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The use of sulfonated alcohols in modifying alkyd resins.

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THE UNIVERSITY OF LOUISVILLE

THE USE OF SULFONATED ALCOHOLS
//

IN

MODIFYING ALKYD RESINS

A Thesis

Submitted to the Faculty

of the Graduate School

of the University of Louisville

in partial fulfillment

of the requirements

for the degree of

MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

by

Harold S. Sell
//

1941

THE USE OF SULFONATED ALCOHOLS
IN
MODIFYING ALKYL RESINS

Harold S. Sell

Approved by Examining Committee

Director
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May 15, 1941

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and helpful guidance of Dr. E. E. Litkenhous, who
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ABSTRACT

The purpose of this research was to investigate the effects of modifying glycerol phthalate resins with high molecular weight sulfonated alcohols.

It was found that as the modification of the alkyd resins were increased their percentage esterification increased, their specific gravity decreased, their acid number decreased, and the resins became darker in color. The incorporation of the sulfonated alcohol into the alkyd resin also caused them to become less brittle and more soluble.

The most important effect of the modification was the marked increase in compatibility of the resins with nitrocellulose, making possible the use of the resins in nitrocellulose lacquer formulations. The greatest possibility for application of the sulfonated alcohol modified alkyd resins lies in the field of nitrocellulose lacquers.

Because the resins still retained their oil insolubility even when modified, they had no varnish application.

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INTRODUCTION

Each year the protective coating industries consume a large percentage of the resins produced for use in paints, lacquers, and varnishes. This consumption has stimulated research in resin manufacture in an effort to produce resins more applicable to the needs of this industry. With this need in mind it was thought that incorporation of sulfonated alcohols in alkyd resins would produce a resin suitable for protective coatings. Before discussing the reasons for this assumption it might be well to discuss synthetic resins briefly.

Ellis (14) defines a resin as a solid or semi-solid, complex, amorphous mixture of organic substances, having no definite melting point and showing no tendency to crystallize. It is characterized by such physical properties as a typical luster and a conchoidal fracture rather than by any definite chemical composition. Resins such as rosin occur in nature and are known as natural resins, but within the past few years synthetic resins have become increasingly important.

Under the term synthetic resins is a growing group of non-crystallizing organic materials of synthetic or semi-synthetic origin which resemble the natural resins in appearance and properties. These synthetic resins divide into two classes; those which serve as plastics and those used as film forming substances in varnishes and other protective coatings.

Resins for use in the coating industries must be hard, soluble, resistant to water, and durable. Although there are many different types of synthetic resins used in protective coatings only the so-called alkyd type was considered in this research. Alkyd resins are resins produced by the reaction of polyhydric alcohols and polybasic acids. If the reactive groups in the alcohol and acid are in the ratio of 2:2, hard resins do not result; but if the reactive groups are 3:2, they form chains which are three dimensional patterns yielding an infusible and insoluble molecule. Resins formed by this latter reaction are usually too insoluble and too brittle to be used in varnishes and lacquers; and various other acids, alcohols, or oils must be incorporated into the resin to obtain the desired properties. Alkyd resins have been modified with butyl alcohol, castor oil (16), linseed oil (19), lactic acid (30), and monobasic substances (6) to obtain useful resins. The presence of these monobasic acids and alcohols hinder the linkage of the chains producing increased solubility, increased flexibility, and decreased brittleness.

In this thesis work a high molecular weight sulfonated alcohol was incorporated with the alkyd resin to make a resin suitable for use as a protective coating. The sodium salts of sulfonated alcohols are being used at present as detergents, wetting agents, and "soapless" soaps. The substance

consists of a sulfonated high molecular weight alcohol, having acid sulfate groups in place of the hydroxyl groups. Monobasic acids or monohydric alcohols which have only one reactive group do not give rise to resinous materials, but incorporation of hydrophylic groups such as hydroxyl or sulfonic groups tend to produce water solubility and compatibility with nitrocellulose while long paraffin-like chains increase the oil solubility.

The sulfonated alcohol (ROSO_3H) differs from the sulfonic acid (RSO_3H) only in one oxygen atom which suggests that they might produce somewhat similar effects. Sulfonic acids in general are used as catalysts in the manufacture of alkyd resins (9)(2), and neutral phenyl benzene sulfonate (10) has been used as a plasticizer with glycerol phthalate resins.

The purpose of this investigation was to determine whether the resin formed by the reaction of the alkyd resin and sulfonated alcohol would produce a more soluble resin, hard but not brittle, flexible, and suitable for use as a varnish or lacquer resin.

HISTORICAL

Synthetic resin manufacture is a relatively new field of chemistry. The principal motive in creating synthetic resins was not to imitate the natural products, but to improve upon them. As useful as the natural resins are, there is not one that is entirely perfect, and all of them have faults which should be eliminated.

The first account of synthetic resin manufacture was in 1901 when Watson Smith (32) discovered while working with glycerol and phthalic anhydride that they did not form a simple ester on reaction as he had expected, but rather a very hard transparent solid. Since the discovery of this reaction between glycerol and phthalic anhydride there have been many investigations into the mechanism of resin formation.

R. H. Kienle and A. G. Hovy (26) in studying the rate of esterification of two mols of glycerol and three mols of phthalic anhydride found that the reaction proceeds rapidly at first yielding within one minute, at the temperature investigated, a product corresponding to 50% esterification. When the esterification is about 60%-70%, the rate falls off but proceeds more slowly up to and beyond the point where gelation occurs.

The preliminary formation of the monoesters was noted by Honel (18) who found that the continued heating of

the infusible resin after gelation decreased its ability to swell with solvents indicating the process of esterification. He concluded resinification was a formation of compounds of high molecular weight solely by continued esterification of the acid esters first formed. Increase of the amount of glycerol caused the acid number of the mixture to decrease until finally the infusible state could not be reached. He also found that when glycerol and phthalic anhydride were taken in such proportions to form mono- or diesters and heated, the reaction proceeded very slowly at 160°C. Above 230°C however, the reaction was more rapid, but the tendency was to form hard resins.

This reaction between dibasic acids and polybasic alcohols was known for a number of years, but it remained for the inauguration of the lacquer industry to stimulate research on the preparation of resins which would be compatible with nitrocellulose to produce a durable lacquer. The development of synthetic resins of the alkyd type supplied the lacquer industry with an adequate source of resinous material and was in part instrumental in aiding the rapid expansion of this industry.

The pure glycerol phthalate resin is in all cases too insoluble, brittle, and infusible for use in varnishes or lacquers, and various plasticisers, either in the form of soft resins or liquids, have been incorporated into the alkyd

resin to improve its properties.

M. J. Callahan (8) and W. S. Arsen (1) used succinic glyceride as a plasticizer. The disadvantage of using the glycerides of aliphatic dibasic acids to increase the flexibility was that the effect was not permanent. When heated for a long time or when aged, the mixed resin became brittle and tended to have a high acid number.

Kienle and Rohlf (27) suggested the incorporation of glycol succinate with phthalic glyceride in such amounts that the composition cured when heated at a high temperature. About one mol of each resin may be used. The resins may be prepared separately and then mixed or all ingredients heated together at 180°C-200°C. Curing was carried out at 150°C and a soft flexible product was obtained.

