Fatty Acid Esters of Polyvinyl Alcohol

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IT is recognized that improved drying oils can be made by esterifying a given type of fatty acids with alcohols having more hydroxyl groups than glycerol. The use of the more highly functional alcohols in place of glycerol permits the use of acids more saturated than linseed acids. Approximately equivalent drying properties, as oils, can be obtained with a reconstituted linseed acid glycerol ester and a soybean acid pentaerythritol ester. Therefore, as the functionality (as measured by the ethylene linkages) of the fatty acids decreases, the functionality of the alcohol (as measured by the hydroxyl groups) must increase to obtain equivalent properties; a relationship exists between these functionality variables. With this concept in mind it should be theoretically possible to produce a drying oil from oleic acid and a highly polyfunctional alcohol.

The hexitols, mono-, di-, and poly-pentaerythritol, and polyallyl alcohols present no difficulties when esterified with fatty acids. When sugars are used as the polyhydric alcohols (6), esterification is accomplished by the reaction of acid chlorides in the presence of tertiary amines.

The degree of improvement possible with the pentaerythritol (2) and pollyallyl alcohols (1, 3) is directly related to their hydroxyl content. Therefore similar fatty acid esters of polyvinyl alcohols would be expected to show greater improvements.

Eighteen carbon unsaturated fatty acid esters of the polyvinyl alcohols can be prepared by the following methods:

a) preparation of monomeric vinyl esters, according to Rinse and Dorst (7), followed by polymerization; or,

b) replacement of *a* functional group in *a* polyvinyl compound with a fatty acid.

Polymerization of the monomer of the first method leads to a cross-linked polymer by reaction of the ethylene linkages of the fatty acid chain and the vinyl group. In the case of vinyl oleate a semi-liquid product with a limited degree of polymerization is possible.

The second method yields a polyvinyl ester of a definite structure in which unsaturation in the fatty acids remains available for oxidation and film formation. Eckey (4) used this method by application of the ester-ester interchange reaction. The work described in this paper applies this method by the direct esterification of 18 carbon unsaturated fatty acids and a polyvinyl alcohol.

Polyvinyl alcohol heated with fatty acids does not react but coagulates to form a product which is no longer soluble in its usual solvents. This suggested the use of a mutual solvent. Such a solvent would necessarily have to possess a high boiling point, 160° C. or higher, and be nonreactive with alcohols and acids. This limitation excludes the commonly used alcohols, esters, and hydrocarbons. Phenol, as used by Hilditch (5) to prepare mono- and di-glycerides, or a cresol was chosen as the mutual solvent; the former is preferred.

The polyvinyl alcohol chosen for this work was du Pont's RH393 (now known as 70-05), a low-viscosity type and 99% hydrolyzed. Other polyvinyl alcohols, e.g., RH623, low-viscosity and 88% hydrolyzed, and RH428, medium viscosity and 92% hydrolyzed can also be used.

The RH393 polyvinyl alcohol is readily soluble in phenol (b.p. 182° C.) at 160° C. up to 20% concentration, forming a clear, dark amber, viscous solution. For convenience in this investigation a 10% to 12% solution was used. The polyvinyl alcohol-phenol solution will tolerate a quantity of fatty acids in excess of that necessary to esterify the alcohol, provided they are added slowly over a period of 30 to 90 minutes with a simultaneous temperature rise to avoid turbidity. Under these conditions some reaction takes place, and the solution will boil between 185° to 188° C. with phenol and water distilling. The ester formed at this temperature undoubtedly acts as a solvent for both free acids and alcohol and compensates for phenol removed by distillation.

