

Chemistry and Technology of Some Drying Oil Fatty Acid Esters of Polyvinyl Alcohol

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Introduction

ONE OF THE SEVERAL WAYS of making improved drying oils involves the replacement of glycerol with more functional polyols. In the case of polyvinyl alcohol, this implies the esterification of unsaturated drying oil-derived fatty acids of the homopolymerization of monomeric vinyl esters of drying oil fatty acids via the vinyl alcohol structure. The presence of the polyvinyl moiety in drying oil fatty acid esters would be expected to yield coating compositions with improved film forming characteristics as based upon functionality concepts (1, 2).

The greater hydroxyl functionality of the polyvinyl alcohol for a given high level of unsaturation, such as found in linseed oils would be expected to yield greatly improved film formers. Conversely, a highly functional polyol esterified with acids of a low degree of unsaturation such as oleic acid or those derived from the non-drying oils, might be expected to yield film forming compounds. Further, the structure of the backbone of a polyvinyl moiety would lead to regularity-oriented fatty oil ester molecules. Film formation would be via oxidative cross-linking and association through intermolecular forces.

Properties of Polyvinyl Alcohol

Since the basic discussion in this paper concerns polyvinyl esters, it is in order to consider first the properties of the polyvinyl alcohols.

According to Kainer (3), polyvinyl alcohols of various mol wt were independently prepared in Germany in 1924, by Hermann and Haehnel and also Staudinger. Schildknecht (4) describes the preparations of polyvinyl alcohols from polyvinyl esters. Hermann and Haehnel (5) prepared polyvinyl alcohol from polyvinyl acetate by reacting the ester with sodium hydroxide in ethanol. Acid catalysts are much slower than alkaline catalysts in the alcoholysis of polyvinyl acetate and tend to favor the formation of intra- and/or inter-ether linkages. It has been generally believed that sodium alkoxide catalysts with ethanol or methanol give more complete replacement of acetate groups.

It was originally believed by Staudinger (6) and Hermann and Haehnel (5) that polyvinyl alcohol consisted of mixtures of the 1,3- and 1,2-glycol structures.

These investigators reported that the oxidation of polyvinyl alcohol yielded both oxalic and succinic acids. Marvel and Denoon (7) in 1938, found that the oxidation of polyvinyl alcohol formed products which confirmed the 1-3 glycol structure.

Fuller (8), in a review of the subject, reported that X-ray investigations by Halle and Hoffmann, showed periods of $2.57 \pm .02$ Angstroms for the $-\text{CH}_2\text{CHOH}-$ group. This also confirms the 1-3 glycol structure.

The ultraviolet absorption spectrum of polyvinyl alcohol has also been shown to be similar to that of 2,4-pentane diol. Further, the dihalide of polyvinyl alcohol has an ultraviolet spectrum similar to that of 2,4 dichloropentane, but differs from that of 2,3 dichloropentane (9). These findings further suggest that polyvinyl alcohols are predominantly 1,3-glycols.

Marvel and Inskeep (10) found that during the alcoholysis of polyvinyl acetate and also during the re-esterification of this same polyvinyl alcohol, a definite change in the alcohol mol wt and end group structure resulted. They felt this was due to a disproportionation with the end group being an enol acetate, which on hydrolysis would yield an aldehyde group.

It has been suggested by McDowell and Kenyon (11) that the polyvinyl acetate or alcohol molecule contains unstable linkages. This was proved by deacylation and dehydration to unsaturated polyvinyl acetylation and dehydration to unsaturated polyvinyl compounds of various molecular sizes. These polyvinyl alcohols when reacylated yielded acetates with various degrees of polymerization and a viscosity less than that of the original polyvinyl acetate. This decrease in the average chain lengths may be due to rupture of unstable linkages within the linear molecule.

Clark and Blout (12) report that polyvinyl alcohol molecules contain carbonyl groups, probably ketonic, randomly distributed along the polymer chain, and independent of chain length. The ketone groups can give rise to ketals which are readily cleaved by acids, and further render the polymer chain susceptible to alkaline cleavage and degradation. This structure may give rise to abnormal viscosity and chemical behavior.

Infrared spectrograms show an absence of a peak at 2.85-2.90 microns for the hydroxyl group. This indicates strong hydrogen bonding (Fig. 3).

In summarizing the properties of polyvinyl alcohol, it can be said that it is essentially a 1-3 glycol with some 1-2 glycol structure and randomly spaced carbonyl groups. It is crystalline with the polymer chains linearly oriented and held together tightly by hydrogen bonding.

Although a secondary alcohol, polyvinyl alcohol is very reactive and shows reactions typical of most alcohols. Some of these are the formation of formals (13,15), ketals (14), ethers (15), urethanes (16), and cyanoethylated products (17). On standing in the presence of traces of mineral acids, it will react with itself to form ethers (6). This is especially true of the sulfuric acid hydrolysed material, and, hence this is stabilized with alkali (4).

Heating polyvinyl alcohols at high temp causes water to split off with the formation of ethylenic groups. In this manner polyvinyl alcohol acts as a true secondary alcohol. When heated above 250C, polyvinyl alcohol and some polyvinyl esters will give polyethenes, insoluble dark-colored products which

¹The work described in this paper is taken from theses submitted in partial fulfillment of the requirements for the Master of Science degree at the N. Dak. State University in March, 1960, and March, 1962, respectively.

probably originate from conjugated unsaturation in the carbon chain (4).

Reactions of polyvinyl alcohol with polyfunctional acids and their anhydrides, e.g. phthalic, maleic, adipic (18,19), and boric acid (20) have been reported.

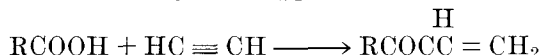
Method for the Preparation of C₁₈ Fatty Acid Esters of Polyvinyl Alcohol

Polyvinyl alcohol was found to react with C₁₈ monocarboxylic acids derived from natural fats and oils in the presence of a suitable solvent (21). The ester was prepared using phenol as a mutual solvent for high mol wt polyvinyl alcohols and various types of drying and semi-drying oil fatty acids. The ester was separated from the unreacted acids by methanol extraction.