High boiling solvents were used to increase the flexibility by Conever (12) who mixed 15 parts of diethyl phthalate with 85 parts of freshly prepared phthalic glyceride and heated the solution to 150°C. A soft light colored resin was obtained which has been converted into a flexible infusible form by heating to a high temperature. R. H. Kienle (28) used dibutyl phthalate, triphenyl phosphate, triacetin, or aniline to overcome the brittleness of the alkyd resin.

The addition of furfural increases flexibility but has the tendency to darken the color. Conever (11) heated a

mixture containing 92 parts of glycerol, 148 parts of phthalic anhydride at 210°C for an hour allowing the temperature to fall to 140°C and added 48 parts of furfural, producing a soft, dark colored mass. This product was converted to the infusible form when heated, the conversion being about ten times as rapid as that of the resin in the absence of furfural.

Blue colored resins of improved mechanical and electrical properties can be formed by the addition of amino carboxylic acids (34) at any stage before the conversion of the resin to its final form.

Harder and more resistant glycerol phthalate resins are prepared by treatment with ketene. The free hydroxyl groups in the glycerol phthalate resin were acetylated under these conditions. The product thus formed was darker in color and had a higher acid number than the original resin but was more resistant to water (7). The ketene treated resin was compatible with nitrocellulose.

A great many other modifying agents have been used in the resin molecule for the same purpose or to produce resins of different properties. The modification of alkyd resins with monobasic acids imparts increased solubility to the resin. Aliphatic acids (butyric, acetic) have a pronounced softening action. Acids from non-drying oils lead to the formation of products of greater flexibility. As a

rule the free acids are used instead of the oils themselves since, with the exception of castor oil, it is difficult to incorporate the glyceride oils into an alkyd resin unless direct methods are used. Other monobasic acids used with alkyd resins include natural resins which increase the solubility and brittleness of the resulting resin.

Other industrial modifying agents for the pure alkyd resin consists of monohydric alcohols (5), ketones (13), and various oils.

The principal use for all of these modified alkyd resins has been in coating compositions, particularly nitrocellulose lacquers. From these previous investigations it was supposed that the incorporation of the sulfonated alcohol into the alkyd resin might produce a resin applicable in the protective coating industry.

THEORETICAL

The rules for resin formation of polybasic acids and polyhydric alcohols given by R. H. Kienle (23) are:

- (1) High molecular weight organic compounds are formed only when the interlinking molecules are poly-reactive.
- (2) The interlinking of the molecules proceeds according to the chance contact of any two reactive points.
- (3) The relative size and shape of the reacting molecules and the position of the reactive points largely determine the physical properties of the resulting polymer, such as, hardness, flexibility, and heat convertibility.

Esterification of a polybasic acid, such as phthalic anhydride, and a polybasic alcohol, such as glycerol, leads to high molecular weight products instead of the pure ester. In studying the reaction of glycerol and phthalic anhydride, R. H. Kienle and A. G. Nevy (25) found that the reaction proceeded by esterification with water and the resin as the only products. No intermediate aldehyde was formed. They stated that the reaction, when carried out at a temperature at which both reactants were liquid, went very rapidly at the start evolving heat, and was apparently half complete within one minute of mixing. This reaction corresponded to the formation of the monoester of phthalic acid.

According to Hönel (18) the internal esterification was responsible for the formation and characteristic properties of the alkyd resins. He regarded the first stage as giving rise to a mixture of the mono- and diglycerides referred to previously. With further heating these react to give condensation products as follows:

Kienle and Hovy (26) also found that as the reaction proceeded under isothermal conditions, the free acidity decreased and the percent esterification and flow point increased. The variation with time was quite irregular although there was a definite trend upward in the reaction.

The resin was clear, colorless, and transparent, and remained so to the end of the reaction when it resembled glass.

Schlenker (31) thought the resins were long chains of glycerol molecules linked at the alpha positions through carboxyl groups of the alternating phthalic acid molecules, while the beta hydroxyl groups were esterified in later stages of the reaction.

According to R. Houwink and K. H. Klaassens (20) only the alpha hydroxyl groups of the glycerol are active below 180°C, but at higher temperatures the beta hydroxyl groups enter into the reaction with the formation of a three dimensional polymer. Further esterification now involving the beta hydroxyl groups might proceed internally, forming such a glyceride.

This is unlikely however, as the limit product is almost completely soluble in very dilute KOH, requiring in fact only as much alkali as is required to neutralize the free acid. The progressive decrease in acidity and corresponding increase in resinlike properties can, however, be far more readily ex-

plained by esterification of a hydroxyl group by the carboxyl group of another molecule.

The continuation of this esterification results in the formation of large molecules containing long branched chains of the type shown, which perhaps further condense to ring structures of higher order. The length of such chains and the corresponding colloidal properties of the resin depend primarily on how long the heat treatment is continued beyond the point at which internal esterification commences. It can be seen that esterification can also take place on the other carboxyl groups of the acid in the molecule as well as the beta hydroxyl group, forming a long chain of linking acid and alcohol molecules, the length and molecular weight of

which are dependent upon the degree of completion to which the reaction was carried. As the size of the molecule becomes greater, it also becomes more complex and more compact with the result that the solubility and fusibility decrease.

The resins have been classified by T. Hedly Barry(4). Accordingly, the resinification products resulting from the condensation of polybasic acids and polyhydric alcohols such as glycerol and phthalic anhydride may be classed in stages as: A-stage which is fusible, soluble in acetone, and not resistant to water. It is converted to B-stage which is fusible, insoluble in acetone, and not resistant to water by heating. This is further converted by heat to C-stage which is infusible, insoluble, and resistant to water.

Substances which have only one reactive group such as monobasic acids and monohydric alcohols, or the sulfonated alcohol used in this research do not give rise to resinous materials. Incorporation of these substances prevents the cross linking of the molecules by decreasing the number of possibilities for reaction, and in general causes the resin to become more soluble and fusible. When a modifying agent is incorporated into the alkyd resin, the possible structure may be represented as;

In the structure, G represents a glycerol molecule with the three hydrogens of the hydroxyl groups replaced, P represents the phthalyl radical, and D represents the modifying agent. If less of the modificant is used, more of the glyceryl radicals tend to unite with phthalyl groups thus approaching the structure of phthalic glyceride.

The effect of conducting the reaction at a higher temperature was to reduce the amount of free acid more rapidly than at a lower temperature. The temperature and time necessary to reach 95% esterification using stoichiometric proportions of glycerol and phthalic anhydride was 1000 minutes at 190°C and 220 minutes at 220°C (25). Shigeru Hirano and Kikinosuke Ohashi (17) reported that one mol of glycerol and one and one-half mols of phthalic anhydride when reacted at 200°C went very fast at first corresponding to one-half reaction. If the same quantities were heated at 180°C, 200°C, and 220°C the reaction became faster, but all the resins formed had the same acid value and softening point. Stiffening occurred at 70% esterification but occurred later when less phthalic anhydride was used, and no stiffening occurred below .88 mols of phthalic anhydride.

EXPERIMENTAL

MATERIALS

The source of the sulfonated alcohol used in this research was from the Procter and Gamble product "Dreft", and the Colgate Palmolive Peet product "Vel". Both products were sodium salts of high molecular weight sulfonated alcohols, but they also contained a quantity of inert material as a filler. These salts were prepared in the following manner according to the Chemical Research Division of Procter and Gamble:

"A fatty acid, for example lauric acid, is treated with hydrogen under tremendous pressure and in the presence of a catalytic agent. The lauric acid is reduced to lauryl alcohol.

