

Production of Polyvinyl Esters by Ester Interchange¹

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VINYL ACETATE has become an industrial chemical, available in large tonnages at a moderate price and used principally for making polyvinyl acetate, polyvinyl alcohol, and polyvinyl acetals. Vinyl esters of various other organic acids have interesting and potentially valuable properties, but none of these appears to have been exploited to any great extent, and few are available commercially (7). The properties of some of the polyvinyl esters of organic acids other than acetic acid suggest that these polymers merit attention and that some of them may be utilized more extensively when their qualities are better known.

For example, polyvinyl esters of the fatty acids from drying and semidrying oils would be expected to have superior drying qualities, in accordance with the well-known fact that the esters of the higher unsaturated fatty acids improve in film-forming properties as the functionality of the alcohol portion is increased; ordinary grades of polyvinyl alcohol have more than 50 hydroxyl groups per molecule. This expectation was verified by the examination of products made by esterifying polyvinyl alcohol with oleic acid, or with the mixed acids from soybean oil, linseed oil, or dehydrated castor oil (5, 6).

Alternative methods can be used to produce polyvinyl esters of various acids. The principal ones are a) polymerization of monomeric vinyl ester, b) esterification of polyvinyl alcohol, c) displacement of acetic acid from polyvinyl acetate by another acid, and d) replacement of acetate in polyvinyl acetate by ester-ester interchange. Vinyl esters of acids such as lauric, stearic, or benzoic can be polymerized successfully (2, 9, 10), but this route is not suitable for making polyvinyl esters of acids or acid mixtures that include components more unsaturated than oleic acid. Unsaturation in a fatty acid chain interferes with the normal course of polymerization of the vinyl ester. Vinyl linoleate yielded only a small proportion of polymer when treated with benzoyl peroxide under conditions which caused a high conversion of vinyl stearate to polyvinyl stearate; moreover the intrinsic viscosity of the polymer was much lower than that of the polyvinyl stearate (3). Under some conditions of polymerization, vinyl oleate, and even the vinyl esters of saturated acids such as vinyl palmitate, produce polymers and copolymers that do not dissolve but only swell in hydrocarbon solvents (4).

Direct esterification with higher fatty acids is made difficult by the insolubility of polyvinyl alcohol in the fatty acids and complicated by susceptibility of the alcohol to dehydration and cross-linking reactions at the relatively high temperatures required for ester-

ification. These difficulties were largely overcome by the use of phenol as a mutual solvent, together with an excess of fatty acid to prevent gelation (5, 6). Similar difficulties attend the acidolysis reaction. The ester-ester interchange reaction likewise requires special conditions; with a favorable choice of reactants and reaction conditions polyvinyl acetate will interchange with esters of higher fatty acids to produce mixed polyvinyl esters that are soluble in aliphatic and aromatic hydrocarbons and that have about the same specific viscosity as the polyvinyl acetate from which they are made (1).

Conditions Favorable for Conversion of Polyvinyl Acetate by Ester Interchange

Unless conditions favoring the desired reaction are used, the interchange between polyvinyl acetate and esters of other acids fails to produce the desired products. Side reactions may cause rapid destruction of catalyst, excessive darkening of color, and the formation of insoluble cross-linked products. Conditions that have been found to be favorable include the use of an active catalyst, a selected mutual solvent for the reactants at the beginning of the reaction, a moderate temperature, a choice of esters capable of reacting readily with polyvinyl acetate, and of course the absence of air and moisture from the system during the reaction.

Catalyst. Active catalysts include organoalkali compounds such as amylsodium and phenylsodium, the alkali metals themselves, and their hydrides and alkoxides. A form of organoalkali compound that is easily prepared for laboratory use is the green solution made by dissolving sodium in a mixture of naphthalene and a selected ether (8); tetrahydrofuran is an effective ether. Alkali metal itself in finely dispersed or dispersible form may be the most practical catalyst. The alkali metal alkoxides, in general, are effective but differ in activity according to the kind of alcohol from which they are made; sodium tertiary butoxide, for example, is more effective than an equivalent quantity of sodium methoxide. Some experimental results indicate that the alkoxy groups introduced with alkoxide catalyst increase the color formed during the reaction.

The catalyst may be pre-mixed with the ester which is to react with the polyvinyl acetate, before mixing with the polyvinyl acetate itself, or it may be added to the mixture. The actual catalyst probably is an anion formed from ester; once the added catalyst has been dissolved in the ester, the catalytic substance probably is the same, whether formed from metallic sodium or from hydride, alkoxide, or organosodium.

