

indicated when high degrees of agitation are used (9). At 150 and 300 p.s.i. selectivity appears to increase slightly with temperature; but at higher pressures, selectivity may decrease with temperature. The present results are not sufficiently accurate though to establish the temperature trend definitely. Rather surprisingly the ratio of k_{12}/k_{13} is fairly constant in all cases at about 1.5–1.7. Also k_{23} and k_{32} are generally 0.10 and 0.05, respectively. Selectivity can be expressed quantitatively as follows:

$$12) \quad N = \frac{k_{LO}}{k_{OS}} = \frac{k_{12} + k_{13}}{k_{24}}$$

Table II indicates variations of N values from 2.3 to 6.1; however, these values may be inaccurate by as much as 10–20% because of small errors in the values determined for the relative reaction rate constants.

The hypothesis (2,9) that isomerization is caused by a hydrogenation-dehydrogenation scheme involving atomic hydrogen is consistent with the present results. Further, the explanation (9) that selective hydrogenation is caused by preferential physical adsorption of polyunsaturated groups as compared to monounsaturated groups still seems probable. In each case an increased concentration of hydrogen at the catalyst surface, as would occur at higher hydrogen pressures, would decrease selectivity and isomerization. In this respect the equilibrium solubility of hydrogen in cottonseed oil was found to be essentially directly proportional to the hydrogen pressure, and to increase slightly with temperature (13). Based only on this information concerning temperature, selectivity and isomerization would be expected to decrease somewhat at higher temperatures when high degrees of agitation are provided. The relative rates

of the various reactions probably change slightly, however, so that actually selectivity is relatively unchanged and isomerization increases to a small extent with increased temperatures. When relatively poor agitation is employed, both selectivity and isomerization increase with temperature, since the overall rates of reaction are increasing and since the high resistances to hydrogen transfer cause the hydrogen concentration on the catalyst to decrease.

Acknowledgments

Emery Industries, Inc., donated the methyl oleate. F. L. Kauffman of Swift and Company helped in regard to the gas-liquid chromatographic analyses. H. K. Hawley of Procter and Gamble Company offered valuable advice during the course of the investigation.

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Properties of the Fatty Acid Esters of Amylose¹

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To help establish the suitability of esters of amylose and fatty acids as dip-coating materials, esters of the even-numbered, saturated fatty acids, acetic through stearic, and of oleic and cottonseed oil fatty acids were prepared, and their properties were determined.

The various esters generally were prepared by the interaction of acid chlorides with the amylose suspended in a suitable mixture of solvents. Analyses for content of free fatty acid groups indicated that high proportions of the hydroxyl groups were esterified. Intrinsic viscosity decreased as the chain length of the acyl group increased, a reflection of the changing nature of the products rather than a decrease in the degree of polymerization of the amylose.

As the chain length of the saturated fatty acid group increased the softening point at first decreased and then increased, the minimum being obtained with the myristate. The stearate softened at 56.2°C. The stearate had a hardness index of 139, which was about equal to the index of 140 for completely hydrogenated cottonseed oil. Densities were greater than those of the corresponding triglycerides and decreased as the chain length of the fatty acid group increased. Permeability to water vapor also decreased as the chain length increased, the index being 620×10^{-12} for

the acetate and 15×10^{-12} for the stearate. The acetate possessed the highest tensile strength, about 4.40 kg./sq. mm., while the palmitate had a tensile strength of about 0.49 kg./sq. mm. Elongation at the break point varied widely, being 632% for the caprate and 0.95% for the stearate.

ESTERS PREPARED from fatty acids and a film-forming polyhydric material like amylose should be useful as dip-type coatings on both foods and nonfoods and such use might provide a new, large-volume outlet for surplus fats and oils. While adequate information on the physiological properties of such esters is not available, presumably they can be shown to be edible, and they might be digestible, at least to some extent.

Among the film-forming polyhydric materials available, amylose is one of the preferred. It can be derived from corn, another surplus commodity, by a relatively simple procedure. Some new varieties of corn yield a starch containing over 70% amylose (12).

Amylose and cellulose have a straight-chain molecular structure of identical chemical composition. However, the d-glucopyranose units of the amylose molecule are joined by alpha-1:4 linkages, while those of the cellulose molecule are joined by beta-1:4 link-

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ages. As a result, the cellulose molecule has a relatively rigid, thread-like spatial configuration, while that of amylose has a helical spatial configuration.

