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Abstract

Over 60 air-dry resins were designed and synthesized to provide prototype resins for cylinder-wipe intaglio inks. Most of the resins contain linseed oil fatty acids as the air-dry part. The polyols used are trimethylol propane, pentaerythritol, dipentaerythritol, and tripentaerythritol. In some cases, sebacic acid was used to extend the polyols to polyesters. In other cases, "super drying oil" resins were synthesized from tripentaerythritol and linseed oil fatty acids. Inks made from the resins must disperse in 1% aqueous alkali. Acid groups were introduced into the resins using trimellitic anhydride, phthalic anhydride or succinic anhydride.

Inks made from air-dry resins must pass two preliminary tests, one for dispersion in aqueous alkali before curing and one for resistance to the same solution after curing. Two resins, one a super-drying-oil type molecule based on tripentaerythritol and one a more typical alkyd based on pentaerythritol, gave inks which passed these tests.

Executive Summary

Various types of air-dry curing resins have been synthesized at NIST for intaglio cylinder wipe inks to be used in printing currency at the BEP. Properties and performance of inks made from these resins have been measured in laboratory tests at BEP.

The properties required of an intaglio ink resin include low toxicity, viscosity of about 25 to 200 poises depending on the amount of solvent used in the ink, the ability to disperse the extenders and pigments during manufacture of the ink, satisfactory pot life of the formulated ink, good flow, satisfactory dispersion of the ink from the wiping cylinder using the liquid cleaning system, reasonably fast cure speed, and good mechanical strength and resistance to aqueous alkali in the cured film.

In work under this program, over 60 air-dry resins have been designed and synthesized. The resins fall into two classes. One class is based on esters of drying oil fatty acids and tripentaerythritol. The second class consists of pentaerythritol or trimethylol propane partially esterified with linseed oil fatty acids and extended using sebacic acid. Both classes contain carboxylic acid groups and alcohol groups to confer water dispersibility or solubility. Several of the resins supplied to BEP had many of the required properties. One resin in each class gave inks which passed BEP's preliminary tests. Some of the resins are of relatively low viscosity so that they need not be diluted with solvent. This looks forward to the day when the limits on added solvent are revised to lower limits.

The program has included the active participation of Thomas F. O'Brien of BEP to aid in the design and synthesis stages, to formulate the inks and to transfer the knowledge and experience of these systems to BEP, where they can be used to design and specify resins purchased from outside suppliers.

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1. Introduction

Air-dry intaglio ink resins are based on a long-established technology which requires that the ink cure under the action of atmospheric oxidation. Few materials will cure this way. The only practical system is one based on the naturally available drying oils. These oils are commonly reacted chemically to make larger molecules known as alkyds (1). Alkyds cure faster than simple drying oils because some of the chemical bonds needed to cure the material are formed in the manufacturing process rather than in the time after printing.

Because alkyds contain large molecules which are essentially polyesters, they are typically so viscous that they must be diluted before use. Air pollution rules (2) limit the amount of volatile organic solvent which can be used for dilution. The current limit for volatile organic compounds in a non-heat set, cylinder wipe intaglio ink in the District of Columbia is 12% based on the weight of the ink. Some of the resins synthesized in this work are of relatively low viscosity so that they need not be diluted with solvent.

This work was a continuation of a small effort begun in FY87 to explore ways to make resins which would met BEP objectives. Various types of air dry resins based on drying oil technology have been synthesized and taken to BEP for evaluation. BEP intaglio inks must be dispersible in Dalmar solution (aqueous alkali containing surfactant). The resins synthesized early in this work were based on polyvinyl alcohol to confer the ability to disperse in water alone, without the need for alkali and surfactant. Later resins were based on carboxylic acid groups to confer dispersibility in aqueous alkali. Such resins are inherently lacking in resistance to aqueous alkali when cured. Several avenues were explored to provide resins which are expected to give more densely crosslinked films after curing. Densely crosslinked films are known to have greatly improved resistance to aqueous alkali.

2. Drying oils and alkyds

Natural oils are based on the esters of long chain fatty acids with polyols (1). The structure of a natural oil is shown in Figure 1. This structure represents the tri-ester of a (saturated) C_{18} fatty acid with the tri-hydric alcohol glycerol (Figure 2). Oils which do not contain double bonds do not dry under oxidation by air. Therefore, only those oils (and their derivatives) which contain fatty acids such as

$HOOC-(CH_2-)_6CH_2-CH=CH-CH_2-CH=CH-CH_2-CH_2-CH_2-CH_2-CH_3$

1 2-7 8 9 10 11 12 13 14 15 16 17 18

Linoleic acid

$HOOC-(CH_2-)_6CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH_3$

1 2-7 8 9 10 11 12 13 14 15 16 17 18

Linolenic acid

$HOOC-(CH_2-)_6CH_2-CH=CH-CH=CH-CH=CH-CH_2-CH_2-CH_2-CH_3$

1 2-7 8 9 10 11 12 13 14 15 16 17 18

Eleostearic acid

will cure as a result of oxidation by air. The products of air oxidation include hydroperoxide groups, -O-O-H. These groups decompose spontaneously under the action of heat and UV to give free radicals. The decomposition is greatly speeded up in the presence of transition metal salts known as driers. The free radicals add to the double bonds in the fatty acid side chains and produce some crosslinking of adjacent oil molecules to give a cured film, as indicated in Figure 3.

Natural oils containing eleostearic acid cure more quickly than other oils. However, cured films containing eleostearic acid derivatives buckle, wrinkle and oxidize so much that they become too brittle. Also, eleostearic acid is not commercially available in bulk. Nearly all synthetic air-dry materials are based on linseed oil fatty acids or tall oil fatty acids, both of which contain appreciable amounts of linoleic and linolenic acids.

To design a resin which will cure more quickly than a natural oil, more than three fatty acids are placed on each molecule. This may be carried by using a higher polyol, examples of which are shown in Figure 4 (pentaerythritol, PE), and Figure 5 (tripentaerythritol, TPE), instead of glycerol. One of our approaches has been to synthesize a family of resins based on TPE.

A second way to place more than three fatty acid side arms on each molecule is to make an extended polyester/polyol, as shown in Figure 6. The tri-hydric alcohol trimethylol propane (Figure 7) is often used instead of glycerol because it contains three primary alcohol groups. This type of molecule is known as an alkyd. We have also synthesized a family of alkyd resins. In this work, we have referred to all our resins as alkyds. An extended polyester chain with fatty acid side chains is what is usually meant by the term alkyd.

The uncured resin must disperse in alkaline aqueous surfactant. Most of the resins described in this work have been made with acid groups. A natural drying oil is difficult to make dispersible, because a significant fraction (one third) of the arms would be lost if the acid groups are placed on the polyol part. Also, a significant part of the double bonds would be lost if the acid groups are placed on the fatty acid side arm. The oil containing the most unsaturation is tung oil, which can be acidified by maleation as shown schematically in Figures 8a and 8b. 80% of the fatty acid in tung oil is eleostearic acid, which contains three conjugated double bonds. If TPE is used as the polyol and is completely esterified, a "super drying oil" molecule with eight fatty acid side chains is obtained (Figure 8c). In this case, it is feasible to forego two or three fatty acid side chains and attach the acid groups to the polyol, as in Figure 8d.

3. Experimental details of alkyd syntheses

All alkyds were designed and synthesized in a similar way.

The main considerations in designing an intaglio resin are:

1) Given the time constraints, the reaction can not be designed to be stoichiometric and to be carried out to 100% completion, so the reaction must be designed so that some hydroxyl groups are left in excess. In our resins, this was typically 5% of the total number of reactive groups (i.e., all acid groups and hydroxyl groups present initially).

2) The reaction mixture must not gel.

3) A large fatty acid content (>55%) will confer more crosslinking in the cured film and lead to a less viscous resin but will make the resin more hydrophobic and thus harder to disperse in aqueous alkali. Therefore the acid number must be increased with the fatty acid content. We used a range of acid numbers from 70 to 130 g KOH per Kg resin.

4) The viscosity must be kept reasonably low, i.e., less than 200 poises. Thus aliphatic materials must be used rather than aromatic materials. We have used sebacic acid in place of the more usual isophthalic acid and succinic anhydride in place of the more usual phthalic anhydride or trimellitic anhydride.

The spreadsheet shown in Figure SS1 was used to arrive at a reaction composition which would:

1) have a gel point near to or above 100% reaction in the first step,

2) provide a resin with the desired acid number and which contains the desired amount of fatty acid (% oil), and

3) have excess hydroxyl groups.

The reactions used are esterification reactions. In the first step, acids are esterified with alcohols. In the second step, an acid anhydride is reacted with unreacted alcohol groups. In the first step, the polyol is either reacted with fatty acids originally from drying oils (typically linseed oil fatty acids) to give a drying oil-like molecule (Figure 8c) or is reacted with a mixture of monofunctional fatty acid and di-functional acid to give the extended structure of an alkyd (Figure 6). In the second step, an acid anhydride attaches to an alcohol group to add a free acid group to the molecule, as shown in Figures 9, 8d and 6.

The polyhydric alcohol, the fatty acids, and any dibasic acid were weighed into a 500 mL three-necked flask equipped with a magnetic stirrer, a water-cooled condenser and a Dean-Stark trap (to measure the quantity of water produced and hence crudely follow the esterification reaction). The flask was surrounded by an electronically-controlled heating mantle. The setup is shown in Figure 10. The flask was flushed with an inert gas (nitrogen) in the direction from the thermometer through the condenser in Figure 10. The contents of the flask were heated to 245 C and held at this temperature with continuous stirring until the acid number of the reaction mixture decreased to about 10 mg KOH per gram of reaction mixture. The reaction mixture was cooled to 175 C and the acid anhydride added. The acid anhydride reacted with unreacted hydroxyl groups to give an ester linkage and one or more free carboxylic acid groups, depending on the anhydride used. The mixture was held at 175 C for 20 minutes and then allowed to cool. The final acid number was taken when the reaction mixture had cooled to room temperature. (In later preparations, xylene was added in step 1 to aid in refluxing and was removed before step 2.)

The reaction of the acid anhydride with a hydroxyl group is much more rapid than the reaction of a carboxylic acid with a hydroxyl group, although both reactions give an ester group. Thus, it is possible to use an anhydride to attach a carboxylic acid group to the resin by esterifying hydroxyl groups. However, if the second step is allowed to continue too long, the carboxylic acid groups formed from the anhydride will also have time to react with unreacted hydroxyl groups and the reaction mixture will gel.

Acid numbers were determined by dissolving the resin in isopropanol and titrating with potassium hydroxide dissolved in isopropanol. Bromothymol blue was used as an indicator.

Resin viscosities were measured at 20 and 35 C using a rotating bob rheometer.