Temperature. In a solution of polyvinyl acetate the concentration of the alkaline catalyst diminishes

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more or less rapidly, depending upon the temperature. At high temperature the rate of loss of catalyst in relation to the rate of the desired interchange may be too great to allow the reaction to proceed to the desired extent without the use of excessive quantities of catalyst. The upper limit of the temperature range considered to be practical is about 120°C.; temperatures in the range 50 to 100°C. give good results when other conditions are favorable.

Solvent. The solubility of polyvinyl acetate in esters of the higher fatty acids, such as those derived from the fatty oils, is small. Unless the reactants include esters having a greater solvent power for polyvinyl acetate, the reaction between the higher fatty acid esters and polyvinyl acetate requires the presence of a mutual solvent, at least at the outset. It is remarkable that the reaction rate is affected to a noticeable degree by the kind of solvent present, even among solvents that produce homogeneous systems. Thus the rate of interchange is about three times as great with dioxane as it is when toluene is used as the mutual solvent. Among the solvents which may be used are various ethers, acetals, and ketones. The reaction has been carried out successfully in dioxane, methylal, tetrahydrofuran, 1,2-dimethoxy ethane, anisole, methyl isobutyl ketone, and other media. Various esters are effective mutual solvents with a favorable effect on reaction rate but, of course, tend to enter into the reaction themselves. Various mixed polyvinyl esters therefore may be made with esters serving as the only solvents.

Type of Ester. The rate of reaction of polyvinyl acetate with an ester of a given kind of acid, such as oleic acid or stearic acid, is determined to a remarkable degree by the alcohol radical of the fatty ester. Esters of secondary and tertiary alcohols, in general, are too sluggish; with these esters as reactants most of the catalyst is lost before much useful reaction has occurred. Even among the primary alcohols considerable differences in activity exist.

Methyl esters react well enough to be satisfactory, but esters of certain other alcohols react several times faster and are preferred to the esters of the simple primary alcohols. The presence of certain groups on the carbon atom in the beta position with respect to the hydroxyl group has a favorable effect. Hydroxyl groups, alkoxy groups, and double bonds in this position appear to be responsible for enhanced activity; esters of methoxy ethanol, ethoxy ethanol, ethylene glycol, glycerol, and furfuryl alcohol are among those which react much more rapidly than the corresponding methyl esters.

Proportion of Reactants and Removal of Reaction Products. The extent of the replacement of acetate by other acid radicals may be influenced by the proportion of the replacing ester used in the reaction, the nearness of approach to equilibrium attained in the reaction, and the extent to which by-product ester is removed from the system during the time when the reaction is continuing. By the use of an excess of replacing ester and conditions which allow by-product ester to be distilled from the reaction mixture during the reaction, 90% or more of the acetate groups originally present in the polyvinyl acetate may be replaced by other acid radicals. A much lower degree of replacement than this is sufficient for the production of many useful products. For example, mixed polyvinyl esters soluble in mineral spirits and having

excellent drying properties can be made by reaction of equivalent quantities of soybean oil and polyvinyl acetate without any forcing of the reaction by removal of products while the reaction is taking place.

Examples of Replacement of Acetate in Polyvinyl Acetate by Ester Interchange

A. Reaction of Polyvinyl Acetate with Methyl Esters of Higher Fatty Acids, with Sodium Alkoxide as Catalyst

MATERIALS

Polyvinyl Acetate. A low viscosity grade of commercial polyvinyl acetate was used (Bakelite Vinylite Resin AYAC). According to the manufacturer's specifications, this grade has an intrinsic viscosity, measured in cyclohexanone at 20°C., of 0.11. The specific viscosity of a solution in benzene (50 g. per liter of solution) at 25°C. was 0.75. The saponification value of the resin was 640; Acid V., 1.4; Moisture, about 1%.

Higher Fatty Acid Esters. These consisted of distilled methyl esters prepared by methanolysis of refined soybean oil, followed by distillation of the washed and dried esters in glassware at a pressure of approximately 1 mm. Acid V., 0.1; I. V., 128; Sap. V., 195.

Catalyst. A suspension of sodium tertiary butoxide in dioxane was prepared by dissolving 8.75 g. of sodium in a mixture of 110 ml. of tertiary butanol and 260 ml. of dry dioxane. The sodium was added in small cubes, and the mixture was stirred and boiled under reflux until the sodium was no longer visible. The excess of tertiary butanol was then removed by boiling the mixture with continuous stirring while vapors were removed through a fractionating column until the temperature at the still head reached the boiling point of pure dioxane.

Solvent. Commercial dioxane was distilled at atmospheric pressure through a fractionating column, and the first runnings were discarded. The portion collected for use distilled within a range of less than 1°C.

