NISTIR 4754

FY 91 Syntheses of Liquid Prototype Air Dry Resins for Use in BEP Intaglio Inks

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Prepared for:
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Executive Summary

BEP ink formulation of intaglio inks was shown to be of paramount importance in determining the press behavior of the inks. Intaglio inks with performances differing widely, from bad to good, were made from the same resin. Therefore, a range of formulations must be tried for each candidate intalgio ink resin.

The viscosity of a carboxylated resin can be greatly changed by adding amines, hydrocarbon solvents, and alcohols or ketones or water. Some of these materials increase the viscosity while others decrease it. Examples are provided.

Tung oil fatty acids were used in alkyd syntheses in an attempt to improve the rate and extent of air-dry cure of inks made from these resins so that the resistance of the cured ink film to aqueous alkali solutions would be improved. Because tung oil fatty acids are not commercially available, the synthesis procedure was more involved than the relatively simple synthesis of alkyds based on linseed oil fatty acids. However, the tung oil fatty acid-containing resins did not perform better than the linseed oil-containing alkyd resins.

Linseed oil fatty acid-containing alkyd resins which passed laboratory tests for washing (ability to emulsify in Dalmar solution) and chemical resistance were successfully designed and synthesized. The key was to increase the average molecular size of the alkyd resin molecules. To accomplish this without increasing the viscosity beyond the usable range of about 10 to 15 Pa s, aliphatic ingredients were used. Most alkyd resins are made from at least some aromatic ingredients. At least three of these resins produced inks which are promising candidates for production intaglio inks.

The synthesis procedure was fine-tuned to make it as reproducible as feasible. The effect of temperature was studied and documented by viscosity measurements and size exclusion chromatographic measurements.

Because the acid numbers of the resins were designed to be about 100 (mg KOH per gram resin), no solubilizing amines were needed. Because of the designed viscosity of the resins, no solvent was needed. Therefore, the resins should meet the requirements of air pollution regulations for the foreseeable future.

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1: INTRODUCTION

1.1: Objective

The objective of the work described in this report was to design and synthesize air-drying resins at the National Institute of Standards and Technology (NIST) for intaglio cylinder-wipe inks to be used in printing currency at the Bureau of Engraving and Printing (BEP). The properties of the prototype resins were measured in laboratory tests at NIST. Inks were formulated and their properties measured at BEP. The aims were to 1) produce material which will give the BEP an improved, known, non-proprietary technology with which to make their intaglio inks and 2) establish principles of intaglio ink resin design.

1.2: Background

Air-dry intaglio ink resins are based on a long-established technology where the ink cures 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, such as linseed oil, and their derivatives. These oils may be used "as is" but are much more commonly reacted chemically to make large molecules known as alkyds. Alkyds cure faster than simple drying oils because some of the chemical bonds needed to cure the material are formed during the manufacturing process of the alkyd rather than in the time after printing.

Because alkyds are large molecules, they are typically so viscous that they must be diluted before use. Air pollution rules limit the amount of volatile solvents which can be used for dilution. Therefore, efforts were made in this work to produce resins which need a minimum of dilution. BEP intaglio inks must be dispersible in water or aqueous alkali (Dalmar solution). To achieve this end, carboxylic acid groups were incorporated into the resins.

The work described in this report is a continuation of work done in FY88 and FY89 in which we designed and synthesized several types of intaglio resins. The syntheses are based on reacting fatty acids from drying oils with various polyols and di-acids. The resultant resins gave inks which in laboratory tests at BEP dispersed well in the alkaline wiping solution used on the press. Initial laboratory tests, designed and carried out by BEP, suggested that the trial inks, after being cured in air for seven days, resisted the wiping solution better than did the standard ink.

1.3: Approach

The properties required of an intaglio ink resin include low toxicity, appropriate viscosity, 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, acceptably low set-off (transfer of ink between adjacent newly-printed sheets), appropriately fast cure speed, good mechanical strength and solvent resistance in the cured film, and little deterioration of film properties on aging.

Drying-oil type molecules and alkyds with reasonable expectations of either providing needed information or meeting BEP's requirements for intaglio ink resins were synthesized. The low toxicity of these air-dry systems is a major reason for their continued use. The resins were based on esters of drying oil fatty acids and contained carboxylic acid groups and alcohol groups to produce stable dispersions of pigments and extenders in the ink and to confer to the ink the ability to disperse in alkaline water. The resins were characterized in terms of molecular size, acid number and viscosity at NIST and, where appropriate, in ink-formulation laboratory tests at BEP. No studies of ink formulation were carried out at NIST.

We have synthesized well over 100 resins in this program and have supplied to BEP several candidate resins which appear from laboratory tests to have the required properties.

1.4: Compliance with the Office of Management and Budget

The activity covered by this agreement consists of work which requires the definition of measurement methods, materials property data, and standards of basic scientific and engineering units to insure equity and comparability in US commerce, international trade, and technical activities. As such, it complies with OMB Circular A-76, revised under paragraph 5f ("Activities classified as Government responsibilities or intimately related to the public interest").

2: BEP PRESS TRIALS OF PROTOTYPE INKS

2.1: Identification of Inks Tested

Several inks made at BEP by Thomas F. O'Brien from prototype resins were subjected to press trials at the end of November, 1990. The inks tested were: two inks made from a resin based on NIST intaglio ink resin WB 27 and made in 208 L (55 gallon) quantity by industry[1]; two inks made from a resin obtained by BEP from the Superior Varnish and Drier Company[1]; and an ink made from a resin obtained from the GEC Company[1]. Table 1 shows the compositions of these inks. The results of the press trial were made available to us by Mark Weiss and Thomas F. O'Brien of BEP and are summarized in Table 2. These results shed some light on the utility of the various laboratory tests used at BEP to gauge the effectiveness of trial inks and resins before the inks are used in trials on the printing press.

2.2: Finger Rub Test and Soak Test

The finger rub test is carried out by spreading a thin ink film on a sheet of glass, covering it with a layer of the Dalmar solution used to emulsify ink on the wiping blade of the press, and rubbing the ink layer until it disperses. The test was used to gauge the ease of dispersion of an ink in the Dalmar solution. Table 3, supplied by Mark Weiss of BEP, shows a high correlation between ease of wiping in the finger rub test and ease of wiping of the ink from the engraved plate using the wiping cylinder, the latter being judged by the amperage used to drive the wiping cylinder on the press. Poorly wiping inks need more pressure from the wiping cylinder and hence more current is necessary to drive the wiping assembly.

The two inks which performed poorly in the finger rub test and amperage requirements were black inks, one made from the NIST-designed resin and one made from the SVD resin. The green ink made from the NIST-designed resin gave the best print quality, had appropriately low amperage requirements, and performed very well in the finger rub test. Since both NIST-based inks (green and black) were made from the same resin, yet one performed well and one poorly in these tests, there must be some explanation other than the nature of the resin for the difference in performance. Obviously, the formulation is critical.

A beaker soak of each ink on a microscope slide suspended in Dalmar solution was also performed to gauge the same property as in the finger rub test, i.e., ease of dispersion of the ink in Dalmar solution. There is very little correlation between the finger rub tests and the beaker soak tests in Table 3. The finger rub test is a dynamic test in that the finger is moving. The beaker test is a static soak. A possible explanation for the difference in performance of an ink in the finger rub and soak

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[1] Commercial names and materials are mentioned to document the procedures. In no case are such mentions to be taken as recommendation or endorsement by NIST or BEP.

Table 1

INK FORMULAS*

	GEC Black 020590-3	NIST Black 062590-3	SVDL Black 020590-4	SVD Black 062590-4	NIST Green 062590-1	SVD Green 062290-4
GEC Varnish	21.1	--	--	--	--	--
Linaqua	9.0	--	10.1	--	--	--
Superior SVD-1788 I-876	--	--	25.3	32.0	--	31.0
Superior SVD-1781 (NIST)	--	32.0	--	--	30.8	--
Petroleum Solvent I-269	3.0	5.0	3.0	5.0	6.9	7.0
Myrj 45 Surfactant	5.0	--	--	--	--	--
Atlas G-3300 Surfactant I-265	--	--	--	0.5	--	--
Cobalt Hydrocure II Drier I-881	0.5	1.0	0.5	0.5	1.0	0.5
Manganese Hydro II Drier I-871	0.5	1.0	0.5	1.0	1.5	1.0
Rare Earth Drier I-982	1.0	1.0	1.0	1.5	1.5	1.5
Clove Oil	0.1	--	--	--	--	--
Furnace Black I-160	2.0	2.0	2.0	2.0	--	--
Black Iron Oxide I-3	25.1	25.0	25.3	25.0	--	--
Blue Base I-291	--	--	2.0	--	--	--
Synthaline Green Base I-281	--	--	--	--	6.0	6.0
Furnace Black Base I-855	--	--	--	--	2.8	2.8
Yellow Iron Oxide I-204	--	--	--	--	9.9	10.0
Amorphous Silica I-154	--	--	--	--	2.0	2.0
Calcium Carbonate I-38	32.7	33.0	30.3	32.5	37.6	38.2

*Formulas are given in wt.%

Table 2

Results for Inks Given Press Trials 11/29/90

	GEC Black 020590-3	NIST Black 062590-3	SVD Black 020590-4	SVD Black 062590-4	NIST Green 062590-1	SVD Green 062290-4
LABORATORY PERFORMANCE						
Emulsification/Washing						
Finger Rub (strokes)	9 9 9	15 16 20	9 10 12	18 20 23	7 9 10	7 8 9
Beaker (5=SICPA >5 worse)	0.5	0 (superb)	5	7.5	1	3
NaOH Resistance						
Q-tip Rub (5=std >5 worse)	8	3.5	8	9	5.5	7.5
Soak (20 hrs) (5=SICPA)	6	7.5	7.5	5	3	6
Inkometer Behavior	see sep shts	sep shts	sep shts	sep shts	sep shts	see sep shts
ON-PRESS PERFORMANCE						
Amps Drawn	37-53	extreme hi	58-81	extreme hi	33-47	30-40
Staining on Print	none	a lot	a lot	a lot	none	yes
Print Quality	a bit mashy	staining	similar	staining	OK	some staining
Negative Aspects Noted	too loose for stable ink key adjustment	tripped breaker	to green 062290-4	tripped breaker	"very unpleasant odor"	dried on duct roll & plate, wiped but did not emulsify
POST-PRESS PERFORMANCE						
Set-Off	excellent	poor	fair	very good	very poor	fair
Blocking	excellent	very poor	poor	poor	very poor	poor
Chemical Resistance (Soak)						
1% Sulfuric Acid	equal	equal	equal	equal	equal	equal
2% NaOH	equal	inferior	inferior	inferior	inferior	equal
1:4 Bleach Solution	equal	equal	equal	equal	equal	equal
Ethanol	equal	equal	equal	equal	equal	equal
Perchloroethylene	equal	equal	equal	equal	equal	equal
Toluene	equal	equal	equal	equal	equal	equal
Acetone	equal	equal	equal	equal	equal	equal
Gasoline (unleaded)	equal	equal	equal	equal	equal	equal
Mineral Spirits	equal	equal	equal	equal	equal	equal
Chemical Rub Resistance						
1% Sulfuric Acid	equal	equal	equal	equal	equal	equal
2% NaOH	inferior	equal	inferior	inferior	equal	equal
1:4 Bleach Solution	equal	equal	equal	equal	equal	equal
Ethanol	superior	superior	superior	superior	superior	equal
Perchloroethylene	superior	superior	superior	superior	superior	equal
Toluene	superior	equal	superior	superior	equal	equal
Acetone	superior	superior	superior	superior	superior	equal
Gasoline (unleaded)	equal	equal	equal	equal	equal	equal
Mineral Spirits	superior	superior	superior	equal	superior	equal
Durability						
Crumple	6-exclnt.	6-exclnt.	4.8 satis.	4.3 accpt.	6-exclnt.	6-exclnt.
Laundry	5.4 V good	5.9 exclnt.	4.8 satis.	4.4 accpt.	5.5 V good	6-exclnt.

Table 3

Inks Given Trials 11/29/90 - Conclusions

Ink	Finger Rub Strokes[A]	Press Amperage[B]	Beaker Test Rating[C]	Ink Rankings by Finger	Amps	Beaker
GEC B 020590-3	9 9 9	37 - 53	0.5	3rd	3rd	2nd
NIST B 062590-3	15 16 20	extreme hi	0	5th	5th	Best
SVDL B 020590-4	9 10 12	58 - 81	5	4th	4th	5th
SVD B 062590-4	18 20 23	extreme hi	7.5	6th	6th	6th
NIST G 062590-1	7 9 10	33 - 47	1	2nd	2nd	3rd
SVD G 062290-4	7 8 9	30 - 40	3	Best	Best	4th

[A] Fewer is better. [B] Lower is better. [C] <5 -- Better than the standard ink; >5 --worse tests is that, for a given resin, low ink viscosity is more important in the finger rub test. Higher viscosities are expected to give higher strokes in the finger rub test.

