

A STUDY OF THE PREPARATION AND PROPERTIES OF
DRYING OILS PREPARED BY THE ESTERIFICATION OF
CERTAIN POLYHYDROXY ALCOHOLS.

A STUDY OF THE PREPARATION AND PROPERTIES OF
DRYING OILS PREPARED BY THE ESTERIFICATION OF
CERTAIN POLYHYDROXY ALCOHOLS

By

ANDREW P. GARRISON

Bachelor of Science

Oklahoma Agricultural and Mechanical College

Stillwater, Oklahoma

1948

Submitted to the Department of Chemistry
Oklahoma Agricultural and Mechanical College
In Partial Fulfillment of the Requirements
for the Degree of
MASTER OF SCIENCE

1949

OKLAHOMA
AGRICULTURAL & MECHANICAL COLLEGE
LIBRARY
NOV 4 1949

APPROVED BY:

Ernest M. Hodnett
Chairman, Thesis Committee

O. Decker

Member of the Thesis Committee

Olto M. Smith

Head of the Department

H. C. W. Zook

Dean of the Graduate School

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. E. M. Hodnett, under whose direction this work was done.

TABLE OF CONTENTS

	Page
Introduction	1
Historical	2
Experimental	17
A. Materials	17
1. Polyvinyl acetate	17
2. Polyvinyl alcohol	18
3. Fatty acid chlorides	18
B. Esters of polyvinyl alcohol and fatty acids	19
1. By transesterification of polyvinyl acetate and fatty acids	19
2. By direct esterification of polyvinyl alcohol and fatty acids.....	20
3. By esterification of polyvinyl alcohol with acid chlorides	22
a. Procedure	22
b. Saponification numbers of esters	23
c. Preparation and properties of varnishes made from esters.....	25
C. Esters of inositol and fatty acids.....	26
1. Esters of inositol and linoleic acid.....	26
2. Esters of inositol and linseed oil fatty acids.....	32
3. Esters of inositol and tung oil fatty acids...	33
Discussion.....	37
Bibliography.....	39
Biography.....	42

INTRODUCTION

Most drying oils used in protective coatings are natural esters of glycerol and various fatty acids, some of which are unsaturated. During recent years synthetic esters have been prepared for use as drying oils. These esters have been prepared from mixtures of various fatty acids and polyhydroxy alcohols, such as sorbitol, pentaerythritol, and dipentaerythritol, which contain more than three hydroxyl groups.

In view of the fact that the synthetic esters prepared from alcohols which contain more hydroxyl groups than does glycerol have better drying properties than the natural drying oils, it seemed profitable to extend the investigation of synthetic drying oils to include the study of the preparation and the properties of synthetic drying oils obtained by esterification of some of the polyhydroxy alcohols which have not been investigated. This work deals with the preparation of synthetic drying oils by the esterification of polyvinyl alcohol and of inositol.

HISTORICAL

A survey of the literature shows that many different methods, with numerous variations of conditions and catalysts, have been employed in the preparation of esters of fatty acids and polyhydroxy alcohols. This review will include examples of various methods and conditions which have been used in preparing esters of fatty acids and alcohols containing more than one hydroxyl group. These examples will illustrate the following types of esterification:

- a. Esterification of polyhydroxy alcohols with fatty acids without catalysts.
- b. Esterification of polyhydroxy alcohols with fatty acids by use of sulfonic acid catalysts.
- c. Esterification of polyhydroxy alcohols with fatty acids in the presence of basic catalysts.
- d. Esterification of polyhydroxy alcohols with anhydrides of fatty acids.
- e. Reaction of polyhydroxy alcohols with fatty acid halides.
- f. Reaction of polyhydroxy alcohols with alkyl esters of fatty acids without catalysts.
- g. Exchange esterification of triglycerides with polyhydroxy alcohols in the presence of alkaline catalysts.
- h. Exchange esterification of triglycerides by polyhydroxy alcohols, by use of metal or metallic oxide catalysts.
- i. Reaction of fatty acids with anhydro derivatives of polyhydroxy alcohols.
- j. Ester formation between polyhalides or haloalcohols and fatty acid salts.

k. Reaction of fatty acids with sulfuric acid esters of polyhydroxy alcohols.

In addition examples will be given in which polyfunctional esters have been prepared which are suitable for use as drying oils.

Chittenden (14) obtained esters of glycerol and fatty acids by heating the reagents for 114 hours at a temperature of 100° , in an open retort, and collecting the water of reaction.

Schalit (49) obtained mixtures of esters, often up to the tetra ester, by heating different equivalent amounts of fatty acids with erythritol in an oil bath at $200-250^{\circ}$.

Blagonravova and Lararev (7) accomplished the esterification of pentaerythritol with oleic acid and linoleic acid by heating equivalent amounts of the acids and alcohol at 180, 200, 220, 230, and 240° for 6 hours.

Konen (35) prepared esters of fatty acids and various alcohols by direct esterification of the alcohols and fatty acids, without the use of catalysts, as described in the following quotation:

"From a chemical standpoint there are quite a number of different ways of forming esters, but from a practical and commercial view, there are only two methods which are economical enough for the use of the drying oil industry. These are: direct esterification, in other words, the uniting of fatty acids directly with polyhydric alcohol; and alcoholysis, in which one alcohol replaces another to form a new type of ester. The one most in use at present is direct esterification and is carried out as follows: Theoretically equivalent amounts of the alcohol and the fatty acids are placed in a large closed vessel which is fitted with a reflux and a condenser to which a source of vacuum is attached. The acids and alcohol are heated to about 450° F. while being agitated with a stream of inert gas and with vacuum applied. Reaction takes place, water being liberated and taken off through the condenser. The reflux serves to condense any alcohol which might vaporize and returns it to the reaction mixture while allowing the water vapor to pass on into the condenser to be discarded. The reaction progresses very rapidly at first and at 450° F. the major portion of the reaction is over within an hour or two, as measured by the drop in acid value. The amount of this drop depends upon the type of alcohol being used. After this initial rapid reaction, however, the decrease in acid value is very slow and if a low final acid value such

as 4 or 5 is desired, heating must be continued for 6, 8, 10 or more hours."

Johnson (24) obtained esters of sorbitol and various higher fatty acids by heating the reaction mixtures in open vessels for 3-10 hours, at temperatures ranging from 200 to 260°.

Berthelot (5) reported poor yields of the esters of glucose and sucrose, obtained by heating these polyhydroxy compounds with fatty acids in sealed tubes for 50-60 hours at a temperature of 120°.

Berthelot (6) obtained esters of trehalose and fatty acids by heating the reaction mixtures in sealed tubes at a temperature of 180°.

Hilditch and Rigg (31) obtained esters of glycol and various fatty acids by using phenol as a solvent and camphor-beta-sulfonic acid as a catalyst. Several runs were made by heating the reaction mixture for 4 hours at temperatures varying from 120 to 180°. For the runs made at 160-180°, 50-70 percent of the fatty acid had reacted after 4 hours.

Ciocca and Semproni (16) esterified higher fatty acids with glycol by using aromatic sulfonic acid catalysts and refluxing in benzene for 4-5 hours.

Kafka and Nalbandova (34) esterified glycol and glycerol with fatty acids in the presence of 2-naphthalenesulfonic acid, forming mono- and diesters.

Ivanov and Klovov (33) prepared glycerides of linolenic acid, oleic acid, and mixtures of various fatty acids, by heating the reagents in the presence of the Twitchell reagent for 5-7 hours at a temperature of 100°, in a stream of carbon dioxide.

Twitchell (53) esterified glycerol with a mixture of palmitic and stearic acids by using naphthalenestearosulfonic acid as a catalyst and heating the reaction mixture in an open flask at a temperature of 100° for 4.5 hours.

Bennett (3) esterified glycol, diethylene glycol and other dihydroxy alcohols with fatty acids containing more than 5 carbon atoms by heating the alcohol and acid under pressure in the presence of a catalyst such as calcium chloride, sodium glycerophosphate, borax, and sodium sulphite, for 2 hours at a temperature of 200°.

Thurman and Crandall (52) esterified glycol and diethylene glycol with higher fatty acids by dissolving 0.01 part of sodium in 2 volumes of the anhydrous alcohol and one volume of a glyceride, and boiling under reflux for a few minutes.

Christensen (15) obtained the mono- and diglycerides of higher fatty acids by heating the acid in the presence of an alkali-forming metal glyceroxide at 100-220° for 1-5 hours.

Lundsgaard (38) esterified the fatty acids obtained by the saponification of sunflower-seed oil, by heating them with a large excess of glycerol and a potassium soap, at a temperature of 180° for 10 hours.

Johnson (25) obtained the esters of glycerol and mixtures of various fatty acids by passing glycerol vapor, at a temperature of 230° and under a pressure of 20 mm., into the acids, which had been heated to a temperature above the boiling point of the glycerol. The reaction was continued for 30 minutes in the presence of metal soaps.