Inks were made at BEP by T. F. O'Brien and M. Weiss of BEP according to their standard formulation. Selection of ingredients other than the resin and tests of washing and alkali resistance were carried out by Messrs. O'Brien and Weiss.

4. Results of alkyd syntheses

The reaction compositions, measured acid numbers, and viscosities of the resins prepared in this work are given in Table 1. The washing indices and resistance indices of inks made at BEP from selected resins are included. For satisfactory performance, the washing index should be 10 or lower and the resistance index should be 5 or lower.

The washing index is estimated using a procedure developed by Mark Weiss of BEP. A thin (0.002 inch) film of ink is spread on a glass plate and an excess of Dalmar solution is poured over the film. The film is then wiped side-to-side with a blunt wiping implement until the ink film is dispersed in the Dalmar solution and the wiping implement has penetrated to the glass below. The index is somewhat variable and may depend on the width of the film and applied pressure. This could be improved by always using a given width of film or perhaps by dividing the number of strokes by the width of the ink film. However, the general trend is clear and was considered acceptable for the purpose. Until this procedure was developed, no simple quantitative index of washing was readily available.

The resistance index depends on the ability of the film to not transfer color to a caustic-soaked cotton swab after seven days of air-drying. The resistance of the cured film is dependent on the formulation (including the solids to resin ratio) of the ink and on the activity of the driers, as well as on the nature of the resin itself.

One of the main variables in these alkyds is the amount of fatty acid incorporated. This is given in Table 1 as the % LOFA (linseed oil fatty acids) in the alkyd. The ranges are (1)

30 to 42% for short oil length alkyds
42 to 54% for medium oil length alkyds
54 to 68% for long oil length alkyds and
more than 68% for very long oil length alkyds.

Short and medium oil alkyds dissolve in aromatic solvents. Long oil alkyds dissolve in aliphatic solvents such as mineral spirits. Short oil alkyds are usually reacted with a crosslinker at stoving temperatures to give hard films. Medium oil alkyds also typically require higher temperatures to dry. Short and medium oil alkyds give hard resistant films but are usually not air-dry type alkyds. Longer oil alkyds give softer, less resistant films and if made from drying oil fatty acids can dry at lower temperatures. It is generally accepted (1) that, for trimethylol propane-based and glycerol-based alkyds, drying time is a minimum for alkyds which contain 48 to 50% fatty acid and that drying time increases with the amount of fatty acid in the alkyd. More fatty acid means lower viscosity, lower film hardness and increased resistance to water, and increased flow and ease of pigment dispersion.

Resins 1 to 8 and 12 to 14 in Table 1 are based on trimethylol propane (TMP, column 2). TMP has three primary alcohol groups and thus can ideally react with one di-basic acid (such as isophthalic acid or sebacic acid) and one mono-basic acid (such as linseed oil fatty acid) to give chains containing ester linkages in the backbone and fatty acids in the side groups (Figure 6). This is the normal route to alkyds. The trihydric alcohol glycerol occurs naturally in drying and other oils, but its esterified secondary alcohol group is less hydrolytically stable than esters based on primary alcohol groups such as in TMP. Alkyds 1 to 5 are based on TMP and were made before we had received good samples of the ingredients. Pending their arrival, we used stock material, most of which was too old to be trustworthy. The first alkyd to be made with new material was 6. Alkyds 4 and 5 were attempts to include tung oil in the reaction by a procedure known as alcoholysis. Those preparations failed.

The presence of a washing index value in Table 1 shows that inks were made from alkyds 6, 7, and 13. The washing was essentially acceptable, with values of 10 to 11. The resistance of a cured film of the inks after seven days was however very low, with indices of 9 to 10.

Alkyds 15 to 18 were made using the polyhydric alcohol tripentaerythritol (TPE), which has 8 hydroxyl groups compared with 3 for trimethylol propane. Thus, more drying oil fatty acid side chains can be attached to each molecule. Experience with alkyds has shown that use of pentaerythritol and its derivatives such as TPE gives alkyds which are harder and have faster drying and better gloss retention and water resistance than alkyds based on glycerol and which contain the same amount of fatty acid. An ink made from alkyd 18 had poor washing but had acceptable resistance to aqueous alkali. What was noteworthy was that this ink gave cured films which had significantly better resistance to organic solvents than did the films from the intaglio ink currently in use at BEP. Specifically, the film was much more resistant to toluene and noticeably more resistant to acetone. Also, the film was much glossier than the film from the standard ink. These properties are expected for an alkyd containing TPE and a high amount of fatty acid, as discussed in the proceeding paragraphs.

Thus, a resin based on TPE is expected to be of reasonably low viscosity and should give films which are more resistant to water, alkali and organic solvents and are harder, glossier and more flexible than alkyds based on glycerol and TMP. An effort was then made to produce an alkyd based on tripentaerythritol which would have better washing characteristics. This effort continued from alkyd 22 to alkyd 50. Of these, only alkyds 44 and 45 gave inks which washed well enough (washing indices of about 9 to 14) to be considered to be within striking distance of success. Alkyds 44 and 45 are "super" drying oils in that they have an average of 4.5 drying oil arms instead of the 3 in a normal drying oil. They also have 3 carboxylic acid groups per molecule, which provide the good washing characteristics. The resistance of the cured ink to alkali was not good (about 7 instead of 5 or less).

Several attempts were made (alkyds 51, 51A, 51B) to make an improved resin out of one of the better washing and more resistant TPE alkyds (29 in small scale preparation, 51 from a large scale preparation). Parts of alkyd 51 were diluted with allowable amounts of a water-soluble solvent. The legal limit is 12% by weight, based on the weight of the ink. The resin was of satisfactory viscosity, and the cured films were sufficiently resistant, but the washing could not be improved sufficiently in the ink formulation used. However, one ink was formulated with 40% resin instead of 33%. This ink washed in about 15 strokes, compared with about 25 strokes for the ink based on 33% resin, which suggests that a formulation with improved washing could be developed for these TPE-based resins. The resistance of the ink based on 40% resin was 1, which is very good. The considerable resistance of the early TPE-based alkyd 18 to toluene and acetone suggest that it may be worthwhile to devote some effort to formulate an acceptable ink from this family of alkyds.

After the work on alkyds based on TPE, attention was then refocussed on the TMP alkyds. Alkyd 54 is a short oil alkyd, 55 is a short/medium oil alkyd. Both are too viscous to be useful. Alkyds 56 to 59 are medium oil alkyds and were made to provide examples of this type of alkyd. Alkyd 57 contains backbone linkages of isophthalic acid and is considerably more viscous than the others, which contain sebacic acid backbone linkages. Sebacic acid has 8 methylene groups between the two carboxylic acid groups and is very flexible. Resins containing sebacic acid tend to be low in viscosity. Isophthalic acid has a benzene ring between the carboxylic acid groups which stiffens the molecule and confers viscosity to the resin.

Resins 56, 58 and 59 are of low viscosity and can be used without solvent. Inks made from these resins all washed well. Alkyd 60 is based on TPE and sebacic acid and is very viscous. Alkyd 61 is based on pentaerythritol and is of satisfactory viscosity. Alkyd 64 is based on dipentaerythritol, and is a little more viscous still. An ink made from resin 61 washed well but the resistance index of 7 indicated poor cure after seven days of drying.

The washing index can be improved in many or all of these resins by making a salt from the carboxylate group. This is the solubilization process which occurs when the resin is dispersed in Dalmar solution. Making the salt beforehand shortens the time needed for solubilization. Volatile amines are typically used so that some of the amine leaves the film during the drying period. The water sensitivity of the film is then less than that of a film from an ink in which the salts were made with non-volatile cations. Some brief trials were carried out with amines. This aspect remains to be developed further.

It was noted at this point that some of the TPE-based alkyds continued to cure well after the one week testing stage. Several films eventually became more resistant to alkali than the standard ink. This suggested to us that there was some problem with the driers, the transition metal salts used to decompose hydroperoxide groups formed in the ink during the drying process. Mr. O'Brien of BEP later independently suggested that the driers may be inactive in these inks. These alkyds contain a high proportion of fatty acid and therefore are soluble in aliphatic solvents rather than aromatic solvents. Thus it would not be surprising to find that the conventional driers, which are naphthonate salts, are not compatible with these resins, which as pointed out above tend to be more soluble in aliphatic solvents than in aromatic solvents. Driers based on aliphatic acid salts are available. Tests at BEP with new aliphatic driers began very late in this stage of the project. The results are given at the bottom of Table 1. The cure of all inks retested in this way improved by about 3 units in the caustic resistance test. In particular, resins 45 and 61 then had both satisfactory resistance and satisfactory washing.

Two families of resins were developed in this project. One was based on TPE to give a "super" drying oil, containing about five fatty acid drying arms compared with the three found in a natural drying oil. The most successful member of the TPE family was the member with the highest acid number, as expected since washing was the problem to overcome in this family of resins.

The second family of resins was based on the alkyds. The most successful member in the alkyd family was the one with an increased number of fatty acid side chains. Washing was not much a problem with this family of resins.

5 Size exclusion chromatography of resins

The chemical reactions used in this work are esterification reactions. The most significant unwanted side reactions are self polymerization of the polyols by etherification during the esterification and further esterification of the acid groups introduced using the acid anhydrides.

The size exclusion chromatograms reveal the distribution of molecular sizes in the resins. Larger molecular sizes elute first and smaller molecular sizes elute later, with the solvent eluting last. Polymeric materials contain a range of molecular sizes which leads to broad peaks in the chromatograms. The chromatograms show that the spreadsheet recipes for resins did indeed lead to larger molecular sizes when di-acid was included and that etherification during step 1 of the synthesis and esterification in step 2 during the anhydride addition were generally not important. The chromatographic results also reinforce our decision to use aliphatic materials to reduce the viscosity of the resins, since the families of resins with the same range of molecular size but different amounts of aromatic components had greatly different viscosities.

Figure 11 shows the relative molecular sizes of alkyd 18, linseed oil, commercially maleated tung oil, and linseed oil fatty acids. Alkyd 18 is an five arm resin based on TPE. Linseed oil is a three arm natural oil. The commercial sample of maleated tung oil contains two main molecular sizes, which are probably the maleated oil and the tung oil dimer produced from letting the temperature of reaction go too high. There are also significant amounts of higher molecular sizes. The free fatty acids from linseed oil represent a one arm molecule.

Figure 12 contains the chromatograms of several resins which are based on TPE and which are not extended with di-acid. All these resins have acid groups attached to the polyol. A little esterification of these acid groups with polyol hydroxyl groups is normal and probably accounts for the (small) amount of higher molecular size material. Linseed oil is provided as reference.

Alkyds 27 and 39 in Figure 13 were extended with 0.3 moles of diacid. Alkyd 50 was extended with 0.2 moles. The first two contain higher molecular size material, as expected. Alkyds 27 and 39 were acidified with different anhydrides but are very similar in molecular size.