As the boiling point rises, the esterification rate increases, and the rate of phenol removal can be increased and adjusted to maintain a homogeneous solution. When the reaction pot temperature reaches 205° to 210° C., about one-half of the phenol is distilled. The remaining phenol can be removed rapidly up to 235° C. without causing turbidity, and esterifi-

TABLE I

Effect of Fatty Acid Concentration on the Viscosity of the Refined Polyvinyl Alcohol Esters

PVA[5] Equivalents	Acids		Phenol Parts[1]	Crude Ester	Required Ester		Times Extracted
	Equivalents	Type		Acid Value	Acid Value	Ester Value[4]	
1	0.75	Linseed	450	Gelled[3]	....	....	....
1	1.00	Linseed	500	Solid[2,3]	....	....	....
1	1.25	Linseed	450	89	21.5	158.5	5
1	1.50	Linseed	450	98	29	161.0	3
1	1.50	Linseed	450	93	12	166	5
1	2.00	Linseed	450	107	11.5	162.5	5
1	2.00	Linseed	400	96.5	10	178	5
1	0.50	Neo-Fat 3R	400	Gelled	....	....	....
1	1.50	Neo-Fat 3R	450	100	4.7	168.3	5

[1] Parts per equivalent weight taken as 42.
[2] Too viscous to handle—probably a gel.
[3] Condition at end of esterification.
[4] Theoretical ester value is 184.
[5] du Pont's RH393.

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TABLE II

Effect of Phenol Concentration Upon the Viscosity of the Refined Polyvinyl Alcohol Esters

PVA Equivalents	Acids[1] Equivalents	Phenol Parts[2]	Acid Value		No. of Extractions	Remarks
			Before Extraction	After Extraction		
1	1.25	None	....	....	....	No reaction
1	1.25	200	....	35.6	2	Solid[3]
1	1.25	260	82	....	4	Gelled
1	1.25	300	80	....	4	Gelled
1	1.25	350	86	12	5	Gel particles
1	1.25	400	89	12	5	OK
1	1.25	450	89	21.5	5	OK

[1] Linseed acids.
[2] Parts per equivalent PVA.
[3] Probably a gel.

cation is continued with carbon dioxide sparge until the acid value remains constant.

Fatty acids are always used in excess of that required by the alcohol. This excess serves two functions

a) to drive the reaction to completion; and
b) to prevent gelation, which is a well-known effect in oil bodying reactions.

The product at this point is a crude ester; it has an acid value between 80 and 90, is somewhat viscous, and has a Gardner color (1933 standards) of about 7-8.

The crude ester is extracted with methanol at room temperature five times with an alcohol volume in each cycle equal to the volume of ester to be extracted. After five cycles approximately equal parts of raffinate and extract are obtained. The raffinate is the low-acid (15 or less) refined polyvinyl ester. Its yield, based upon the fatty acids, varies between 50% and 60%, depending upon esterification conditions. The extract has a high acid value and can be recycled in succeeding runs after removal of the methanol.

Since efforts were concentrated on making a product and studying its properties, only a limited amount of work has been undertaken to determine the optimum methods of synthesis. However the preliminary runs indicated the following:

a) an excess of fatty acids, during the esterification, was necessary to prevent gelation, and
b) the quantity of phenol used as solvent influenced the viscosity of the final product.

These factors were investigated, using constant esterification conditions.

In Table I the data showing the effect of fatty acid concentration on the viscosity (or gelation tendency) of the refined ester are indicated. Increasing amounts of free fatty acids have a stabilizing effect in preventing gelation. Judging from these data, if the molecular ratio of acid/alcohol is less than 1, the final product will be a gel; a ratio of 1 is borderline. The optimum ratio appears to be 1.25/1.

An attempt was made to reduce the quantity of phenol in order to simplify and reduce the cost of the process. The results of this work are indicated in Table II and are based on the results of Table I. The mole ratio of fatty acid to polyvinyl alcohol was held constant at 1.25/1. The phenol was varied from 200 to 450 parts by weight per one equivalent of alcohol. All the crude esters prior to extraction had practically constant acid values. The viscosity of the refined ester was influenced by the number of methanol extraction steps used to recover it. The viscosity of the refined ester increased inversely as the amount of phenol used as the mutual solvent at the beginning of the reaction. The ester prepared with 350 parts of phenol showed gel particles after five extractions. Esters made with 300 and 260 parts of phenol (extracted four times) gelled after being thinned in xylene. Only two extractions were possible in the ester made with 200 parts of phenol; at this point the ester was almost solid. The practical results obtain when 350 to 400 parts of phenol are used. The phenol used acts either as a depolymerizing agent on the polyvinyl alcohol or as a diluent which prevents polymerization of the polyvinyl esters through the unsaturation in the fatty acid chains.