The alcohol is sulfated by treatment with sulfuric acid.

The lauryl acid sulfate is treated with sodium hydroxide to form the neutral sodium salt.

To liberate again the lauryl acid sulfate, the sodium salt has only to be treated with a dilute hydrochloric acid solution containing just enough acid to displace

any equilibrium tending to hydrolyze back to lauryl alcohol and sulphuric acid.

Pure long chain acid sulfates were not available as such because the acid was somewhat unstable and could not be kept for a long period of time; but the compound was very stable as the sodium salt.

Mr. E. E. Dreger, director of research of Colgate Palmolive Peet Co. in Jersey City, New Jersey, wrote that "Vel" was the sodium salt of the sulfated monoglycerides of coconut oil fatty acids, and the commercial product contains 35% to 36% active ingredient and 64% to 65% sodium sulfate filler. This was in reality a long chain of carbon atoms containing the acid sulfate groups on the remaining two hydroxyl groups of the glycerol.

In test runs it was found that the sulfonated alcohol extracted from "Vel" was more stable than that extracted from "Dreft" and reacted in the resin mixture more readily probably because of the presence of the glycerol base. Pure sodium lauryl sulfate was obtained from duPont under the trade name "Duponol" and contained no filler whatsoever. This had only to be treated with the dilute acid to separate the pure lauryl acid sulfate. The extracted product was more unstable than the sulfonated glycerol ester and decomposed much more

readily on heating.

The extracted sulfonated alcohol from "Vel" was a brownish oily liquid which was soluble in water forming a soaplike solution similar to that of the sodium salt; but by using large amounts of the sodium alkyl sulfate in small volumes of water and saturating the solution with salt, the acid sulfate was separated. By warming the solution during the salting out, the components were separated more readily. Since the sulfonated alcohol solidified when cooled slightly below room temperature, it could be separated and purified by a process of freezing, removing the liquid portion, and re-melting.

Coconut oil fatty acid has a density of .843, a melting point of 62.6°C , is insoluble in water, and decomposes when heated to a high temperature. Glycerol has a density of 1.26, boils at 290°C , is very soluble in water, and melts at 17°C but solidifies at a much lower temperature. The sulfonated product of the monoester of coconut oil fatty acid and the glycerol had the following physical constants.

Color	brown oil
Density	.971
Melting Point	$26^{\circ}\text{C} - 28^{\circ}\text{C}$

When this product was heated in a distilling flask, it decomposed evolving water and a yellowish green liquid. This liquid,

which was very insoluble in water, distilled from the flask and left a gummy black residue.

The other components used in the cooking of the resins were C. P. flake phthalic anhydride and 95% glycerol.

APPARATUS

All the resins were cooked in a 500 ml. three necked flask set in a constant temperature oil bath so that the temperature of the reaction could be maintained as constant as possible. A 0°C - 360°C thermometer dipped into the reaction mixture through the center neck and recorded the temperature of the reaction mass. A hand stirrer also fit around the thermometer and came through the center neck. This was operated in an up and down motion permitting stirring of the reaction mass.

A slow stream of carbon dioxide gas from a tank of compressed carbon dioxide was bubbled through the resin during the reaction to provide an inert atmosphere and prevent any oxidation from the air. The gas was led into the flask through a tube in one of the small necks, the tube dipping into the reaction mixture and also serving to remove small samples of the cook onto a glass plate for testing purposes. The other small neck was equipped with a water condenser to condense the water evolved in the reaction of the glycerol, sulfonated alcohol, and phthalic anhydride. By measuring the water evolved it was possible to follow the progress of the reaction.

The oil in the oil bath completely covered the flask to prevent the water of reaction from condensing on the sides

of the flask and running back into the reaction mass. In this manner most of the water of reaction was removed from the flask. The carbon dioxide also helped to carry the water vapor from the flask and aided in the agitation of the resin mass.

The source of heat for the oil bath was an electric pad or a bunsen burner.

Fig. 1 Apparatus for Cooking Resins.

PROCEDURE

All the resins were prepared in the apparatus previously described using a constant temperature of 200°C for each run. This temperature was chosen from a study of similar resin reactions in order to determine the best reaction temperature. The range of temperatures generally used in the cooking of alkyd resins was from 180°C to 230°C depending upon the speed of reaction desired. A rather low temperature was chosen to minimize the possibility of any decomposition of the sulfonated alcohol. The resins were all cooked in an inert atmosphere of carbon dioxide to prevent any oxidation from the air and to obtain the lightest colored resin possible. The carbon dioxide gas also served two other purposes: it helped to stir the liquid in the flask, and it helped to carry the water of reaction from the flask.

The three components of the resin were placed in the reaction flask at the start of the run, and the temperature was raised to and held at the reaction temperature until the cook was completed. Extreme care had to be taken in cooking the resins because the sulfonated alcohol and resin mixture were somewhat immiscible at room temperature. At a temperature around 150°C the liquids became miscible and the mixture reacted. The carbon dioxide inlet tube served to remove small samples of the resin from the flask at definite intervals; these samples were placed on a glass plate and

allowed to cool in order to determine how the reaction was proceeding. At the outset of the reaction the cooled test drops of resin had a cloudy appearance, but as the reaction progressed the drops became less cloudy until at the end of the cook the resin had a clear appearance. All the sulfonated alcohol must be reacted or removed from the mixture before the resin thickens, or the components upon cooling will give the resin a cloudy color. R. Houwink and K. H. Klaasens (20) stated that only the alpha hydroxyl groups of the glycerol are active below 180°C , but at a higher temperature the beta hydroxyl groups enter into the reaction with the formation of the three dimensional polymer. Thus by keeping the temperature of reaction below 180°C and taking samples on a test plate at intervals, it was possible to determine when all the alcohol had reacted from the appearance of the cooled resin.

After all the sulfonated alcohol had reacted, the temperature was raised to 200°C and the resin cooked until the thickening point was reached. At times during the course of the reaction some of the sulfonated alcohol distilled over with the water before it had reacted and this had to be subtracted from the original amount of sulfonated alcohol to obtain the actual amount incorporated in the resin.

Stirring is an important factor in the production of a good resin. If the resin batch was not stirred

thoroughly throughout the cooking time, the sulfonated alcohol did not become thoroughly mixed and consequently did not react completely causing the cooled resin to have a cloudy appearance due to the unreacted component. A test cook was conducted on two resins of the same composition and under the same cooking conditions, stirring one but not stirring the other. At the completion of the run it was found that the unagitated resin had a more pronounced cloudy appearance than the stirred resin.

In a comparison of the resins cooked from "Vel" and "Dreft" it was found that the product extracted from "Vel" seemed to react more readily than that extracted from the "Dreft". These resins cooked from the straight chain sulfonated alcohols extracted from "Dreft" and "Duponol" produced very dark colored resins which would be of limited application because of their color. This more pronounced darkening of the resin can be accounted for by the greater instability of these products than the sulfonated alcohol from the "Vel". For this reason the sulfonated alcohol from "Vel" was used throughout this research.