Figure 14 contains chromatograms of several alkyds based on TMP. TMP contains three hydroxyl groups (Figure 7). Extending TMP with a diacid consumes two of these hydroxyl groups. To provide enough fatty acid side chains per molecule, a considerable amount of diacid has to be used to give long enough polyester chains. Many of these alkyds are very viscous when aromatic diacids are used. However, the actual molecular size is seen to be not much different from the TPE based resins.

Figure 15 contains chromatograms of several alkyds based on pentaerythritol. Use of this polyol allows two fatty acid side chains per polyol unit in the alkyd backbone. These resins all contain higher molecular weight material than the other alkyds, which may account for their more satisfactory cure behavior.

6. Air-dry resins based on polyvinyl alcohol

6.1: Introduction

Resins based on nonionic water-soluble polymers have the advantage of washing with plain water instead of caustic solutions such as Dalmar. This eliminates the cost of mixing the Dalmar solution and poses less of a disposal problem. Work in FY87 involved synthesis of polyethylene glycols (PEG) capped with polymerizable groups. Comb type polymers were also made with a methacrylate backbone and PEG branches.

Nonionic water-soluble polymers such as PEG are less efficient than carboxylic acid groups at solubilizing resins. Our work on polyurethane resins polymerizable by electron beams has indicated that up to 70% by weight of PEG is necessary to obtain reasonable washing characteristics. Typical alkyd resins can be solubilized with acid numbers between 50 and 100 mg KOH/g resin. The carboxyl group COOH has a formula weight of 45. The above acid numbers therefore translate to a carboxylic acid content of 4 to 8 wt%.

Nonionic air-dry resins were made by reaction of low molecular weight poly vinyl alcohol (PVA) with linolenic acid. PVA is very hydrophilic and therefore is expected to be able to solubilize a high fatty acid content.

6.2: Synthesis

Typically 40 g of PVA (75% hydrolyzed, MW = 2000) and 20 g of linolenic acid are dissolved in 200 ml of dimethyl formamide (DMF), and 0.02 g of p-toluene sulfonic acid monohydrate is used as a catalyst. The temperature is raised to 152 °C over one hour and the DMF is distilled off over an additional 2 hours. The cooled resin is a waxy solid which can be made fluid by addition of between 25% and 50% solvent such as water or butyl cellosolve. Reactions were carried out with 33%, 40%, 50%, 60% and 67% linolenic acid content, but only those with 50% or less linolenic acid remained as a single phase. The others separated into two phases during the synthesis and the reaction did not go to completion.

6.3: Cure Studies

Samples of the PVA/fatty acid resins diluted with water were taken to BEP and formulated into air-dry inks containing naphthonate driers. The inks were drawn down on a glass plate along with other inks based on alkyds. The washability was good at less than 10 strokes. The films "set" very rapidly, probably due to loss of solvent water, to form dry, hard films that had a much duller finish than those from the alkyds. After one week the films were tested for solvent and alkali resistance. The films had very poor resistance indicating little crosslinking. This may have been because the driers used are inactive in the aqueous environment conferred by the water present as diluting solvent. However, due to the significantly better results from the alkyds, emphasis was switched to the alkyds at this point. Tests of these resins should be carried out using the newer driers.

7. Aspects of formulation: Dispersing solids in liquids

Two aspects of dispersion of solids in liquids must be overcome to make an intaglio ink which will disperse in a medium such as Dalmar solution. The first is to disperse the pigments and extenders in the varnish. The second is to disperse the uncured ink in Dalmar solution. The main differences between the two cases seem to be the obvious one of the vastly different solvent properties of the organic liquid ink vehicle and the aqueous Dalmar solution, and the less obvious one of the higher ionic strength of the Dalmar solution.

Dispersion of solids in liquids is not the normal course of events because solid particles inherently attract one another, as discussed in detail in reference 3. The source of the attractive forces is the so-called dispersion force, i.e., the individually weak interactions of polarizable (movable) electrons. These forces are between induced dipoles, where some very short term separation of charge has caused a "sympathetic" separation of charge elsewhere. This type of force is normally considered to be weak and active only over short distances, but when the effect is summed up over the trillions of molecules or ions in a small particle of say one micron, it becomes dominant.

Several aspects of the above discussion are pertinent. First, dispersion forces between pigment particles are expected to be stronger than forces between particles of most colorless solids. This occurs because pigments are materials which interact electronically with light waves, which means that there are electrons in pigments which are not strongly localized. Therefore, it is unusually difficult to keep suspensions (dispersions of solids in liquids) of pigments from coalescing into larger and larger particles.

Second, the attractive forces between particles stretch out about as far as the diameter of the particles. Particle size considerations are important in deciding whether a suspension can realistically be stabilized and in deciding how to attempt to stabilize the suspension. If the particle size is small enough and the suspension is in a medium of low dielectric constant, such as an organic liquid of low polarity, then absorbing a charged species onto the particles is very effective. The particles then all have the same charge, with a high charge density if enough adsorption of the charged species has taken place, and repel each other over large enough distances to keep the suspension dispersed, at least over limited time.

Third, a suspension stabilized by adsorbed charge is inherently unstable because the charge on the particles is easily changed. Also, if the medium is changed to a medium of high dielectric strength, then the charge on the particle is made much less effective by the charges in the medium, and the particles then experience larger attractive forces from the dispersion forces than the repulsion they experience from electrostatic forces between like charges.

Fourth, the mechanism used to keep particles apart (suspended) in a medium of high dielectric strength such as an aqueous salt solution is to coat them with a block copolymer, parts of which are compatible with the medium and which therefore extend out into the medium about one particle diameter to stabilize the suspension. How far the polymer molecules will extend out from the particles depends on many things, including the molecular weight of the polymer molecules. As a general rule, the particles must be five microns or less in size (one micron or less is better) for this to be effective.

Thus:

1) The solid particles to be dispersed should be fine so that the range over which the attractive forces act is small.

2) Pigments differ in the strength of their attractive forces. Since these forces are among the strongest of inter-solid forces, some pigments will be more difficult to disperse than others.

3) It may be worth adding a charge-conferring material such as sodium pyrophosphate, which will adsorb on the solids and confer a net negative charge. This principle is used in dishwasher detergents so that the particles will not aggregate to sizes visible to the naked eye. It should be noted that particles re-aggregate during grinding unless the new surfaces are immediately covered with dispersing agent, so intermittent grinding over an extended period is much better than grinding all at one time.

4) So-called steric stabilization using a polymeric adsorbent should be considered. Two companies make additives which are useful in aqueous dispersions: Dupont makes the Elvacite series of dispersants and ICI makes the Solsperse system of dispersants.

When the uncured ink is dispersed in aqueous alkali during cleaning of the wiping roller of the press, the resin component of the ink must be dispersed in micelles in the aqueous phase. Here, at least two factors come into play. One is the critical micelle concentration of the surfactant used in the surface of the micelles. Non-ionic surfactants such as BRIJ 35 and TWEEN 80 have very low critical micelle concentrations, lower than the critical micelle concentrations of C16 and C18 long chain acids.

The second factor is the compatibility between the resin and the surfactant. Resin-surfactant combinations should be tested. Since the pigments greatly perturb the behavior of suspensions, this means that the pigment has also to be present when the tests are carried out. Thus, the necessity to test several combinations of surfactants and dispersing agents must be recognized.

8. Conclusions

Much of our work on air-dry intaglio ink resins has concentrated on preparing alkyd resins based on tripentaerythritol. Such alkyd resins are known to be more stable to hydrolysis than the standard types based on trimethylolpropane and glycerol. The viscosities of alkyds based on tripentaerythritol are less than the viscosity of a standard type of alkyd. Low viscosity seems to be an important parameter in making an intaglio ink which will disperse successfully in Dalmar solution. It allows a higher pigment/extender (solids) loading in an ink without making the ink too viscous.

Our tripentaerythritol-based resins are somewhat like extra large or bodied drying oil molecules. Thus, inks made from this kind of alkyd should dry more quickly than inks made from other low-viscosity alkyds. The final films should be more resistant to solvents because more crosslinks will be formed.

We have made tripentaerythritol-based resins with a range of acid numbers from 40 to 130. Few of the inks made with the standard formulation from our tripentaerythritol-based resins have dispersed satisfactorily (i.e., quickly enough) in Dalmar solution. The best inks contained alkyds 44 and 45. Experience at BEP with inks made from NIST resins based on trimethylolpropane has shown that these inks disperse more easily in Dalmar solution. This may be because the tripentaerythritol-based resins contain fewer hydrophilic groups such as ester groups than do the alkyds based on trimethylolpropane (see Table SS3 for an estimate of relative hydrophilicities of TPE-based and alkyd resins) and because the solubilizing acid groups in tripentaerythritol-based resins are more sheltered from the alkaline environment in which they are to disperse. Therefore, we have synthesized and provided to BEP several alkyds based on trimethylol propane and pentaerythritol.

It is standard in the water-borne coatings industry, and apparently also common in intaglio inks, to include amines and co-solvents in the formulations (1). It may be appropriate to include these ingredients in BEP formulations if it is necessary to use medium viscosity alkyds.

Some inks also contain wax. Wax plays many roles. It is typically used to reduce tack. If it remains as a solid, it limits the amount of solids which can be loaded into the ink, thus acting as an inert filler. If it dissolves in a solvent contained in the ink, it produces a fast thermoplastic set when it solidifies as the solvent evaporates or is absorbed by the substrate. It provides a hydrophobic coating which is the first line of defense against caustic solution and reduces transfer of wet ink to adjacent sheets of paper. It reduces abrasion losses of printed ink.

An ink made at BEP with 40% resin (and without added amine) washed as well as an ink made with 33% resin and 6% non-reactive surfactant. We currently do not know whether the improvement in washing arises in both cases from decreased viscosity because of lower solids content in the finished ink or from some effect between solid particles, but it warrants further investigation by BEP. For example, additional resin could be added to inks which wash poorly (25 strokes) and the washing and viscosity of the inks correlated. The effect of additional resin in the above case was to increase the resistance of the cured ink to aqueous caustic solution. It is well known that the durability of a coating is greatly reduced at high solids contents.

In other tests conducted at BEP on inks drawn down by BEP, inks made with NIST alkyds based on tripentaerythritol were shown to be more resistant to 2% caustic solution after two weeks of air-dry than the standard ink was. Earlier tests had shown that the inks based on the NIST resins are more resistant to organic solvents such as toluene. This suggests that the drying process slows down dramatically after the first day or so, because during the first few hours, NIST inks dry more quickly than the standard ink. The tests should be carried out to select a good drier system. An ink made from a resin based on TPE washed and cured satisfactorily.