Du Pont de Nemours and Company (21) patented the preparation of esters of pentaerythritol and fatty acids containing more than 16 carbon atoms by heating the alcohol and acids for 1-4 hours at temperatures ranging from 150 to 275°, in the presence of a small proportion of a base, such as the oxides of lead, calcium, zinc, and sodium.

Shen and Kuo (50) made the ester of mannitol and eleostearic acid by heating the alcohol and acid with lead oxide, in a current of carbon dioxide, at a temperature of 180° for 8.5 hours.

Du pont de Nemours and Company (22) claim the preparation of mixed esters of fatty acids and cellulose by treating the alcohol and an excess of the acids with ketene in the presence of sulfuric or hydrofluoric acid, at a temperature not exceeding 100°.

Lorand (37) prepared esters of starch, dextrans and various sugars by heating them at a temperature of 90° for several hours, with anhydrides of higher fatty acids, in the presence of catalysts such as sulfuryl chloride or magnesium perchlorate.

Young and Black (55) obtained the dipalmitate of ethylene glycol by placing ethylene glycol, together with quinoline, in an ice bath, after which palmityl chloride was added and the mixture shaken vigorously until it set to a hard mass. The mixture was then allowed to stand at room temperature for 48-72 hours.

Pfeiffer and Goyert (43) made ethylene dipalmitate by heating palmityl chloride with ethylene glycol up to a temperature of 180°, without the use of a solvent.

Malkin, Shurbagy, and Meara (39) obtained the dilaurin by first adding lauryl chloride to a cold solution of alpha-monolaurin in dry benzene, and then slowly adding pyridine while shaking, after which the mixture was allowed to stand overnight.

Cantor (12) made esters of glucose by heating the sugar with higher fatty acid halides in pyridine for 8-12 hours, at a temperature of 60°.

Hoglan and Bartow (32) obtained solid hexa-ester derivatives of inositol and acetic, propionic, n-butyric, isobutyric, n-valeric, and 3,5-dinitrobenzoic acids. The esters were prepared by refluxing an excess of the acid chloride with inositol on an oil bath at 110-120° for 45 minutes to one hour, in the presence of a small amount of zinc chloride. The reaction would not occur in the absence of zinc chloride.

Adams (1) prepared the esters of pentaerythritol and fatty acids by first allowing the acid halide and pentaerythritol to react in the cold, then at a temperature of 60° , for a total of 24 hours, using pyridine as a solvent.

Oden (40) obtained fatty acid esters of l-arabinose by reacting the sugar with the acid halides at a temperature of 50° , using either quinoline or chloroform as a solvent.

Goss and Johnstone (28) prepared fatty acid esters of compounds containing more than 3 hydroxyl groups by replacing the alcohol in glycerides with other polyhydroxy compounds. Alcoholysis was effected between a glyceride and methyl, ethyl or propyl alcohol. Alcoholysis was then effected on the resulting ester by causing it to react with various polyhydroxy compounds, such as mannitol, sorbitol, erythritol, arabitol, and xylitol.

Grun, Wittka, and Schelze (30) reported the alcoholysis of fatty acid esters of ethanol by reacting the ester with glycerol, in an open vessel at a temperature of $270-280^{\circ}$ for a period of 15 hours. The conversion was 94 percent complete.

Rewadikar and Watson (47) prepared esters of fatty acids and glycerol by heating esters of methyl alcohol with glycerol at a temperature of 100° for 24 hours, using pyridine as a solvent and in the presence of sodium methoxide.

Blagonravova, Antipova, Savvina, and Svetlichnaya (9) prepared mixed esters of pentaerythritol by alcoholysis of various vegetable oils. Numerous runs were made, using calcium oxide as a catalyst and heating the mixture for 3 hours at temperatures ranging from 220 to 270° . The extent of exchange esterification was found to increase with increase in proportion of pentaerythritol, the maximum tolerance of pentaerythritol being 2

moles per mole of linseed oil. When sodium hydroxide was used as a catalyst, the reaction was completed in a shorter time, and at a lower temperature.

Rikagaku (48) effected exchange esterification of vegetable oils by heating the glycerides with 5 to 50 percent glycerol at a temperature of 200° for 1-2 hours, while stirring. The presence of ethanol, benzene, and hydrogen gas under a pressure of 90 atmospheres had no effect on the extent or rate of the reaction. The reaction was slowed down by the presence of water.

Young and Black (55) obtained monolaurin from trilaurin by refluxing glycerol with trilaurin. When 10 grams of glycerol and 10 grams of trilaurin were refluxed for 30 minutes under anhydrous conditions in an atmosphere of nitrogen, 1.0 gram of monolaurin was isolated from the reaction mixture.

Mixtures of diglycerides and triglycerides of fatty acids have been prepared (44) by heating glycerol with triglyceride esters at a temperature of 225-250° for 1-5 hours, with agitation of the mixture during the reaction.

Blagonravova and Antipova (8) performed exchange esterifications between various vegetable oils and glycerol or pentaerythritol, using various basic catalysts. They found calcium oxide and lead oxide to be effective catalysts, magnesium oxide to be less effective, and the oxides of zinc, iron and cobalt to be ineffective. Caustic alkali, in the form of an alcoholate of the alcohol used, was found to be more effective than the metal oxides. Water-absorbing salts were found to be ineffective.

Exchange esterifications between triglycerides and glycerol have been effected (45) by heating the two substances in the presence of an alkali

catalyst, such as an alkoxide or soap, at a temperature of 175° . Any water formed during the reaction was removed by bubbling a stream of inert gas through the reaction mixture, or by carrying out the reaction under vacuum.

Esters of polyglycerol and mixtures of fatty acids have been obtained (23) by first polymerizing glycerol with heat, then reacting the resulting polyglycerol with triglycerides, by heating the mixture in the presence of an alkaline catalyst.

Gran (29) obtained esters of glycerol and various fatty acids by exchange esterification of triglycerides with glycerol. The reactions were run at a temperature of $170-250^{\circ}$ for 3-5 hours, in the presence of metal catalysts, such as tin, zinc, and aluminum.

Orthner and Heuck (41) prepared esters of glycerol and fatty acids by reacting glycidol with various fatty acids. The reaction was found to take place either with or without the use of heat or pressure, and catalysts such as alkalies, alkaline salts, organic acids, and acid-reacting salts.

Monochlorohydrin esters of fatty acids containing 4 or more carbon atoms have been obtained (26). The reaction is carried out by slowly adding an equivalent amount of epichlorohydrin to the fatty acid in the presence of Friedel-Crafts catalysts, such as aluminum chloride, ferric chloride, and boron trifluoride.

Esters of various fatty acids have been obtained (27) by reacting ethylene and propylene oxides with the fatty acids at a temperature of $130-140^{\circ}$, using at least 2 moles of the oxide per mole of fatty acid.

Renshaw (46) prepared 2,3-distearin by sealing 20 grams of sodium stearate and 6.5 grams of 2,3-dibromopropanol in a glass tube and heating at a temperature of $140-150^{\circ}$ for 7 hours, in an air bath. The same writer also made this compound by heating 20 grams of lead stearate and 5.5 grams

of 2,3-dibromopropanol in a pressure bottle at a temperature of 122°, in an air bath with constant shaking.

Schalit (49) obtained esters of erythritol by reacting 1,4-dichloro-2,3-butanediol with sodium salts of fatty acids. The resulting mixtures contained decomposition products in addition to the esters.

Thomson (51) reported the formation of esters by heating 1,3-dichlorohydrin with potassium salts of fatty acids at a temperature of 160-170° for 3.5 hours, using xylene as a solvent for the reaction mixture.

Veikhertz (54) prepared the distearate of glycerol by dissolving glycerol and stearic acid in concentrated sulfuric acid, and then heating the two resulting mixtures together at a temperature of 70° for 3 hours.

Overholt and Elm (42) obtained glycol esters of oleic, linoleic, linolenic, and eleostearic acids by effecting an interchange between glycol acetate and the methyl esters of these fatty acids, the resulting volatile ester being removed from the reaction mixture by distillation.