APPARATUS AND PROCEDURE

The reaction vessel was a four-necked, round bottom, 300-ml. Pyrex flask equipped with a motor-driven stirrer, reflux condenser, thermometer, and a glass tube arranged for withdrawal of samples and addition of reagents. The apparatus was connected by suitable lines and cocks to a vacuum pump, manometer, and nitrogen cylinder, to allow the reaction to occur in an atmosphere of nitrogen. A three-necked flask similarly equipped except for the condenser was used for premixing the catalyst suspension with the fatty esters.

A solution of polyvinyl acetate in dioxane was dried in the manner described for the purification of dioxane and put into the main reaction flask. In the separate flask a portion of the catalyst suspension was mixed with soybean methyl esters at room temperature. The alkalinity of the mixture was determined by titration and found to be equivalent to 0.007 g. of sodium per ml. The main reaction flask was heated by means of an oil bath. With the stirrer operating in the reaction flask, the suspension of catalyst in fatty esters was transferred to the reaction flask by

means of a 20-ml. glass syringe, followed by a sufficient additional quantity of fatty ester to make the total mix in the reaction flask consist as follows: Polyvinyl acetate, 20 g.; dioxane, 60 g.; soybean methyl esters, 77.5 g.; sodium tertiary butoxide, 1.9 g. (equivalent to 0.46 g. of sodium). The equivalent ratio of soybean methyl esters to polyvinyl acetate was 1.17. The transfer occupied a period of approximately seven minutes, at which time the temperature of the whole mixture was 80°C. The mixture became clear and assumed a dark red color. It was stirred at 80°C. for 90 min., then left overnight without heating or stirring, after which it was stirred for 30 min. longer at 80°C., then acidulated by the addition of 85% H_3PO_4 in a quantity amounting to one mole of phosphoric acid per atom of sodium compound in the mixture. During the reaction, samples were taken at intervals to test the solubility of the mixture in petroleum ether,² its viscosity when diluted with a fixed proportion of benzene (containing acetic acid to acidulate the catalyst), and its alkalinity. These tests showed that the polyvinyl ester became soluble in petroleum ether within 40 min. and reached maximum viscosity in about 85 min. The titrations showed a continuous loss of alkalinity, rapid at first and gradually diminishing as the reaction proceeded. Approximately half of the catalyst had disappeared in the first 20 min., and two-thirds had disappeared within 1 hr.

The acidulated reaction mixture was filtered with suction with the aid of diatomaceous earth. The clear cherry red filtrate was subjected to a stripping distillation at reduced pressure with a stream of steam bubbles to prevent bumping and to assist the distillation; final temperature, 250°C.; pressure, 1 mm. Under these conditions all of the solvent and nearly all of the unreacted methyl esters were removed. The product was a heavy bodied oil having the characteristics shown in Table I.

TABLE I
Characteristics of Products of Reactions Described

	A	B	C
Saponification V.	304	233	213
Acid V.	0.6	0.9
Iodine V.	106
Color, Gardner.	13	12	12
Viscosity, Gardner.	Over Z-10	Z-7	Z-5
Sp. Visc., benzene, 50 g./l. of soln., 25°C.	1.05
Cloud Point, °C.	Below -70	Below -70	Below -70

B. Polyvinyl Acetate and Hydrogenated Sardine Oil

MATERIALS

The same grade of polyvinyl acetate was used as described above.

Hydrogenated Sardine Oil. A partially hydrogenated sardine oil supplied by a commercial firm was used to dry the polyvinyl acetate, and a portion of the reaction mix consisted of the dioxane introduced in the polyvinyl acetate solution.

Solvent. The principal solvent was tetrahydrofuran purified by distillation through a fractionating column. Dioxane, purified as described above, was used to dry the polyvinyl acetate, and a portion of

² Polyvinyl acetate is insoluble in petroleum ether; long-chain fatty acids combined in the polymer increase the solubility. Mixed polyvinyl esters of acetic acid and soybean acids are completely soluble in petroleum ether when the soybean ester groups amount to about 25% or more of the total ester groups.

the reaction mix consisted of the dioxane introduced in the polyvinyl acetate solution.

Catalyst. A catalyst mixture was prepared by stirring a mixture of tetrahydrofuran, 46 g., naphthalene, 8.4 g., and metallic sodium, 1.5 g., for about 1 hr. at room temperature in an atmosphere of nitrogen. Titration of a sample of the dark green solution obtained showed that all of the sodium had dissolved.

APPARATUS AND PROCEDURE

The reaction was carried out in a 1-liter flask equipped as described above. All of the ingredients, except the catalyst solution, were brought to a temperature of 60°C. in the reaction flask in an atmosphere of nitrogen. The catalyst solution was then transferred to the reaction flask by means of a 20-ml. glass syringe.