On outdoor exposure trials in Florida, these esters showed remarkable durability as clear coatings (21). More work was indicated in this study. There was a need for a better esterification technique to obtain a higher ester yield and further evaluation of the dried films in various modifications and applications, especially as vehicles in pigmented systems. This previous work used du Pont's polyvinyl alcohol RH393 and Elvanol 70-05 (mol wt of 12,000 to 15,000).

Polyvinyl esters of linseed, soya, tall oil, and tallow fatty acids have also been prepared by other techniques. Eckey (22) prepared the corresponding esters by an interchange technique, using a low mol wt polyvinyl acetate and methyl fatty acid esters. A basic catalyst and special solvent systems are needed to effect the reaction.

The polymerization of monomeric vinyl esters of fatty acids has also been described. The monomers can be prepared by the Reppe reaction (23)



Zinc soaps are the catalyst. The reaction is run at 200C under a slight pressure with nitrogen diluted acetylene. Another method for monomer preparation is the interchange method described by Toussant and McDowell (24), thus:



The mercuric sulfate catalyst gives the best results when freshly prepared in situ.

The polymerization of the saturated fatty acid-vinyl esters proceeds with some difficulty with peroxides to yield semi-solid waxy masses (2-5). The unsaturated fatty acid esters appear very reluctant to homopolymerize (26). Their reaction rate is related to the degree of unsaturation according to Harrison and Heeler (27). In the unsaturated esters, the fatty acid ethylene groups interfere with the vinyl-polymerization to yield a poor drying low mol wt undesirable, unoriented structure in contrast to the regular zig-zag polyvinyl structure.

The phenol esterification process has several disadvantages also, but nevertheless yields product with oriented structures. The flow diagram for this process is shown in Figure 1.

From this work it was felt that the direct esterification process should be reconsidered if a lower mol wt polyvinyl alcohol should become available. It was hoped that the use of this polyol would:

1. Eliminate or reduce the amount of solvent phenol;
2. Eliminate the methanol extraction step; and
3. Improve ester yield.

In 1958, the E. I. du Pont de Nemours and Company introduced a low mol wt polyvinyl alcohol which was used in this investigation. It is known as LMPVA, Elchem 1445.² With a mol wt of about between 3000-5000. Accordingly, a project was started to improve the esterification technique and evaluate the esters as clear and pigmented finishes.

Preparation of Esters by Direct Esterification

In order to make esters of a polyvinyl alcohol and C₁₈ fatty acids a strong mutual solvent which is non-reactive with both components is necessary. This solvent must be able to overcome the hydrogen bonding in the polyvinyl alcohol to enable the fatty acids to contact the sheltered hydroxyl groups. Before too much was known about the polyvinyl alcohol structure, phenol was found to be a good solvent for this reaction. (Details on this follow.) It was used again in the subsequently described work.

Various esters were prepared with different ratios of LMPVA, to fatty acids using phenol as a solvent (21).

The esterification equipment consisted of a three-neck flask, a mechanical stirrer, thermometer, dropping funnel and a Dean-Stark trap with condenser. The heat was supplied with a heating mantle and powerstat.

One equivalent wt (44.0 g.) of LMPVA was added to phenol at 160C to make a solution of approximately 10% concentration. When the temp of the mixture reached 180C, the dropwise addition of fatty acids was begun and continued at a rate such that no turbidity formed. After this addition, the phenol was removed slowly until the reaction was completed as indicated by a constant acid number usually between 60 and 80.

Most of the phenol was removed by sparging the mixture with carbon dioxide. The resulting crude high acid number ester was insoluble in methanol.

The unreacted fatty acids and the small amount of residual phenol was removed by five methanol washings to obtain products useful as coatings. These had an acid number of 10 or less. Each washing used a volume of methanol equal to the volume of the ester. The methanol was heated to about boiling in order to

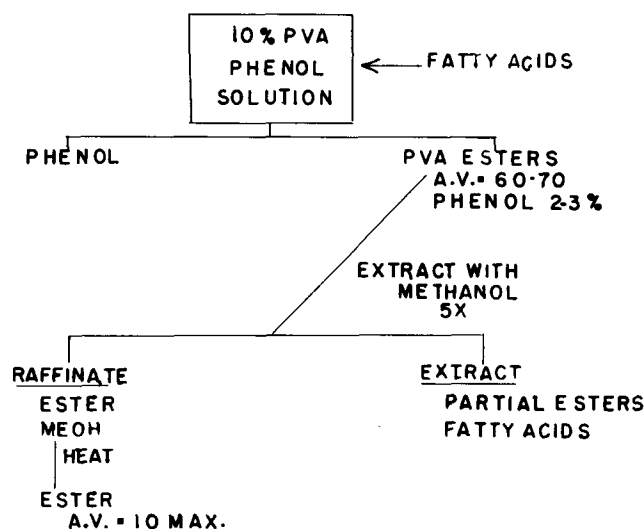


Fig. 1. Flow diagram for phenol process.

²In the discussion which follows, this product will be designated as LMPVA.