The following quotation taken from a paper by Konen (35) describes the relationship between the drying properties of a compound and its molecular structure:

"The preceding oils described have been modified by altering the fatty acid portion of the oil molecule. There is another class of oil now in restricted use that has been made by modifying the alcohol portion of the oil molecule. These are the so-called ester oils, such as pentaerythritol or sorbitol esters. The purpose of altering the alcohol portion is to cause an improvement in the drying properties of the oil by increasing the functionality of the molecule. Perhaps we should explain this term briefly. All natural drying oils are fatty acid esters of glycerine. Glycerine is a trihydric alcohol, i.e., it has three hydroxyl groups at which points fatty acids can be joined to the glycerine nucleus; hence glyceride oils are trifunctional, and if there is sufficient unsaturation in the fatty acid portions, these oils will dry to a solid film. If, however, these fatty acids were attached to glycol which has only two hydroxyl groups, thus giving a bifunctional molecule, a drying oil would not be formed. Upon oxidation, this bifunctional oil might become gummy and very viscous but it would not set to a hard film. To go further, if the same fatty acids were attached to ethyl or methyl alcohols which are monohydric, thus being

monofunctional, they would show no drying properties whatsoever and would remain liquid upon oxidation. However, to go in the other direction, if we were to attach the same fatty acids to pentaerythritol, which is tetrahydric, we would find that the drying properties of the oil resulting would show an improvement over one made with glycerol. Sorbitol contains six hydroxyl groups and therefore should give an even better drying oil than does pentaerythritol. However this is not the case because two of the hydroxyl groups in sorbitol do not readily esterify with fatty acids but, rather, form an interlinkage between themselves and thus are not readily available for the attachment of a fatty acid chain. Therefore, sorbitol, in effect, is tetrafunctional as is pentaerythritol. It is possible to react 5.5 mols of fatty acid with sorbitol but at present the process is not commercially feasible."

Konen (35) prepared the fatty acid esters of sorbitol, glycerol, pentaerythritol, and di-pentaerythritol, and studied their drying properties with the results shown in the following quotation, taken from the same paper as above:

"The testing of these esters in varnishes is now going forward but as yet not enough data are available for a comprehensive report. In general, the improved drying and hardness shown by the oils is carried over into the varnishes made from them. All of the synthetic esters show an improvement in bodying speed over the corresponding glycerol ester. In the same fashion, improved water and alkali-resistance is shown. The sorbitol esters do not show as much improvement as the pentaerythritol esters, however, are slightly inferior to pentaerythritol esters in soap and alkali resistance. Di-pentaerythritol shows an advantage over pentaerythritol in hardness, mar resistance and alkali resistance. All the synthetic ester varnishes have better abrasion resistance than corresponding glycerol ester varnishes. Sorbitol ester vehicles do not respond well to baking but show excellent adhesion properties. This might suffice their use in primer surfaces. Taste and odor qualities of the sorbitol esters are good, therefore they might well be useful in can coatings and food wrapper inks."

Burrell and Vander Valk. (11) produced esters which can be used to prepare low-cost, rapid-drying varnishes from polypentaerythritol, maleic anhydride, and tall oil. A Diels-Alder reaction was first carried out between tall oil and 3.5-6.0 percent maleic anhydride, based on the weight of the tall oil. By the time the reaction mixture had reached a temperature of 250° C. more than 98 percent of the maleic anhydride had reacted with the tall oil.

Enough polypentaerythritol was added to the resulting compound to react with the acid groups of the tall oil and maleic anhydride product. This re-

action was best carried out at 275° in a closed container and with agitation of the reaction mixture. The use of a high-boiling petroleum naphtha aided in the removal of water formed during the reaction.

Five samples of tall oil of various compositions were reacted with 4.5 percent maleic anhydride and the resulting products esterified with dipentaerythritol. The resin acids of the esters varied from 40 percent to 55 percent and the fatty acids from 38 percent to 53 percent. Data on the oils and the varnishes prepared from the oils are recorded in Table I which was taken directly from the above reference.

Storing of the varnish in the presence of driers improved the drying ability. The tack-free drying times of a sample of one of the varnishes after various intervals of storage are given in Table II.

All the varnishes had excellent gloss which was retained with aging of the film. The durability of the various varnishes was tested, the results indicating that the dipentaerythritol varnish was suitable for inside work, and that the outside durability was fair and superior to that of varnishes prepared from the glycerol and mannitol esters.

Table I.

Esters of Dipentaerythritol and Varnishes Prepared from these Esters

Sam- ple No.	Acid No.	Ash (%)	Sterols (%)	Fatty Acids (%)	Resin Acids (%)	Iodine Value	Varnish (50% Solids)			Color (Gardner)
							Dust Free	Tack Free	Viscosity (poises)	
1	162	0.20	7.4	38	55	152	1/4	4.5	1.30	16
2	158	0.20	8.4	41	51	147	1/4	4.5	1.00	17
3	157	0.10	8.0	41	51	152	1/4	4.5	1.33	16
4	165	0.16	8.8	45.4	45.8	146	1/4	5	0.50	13
5	165	0.19	6.5	53.1	40.4	143	1/4	5.5	0.22	16

Table II.

Varnish from Polypentaerythritol, Maleic Anhydride, and Tall Oil

Time of storage (days)	Tack free drying time (hours)
1	11.5
4	6.5
7	4.5
(1 year)	8.0

Cowan and Falkenburg (17) prepared drying oils by first polymerizing the drying fraction of the fatty acids of certain oils to form dimeric and trimeric acids, after which these polymerized acids were removed from the mixture and heated with polyhydroxy alcohols to form polymeric esters. The remaining hydroxyl groups of these esters were then reacted with fatty acids to give a synthetic oil.

One of the synthetic oils was prepared by reacting dimerized fatty acids with glycerol in the presence of lead oxide, then further esterifying the resulting ester with linseed oil fatty acids. Mannitol, pentaerythritol and soybean oil fatty acids were also used in the preparation of the various oils.

Varnishes were prepared from the synthetic oils; the properties of these varnishes are shown in Tables III, IV, and V prepared by these workers. Also included in the tables are one or more linseed oils of different viscosities, for comparison purposes. The results indicate that these synthetic oils give films which are faster drying and are more resistant to water and alkali than are linseed oil films. It is thought that this increase in resistance to alkali and water may result from a greater number of carbon-carbon bonds present in the film. Ester gum varnishes prepared by the investigators gave little indication of being superior to similar varnishes prepared from linseed oil.

Table III.

Drying of Varnishes from Synthetic Oils

Varnish from Oil No.	Designation of oil	Time required for Film condition after			
		Initial set (min.)	Dust-free (min.)	Eight hours	Twenty-four hours
1	1SG ¹	150-180	270-300	Tacky	Sl. Tacky
2	2SG	120-150	330-360	Tacky	Tacky
3	1LG	120-150	300-330	Sl. Tacky	Sl. Tacky
4	2LG	90-120	210-240	Sl. Tacky	V. Sl. Tacky
5	2SPE	90-120	210-240	V. Sl. Tacky	V. Sl. Tacky
6	1SM	30-60	150-180	Not Tacky	Not Tacky
7	2SM	90-120	150-180	Not Tacky	Not Tacky
8	2SM	120-150	330-360	V. Tacky	V. Tacky
9	2CSMG	120-150	270-300	Sl. Tacky	V. Sl. Tacky
10	2SGFA	150-180	330-360	Tacky	Tacky
11	2SGMA	120-150	240-270	Sl. Tacky	V. Sl. Tacky
12	2SGMA	210-240	330-360	V. Sl. Tacky	V. Sl. Tacky
13	2LGMA	60-90	240-270	V. Sl. Tacky	Not Tacky
14	2SPMA	60-90	210-240	V. Sl. Tacky	Not Tacky
15	Linseed X	60-90	240-270	V. Sl. Tacky	Not Tacky

¹The oils have been designated by symbols for ease in referring from table to table: For example, 2SPE designates the oil made from 1 part residual dimerized fat acids, 2 parts soybean fat acids with pentaerythritol.

Table IV.

Water Resistance of Varnish Films

Varnish No.	Designation	Appearance of Film after Exposure to Cold Water for			Recovery after 48 hours immersion (min.)
		6 Hours	24 Hours	48 Hours	
1	1SG	V. Sl. Blush	Blush	Blush	30-35
2	2SG	Blush	B. Blush	Blush	30-35
3	1LG	Sl. Blush	Blush	B. Blush	30-35
4	2LG	Blush	Blush	B. Blush	30-40
5	2SPE	V. Sl. Blush	Sl. Blush	Sl. Blush	15-20
6	1SM	V. Sl. Blush	V. Sl. Blush	V. Sl. Blush	5-10
7	2SM	V. Sl. Blush	Sl. Blush	Blush	30-35
8	2SM	V. Sl. Blush	Sl. Blush	Blush	15-20
9	2CSG	B. Blush	B. Blush	V. B. Blush	60
10	2SGFA	B. Blush	B. Blush	V. B. Blush	60
11	2SGMA	B. Blush	B. Blush	V. B. Blush	30-35
12	2SGMA	V. Sl. Blush	V. Sl. Blush	Blush	15-20
13	2LGMA ^A	V. Sl. Blush	Sl. Blush	Blush	25-30
14	2SPMA	V. V. Sl. Blush	V. Sl. Blush	V. Sl. Blush	5-10
15	Linseed X	Blush	B. Blush	B. Blush	30-35

Table V.