From the compositions of the inks, Table 1, it is obvious that the two black inks requiring high amperage had 1.9% less petroleum solvent than the green inks. The other black inks, made from the GEC and the SVD resins, had much more solvent, i.e., 9% and 10% Linaqua solvent, respectively.

The viscosities of the inks were:

GEC black: 0.35 Pa s (contained Linaqua)
NIST black: 1.19 Pa s
SVD black 1: 0.99 Pa s (contained Linaqua)
SVD black 2: 1.89 Pa s
NIST green: 0.90 Pa s
SVD green: 1.30 Pa s

These inks and viscosities are listed in the same order as the inks in Table 2. There is little correlation of the washing and amperages values in Table 1 with these viscosity values. This shows that ink viscosity, while important, is not the most important parameter controlling differences in performance in the finger rub and soak tests and amperage requirements. Otherwise, it would be possible to bring an ink into compliance in the finger rub test by adding solvent. Confirmation of this view was obtained in several tests conducted on inks which had performed poorly in the finger rub test. Some of these inks were based on resins with acid numbers of about 100 mg KOH/ g resin, which is high enough to make the resin dispersible in Dalmar solution. Some improvement in the finger rub test results was made by adding mineral spirits to the inks, but it proved to be impossible to bring the inks into compliance (10 strokes or less).

Equally clearly, although the acid number of the resin must be high enough, it also is not the determining parameter in governing washing. Because the NIST and SVD resins gave widely differing black and green inks, formulation must be the governing factor.

2.3: Chemical Resistance Tests and Durability Tests

Chemical resistance of the ink film after one week of cure in air was checked at BEP against nine common aggressive liquids: mineral spirits, gasoline, acetone, toluene, perchloroethylene, ethyl alcohol, 1:4 aqueous bleach solution, 2% aqueous sodium hydroxide, and 1% aqueous sulfuric acid. Durability was checked in crumple and laundry tests. The results are given in Table 2.

The problem for all inks was lack of satisfactory resistance to 2% aqueous sodium hydroxide, where the ink was required to withstand an abrasion test, both after immediate application of the caustic to the printed ink film and after the film had undergone a 24 h soak in the caustic solution. In earlier bench-top tests at BEP, resistance to caustic solution had been estimated using a rub test immediately after applying the caustic solution (Q-tip rub test). In the case of the inks used in the press trials, a long soak (20 h) in aqueous caustic was also carried out by BEP personnel. This was the first long soak test performed during the development of these alkyd resins. Up to this point, we were unaware that 24 h soaking with subsequent testing was a necessary test.

The NIST inks were the two most resistant inks in the laboratory Q-tip rub test. The green NIST-resin based ink was the most resistant in the soak test. However, the NIST-resin based black ink, which was the most resistant ink in the Q-tip test, was the least resistant ink (equal with one other ink) in the soak test. Clearly, the Q-tip rub test and the soak test measure different ink properties and one cannot be substituted for the other.

The NIST-resin based green ink was significantly worse than the NIST-resin based black ink in the Q-tip rub test but was significantly better in the soak test. These inks were made from the same resin, which again clearly points out the importance of the formulation on the ink properties, the difficulty of assessing any particular resin because the formulation of the ink is so important in determining the properties of the ink, and the need for an extensive study of the formulation of an ink. Both inks passed the press trial rub test, and both were inferior to the standard ink in the aqueous caustic 24 h soak test.

2.4: Improving Resin Resistance to Aqueous Caustic

The resistance results pointed to a need to increase the resistance of the newly-cured ink films. To the extent that solvent resistance is dependent on the resin and not on the formulation, this may be achieved by 1) reducing the acid number of the resins, 2) increasing the rate and extent of cure by incorporating more drier in the inks, or tung oil fatty acids in the alkyd, or tung oil as a reactive diluent in the formulation, or 3) using higher molecular weight or more viscous alkyds.

Resistance and other properties are also governed by such parameters as the solid to resin ratio in the ink, too much solid being particularly deleterious.

If the acid number of the resin is reduced, the dispersibility in Dalmar solution will be reduced. However, it was not clear that we had been able to optimize the acid number of the resin, because all our design work concerning the acid number of the resin had been based on the finger rub test, which is greatly influenced by the formulation as well as the acid number of the resin used in the ink. The acid number of the NIST-based resin used in the press trial inks was about 100 mg KOH/g resin.

Salts of carboxylic acids are more hydrophilic than un-ionized carboxylic acids and thus disperse more easily in aqueous solutions such as Dalmar solution. Dispersibility can therefore be conferred to inks with low acid numbers by converting the acid groups in the resin to salts by neutralization with volatile amines. These amines are slowly lost as the ink cures and the less hydrophilic un-ionized carboxylic acid groups are reformed. The inks formulated at BEP from NIST resins have not included amine. Since the solubilizing contribution of the amine-derived salt (often used in inks and paints) was absent in the BEP inks made from NIST resins, it was therefore necessary to increase the acid number of the NIST resins considerably to confer the needed water dispersibility to the inks. This makes the inks more susceptible to long-term immersion in caustic solutions.

Improved resistance can be conferred to the ink by incorporating tung oil fatty acids in the resin along with the linseed oil fatty acids commonly used. Resins and inks of this type are expected to crosslink more extensively than the resins based solely on linseed oil fatty acids. Thus the cured ink films are expected to be somewhat more resistant to long-term immersion in aqueous caustic solution.

In the work described in this report, we synthesized several resins which contained tung oil fatty acids along with linseed oil fatty acids. Because of reorganizational delays at BEP, these resins were not tested until three months after their preparation. During that time, the resins became significantly more viscous and seemed to have undergone some curing.

We also conducted laboratory tests in which amines and solvents were added to intaglio ink resins. Several inks were made by Mark Weiss at BEP from alkyds which had lower acid numbers and contained solubilizing amines, including ammonia. The washing behavior of the inks was not acceptable (the best result was about 16 strokes) but the resistance after being soaked for 20 h in aqueous caustic was judged to be comparable to that of the standard ink. The most resistant films were those of lower acid number originally containing ammonia, and those containing some tung oil fatty acid in the alkyd. There was little correlation between strokes to wash and ink viscosity.

Other ink resins which were synthesized had much higher molecular weights. Several of these resins were formulated by John Moynihan at BEP into inks which performed satisfactorily in laboratory tests.

2.5: Brittleness

It must be emphasized that a more highly cured ink film is be more brittle. Crumple tests must be included in the tests run on inks made from resins including tung oil or tung oil components to ensure that the films are not too brittle. In the press trials, the NIST-resin based inks passed the crumple tests with grades of excellent and very good. With tung oil components, brittleness may increase significantly with time and crumple tests should be carried out on one and two year old samples.

2.6: Set-off

Presumably tack plays some part in determining "set-off" and the related "blocking", where there is transfer of printed ink from one sheet to the neighboring sheet in the first case and adhesion between sheets in the second case. Tack is necessary to allow the paper to pull the ink out of the grooves on the engraved cylinder on the press. Lower tack is presumably appropriate to prevent set-off and blocking.

Tack values for the various inks at 60 seconds are shown in Figure 1. The NIST-resin based inks were the worst in set-off and blocking. The best, the GEC-resin based ink, had low tack values, but did not print as well as the NIST-resin based green ink. The NIST-resin based inks are in the middle of the range of tack values found. The NIST-resin based green ink had almost the same tack values as reconstituted standard ink, which is known to behave satisfactorily on the press. The extent to which set-off and blocking are correlated with tack is not clear.

The typical industrial solution to the problem of high tack at one point in the printing process and lower tack at a subsequent point is to make the tack sensitive to temperature by incorporating wax in the ink. At the temperature of the press (about 80°C), the wax is molten and dispersed in the ink. As the ink cools on the newly-printed paper on its way to the stock pile, the wax solidifies and changes the properties of the ink, in particular reducing the tack. Measured tack values should be obtained at different temperatures to monitor the change in tack during the printing process.

Physically, the tack manifests itself as "stringiness" of the resins. Stringiness is a function of molecular weight of the resin and of polar, hydrogen-bonding groups such as hydroxyl and carboxylic acid groups on the resin molecules.

It may therefore be that set-off is advantageously affected by a decrease in acid number and perhaps by the use of amines. Carboxylic acid groups are known to promote adhesion by forming ionic bonds and hydrogen bonds. Reducing the concentration of carboxylic acid groups would to some extent make the ink less

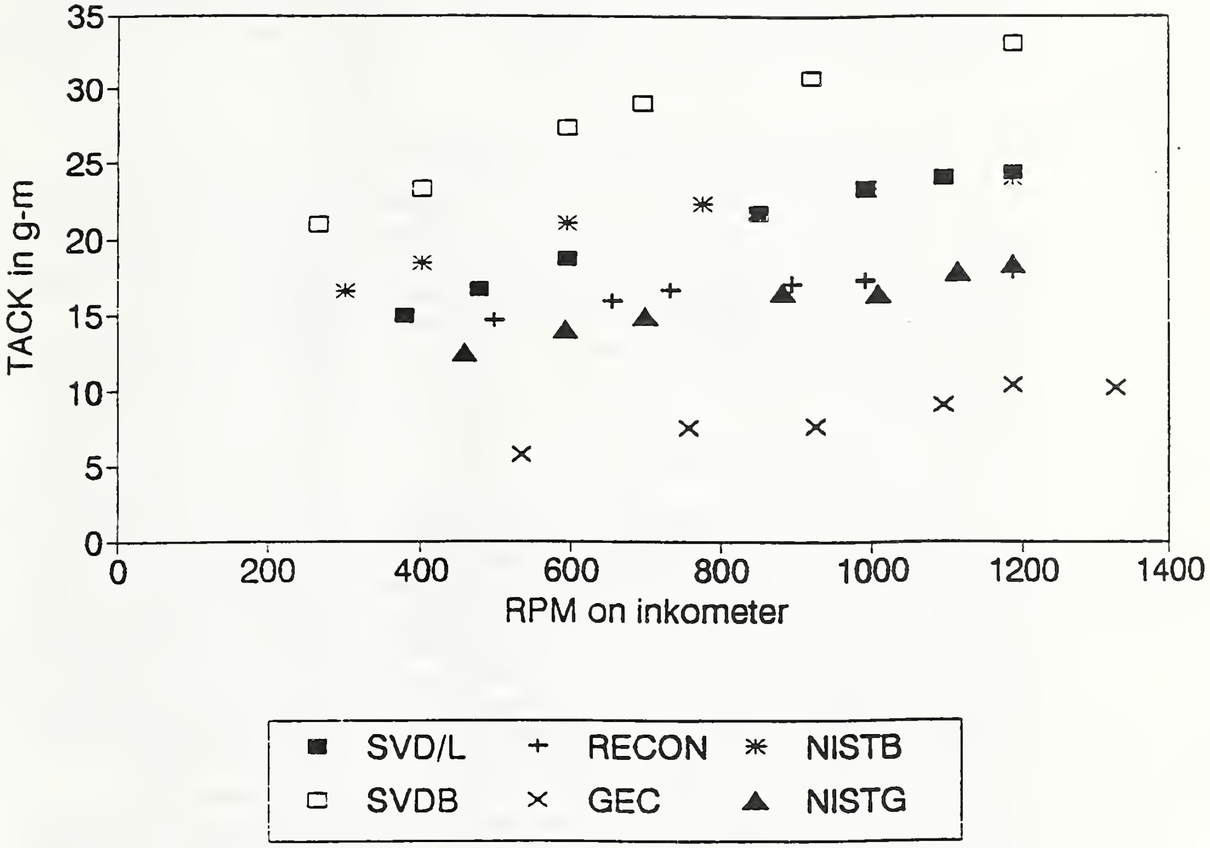


Figure 1: 60 second tack values for selected inks.

sticky by reducing the number of these bonds. Making the acid groups into salts using amines would remove their ability to enter into hydrogen bonds and would allow the addition of water, which would reduce tack. Of course, numerous other factors also contribute to reducing set-off.

2.7: Use of Amines in Ink Formulations

Amines are used to form carboxylic acid salts in water-dispersible coating materials such as paints and inks. If used in air-dry inks, they tend to complex with the transition metal driers and retard the drying rate of the ink. Also, if volatile, they contribute to environmental pollution. If a suitable ink formulation can be found, the use of amines should be avoided.