TABLE I
 Esterification Data of LMPVA Esters at 230C

Code number.....	X-100-17	Y-200-118	X-100-33	X-100-64	X-200-3	X-100-48	X-100-58	Y-200-108
Fatty acid used.....	linseed	linseed	tall oil	soya	linseed	tall oil	tall oil	soya
Ratio of fatty acid/LMPVA.....	1/1	1/1	1/1	1/1	1.25/1	0.5/1	0.4/1	0.1/1
% LMPVA ^b	10	10	10	10	10	10	10	5
Reaction in time in hours.....	9.0	5.25	12.0	10.5	8.5	7.3	7.0	3.5
Acid number before washing.....	76.6	66.5	87.7	81.5	85.5	14.3	9.7	9.8
Acid number after washing.....	9.5	11.8	8.3	8.3	14.3
% yield of ester.....	55.7	66.7	59.7	57.0	51.6	93.0	95.0	95.0
Dry time of flowed out film (hr).....	1.5	2.0	2.0	2.0	1.5	2.0
G. H. Viscosity.....	Z-1	Y	Z-2	Z-3	Z-4	F ^a
G. H. Color.....	13	14	13	13	15	15	16	11

^a Viscosity in a 50% xylene solution by weight.

^b LMPVA per cent dissolved in phenol.

aid the extraction. The last traces of methanol were removed from the ester by heating gently to not over 100–110C and together with a carbon dioxide sparge.

In the original work (21) gels were obtained when the ratio of fatty acids to polyvinyl alcohol RH393 was less than 1/1. Seavell (24) also used a high ratio. With the advent of LMPVA it was felt that the ratio of fatty acid to the polyol might be at least equal to or less than 1/1. This assumption was found to be correct. Lower ratios of fatty acids to polyvinyl alcohol, i.e. from 1/1 to 0.1/1, could be successfully esterified without gel formation as shown in Table I.

In the acid polyol ratio range 1/1–.5/1, the acid numbers still remained high. Below .5/1 they were not generally higher than 15.

The procedure and apparatus for the esterification of the 0.5/1 and 0.1/10 fatty acid to polyvinyl alcohol esters, is similar to that previously described. However, the esterification reaction must be handled very carefully since the rate of reaction seems to be dependent, to some extent, on the rate at which phenol is removed. It is desirable to remove phenol as quickly as possible in order to obtain the fastest reaction, but if phenol is removed too fast haziness results. Also, if insufficient phenol is used the product will not be clear.

In the typical esterification, Table I, using a 1/1 ratio of fatty acid to polyol, the per cent of hydroxyl groups esterified was about 50–60%, based on the theoretical yield of ester, as determined by acid numbers of 76–86. The yield was in a range which is no better than that described earlier (21). Therefore, the optimum ratio of fatty acid to LMPVA appeared to be approximately .5/1.

From the data in Table I, it can be seen that the products are reproducible. It can also be seen that when a lower acid/polyol ratio, i.e. .5/1, was used, the time required to obtain the minimum acid number or maximum extent of reaction was decreased considerably, and it was not necessary to methanol-extract the product.

The reason for low ester yield or high acid number was now explored. An equilibrium situation at this point was not considered likely. It was felt that hydroxyl groups of the polyol were lost by some process, e.g. dehydration, etherification, and/or the esterified polyol was deacylated. Probably some hydroxyl groups are not available for fatty acid esterification

due to the presence of ketal and formal structures which the fatty acids cannot split or they may be sterically hindered. In the work which follows an attempt is made to clarify this situation.

In the 1/1 reaction (X-100-17, Table I), the excess unreacted acids were extracted from the crude esters in order to obtain an acid number of ten or less. It was observed that lower yields of the ester were obtained after the five washings with methanol than were calculated from the per cent of acids reacted before extraction. An acid number of 76.6 (before washing) indicated 61.7% yield, as compared to the actual yield (after washing) of 55.7%. Thus, some ester was removed in the methanol washing procedure.

In order to study the reaction in more detail, a typical esterification, X-100-71, Table II, and Figure 2, used five equivalents of linseed fatty acids with five equivalents of LMPVA and 2000 g. of phenol. Samples were removed at regular intervals. These samples were not methanol extracted, rather they were steam distilled to free them of phenol. The hydroxyl, acid, and iodine numbers were determined.

There is a net decrease of about 7–8 points in iodine value. This is the sum of the unsaturation caused by

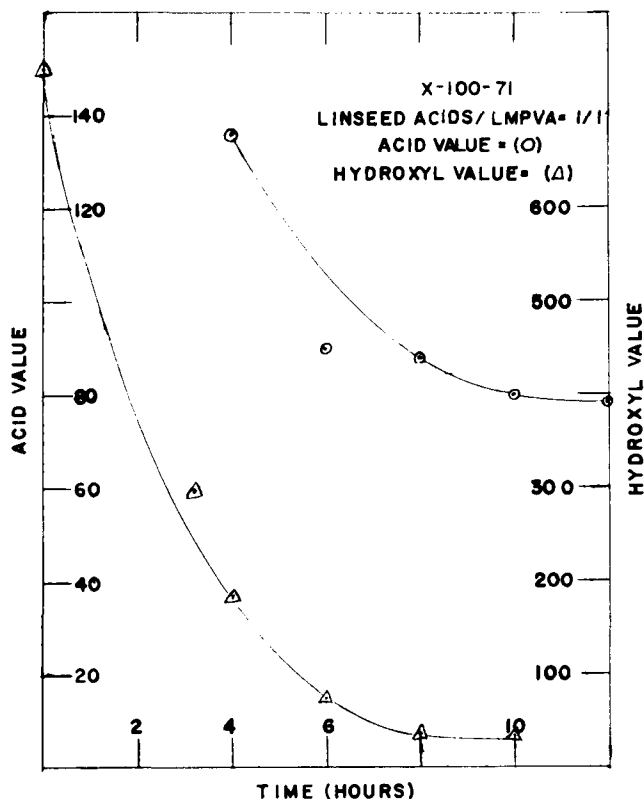


FIG. 2. Relationship of acid and hydroxyl numbers with time for 1/1 FFA/LMPVA ester.