Alkali Resistance and Hardness of Varnish Films

Varnish Number	Designation of oil	Rocker Hardness of Varnish Films		Time Required for Film Failure ² in 3 % NaOH (min.)
		24 Hours	72 Hours	
1	1SG	8	10	65
2	2SG	10	14	50
3	1LG	8	10	55
4	2LG	8	12	60
5	2SPE	10	14	135
6	1SM	26	30	60
7	2SM	16	23	120
8	2SM	23	28	50
9	2CSG	2	2	40
10	2SGPA	6	10	50
11	2SGMA	8	12	50
12	2SGMA	8	10	55
13	2LGMA	12	15	65
14	2SPEMA	10	16	90
15	Linseed X	8	14	45
Plate Glass		100		

²The time required for the film to dissolve or break while immersed in the three percent alkali was recorded as failure.

The following data were taken from a paper presented by Barrell (2).

The data are concerned with results obtained when synthetic drying oils were prepared by esterification of certain fatty acids with the technical grade of pentaerythritol, trademarked "Pentek". This substance has an average hydroxyl content of 47.2 percent instead of the value of 50 percent for the pure compound. The decrease in hydroxyl content is partly caused by the presence of some dipentaerythritol.

Table VI gives the drying times and outdoor durability of pentaerythritol esters to which had been added cobalt, manganese, and calcium salts as driers. Table VII shows a comparison between pentaerythritol esters of linseed oil acids and soybean oil acids with other polyhydroxy esters, all the esters being bodied to a certain viscosity before exposure. These tables were taken from the above reference.

Where pentaerythritol is substituted for glycerol in the preparation

of drying oils, films are obtained which are faster drying, quicker bodying, harder, tougher, have higher gloss, better aging qualities, and are more resistant to water.

Table VI.

Drying Time and Durability of Pentaerythritol Esters

Oil Acids	Tack Free Drying Time (hrs.)	Durability (months)
Citicica.....	5	19
Dehydrated castor.....	5	7
Fractionally distilled fish oil.....	5	12
Fractionally distilled soy oil.....	(7 days)	3

Table VII.

Polyhydroxy Alcohol Esters

	Tack Free Drying Time	% Yellowness Increase	
		Light	Dark
Linseed acids ester of:			
Pentaerythritol.....	15 hours	4.7	4.1
Erythritol.....	32 hours
Trimethylolpropane.....	15 days
Glycerol.....	7 days
Soy acids ester of:			
Pentaerythritol.....	18 days	5.3	2.9
Erythritol.....	24 days
Natural glycerides:			
Linseed oil.....	7 days	33.4	16.8
Soy oil.....	More than 30 days
Tung oil.....	3 hours

Bolley (10) claims the preparation of drying oils by the esterification of erythritol, inositol, and pentaerythritol, and states that these drying oils have better drying qualities than natural drying oils. Detailed information is given only on the esters of pentaerythritol which indicates that, compared to natural drying oils, these esters impart to varnishes (1) shorter drying times, (2) lower resistance to alkali, (3) lower solubility in organic solvents.

EXPERIMENTAL

A. Materials.

Under this heading are included those compounds used in this work which were not readily available but which were prepared from other substances. These include polyvinyl acetate, polyvinyl alcohol, and the acid chlorides of various fatty acids or mixtures of fatty acids.

1. Polyvinyl acetate.

The method used for the preparation of polyvinyl acetate was essentially that of D'Allelio (19), but it was found that the best yields were obtained when the reaction mixture was heated for a much longer period of time than that stated in this reference.

First run: One hundred milliliters of distilled water, 5 g. of Aerosol OT, 24 ml. of vinyl acetate, and about 0.1 g. of potassium persulphate were placed in a 250-ml. round bottom, 3-neck flask equipped with a mercury-sealed mechanical stirrer. The mixture was heated at 60-65° and stirred continuously for 1 hour. The yield of polyvinyl acetate obtained by filtration was 4.67 g.

Second run: Conditions and amount of reactants were the same as for the first run, but the mixture was heated for 3 hours and 20 minutes. Twenty and three-tenths g. of product was obtained, representing a 90.5 percent yield.

Third run: This run was the same as the second run, except that the reaction mixture was heated for 5.5 hours. The yield was 15.2 g. which represents 67.9 percent of the theoretical.

None of the polyvinyl acetate obtained during the above runs was used in the research. Some polyvinyl acetate was found in the store room which had formed by the spontaneous polymerization of a bottle of vinyl acetate at room temperature. Since this polymer was more uniform than the ones pre-

pared by the above operation, it was used as one of the materials for this work.

The specific viscosity of a 0.0101 molar benzene solution of the polyvinyl acetate used in this investigation was determined. The value of 0.015 was found for the specific viscosity, defined as:

$$\frac{(\text{Time of efflux of polymer solution at } 20^{\circ} \text{ C.})}{(\text{Time of efflux of solvent at } 20^{\circ} \text{ C.})} - 1$$

B'Allelio (18) employed the specific viscosity as a means of determining the molecular weight of polymers, but since the necessary constants were not available, the molecular weight of this particular polymer could not be determined by this method.

2. Polyvinyl alcohol.

The polyvinyl alcohol used was prepared by alcoholysis of polyvinyl acetate with methyl alcohol (20). Twenty five grams of polyvinyl acetate was dissolved in 700 ml. of absolute methanol and this solution was added to a 1,000-ml., 3-neck round-bottom flask equipped with a mercury-sealed stirrer, a thermometer and a gas dispersion tube. Hydrogen chloride gas was bubbled through the mixture while it was heated at reflux temperature for 15 minutes. The polyvinyl alcohol which precipitated out at the end of this period of time was washed with ethanol and then allowed to dry.

3. Fatty acid chlorides.

Three attempts were made to prepare acid chlorides. The third attempt was considered the most successful and was the one adopted for use throughout this research. The three runs made are described as follows:

First run: The acid chlorides were prepared by placing 40 g. of linseed oil fatty acids in a 250-ml. round-bottom flask and adding thionyl chloride slowly through a dropping funnel, after which the mixture was heated on a water bath at $75-85^{\circ}$ for 1 hour. A beaker containing a so-

lution of potassium hydroxide was used as a trap to catch the hydrogen chloride and sulfur dioxide formed during the reaction. The acids turned dark immediately upon addition of the thionyl chloride. After the completion of the reaction, an attempt was made to purify the acid chlorides by distilling them under reduced pressure, but the product decomposed at the boiling point, resulting in a relatively large amount of black, tar-like material.

Second run: An attempt was made to prepare the acid chlorides by the method of Krofft and Tritsler (36). To a 250-ml. round-bottom flask was added 40 g. of linseed oil fatty acids and 8 g. of phosphorus pentachloride. A beaker containing an aqueous solution of potassium hydroxide was used as a trap for the hydrogen chloride formed. The fatty acids turned dark on coming in contact with the phosphorus pentachloride. A gas slowly escaped from the solution during the first 5 minutes. At the end of this time the mixture was heated at 45-50° for 15 minutes. The mixture was then heated in an electric heating mantle, under a pressure of 20 mm. of mercury, in order to distil off any phosphorus oxychloride formed. By the time distillate started coming over a relatively large amount of tar-like substance had formed in the distillation flask.

Third run: This run was the same as the first run, except that no attempt was made to purify the acid chlorides after they had been prepared from the fatty acids of linseed oil and thionyl chloride. The crude mixture was used directly for esterification, as described later.

B. Esters of polyvinyl alcohol and fatty acids.

1. By transesterification of polyvinyl acetate and fatty acids.

First run: Nine grams of polyvinyl acetate, 31.25 g. of linseed oil fatty acids, 100 ml. of toluene, and 2 g. of zinc stearate were added to a 250-ml. round-bottom flask equipped with a water-cooled reflux condenser.

The toluene was used as a solvent for the reaction mixture. It also forms an azeotropic mixture, which boils at 104.9° , with acetic acid. The reaction mixture was heated at reflux temperature for 2 hours, after which it was distilled through a fractionating column. At a temperature of 84° , 2.3 ml. of distillate came over. The temperature of the vapors then rapidly rose to 106° . At the end of 4.5 hours 33.6 ml. of distillate had been collected at a temperature of 106 to 109.7° . After the first 15 ml. of distillate had been collected, an additional 20 ml. of toluene was added to the reaction mixture. The distillate collected was titrated with a standard sodium hydroxide solution, using phenolphthalein as an indicator, to determine the amount of acetic acid produced. The distillate required 31.25 ml. of 0.203 N sodium hydroxide solution for neutralization of the acid present. According to these results only 6.14 percent of the polyvinyl acetate reacted to liberate acetic acid. The residue in the flask was made basic with sodium hydroxide solution, sodium chloride was added, then the mixture was extracted with diethyl ether. None of the desired product was found after the evaporation of the ether.