The initial resin was cooked using stoichiometric proportions of glycerol and phthalic anhydride; that is, a ratio of one mole of glycerol to one and one-half mols of phthalic anhydride. All the resins were cooked using 46 grams ($\frac{1}{2}$ mol) of glycerol and in each succeeding resin part of the

phthalic anhydride was substituted for by the sulfonated alcohol. The amounts of sulfonated alcohol were calculated assuming the sulfonated alcohol to be entirely lauryl acid sulfate. This assumption is not entirely accurate because it assumes one reactive acid sulfate group for every molecular weight of 266 while the actual product contains two reactive groups and a molecular weight of 490; or one reactive group for every 245 units of molecular weight. Such an assumption had to be made because the composition of the sulfonated alcohol from "Vel" was not known at the outset of the research.

The sulfonated alcohol would be expected to have acidic properties because glycerol itself exhibits acidic properties due to the accumulation of the hydroxyl groups in the structure. With these groups replaced by acid sulfate groups, it definitely would exhibit acid characteristics.

The sulfonated alcohol and phthalic anhydride both being acids, they would be expected to react with glycerol in the following manner.

Phthalic acid and glycerol:

Straight chain sulfonated alcohol and glycerol:

Glycerol sulfonated alcohol and Glycerol:

Since the phthalic acid and sulfonated alcohol both evolve water when they react with glycerol, it was possible to calculate the theoretical amount of water which should be evolved in the reaction. By collecting the water condensed from the reaction, it was possible to follow the reaction and to measure its extent.

As a means of comparing the reactions, each resin was cooked to the stiffening point and then its esterification was measured. Klenle and Furgusen (24) found that glycerol and phthalic anhydride have only a moderate degree of esterification (75% - 80%) and was heat convertible even when replaced with some monobasic acid. Shigeru Hirano and Kinisuke Ohashi (17) found that stiffening occurred at 70% esterification at all temperatures when stoichiometric proportions of glycerol and phthalic anhydride were used. After

stiffening occurred very little water was evolved, and further esterification could be obtained only by prolonged heating.

DATA AND RESULTS

ESTERIFICATION

In each run the resins were cooked until they reached the stiffening point and the percentage esterification was measured by dividing the actual water collected by the theoretical water which should be evolved. The proportions used in each run were 46 grams ($\frac{1}{2}$ mol) of glycerol and stoichiometric proportions of phthalic anhydride and the sulfonated alcohol. The following table (Table I) shows the effect of the sulfonated alcohol modification on the esterification of the resin.

It can be seen from the data that the sulfonated alcohol tended to increase the percentage esterification which could be obtained in the resin, and this property is shown graphically on Figure 2. This was quite in accordance with the findings of Hirano and Ohashi (17) who found that stiffening occurred at 70% esterification when stoichiometric proportions of glycerol (1 mol) and phthalic anhydride (1.5 mols) were used, and no stiffening occurred below .88 mols of phthalic anhydride. When the sulfonated alcohol was incorporated in the resin, the point of non-stiffening was raised to 1.2 mols of phthalic anhydride as compared to .88 mols when just the glycerol and phthalic anhydride were used.

TABLE I
Modification vs. Esterification

<u>Run #</u>	<u>Mols Glycerol</u>	<u>Mols Phthalic Anhydride</u>	<u>Grams</u>	<u>Modification</u>	
				<u>Mols</u>	<u>Mol Fraction</u>
#1	.5	.75	0.0	.00	.000
#2	.5	.75	0.0	.00	.000
#3	.5	.75	0.0	.00	.000
#4	.5	.73	5.16	.009	.007
#5	.5	.73	12.6	.024	.019
#6	.5	.71	18.6	.035	.028
#7	.5	.73	4.96	.009	.007
#8	.5	.68	27.1	.051	.042
#9	.5	.72	16.0	.030	.024
#10	.5	.67	40.0	.075	.060
#11	.5	.69	28.8	.054	.043
#12	.5	.67	39.2	.074	.060
#13	.5	.65	----	----	----
#14	.5	.68	34.8	.066	.053
#15	.5	.70	25.6	.048	.038
#16	.5	.627	51.6	.097	.078
#17	.5	.609	58.8	.111	.090

<u>Run #</u>	<u>Grams Glycerol</u>	<u>Grams Phthalic Anhydride</u>	<u>Modification</u>		<u>Percent Esterification</u>
			<u>Grams</u>	<u>Wt. %</u>	
#1	46.0	111.0	0.0	0.0	55.6%
#2	46.0	111.0	0.0	0.0	55.0
#3	46.0	111.0	0.0	0.0	56.1
#4	46.0	108.0	5.16	3.22	58.5
#5	46.0	108.0	12.6	7.6	68.9
#6	46.0	105.0	18.6	10.9	72.1
#7	46.0	108.0	4.96	3.12	60.7
#8	46.0	101.0	27.1	15.6	75.8
#9	46.0	106.5	16.0	9.5	63.8
#10	46.0	99.0	40.0	21.6	79.4
#11	46.0	102.0	28.8	15.4	52.2
#12	46.0	99.0	39.2	21.2	77.2
#13	46.0	96.0	----	----	----
#14	46.0	101.0	34.8	19.1	water lost
#15	46.0	104.0	25.6	14.6	72.0
#16	46.0	93.0	51.6	27.1	77.1
#17	46.0	90.0	58.8	30.2	85.1*

* no stiffening

FIGURE 2 Percent Esterification vs. Modification

The question arises whether the components are reacting or just admixing into the resin. Whether the resulting resin is caused by a reaction or just admixing is of secondary importance to the fact that the modification has produced a resin usable in lacquer formulations, which was the original goal of the research. However, there are a number of evidences which indicate that there is a reaction.

(1) In the original unmodified resin it was found that only about 60% esterification took place before the resin stiffened and only 7.1 grams of water were evolved; but in the case of the resin modified with 30 wt. % of sulfonated alcohol and using the same amount of glycerol, there were evolved 12.7 grams of water even though the amount of phthalic anhydride was reduced. The only place this increased water could come from would be from the reaction of the sulfonated alcohol and the glycerol, or from the increased esterification of the glycerol and phthalic anhydride; but had all the phthalic anhydride in the resin reacted, there would have been only 11.0 grams of water evolved. A proof that all the phthalic anhydride had not reacted was shown by the resin having an acid number of 34, and this was a good indication that the sulfonated alcohol reacted.

(2) If the process were one of admixing, one would suppose that if the resins were ground finely they would have the characteristic oily feeling of the sulfonated alcohol;

but this is not the case, for the stiffened resins were hard and ground into a fine powder.

There were also a number of facts that supported these conclusions.

(1) In many cases the sulfonated alcohol occupied an initial volume approximately equal to the volume of glycerol and melted phthalic anhydride. In run #17 the resin mixture occupied 100 ml. and the sulfonated alcohol 75 ml., which would make it extremely difficult to admix this volume of liquid in such a small volume of solidified resin. Resins have been made incorporating as high as 90 ml. of sulfonated alcohol in the same volume of resin mixture.

(2) It was previously discussed that during the cooking of the resin the appearance of the resin mixture changed from cloudy to clear as the cooking proceeded and remained clear at the completion of the reaction. The cloudy appearance at the start of the reaction was accountable to the immiscibility of the resin components and the sulfonated alcohol. The disappearance of this cloudy color was accounted for by the reaction of the sulfonated alcohol, or by the miscibility of the sulfonated alcohol and the finished resin.

(3) When a sample of a highly modified resin was dissolved in a solvent and the solvent evaporated very slowly from it, the original resin was recovered indicating a more

intimate bond than just admixing.