The exact molecular size of the esterified polyvinyl alcohol is unknown. However it is fair to presume that it is not as high as the original starting material, which had a mole weight of about 6,000 and with probably 130 hydroxyl groups.

Several semi-pilot plant lots were prepared for evaluation purposes. The constants of these esters are shown in Table III.

The refined esters have strong gelation tendencies. In some instances they gelled by standing overnight and always skinned. This was overcome by storing the esters preferably as a xylene solution with an anti-skinning agent and in an inert atmosphere.

A study to determine optimum drier and inhibitor concentrations was undertaken. The results indicate that lead drier is incompatible and manganese has little or no effect. Between 0.025% and 0.05% cobalt

TABLE III

Summary of Constants of Polyvinyl Linseed Esters Using 400 Parts Phenol Per Equivalent of Alcohol Prepared in Semi-Pilot Plant Lots

Equivalent Acids[1]	Crude Ester		Constants						
			MeOH Soluble			Refined Ester			
	Acid Value	% OH	%	Av.	% OH	%	Acid Value	% OH	Viscosity[2]
1.40	69.5	1.95	45.5	136	2.90	54.5	3.0	.20	I
1.25	81.5	2.05	55.5	126	4.20	44.5	5.4	.20	B/C
1.50	92.0	2.15	64.5	128	3.65	35.5	3.5	.15	C

[1] Linseed acids—equivalent acid/equivalent PVA.
[2] 50% nonvolatile in xylene (Gardner-Holdt).

TABLE IV

Typical Evaluation Results of Various Polyvinyl Alcohol Esters as Compared With Standard Products

	1	2	3	4	5	6	7	8	9
Type	PVA Linseed	PVA Soybean	PVA Dehydrated Castor Oil	PVA Linseed	Automotive Lacquer (5)	33-Gal. Phenolic Tung Varnish	30-Gal. Dehydrated Castor Oil Ester Gum Varnish	35-Gal. Linseed Pentalyn M Varnish	Alkyd 52R13 Specification
Drier	0.05% Co	0.05% Co	0.05% Co	0.05% Co	....	0.03% Co 0.2% Pb	0.07% Co. 0.5% Pb	0.07% Co 0.5% Pb 0.05% Ca	0.03% Co
Dry Time (hrs.: min.)									
Set to Touch	:15	1:00	:50	:25	....	:45	2:30	2:30	2:30
Cotton-Free	:30	2:00	1:30	:50	....	3:00	4:30	4:30	7 hrs.+
Foil Free	5:30	24 hrs.	Overnight	4:30	....	Overnight	Overnight	Overnight	24:00
Hardness—Sward, %									
6 Hours	4	4	6	4	42	4	....	....	....
24 Hours	9	4	7	11	46	12	8	8	5
1 Week	12	4	9	17	40	19	12	12	9
Alkali Resistance (1)									
Time in Hrs.: Min.									
White	:10	:05	:05	:03	....	....	:15	:10	:05
Blister	:15	:10	:20	:25	2.00	....	:20	:20	:10
3 Hours	(3)	(3)	(3)	(3)	Good	Good	(6)	(6)	(6)
Flexibility—Kauri Red									
Pass, %	140	160	100	120	....	120	40	60	100
Fail, %	160	180	120	140	....	140	60	80	120
Flexibility (2)									
Conical Mandrel	Failed	Passed	Passed	Failed	Failed	Passed	Failed	Failed	Passed
Rating	Poor	Chalked	....	Poor	Poor	....	Brittle	Brittle	....
Remarks	Adhesion			Adhesion	Adhesion				
Discoloration (rating)									
Baking (10)	4	3	3	2	1	6	3	5	2
Ultraviolet Exposure	4	1	2	5	7	3	9	8	6
Cold Water Resistance (24 hours)									
Remarks	Sl. Bl. (4)	Bad Bl.	Sl. Bl.	Bl.	Bl.	Sl. Bl.	Bl.	Bl.	Sl. Bl.
Recovery Time	:20	:20	:30	:30	:20	:30	:20	:20	:20
Hot Water Resistance (1-hour boil)									
Remarks									
Blush Recovery (hr.: min.)	:10	:05	.05	:05	:10	:05	:05	:05	:05
Hardness	:20	:10	:10	:05	:20	:05	:05	:05	:03
Outdoor Exposure									
43 Weeks (Florida)	Failed	....	Failed	....	(7)	....	Failed (8)	Failed	....
Failure	....	....	Peeled	....	Checked	....	Checked	Checked	....
Dirt Collection	Yes	Yes	....	Spotty	....	Less than 4	....	....	More than 4
Color—Rating		1		2		3 (9)			2
Gloss		2		2		3			1
Remarks				OK		OK			OK