2.8: The Research Press

The results of the press trials show that formulation is the key to making a suitable resin into a successful ink. No clear relationships were found between measured parameters and performance on the press. Therefore, many formulations will have to be carried out to evaluate a particular resin and the formulations will have to be tested in press trials. Because the production presses are heavily used, a substitute must be found if one exists. The best candidate is the research press at BEP, but the extent to which performance on the research press correlates with performance on the production presses is unknown. The easiest way to establish whether there are indeed such correlations (without which the research press is useless and should be discarded) is to run many samples of the standard ink on the research press as well as on the production presses. It will then be feasible to establish whether the research press can be used to carry out realistic tests of the many formulations required to test a potential ink resin. If the research press can be used, the 208 L (55 gallon) quantities of resin available from these studies should be used in a series of formulation studies to learn 1) the interactions between ink components and ink properties and 2) which laboratory measurements correlate with performance on the press.

3: TUNG OIL FATTY ACID-CONTAINING ALKYDS

The press trials pointed to a need to increase the resistance of the inks to alkaline solvents. One of the ways in which to do this is to incorporate tung oil in the ink, either as a reactive diluent or as fatty acids in the alkyd synthesis. The synthesis activities to be described next focussed on the incorporation of tung oil components in alkyd resins. Tung oil fatty acids (TuOFA) are not commercially available. Consequently, our first efforts were directed to the hydrolysis of tung oil to produce tung oil fatty acids. A search of the literature on fats and oils was conducted and several hydrolysis methods were found.

3.1: Tung Oil Hydrolysis

The saponification reaction for oils was generally described as refluxing, for approximately six hours, the following proportions of components:

100 parts of fat or oil
60 parts of potassium hydroxide
500 parts of 95% to 100% ethanol

A trial saponification reaction was carried out using 50 g of tung oil, 30 g of potassium hydroxide and 250 g of 100% ethanol. Reaction glassware consisting of a 500 mL round-bottomed three neck flask, condenser, and thermometer was assembled. A continuous flow of nitrogen gas was swept through the reaction flask and condenser. The reaction components were stirred continuously by a magnetically-driven teflon-covered stirring bar. As the temperature of the reactants was increased, solvent reflux started at 83°C. Samples were removed from the flask periodically to monitor the progress of the saponification reaction. After approximately seven hours of refluxing, the saponification reaction was considered complete and the recovery of tung oil fatty acids from the reaction mixture was started.

The first step in the recovery process was to remove by distillation approximately one half of the ethanol in the reaction mixture. The mixture was then cooled, poured into a large separatory funnel and diluted by the addition of 250 mL of de-ionized water to remove glycerol, potassium hydroxide and some of the ethanol. It is particularly important to remove the glycerol from the saponification mixture because it is a trihydric alcohol and re-esterification would give no advantage over using tung oil initially.

The aqueous mixture was then extracted with 1,2-dichloroethane (DCE). Glycerol is not soluble in DCE. After the addition of 150 mL of DCE, two phases appeared. The funnel was shaken for approximately five minutes and the phases allowed to separate. The lower phase (DCE) was drawn off and 100 mL of fresh DCE added. This DCE extraction was repeated four times. The residual potassium hydroxide in the solution was then neutralized by the addition of numerous small aliquots of hydrochloric acid. The pH of the solution was monitored by pH paper and acid addition stopped as the solution became neutral (this should have been continued until the layer was definitely acid, at a pH of about 2). At neutral pH, the solution separated into two phases, a cream-white aqueous upper phase and a tan-brown oily lower phase containing the tung oil fatty acids. The lower phase was drained into a storage bottle and the head space flushed with nitrogen gas before the bottle was capped.

Samples of the tung oil fatty acid solution were weighed into vials and the solvent driven off in a warm (80 to 82°C) oven. The solution contained 30% tung oil fatty acids (TuOFA) and 70% volatile solvents.

3.2: Synthesis of 100% Tung Oil Fatty Acid Alkyd

Earlier tests at BEP in FY90 had shown a NIST alkyd resin known as WB 27 to be promising. WB 27 was based on linseed oil fatty acids (LOFA). Using the formula for WB 27 as a starting point, a tung oil alkyd was synthesized by completely substituting tung oil fatty acids for linseed oil fatty acids in the formula. The tung oil hydrolysis yielded 37.2 g of tung oil fatty acids, so the amounts of other alkyd components were scaled appropriately (Table 4) to maintain the same ratios of components as that of alkyd WB 27.

Table 4: 100% TuOFA Alkyd Based on WB 27

Alkyd WB 27		100% TuOFA Tung Oil Alkyd	
Linseed Oil Fatty Acids	86.7 g	Tung Oil Fatty Acids	37.2 g
Sebacic acid	18.0 g	Sebacic acid	7.73 g
Pentaerythritol	30.3 g	Pentaerythritol	13.0 g
Succinic anhyd.	30.1 g	Succinic anhyd.	12.9 g

The tung oil alkyd synthesis was started by combining the tung oil fatty acids, sebacic acid and pentaerythritol and driving off excess ethanol/DCE solvent from the reaction mixture. As the temperature of the reaction components was slowly increased and reached 82°C, ethanol/DCE began to condense in the apparatus side arm. Solvent continued to condense until the temperature reached 130°C, at which point 55 mL of solvent had been removed. The apparatus side arm was then filled with xylene and 20 mL of xylene was added to the reaction flask and heating continued. Reflux of the xylene started at 162°C. The reaction temperature increased slowly to 183°C as the reaction proceeded and the acid number dropped from 160 to 19 mg KOH per gram of reactants.

After it had reached an acid number of 19, the reaction mixture was cooled to 125°C. The acid number was not reduced further to prevent gellation of the alkyd. Succinic anhydride was added. The temperature was increased to 180°C and maintained there for 15 minutes. Heating was stopped and the resin cooled and poured into a storage jar. The storage jar headspace was flushed with nitrogen gas before the jar was capped.

The tung oil alkyd had a high viscosity at room temperature, too high to measure on the equipment we use for viscosity measurements. The acid number of the finished alkyd was relatively high, 175 mg KOH per g of resin. The alkyd did not dissolve completely in the isopropanol used as solvent in the determination of acid number. The alkyd also did not completely dissolve in the THF used as solvent in the size exclusion chromatograph. These results, taken together with the high viscosity, suggest that the alkyd contained a gel component.

The fact that the TuOFA had not been completely acidified meant that some potassium ions were present, which probably contributed to the observed insolubility and apparent gelation through the formation of potassium salts.

3.3: Larger Scale Tung Oil Hydrolysis

Following the successful saponification of a small quantity of tung oil and the subsequent synthesis of a tung oil alkyd, the saponification process was scaled up to provide a larger supply of tung oil fatty acids (TuOFA). 200 g of tung oil, 120 g of potassium hydroxide and 1000 g of 100% ethanol were used. Reaction glassware comprised of a 2000 mL round-bottomed three neck flask, condenser, and thermometer was assembled. A continuous flow of nitrogen gas swept the reaction flask and exited the glassware through the condenser during the reflux period. The reaction components were heated to about 85°C for about 7 h and then the tung oil fatty acids were extracted as before.

Just prior to use in an alkyd synthesis reaction, the tung oil fatty acid solution was further processed. Six to 8 mL of concentrated HCl were added to 250 mL of the TuOFA solution. As the solution turned acidic, two phases appeared. The upper phase was presumably an ethanol-rich phase which had been emulsified in the DCE by the potassium salt of the tung oil fatty acids. When the solution was made appreciably acid (pH about 1 to 2), the tung oil fatty acids no longer existed as the potassium salt. Thus the soap action of the fatty acid salt was lost and the ethanol phase separated.

Five hundred mL of water were then added and the mixture was mixed vigorously and allowed to separate. The upper aqueous layer was removed by suction and two more water washes of the lower phase were performed. After removal of the upper water layer, the TuOFA lower phase was poured into a bottle for storage. TuOFA solution samples heated to dryness in a 100°C oven revealed the solution contained approximately 30% TuOFA solids, the remainder being ethanol/DCE solvent.

Tung oil fatty acids are light brown solids, melting at about 50°C for the naturally occurring cis isomer and 75°C for the trans isomer. It proved convenient to keep them in DCE solution rather than precipitate them and filter them off and risk polymerization of the solid fatty acids in air.

3.4: Cold Saponification of Tung Oil

A second "cold" method of saponification was also tried. The reaction consists of mixing 10 mL tung oil, 2.6 g potassium hydroxide, 2.5 g water and about 0.1 mL ethanol, and is said to be complete within minutes. The reaction proceeded with a considerable exotherm. After five minutes, the viscosity had increased significantly. After 10 minutes, the mixture was almost impossible to stir. About 1 liter of water was added slowly and the mixture was acidified. Free tung oil fatty acids separated as a brown solid. However, the extent of saponification proved to be less than 10%, as judged from the amount of recovered tung oil. Therefore, it seemed more reasonable to carry out the saponification at higher temperatures and for far longer times as described above.

3.5: Synthesis of 10%, 20%, 30% TuOFA alkyds

Using the formula for alkyd WB 27 as a starting point, several more tung oil alkyds were synthesized by partially substituting tung oil fatty acids (TuOFA) for linseed oil fatty (LOFA) acids. The total fatty acid content of the alkyds remained constant. Syntheses were carried out with TuOFA replacing 10%, 20% and 30% of the LOFA. Syntheses were carried out later with TuOFA replacing 5%, 30% and 50% of the LOFA.

The total quantities of materials used in the TuOFA/LOFA alkyds were increased by two times the original alkyd WB 27 amounts to reduce the air space in the reaction flask due to concerns about the increased air sensitivity of TuOFA as compared to LOFA. A formula comparison chart for the different alkyds is given in Table 5.

TABLE 5: TuOFA/LOFA Alkyds

Quantities in grams

Alkyd WB 27		Linseed Oil/Tung Oil Alkyds			
			10%	20%	30%
Linseed Oil		LOFA	156.0	138.7	121.3
Fatty Acids	86.67	TuOFA	17.3	34.7	52.0
Sebacic acid	18.0	Seb. acid	36.0	36.0	36.0
Pentaerythritol	30.28	Pentaeryth.	60.6	60.6	60.6
Succinic anhyd.	30.1	Suc. anhyd.	60.2	60.2	60.2

Xylene was added at 10% by weight of the first step reactants.

The TuOFA/LOFA alkyd syntheses were started by combining the linseed oil fatty acids and tung oil fatty acids solution (30% TuOFA solids), sebacic acid and pentaerythritol. Refluxing of the xylene/ethanol/DCE mixture began at progressively lower temperatures as the proportion of TuOFA increased, reflecting the higher amounts of ethanol/DCE added to the flask with increasing amounts of TuOFA (Table 6).

TABLE 6

Boiling point depression in alkyd syntheses

Composition of Alkyd	ID #	Initial Reflux Temperature
10% TuOFA, 90% LOFA	(WB 48)	155°C
20% TuOFA, 80% LOFA	(WB 49)	135°C
30% TuOFA, 70% LOFA	(WB 50)	100°C

These reflux temperatures are below the minimum 160 to 170°C temperature needed to cause the esterification reaction to proceed at a reasonable rate. To increase the reflux temperature of the reaction mix, solvent was drained from the Dean-Stark side arm of the apparatus before the side arm completely filled and solvent started returning to the reaction flask. Fresh xylene was added to the reaction mixture through one of the flask necks. After three to four 25 mL volumes of xylene had been flushed through the flask in this way, the reflux temperature increased to 184°C, 174°C and 160°C, respectively, for the 10%, 20% and 30% TuOFA levels in the alkyds. The synthesis of the 30% TuOFA alkyd, refluxing at 160 to 165°C, was very slow. After over nine hours of refluxing, the first step of the reaction was only 68% complete. Thirteen more hours of refluxing were needed to react enough material to produce an acid number of 9, permitting the second step of the reaction to proceed. Clearly, not enough low-boiling solvent had been removed.

After reaching an acid number of 10 mg KOH or less per gram of alkyd, the reaction mixture was cooled to 125°C and succinic anhydride was added. Following succinic anhydride addition, the temperature was increased to 180°C and maintained there for 30 minutes. Heating was then stopped and the resin cooled and poured into a storage jar. The storage jar headspace was flushed with nitrogen gas before the jar was capped.

To overcome the problem of low reflux temperatures and very slow reaction rates caused by the relatively high solvent content of the TuOFA solution, flash evaporation of the solvent from the TuOFA solution under vacuum was performed. The TuOFA solution was warmed in a round bottomed flask to about 50°C in a pan of water and subjected to vacuum. Solvent was readily removed from the TuOFA solution. After approximately one hour under vacuum, the TuOFA solution contained 85.6% solids and 14.4% volatiles, as determined by drying a sample in an oven at 102°C.