Several alkyds based on trimethylol propane were made. The rationale was that such alkyds are inherently more hydrophilic than the tripentaerythritol-based alkyds. An ink made from a very low viscosity "long oil" alkyd with an acid number of 90 washed in Dalmar solution in about 10 strokes without added surfactant and without added amine. The viscosity of the resin used to make the ink is 30 poises at 25 C. The ingredients used to make the resin contained 50 weight % of linseed oil fatty acids. An ink made from a resin based on pentaerythritol washed and cured satisfactorily.

One of our approaches is to make alkyds which are sufficiently low in viscosity to be used alone, i.e., without added solvent and without added amine. This would certainly comply with Air Quality Regulations for the foreseeable future. Using a more viscous resin with added solvent would give an enhanced rate of touch drying in air. It is now clear that in most cases (the low viscosity alkyd described above being an exception) the solubilizing salts formed when a resin such as those based on tripentaerythritol is dispersed in Dalmar solution must be formed, at least in part, in the ink before it comes into contact with the Dalmar solution. Thus, future formulation efforts should include the addition of amines to our more viscous resins.

9. References

1. "Resins for Surface Coatings", P. Olding and G. Hayward, Eds., in 3 volumes, SITA Technology, London, (1987).

2. "District of Columbia Air Quality Control Regulations, Effective March 15, 1985", Environment Reporter, Bureau of National Affairs, publ., 341:0501 Appendix 3.

3. "Colloidal Systems and Interfaces", S. Ross and I.D. Morrison, Part III: pp 205-263.

Table 1: Composition of synthesized alkyds

Alkyd #	TMP	TPE	LOFA	Isoph	Sebac	TM Anh	Phth Anh	Succ Anh	acid #	viscosity		comment	Wash test	NaOH res	% LOFA	cal acid#
										20C	35C					
1	1	0	.80	0	0	.33	0	.77		7000	1500				48	161
2	1	0	.80	0	0	.36	0	.80	34	45	20				47	168
3	1	0	.80	0	0	.33	0	.90	77	1950	390				47	171
4	1	0	(1.15)	0	0	.43	0	1.07	tung oil			aborted				
5	1	0	(1.15)	0	0	.43	0	1.07	tung oil + Ca Acetate			aborted				
6	1	0	1.15	.38	0	.21	0	0	59	195	57		10	9	62	42
7	1	0	1.16	.57	0	.23	0	0	73	2000	350		11	10	59	43
8	0	0	.69	0	0	.19	0	.67							72	199
12	1	0	2.46	1.76	0	.62	0	0	33						62	56
13	1	0	.81	.78	0	.22	0	0	64				11	9	46	46
15	0	1	3.99	0	0	.77	0	0	63	1900	390				72	53
16	0	1	2	0	0	.24	0	0							60	28
17	0	1	2.98	0	0	.63	0	0	64	12000	1100				66	53
18	0	1	5	0	0	.93	0	0	65	270	90		23 to 3	5	76	54
19	1 PVA + 4.75 linolenic acid + DMF								5							
20	1 PVA + 14.5 linolenic acid + DMF								221			two phases				
21	1 PVA + 10.7 linolenic acid + DMF								241			two phases				
22	0	1	5.10	0	0	1.26	0	0	90	3500	800				74	69
23	0	1	5.10	0	0	1.88	0	0	133	38000	45000	w linolenic acid	8	9	70	98
24	0	1	5.11	0	0	0	0	2.51	40			2 phases			75	69
25	0	1	5	0	0	0	0	2.10	71	50	20		25	5	75	60
26	0	1	5.80	0	0	0	0	1.50	52	180	100		26	4	80	39
27	0	1	4.30	0	.30	0	0	2	70	130	50		25	3	70	61
28	0	1	4.70	0	.30	0	2	0	71	360	100		27	3.50	69	55
29	0	1	5	0	.45	1	0	0	81	350	100		14 to 17	3.5 to 7	72	55
30	0	1	4.80	0	0	0	0	2.70	94	80	30		21	5	72	77
31	0	1	6	0	0	2	0	0	133	12000	3000				73	92
33	0	1	5	0	0	0	0	2.10	86	75	32	tall oil	22	7	75	60
34	0	1.	4.88	0	0	0	0	2.10	63	120	42	tall oil	17	10	75	61
35	0	1	5	0	0	0	0	2.10	73	59	26	linseedFA like 33	21	5	75	60
36	0	1	5	0	0	0	0	2.10	75	52	24	linseedFA like 35			75	60
37	0	1	5	0	0	0	0	2.10	71	55	22	linseedFA like 35			75	60
38	0	1	4.70	0	.30	0	2	0	68	260	100	linseedFA like 28	20	6	69	55
39	0	1	4.70	0	.30	0	0	2	91	135	45	linseedFA like 27	18 to 24	4 to 5	72	58
41	0	1	4	0	.50	2.50	0	0	199			scorched			58	136
43	0	1	4	0	.50	1.20	0	0	100			linseed			65	74
44	0	1	4.50	0	0	0	0	3.20	115	175		linolenic acid	11	7	69	92
45	0	1	4.50	0	0	0	0	3.10	133	135		linseedFA	9 to 14	7 to 8	70	90
46	0	1	5.60	0	0	1.90	0	0	161	14000		linseedFA bad stirrer			72	93
47	0	1	6.10	0	0	1.70	0	0	84	1100		linseedFA	15/1	5/7.5	75	80
48	0	1	4.50	0	0	0	0	2.10	94	110		linseedFA	13/2	5/7.5	73	64
49	0	1	5.40	0	0	0	0	2.50	101	35		linseedFA	14/2	5/8	76	66
50	0	1	5	0	.20	0	0	2.50	85	100		linseedFA 49+sebac	26/1	4/6/5.5	73	68
51	scale up of #29								79	2000						
51A = 116-1 = #51 with 5% cellosolve													20/2	1-3		
51B = 116-2 = #51 with 10% cellosolve													20/3	2-4		
52	second scale up of #29, done in one day - product gelled															
53	smalsmall scale repeat of #51 with same heating								101	3200						

54 & 54B	1	0	.51	.72	0	.21	0	0	84	v. high		short oil alkyd	13	6.3	36	54
55 & 55B	1	0	.79	.77	0	.22	0	0	58			short/medium alkyd	10	3.7	46	47
56	1	0	1.10	0	.50	0	0	.75	90	29		medium oil alkyd	10-12	10	54	68
57	1	0	1.10	.60	0	0	0	.75	99	390		medium oil alkyd	11		55	68
58	1	0	1.20	0	.50	0	0	.50	75	16	7	medium oil alkyd	10-12	10	59	45
59	1	0	1	0	.60	0	0	.50	71	28	14	medium oil alkyd	11-13	10	52	48
60	0	1	3.50	0	.40	0	0	3	129	2300	690	TPE alkyd			61	97
61	0	1 PE	1.50	0	.55	0	0	1	107	165	62	PE alkyd	8-10	7	60	73
62	0	1	3	0	.30	0	0	2	44	2 phases		TPE alkyd			61	76
63	0	1 Di	2	0	.25	0	0	1.70	71	gelled		diPE alkyd			58	92
64	0	1 Di	2.50	0	.40	0	0	2	122	540	175	diPE alkyd	14		61	91

NEW DRIER SYSTEM:

45	4.5
59	6-8
61	3.5
64	6

```
SS1: From molecules in formulation to weights in recipe

Weights of material needed to make condensation oligomers
Sep 29, 1988        10:48 AM
                            USER TYPES HERE       formula  weights  weights
   cmpd   acid/OH  molecular    recipe  f(i)A(i)  weights   scaled   scaled
          gps/mol   weights  (molecules)                    to vol    to wt

LinseedFA      1        278        1.20    1.20   333.60  593.210    80.89
MaleicAnh      2         98           0       0        0        0        0
Isophthal      2        166           0       0        0        0        0
SebacicAc      2        202         .50       1      101  179.599    24.49
  PEG 400      2        400           0       0        0        0        0
TriMPropa      3        134           1       3      134  238.280    32.49
PentaEryt      4        136           0       0        0        0        0
DiPentaEr      6        254           0       0        0        0        0
TriPentaE      8        372           0       0        0        0        0
PhthalicA      1        148           0       0        0        0        0
Trimellit      1        192           0       0        0        0        0
ParaMelli      2        218           0       0        0        0        0
SuccAnhyd      1        100         .50     .50       50   88.910    12.12

    f(e)=   1.45       g(e)=          3
gel pt^2=   1.10     gel pt=       1.05
 Acid # =  45.26              Net OH at end of reaction =     .30
%XS OH at end  =       5.26  %XS OH in 1st step =           14.04

alkyd # =   1.19     % oil =         54

mLs water formed in first step =         38.409

Final volume =         1000             Total volume of reactants   562.36
Final weight =                      150 Total weight of reactants   618.60
 additive 0.05% =      .550        .075
 additive  0.10%      1.100        .150

INSTRUCTIONS:
Type the numbers of molecules in the recipe in column D
Type total volume required in C30 or total weight in D31
Press F5 to recalculate the formulae.
The weights to use are given in columns G and H
Press Ctrl P then B to print out the results.
```

Legend to SS1

The spreadsheet in Table SS1 is used to calculate the weights of ingredients in an alkyd preparation which was designed from the numbers of molecules of each type of ingredient to be included in the final product.

The total amount of material to be prepared is supplied at the bottom of the spreadsheet as a volume and as a weight. the amounts to weigh out are then given in the two right-hand-most columns. The first of these columns is the weights of reactants to use to achieve the specified volume of product and the second of the columns is the weights of reactants needed to arrive at the total weight of product specified.

The proportions of reactants are then adjusted if necessary to produce a reaction mixture which will not gel, as shown by the gel point parameter being close to or greater than 1. This is the extent of reaction at which gelation is expected to occur.

The acid number is similarly adjusted. The remaining equivalents of OH must also be positive for the reaction to proceed to near completion.

The amount of water produced in the first step, which is the reaction of the polyol with the fatty acid and the di-acid which forms the ester groups in the backbone of the alkyd chain, is calculated and may be used to follow the extent of reaction by catching the evolved water in a Dean-Stark trap.