The quantities of ingredients in grams in the complete mixture was as follows: polyvinyl acetate, 39.8; dioxane, 93.6; partially hydrogenated sardine oil, 280; tetrahydrofuran, 303; naphthalene, 6.8; sodium, 1.2. The equivalent ratio of sardine ester to polyvinyl acetate was 2.09:1. The mixture was stirred at atmospheric pressure, 60°C., for 2.3 hours, after which the pressure was gradually reduced and the temperature raised to a maximum of 90°C. over a period of 1.4 hrs. The distilled solvent was condensed and collected in a receiver. The catalyst was then neutralized by the addition of 3.1 ml. of glacial acetic acid.

Observations on samples taken during the first stage of the reaction showed that the concentration of catalyst remaining in the mixture 5 min. after the addition of catalyst had been completed was equivalent to .075 g. of sodium per 100 ml. of mixture; 2 hrs. later the concentration was .065. Within 36 min. from the time when the addition of catalyst was completed, the reaction had proceeded far enough to make the resin soluble in petroleum ether.

After neutralization of the catalyst the reaction mixture was extracted with anhydrous ethanol (Formula 3A) in order to separate the triglycerides in the mixture from the polyvinyl esters. The contents of the reaction flask were stirred thoroughly with three times their weight of ethanol, and the two liquid layers were separated by decantation after settling for several hours. The alcohol-rich layer contained approximately three-fourths of the total quantity of triglycerides in the mixture. The lower layer contained a small proportion of alcohol together with residual glycerides and nearly all of the polyvinyl ester. The lower layer was re-extracted with fresh ethanol three times, making a total of four extractions. The quantity of extract obtained in the fourth extraction was approximately 2% of the weight of the product. The extracted product was heated at a pressure of 15 mm. to a temperature of 190°C. Characteristics of the product are given in Table I.

C. Polyvinyl Acetate and Methoxyethyl Esters of Soybean Fatty Acids. Reaction Forced by Distillation of Methoxyethyl Acetate

MATERIALS

Methoxyethyl esters were prepared from methyl esters which had been made by reaction of refined dried soybean oil with 3.1 equivalents of methanol at 65°C. in the presence of an alkaline catalyst consisting of .02 equivalent of KOH predissolved in the

methanol. The methyl esters after washing and drying, but without distillation, were converted to methoxyethyl esters by reaction with methoxyethanol in the presence of an alkaline catalyst. The reaction was carried out at 60-80°C. with the pressure gradually reduced, and was forced to completion by the use of a 50% excess of methoxyethanol over the equivalent quantity and by removal of methanol through a fractionating column during the reaction. After neutralization of the catalyst with acetic acid the esters were washed with hot water followed by several washes with aqueous alcohol. A small quantity of KOH was added to the first of the aqueous alcohol washes to extract any free acid from the fatty esters. The esters used in the reaction with polyvinyl acetate consisted of esters prepared in this way and distilled at 1-mm. pressure, together with approximately an equal quantity of esters that were dried but not distilled; Gardner colors were 1 for the distilled esters and 11 for the undistilled.

The solvent used was diethylene glycol diethyl ether prepared by fractional distillation of the commercial material. The catalyst consisted of a solution of sodium prepared by dissolving 7.6 g. of sodium at room temperature in a mixture of 222 g. diethylene glycol diethyl ether and 41 g. naphthalene. The solution was prepared in a separate flask with exclusion of air, and a portion was transferred to the main reaction flask after the sodium had dissolved. Polyvinyl acetate was the same grade as that described for the preceding experiments.

APPARATUS AND PROCEDURE

The reaction was carried out in a 5-liter, three-necked Pyrex flask equipped with a motor-driven stirrer, thermometer, a tube leading into the reaction mix for the addition of catalyst and for removal of samples, a short column connecting through a still head and suitable lines to condensers, traps, distillate receiver, manometer, and vacuum pump.

Polyvinyl acetate, 303 g., diethylene glycol diethyl ether, 505 g., and methoxyethyl esters of soybean acids, 1336 g., were put into the reaction flask and dried by heating to 100°C. and distilling off about 20 ml. of the solvent at a reduced pressure. The mixture was then cooled to 60°C., and the catalyst solution was added. The total dried mixture consisted of the following ingredients, not including additional solvent used for sparging later in the reaction: polyvinyl acetate, 300 g.; diethylene glycol diethyl ether, 685 g.; methoxyethyl soybean esters, 1336 g.; naphthalene, 36.8 g.; sodium, 4.8 g. The equivalent ratio of higher fatty acid esters to polyvinyl acetate was 1.17:1.