In addition to the three alkyds described above, two additional TuOFA/LOFA alkyds were synthesized using the TuOFA solution with the solvent content reduced by vacuum evaporation. The first of these alkyds (WB 51) was a repeat of the 10% TuOFA /90% LOFA alkyd (WB 48) based on the formula for alkyd WB 27. This alkyd was chosen to evaluate the effect of a shorter, higher temperature first reaction step on the molecular weight distribution and viscosity of the finished alkyd. The viscosity of the alkyd prepared this way is comparable with that of the alkyd prepared without solvent evaporation (WB 51 vs. WB 48 in Table 7). WB 48 contains less solvent than WB 51 and is expected to be a little more viscous.

The second of these alkyds, containing 20% TuOFA and 80% LOFA (WB 52), was based on the formula for alkyd WB 31 (formulas shown below in Table 8), which contains less sebacic acid than WB 27. The goal in using the WB 31 formula was to reduce the viscosity of the finished alkyd (Table 7). The amount of available TuOFA did not allow a gram for gram equivalent copy of the WB 31 formula so the weights of other constituents were scaled to that of the TuOFA. The goal was to provide an alkyd which would need less solvent to provide the appropriate viscosity and hence would produce less volatile organic content (VOC) emission in line with the Clean Air Act, but which would be expected to produce a fairly hard film after the initial air dry.

TABLE 7

Acid numbers, viscosities and residual solvent contents of the TuOFA/LOFA alkyds.

Alkyd ID #	Acid Number	Viscosity, Pa s		Residual Solvent
		20°C	30°C	
WB 48	111	40	22	0.2% to 0.3%
WB 49	120	41	22	0.8%
WB 50	120	53	33	1%
WB 51	116	34	19	1%
WB 52	100	10	5	2%

TABLE 8

Alkyd WB 31		Alkyd WB 52	
Linseed Oil		LOFA	145.6 g
Fatty Acids	98.2 g	TuOFA	36.4 g
Sebacic acid	10.5 g	Sebacic acid	19.5 g
Pentaerythritol	28.3 g	Pentaerythritol	52.5 g
Succinic anhyd.	28.0 g	Succinic anhyd.	51.9 g

Xylene was added at 10% by weight of the first step reactants.

Inks were made from these resins by Mark Weiss at BEP at the same time that inks were made from the amine- and solvent-containing resins. The results are given together with those of other resins in Table 13.

3.6: Size Exclusion Chromatographic Examination of Tung Oil Alkyds

The preparations of the tung oil-containing alkyds were monitored using size exclusion chromatographic analysis. A cross-linked divinylbenzene mixed-bed size exclusion column with a linear range of 100 to 20,000,000 daltons was used. The eluting peaks were examined using a UV absorption detector capable of monitoring four wavelengths simultaneously and by a mass sensitive evaporative detector. Both THF and 1,2 dichloroethane were used as solvents. Solvent flow rate through the chromatographic column was 1 mL per minute.

Our scheme involved as a first step the hydrolysis of tung oil to provide free tung oil fatty acids, analogous to the free linseed oil fatty acids used in our previous syntheses. The chromatographic results of the hydrolysis reaction are shown in Figure 2. In Figure 2, the chromatograms are, from the bottom of the figure, of tung oil fatty acids (TuOFA) from reaction 1, TuOFA (TuOFA solution) from reaction 2, a commercial sample of linseed oil fatty acids, and a commercial sample of linolenic acid. Lower molecular size is to the right side in these chromatograms.

The chromatogram for linolenic acid shows where fatty acids are expected to elute. The chromatogram for LOFA shows a peak corresponding to free fatty acids, as expected. A second peak in the "fatty acid region", just to the left of the first peak, shows that in this material there is in some other species close in size to the free fatty acids. There is also some unhydrolyzed linseed oil, as indicated in the figure. In comparison, the second hydrolysis reaction of tung oil, labelled TuOFA solution, produced very pure TuOFA as seen from the fact that there is only one peak in that chromatogram. The TuOFA are solids which we typically keep dissolved in the solvent 1,2 dichloroethane; hence the label TuOFA solution. The first hydrolysis reaction obviously contains unhydrolyzed tung oil (the left hand peak on the bottom chromatogram) and some other species not as low in molecular weight as TuOFA. Thus, the first hydrolysis reaction was not satisfactory. The fully hydrolyzed TuOFA was used in the synthesis of the alkyds WB 48 to WB 52.

A comparison of tung oil and linseed oil is given in Figure 3 and serves to identify the left hand peaks in Figure 2 (at an elution volume of about 24 mL) as being from tung oil and linseed oil, respectively. The two lower chromatograms in Figure 3 are from an evaporative detector, which measures only those materials that remain as particles at about 100°C. The solvent and BHT stabilizer evaporate under these conditions. Both tung oil and linseed oil (the second chromatogram in Figure 3) have only one peak. The UV chromatogram of linseed oil (top chromatogram), taken in solution at 254 nm, shows two peaks. The left hand peak is from a material which either evaporated in the evaporative detector (which is unlikely, given that its molecular size is larger than that of linseed oil) or is an intense absorber of 254 nm radiation but present in very small quantity (much more likely). Thus it is possible to conclude, from comparing the results of the two different detectors, that this sample of boiled linseed oil did not contain any discernible quantity of linseed oil dimer.

A total of seven tung oil fatty acid containing alkyds had been synthesized at this point, five of them being from mixtures of TuOFA and LOFA. Table 9 below summarizes the fatty acid composition of those alkyds based on mixtures of TuOFA and LOFA.

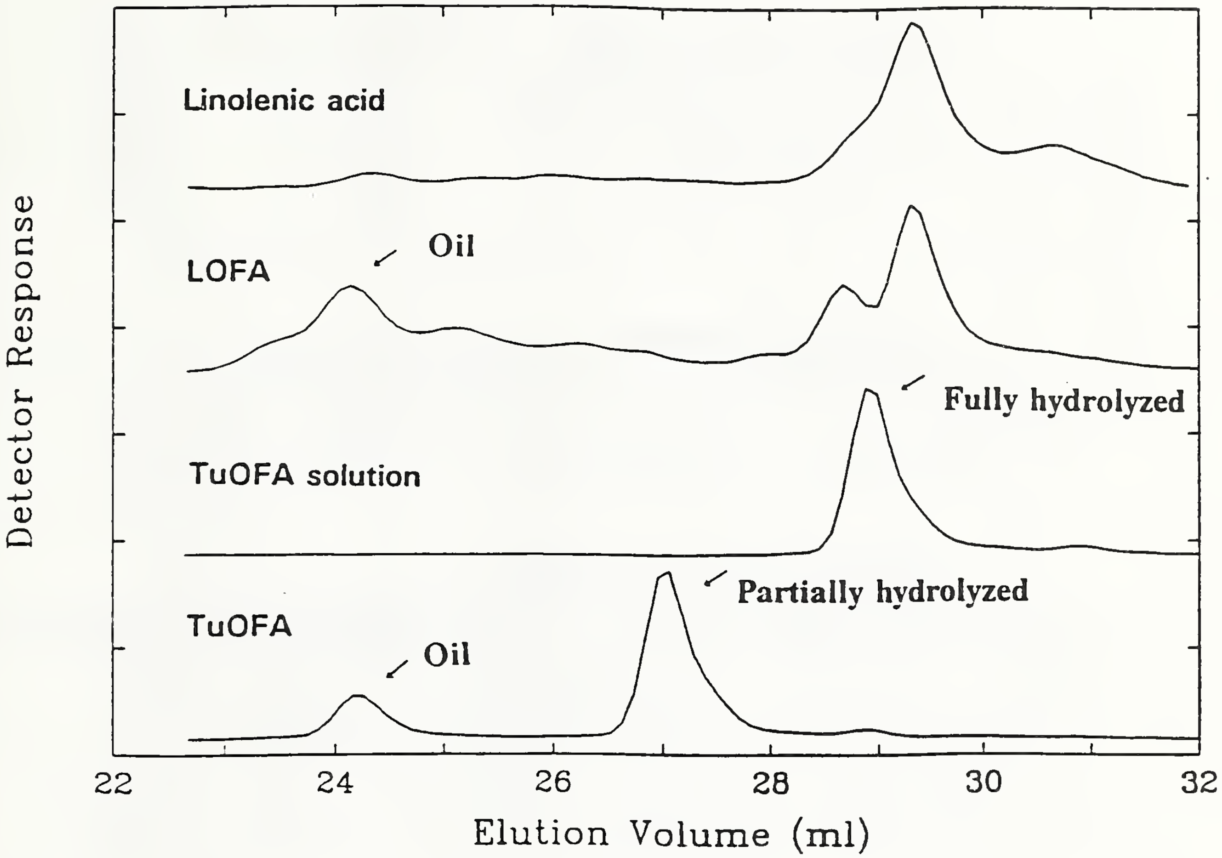


Figure 2: Size exclusion chromatographic analysis of tung oil hydrolysis reaction.

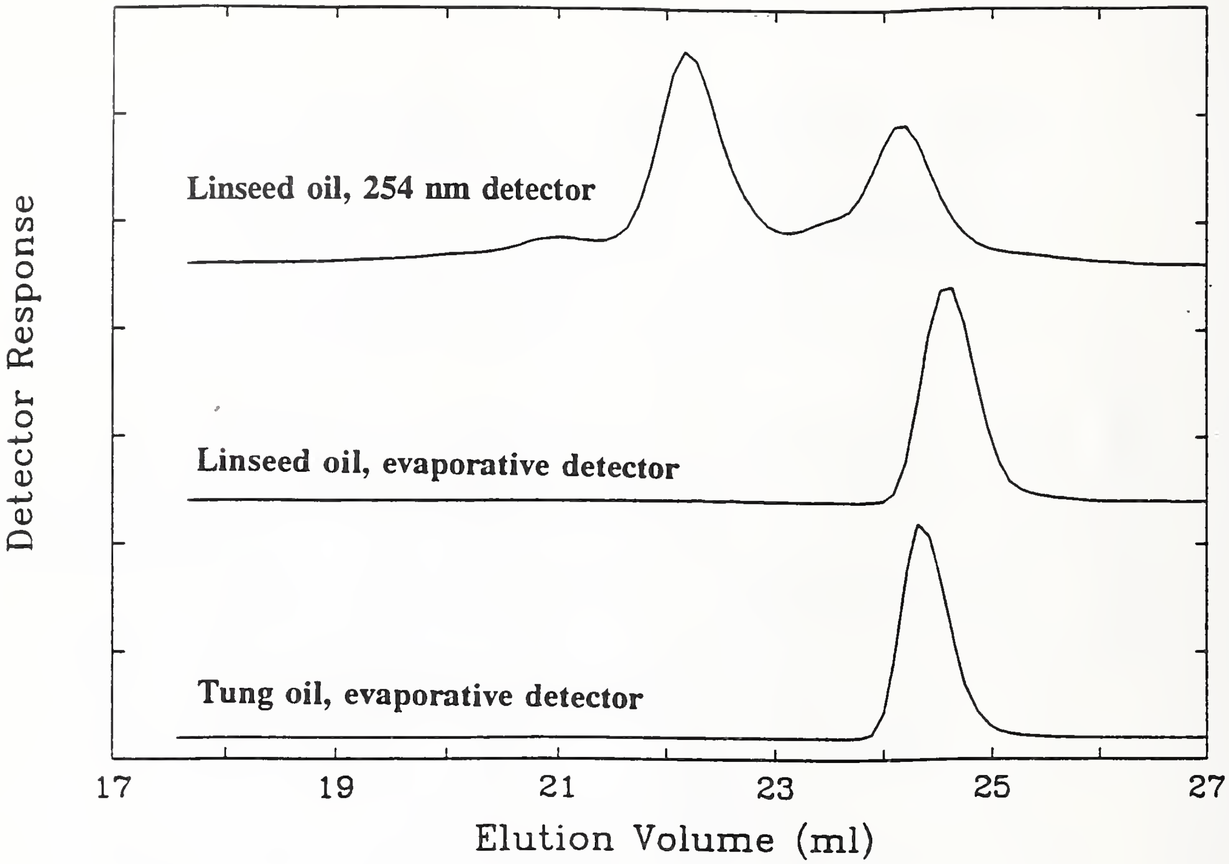


Figure 3: Size exclusion chromatographic comparison of linseed oil and tung oil

Table 9

Alkyd ID	TuOFA/LOFA Ratio	TuOFA Solids/Solvent Ratio
WB 48	10% / 90%	Dilute solution: 33% TuOFA, 67% Solvent
WB 49	20% / 80%	Dilute solution: 31% TuOFA, 69% Solvent
WB 50	30% / 70%	Dilute solution: 30% TuOFA, 70% Solvent
WB 51	10% / 90%	Conc. solution : 86% TuOFA, 14% Solvent
WB 52	20% / 80%	Conc. Solution : 78% TuOFA, 22% Solvent

These alkyds are compared with alkyd WB 27 in Figures 4 and 5.