SS2: From weights in formulation to molecular ratios

```
# molecules from weights of material in alkyd recipes
Sep 29, 1988        11:32 AM                             USER TYPES HERE
ALKYD NUMBER :           57                       formula  weights
   cmpd   acid/OH  molecular    recipe  f(i)A(i)  weights  used in
          gps/mol   weights  (molecules)                    recipe

LinseedFA      1        278      1.1015    1.10   306.21   74.500
MaleicAnh      2         98           0       0        0        0
Isophthal      2        166       .6091    1.22   101.11   24.600
SebacicAc      2        202           0       0        0        0
  PEG 400      2        400           0       0        0        0
TriMPropa      3        134       .9999    3.00   133.99   32.600
PentaEryt      4        136           0       0        0        0
DiPentaEr      6        254           0       0        0        0
TriPentaE      8        372           0       0        0        0
PhthalicA      1        148           0       0        0        0
Trimellit      1        192           0       0        0        0
ParaMelli      2        218           0       0        0        0
SuccAnhyd      1        100       .7522     .75    75.22   18.300
                  Divider =         .24
    f(e)=   1.53       g(e)=          3
gel pt^2=    .95     gel pt=        .98
 Acid # = 68.32              Net OH at end of reaction =    -.07
%XS OH at end  =      -1.19  %XS OH in 1st step =           11.20

alkyd # =   1.13     % oil =         50

mLs water formed in first step =         10.159

Final volume =         1000             Total weight of reactants   616.52
Final weight =                      150
 additive 0.05% =      .075       1.267
 additive  0.10%       .150       2.534

INSTRUCTIONS:
Type the weights in column G
Put 1 in the divider cell
Press F5, then enter the number of TMP or TPE or PE molecules in the divide
Press F5 again.  The numbers of molecules will be normalized to TMP, etc.
Enter the alkyd number in C3.  Press CtrlP then B to print out a copy.
```

Legend to SS2

SS2 is used find the molecular ratio of reactants from the weights of reactants used to make an alkyd. The weights are typed into the right hand column of the spreadsheet. The spreadsheet is recalculated (by pressing the appropriate function key on the computer keyboard). The ratios are more meaningful if they are normalized to some molecular abundance of one, so our custom is to start with a divider value of 1, press the recalculate key, then put as divider the number of molecules of polyol. The recalculate key is pressed again. The ratio of reactants is then given in the fourth column of the spreadsheet. The other numerical information supplied at the bottom of the spreadsheet is the same as that given in SS1 and provides information on the design parameters of the alkyd.

SS3: Estimates of water solubilities of alkyds

Hydrophobic/hydrophilic partition estimated for 2 air-dry alkyds

Sep 26, 1988 1:36 PM

Contributions to Log Partition Coefficient between octanol and water:

group	factor	group	factor
C6H5	1.90	LOFA	7.57
H	.23	TPE	5.88
C	.20	TMP	4.13
øø	-.09	Sebacic acid	.50
øOH	-.44	OH	-1.64
CH2	.66	Succinic an	-1.25
OH	-1.64	TMA	-1.59
-O-	-1.82		
EO -O-	1.54		
ø-O-	-.61		
>C=C<	-.55		
-C(O)-O-	-1.40		

(A)
Alkyd containing tripentaerythritol

group	number	subtotal
LOFA	5	37.85
TPE	1	5.88
TMP	0	0
Sebacic acid	.50	.25
Succinic An	2	-2.50
TMA	0	-0
total =		41.48

(B)
Alkyd containing trimethylol propane

group	number	subtotal
LOFA	1	7.57
TPE	0	0
TMP	1	4.13
Sebacic acid	1	.50
Succinic An	0	-0
TMA	1	-1.59
total =		10.61

KEY: LOFA = Linseed oil fatty acids; TPE = tripentaerythritol
TMP = trimethylol propane; An = Anhydride; TMA = Trimellitic anhydride

RESULT:	Alkyd A	Alkyd B
Hydrophobic vs. Hydrophilic Log Partition Coefficient	41.48	10.61

CONCLUSION:
Alkyd A is much more hydrophobic than alkyd B and will be much more difficult to disperse in an aqueous environment.

Legend to SS3

SS2 is a printout of a spreadsheet which estimates to a first approximation the relative solubility of materials in octanol and water. The higher the number obtained, the more soluble the material is in octanol and the less it is in water.

The top part of the table shows the group contributions of selected chemical groups in the molecules to the logarithm of the octanol/water partition coefficient. The bottom part of the table shows the logarithms of the octanol/water partition coefficients using these groups to represent an alkyd based on tripentaerythritol (TPE), on the left, and one based on trimethylol propane (TMP), on the right.

The results show that the alkyd based on trimethylol propane is significantly more soluble in water than the alkyd based on tripentaerythritol. The inference is that alkyds based on TMP will be easier to disperse (for a given acid number) in Dalmar solution than will alkyds based on TPE.

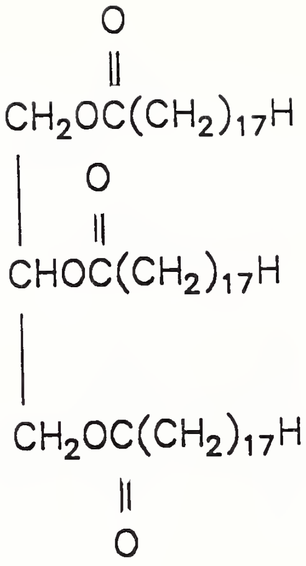


Figure 1: The chemical structure of a natural oil.

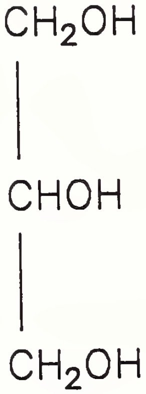


Figure 2: The polyol glycerol. Note that the middle OH group is on a secondary carbon atom.

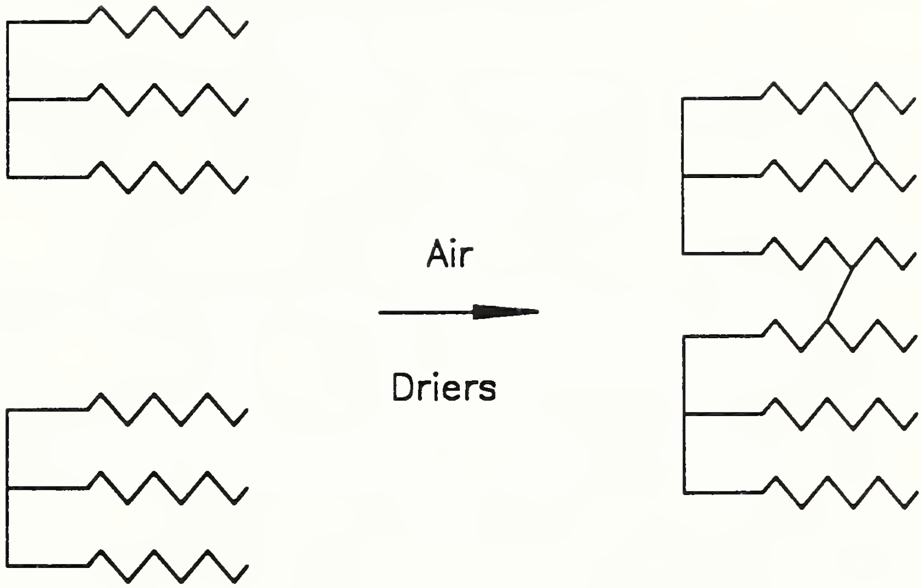
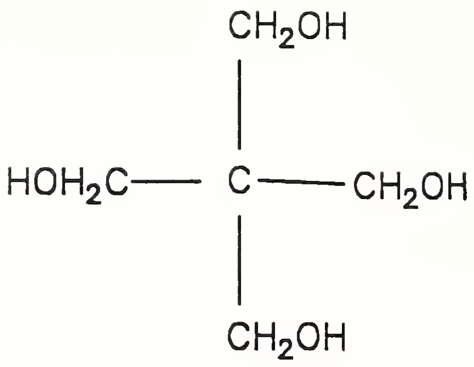
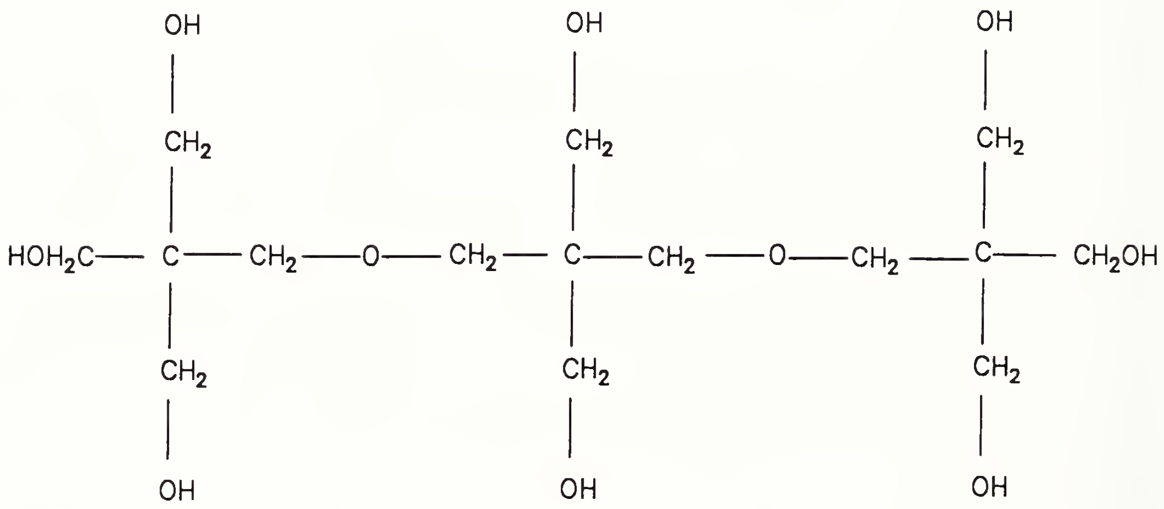


Figure 3: A schematic representation of the cure process for air-dry resins.



$$HOH_2C-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CH_2OH$$

Figure 4: The polyol pentaerythritol, which has four primary OH groups.



$$HOH_2C-\underset{\underset{OH}{CH_2}}{\overset{\overset{OH}{CH_2}}{C}}-CH_2-O-CH_2-\underset{\underset{OH}{CH_2}}{\overset{\overset{OH}{CH_2}}{C}}-CH_2-O-CH_2-\underset{\underset{OH}{CH_2}}{\overset{\overset{OH}{CH_2}}{C}}-CH_2OH$$

Figure 5: The polyol tripentaerythritol, which has eight primary OH groups.