Second run: The process was the same as for the first run, except that 1 g. of sodium benzenesulfonate was used as a catalyst instead of zinc stearate. After the mixture was refluxed for 2 hours, it was fractionally distilled. The first distillate came over at a temperature of 107° . Thirty and five tenths milliliters of distillate was collected over a period of 5 hours, at a temperature of 107 to 110.2° . Twenty nine and three tenths milliliters of 0.203 N sodium hydroxide solution was required to neutralize the acid in the distillate, indicating that 5.76 percent of the acetic acid was liberated from the polyvinyl acetate used. No attempt was made to obtain any pure product from the reaction mixture.

2. By direct esterification of polyvinyl alcohol and fatty acids.

First run: Six grams of polyvinyl alcohol, 40.6 g. of linseed oil fatty acids, 150 ml. of toluene, and 1 g. of zinc stearate were added to a 500-ml. round-bottom flask equipped with a reflux condenser and a Bidwell-Sterling tube, in which water formed during the reaction was collected and separated from the mixture. This mixture was refluxed for 12 hours. One and five-tenths milliliters of water was collected during the first 5 minutes of this period, but thereafter no water formed, and there was no apparent decrease in the amount of solid polyvinyl alcohol contained in the reaction mixture. At the end of the first 2 hours and 10 minutes the liquid part of the reaction mixture had become slightly yellow. After the termination of the 12-hour period the ferric hydroxamate test for esters was applied to both the liquid and the solid portions of the reaction mixture. The test was negative in both cases. The small amount of water collected during the first 5 minutes of the reflux period might have been present as an impurity in the fatty acids used.

Second run: Conditions were the same as for the first run, except that sulfuric acid was used as a catalyst instead of zinc stearate, and the fatty acids used were dried overnight with Drierite. Ten drops of concentrated sulfuric acid was added to a flask containing fatty acids of linseed oil, toluene, and polyvinyl alcohol in the same proportions as in the first run. The reaction mixture turned slightly dark immediately upon addition of the sulfuric acid. Two and one tenth milliliters of water formed during the first 10 minutes of the reflux period. After the mixture had been refluxed for 4 hours the liquid portion had turned slightly yellow, with no apparent decrease in the amount of solid particles present. Ten more drops of concentrated sulfuric acid was then added, and the mixture turned very dark. An additional 1.7 ml. of water was collected during the first 10 minutes after the addition of the second portion of concentrated

sulfuric acid. After this mixture had been refluxed for 10 hours, the dark liquid and solid particles gave a negative test for an ester.

Third run: A 500-ml., 3-neck flask equipped with a gas-dispersion tube and a water bath were used for this run. Six grams of polyvinyl alcohol, 40.6 g. of linseed oil fatty acids, and 2 drops of dilute sulfuric acid were heated in a round-bottom flask on a water bath at a temperature of 100° for 5 hours. Nitrogen gas was bubbled through the mixture during the period of heating, to help remove any water formed. Apparently none of the polyvinyl alcohol dissolved in the fatty acids, and there was no change in the appearance of the mixture during the period of heating. The mixture gave a negative test for esters.

Fourth run: The equipment was the same as for the third run, except that the mixture was heated on an oil bath at a temperature of 130-135° (polyvinyl alcohol rapidly decomposed at 140°). The polyvinyl alcohol started turning dark after the first nine minutes of heating. Apparently it was gradually decomposed by the heat. The mixture was heated for a total of 20 minutes, after which the run was discontinued. The test for the presence of an ester was not applied.

3. By esterification of polyvinyl alcohol with acid chlorides.

The preparation of esters from the alcohol and acid chloride had not previously been attempted because of the fear that hydrogen chloride formed during the reaction would react with the unsaturated fatty acids contained in the reaction mixture, but since previous attempts to form the ester had been unsuccessful it was decided that this method would be tried next.

a. Procedure.

First run: Using the same setup that was used to prepare the acid chloride, 4.4 g. of polyvinyl alcohol was added to the acid chloride prepared as previously described, and the mixture was heated on a water bath

at 100°. Immediately after the addition of the polyvinyl alcohol to the acid chloride a gas started bubbling out of the mixture. After 10 minutes the acid chloride seemed to have disappeared completely and the volume of the solid portion of the mixture had increased to several times the original volume. The resulting substance was washed three times with methanol then allowed to dry in an open dish. The product formed was a spongy, slightly yellow solid.

The solubility of the product was tested in ethanol, petroleum ether, and ethyl acetate, by filtering off the excess solute after it had reached equilibrium with the solvent and then allowing the solvent to evaporate. The amount of solid remaining after evaporation of the solvent in each case was so small that no attempt was made to determine the weight, since it probably would not have been significant.

The substance turned slightly brown after it had been heated to a temperature of 130°, and with continued increase in temperature it did not melt but charred completely.

b. Saponification numbers of esters.

The saponification equivalent of the ester was determined by saponifying a sample of it in an excess of alcoholic potassium hydroxide, then back-titrating the basic mixture with hydrochloric acid solution. The first run was made in order to determine the amount of time necessary for the reaction to reach completion. The second run was made to determine the saponification equivalent of the ester.

First determination: Two hundred milliliters of a 0.691 N solution of potassium hydroxide in ethanol and 13.14 g. of the ester were added to a 500-ml., round-bottom flask equipped with a reflux condenser. The two substances were well mixed, then 5 ml. of the liquid was withdrawn and titrated with 0.102 N hydrochloric acid. The mixture was then refluxed, with 5-ml.

samples being withdrawn at various intervals and titrated with the standardized hydrochloric acid solution, with the results shown in Table VIII.

Table VIII.

Saponification of Ester of Polyvinyl Alcohol and Acids of Linseed Oil

Reaction time (min.)	Volume of acid required for back titration
0	30.31
6	27.10
12	20.80
21	20.39
36	20.10
56	19.55
70	19.53

According to these data, the reaction was very near completion after a period of one hour.

Second determination: Eleven and ninety-eight hundredths grams of the ester were mixed with 200 ml. of the alcoholic potassium hydroxide as in the first determination, and 5 ml. of the liquid was withdrawn and titrated with 0.102 N hydrochloric acid, requiring 32.90 ml. of the acid for neutralization of the basic solution. The mixture was refluxed for 1 hour; then 5 ml. was withdrawn and back-titrated as before. Twenty-three and three tenths milliliters of 0.102 N hydrochloric acid was required for neutralization. The saponification equivalent was calculated from these data to be 313.7. The extent of esterification of the polyvinyl alcohol as determined from the equation $313.7 \text{ equals } (44.05/X \text{ plus } 278.8 \text{ minus } 18.0) (100)$, where 278.8 is the calculated average molecular weight of linseed oil fatty acids, was 83.3 percent.

The ester was tested for the presence of halogen by the Beilstein method and also by fusing some of the product with sodium and testing the resulting filtrate for halide ions (13). Both tests were negative, indicating that none of the hydrogen chloride formed during the reaction had reacted with the unsaturated fatty acids.

c. Preparation and properties of varnishes made from esters.

Two varnishes were prepared according to the method of Bennett (4). The first of these contained some of the ester as one of the components. The second varnish did not contain any of this substance, but was used only for comparison purposes during the testing of the drying properties of the first varnish. The ester at first appeared to be very soluble in turpentine, which was used as a solvent for the varnish, but later proved to be only slightly soluble when a varnish containing this substance as one of the components was filtered and most of the ester remained behind on the filter paper.

Several attempts were made to prepare a varnish which could be used as a comparator for the varnish containing the synthetic ester. A varnish could have been obtained already prepared for this purpose, but it was deemed necessary to obtain experience in the preparation of varnishes before attempting to prepare and study the drying properties of varnishes prepared from the synthetic ester. Only the most successful attempt to prepare one of these varnishes will be recorded here.

Five grams of nevillac (a resin obtained by the polymerization of formaldehyde and phenol) was added to 21 ml. of boiled linseed oil, and the mixture was heated at a temperature of 190-200° for 30 minutes. Then 5 g. more of the resin was added and the mixture was heated at 190-200° for 1 hour and 10 minutes. The mixture was then dissolved in 33.5 ml. of turpentine and 3 ml. of japan drier was added. A layer of this varnish was applied to a test panel containing a coating of shellac. The varnish remained quite tacky for 18 hours. It was only slightly tacky after a period of 28 hours, and after being exposed for 37 hours it had set to a hard film.

Other varnishes were prepared by substituting some of the polyvinyl ester for the resin. It was hoped that the synthetic ester would not only

serve as a resin, but would also contribute to the drying properties of the varnish.

First Varnish: Two and five tenths grams of the ester was added to 21 ml. of boiled linseed oil and this mixture was heated at 160-185° for 30 minutes. Then 1 g. more of the ester was added to the mixture and it was heated at 150-185° for 55 minutes. Three milliliters of japan drier and 33.5 ml. of turpentine were added to this mixture. A layer of this varnish was applied to a test panel which had been previously coated with a layer of shellac, as for the other tests. After 5 hours of exposure the coating was only slightly tacky, but a rough surface had formed, due to the presence of the polyvinyl ester which had not dissolved during the preparation of the varnish. The rough film had completely dried after a period of 26 hours.