The chromatogram of WB 27 is the one which extends most to the left hand side in Figure 4, i.e., to the high molecular weight side. The chromatogram which extends least to the left hand side in Figure 4 is that of alkyd WB 52. The other alkyds are very similar to each other, as shown by the remaining chromatograms, and are intermediate between alkyds WB 27 and WB 52.

Figure 5 shows other chromatograms of the same materials. The difference is that the 4 mg alkyd samples were kept on the side of the SEC vial for up to 0.5 h before the solvent was added and thus had time to air-dry and extend (to the left in Figure 5) to produce more high molecular weight material than was present in the bulk material. Figure 4 contains chromatograms from specimens that were immediately covered with and dissolved in solvent so that air-drying could not occur. The molecular weights are more in accord with expectations. Thus, some care is necessary to ensure that the chromatographic results are meaningful.

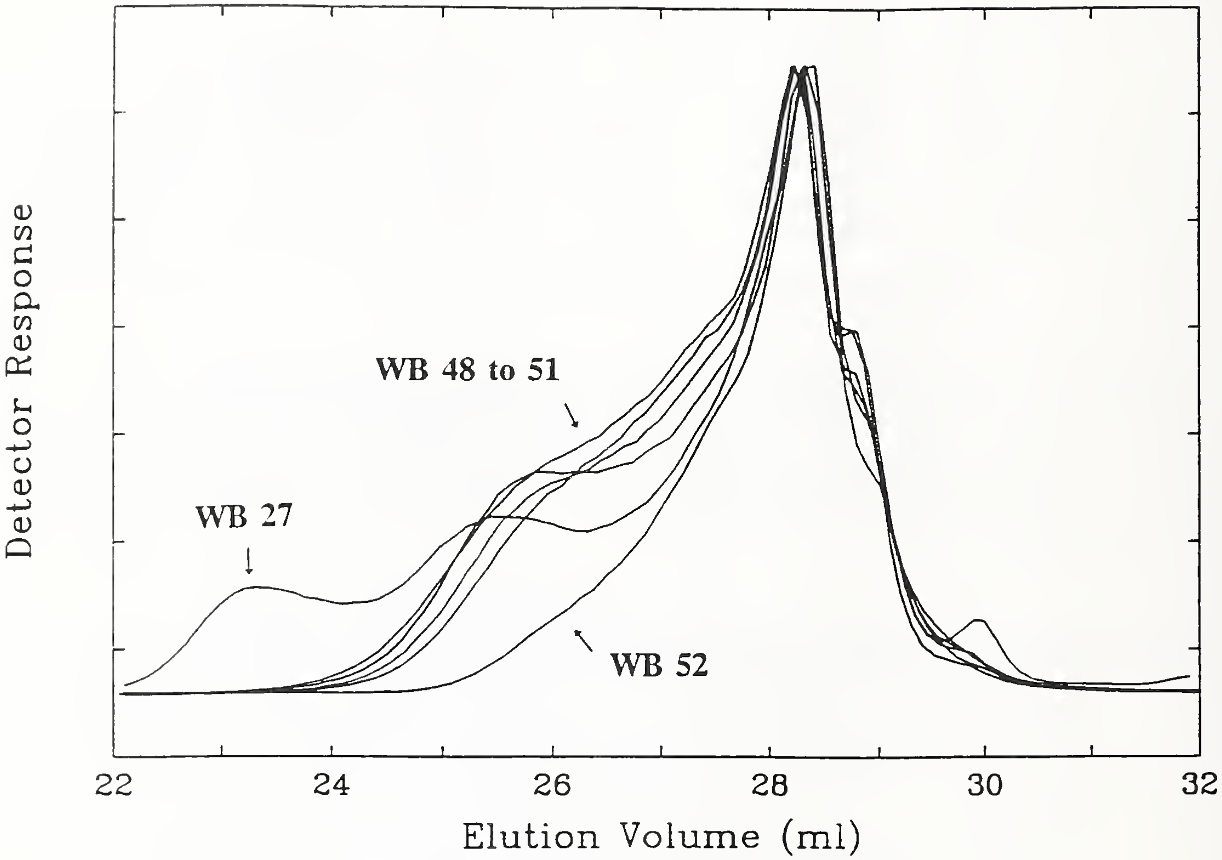


Figure 4: Size exclusion chromatographic comparison of alkyd WB27 and the TuOFA-containing alkyds WB48, WB49, WB50, WB51 and WB52.

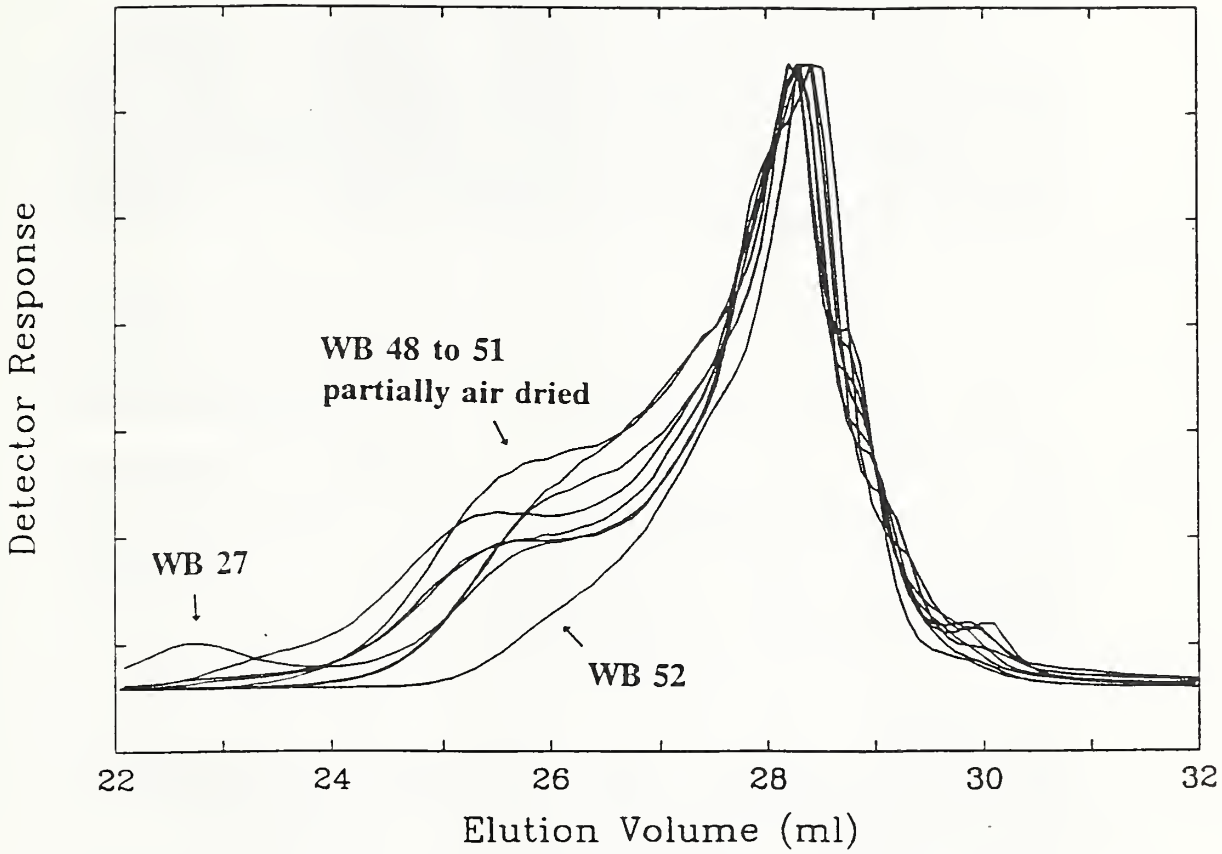


Figure 5: As in figure 4, except that alkyds WB48 to WB51 had partially air-dried on the walls of the sample vials.

3.7: Synthesis of 5%, 30%, 50% TuOFA Alkyds

The tung oil fatty acid-containing alkyds just described were based on WB 27, a successful resin developed in FY90. The formula of WB 27 in terms of moles of reactants is given in Table 10. Three more TuOFA-containing alkyds were synthesized. The TuOFA contents were 5%, 30% and 50%, the required fatty acid content being made up to 100% with LOFA. Details of the results of the preparations are given in Table 11.

Table 10: Molecular Composition of WB 27 and Related Alkyds

First step:

React fatty acids, diacid and polyalcohol

Fatty acids	1.4 moles
Sebacic acid	0.4 moles
Pentaerythritol	1.0 moles

Second step

Add pendant acid groups, some further chain extension occurs by esterification.

Succinic anhydride	1.35 moles
Target acid number	102 mg KOH/g resin

OH remaining unreacted at end of first step: 23.8% of original
OH remaining unreacted at end of second step: 6.0% of original

Table 11: Details of tung oil fatty acid-containing alkyds

	TA 5(I)	TA 5(II)	TA 30	TA 50
LOFA, g	212.1		156.3	55.8
TuOFA, g	11.2		67.0	55.8
Sebacic acid, g	46.4		46.4	23.2
Pentaerythritol, g	78.0		78.0	39.0
Succinic Anhyd., g	77.5		77.5	38.7
Max Temp, first step,°C	200		225	210
Acid #, mg KOH/g				
First step:	10		2	10
Final:	104	97	89	92
Time of second step, min	20	30	30	30
Solvent content, wt%	1.0	0.9	2.6	3.0
Viscosity at 25°C, Pa s	17	25	62	100

The preparation of the alkyds closely paralleled that of WB 27. The ingredients for the first step were weighed into a round bottomed flask fitted with condenser, Dean-Stark trap, and provision to flow nitrogen from the flask through the condenser. The trap was filled with xylene and xylene was added to the flask in an amount of about 20% of the fatty acid content. The contents of the flask were refluxed until the acid number became acceptably low - i.e., about 10 mg KOH/g resin or less. The xylene served to carry off the water formed during the esterification and to reduce the tendency of the reaction mixture to "bump".

After the acid number had indicated that the first step had progressed sufficiently far, the xylene was distilled off, the reaction mixture was cooled to 120°C, and succinic anhydride was added to begin the second step of the synthesis. The addition of succinic anhydride is exothermic, but some additional heat was supplied externally to bring the contents of the flask rapidly up to 180°C. Typically, the reaction mixture was held at 180°C for 30 minutes. In the case of the alkyd containing 5% TuOFA, half the reaction mixture was removed from the flask after 20 minutes at 180°C in the second step and the rest was reacted for a total of 30 minutes.

Size exclusion chromatograms of the alkyds are shown in Figure 6. There is more high molecular weight material (to the left in Figure 6) in the alkyds as the viscosities in Table 11 increase, as expected. The presence of more high molecular weight material increases with the TuOFA content of the alkyds. This is as expected because of the likelihood of further bodying of the TuOFA during the alkyd syntheses and subsequent storage of the alkyds. A second consideration is that no tung oil remains in the TuOFA synthesized as described above (see Figure 7) but previous results have shown that there is some linseed oil in the commercial sample of linseed oil fatty acids used. Extra oil would introduce more hydroxyl groups which would in this case reduce the average functionality of the polyol and change the stoichiometry of the reaction in the direction of lower molecular weight.

The alkyds were taken to BEP, where they were made into trial inks by John Moynihan. The resistance of the printed inks to a 24 h soak in caustic soda solution was followed by immediately pressing the printed paper between filter papers for one hour. Some transfer of the print material occurred unless tung oil was added to the formulations. The viscosities of the resins were very high (Table 11) but in the case of TA 30 addition of about 25% tung oil to the resin allowed the formulation of an ink of excellent viscosity and flow which printed well and passed all resistance, set-off and blocking tests. The TA 50 resin was too viscous for a successful ink to be made.

4: AMINES AND SOLVENTS IN INTAGLIO INK RESINS

The press trials described earlier in this report indicated that improvement was necessary in the NaOH resistance of the cured ink films. The resin used in the ink trials and most of the other NIST resins made more recently have acid numbers greater than 100 mg KOH/ g resin. In an effort to improve the resistance to aqueous alkali, two WB 27-type alkyd resins were made with lower acid numbers (resin A with an acid number of 50 mg KOH/ g resin and resin B with an acid number of 63). Such resins are more hydrophobic than WB 27 and are not expected to wash well in Dalmar solution. To improve the washing, amines and ammonia were added to make ammonium salts from the acid groups in the resin. The amine evaporates during the drying, leaving a hydrophobic, resistant film.