The literature on the simple and mixed lower fatty acid esters of cellulose is extensive. That on the higher fatty acid esters is less extensive, but numerous descriptions can be found. A series of cellulose esters from the acetate through the palmitate was prepared and described by Malm *et al.* (6, 7) and Sheppard and Newsome (14). The data indicate that the higher members of the series, which on a weight basis are composed predominantly of fatty acid groups and can be regarded as fatty products, possess some of the properties desired in dip-coating materials.

The literature on the lower fatty acid esters of starch and amylose also is fairly extensive. However, relatively little has been published concerning esters of amylose and the higher fatty acids. With the exception of a report of some properties of amylose acetate, butyrate, caproate, and palmitate (19), there apparently is no report on a reasonably complete homologous series of fatty acid esters. Investigators generally have confined themselves to one or two unfractionated esters (1, 11, 17). Frequently the details of the preparation, purity of the product, or physical properties are not described. Because different methods of preparation are often used, the reported data are difficult to correlate. The number-average molecular weight and distribution of molecular size of the amylose molecules probably varies as well as the nature and amount of the impurities and the degree of acylation. Sheppard and Newsome (14) point out that the esters described by different investigators may be identical in over-all composition and yet differ considerably in molecular weight.

The present investigation was concerned primarily with the preparation and examination of a homologous series of fatty acid esters of a commercially available amylose. Tests bearing on the possible use of the esters as dip-coating materials were made, and the effect of chain length and unsaturation of the fatty acid groups was established.

Materials and Methods of Preparation

Materials. The amylose employed was the Superlose product manufactured by Stein, Hall and Company. The product was said to be derived from potato starch and to contain 95% amylose. The degree of polymerization was claimed to be 800–1,000 and the molecular weight about 150,000. Analysis by the Karl Fischer method (3) indicated 10.06% moisture. Attempts to "uncoil" the amylose molecules by dispersing the amylose in a pyridine solution, distilling off the pyridine-water azeotrope, and adding more pyridine appeared to be ineffective. This treatment lowered the moisture content to 0.71%. Esters were prepared from amylose which was not pretreated other than sieving through a 100-mesh stainless steel gauze to remove coarse particles and stripping at 110°C. with an inert gas under reduced pressure to lower the moisture content to 0.50%.

Acetyl chloride, obtained as Baker's analyzed grade from the J. T. Baker Chemical Company, was used without further purification. The butyryl, caproyl, lauroyl, myristoyl, and palmitoyl chlorides employed were Eastman grade, obtained from the Eastman Organic Chemicals Department, Eastman Kodak Company. The chlorides of caprylic, capric, and the cottonseed oil fatty acids (both hydrogenated and

unhydrogenated) were prepared by dissolving the fatty acids in benzene and treating with a 50% excess of oxalyl chloride. Oleoyl chloride was prepared by the action of phosphorus pentachloride on oleic acid dissolved in petroleum ether, according to the method of Youngs *et al.* (21). Stearoyl chloride was prepared by the action of phosphorus trichloride on stearic acid followed by stripping with an inert gas at a relatively low temperature and low pressure and decantation from the immiscible by-products.

The acetic anhydride and acetic acid used were Baker's analyzed grade; the anhydride assayed 97.0%. The butyric anhydride and butyric acid used were Eastman grade.

Other reagents and various solvents employed were reagent grade and were specially purified when this was deemed necessary. The p-dioxane was freed of traces of moisture and peroxides by passage through a long column containing an equal weight of Woelm aluminum oxide, basic, activity grade 1. Pyridine was refluxed and distilled over porous barium oxide to remove all traces of moisture. The chloroform was washed to remove the ethanol which had been added as a preservative, dried over Drierite, decanted, and distilled. Toluene was dried over Drierite and decanted.

Methods of Preparation. Because of the fairly low boiling point of acetyl chloride and somewhat limited solubility of amylose acetate (18), this ester was prepared by vigorously mixing 1 part amylose with 3.2 parts acetic anhydride and 3.7 parts pyridine for 4 hrs. at 110–115°C., according to Whistler's method for starch (18). According to him, amylose should contain some moisture, but not over 3%, when treating it with acetic anhydride. Anhydrous conditions produce strong intermolecular forces which cause the molecules to be highly associated. Therefore, special drying of some of the reagents was not deemed necessary. A few per cent of acetic acid were added after the reaction had proceeded about 1 hr. The reaction product was isolated by precipitation in distilled water. The fibrous mass which resulted was ground with water in a ball mill and dried by stripping with an inert gas while being heated at 110°C. under reduced pressure.