Second Varnish: This preparation was essentially the same as the first, except that after the varnish was prepared it was filtered to remove any undissolved ester. A total of 3.4 g. of the ester was used in the preparation of the varnish, and 3.1 g. was recovered on the filter paper, leaving only 0.3 g. of the substance in the varnish. This varnish was not applied to a test panel, since it contained only a relatively small amount of the synthetic ester.

6. Esters of inositol and fatty acids.

It was thought that since inositol contains 6 hydroxyl groups an ester might be prepared from this polyhydroxy alcohol which would be useful as a drying oil. Various methods and conditions were employed in attempts to esterify this alcohol with linoleic acid and the acids contained in linseed and tung oil. From the products obtained varnishes were prepared and applied to test panels. Several of the substances obtained were also saponified and their saponification equivalent thereby determined.

1. Esters of inositol and linoleic acid.

First run: For preparation of the acid chloride, 13 ml. of thionyl chloride was added to 42 g. of linoleic acid in a 250-ml. round-bottom flask, as was previously done for the preparation of the polyvinyl ester. This mixture was heated on a water bath for 1 hour at 100°, the gases formed being caught in a trap containing potassium hydroxide solution. At the end of a period of 1 hour, 2 g. of inositol (slightly less than 0.5 equivalent per equivalent of acid chloride) and a small amount of zinc chloride as a catalyst were added to the dark liquid. By use of the same setup, this mixture was then heated on an oil bath at 120-130° for 1 hour. The mixture reacted quite vigorously during the first 20 minutes, with the expulsion of a large amount of gas. The reaction was much slower during the last 40 minutes of heating. After being heated 1 hour at this temperature, the mixture was a dark viscous oil. In order to remove the excess linoleic acid, the dark mixture was added to a beaker containing a solution of sodium bicarbonate and sodium chloride. The oil and basic solution were mixed thoroughly until all the excess acids were neutralized. Most of the aqueous layer was then decanted from the mixture, after which the ester was extracted with diethyl ether. The solution was then filtered to remove undissolved solid particles present. After evaporation of the ether a yellow viscous oil remained, mixed with a dark colored substance which probably resulted from the decomposition of fatty acids during the heating of the reaction mixture.

In order to determine the extent of esterification of the inositol, the saponification equivalent was determined as previously described for the ester of polyvinyl alcohol. Two hundred milliliters of a 0.859 N solution of potassium hydroxide in ethanol was mixed with 11.23 g. of the product in a 500-ml. flask. Five milliliters of the liquid was withdrawn and titrated with 0.1173 N hydrochloric acid, requiring 35.15 ml. of the

acid for neutralization of the base. The mixture was refluxed for 1.5 hours and another 5-ml. sample was removed from the mixture and titrated, requiring 28.26 ml. of the hydrochloric acid for neutralization. The mixture was then refluxed for an additional 30 minutes, with no appreciable change in the alkalinity of the mixture, a 5-ml. sample requiring 28.29 ml. of the acid for neutralization. From these data the saponification equivalent of the ester, calculated by $(5) (11.23) (1,000) / (195) (0.1173) (35.13 - 28.26)$ is 357.2. The percentage esterification, calculated as previously described, was 31.7. From these results it can be seen that most of the ester molecules contained no more than two acid radicals. It is recognized that this method of determining the saponification equivalent is not so accurate as desired, since the sample weighed out for saponification contained a small amount of decomposed substance which could not be removed from the mixture.

Some of the above ester was used to prepare a varnish. Twenty milliliters of the product was mixed with 4.3 g. of nevilleac resin in a 250-ml. beaker. The mixture was heated on an oil bath at 200-210° for 30 minutes. Then 4.3 g. more of the resin was added, and the heating was continued at 200-210° for 35 minutes. During this time considerable polymerization occurred on the sides of the beaker. The mixture was dissolved in 29 ml. of turpentine, and 3 ml. of japan drier was added.

Some of this varnish was placed on a test panel of the type used for testing the varnishes prepared from the polyvinyl ester. After being exposed for 6 hours the varnish had dried somewhat but remained very tacky. No further drying of the film was evident during the following 3 days.

Second run: The acid chloride was prepared from 42 g. of linoleic acid and 13 ml. of thionyl chloride in the same manner as in the first run. The ester was prepared from this acid chloride by the same method used during the first run, except that 4 g. of inositol was used, which is slightly

less than one equivalent per equivalent of acid chloride, and the reaction mixture was heated for 2 hours.

The product was purified as before, and a 12.10 g. sample was saponified with 200 ml. of 0.8485 N alcoholic potassium hydroxide as in the first run. The initial 5-ml. sample required 36.04 ml. of 0.1173 N hydrochloric acid, and a 5-ml. sample removed after the mixture had been refluxed for 1.5 hours required 28.00 ml. of the acid for neutralization. The saponification equivalent was calculated to be 329.1, and the percentage esterification was 45.0.

A varnish was prepared from some of this ester by use of the same components and in the same proportion as for the varnish prepared during the first run. The ester polymerized extensively during the process of heating. Therefore the mixture was heated at first at 185-195° for only 20 minutes, then after the addition of the second half of the resin the temperature was lowered to 165° and heated at 165-175° for 18 minutes. The resulting product was much more viscous than that prepared during the first run. The usual proportions of turpentine and japan drier were added to the mixture, and a coating of the varnish was applied to a test panel with the results shown in Table IX.

Table IX.

Drying Properties of a Varnish Prepared with an Ester of Inositol and Linoleic Acid.

Time of exposure (Hours)	Condition of film
5	Somewhat dry but quite tacky.
10	Slightly tacky.
18	Same as above.
24	Very slightly tacky.
29	Same as above.
33	Dry.

The dried film had a slightly dark color, due to decomposition products

contained in the ester.

Third run: The acid chloride of linoleic acid was prepared by the same method used in the first run, 42 g. of acid and 13 ml. of thionyl chloride being used for the reaction. An ester of inositol and linoleic acid was prepared and purified by the same method used in the first run, except that the mixture was heated for a longer period of time. Two grams of inositol was added to the acid chloride, and the mixture was heated at 120-130° for 2 hours and 20 minutes. A gas was continuously given off at a slow rate during the period of heating, and was still coming off when the heating was discontinued to prevent further decomposition.

After the ester was purified as in the previous manner, the saponification equivalent was determined from a 11.74-gram sample of the product. Everything except the weight of the sample was the same as for the second run. The initial 5-ml. sample of the mixture and a 5-ml. sample removed after the mixture had been refluxed for 1 hour and 10 minutes required 35.40 and 27.30 ml. of the acid respectively for the back titration. The saponification equivalent was found to be 316.8, corresponding to 55.2 percent esterification.

A varnish was prepared from the above ester, using the same proportions of components and the same conditions as during the first run, except that the final period of heating was for 32 minutes. The usual test was made by placing a coating of the varnish on a test panel, with the results shown in Table X.

Fourth run: This run was quite different from the preceding three runs in that linoleic acid was used directly, instead of the acid chloride. The equipment used was a 500-ml. round-bottom flask equipped with a reflux condenser and a Bidwell-Sterling tube, as used in the attempt to esterify poly-

Table X.

Drying Properties of a Varnish Prepared with an Ester of Inositol and Linoleic Acid.

Time of exposure (hours)	Condition of film
3	Quite tacky.
6	Same as above.
22	Somewhat drier.
32	Same as above.
46	Slightly tacky.

There was no further change in the condition of the film after it had been exposed to the air for 46 hours.

vinyl alcohol. Two grams of inositol, 20 g. of linoleic acid, and 0.5 g. of *m*-benzenedisulfonic acid were added to the flask. The mixture was heated at 150-160° for 3.5 hours. After 5 minutes of heating at this temperature the mixture started bubbling, and water began forming on the wall of the reflux condenser. The reaction mixture also started turning dark. Within 10 minutes the mixture had turned very dark and a tar-like substance had begun to form in the flask. The mixture bubbled slowly during the first hour and 20 minutes. Water vapor slowly formed during the entire 3.5 hours, a total of 1.8 ml. being collected.

The same method of purification of the product was used as for the previous runs. The ester was a yellow, viscous oil, and was not colored with decomposition material as were the esters made by using the acid chlorides of the various acids.

During the determination of the saponification equivalent everything was the same as for the third run, except that 10.26 g. of the sample and 0.5454 N base were used. The initial and final 5-ml. samples of the mixture required 20.30 and 15.16 ml. of the acid respectively for neutrali-

sation. The saponification equivalent as calculated from these data was 436.2, which is slightly less than the value for the monoester. The percentage esterification was found to be 17.3.

A varnish was prepared as for the previous esters, the temperature being kept between 200 and 210° for 30 minutes and then between 200 and 210° for 37 minutes after the second half of the resin had been added. A portion of the varnish, when applied to a test panel, had dried somewhat after 10 hours, but remained quite tacky. Two weeks later the film was still in the same condition.