A study was made of the effects of amine and solvent addition on resin viscosity. Figure 8 shows the viscosity change of alkyd A upon addition of up to 5 wt % aqueous ammonia and mineral oil. Ammonia causes association of the acid groups on the alkyd, increasing the viscosity by about a factor of 4. Mineral oil acts only as an inert diluent.

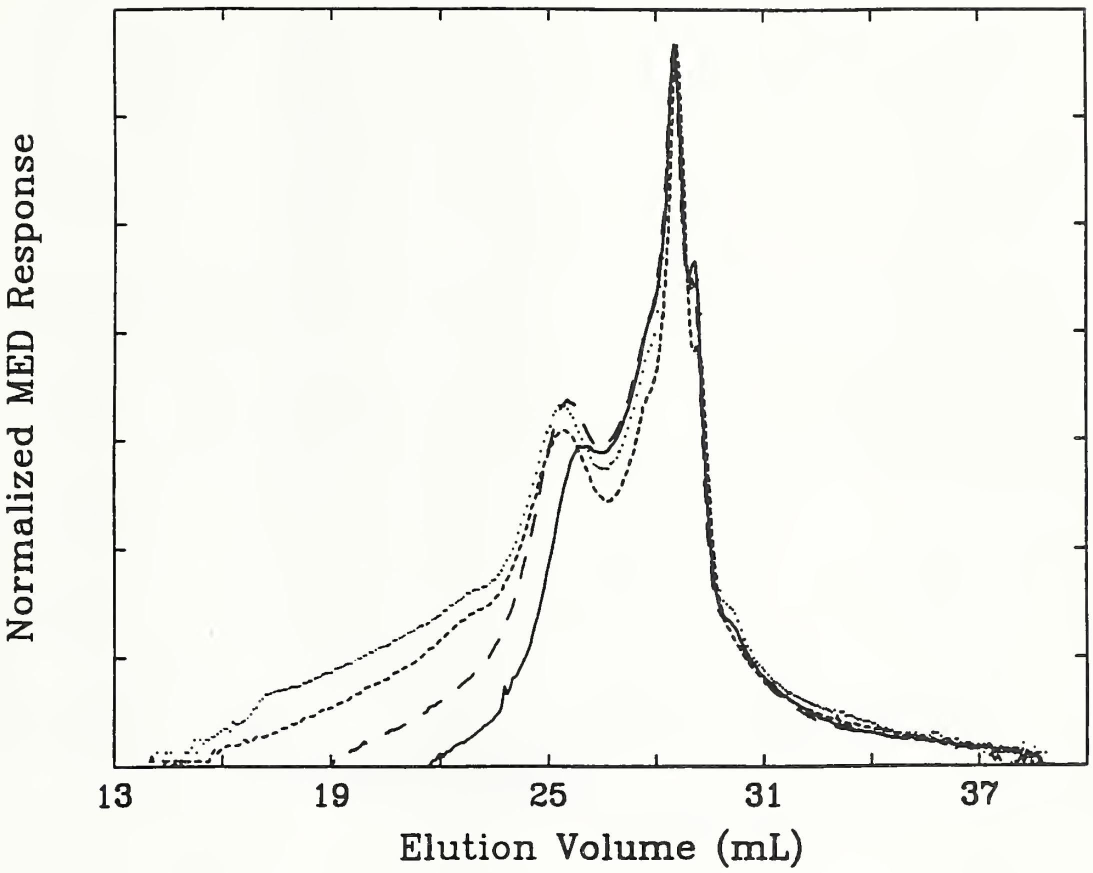


Figure 6: Size exclusion chromatograms of four tung oil fatty acid-containing alkyds. In order from the left hand side of the plot, the alkyds are: %50 TuOFA, 50% LOFA; 30% TuOFA, 70% LOFA; 5% TuOFA, 95% LOFA, 30 minutes at 180°C in second step of alkyd synthesis; 5% TuOFA, 95% LOFA, 20 minutes at 180°C in second step of alkyd synthesis.

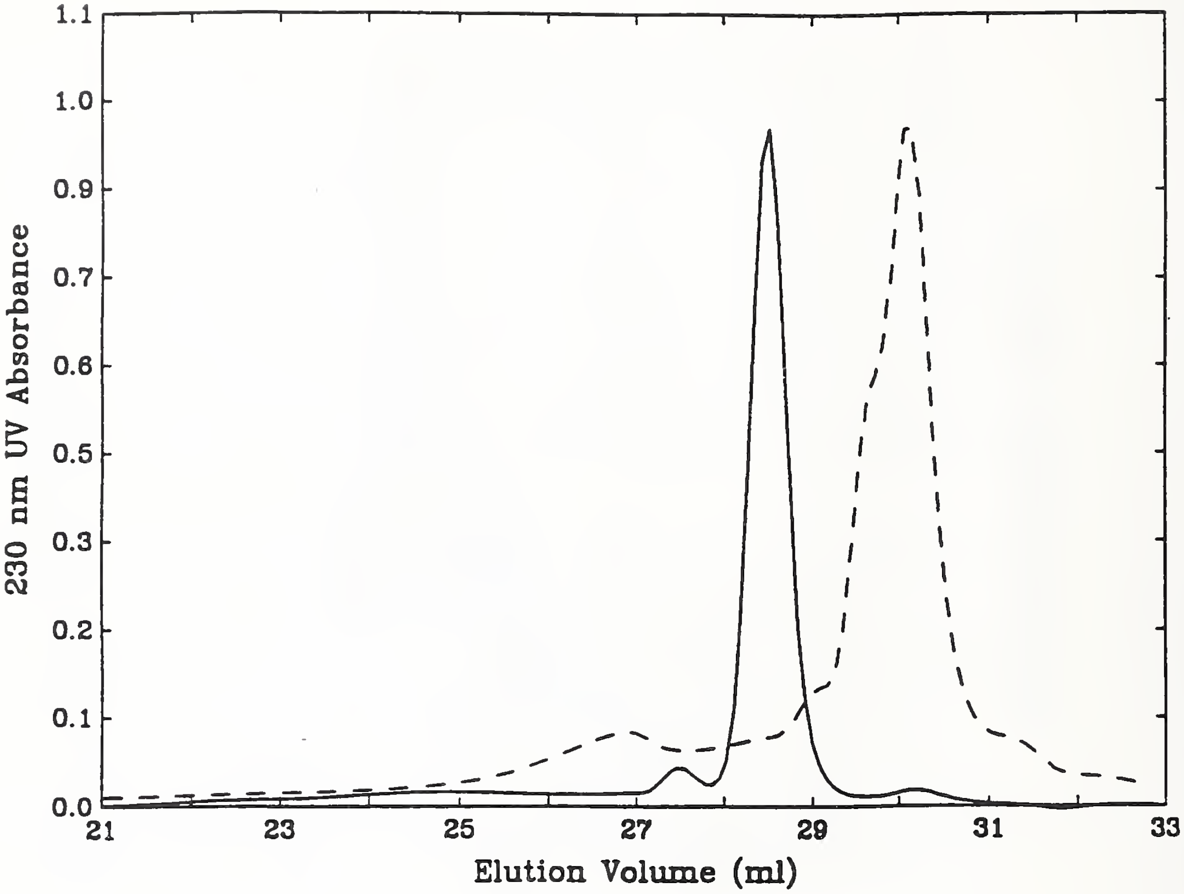


Figure 7: Size exclusion chromatograms of tung oil (solid line) and tung oil fatty acids (dashed line) produced by the procedure described here.

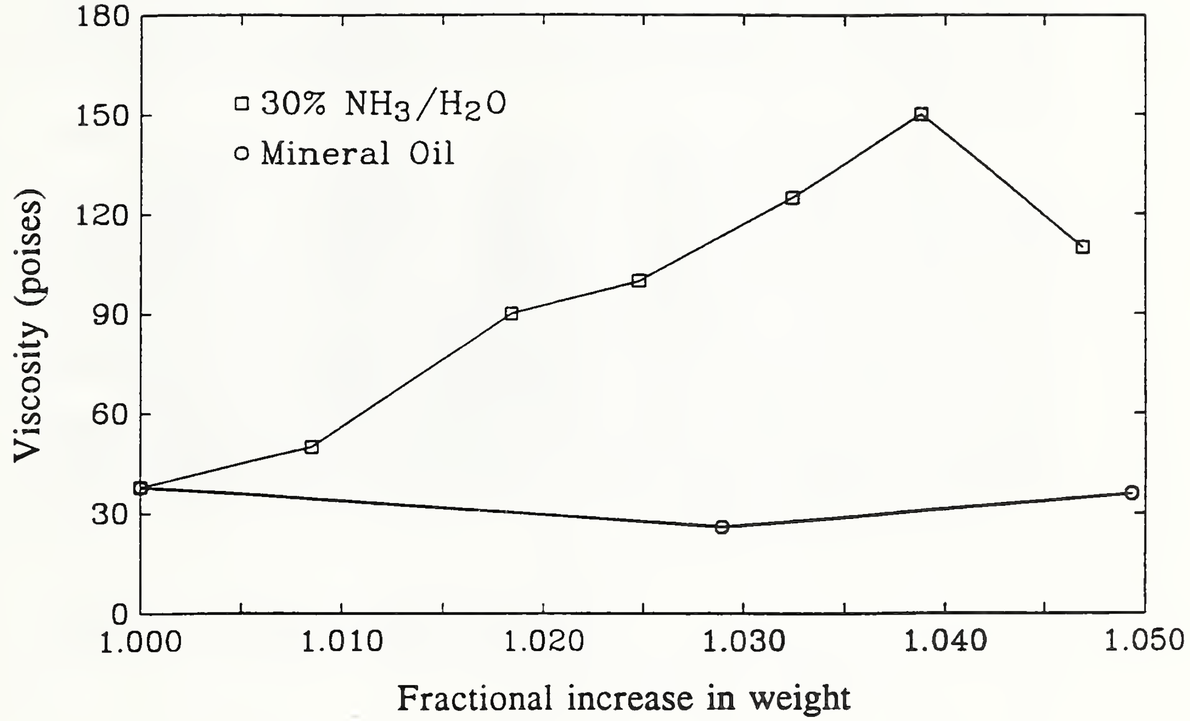


Figure 8: **Effect on resin viscosity of adding aqueous ammonia and mineral oil to alkyd A.**

Figure 9 shows the effects of solvent addition on a sample of alkyd A that had been mixed with 90% of the stoichiometric amount of N,N-dimethylethanolamine. The viscosity is greatly increased when either very hydrophilic or very hydrophobic solvents are added. In the case of the hydrophilic solvent, the viscosity increase is caused by the very hydrophilic regions of the resin (the salts) dissolving in small isolated globules of the hydrophilic solvent. In the case of the hydrophobic solvent, the salt regions are forced to associate with each other because the remainder of the resin has become significantly more hydrophobic. Butyl cellosolve, however, which is intermediate between mineral oil and water in hydrophilicity, is compatible with both the hydrophilic parts and the hydrophobic parts of the resin molecules. It thus acts as a diluent and reduces the viscosity.

Combinations of amine, water, mineral oil, and butyl cellosolve may be necessary to control both the washability and viscosity of this type of lower acid number resin. Figure 10 shows the viscosity change of alkyd A upon addition of these four liquids. The viscosity increases by the amine addition and by further additions of both very hydrophobic and very hydrophilic solvents. Small additions of butyl cellosolve greatly decrease the viscosity, apparently breaking up the associations formed by the other additives. By controlling the amount and type of additive, the viscosity of an alkyd can be made to be higher or lower than that of the neat resin, the range of attainable viscosities being quite large. Table 12 gives the composition of 15 mixtures taken to BEP.

Table 12. Samples of alkyd resins delivered 2/28/91.

Name	Alkyd	Amine	Ammonia	Water	Min-Spirit	But-Cell
A	A	---	---	---	---	---
B	A	7.3	---	---	---	0.8
C	A	7.3	---	7.3	---	2.4
D	A	7.3	---	---	7.3	2.4
E	A	---	4.6	---	---	0.4
F	B	---	---	---	---	---
G	B	9.0	---	---	---	0.9
H	B	9.0	---	9.1	---	2.6
I	B	9.0	---	---	9.0	1.5
J	B	---	5.7	---	---	0.3

Name	Alkyd	TuOFA	LOFA	TuOFA(pumped)	Acid #
K	WB 48	10%	90%	no	111
L	WB 49	20%	80%	no	120
M	WB 50	30%	70%	no	120
N	WB 51	10%	90%	yes	120
O	WB 52	20%	80%	yes	100

All mixtures based on 100 g alkyd

TuOFA = tung oil fatty acids
LOFA = linseed oil fatty acids

Alkyd B had an acid number of 63, alkyd A had an acid number of 51.