TABLE II

Analytical Data Obtained from Reaction X-100-71
FFA/LMPVA = 1/1 (Run at 230C)

Hours of reaction	Hydroxyl values	% Free hydroxyl	Iodine values	Acid values
1	750.0	22.8	200.0
3	300.0	9.0	177.5
4	165.0	4.9	170.0	137.0
6	75.0	2.2	163.3	90.6
8	34.8	1.0	165.5	88.6
10	33.0	1.0	165.5	79.1
13	27.5	0.83	165.5	76.3

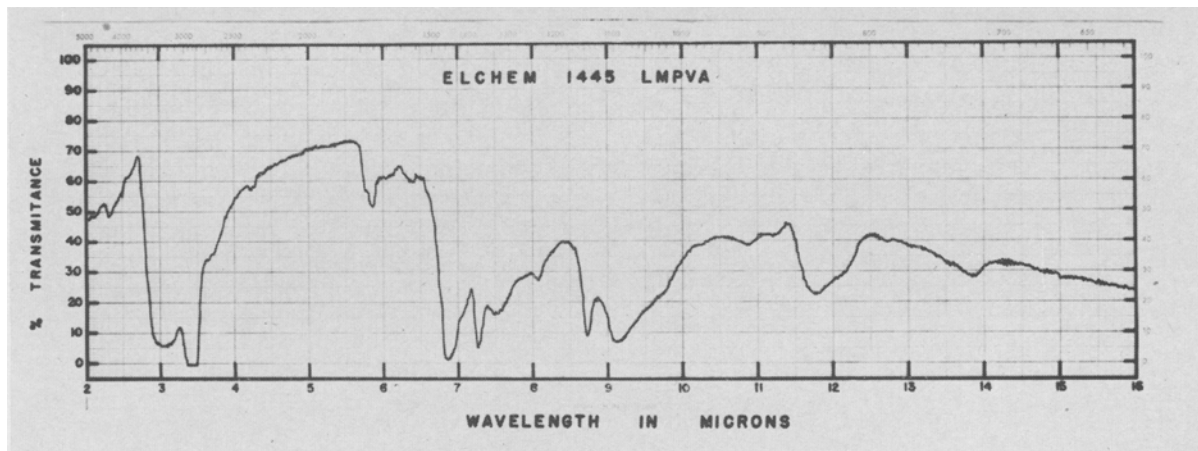


FIG. 3. IR spectrogram of LMPVA.

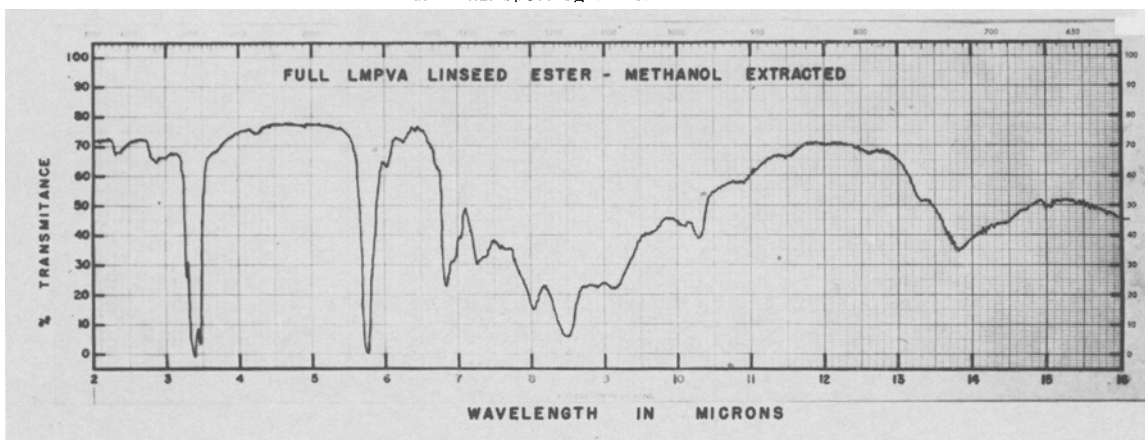


FIG. 4. IR spectrogram of 1/1 linseed LMPVA ester.

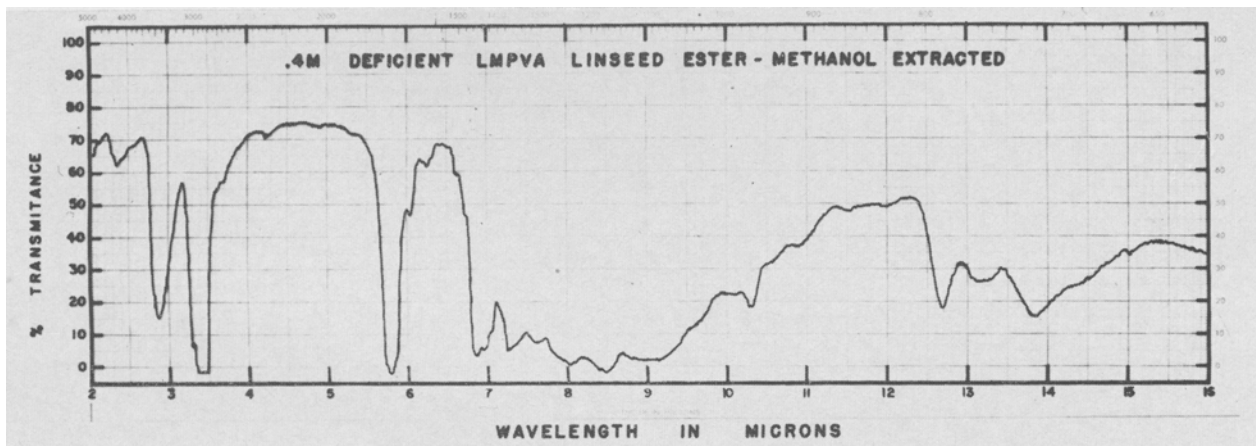


FIG. 5. IR spectrogram of .4/1 linseed LMPVA ester.