With continuous stirring the pressure was reduced on the system until distillation was rapid. At the end of 23 min. the pressure had been reduced to 5 mm. Thereafter the temperature was raised gradually and pressure further reduced to cause continued rapid distillation. At the end of 50 min. of reaction time, the temperature had reached 80°, pressure 1 mm.; 432 g. of distillate had been collected, containing 178 g. of methoxyethyl acetate as estimated from the saponification value. After an additional 23 min., at approximately the same temperature and pressure, an additional 377 g. of distillate had been collected containing 64 g. of methoxyethyl acetate. At this point the quantity of methoxyethyl acetate distilled from

the mixture corresponded with 60% of the total available acetate groups. Thereafter the reaction was continued for another hour, during which time the temperature was gradually raised to 87°, and 525 ml. of additional solvent was gradually introduced to encourage continued distillation. The additional methoxyethyl acetate recovered brought the total to a quantity equivalent to 78% of the total acetate originally present. The catalyst was neutralized by addition of 13 ml. of acetic acid, after which most of the remaining solvent was distilled.

The product was given three extraction treatments with anhydrous ethanol to remove monomeric esters and naphthalene, and a wash with 75% aqueous ethanol to insure removal of any residual salts. Approximately three volumes of ethanol per volume of product were used in each extraction, which was accomplished by stirring the mixture thoroughly, settling and decanting the alcohol-rich layer. The quantity of material removed in the third ethanol extraction amounted to 3.4% of the weight of the product from the second extraction, indicating that the quantity of monomeric ester remaining in the final product was negligible. The product after heating under vacuum to 110°C. to remove the last of the solvent was a viscous, reddish colored oil, Gardner color 15. Further heating to 220°C., at which temperature the oil was held for 30 min. with continuous stirring, reduced the color to 12 (Table I).

Discussion of Experimental Results

Experiments A and B illustrate reactions uninfluenced by removal of reaction product during the course of the reaction while experiment C illustrates the effect of removal of one of the products during the reaction. Calculation of the composition of the mixed polyvinyl ester of acetic acid and higher fatty acid obtained in reaction A on the basis of its saponification value indicates that, in equivalents, the product consists of 54% acetate and 46% of higher fatty acid ester; on a weight basis this corresponds with approximately 25% acetate and 75% higher fatty acid esters. In other words, the reaction resulted in the replacement of 46% of the acetate groups originally present in the polyvinyl acetate by soybean fatty acid radicals. This is a little short of the equilibrium proportion if it is assumed that no preferential affinity exists which would influence the ratio of acetate to higher fatty acid radicals in the mixed ester at equilibrium. Calculated on this assumption, the replacement would have been 54% instead of 46% if equilibrium had been attained.

A greater degree of replacement was obtained in experiment B because a larger ratio of higher fatty acid ester was used and because the calculated equilibrium value was reached or exceeded. As calculated from the saponification value of the product, 71% of the acetate groups were replaced by the higher fatty acid radicals of the partially hydrogenated sardine oil as compared with a calculated equilibrium value of 68%. On a weight basis, the product consists of approximately 10% acetate ester and 90% high fatty acid ester.

In reaction C the proportion of soybean ester to acetate at the beginning of the reaction was the same as in reaction A, but because of the removal of methoxyethyl acetate by distillation during the reaction a much higher degree of replacement was obtained.

The saponification value of the product indicates that 83% of the acetate was replaced and that, on a weight basis, the mixed polyvinyl ester corresponds with 94% polyvinyl ester of soybean fatty acids and 6% polyvinyl acetate.

The reaction rate in experiment B was as great or greater than that in reaction A in spite of the fact that a reaction temperature 20° lower and a substantially smaller quantity of catalyst was used. The results of various other experiments show that the principal factor accounting for this more favorable reaction rate is the difference between glyceryl esters and methyl esters.

Properties of Polyvinyl Esters of Higher Fatty Acids

Polyvinyl esters covering a wide range of physical properties can be prepared by ester interchange. The principal variables determining the properties of these products are the viscosity or molecular weight of the polyvinyl acetate entering the reaction, the kind of acid radicals in the reacting esters, and the proportion of the acetate replaced by other acid radicals. When these radicals are derived from ordinary fatty oils and replace the greater part of the acetate from polyvinyl acetate of low or medium viscosity, the products may be described as heavy-bodied oils. They mix in any proportion with petroleum ether, mineral spirits, or benzene but are nearly insoluble in methanol, ethanol, or acetone. They may be separated from the fatty oils and other non-polymeric fatty esters by extraction with selected solvents.

High-viscosity grades of polyvinyl acetate yield products having similar properties, except that they are so very viscous at room temperature that they seem more like solids than oils. With a given grade of polyvinyl acetate to start with, the viscosity of the product is smaller, the smaller the proportion of acetate remaining unreplaced by higher fatty acid. When a large proportion of the acetate remains, the product is likely to be tacky and extremely viscous with a long stringy texture. Nevertheless such products are soluble in mineral spirits, provided that about 25% or more of the acetate has been replaced by higher fatty acids. The viscosities of dilute solutions are much less influenced by the proportion of acetate than are the viscosities of the undiluted products; the specific viscosities of benzene solutions of the mixed esters do not differ much from those of the polyvinyl acetate from which they are made. Some of these relationships are illustrated in Table II.