(1) 1% NaOH after 48 hours.
(2) After 100 hours. Exposure in Weather-Ometer.
(3) Badly wrinkled, not destroyed.
(4) Sl. = Slight, Bl. = Blush.
(5) Automotive lacquer nitrocellulose + castor oil alkyd.
(6) Destroyed.
(7) Failed in 16 weeks.
(8) Failed in 25 weeks.
(9) Yellowed.
(10) Baked 2 hours at 150°F.

as metal, introduced as the naphthenate, is the optimum. Up to 0.04% guaiacol appears effective as an anti-skin agent. A refined linseed ester so treated will dry dust-free in 35 to 45 minutes and foil free in 5 to 6 hours. It will bake dry in 5 minutes at 100°C. The guaiacol has no appreciable effect on the final drying of the ester although it appears to slow the cotton-free time.

The dried film of the linseed ester shows good depth of finish and scuff resistance, fair water resistance, good grease resistance, but poor alkali resistance. Upon aging, the films become tougher but not brittle. Generally the properties seem to lie between those of an oleoresinous and lacquer finish.

Several polyvinyl alcohol esters were prepared from different types of fatty acids; an acid/alcohol ratio of 1.25 and 400 parts of phenol per equivalent of alcohol was used. These esters were evaluated as varnishes. The performance data compared with several standards are given in Table IV. This preliminary information indicates that the polyvinyl linseed esters as varnish films compare very favorably in chemical resistance, outside exposures in Florida for 43 weeks, and physical properties with such products as a 33-gallon tung oil-phenolic varnish and an alkyd resin corresponding to Bureau of Ships Specification 52R13.

When the esters were used as a varnish, they showed better holdout than lacquer sealers but did not develop early hardness to permit sanding.

Attempts were made to use the extracted polyvinyl esters as varnish oils. The only resins with which it was possible to combine these esters were ester gum or the rosin ester of pentaerythritol. The more complex resins, e.g., phenolics and maleated ester gums, were incompatible. An ester gum varnish can be made by merely heating the resin and ester to 225°C. and thinning immediately. Higher temperatures or longer heating time resulted in gels in each case.

The drying properties and film characteristics of this varnish were not so good as those obtained by using the ester alone. These varnishes did not show any outstanding improvement over a linseed oil varnish of similar length. Apparently the presence of the resin detracts from the oil properties.

In order to eliminate the methanol extraction step, several attempts were made to esterify the crude ester with pentaerythritol. No gelation difficulties were encountered. However the ester so prepared did not have any of the outstanding characteristics of the extracted product; rather it resembled the corresponding pentaerythritol esters in properties.

An oleic acid ester prepared by the method of this paper dried cotton-free in 1½ hours and foil-free in 24 hours with .05% cobalt drier. After two days the film showed good adhesion and through-dry. Further aging showed good toughness and hardness without embrittlement. This was compared with an ester made by the peroxide polymerization of vinyl oleate (8), from which unreacted monomer was removed. The polymerized vinyl oleate ester did not dry hard or tough but remained soft or "cheesy," and did not compare favorably with the product made by direct esterification of the polyvinyl alcohol. This observation apparently verifies the fact that in the polymerized vinyl oleate, the molecular size (degree of polymerization) was not as great as that obtainable by direct esterification.