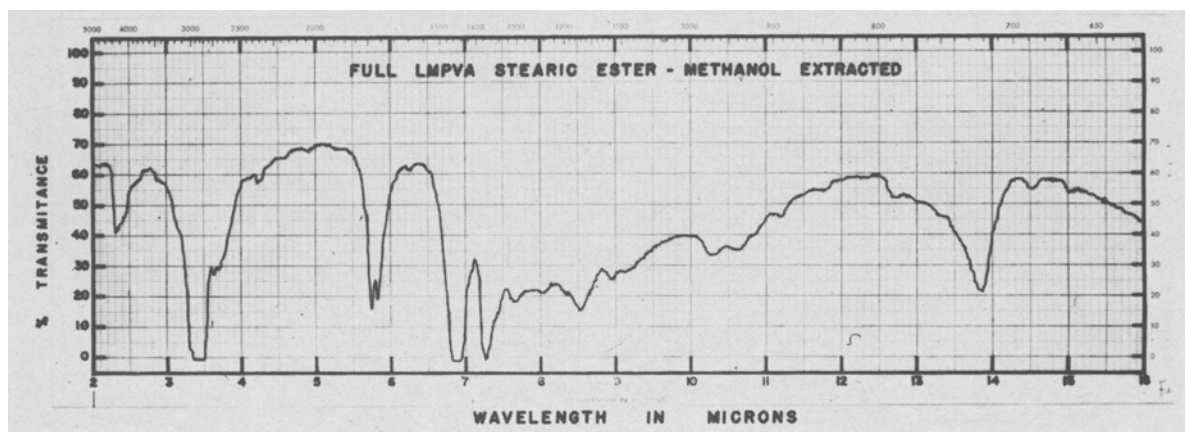


FIG. 6. IR spectrogram of 1/1 stearic LMPVA ester.

deacylation and dehydration and that lost by polymerization within the fatty acid structure.

The hydroxyl values indicate that essentially all of the hydroxyl groups disappeared while the acid values indicate that the esterification is still incomplete. It is quite possible, that etherification is occurring and that the rate of etherification probably coincides very closely with the decrease in acid value. If this is the case, it would explain the disappearance of hydroxyl groups while the acid value is still quite high.

Infrared analysis on LMPVA, Figure 3, and the 1/1 and .4/1 linseed LMPVA esters, Figures 4 and 5, respectively do not conclusively detect the presence of ether groups.

The possibility of deacylation was next investigated. Previous work on unsaturated fatty acid esters was inconclusive concerning the probability of a deacylation reaction. The top temp of the esterification reaction was 240C. It was felt that the presence of a dehydration or deacylation reaction might be more readily determined on a stearic acid LMPVA ester. Therefore, if unsaturation was detected by the infrared study or iodine numbers, it would have to be present in the LMPVA moiety.

A full LMPVA stearic acid ester was prepared by the standard method. This stearic acid ester with an acid number of 15 was heated to 275C for one hr. The acid value rose to 50, indicating deacylation.

Seavell (28) observed deacylation at 280C on linseed esters. Our products gelled too rapidly at this temp to confirm his work.

In a second experiment a polyvinyl stearate was prepared at a temp of not over 240C which was standard for the linseed ester. The iodine number increased 13 points over that of the starting material.

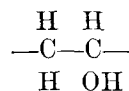
The formation of unsaturation was further confirmed by infrared absorption measurements. In the spectrogram of the starting LMPVA, Figure 3, there is no indication of unsaturation to the 10-11 micron range. In Figure 6, characteristic peaks at 10.3 and 10.7 μ show the presence of unsaturation in the stearic acid ester. The formation of unsaturation in the polyvinyl structure was further confirmed by completely saponifying a .4 mole ratio linseed-LMPVA ester. The polyol was recovered from the alcoholic potassium hydroxide and potassium soap solution. After a thorough washing, the infrared spectrogram of the cleaved product was determined as shown in Figure 7. An inspection of this figure shows a peak at 10.3 μ which further confirms the formation of a

double bond in the polyvinyl alcohol structure during esterification with linseed fatty acids.

In connection with the infrared spectrograms, the hydroxyl peak at 2.85-2.90 μ should be considered. The full LMPVA esters as in Figures 4 and 6, show no hydroxyl peaks as expected. The unesterified LMPVA, Figure 3, shows a broadened band between 2.9 and 3.5 μ . The partial LMPVA ester in Figure 5 shows a distinct hydroxyl peak indicating that partial esterification has overcome hydrogen bonding, when this is compared with the spectrogram of Figure 7, for the cleaved ester, the absence of the hydroxyl peak indicates a resumption of the effectiveness of the hydrogen bonding.

Use of Other Solvents

Polyvinyl alcohol is highly hydrogen bonded and has a solubility parameter calculated by Small's (29) method to be 9.1 for the unit



Burrell (30) lists a number of parameters for solvents. According to Small the parameter can be calculated from the sum of the groups or elements;

$$S = \frac{d \sum G}{M}$$

For polyvinyl alcohol this is:

$$\begin{aligned} M &= \text{molecular per unit, } 44 \\ d &= \text{density, } 1.21 \\ &= \text{CH}_2 \quad 1.33 \\ &= \text{CH} \quad .28 \\ &= \text{OH} \quad 1.70 \\ \sum G &= 3.31 \end{aligned}$$

Parameters can also be calculated from ΔE , the energy of evaporation (30) as follows:

$$S = \left(\frac{\Delta E}{M/d} \right)^{1/2}$$

Table III summarizes the parameters of solvents as calculated or listed by Burrell (30). Since most of these are highly hydrogen bonded, these should be good solvents for polyvinyl alcohol.