The polyvinyl esters of higher fatty acids melt at temperatures lower than the melting points of the fatty acids themselves or of their triglycerides. Polyvinyl stearates made by ester interchange have capillary melting points in the range 40-50°C. The melting point depends to a slight extent upon the completeness of replacement of acetate by stearate and upon the grade of polyvinyl acetate used in the reaction. Mixed esters in which the higher fatty acid por-

TABLE II
Properties of Some Mixed Polyvinyl Esters of Acetic and Higher Fatty Acids

Code No.	Kind of higher fatty acids	Saponification Value	Viscosity ^a	Specific Viscosity ^b	
				Of product	Of polyvinyl acetate used
18-112	Soybean	203	33	0.38	0.28
19-103	Soybean	226	190	0.96	0.75
21-37	Soybean	256	391	1.8	0.75
19-29	Lard	273	1,100	1.08	0.75
18-131	Soybean	304	3,800	1.06	0.75
18-114	Soybean	268	Extremely viscous	7.2	7.3
18-122	Soybean	247	Extremely viscous	11.3	9.5

^a Comparative viscosity tests on undiluted product. Seconds for bubble to rise in Gardner viscosity tube, 25°C.

^b Specific viscosity in benzene, 50 g./liter of solution, 25°C.

tion consists of a mixture of solid and liquid acids melt at lower temperatures. A notable feature of the mixed esters is that they have the property of remaining clear and unclouded at all temperatures to as low as -70°C. even when the composition includes a substantial proportion of solid acids. Thus the polyvinyl esters containing the mixed fatty acids of such fats as soybean oil, cottonseed oil, coconut oil, partially hydrogenated fish oils, and lard do not cloud or crystallize at any ordinary temperatures nor when chilled to -70°C. The same is true of air-dried films made from such polyvinyl esters. Table III gives a few illustrative data.

The air-drying properties of the polyvinyl esters of mixed higher fatty acids are better than those of the corresponding triglycerides. Films of the polyvinyl esters dry more rapidly and become tougher, stronger, more scuff-resistant and weather resistant, with less tendency to yellow than films of the fatty oils from which they are derived. The contrast is especially great with fatty esters which are incapable of forming satisfactory dried films in the triglyceride form, as, for example, in the case of lard or partially hydrogenated fish oil.

The product of reaction B, described above, derived from partially hydrogenated sardine oil, dried to a

TABLE III
Melting Points of Some Mixed Polyvinyl Esters Made from Polyvinyl Acetate^a

No.	Source of higher fatty acid radicals used to displace acetate	Estimated % solid acids in the mixed higher f.a.	Polyvinyl ester		
			Sap. V.	I. V.	M. P., °C.
1	Hydrogenated Soybean Oil (I. V., 6)	93	186	50
2	Hydrogenated Soybean Oil (I. V., 6)	93	270	44
3 ^a	Hydrogenated Soybean Oil (I. V., 1)	99	256	40
4	Hydrogenated Soybean Oil (I. V., 1) + Soybean Oil, ratio, 66.7:33.3	71	238	32
5	Same fats as No. 4, ratio, 40:60	48	236	19
6	Same fats as No. 4, ratio, 26:74	36	252	70	-10
7	Same fats as No. 4, ratio, 16:84	28	212	93 ^b
8	Hydrogenated Soybean Oil (I. V., 1) + lard, ratio, 40:60.	64	243	34	21
9	Same fats as No. 8, ratio, 20:80	52	233	47	-13
10	Lard, I. V., 66	41	273 ^b
11	Winterized Cottonseed Oil	26	265 ^b
12	Partially Hydrogenated Sardine Oil (I. V., 123)	32	233	106 ^b

^a Same grade of polyvinyl acetate as was used to make products of Table I, except No. 3, which was a higher-viscosity grade (Bakelite's Vinylite AYAT), Sp. Visc., benzene, 50 g./l., 25°, 9.5.

^b Does not cloud or crystallize at temperatures to -70°C.