The same method when used for the preparation of amylose butyrate gave after 6 hrs. reaction time a product containing 41.1% butyryl groups, theoretical 57.3%.

Consequently, amylose butyrate and the other members of the series were prepared by the acid chloride-pyridine procedure. Amylose is insoluble in anhydrous organic solvents but it can be dispersed in pyridine. Carbohydrates such as amylose are extensively susceptible to degradation, but this can be minimized by the use of inert solvents (11). p-Dioxane was used as the diluent. The higher amylose esters were more soluble in nonpolar solvents; therefore, a mixed solvent system composed of p-dioxane and toluene was used.

A typical preparation was conducted as follows: 0.1 mole of amylose was dispersed in 200 ml. of p-dioxane and 0.6 mole of pyridine. This dispersion was transferred to a reaction flask equipped with a thermometer, magnetic stirring bar, and condenser and containing 0.45 mole of acid chloride dissolved in 200 ml. of toluene. The reaction was conducted under an inert atmosphere for 6 hrs. at 100°C. The solvents then were removed by stripping at this temperature with an inert gas under reduced pressure.

TABLE I
 Properties of Amylose Esters

Ester	Appearance	Acyl, %		Reaction %	Intrinsic viscosity		Softening point, °C.	Hardness index	Density, g./ml. at 30°C.	Tensile strength, kg./sq. mm.	Elongation, %	Permeability constant x 10 ¹² a
		Actual	Theoretical		Chloroform	Benzene						
Acetate.....	Clear, hard	43.6	44.8	95.3	1.32	295	508	1.348	4.40 b	16.1 b	620
Butyrate.....	Clear, fairly hard	54.7	57.3	90.2	1.82	175	191.0	1.253	2.45 b	10.6 b	481
Caproate.....	Clear, soft	59.2	65.2	77.9	1.74	1.45	142	16.0	1.196	0.62 c	135 c	375
Caprylate.....	Clear, soft	64.1	70.6	74.8	1.70	1.30	118	1.3	1.119	0.42 c	483 c	295
Caprate.....	Clear, soft	69.0	74.5	66.1	1.68	1.25	95.8	0.8	1.110	0.24 c	632 c	200
Laurate.....	Clear, soft	74.1	77.6	83.1	1.23	1.05	70.0	2.2	1.059	0.22 c	306 c	110.1
Myristate.....	Clear, tacky	77.1	79.9	84.7	0.90	0.86	49.8 d	1.036	67.4
Palmitate.....	Clear, plastic	75.2	81.9	67.6	0.86	0.66	51.5	5.9	1.022	0.49 b	21.1 b	30.3
Stearate.....	Translucent, brittle	81.8	83.4	89.2	0.51	0.74	56.2	139	1.012	0.37 b	0.95 b	15.0
Acetate-stearate.....	Translucent, hard	2.0 e 63.0 f	38.3	0.57	60.0	168	1.089	41.8
Acetate-stearate.....	Translucent, hard	11.6 e 49.1 f	35.7	0.64	88.8	300	1.111
Oleate.....	Clear, viscous liquid	81.7	83.3	89.4	0.32	0.30	17.8 d	1.003
(Cottonseed oil).....	Clear, viscous liquid	78.7	82.9	76.5
(Hydrogenated cottonseed oil) g.....	Translucent, fairly brittle	79.6	83.0	80.6	0.41	46.0	54.5	128

a Permeability to water vapor at 21.1°C.

b Rate of grip separation, 0.5 in./min.

c Rate of grip separation, 20 in./min.

d Extremely viscous liquid.

e Acetyl, %.

f Stearoyl, %.

g Iodine value, 20.

The reaction product was washed with hot water in the case of the butyrate and caproate and with hot, absolute ethanol in the case of the other esters of the series. After six successive washings, the esters were dried in a vacuum oven below 100°C. Then they were dissolved in a suitable solvent, chloroform for the butyrate and caproate and commercial hexane for the others, and filtered through a fritted glass funnel. The solvent was removed by evaporation over a steam bath followed by heating in a vacuum oven.