In addition to the parameter requirements, the solvents must be non-reactive with both fatty acids and the polyvinyl alcohol. This immediately eliminates amines, alcohols, esters, and acids. The solvents

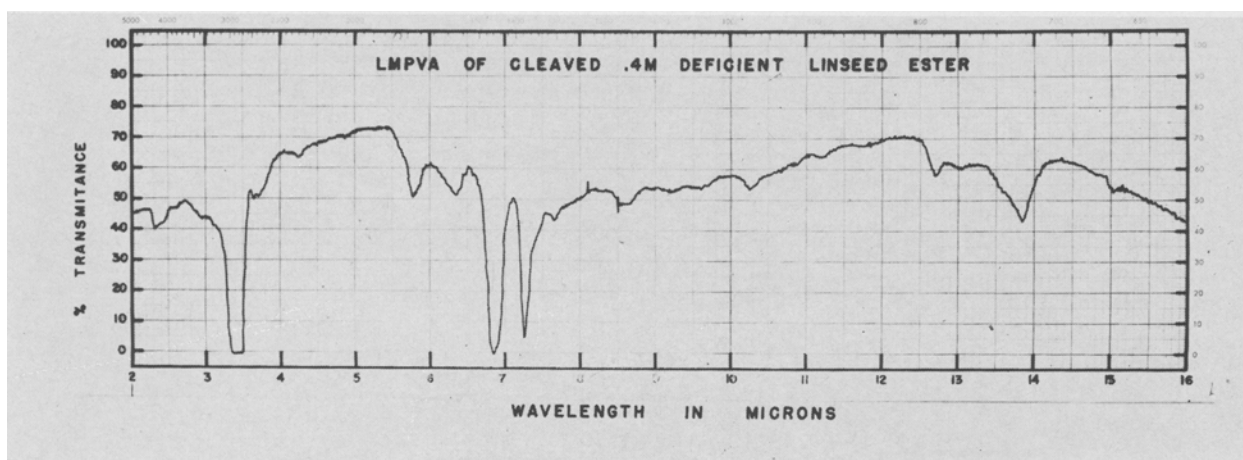


Fig. 7. IR spectrogram of LMPVA recovered from .4/1 linseed ester.

TABLE III
 Parameters of Polyvinyl Alcohol Solvents

Compound	Parameter	B.P.°C	Source
Phenol.....	10.3	182	Formula
Cresol.....	10.7	191	Small (29)
Diphenyl ether.....	9.7	252	Small (29)
Pyridine.....	9.9	115	Formula
Cyclohexanone.....	9.9	157	Burrell (29)
N,N dimethyl acetamide.....	10.1	165	Formula
Cyclopentanone.....	10.4	130	Burrell (30)
Acetonitrile ^a	11.9 ^a	82	Small (29)
N,N dimethyl formamide.....	12.1	153	Burrell (30)
Water.....	23.9	100	Burrell (30)
Fatty acids.....	7.5	Small (29)

^a Low hydrogen bonding.

must have a boiling point of at least 165°C since C₁₈ fatty acids do not esterify at temp much below this point. Further, the solvents must not decompose in the temperature range necessary for this reaction, namely, 165–224°C. The following were tried: pyridine, dimethyl formamide, diphenyl ether, cresol, phenol-water mixture, and acetonitrile.

The conditions used were as previously described with 1/1 ratio fatty acids to polyvinyl alcohol.

The esters obtained from dimethyl formamide and acetonitrile had an extremely dark color. The reaction was incomplete and they were very difficult to recover by methanol extraction. Yields were less than 10%.

The reaction using a phenol-water mixture gave an ester having an improved color, but the time needed to obtain it with no improvement in yield made this method impractical. The phenol-water mixture was used because it was thought that water might aid in breaking the hydrogen bonding in the polyvinyl alcohol. The phenol, water, and polyvinyl alcohol were mixed together and allowed to stand for a day prior to running the reaction. The results indicated no improvement in the degree of esterification.

From these results it was concluded that phenol is so far, still the best solvent for this reaction and that it does not promote or inhibit the reaction.

Use of Catalysts

A study was made to determine the use of acid and basic catalysts in the presence of phenol. In the preliminary work the ratio of fatty acid to LMPVA was

kept constant at 1/1 with a 10% LMPVA-phenol solution. Data for these esters are shown in Table IV.

The acid catalysts used were:

1. p-Toluenesulfonic acid.
2. Mono-n-butyl acid orthophosphate,

The product obtained when p-toluenesulfonic acid was used was very dark, viscous, and had very poor drying properties. It is very possible that there was some other reaction with the phenol and LMPVA and/or fatty acids since all of the phenol was not recovered. The product was not identified.

Mono-n-butyl acid orthophosphate seemed to inhibit the reaction since the acid value remained constant at 118 after 7½ hr.

The basic catalysts used were:

1. Litharge.
2. Lithium hydroxide plus zinc oxide.
3. Sodium acetate.

In most cases these catalysts improved the color of the product. It was found that 0.5% basic catalyst (based on the wt of the ester obtained) produced a product with good color and reduced the reaction time as shown in Table IV. Acid numbers of the final products were not improved.

The second phase of the catalyst studies involved esterification of LMPVA and Elvanol 70-05 with a deficient amount of fatty acids. The following basic catalysts were tried and a portion of these esters are listed in Table V.

1. Sodium borate
2. Sodium acetate
3. Lithium hydroxide
4. Calcium acetate
5. Zinc oxide

Of these five catalysts, sodium borate was the only one which failed to give an ester. It is quite possible that a boron complex was formed (20) which caused the polyvinyl alcohol to be thrown out of the solution. Although zinc oxide speeded up the formation of ester, the product was hazy. Calcium acetate produced an ester without haziness, but it did not speed up the reaction compared with the other catalysts in spite of the greater polyol excess.