COOKING TIME

Each increase in modification of the pure alkyd with the sulfonated alcohol had a tendency to increase the time of cooking. It was found that it took only 110 minutes for the pure alkyd to reach the thickening point at 200°C, whereas the resin with 30.2 wt. percent of the sulfonated alcohol incorporated in it did not thicken and "set" in the flask even after heating approximately four hours at the same temperature.

COLOR

When cooked in an inert atmosphere, the pure alkyd resin has a clear, water-white, glass-like appearance; but as the resin is modified the color becomes progressively darker until the resin in run #17 (30.2 wt. % modification) is a brownish color but still retains its clear appearance.

HARDNESS

The hardness of the resins change from a very hard, brittle, pure alkyd resin to a soft, tough, and flexible resin when modified with 60 grams (30.2 wt. %) of the sulfonated alcohol. When 80 grams (38.1 wt. %) were incorporated into the resin, it was found that a rubbery resin resulted which would not harden but retained its sticky feeling. Because of its very tough and rubbery properties, it may have

some applications in the adhesives field.

It was apparent that the sulfonated alcohol acted as a plasticiser in the alkyd resin, and this property was very important if the resins were to have any applicability in protective coating applications.

SPECIFIC GRAVITY

As was expected, the specific gravity of the resins decreased as they were further modified because the sulfonated alcohol was a liquid with specific gravity less than unity, and retarded the formation of large, complex, high molecular weight molecules.

The specific gravities of the resins were determined by the water displacement method, by measuring the water displaced by a known weight of resin. The data are listed below and are shown graphically on Figure 3.

TABLE II
Specific Gravity vs. Modification

<u>Run #</u>	<u>Modification</u> <u>Grams</u>	<u>Wt. %</u>	<u>Sample</u> <u>of resin</u>	<u>cc. water</u> <u>displaced</u>	<u>Sp. Gr.</u> <u>Gms./cc</u>
#2	0.0	0.0	9.829	7.40	1.330
#3	0.0	0.0	15.027	11.10	1.356
#4	5.16	3.22	12.329	9.31	1.332
#5	12.6	7.6	12.208	9.15	1.338
#6	18.6	10.9	12.589	9.80	1.299
#7	4.96	3.12	12.619	9.51	1.329
#8	27.1	15.6	13.328	10.39	1.280
#9	16.0	9.5	8.604	6.50	1.325
#10	40.2	21.6	9.834	8.30	1.185
#11	28.8	15.4	10.859	8.50	1.276
#12	39.2	21.2	5.836	4.90	1.195
#14	34.8	19.1	11.932	9.28	1.273
			11.885	9.20	1.270
#15	25.6	14.6	13.795	10.61	1.301
#16	51.6	27.1	14.026	11.60	1.210
#17	58.8	30.2	13.399	11.42	1.172

FIGURE 3 Specific Gravity vs. Modification

ACID NUMBER

At the start of a resin cook a definite amount of acid (phthalic anhydride) and the other constituents of the resin were placed in the reaction flask, and as these reacted the amount of unreacted acid decreased because the carboxyl groups of the phthalic acid were being esterified by the hydroxyl groups of the glycerol. During the cooking of the resin the mass usually gelled or reached the infusible state before all the carboxyl groups were reacted, leaving the resin with a certain amount of free acid. Previous references have shown this to be about 60% - 70% reaction.

The acid number of a resin is a measure of the free acidity in the resin and is defined as the number of milligrams of potassium hydroxide necessary to neutralize the free acid in a one gram sample of the resin. It is desirable to have as low an acid number as possible in the resin, for the greater the free acid the more vulnerable is the resin to deterioration.

The procedure used in determining the acid values was to weigh a known weight of resin (approx. one gram) into a 500 ml. erlenmeyer flask; this was treated with 25 ml. of acetone and allowed to stand (preferable overnight) until all the free acid was dissolved. The acid solution was taken up in 250 ml. of distilled water and the solution heated to remove most of the acetone. This solution was titrated with a

previously standardized potassium hydroxide solution of about five units of acid number per cubic centimeter, using phenolphthalein as the indicator and titrating to the first pink tinge. The indicator color will always disappear as the solution stands since an excess of base will always saponify the resin in the bottom of the flask until this resin entirely disappears. From the weight of sample and the cubic centimeters of base used, the acid numbers of the resins were calculated. Three samples were run on each resin and the average taken. The trend of the acid numbers are as follows, and are shown graphically on Figure 4.

TABLE III
Acid Value vs. Modification

<u>Run #</u>	<u>Modification</u>		<u>Acid Value</u>
	<u>Grams</u>	<u>Wt. %</u>	
#2	0.0	0.0	160.0
#3	0.0	0.0	175.0
#4	5.16	3.22	125.7
#5	12.6	7.6	118.0
#6	18.6	10.9	114.0
#7	4.96	3.12	109.4
#8	27.1	15.6	67.0
#9	16.0	9.5	82.7
#10	40.2	21.6	
#11	28.8	15.4	56.0
#12	39.2	21.2	32.1
#13			
#14	34.8	19.1	75.8
#15	25.6	14.6	55.9
#16	51.5	27.1	41.5
#17	58.8	30.2	34.0
#18	80.0	38.1	34.0

Figure 4 Acid Number vs. Modification

It can be seen from the data that the acid number decreased as the resin was modified. This was to be expected since it has been seen that the esterification increased as the resins were modified, which necessitated more of the phthalic anhydride to react. The effect of the sulfonated alcohol was presumably to retard the gelling of the resin allowing more of the phthalic anhydride to react.

It must be remembered when considering the acid numbers of these resins that each resin was cooked using stoichiometric proportions of material; and in order to obtain an acid number of zero, the reaction would have to go to completion. The object was not to obtain as low an acid number as possible in each resin, but rather to find how the acid number changed as the resin was modified.

Lower acid numbers could be obtained in each of the resins in a number of ways. First, if an excess of glycerol were used over the theoretical amount, there would be more hydroxyl groups for the carboxyl groups of the phthalic anhydride to react with, and consequently there would be less free phthalic anhydride in the resin. Second, in industry, before the resin is finished cooking, a stream of inert gas is bubbled vigorously through the resin which carries the unreacted phthalic anhydride with it and sublimates it on a cold wall outside of the reaction vessel. In this manner most of the unreacted phthalic anhydride was removed, leaving a resin

with a low acid number. This effect was not apparent in this research because the velocity of the carbon dioxide gas was too low to force the phthalic anhydride vapor from the flask.

The theoretical relationship between molecular weight and acid number representing various stages in the esterification of phthalic anhydride and glycerol was given by Ellis (14) and is shown below where P represents phthalic anhydride, and G represents glycerol. A terminal P implied the presence of a carboxyl group, and a terminal G represented a dihydroxy group.

TABLE IV

Molecular Weight vs. Acid Number

<u>Formula</u>	<u>Molecular Weight</u>	<u>Acid Number</u>
GP	240	233
GPGP	462	121
GPGPGP	684	82
GPGPGPGP	906	62
PGP	388	289
PGPGP	616	184
PGPGPGP	832	135
PGPGPGPGP	1054	106

SOLUBILITY

The solubilities of the various resins were taken using several different solvents to show their trend. Since the resins were cooked to the stiffening point, the solubilities were very low, but each modified resin showed an increase in solubility as more sulfonated alcohol was incorporated.