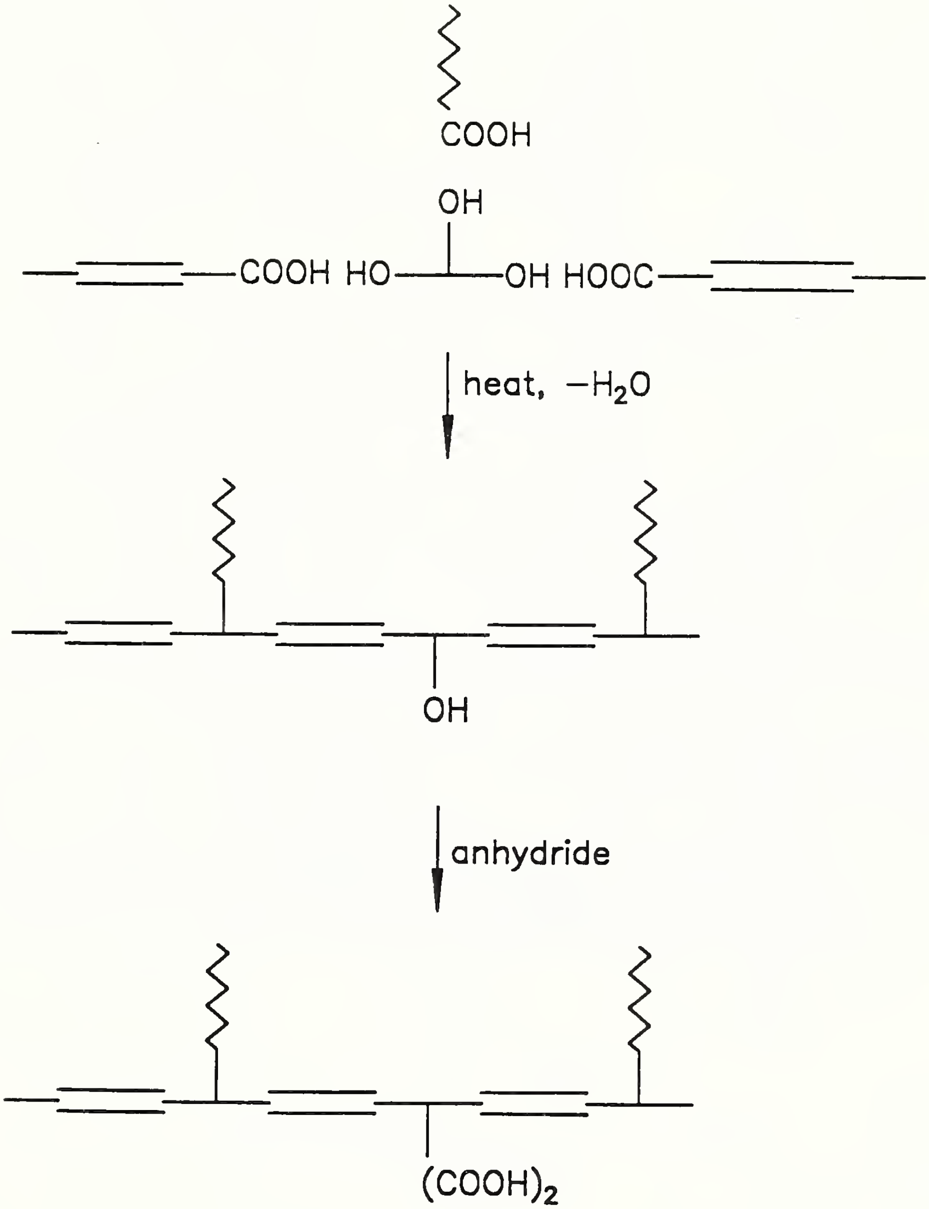
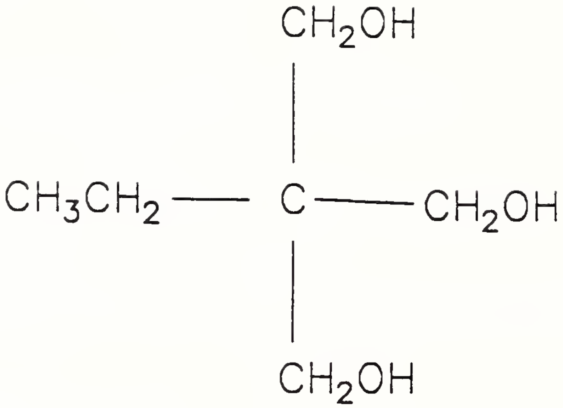
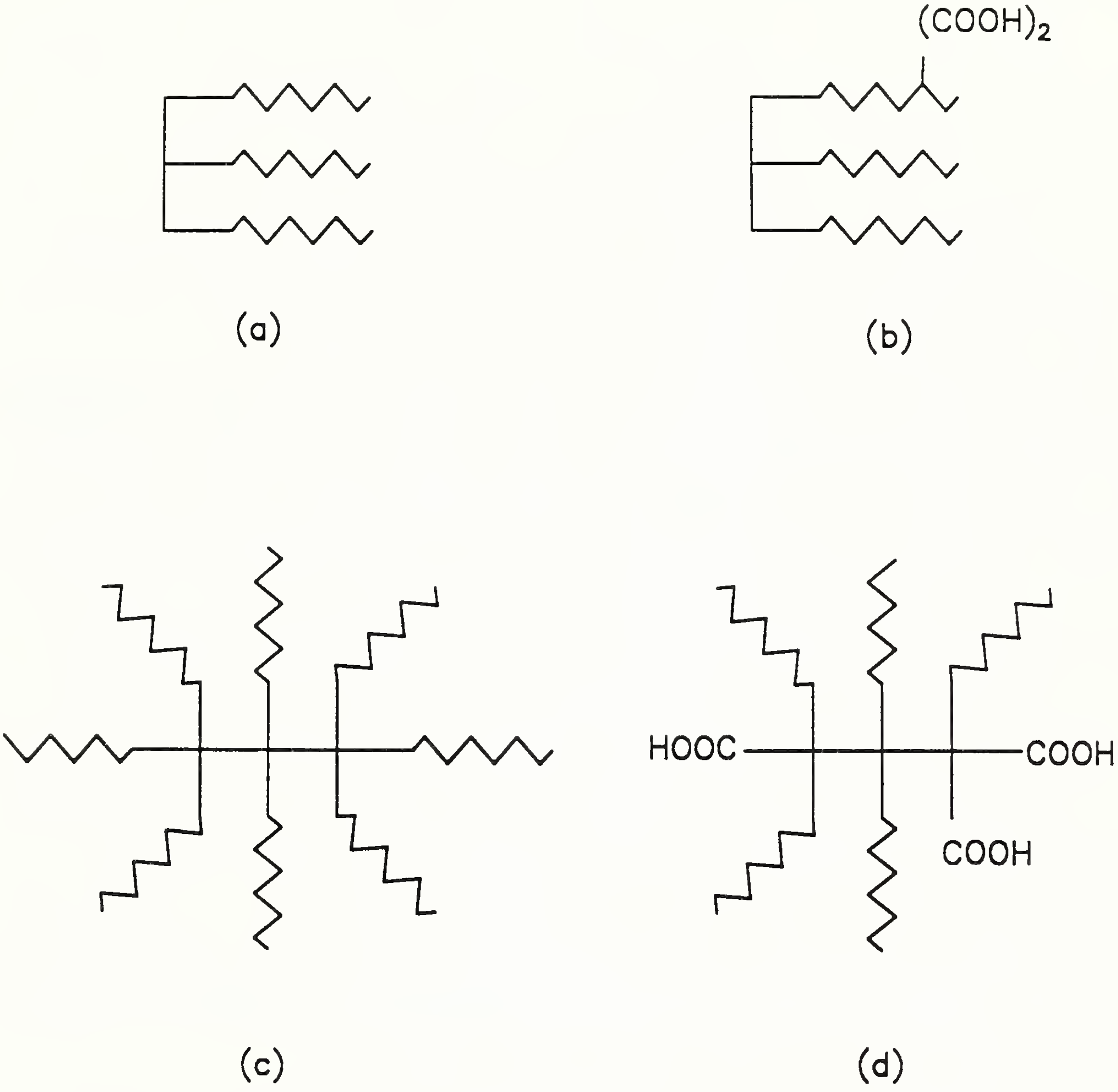


Figure 6: Synthesis scheme for a typical alkyd. The double lines represent a diacid; only one acid group is shown. The anhydride is trimellitic anhydride which contains one anhydride and one free acid group, thus providing two free acid groups after reaction of the anhydride group.



$$\mathrm{CH_3CH_2}-\overset{\displaystyle \mathrm{CH_2OH}}{\underset{\displaystyle \mathrm{CH_2OH}}{\overset{|}{\underset{|}{\mathrm{C}}}}}-\mathrm{CH_2OH}$$

Figure 7: The polyol trimethylol propane, functionally equivalent to glycerol, Figure 2, but with three primary OH groups.



(a) (b)

(c) (d)

Figure 8: Adding acid functionality to (a & b) tung oil and (c & d) a resin based on tripentaerythritol (Figure 5).

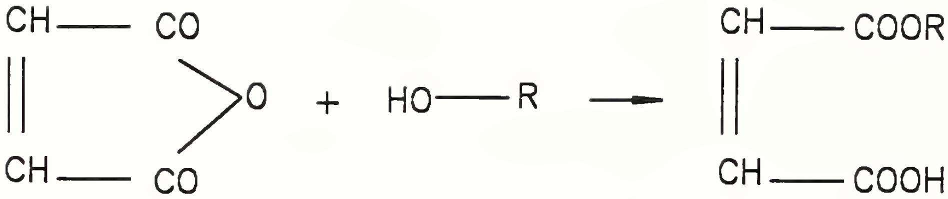


Figure 9: Reaction of an acid anhydride with an OH group to give an ester linkage and a free acid group.