 TABLE IV
 Esterifications Using Acid and Base Catalysts in Phenol at 230°C
 Fatty Acids/Polyvinyl Alcohol = 1/1^c

Code number	Catalyst	Fatty acid used	Time of cook (hr)	Acid value before washing	Acid value after washing	G.H. visc.	G.H. color	Yield on ester	Dry time
X-100-35	p-Toluene sulfonic.....	Linseed	6½	31.3	9.93	Z-6	18 ^a	84.4	3 days
X-100-92	Mono-n-butyl ortho-phosphate.....	Tall oil	7½	118	no effect
X-100-94	Litharge.....	Tall oil	4¼	83	58.0
X-100-97	Lithium hydroxide plus zinc oxide ^a	Tall oil	6½	61.7	7.3	Z-3	12	69.0	2 hours
X-100-111	Sodium acetate ^b	Tall oil	3¾	63	68.5
X-100-33	None.....	Tall oil	7	87.7	8.3	Z-2	13	59.7

^a 0.5% based on the ester to be produced.

^b 1% based on the ester to be produced.

^c Used 400 g phenol/mole PVA.

 TABLE V
 Esters Formed Using an Excess Polyvinyl Alcohol and a Catalyst
 Linseed Acids Elvanol 70-05

Reaction number.....	Y-100-19	Y-100-24	Y-100-26	Y-100-27	Y-100-31	Y-100-32	Y-100-35	Y-100-36
Fatty acid to polyvinyl alcohol ratio.....	0.4/1	0.6/1	0.4/1	0.6/1	0.5/1	0.6/1	0.5/1	0.4/1
Catalyst	calcium acetate	sodium acetate	sodium acetate	sodium acetate	zinc oxide	lithium hydroxide	lithium hydroxide	lithium hydroxide
% Catalyst used (based on wt of ester).....	1	1	1	2	1	.5	.5	.5
Acid values after time indicated								
4 hr.....	24.6	14.7	22.8	14.3	9.65
4½ hr.....	13.6	11.4	15.7	16.3
5 hr.....	12.4	19.0	21.5
6 hr.....	16.3	11.2
7 hr.....	13.2

TABLE VI
Esterification of Elvanol 70-05 with Linseed Acids at 230C
Fatty Acid to Polyol Ratio: 0.5/1

Reaction number	Phenol g	Reaction time, hr	Final acid value	Catalyst	Per cent catalyst by wt	Result
Y-200-62	250	4.5	16.3	Lithium hydroxide	0.5	Viscous soln.
Y-200-70	250	5.0	16.8	Sodium acetate	0.5	Viscous soln.
Y-200-71	250	5.0	11.3	None	Gelled

Considerable work was undertaken using lithium hydroxide and sodium acetate at 0.5% and 1% levels. The rates of reaction of lithium hydroxide and sodium acetate were found to be very much the same, with the exception that the product obtained from the former was slightly hazy in appearance while the one from the latter was clear. The color of the catalyzed products was considerably lighter than those prepared without a catalyst, but the viscosity appeared to be much higher in spite of the shorter esterification time. This change in physical properties indicates that the esters formed with the aid of a catalyst must be somewhat different in structure from those obtained without a catalyst. The amount of catalyst appeared to have no effect on the reaction rates in these excess polyol esters. The presence of unreacted hydroxyl groups is responsible for viscosity increase.

It was found that there is no great beneficial effect with a catalyst for the esterification of Elvanol 70-05 with linseed acids in a ratio of one-half equivalent of acids to one equivalent of polyol. This can be seen by the reaction times comparing basic catalyzed to uncatalyzed reactions of Table VI.

In the case of stearates, Figure 8, at the 1/1 acid/polyol ratio, the lower acid number in the final product i.e., 53 compared to 75. In the .5/1 ratio no advantages were noted.

Preparation of Coatings

The first evaluation studies (21) on polyvinyl fatty acid esters were described in 1951. Esters of linseed, soybean, and dehydrated castor oil fatty acids were prepared and evaluated as clear finishes using a 33-gallon tung-phenolic varnish, 30-gallon dehydrated castor ester gum varnish, a 35-gallon linseed maleic-phenolic resin varnish, an automotive exposure for 52R13 alkyd resin as controls. Outdoor exposure for 43 weeks in Florida showed that the linseed and soya

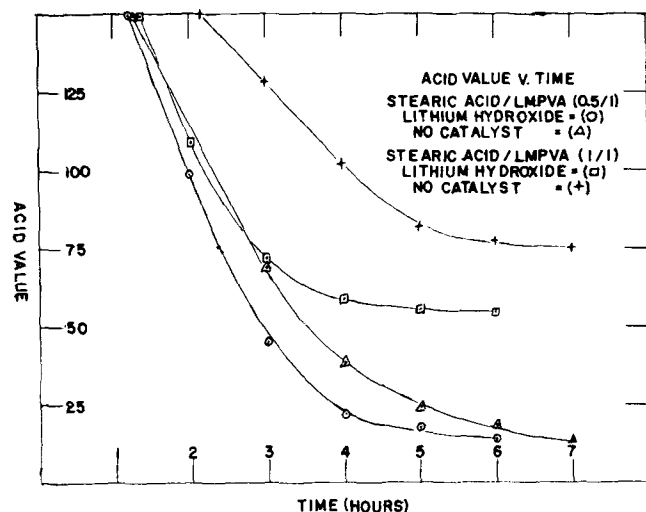


Fig. 8. Decrease in acidity with time for .5/1 and 1/1 stearic acid LMPVA reaction.

TABLE VII
Typical Constants of LMPVA Esters Used in Coating Evaluation
1/1 Acid LMPVA Ratio

Fatty acid	Acid value MgKOH g	Vis. G-H	% N.V.	Color G-H
Linseed.....	9.6	Z-2	100	12
Soya.....	7.0	Z-2	100	13
Tall oil.....	8.0	Z-2	100	13

* Esters were composites of several batches.

esters were equal to the tung-phenolic varnish and alkyd controls.

In the present study, the full and partial esters were evaluated as clear finishes. Only the full esters were evaluated in pigmented coatings.

The esters which were used in the evaluation studies were made by the standard procedure previously described. Tables VII and VIII summarize the typical properties of the esters used in this work. All esters were 5-liter laboratory cooks.