Ammonia is 30 wt % NH_3, 70 wt % H_2O
Amine is N,N-dimethylethanolamine

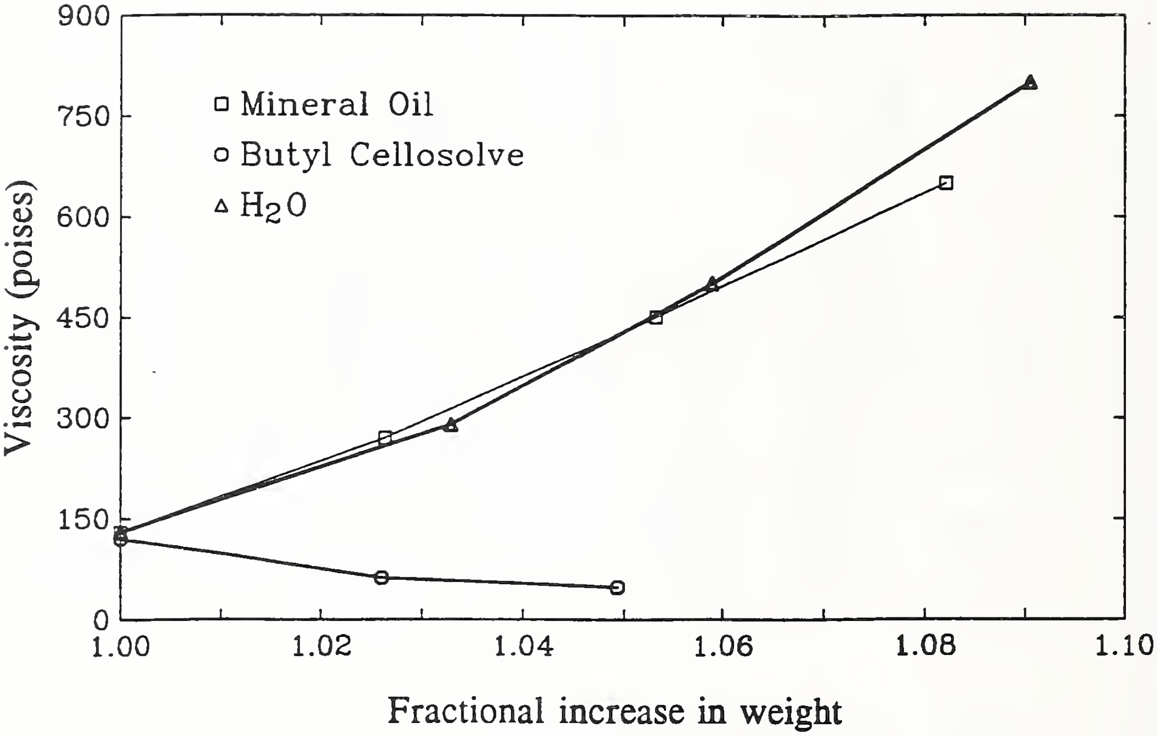


Figure 9: Effect on the viscosity of adding mineral oil, butyl cellosolve and water to a sample of alkyd A which had been 90% neutralized with N,N-dimethylethanolamine.

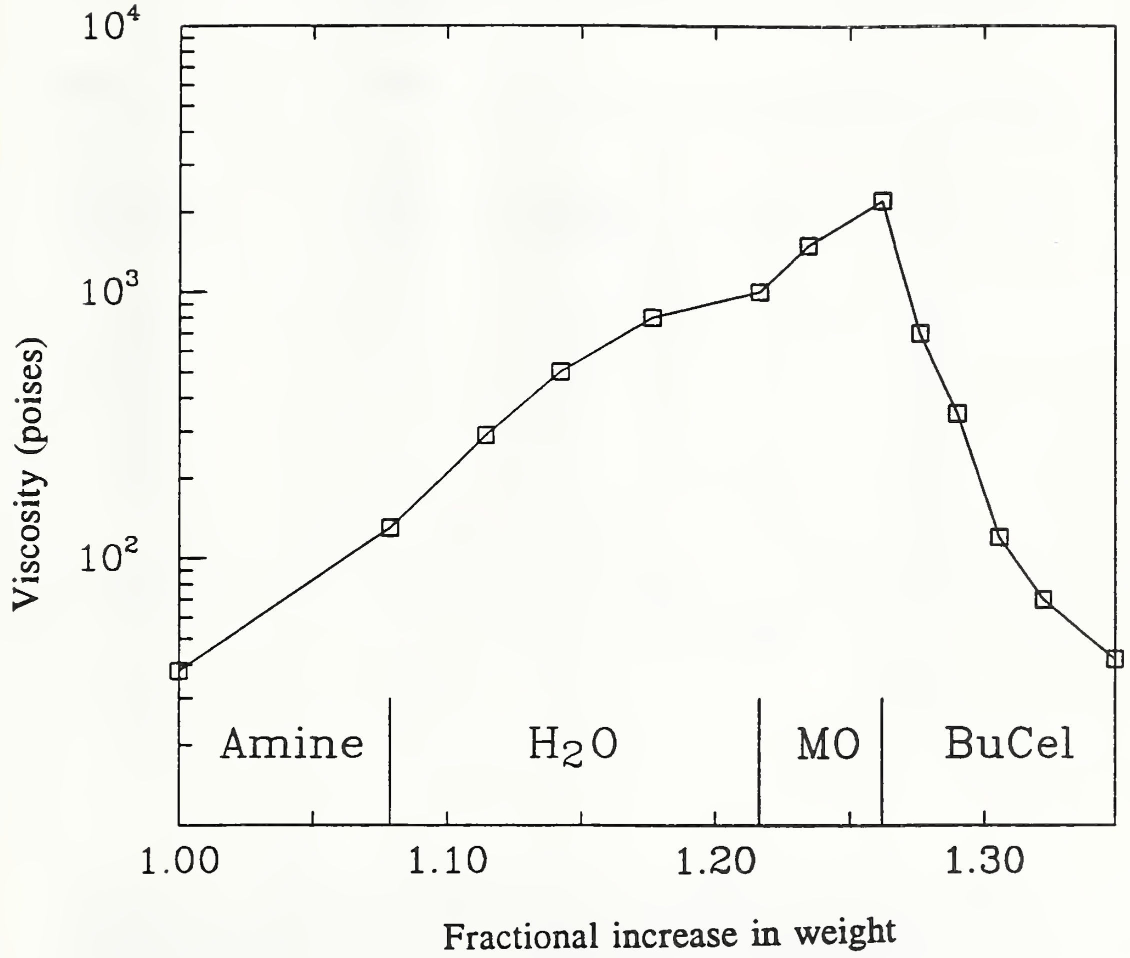


Figure 10: Effect of successive addition of N,N-dimethylethanolamine, water, mineral oil, and butyl cellosolve on the viscosity of alkyd A.

Inks were made by Mark Weiss at BEP from the mixtures in Table 12. The results are given in Table 13. None of the inks made from the amine/solvent/alkyd resins washed well, partly perhaps because a new ink formulation was used. The least unsatisfactory inks were those made from resins N and O. The importance of the influence of the ink formulation makes it very difficult to evaluate a resin. Testing with only one formulation measures the fit of the resin to the formulation.

Table 13: Characteristics of inks made from the resins in Table 12 (data from Mark Weiss of BEP).

Resin	Skin	Viscosity (Pa s)	Washing (strokes)	Q-tip resistance	Alkali (24 h soak)
A	thin	4	> 35	2.5	6
B	none	10	> 35	3	6
C	none	21	> 35	4	7.5
D	none	5	> 35	2	5.5
E	thick	13	> 35	1	5.5
F	thin	2.5	33	5	7
G	none	9	> 35	6	5.5
H	none	10	30	5	5.5
I	none	3.5	> 35	7	7
J	thick	7	> 35	4.5	7
K	thick		> 35	1.5	6.5
L	thick	80	35	2.5	5.5
M	thick		31	1.5	6
N	thick		19	3.5	5
O	thick		20	3.5	5.5
Standard ink	thick		10	5	5

5: NEW TEMPERATURE PROGRAM IN LOFA RESIN SYNTHESES

Because later attempts at BEP to remake inks with the SVD 1781 varnish commissioned from industry had not been satisfactory, the SVD 1781 varnish was examined using size exclusion chromatography to see (1) if it had changed over the year which has elapsed since it was made, and (2) how it differed from the other resins used in these studies.

Figure 11 shows the pertinent size exclusion chromatograms. High molecular weight is to the left in Figure 11. The solid line in Figure 11 is from alkyd WB 27, which is the NIST lab sample on which the SVD varnishes were based. The dashed line is the SVD lab sample. Alkyd WB 27 and the SVD lab sample produced similar chromatograms and have similar distributions of molecular size. The NIST sample was made using refluxing xylene in the first step of the two step alkyd synthesis and carrying out the

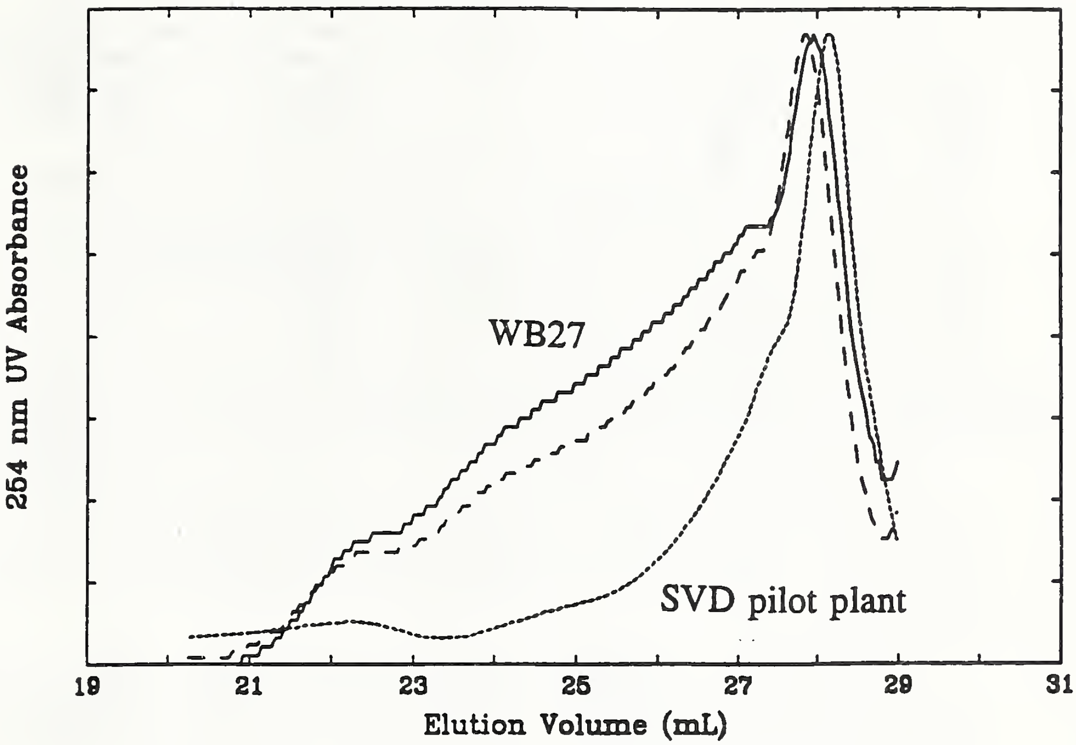


Figure 11: Size exclusion chromatograms of, from left to right, alkyds WB27, SVD1781 lab sample, and SVD1781 pilot plant sample.

succinic anhydride addition in the second step at 180°C for 30 minutes. The SVD sample was made by the fusion process, where no refluxing agent is used. The temperature program in the second step in making the SVD lab sample is not known to us.

A 208 L (55 gallon) drum sample of the alkyd was made at SVD from the same starting composition of ingredients as were used for the lab sample and WB 27. The drum sample, also called SVD 1781, is the sample which was later used in press trials and other tests at BEP. The drum alkyd was not subjected to chromatographic scrutiny when it was first delivered to BEP. The recently measured chromatogram is shown as the dashed line in Figure 11. It is clear from Figure 11 that the drum alkyd is significantly different from the SVD lab sample and from the target WB 27 sample. In particular, it has less material in the middle of the molecular weight range. These higher molecular weight components are expected to speed up the drying time and perhaps improve resistance of the air-dried film to solvent attack. Inks made from SVD 1781 are weak in solvent resistance.