Amylose esters containing both acetyl and stearoyl groups were prepared by acetylation followed by stearoylation and by the reverse procedure. When acetylation with acetyl chloride was performed first, chloroform had to be used as a solvent instead of toluene, which necessitated reducing the reaction temperature.

Analysis of Products

Degree of Acylation. The analytical procedure of Matchett and Levine (8) was used to determine the contents of acetyl and butyryl groups, while an alcoholic alkali procedure (4) was used for determining acyl contents of the other esters. As the esters are not soluble in alcoholic alkali, they were first dissolved in a volume of benzene equal to the volume of alcoholic alkali to be used. Saponification was conducted at room temperature for 48 hrs. while gently shaking the mixtures. Contents of all acyl groups with the exception of acetyl, butyryl, and caproyl were also determined by a procedure consisting of saponification, acidulation, petroleum ether extraction and washing of the free fatty acids, and titration. From the percentages recorded in Table I it is evident that for each product the content of acyl groups was below the theoretical, though for the acetyl, stearoyl, and oleoyl groups the difference is less than two units. On a weight basis and from a practical standpoint all of the products may be regarded as being well acylated. By way of comparison, commercial cellulose acetate usually contains about 39% of acetyl group, theoretic-

cal 44.8%. However, when the percentage completion of each reaction is calculated (Table I), it becomes evident that in some instances a sizable proportion of the hydroxyl groups was not acylated.

Reacylation was found to increase the percentage of acyl groups, but degradation also increased. Data on reacylated products are not reported.

One or more of several factors may be responsible for the reaction not going to completion. The amylose used in the present work had been prepared from potato starch by a process involving precipitation from an aqueous salt solution (2), and was claimed by the manufacturer to have a helical structure. Such a helical structure plus hydrogen bonding should result in steric hindrance, particularly when longer chain acyl groups are to be introduced into the chain.

The reactivities of the three hydroxyls on a glucopyranose unit are not identical. The primary hydroxyl is the most reactive.

Amylose can complex or form occlusion compounds with fatty acids (10). These complexes are composed of helices of glucopyranose units wrapped around fatty acid chains. Based on the original weight of the amylose only a few per cent of fatty acids can be complexed (10), but this could conceivably interfere with acylation. Because linear alcohols can enter the helix and compete with the fatty acids for space (10), the fatty acids, if complexed, should be extracted by the ethanol washing used to purify the amylose esters and should not appear in the final product.

Intrinsic Viscosities. Because ebullioscopic and cryoscopic methods for determination of molecular weights of polymeric materials such as the amylose esters are unsatisfactory, intrinsic viscosities, or limiting viscosity numbers, were determined. The apparatus described by Wagner and Russell (16) was employed, and measurements were made in chloroform solution for the entire series and in benzene solution for those esters soluble in benzene. Measurements were made at a minimum of three concentrations, ranging from

0.25 to 1%; and calculations were made using Kramer's equation,

$$\left\{ \eta \right\} = 1n \eta_r / C.$$

The intrinsic viscosities, which are recorded in Table 1, decrease as the chain length of the acyl group increases. The value for the acetate in chloroform is inconsistent with the other values, possibly because the acetate was made by a different procedure and may have a different degree of polymerization but probably because it is the first member of the homologous series. The first member frequently is not typical of a series. The intrinsic viscosities in benzene solution differ from those in chloroform solution. The variations indicate changes in the configuration or size of the helix. The decrease in viscosity as the chain length of the acyl group increases does not indicate a progressive degradation of the amylose moiety; rather it indicates a progressive change in the nature of the products. Actual molecular weights are not reported because constants are not available for use in Staudinger's equation, $[\eta] = kM$.

Properties of Products

Softening Points. As the esters did not have sharp melting points and were extremely viscous when melted, capillary melting points were not determined. Instead, softening points were determined by the ring and ball method, ASTM Designation E 28-51T (1a), which is normally used for asphalts, tars, pitches, resins, and similar materials. Examination of the data in Table I and Fig. 1 reveals that the softening points of the amylose esters of the saturated fatty acids decreased from 295°C. for the acetate to 49.8°C. for the myristate as the chain length of the acyl group increased; then the softening point increased to reach a value of 56.2 for the stearate. The high softening point of the acetate is an indication of a high degree of association between the molecules. The softening points may be somewhat low because of the presence of a small proportion of amylopectin in the original amylose. Wolff *et al.* (20) observed that amylose esters