From work on the preparation and evaluation of the polyvinyl fatty acid esters certain facts are concluded, thus:

a) a better method of synthesis is to be desired in order to increase the yield; and

b) the performance data indicate that the final product has ultimate properties which are equal to or better than standard oleoresinous varnishes and alkyd resins.

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Spectrophotometric Studies of the Composition of Lespedeza Seed Oil

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METHODS of isolation of lespedeza seed oil and a preliminary description of the properties of the oil have been reported in previous papers from this laboratory (1, 2). The oil has an iodine number of approximately 150, which is reflected in its drying properties and indicates the presence of a significant fraction of unsaturated acid glycerides. In this communication we wish to report data obtained on analysis of the ultraviolet absorption spectra of the oil before and after alkali isomerization in terms of the nature and relative quantities of various types of unsaturation present.

Experimental

Isolation of the oil. The seeds used in this study were obtained from the Ross Seed Company and from the Louisville Seed Company, both of Louisville, Kentucky. Dehulling was accomplished by filling a one-quart capacity pebble mill one-third full with pebbles (average size 1") and then adding just enough seeds barely to cover the pebbles. The mill was run for one hour, the hulls were blown out with an air stream, and this treatment was repeated except that the mill was run for only 30 minutes. After this treatment the seeds were approximately 90% hulled. The remaining seeds with hulls were removed manually. The grinding operation in all cases consisted of charging the mill with seeds and pebbles and running the mill until the seeds were ground to a fine powder. This powder was transferred to a 500-ml. Soxhlet extractor and extracted with petroleum ether, b.p. 60-80°C., until the circulating solvent was colorless. After extraction most of the solvent was removed by distillation on a water bath at about 80°C., and the last traces of solvent were removed under vacuum. Stainless steel balls were used to grind a few of the *L. stipulacea* seed samples as described in the discussion. Some of the *L. stipulacea* seed were not separated from the hulls prior to grinding. Operations under nitrogen were done as previously described (2).

Isomerization of the oil. The procedure of Mitchell, Kraybill, and Zscheille (3) was employed except that 95% ethanol checked for optical purity was substituted for 98% ethanol as a solvent. All measurements were made in duplicate and rechecked by different investigators working independently. Standardized sample weights, alkali concentration, and procedural details were used to make the measurements clearly comparable with one another. The original constants (3) were used in the calculations.

Ultraviolet absorption. Measurements were made, using a Beckman Model DU quartz spectrophotometer with 1.00-cm. cells.

Iodine numbers (Wijs). Iodine numbers were found, using the procedure described in A.O.C.S. Official Method Cd. 1-25.

Isolation of the white solid from the hulls. The hulls were ground and extracted as described above for the seeds. The white solid also separates from

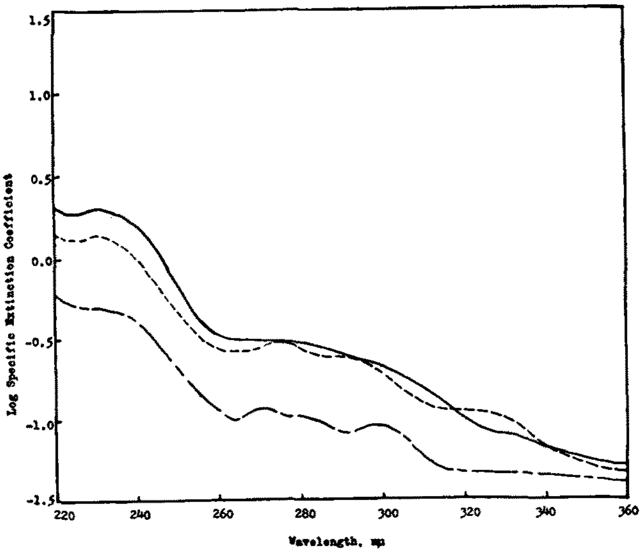

FIG. 1. Ultraviolet absorption spectra of lespedeza seed oil and linseed oil as isolated.

Kobe - - - - - -
Sericea ————
Linseed—— - —— - —— -