The technology of the polyvinyl esters is lengthy but a short summary is in order.

These esters were evaluated as varnish oils with typical varnish resins, house paint vehicles, can coatings, floor paints, and enamels. Compared to standard controls, the polyvinyl esters showed advantages in house paints and can coatings. In varnishes, floor paints, and enamels the property differences were marginal, i.e. in some tests the new esters were better than the controls and in others, not as good.

Conclusions

1. No substitute for phenol as the mutual solvent was found. Other solvents which were tried produced deleterious side effects such as bad color and product recovery difficulties. Furthermore, the yields of ester were not as good as those in the phenol process.
2. At the present time, the yield of ester using the standard procedure cannot be improved. The final product analyses seem to indicate polyethers are formed simultaneously with the fatty acid esters, and that polyvinyl alcohol undergoes chain cleavage with the formation of non-hydroxyl groups, or a deacylation of one of two 1-2 hydroxyl groups which results in a ketone group.
3. Esters of high and low mol wt polyvinyl alcohol based on 0.5/1 (fatty acid/polyol) equivalents as the optimum can be successfully prepared with and without basic catalysts. An ester as low as 0.1/1 fatty acid/LMPVA can be prepared without a gel. This ester is barely soluble in aromatic solvents.
4. The evaluation data on several coatings indicates that improved clear varnishes and house paints are possible and that further evaluation of these esters as can coatings or industrial bakes should be considered. Linseed esters showed better properties than the soya and tall oil esters. No particular advantages were seen in the other pigmented coatings.

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TABLE VIII
Constants of Polyvinyl Alcohol Esters
0.5/1 Acid/Polyol Ratios

Code number	Polyvinyl alcohol	Fatty acid	Acid value	V.N.V. %	G.H. color
X-100-44	LMPVA	Tall oil	14.3	100	11
Y-200-74	LMPVA	Linseed	14.5	50	11
Y-200-62	Elvanol 70-05	Linseed	16.3	50	8

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Practical Aspects of Hydrogenation

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THE HYDROGENATION of fats and oils remains the largest single chemical reaction of the industry. The purpose of the reaction is two-fold. First, a liquid oil is converted into a semisolid or plastic fat and secondly, since the unsaturation of the oil is reduced, the rate of reaction with oxygen is decreased.

The reaction has been carried out for many years with very little change. Converters holding 10,000 to 60,000 lb. of oils are used, heated with internal coils and agitated mechanically using usually a flat blade or turbine agitator. The oil and catalyst are mixed in the converter, heated near operating temp and hydrogen admitted through a spider in the bottom of the vessel. The temp increases rapidly due to the exothermic reaction and may or may not be controlled during the reaction. Excess hydrogen may be allowed to accumulate in the head space of the tank and may or may not be purged, depending on the type of system used. The reaction is followed usually by a change in refractive index of the oil which can be related to the iodine value. When the desired end point is reached, the hydrogen flow is stopped and the charge cooled, filtered to remove the catalyst and then can be bleached with a small amount of clay to remove the last traces of catalyst.

There are three parameters that may be changed to give different characteristics to the products, catalyst, temp and hydrogen pressure. These three parameters cause changes in the rate of hydrogenation, ratio of the rate of saturation vs. isomerization of the double bonds and the selectivity, i.e., the rate of reduction of

polyenes to monoenes vs. the rate of reduction of monoenes to saturated.

With the increasing supply of soybean oil with its linolenic acid which presumably gives it a flavor defect, the question of selectivity has received much attention.

Figure 1 shows the analytical characteristics at the same IV of a soybean oil hydrogenated with the same catalyst under two different reaction conditions that may be used in commercial equipment. It is apparent the reaction at high temp and low pressure (II) is more selective, lower linoleic and lower stearic but has more trans isomers and thus a somewhat steeper solids slope. Also, the more selective reaction (II) has a smaller proportion of the linoleic acid in the cis cis methylene interrupted system as shown by the analysis for "Essential Fatty Acids" using lipoxidase.

The effects of the operating parameters on selectivity and isomerization are: increased pressure decreases selectivity and trans isomers, increased temp under low agitation, increases selectivity and isomerization. However, under very efficient mixing of the oil and hydrogen, the temp effect on selectivity is slight and only an increase in the reaction rate occurs.

From a study of the reaction rates of hydrogenation of cottonseed oil, Wesniak and Albright (10) concluded the mechanism was the reaction between unsaturated in the liquid phase and atomically chemisorbed hydrogen with the surface reaction controlling. This mechanism is consistent with other observations. Kokes and Emmet (7) have shown Raney nickel catalysts hold 45-100 cc of hydrogen/g. catalyst as hydrogen atoms in a substitutional solid solution. Also Beek (2) has shown the hydrogenation of ethylene occurs when it approaches a catalyst film that holds two atoms in a favorable geometric position.

When a catalyst is saturated with hydrogen as in relatively high pressure hydrogenations, most of the "active" sites will hold hydrogen atoms and the probability is large that two atoms are in the correct geometrical position for reaction with any double bond as it approaches the catalyst. Conditions which favor a continuous saturation of the catalyst will thus favor low selectivity because any unsaturated bond that approaches the two hydrogen atoms will be

TABLE I
Composition of Two Hydrogenated Soybean Oils

	I	II
% Solids at 50 F.....	12.0	12.3
70 F.....	5.1	3.8
80 F.....	2.9	0.8
92 F.....	0	0
Essential fatty acids, %.....	19.0	11.7
Trans, %.....	27.8	36.1
Palmitic, %.....	11.7	11.8
Stearic, %.....	8.1	5.7
Oleic, %.....	57.1	61.5
Linoleic, %.....	22.1	20.1
Linolenic, %.....	1.0	1.0

I—Hydrogenated at 285 F, 30 psig to 92 IV.
II—Hydrogenated at 330 F, 10 psig to 92 IV.