2. Esters of inositol and linseed oil fatty acids.

Various attempts were made to prepare esters of inositol and the acids from linseed oil and tung oil. No saponification equivalents were determined since all the successful runs were made under the same conditions as were previous runs in which linoleic acid was used.

First run: The acid chloride was prepared in the usual manner, from 20 g. of linseed oil fatty acids and 6.5 ml. of thionyl chloride. This mixture was heated with 1 g. of inositol at 120-130° for 1 hour, as in previous runs. The unreacted inositol was recovered by adding diethyl ether to the mixture and filtering it with a suction funnel. The failure of the substances to react was probably due to the absence of zinc chloride.

Second run: This was a repetition of the first run, except that zinc chloride was used as a catalyst. After purification of the product, a varnish was prepared as in the fourth run above, the final period of heating being 41 minutes. When this varnish was applied to a test panel it dried only slightly within a period of 24 hours, and after 8 days it was still quite tacky.

Third run: This was the same as the second run, except that 2 g. of

inositol was used with the acid chloride prepared from 20 g. of acid, instead of 1 g. as used in the previous run. A varnish prepared in the usual manner by heating the mixture for a total of 64 minutes showed very poor drying properties. The film remained very tacky after 7 days of exposure.

Fourth run: The acid chloride was prepared from 20 g. of acid and 6.5 ml. of thionyl chloride, as in the third run. This was heated with 1 g. of inositol and 50 ml. of pyridine in the presence of zinc chloride, for 1 hour at 120-130°. No hydrogen chloride was expelled during the heating owing to the presence of pyridine. The reaction mixture was then allowed to stand for 2 hours. During this period of time a relatively large amount of pyridine hydrochloride crystallized out. These crystals were filtered off and the remainder of the pyridine was removed by washing the mixture with hydrochloric acid solution. The excess fatty acids were then removed by the same method used in previous runs. Owing to an accident the product was lost before it was used in the preparation of a varnish. No further attempts were made to prepare esters of the fatty acids of linseed oil, as no more of these acids were available.

3. Esters of inositol and tung oil fatty acids.

The following attempts were made to prepare esters of tung oil fatty acids. The acids were prepared by the saponification of tung oil, and consequently contained large amounts of water.

First run: Seventy grams of the acids and 200 ml. of benzene were added to a 500-ml. flask equipped with a Midwell-Sterling tube and a reflux condenser. The mixture was refluxed, the benzene returning to the distilling flask and the water being removed through the side arm of the Midwell-Sterling tube. The distillation was continued as long as two phases formed in the side arm. Sixteen and four tenths milliliters of water was removed, leaving 53.6 g. of acids (if all the water was removed). Sixteen and seven

tenths milliliters of thionyl chloride was added to the flask, and the mixture was refluxed for 30 minutes. Gas was expelled much more rapidly during the first 15 minutes of this period than during the previous runs. The water might not have been completely removed from the acids. A small amount of zinc chloride and 2.57 g. of inositol were added and the mixture was refluxed for 2 hours. Much unreacted inositol was obtained by filtration of the mixture. The reaction might not have occurred owing to the presence of water in the acids, or the benzene might not have permitted the mixture to reach a high enough temperature.

Second run: This was the same as the first run, except that most of the benzene was removed by distillation before the acid chloride was prepared, and the acid chloride and inositol were heated for 2 hours at 120-130°. A varnish prepared by the usual method required a total of 59 minutes of heating at 200-210°. A coating of this varnish had dried slightly after remaining on a test panel for 9 hours, but remained very tacky. No further change in the condition of the film was noted during the next 11 days.

Third run: Water was removed from the acids and the benzene was distilled off, as in the second run. Then 48 g. of the acids were heated with 3.43 g. of inositol in the presence of m-benzenedisulfonic acid for 2.5 hours at 150-160°. During this time 2.1 ml. of water was collected, but there was no apparent decrease in the amount of unreacted inositol.

Seventy milliliters of xylene was then added to the mixture and it was refluxed for 1 hour and 50 minutes. Only 0.4 ml. of water formed during this this period, but from the appearance of the mixture the inositol did not react with the acids.

The xylene was distilled off and the mixture was then heated at 180-190° for 1 hour and 15 minutes. The substance was filtered, and much unreacted inositol was recovered on the filter paper.

Table XI.

Preparation and Properties of the Esters

Number	Reactants		Conditions of Reaction	Appearance	Saponification Equivalent	Number of Ester groups Per unit
I	Polyvinyl alcohol	Linseed oil fatty acid chlorides	100°, 10 min.	Spongy solid	313.7	0.833
II	Inositol	Linoleic acid chloride	120-130°, 1 hour, ZnCl ₂ catalyst	Viscous oil	357.2	1.901
III	Inositol	Linoleic acid chloride	120-130°, 2 hours, ZnCl ₂ catalyst	Viscous oil	329.1	2.702
IV	Inositol	Linoleic acid chloride	120-130°, 2.3 hours, ZnCl ₂ catalyst	Viscous oil	316.8	3.313
V	Inositol	Linoleic acid	150-160°, 3.5 hours, m-benzenedisulfonic acid catalyst	Viscous oil	436.2	1.036
VI	Inositol	Linseed oil fatty acid chlorides	120-130°, 1 hour, ZnCl ₂ catalyst	Viscous oil	Not determined	
VII	Inositol	Linseed oil fatty acid chlorides	120-130°, 1 hour, ZnCl ₂ catalyst	Viscous oil	Not determined	
VIII	Inositol	Tung oil fatty acid chlorides	120-130°, 2 hours, ZnCl ₂ catalyst	Viscous oil	Not determined	

Table XII.

Drying Qualities of the Varnishes

Time of exposure (hours)	Varnish from ester I	Varnish from ester II	Varnish from ester III	Varnish from ester IV	Varnish from ester V	Varnish from ester VI	Varnish from ester VII	Varnish from ester VIII
3-5			Somewhat dry, quite tacky.	Somewhat dry, quite tacky.				
6-8	Slightly tacky, very rough.	Somewhat dry, very tacky.		Same as above.				
9-10			Slightly tacky.		Somewhat dry, quite tacky.			Slightly dry, very tacky.
18			Same as above.					
22				Slightly drier, quite tacky.				
24	Almost dry.		Very slightly tacky.			Slightly dry.		
28-29	Dry.		Same as above.					
32-33			Dry.	Same as above.				
46				Slightly tacky				
(7 days)		Same as above.		Same as above.	Same as above.	Same as above.	Very tacky.	Same as above.

DISCUSSION

The preparation of drying oils by esterification of polyvinyl alcohol and inositol has not been achieved in this research.

It was found that the polyvinyl esters of the higher fatty acids containing at least 16 carbon atoms could not be obtained by many of the common methods of preparing esters. Only a slight reaction occurred when attempts were made to prepare the desired ester from linseed oil fatty acids and polyvinyl acetate, with either zinc stearate or sodium benzenesulfonate as a catalyst.

Various attempts at direct esterification of polyvinyl alcohol with higher fatty acids were not successful. In one run toluene was used as a solvent and zinc stearate as a catalyst. Then the same method was repeated with sulfuric acid as a catalyst. Runs were also made at various temperatures, using sulfuric acid as a catalyst and sweeping out the reaction flask with nitrogen gas. None of these reactions were successful. Reasons postulated for the failure of esterification to occur in these cases are: (1) low solubility of polyvinyl alcohol in the reaction mixture, (2) necessity of keeping the reaction temperature below the decomposition temperature of polyvinyl alcohol (about 140°), and (3) the large number of secondary hydroxyl groups in the polyvinyl alcohol.

It was learned that the ester could be very easily prepared from polyvinyl alcohol and acid chlorides. Although esters prepared by this method gave a negative test for halogen there is a danger that hydrogen chloride formed in the reaction mixture will react with the unsaturated fatty acids. About 80 percent of the hydroxyl groups in the polyvinyl alcohol were esterified by this method, but the esters formed were found to be unsatisfactory for use in the preparation of varnishes because of their slight solubility in common varnish solvents.

Several esters of inositol were prepared from the acid chloride of linoleic acid by varying the proportions of reactants and time of reaction. Decomposition occurred to a great extent during these reactions and the resulting esters could not be obtained in a highly purified form. No more than 50 percent of the hydroxyl groups of inositol were esterified. Only one varnish prepared from these esters dried completely, and it was dark-colored owing to the presence of decomposition products.

An ester prepared by direct esterification of inositol with linoleic acid did not contain as much decomposition material as did the esters made from the acid chloride, but the extent of esterification of the inositol was much less than by the above method. The resulting product was mostly the monoester.

Various attempts were also made to prepare esters of inositol, using linseed oil fatty acids and tung oil fatty acids. Some of these were successful, but none of these esters were good drying oils.