TABLE IV
Observations on Drying Qualities of a Polyvinyl Soybean Ester^a

Type of rosin ester	Polyvinyl soybean ester		Long oil P. E. soya alkyd	Cold cut varnishes made with polyvinyl soybean ester.			Modified p.e. ester ^c
	None	None	None	Pentaerythritol ester ^b			
Per cent oil in oil resin blend.....				75	66.6	59	66.6
Per cent non-volatile.....	100	57.2	52	55	55	55	55
Viscosity.....	Z7	G-H	F-G	E	E	F	F
Viscosity, after 3 wks. with drier.....				G	Partly gelled	F	H
Color.....	11	10	5	10	10	10	10
Set-up time, hrs. ^d		5.9	3.5	1.6	1.9	2.4	3.2
24 hr. tack ^d		Light	Tack free	Tack free	Tack free	Tack free	Tack free
Sward hardness ^d							
24 hr.....		6	12	18	26	32	24
72 hr.....		6	16	26	26	40	34
1 wk.....		6	18	26	26	44	38
2 wk.....		6	18	28	30	44	40
Cold water. Blush.....		No	Light	Light	Light	Light	V. Sl.
Recovery, min.....			12	4	5	5	5
Boiling water. Blush.....		No	No	No	No	No	No
3% NaOH solution							
Blush, min.....			2	5	45	1.5 hr.	2 hr.
Wrinkle, min.....		1 ^e	4	10	65	8 hr.	5 hr.
Fail, min.....		90	50	5 hr.	12 hr.	8-24 hr.	8-24 hr.
Kauri reduction							
Pass.....		280	130	140	70	10	70
Fail.....		290	140	150	80	20	80
Remarks.....							

^a Observations made at laboratories of the Archer-Daniels-Midland Co., using polyvinyl ester submitted under Code No. 21-94.

^b Pentalyn A.

^c Pentalyn G.

^d With added drier, 0.2% Pb, 0.025% Co. Wet film thickness, 1.5 mils (at indicated % non-volatile). Temperature, 77°F.; humidity, 50%.

^e Severe wrinkling. Film almost loose, but not softened.

^f Gelled in partially filled container some time between 1 and 3 mo.

^g Very good mar resistance at 24 hrs. and no brittleness at 3 wk. The general film properties including dry, hardness, water- and alkali-resistance and flexibility were considered very good on the basis of the type of modification present. The mar resistance of these films was noted as being better than usual for normal, bodied oil-"cold cut" resin blends.

smooth clear film of considerable toughness when a solution in an equal weight of mineral spirits, with 0.05% cobalt in the form of cobalt naphthenate added, was spread on a glass plate with a doctor blade set at 0.002 in. The film was set to touch in 90 min. and tack-free in 5 hrs. A corresponding film of partially hydrogenated sardine oil became cloudy and grainy, because of crystallization of part of the fat, and remained soft and smeary indefinitely. A polyvinyl ester containing fatty acids of lard (Table III, No. 10) tested in the same way formed a clear slightly tacky film in 20 hrs. whereas lard itself, of course, formed a cloudy film devoid of useful drying properties. The polyvinyl lard ester does not form films approaching the quality of those formed by the polyvinyl esters of cottonseed or soybean acids, but its drying ability may be indicated by the fact that in this simple type of comparative test, it dries more rapidly and forms a tougher, stronger film than either soybean oil or linseed oil.

Of the various polyvinyl esters that may be made, those containing soybean or cottonseed acids appear to be among those most suitable for use as drying oils. They dry rapidly to form films having good resistance to marbling, water-spotting, and weathering. They mix with ester gum and other rosin-based resins to make varnishes. Without added resin the films are not as hard as varnish films, and in this respect these polyvinyl esters resemble oils more than resins. Hard films can be obtained by adding the ester gum type of resin, or by modifying the polyvinyl ester in the ester interchange reaction by incorporating radicals of benzoic, furoic, or similar acids along with the radicals of the higher fatty acids.

Addition of triglyceride oils, or other fatty esters of low functionality to the polyvinyl esters, even in small percentages, diminishes the quality of the dried films, especially the strength and scuff-resistance. For this reason it is important to separate residual monomers from the polyvinyl esters as completely as is

practicable at the end of the interchange reaction if the best drying qualities are to be obtained in the products.

Some observations on the drying qualities of a polyvinyl ester containing the fatty acids of soybean oil are recorded in Tables IV and V. The data were ob-

TABLE V
Weatherometer Durability of Varnish Made from Polyvinyl Soybean Ester^a
(37½ gal. oil length, pentaerythritol rosin ester. Three coats on edge grain cedar.^b)

	60° Gloss		Checking ^c	
	Experimental varnish	Commercial varnish (control) ^d	Experimental varnish	Commercial varnish (control) ^d
Initial.....	95	100
109 hrs.....	90	74	10	10
200 hrs.....	70	31	10	3
280 hrs.....	37	8	8	1

^a See Note a, Table IV.

^b Varnish made by melting resin with polyvinyl ester at 400°F. and thinning to 55% non-volatile. Viscosity, F.

^c Visual checking rating on scale of 10 = no checking failure to 0 = complete failure.