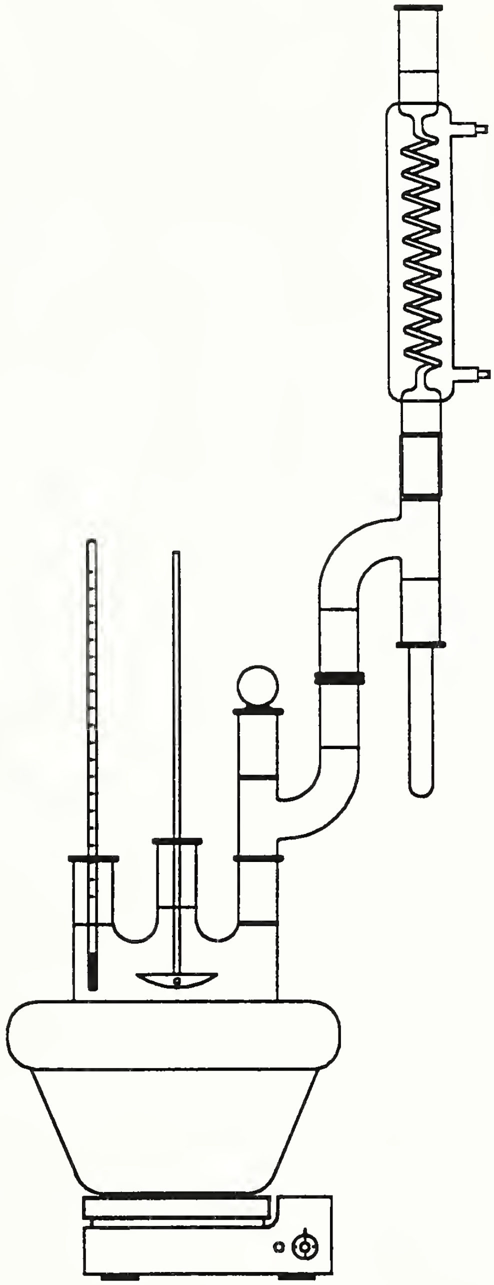
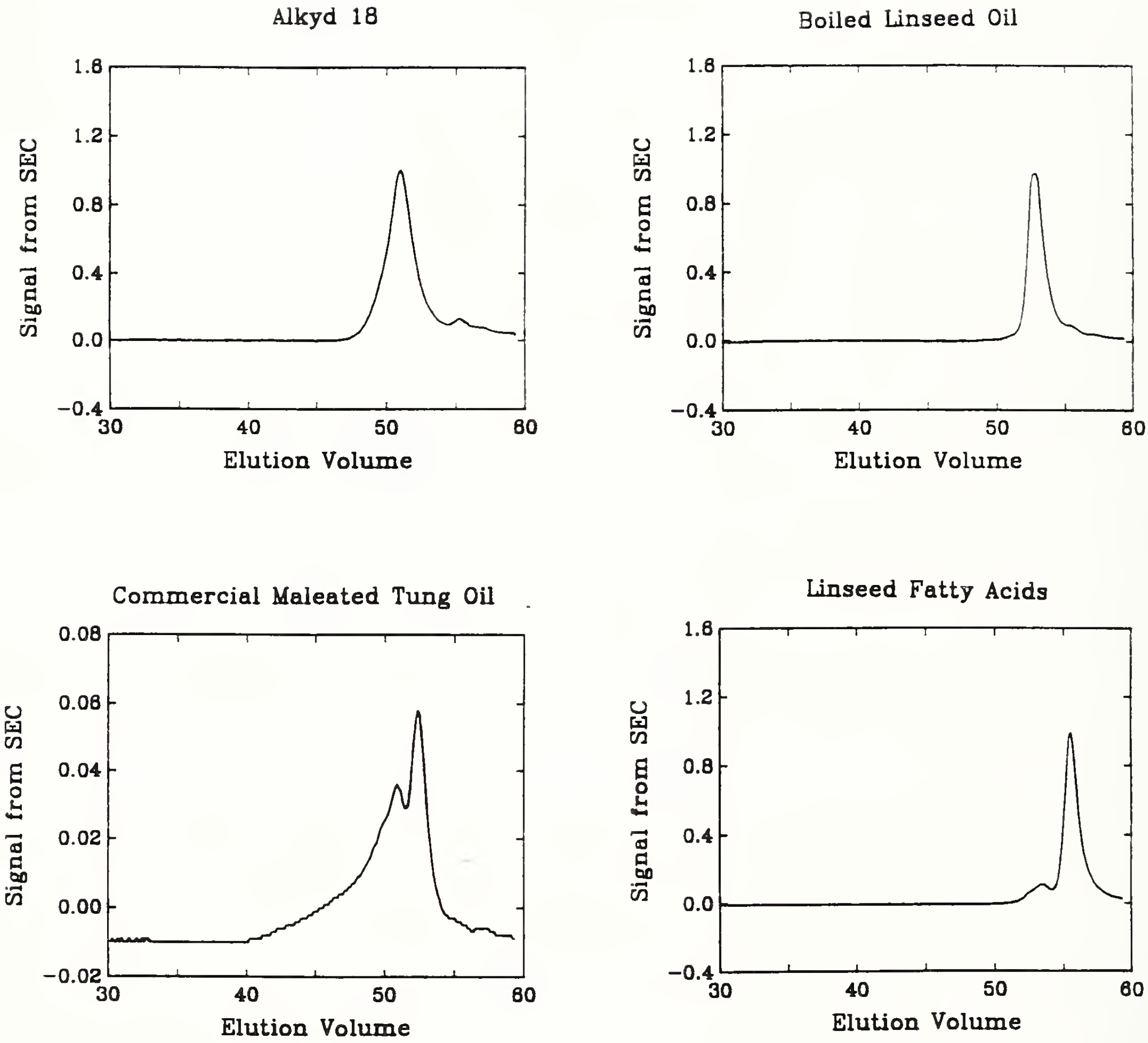


Figure 10: Schematic of apparatus used for resin synthesis.


Alkyd 18

Boiled Linseed Oil

Commercial Maleated Tung Oil

Linseed Fatty Acids

Figure 11: Size exclusion chromatograms of alkyd 18 (tripentaerythritol fully esterified with linolenic acid), linseed oil, maleated tung oil, and free fatty acid.

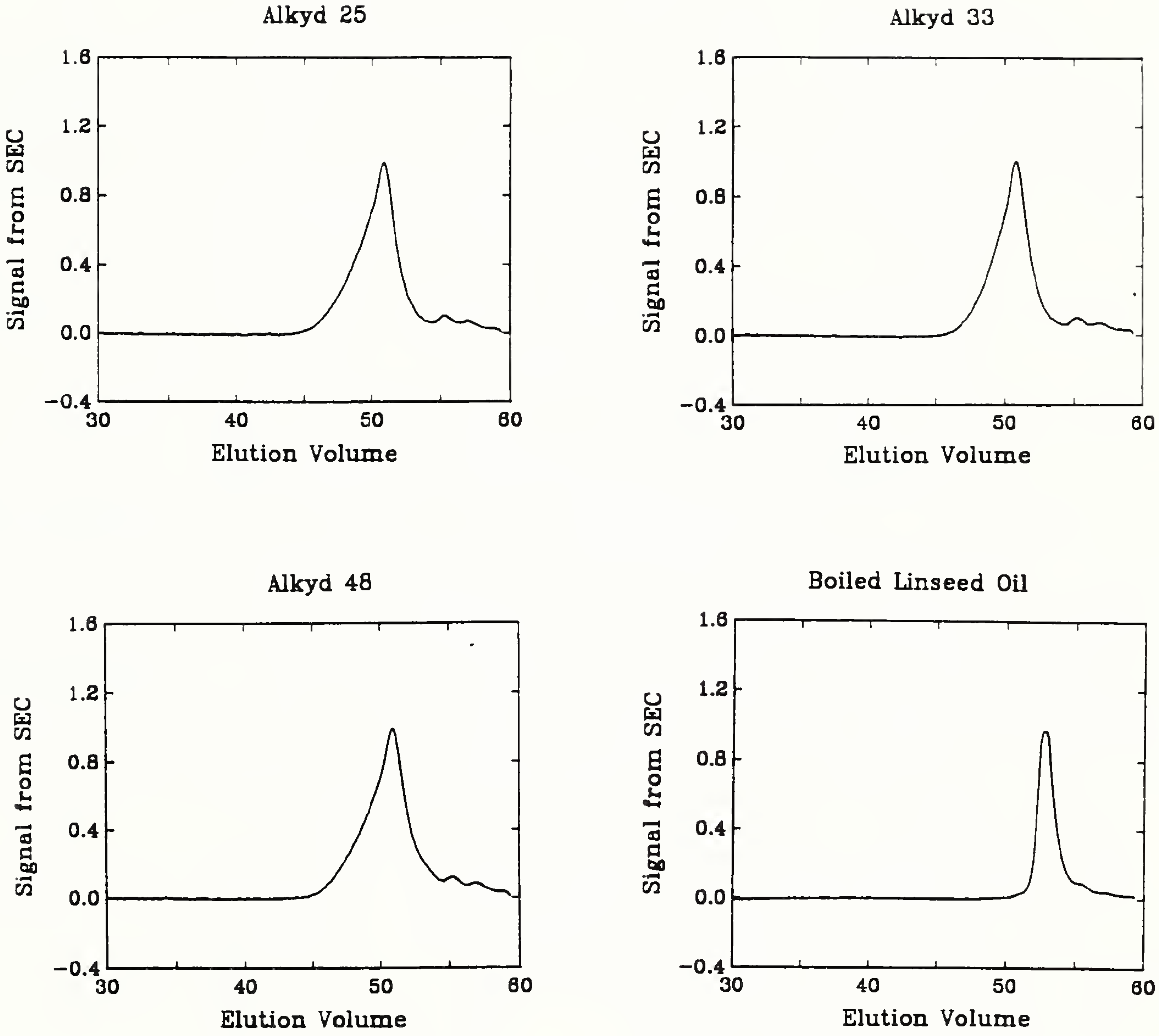


Figure 12: Size exclusion chromatograms of several tripentaerythritol-based resins with 4 to 5 fatty acid residues compared to linseed oil.