The solubilities were determined by refluxing an excess of resin for one half hour in approximately 150 ml. of solvent, after which time the solution was allowed to settle and the clear liquid decanted from the undissolved resin. The clear liquid was placed in a previously weighed flask and the solvent distilled from the resin. After drying the flask in an electric oven to remove the last trace of solvent, it was weighed again and the weight of resin in the known amount of solvent was determined (15). All the solubilities were converted to grams of resin dissolved in one liter of solvent, and they are plotted as such on Figure 5.

In all solvents there was an increase in solubility even though the reaction had proceeded to a greater amount of esterification, showing that the sulfonated alcohol had increased the solubility. After sixty grams (30.2 wt. %) were incorporated, the resin no longer reached the stiffening point and there was a marked increase in the solubility. From

observation of the unstiffened resins it has been noted that those resins having the greatest modification dissolved more readily than those of lower modification. The solubility data are tabulated below and are expressed graphically on Figure 5.

TABLE V
Solubility vs. Modification

<u>Run #</u>	<u>Modification</u>		<u>Solubility</u>	
	<u>Grams</u>	<u>Wt. %</u>	<u>Butyl Acetate</u>	<u>gas./l. Toluene</u>
#2	0.0	0.0	7.45	.116
			10.05	
#3	0.0	0.0	7.6	
#4	5.16	3.22	9.79	
#5	12.6	7.6	11.71	.362
#7	4.96	3.12	8.55	.200
				.192
#8	27.1	15.6	14.63	.447
#9	16.0	9.5	12.4	.458
#10	40.2	21.6	17.25	.559
#11	28.8	15.4	13.62	.757
#11			17.50	.769
#12	39.2	21.2		.840
#14	34.8	19.1	6.98	.850
			6.69	.968
#15	25.6	14.6	4.7	
#16	51.6	27.1	14.35	
#17	58.8	30.2	very soluble	
#18	80.0	38.1	very soluble	

As a result of cooking the resins to the stiffening point, it was apparent that the solubilities were very low. In most cases they were so small that it was difficult to obtain very accurate data, but from the data gathered it was shown that the solubilities increased as the alkyd resins

Figure 5 Solubility vs. Percent Modification

were modified. However the data did show the insoluble and the infusible form of the stage C resin. They also showed that butyl acetate was a much better solvent for the alkyd resins than the ring solvent toluene.

Since the previous resins were cooked to the thickening point, it was impossible to dissolve them in any solvent to a great enough degree to cast a film from them. Before the resins could be applied in varnishes and lacquers, recooks had to be made by taking test drops of the resin onto a glass plate in order to determine when the correct viscosity had been reached, and stopping the reaction just before it came into the infusible and insoluble state. In this manner an acid number as low as possible was obtained without the resin becoming infusible and insoluble.

The recooked resins contained the following modification: no sulfonated alcohol, 21 grams, 40 grams, 58.8 grams, and 80 grams of the sulfonated alcohol all based on one half mol of glycerol and three fourths mol of phthalic anhydride.

COMPATIBILITY

An important factor in the production of lacquers was the question of the compatibility of the resins with nitrocellulose, ethyl cellulose, or other cellulose lacquer bases. Compatibilities were a measure of the amount of resin

which could be mixed with the cellulose derivative without producing a cloudy lacquer.

Compatibilities were tested by preparing a 50% solution of resin in a solvent, and adding this to a 5%-10% solution of nitrocellulose or cellulose derivative in the same solvent until the solution showed a slight haze due to the incompatibility. Butyl acetate was used as the solvent because all the resins dissolved in it more readily than in any other solvent. A mixture of 90% toluene and 10% ethyl alcohol is generally used for compatibility runs, but all the resins were not soluble enough in this mixture to permit its use.

After each small addition of resin solution to the nitrocellulose solution, a film was cast on a glass plate and allowed to dry. Two effects of resin incompatibility were recognized in determining the compatibility limits with the resins. The content of resin which imparted a permanent slight haze to the film was noted as the limit of haze free compatibility. Since many of the hazy films are apparently homogeneous and often possessed a high gloss, a second compatibility limit was determined as the resin content at which the film began to lose gloss. Many resins would be satisfactory in pigmented lacquers at concentrations considerably higher than the haze free limit required by clear films.

The compatibilities were expressed as the percentage of resin as compared to the weight of nitrocellulose or ethyl cellulose. This means that a 50% compatibility indicated that 5 grams of resin were compatible with 10 grams of nitrocellulose in the lacquer. The results of the compatibility tests are shown on Table VI.

The results of the compatibility tests showed the increase in compatibility of the resins with both ethyl cellulose and nitrocellulose as the alkyd resins were modified. It also showed a marked difference in compatibility in the two cellulose derivatives, it being much more compatible with nitrocellulose than the ethyl cellulose.

The fact that more than an equal amount of 30.2 wt. percent modified resin was compatible with a definite weight of nitrocellulose suggested the possible use of the resin in nitrocellulose lacquers.

TABLE VI

Compatibility vs. Modification

Resin Solutions

<u>Modification</u>	<u>Gms. Resin</u>	<u>cc Solvent</u>	<u>Gms./cc (sol)</u>
0.0	14.102	21.0	.444
21.0	15.965	23.2	.437
58.8	9.71	13.5	.410

Compatibility Tests

<u>Modification</u>	<u>Gms. Deriv. in 10% solution</u>		<u>Liquid Haze Limit</u>	
	<u>Ethylcel</u>	<u>Nitrocel.</u>	<u>cc</u>	<u>%</u>
0.0	6.102		.1	.72%
21.0	6.053		.2	1.47
58.8	6.003		.4	3.0
0.0		6.472	.1	.68%
21.0		5.335	.4	3.33
58.8		8.559	5.3	27.9 s

<u>Modification</u>	<u>Film Haze Limit</u>		<u>Loss of Gloss</u>	
	<u>cc</u>	<u>%</u>	<u>cc</u>	<u>%</u>
0.0	.1	.72%	.2	1.44%
21.0	.2	1.47	.4	2.94
58.8	.4	3.0	1.0	7.50
0.0	.2	1.36	.6	4.08
21.0	1.0	8.31	2.2	18.3
58.8	>22.8	>110.0	>22.8	>110.0

s very slight

APPLICATIONS

LACQUERS

Since the modification of the alkyd resins had produced compatibility with nitrocellulose, the possible use of these resins in lacquers was considered. Because of only limited compatibility below 26 wt. % (50 grams) of sulfonated alcohol, only those resins above this modification were applied in the lacquer work.

While the addition of fossil resins increases the viscosity and shortens the life of the lacquer film formed, the addition of synthetic resins prolongs the life of the films. Synthetic resins are used for their effect upon the gloss, hardness, and adherence of the deposited film, and to increase the solids content of the solution without materially increasing the viscosity.

There are two types of synthetic resins used in lacquer formulations: hard resins and plastic resins. Hard resins exhibit such qualities as high melting point, hardness, rapid release of solvent, low viscosity in solution, high gloss, and good durability, and lend themselves to low ratio introduced to the nitrocellulose content. They require plasticiser addition. Plastic resins are very flexible and permit the use of a relatively high ratio of resin to nitrocellulose. They do not act as plasticisers however, and a plasticiser must be added. All the modified resins used in the following lacquer formulations in this thesis would be

classified as plastic or soft resins.