All the hydroxyl groups in inositol and most of the ones in polyvinyl alcohol are secondary. It is known that esterification of secondary and tertiary alcohols is more difficult than that of primary alcohols. Pentaerythritol has four primary hydroxyl groups; glycerol and sorbitol have two primary groups each. It may be that the greater proportion of primary hydroxyl groups in the latter three compounds makes their esterification more rapid and complete.

All of the above can be summed up as follows: The polyvinyl ester may have drying properties, but it could not be used because of its slight solubility in various solvents. None of the esters of inositol were good drying oils, probably due to incomplete esterification of the alcohol. The hexa-ester of inositol and appropriate fatty acids should be an excellent drying oil. The problem is to find a means of completely esterifying the alcohol.

BIBLIOGRAPHY

1. Adam and Dyer, Proc. Roy. Soc., (London) A106, 694-709 (1924). Via Chem. Revs. 33, 266 (1943).
2. Barrell, Oil and Soap 21, 206-11 (1944).
3. Bennett, Can. patent 322,765 (May 31, 1932). Via C. A. 26, 4143 (1932).
4. Bennett, "The Chemical Formulary," Vol. II, D. Nostrand Co., Inc., New York, N. Y., 1935, p. 114.
5. Berthelot, Compt. rend. 41, 452 (1855). Via Chem. Revs. 33, 260 (1943).
6. Berthelot, Ann. chim. phys. (3) 60, 93 (1860). Via Chem. Revs. 33, 260 (1943).
7. Blagonravova and Lararev, J. Applied Chem. (U.S.S.R.) 13, 879-82 (1940). Via C. A. 35, 2060 (1941).
8. Blagonravova and Antipova, Byull. Obmana Opyt. Lakokresoch. Prom., 1940, No. 10, 18-19. Via C. A. 35, 5731 (1941).
9. Blagonravova, Antipova, Savvina, and Svetlichnaya, J. Applied Chem. (U.S.S.R.) 14, 192-7 (1941). Via C. A. 36, 1590 (1942).
10. Bolley, Ind. Eng. Chem. 41, 287-294 (1949).
11. Burrell and Vander Valk., Paint, Oil Chem. Rev. 107, No. 25, 14-20, 33 (1944).
12. Cantor (assigned to Corn Products Refining Co.), U. S. patent 2,147,241 (Feb. 14, 1939), Reissue 21,291. Via Chem. Revs. 33, 267 (1943) and C. A. 34, 2500 (1940).
13. Cheronis and Entrikin, "Semimicro Qualitative Organic Analysis," Thomas Y. Crowell Co., New York, N. Y., 1947, p. 93-94.
14. Chittenden and Smith, Am. Chem. J. 6, 217-34 (1884). Via Chem. Revs. 33, 260 (1943).
15. Christensen (assigned to Armour and Co.), U. S. patent 2,022,494 (Nov. 26, 1935). Via C. A. 30, 894 (1936).
16. Ciocca and Semproni, Ann. chim. applicata 25, 319-23 (1935). Via Chem. Revs. 33, 262 (1943).
17. Cowan and Falkenburg, Oil and Soap 20, 153-7 (1943).
18. D'Alelio, "Experimental Plastics and Synthetic Resins," John Wiley and Sons, Inc., New York, N. Y., p. 69.
19. Ibid., p. 63.
20. Ibid., p. 65.

21. Du Pont de Nemours and Co., Brit. patent 405,826 (Feb. 15, 1934). Via Chem. Revs. 33, 263 (1943) and Brit. C. A., B, 334 (1934).
22. Du Pont de Nemours and Co., Brit. patent 436,885 (Oct. 21, 1935). Via Chem. Revs. 33, 265 (1943) and Brit. C. A., B, 11 (1936).
23. Duulsol Corp., Brit. patent 452,138 (Aug. 10, 1936). Via Brit. C. A., B, 1081 (1936).
24. Farbenindustrie, Brit. patent 350,992 (June 16, 1931). Via Brit. C. A., B, 819 (1931).
25. Farbenindustrie, Brit. patent 336,276 (Oct. 6, 1930). Via Brit. C. A., B, 125 (1931).
26. Farbenindustrie, Fr. patent 850,709 (Dec. 23, 1939). Via C. A. 36, 1947 (1942).
27. Farbenindustrie, Brit. patent 443,631 (Feb. 17, 1936). Via Brit. C. A., B, 684 (1936).
28. Goss and Johnstone (assigned to Sec., U. S. Dept. of Agri.), U. S. patent 2,290,609 (1942). Via C. A. 37, 546 (1943).
29. Grun (assigned to Georg Schicht, A.-G.), U. S. patent 1,505,560 (Aug. 19, 1924). Via Chem. Revs. 33, 271 (1943).
30. Grun, Wittka, and Scholze, Ber., 54, 290-9 (1921). Via Chem. Revs. 33, 268 (1943).
31. Hilditch and Rigg, J. Chem. Soc. 1774 (1935).
32. Hoglan and Bartow, Ind. Eng. Chem. 31, 749 (1939).
33. Ivanov and Klovov, J. Applied Chem. (U.S.S.R.) 7, 171-7 (1934). Via C. A. 28, 7571 (1934).
34. Kofka and Halbandova, Trudy Tsentral. Nauch. Issledovatel. Inst. Konditerskoi Prom., I, 27-55 (1939). Via C. A. 35, 3727 (1941).
35. Konen, Official Digest of the Federation of Paint and Varnish Production Clubs 246, 240-247 (May, 1945).
36. Krofft and Tritschler, Ber. 33, 3584 (1900).
37. Lorand (assigned to Hercules Powder Co.), U. S. patent 1,959,590 (May 22, 1934). Via Brit. C. A., B, 694 (1935).
38. Lundsgaard, Brit. patent 455,540 (Oct. 22, 1936). Via Brit. C. A., B, 21 (1937).
39. Malkin, El Schurbagy, and Meara, J. Chem. Soc. 1409-13 (1937).
40. Oden, Arkiv Kemi, Mineral Geol., 7, No. 15, No. 16 (1918); Chem. Zentr., III, 254,541 (1919). Via Chem. Revs. 33, 266 (1943).

41. Orthner and Heuck (assigned to General Aniline Works), U. S. patent 2,089,569 (Aug. 10, 1937). Via C. A. 31, 7147 (1937).
42. Overholt and Elm, Ind. Eng. Chem. 32, 1348 (1940).
43. Pfeiffer and Goyert, J. prakt. Chem., (M. F.) 136, 299-313 (1933). Via Chem. Revs. 33, 266 (1943).
44. Procter and Gamble Co., Brit. patent 425,980 (Mar. 13, 1935). Via C. A. 29, 5943 (1935).
45. Procter and Gamble Co., Brit. patent 421,284 (Dec. 13, 1934). Via Brit. C. A., B, 194 (1935).
46. Renshaw, J. Am. Chem. Soc. 36, 537-45 (1914).
47. Rewadikar and Watson, J. Indian Indian Inst. Sci. A13, pt. 11, 128-40 (1930). Via Chem. Revs. 33, 268 (1943).
48. Hikagaku (inventor, Ryohei Oda), Japanese patent 101,534 (June 14, 1933). Via Chem. Revs. 33, 269 (1943) and C. A. 28, 5270 (1934).
49. Schalit, Wiss. Mitt. Osterreich. Heilmittelstelle, 42 (1929), 5 (1930). Via C. A. 26, 4303 (1932).
50. Shen and Kuo, Chiao-Tung Univ. Research Inst. Ann. Rept. Bur. Chem. 3, 40-51 (1936). Via C. A. 31, 3308 (1937).
51. Thomson, Trans. Roy. Soc. Can. (3) 20, III, 445-58 (1926). Via Chem. Revs. 33, 278 (1943).
52. Thurman and Crandall, Ind. Eng. Chem. 20, 1390-2 (1928).
53. Twitchell, J. Am. Chem. Soc. 29, 566 (1907).
54. Veikhertz, Khim. Farm. Prom., 284-6 (1932). Via C. A. 27, 270 (1933).
55. Young and Black, J. Am. Chem. Soc. 60, 2603 (1938).

BIOGRAPHY

Andrew Garrison was born at Wilburton, Oklahoma, April 14, 1918. He attended the Public Schools of Ryan, Oklahoma, and graduated from the Ryan High School in May, 1938. He entered Oklahoma A. and M. College in September of 1939 and attended that school for one and one half years.

He entered the U. S. Army in July of 1941, and received his discharge from the service in November of 1945, after serving overseas for twenty-six months.

He reentered Oklahoma A. and M. College in January of 1946. On September 1, 1946 he was married to Alma Robeson. On October 18, 1947 a daughter, Reta Helen, was born. He was graduated from Oklahoma A. and M. College in May of 1948, receiving a Bachelor of Science degree. He entered the Graduate School of Oklahoma A. and M. College in June of 1948.

Typed by:

Alma Garrison