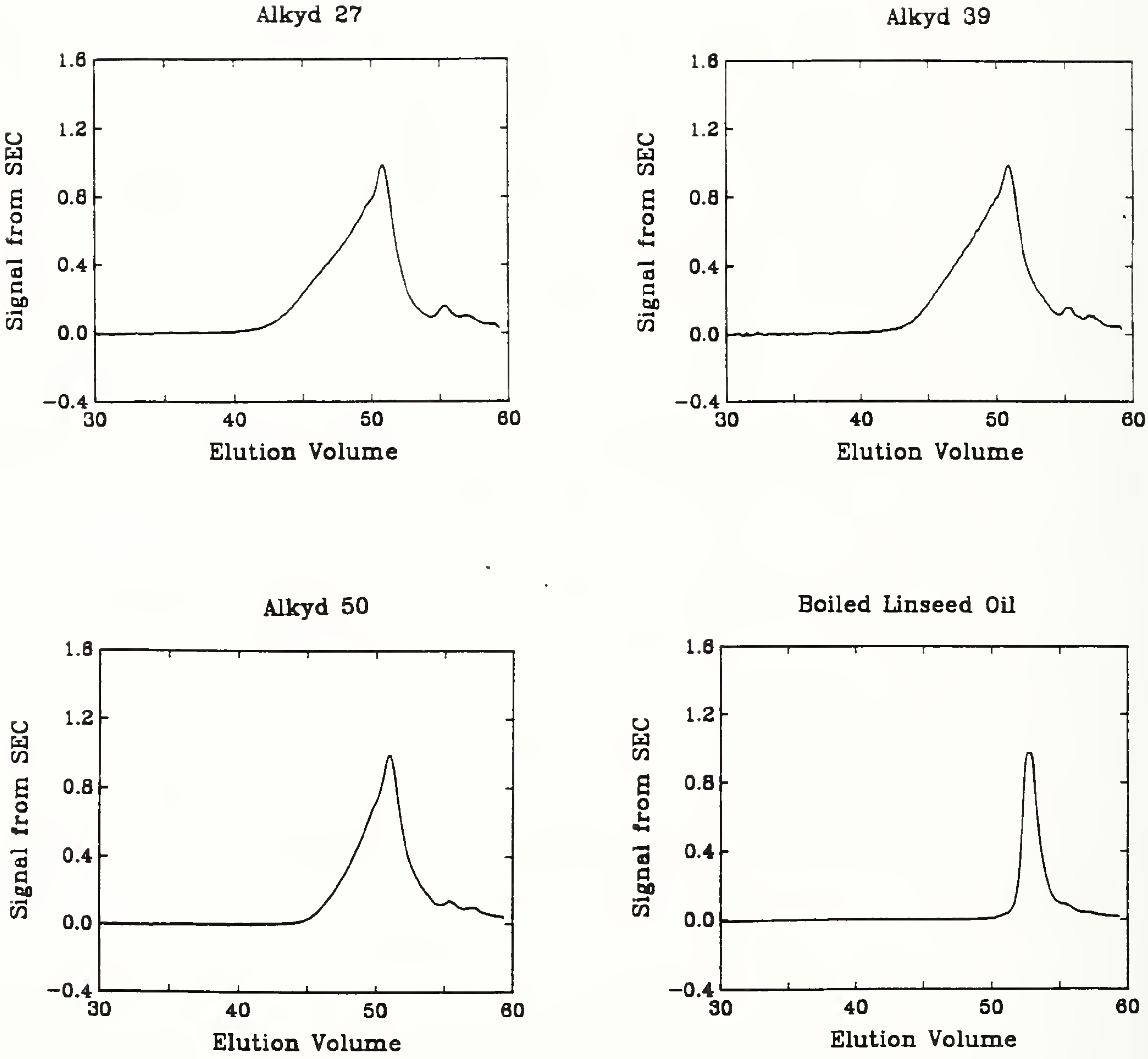


Figure 13: Size exclusion chromatograms of several tripentaerythritol-based resins extended with sebacic acid, compared with linseed oil.

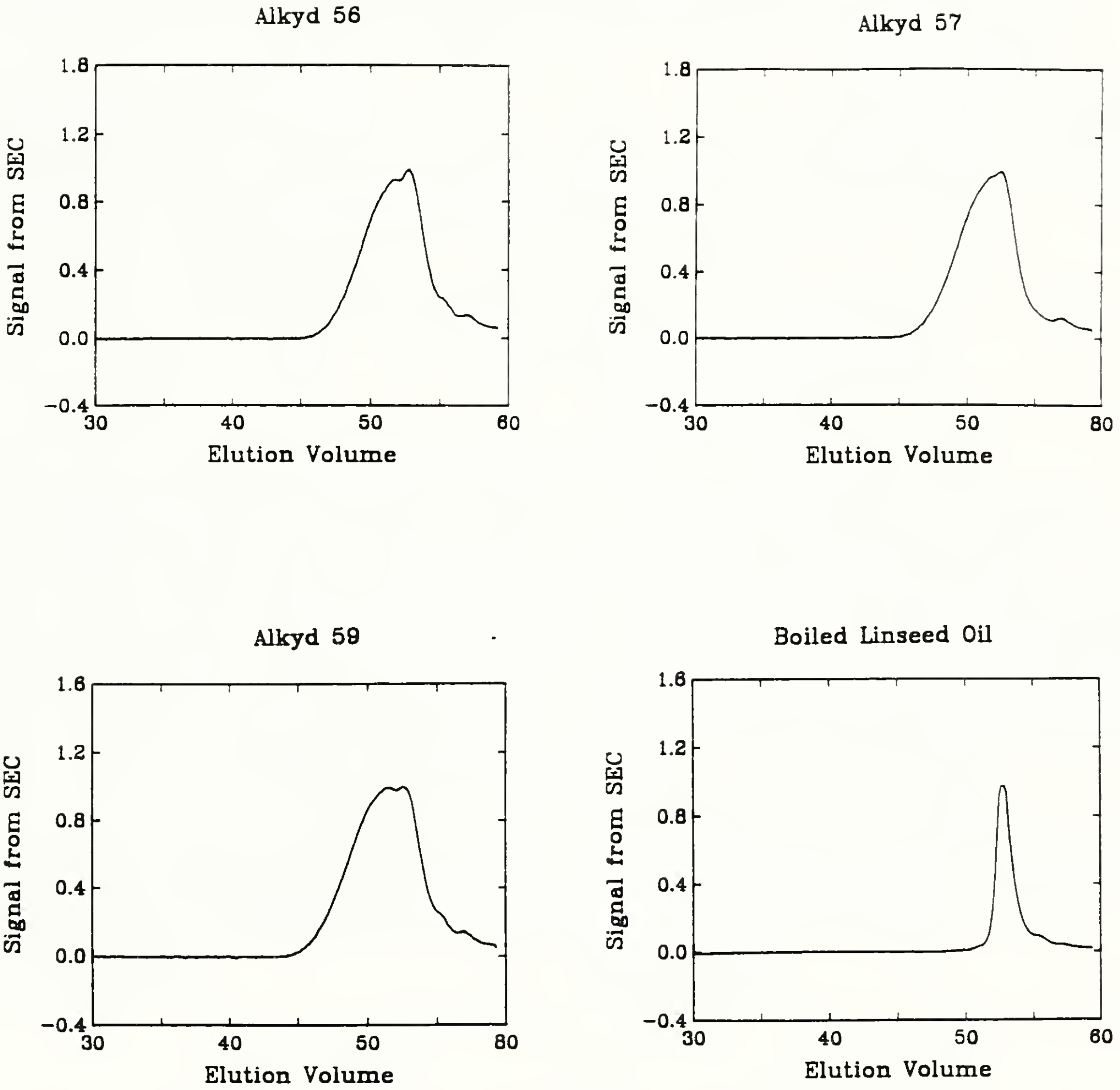


Figure 14: Size exclusion chromatograms of several alkyd resins based on trimethylol propane extended with sebacic acid, compared to linseed oil.

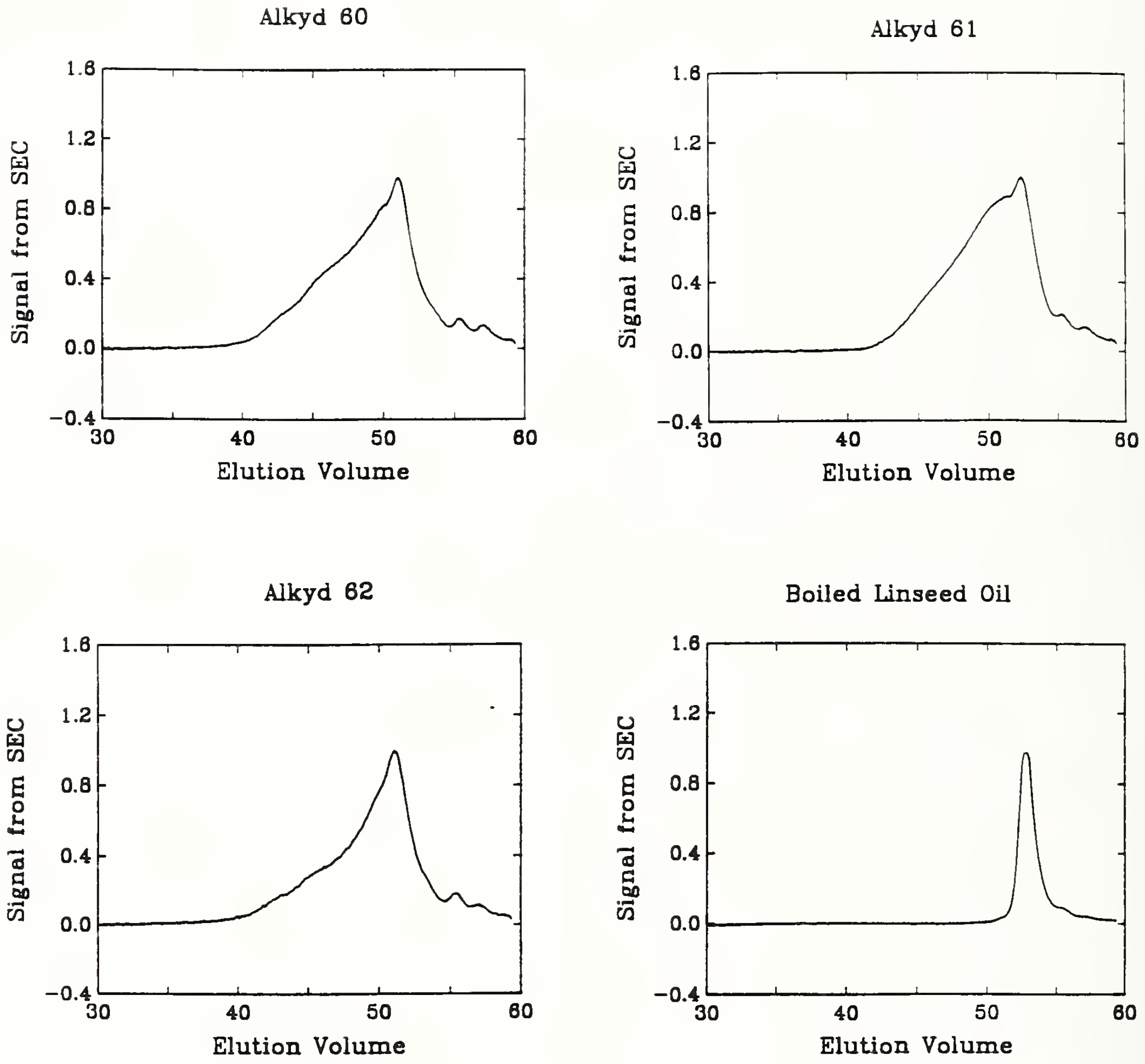


Figure 15: Size exclusion chromatograms of several alkyd resins based on pentaerythritol extended with sebacic acid, compared to linseed oil.

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10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

Over 60 air-dry resins were designed and synthesized to provide prototype resins for intaglio inks. Most of the resins contain linseed oil fatty acids as the air-dry part. The polyols used are trimethylol propane, pentaerythritol, dipentaerythritol, and tripentaerythritol. In some cases, sebacic acid was used to extend the polyols to polyesters. In other cases, "super drying oil" resins were synthesized from tripentaerythritol and linseed oil fatty acids. Inks made from the resins must disperse in 1% aqueous alkali. Acids groups were introduced into the resins using trimellitic anhydride, phthalic anhydride or succinic anhydride.

The inks must pass two preliminary tests, one for dispersion in aqueous alkali before curing and one for resistance to the same solution after curing. Two resins, one a super-drying-oil type molecule based on tripentaerythritol and one a more typical alkyd based on pentaerythritol, passed these tests.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

air-dry; alkyd; drying oil; intaglio inks; resin design; water-dispersible

13. AVAILABILITY

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