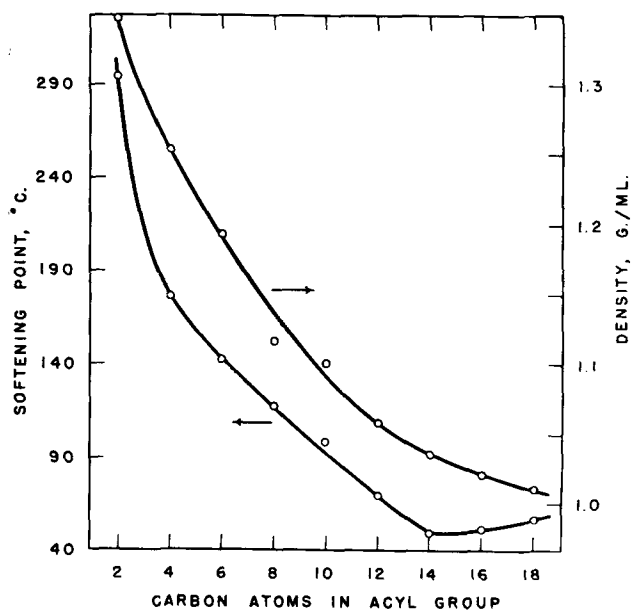


FIG. 1. Amylose esters of saturated fatty acids. Density at 30°C. and softening point.

usually had a higher melting range than did the corresponding amylopectin esters. All of the amylose esters were colorless or had a very light color. At the softening point of the acetate some darkening or charring occurred. The myristate was soft and tacky at room temperature, and on being heated it softened at a rather gradual rate. Amylose oleate did not appear to crystallize on being cooled; it seemed to become merely more viscous. The softening point decreased as the degree of unsaturation increased. On comparing data on the esters containing acetate only, acetate and stearate, and stearate only it is apparent that the softening points increased almost linearly with the content of acetate.

Hardness. Hardness indices of the solid amylose esters were determined at 30°C. by a modification (5) of ASTM Method E 10-54T. Discs of the esters melting below 150°C. were prepared by casting the molten esters in small cylindrical forms. The others were prepared by casting concentrated chloroform solutions and allowing slow but complete evaporation of the chloroform. Hardness indices, calculated from the formula

$$H = \frac{P(100)}{\frac{\pi D}{2} (D - \sqrt{D^2 - d^2})}$$

where H is the hardness index, P is the weight on the ball in kilograms, D is the diameter of the ball in millimeters, and d is the diameter of the depression in millimeters, are shown in Table I.

The acetate is extremely hard, having an index greater than that of carnauba wax. The hardness index of amylose stearate is equivalent to that of completely hydrogenated cottonseed oil. The esters from the caproate through the palmitate were relatively resilient, making it difficult to determine the diameter of the depression. Hence these indices are not reliable. Esters containing acetyl groups in addition to stearoyl groups were harder than amylose stearate.

Density. Densities were determined at 30°C. with a special pycnometer using mercury as the displacement liquid. Sheppard and Newsome (14) used methanol as the displacement liquid. Data obtained for the amylose esters are recorded in Table I and plotted in Fig. 1. The densities of the esters decrease regularly as the chain length of the fatty acid group increases, similar to the behavior characteristics of free fatty acids and glycerides. However, the densities were greater than those of the corresponding free fatty acids and glycerides. The presence of acetyl groups in addition to stearoyl groups increased the density proportionately with the content of acetyl groups. The presence of unsaturated groups lowered the density of the amylose esters, the effect being the reverse of that encountered with glycerides and free fatty acids.

Tensile Strength. Several methods of casting films from solutions of the esters were examined. Apparently the esters formed very viscous, grain-free dispersions rather than true solutions. The acetate could not be dissolved in acetone but was soluble in acetic acid. The esters of the higher fatty acids could be dissolved in hydrocarbons such as hexane, benzene, and toluene. All of the esters were readily soluble in chloroform and pyridine. The selected method of forming films consisted of dissolving the ester in chloroform, filtering the solution at room temperature,

