are available for many other organic compounds. To provide a basis for comparing acetostearin products and other organic compounds, some of the literature data are reproduced in Table V. The permeability constants shown were recalculated to conform to the dimensions used in the present investigation.

It is evident from Tables III and V that the permeability constant for the acetostearin films is less than that of cellulose acetate and only slightly greater than that of nylon, ethylcellulose, polystyrene, and soft vulcanized rubber.

Cellophane, polyethylene, and paraffin wax have permeability constants equal to 1/100 or less of those found for the acetostearin products.

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ALFALFA CAROTENOIDS

Xanthophylls in Fresh and Dehydrated Alfalfa

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The carotenoids of fresh and dehydrated alfalfa were separated chromatographically. Five xanthophylls (lutein, violaxanthin, cryptoxanthin, zeaxanthin, and neoxanthin) comprised 99% of the xanthophylls in fresh material. In addition, seven minor bands were present. The same five pigments comprised 87% of the xanthophylls of a dehydrated alfalfa meal. A total of more than 40 xanthophyll bands were shown to be present in dehydrated meal.

DEHYDRATED ALFALFA MEAL or another rich source of xanthophyll is required in chick feeds to give the finished poultry a desirable yellow color. However, until the kinds and amounts of the separate xanthophylls in the feed additives are known and their relative pigmentation value is assayed, it is difficult to make an accurate estimate of the amount of alfalfa or other supplement required in the diet.

The effect of dehydration on the formation of stereoisomers of β -carotene in alfalfa has been reported (4, 8), but the literature reveals no comparable information on the xanthophylls present in fresh and dehydrated alfalfa. There is incomplete agreement in the literature in regard to the nature of the xanthophylls found in fresh leaf tissue. Strain (7) in an investigation of the leaves of some 50 dif-

ferent species of plants, observed the following xanthophylls in each: lutein, violaxanthin, neoxanthin, zeaxanthin, and cryptoxanthinlike pigments. Karrer *et al.* (5) were unable to confirm the presence of neoxanthin and zeaxanthin in fresh leaves and stated that leaves contain only two principal xanthophylls which they called xanthophyll (lutein) and xanthophyll - epoxide (violaxanthin). More recently, Moster, Quackenbush, and Porter (6), working with corn seedlings, confirmed the presence of neoxanthin and zeaxanthin in fresh leaf material. In addition, they found small amounts of other carotenoids hitherto not observed in green leaves. The present paper describes the separation, characterization, and quantitative determination of the xanthophylls present in fresh green alfalfa, and the changes that

occur in the xanthophylls during the dehydration process.

Fresh Alfalfa

Extraction The alfalfa employed was a Chilean variety grown in a small plot near the laboratory. Alfalfa was harvested at the prebloom stage, taken immediately to the laboratory, and the pigments were extracted by a slight modification of a method published previously (3).

In this method, 30 grams of fresh plant material were blended with 100 ml. of acetone for 1 minute. A 50-ml. aliquot of the acetone solution was added to 50 ml. of hexane and 30 ml. of water in a separatory funnel. Gently swirling the funnel for a minute transferred most of the acetone into the lower water layer which was then withdrawn and dis-