^d Commercial marine spar varnish, based on China wood oil, linseed oil and phenolic resin. Kauri reduction, 110/120.

tained in the laboratories of a manufacturer of oils and vehicles,³ on a sample submitted by the authors. The ester was made by methods similar to that used for reaction C, described above, but differing in some respects. One difference was that only two ethanol extractions were used, instead of three, so that this product probably contained between 3 and 4% of residual monomeric esters, which would detract from the quality to some extent. This product (Code No. 21-94) had the following characteristics: Acid V., 1.4; Sap. V., 234; Viscosity, Z6; Color, 11+.

Presumably the amount of oxidation and cross-linking required to cause films of polyvinyl esters to solidify is considerably smaller than it is with the corresponding triglyceride oils. The good durability

³ The Archer-Daniels-Midland Company, Minneapolis, Minn.

to weathering and some of the other qualities may be attributed in part to this factor. Similarly the polyvinyl esters are more readily gelled by heat treatment, or by being allowed to stand in partly filled containers with driers present, than are the corresponding glycerides. Gelation by the influence of heat alone occurs rapidly at temperatures above about 250°C. with polyvinyl soybean esters, and at considerably lower temperatures than this when the acid radicals of the esters include conjugated fatty acids. The partially hydrogenated sardine ester, B, Table I, gelled in 9 min. in a Browne heat test, in comparison with a very slightly shorter time for a sample of tung oil tested at the same time. High temperature cooking with varnish resins therefore is not appropriate for these polyvinyl esters. At room temperatures in filled containers the esters apparently will keep indefinitely without gelation. Solutions with added drier are susceptible to gelation when held in partly filled containers. Varnishes containing rosin esters appear to be less subject to this than solutions not containing the resin.

Summary

Mixed polyvinyl esters of acetic acid and higher fatty acids can be made by ester interchange between polyvinyl acetate and fatty esters. Their properties indicate that some of these products merit attention as materials for use in the drying oil industries. Because of their enhanced drying qualities and greater tolerance of the presence of saturated acid components, in comparison with the corresponding glycerides, they potentially broaden the range of fatty materials utilizable as drying oils.

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The Countercurrent Distribution of Pure Monoglycerides and Some Related Substances¹

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THE COUNTERCURRENT distribution characteristics of several monoglycerides both of natural and synthetic origin have been determined and reported (1, 2). They were used to help identify the intermediate products formed during digestion of triglycerides by the rat (3) as well as to study the isolation and identification of monoglycerides in lard and breads (2) and from the intestinal contents of humans (4).

The present investigation was set up to determine the countercurrent distribution curves for a selection of pure monoglycerides, which served as a basis for a study of 2-monoglycerides (5) as well as for those mentioned above (2, 4). Nine monoglycerides were thus examined, from which certain effects due to the structural variations could be ascertained. Countercurrent distributions were also made for a diglyceride and for a diglycerol monoester.

Experimental

Procedure. The countercurrent distributions were carried out in a 50-tube, all-glass apparatus similar to that described by Craig (6). The apparatus was modified slightly in connection with the incorporation of an automatic drive (7). The procedure used to determine the distribution curves for the present study was essentially that reported in the previous publication. The solvent system employed consisted of Skellysolve B and an aqueous methanol solution containing 15% water by volume. The sample for distribution, about 120 mg., was weighed directly into a 12-ml. volumetric flask and dissolved in the petroleum solvent

phase. A 10-ml. aliquot was transferred by pipette to the first tube of the apparatus. At the end of the distribution the entire contents of each tube was syphoned into tared cups. After complete removal of solvents, first by warm air and finally by vacuum, the net weight of each cup was determined. A plot of this weight against the tube number gave the distribution curve.

Materials. The 1-monoglycerides of myristic, palmitic, and stearic acids were synthesized from glycerin and the pure acid. The reaction mixture was molecularly distilled to isolate the monoglyceride component. This fraction was further purified by crystallization from methanol until the monoester content by periodic acid analysis reached 99% or better. Monobutyryn was an Eastman Organic Chemical (Cat. No. 4695). The 2-monostearin was prepared by hydrogenolysis of 1,3-benzylidene-glycerol-2-monostearate (8). The 2-mono-olein was isolated from the molecularly distilled mono-olein by solvent crystallization as explained in the following paper (5).

Distilled monoglycerides of lard fatty acids were prepared from the reaction of lard with glycerol. Using repeated molecular distillation as the sole method of purification, it was not possible to increase the monoester content above 92 to 94% as indicated by periodic acid analysis. This particular sample was once redistilled, and contained 92% monoglycerides.

Diglycerol monoesters of "cottonseed oil" were synthesized by reacting with diglycerol the acids obtained by saponification of the cottonseed oil. The monoester fraction was obtained by molecular distillation.

The diglyceride sample is essentially a mixture of

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