Resins perform the function of adhesion to an applied surface, increase the lustre, permit rubbing of the film to a relatively greater depth, and add solids or film building properties.

Nitrocellulose is the basic film forming component and improves the drying time, hardness, and water resistance of the resulting lacquer.

Plasticisers increase the elongation of the film. Plasticisers also increase the flow of the lacquer just before it sets to produce a level film and prevent blushing. They play an important part in fusing the resin and nitrocellulose into a wholly homogeneous film. Excess of plasticiser has no bearing on gloss, and there is an optimum plasticiser content beyond which no increase in adherence, tensile strength, or gloss of the film occurs. It will be noted that each ingredient imparts to the lacquer certain specific properties peculiar to that ingredient, and it is almost hopeless to expect to obtain all the desirable properties in one lacquer with the same raw materials.

Lacquers were made in various formulations using the modified resin, $\frac{1}{2}$ second nitrocellulose, and castor oil as the plasticiser. Butyl acetate was used as the solvent throughout the work, and all the viscosities were maintained

as nearly the same as possible and comparable to an 8% solution of $\frac{1}{2}$ second nitrocellulose in butyl acetate. These lacquers were subjected to various tests to determine the effects of the resins on the resulting films.

Adherence: (33)

Films of each lacquer were cast on tin plates using a .008 inch film doctor blade and allowed to dry overnight. Each plate was cleaned thoroughly using toluene and a clean rag before the lacquer was cast upon it. The dried lacquer was crisscrossed into $\frac{1}{16}$ inch squares with a razor blade. If the lacquer flaked or peeled in cutting, the adherence was very poor. If it remained on the panel but could be removed easily with the thumb nail, it was rated poor. If a fair amount of effort was required to remove the squares with the thumb nail, the adherence was fair. If a knife blade was required, the adherence was rated as good.

The chemical structure of the plasticiser has a definite bearing upon the adherence. In general phosphates have a better adherence than do other types of plasticisers. Adherence of a lacquer is also greatly affected by the surface to which it is applied. A lacquer that is adherent to one type of surface will not necessarily be adherent to another.

Brittleness: (33)

A measure of the brittleness of the lacquers was made by bending the previously prepared tin plates at a sharp angle and rating the films as passed or failed according to whether the film cracked or not. The brittleness of a lacquer is increased with the greater amount of resin in the formulation, and it is the function of the plasticiser to reduce this tendency.

Pencil Hardness: (33)

As a means of determining their relative hardness, films of each lacquer were cast on cleaned and dried tin panels and allowed to dry overnight. The lacquers were tested by scratching the films with a number of pencils of varying hardness (2B to 8H). By writing on each film using the same writing pressure and using successively pencils with harder lead (3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, 6H, 7H, 8H), one could observe what hardness of lead was necessary to scratch the film. The hardness recorded was the softest lead which would cut the film.

This test gives only a measure of the relative hardness of the films, and is dependent upon the person doing the testing. It was generally considered that a hardness of 4H is a good film hardness, and all lacquers harder than 4H have been rated as passing.

Cold Check Test: (33)

Lacquer films are generally subjected to the cold check test to determine their durability and flexibility. Films were cast on 4 x 6 inch steel plates which had previously been well cleaned with toluene. The plates were then subjected to alternate periods of one hour at 150°F and one hour at -5°F, care being taken that they were transferred as rapidly as possible from the high to low temperatures, a period of one hour at each temperature, or two hours in all, constituted one complete cycle. This caused a continued rapid expansion and contraction of the panel and film. Those lacquers which withstood twenty cycles were rated as passing, and those that developed checking during that period were considered failures.

Two formulations of lacquers were made, one using the resin containing 30.2 wt. % (58.8 grams) of the sulfonated alcohol, and the other containing 38.1 wt. % (80 grams) of the sulfonated alcohol. Lacquers made from the 21.1 wt. % (40 grams) modified resin exhibited incompatibility haze, showing that resins must be modified with at least 26 wt. % of sulfonated alcohol to be useful in lacquers. The tables following list the lacquer data, and they are also presented graphically on the trilinear Figures 7 and 8, respectively. Lacquers need not fulfill all the requirements for

any special purpose, and the region meeting any specific specifications can be found by a study of the curves.

TABLE VII

Lacquer Properties vs. Lacquer Composition

30.2 Wt. % Resin

<u>Lacquer</u> <u>No.</u>	<u>%</u> <u>Resin</u>	<u>%</u> <u>Nitrocel.</u>	<u>%</u> <u>Plast.</u>	<u>Adherence</u>	<u>Brittleness</u>
#0	0.0	100.0	0.0	good	passed
#1	29.4	70.6	0.0	fair	failed
#2	39.0	61.0	0.0	poor	failed
#3	22.2	77.8	0.0	good	passed
#4	44.2	55.8	0.0	poor	failed
#5	52.5	47.5	0.0	poor	failed
#6	100.0	0.0	0.0	fair	passed
C10	0.0	90.0	10.0	good	passed
C20	0.0	80.0	20.0	good	passed
C30	0.0	70.0	30.0	good	passed
C40	0.0	60.0	40.0	fair	passed
C50	0.0	50.0	50.0	fair	passed
#7	35.0	35.0	30.0	fair	passed

<u>Lacquer</u> <u>No.</u>	<u>Hardness</u>	<u>Cold</u> <u>Cheek</u>	<u>Color</u>	<u>Gloss</u>	<u>Print Test</u>
#0	8H	passed	clear	fair	passed
#1	7H	passed	clear	fair	passed
#2	7H	passed	clear	fair	passed
#3	8H	passed	light	good-f	passed
#4	6H	passed	light	good	passed
#5	5H	passed	tan	good	passed
#6	soft	passed	tan	v good	failed
C10	7H	passed	clear	good-f	passed
C20	6H	passed	clear	good-f	passed
C30	5H	failed	clear	fair	passed
C40	3H	passed	clear	fair	passed
C50	F	passed	clear	fair	passed
#7	2H	passed	light	good	failed

FIGURE 6

Lacquer Properties vs. Lacquer Formulation

30.3 Wt. % Resin

TABLE VIII
 Lacquer Properties vs. Lacquer Composition
 38.1 Wt. % Resin

<u>Lacquer No.</u>	<u>% Resin</u>	<u>% Nitrocel.</u>	<u>% Plast.</u>	<u>Adherence</u>	<u>Brittleness</u>
80- 0	0.0	100.0	0.0	good	passed
80- 10	10.0	90.0	0.0	good	passed
80- 20	20.0	80.0	0.0	good	passed
80- 30	30.0	70.0	0.0	fair	passed
80- 40	40.0	60.0	0.0	fair	failed
80- 50	50.0	50.0	0.0	poor	failed
80- 60	60.0	40.0	0.0	poor	failed
80- 70	70.0	30.0	0.0	poor	failed
80- 90	90.0	10.0	0.0	soft	passed
80-100	100.0	0.0	0.0	soft	passed
010	0.0	90.0	10.0	good	passed
020	0.0	80.0	20.0	good	passed
030	0.0	70.0	30.0	good	passed
040	0.0	60.0	40.0	fair	passed
050	0.0	50.0	50.0	fair	passed
060	0.0	40.0	60.0	poor	passed
#10	30.0	50.0	20.0	poor	passed
#11	32.0	48.0	20.0	fair-p	failed
#12	20.0	60.0	20.0	fair	failed
#13	33.0	33.0	34.0	fair-g	passed
#14	35.0	35.0	30.0	fair	passed
#15	30.0	60.0	10.0	good	passed
#16	40.0	50.0	10.0	good	failed
80- 40	40.0	60.0	0.0	fair	failed
10010	10.0	80.0	10.0	good	passed
10020	10.0	70.0	20.0	good	slight
10030	10.0	60.0	30.0	fair	passed
10040	10.0	50.0	40.0	poor	passed
10050	10.0	40.0	50.0	good	failed