pouring the filtered solution on a glass plate, and evaporating the chloroform. The clear films which were obtained were cured for at least 24 hrs. in a current of air at 50°C. to decrease residual solvent content to a minimum. X-ray diffraction patterns indicated the films consisted of isotropic crystalline polymers. No attempt was made to orient the crystal structure prior to determining tensile strength. For each ester at least ten tests were made with dumbbell-shaped specimens measuring 5 in. in over-all length and 0.25 in. in width. The thickness ranged from 0.1 to 1.0 mm. The lower fatty acid esters could be cast in extremely thin films while the higher fatty acid esters, particularly the stearate, had to be thicker. The static weighing-constant rate of grip separation test described in ASTM Method D 882-56T (1b) was followed. An Instron tensile tester with a grip separation of 2 in. was used. For the esters having an ultimate elongation smaller than 20%, a rate-of-grip separation of 0.5 in. per min. was used, while for those having a greater elongation a rate of grip separation of 20 in. per min. was used. Just prior to the tests, specimens were conditioned for 10 days at $21 \pm 1^\circ\text{C}$. and $65 \pm 2\%$ relative humidity. Typical stress-strain curves are shown in Figs. 2 and 3.

Results obtained with the two different stretching rates are not comparable. The shapes of all the curves with the exception of that for the stearate are alike at the beginning; that is, the load builds rapidly to a maximum and then decreases as the film is being elongated. In the case of the films represented in Fig. 3 the strengths gradually increase due to molecular orientation on elongation. Breaking loads for the caprylate and caprate are much greater than the original stretching loads. Average tensile strengths and elongations at the break point are recorded in Table I. The caprate exhibited the maximum elon-

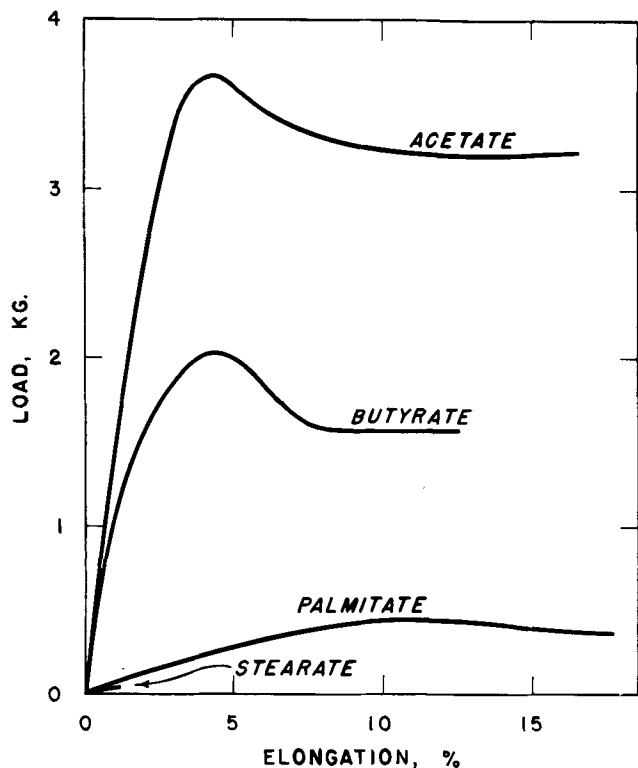


Fig. 2. Typical stress-strain curves of amylose esters of saturated fatty acids; stretching rate, 0.5 in./min.; cross-sectional area, 0.895 sq. mm.

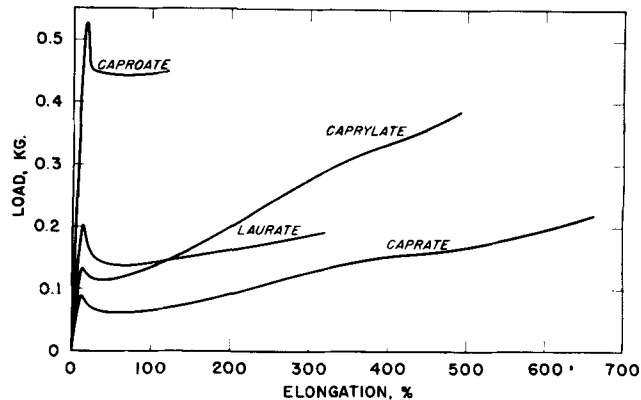


Fig. 3. Typical stress-strain curves of amylose esters of saturated fatty acids; stretching rate, 20 in./min.; cross-sectional area, 0.895 sq. mm.

gation, while the stearate exhibited the least, less than 1%. Data were not obtained for the acetate-stearate products, which were too brittle; for the myristate, which was too soft; and for those unsaturated products which were liquid at room temperature.