TABLE VIII (con't)

Lacquer Properties vs. Lacquer Composition

38.1 Wt. % Resin

Lacquer					
<u>No.</u>	<u>Hardness</u>	<u>Cold</u> <u>Check</u>	<u>Color</u>	<u>Gloss</u>	<u>Print Test</u>
80- 0	8H	passed	clear	fair	passed
80- 10	8H	passed	clear	fair	passed
80- 20	8H	passed	slight	fair	passed
80- 30	7H	passed	slight	fair-g	passed
80- 40	5H	passed	slight	good	passed
80- 50	3H	passed	slight	good	passed
80- 60	2H	passed	tan	good	passed
80- 70	F	passed	dark	fair	passed
80- 90	soft	passed	dark	poor	failed
80-100	soft	passed	dark	poor	failed
C10	7H	passed	clear	good-f	passed
C20	6H	passed	clear	good-f	passed
C30	5H	passed	clear	fair	passed
C40	3H	failed	clear	fair	passed
C50	F	passed	clear	fair	passed
C60	soft	passed	clear	fair	failed
#10	4H	passed	slight	good	passed
#11	5H	passed	slight	good	passed
#12	6H	passed	clear	fair	passed
#13	HB	passed	slight	good	passed
#14	HB	passed	slight	good	passed
#15	7H	passed	slight	fair	passed
#16	5H	passed	tan	good	passed
80- 40	6H	passed	slight	good	passed
10010	8H	passed	clear	fair	passed
10020	6H	passed	clear	fair	passed
10030	6H	passed	clear	fair	passed
10040	3H	passed	clear	fair	passed
10050	F	passed	clear	fair	failed

FIGURE 7

Lacquer Properties vs. Lacquer Formulation

38.1 Wt. % Resin

VARNISHES

As a means of determining the usability of the resins in varnishes, it was decided to cook the resins into varnishes and compare the resulting films. All the varnishes were to be cooked using the following formulation:

Resin	100 parts
Tung Oil	200 parts
Bodied Linseed Oil	100 parts
Mineral Spirits	375 parts

The resin was dispersed into the tung oil and heated to 175°C, then to 260°C in ten minutes, and to 295°C in ten more minutes. The bodied linseed oil was added to chill back the reaction and the mixture was thinned with mineral spirits at 200°C. To the resulting varnish was added driers in the following proportions, based on the oil:

.02%	cobalt metal drier
.10%	manganese metal drier
.50%	lead metal drier

The resins were not oil soluble and other methods had to be resorted to if the resins were to be utilized. Difficulty was encountered in the dispersion of the resin into the tung oil, for heat would not disperse the solid resin into the oil. Even in the case of the resins which would melt the same difficulty was encountered, for after the varnish was cooked and thinned, the resin would be found in small pieces on the bottom of the varnish kettle. It was thought that grinding the resin very finely into the oil before

heating might cause dispersion, but this also failed.

Joachim (21) said that drying oils cannot be easily incorporated with glycerol phthalate. Mere addition of a common solvent or adding the drying oil to the melted resin was not sufficient. To combine drying oils directly high temperatures are resorted to in an autoclave or long reactions through the use of high boiling liquids.

Ellis (14)(1) also stated that drying oils cannot be blended with phthalic glyceride by merely mixing in a common solvent or by adding the oils directly to the fused resin. When a drying oil was heated with a mixture of phthalic glyceride and glycerol, the combination of the oil occurred so slowly that the resin usually gelled before the resin reacted. However glycerol phthalate could be combined with a drying oil in any proportion by heating the two in the presence of a high boiling solvent. For example, when tung oil was heated with a solution of phthalic glyceride in benzyl benzoate and heated for a long time at 200°C , the oil gradually thickened and finally dispersed into the resin. Upon removal of the solvent by distillation a product of the resin and drying oil was obtained.

An attempt was made to disperse the resin into the tung oil using tetralin as the high boiling solvent and heating the mixture for a long time at 200°C . In each case

it was found that upon distilling the solvent off that the resin had not completely dispersed into the oil and consequently could not be used in correlating data on varnishes cooked using these resins. It was apparent, however, that the resins with the greater modification were more easily dispersed but would not disperse completely even with long cooking.

In a study of the various modified alkyd resins used in varnish production, it was found that the great majority of them were modified with drying, semi-drying, or non-drying oils, or the fatty acids of these oils. Incorporation of a definite amount of oil into the resin was necessary in order to make it soluble in oil and suitable for varnish use.

Because of the difficulty of dispersing the modified resins into the tung oil, it was unlikely that the sulfonated alcohol modified resin could be applied in varnish manufacture. The resin might be modified with some oil along with the sulfonated alcohol to make it oil soluble, but that was beyond the scope of this thesis, which deals only with the pure sulfonated alcohol alkyd resin.

INTERPRETATION OF RESULTS

A survey of the data on the modification of the alkyd resin by the sulfonated alcohol indicated that the incorporation had a softening and plasticising effect in the resin; the effects becoming more noticeable as the modification was increased. This plastification had been accompanied by an increase in esterification, decrease in specific gravity, decrease in acid number, decrease in hardness, increase in solubility, and gradual darkening of the color of the resins as the resins were further modified with the sulfonated alcohol.

By far the most important result of the modification was the increased compatibility with cellulose derivatives imparted by the sulfonated alcohol, producing resins suitable for use in lacquer formulations.

The lacquers formed from the modified resins proved to meet most of the specifications required for a usable lacquer. These properties have been plotted on the enclosed trilinear charts, and the properties of any formulation of resin, nitrocellulose, and castor oil can be found by referring to that point on the chart. One disadvantage of the lacquers was the slight brown color imparted by the resin, but the gloss was good, and they would be suitable for pigmented lacquer films. The results of the lacquer work can best be expressed by the use of the following trilinear diagram:

FIGURE 8
Variation of Lacquer Properties

The resulting sulfonated alcohol modified resins had no use in varnish applications because of their insolubility in varnish oils.

CONCLUSIONS AND RECOMMENDATIONS

A number of effects were apparent as the alkyd resin was modified with the sulfonated alcohol, using stoichiometric proportions of materials. These were with increasing modification:

1. Increase in esterification before thickening
2. Decrease in acid number
3. Decrease in specific gravity
4. Increase in solubility
5. Plastification of the resin
6. Increased cooking time at the same temperature
7. Gradual darkening of the resin
8. Increased compatibility with nitrocellulose making possible the use of the resins in nitrocellulose lacquer formulations.
9. Poor oil solubility eliminating the possibility of varnish application.

Generally saturated fatty acid modified alkyd resin lacquers are superior in adherence, toughness, and resistance to oils and alcohols (29). They form lacquers of exceptional durability on exposure to weather. Further work could possibly be done on prolonged weathering tests to check the analogy between the sulfonated alcohol modified alkyd resin lacquers and the fatty acid modified resin lacquers.

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