The tensile strengths plotted in Fig. 4 indicate that the strength decreases as the chain length of the acyl group increases. The same trend has been reported for an homologous series of cellulose esters (7). The tensile strengths are lower than those reported previously for some amylose esters (20). Possibly the chain lengths of the amylose moieties are different, but probably the differences are the result of the presence of a small amount of amylopectin in the amylose used in the present investigation.

Permeability to Water Vapor. For use as protective coatings on foods and other items, amylose esters should be relatively impermeable to moisture. To obtain data on permeability, measurements were made on thin films at 21.1°C. The standard cup method was

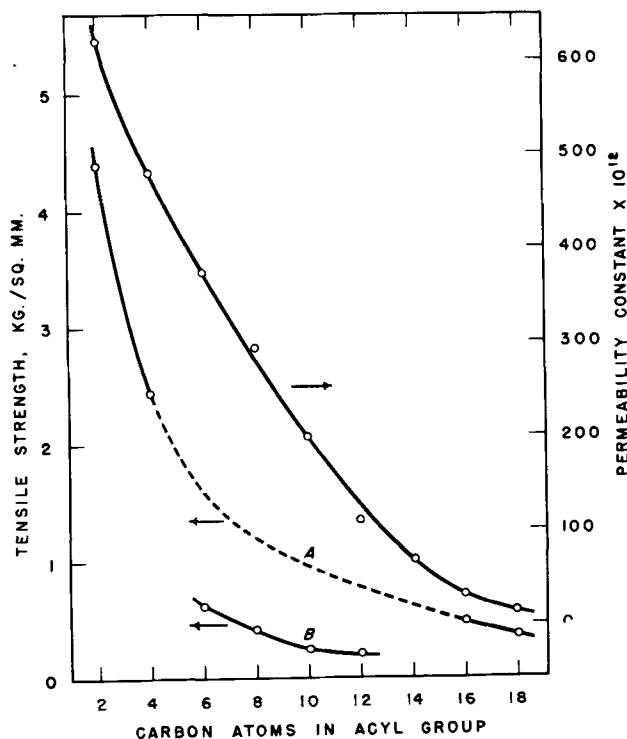


Fig. 4. Amylose esters of saturated fatty acids. Permeability to water vapor at 21.1°C. and tensile strength (A, stretching rate, 0.5 in./min.; B, stretching rate, 20 in./min.).

employed. A 100% difference in relative humidity was maintained across the films. The permeability constant, P , was calculated using the equation,

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

where w is the weight of water vapor, 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. The permeability constants obtained are recorded in Table I and those for the saturated acyl groups are shown graphically in Fig. 4.

Permeability decreased as the chain length of the fatty acid group increased. The presence of unreacted hydroxyl groups apparently had no significant effect on permeability, which is in agreement with data on glycerides obtained in our laboratory. Heretofore, no data on the permeability of amylose esters have been published. Using slightly different test conditions, Rankin *et al.* (12) obtained a permeability constant of 760×10^{-12} for a film of amylose. The permeability of amylose acetate is slightly higher than that reported for cellulose acetate (17). The lowest value obtained, 15×10^{-12} for the stearate, was slightly larger than that of polystyrene (1,5). The value for paraffin wax, probably the most impermeable of organic compounds, has been reported to be 0.17×10^{-12} (15).

When the amylose ester films were removed from the moisture cups after the measurements had been completed, it was observed that the more permeable films had become hazy.

Report of the Uniform Methods Committee, 1961

The meeting of the Uniform Methods Committee was held at 2 p.m., October 30, 1961, during the Chicago fall meeting. K. E. Holt, R. J. Houle, R. A. Marmor, L. D. Metcalf, E. F. Sipos, E. M. Sallee, editor, and D. L. Henry were present. Visitors were: R. W. Bates, L. A. Baumann, R. C. Stillman, and M. E. Whitten.

Progress reports submitted by many of the Technical

Acknowledgments

The authors wish to express their appreciation to Joyce P. Whitley for determining moisture, acetyl, and butyryl contents; to Donald Mitcham for obtaining X-ray diffraction data; to Wilbur F. McSherry for measuring the tensile properties, and to R. C. Hebert for assisting in a portion of the work.

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Committees were discussed with interest. These reports indicate that much good work is being done on needed methods. No recommendations were received to change existing methods or to adopt new ones, and no changes are recommended by the Uniform Methods Committee.

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