The chromatogram (Figure 12) of an extract from the standard ink shows that the standard varnish contains appreciable amounts of high molecular weight components (eluting at 20 to 24 mLs, Figure 12). This molecular weight range is present in the WB 27 and SVD lab samples but is conspicuously missing from the SVD drum sample.

Conversation with SVD chemists revealed that it had not been possible for SVD to follow the temperature program in their pilot plant synthesis of SVD 1781. The acid number and viscosity, the two measures used by SVD to monitor the course of the reaction, reached their target values in the second step before a temperature of 180°C was attained, so the reaction was not held at 180°C for the required 30 minutes. It is known (see next section) that the second step of these alkyd syntheses is important in two respects: 1) the nominal one of adding carboxylic acid groups to the alkyd by reacting free hydroxyl groups on the alkyd with the acid anhydride, and 2) creating esterification of some of these newly added carboxylic acid groups to give an appreciable amount of non-equilibrium chain extension. The temperature of 180°C in the second step was chosen to allow the chain-extending esterification reaction to be carried out in a short time and to the appropriate amount. If this temperature can not be attained in the second step in practice, then much of the esterification aspect must be carried out in the first step by adding more diacid in the first step and proportionately reducing the amount of anhydride in the second step.

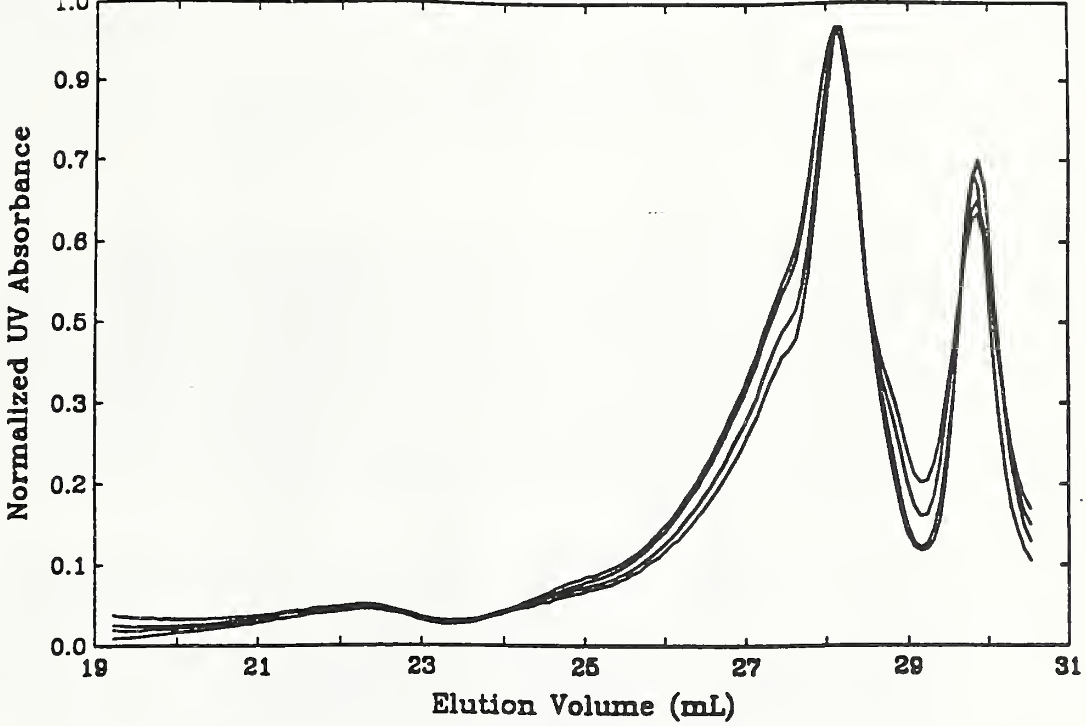


Figure 12: Size exclusion chromatograms of SVD1781 (pilot plant) at four UV wavelengths. The chromatograms are all very similar.

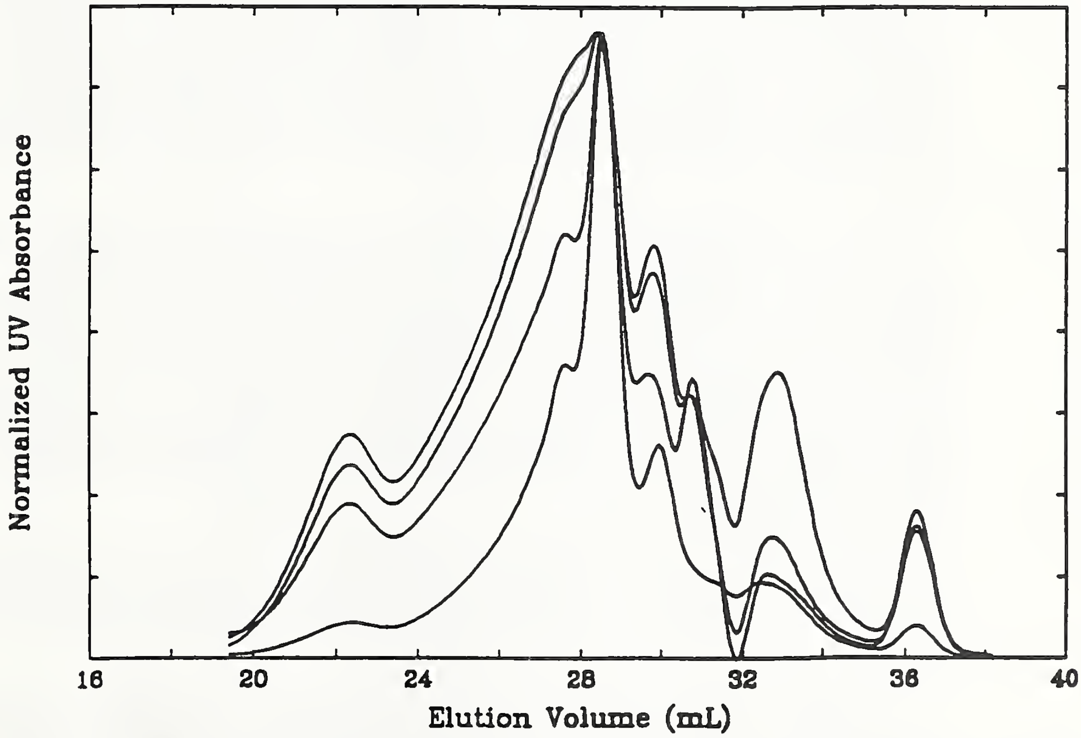


Figure 13: Size exclusion chromatograms of standard black currency ink resin at four UV wavelengths. The chromatograms are appreciably different from each other.

Figures 12 and 13 show other features pertinent to ink formulation. The SVD resin (Figure 12) is the product of a single reaction. Therefore, the multi-wavelength UV detector chromatograms obtained in the size exclusion chromatographic analysis are all very similar when the size of the maximum peak is made the same in each case - this is merely scaling the different detector responses to each other to compensate for the different UV absorptions of the sample at each of the UV wavelengths used - 230, 240, 254 and 275 nm.

The extract from one of the standard inks shows (Figure 13) a wide variation of detector response with molecular size, showing that this varnish is a mixture of several resins of different compositions. Different compositions give different physical properties and allow both fine tuning of ink parameters and also the possibility of erratic changes in ink behavior if the mixture is changed without an understanding of how the changes affect the properties of the ink.

5.1: SEC Analysis of the Effect of Temperature in the Second Step

The effect of the temperature in the second step of the alkyd synthesis on molecular size distribution was followed by size exclusion chromatography, resin viscosity, and acid number determinations. The last two quantities are those typically used in industry. Heat treatment causes esterification to occur. Because the resin molecules contain both free acid groups and free hydroxyl groups, continued esterification produces higher and higher molecular size material in the resin until the resin finally gels.

Two alkyds were heat treated at temperatures of 160°C and 180°C. The first alkyd is the SVD 1781 alkyd, industrially synthesized in 208L (55 gallon) quantity and nominally equivalent to NIST resin WB 27. Because it was made at too low a temperature, SVD 1781 contains less high molecular size material than the target resin WB 27. The heat treatment of SVD 1781 was essentially a prolongment of the second step (no more reactants were added) and was an investigation into whether the lack of high molecular size material could be corrected by inducing further esterification.

The second alkyd was synthesized according to the protocol for WB 27 in the first step of the synthesis but was then divided into parts to allow the second step of the synthesis to be carried out at different temperatures.

Figure 14 shows the size exclusion chromatographic results of the heat treatment of SVD 1781. There is a gradual increase in high molecular size material in the chromatograms (high molecular size is to the left).

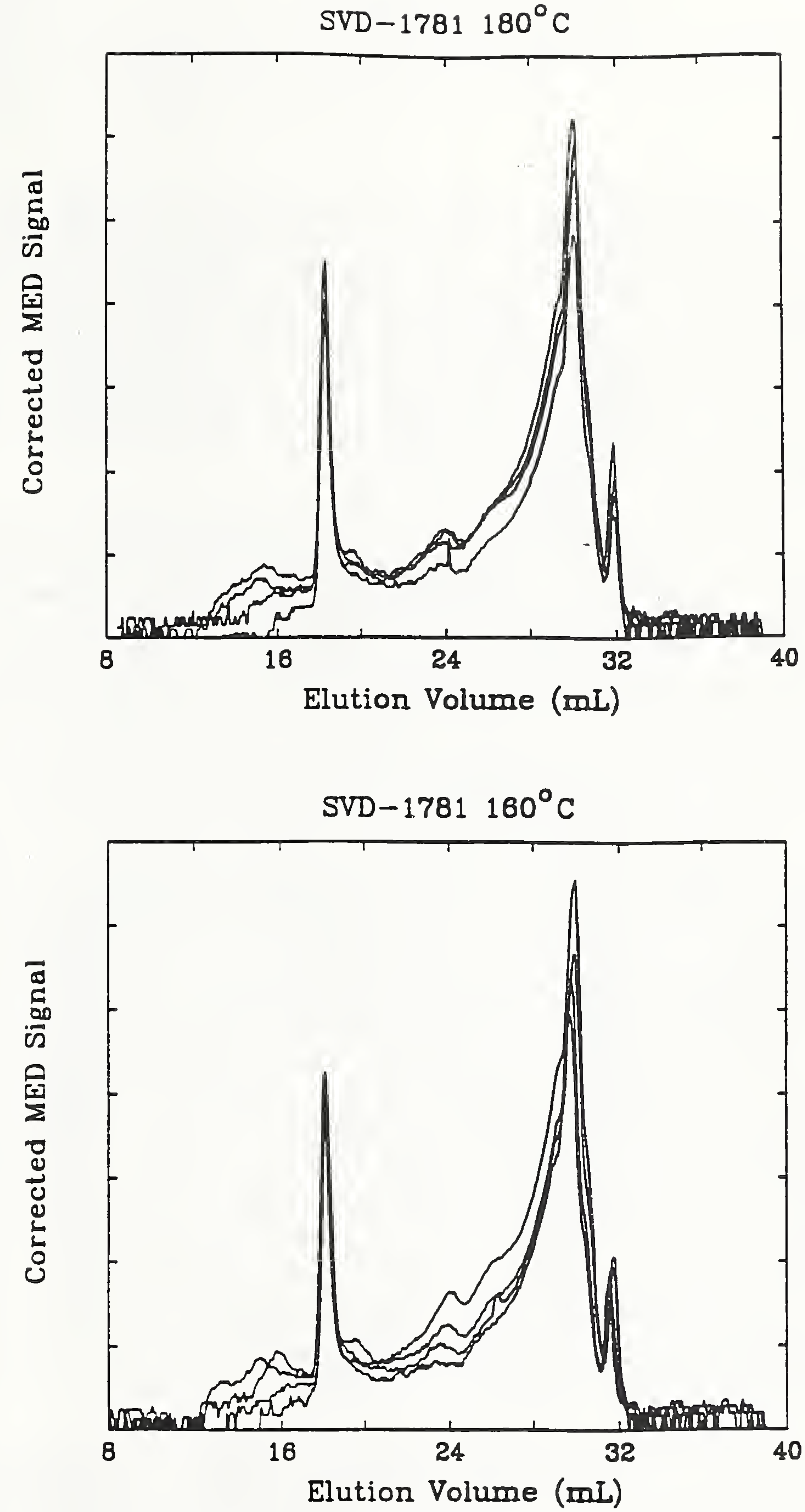


Figure 14: Size exclusion chromatographic examination of the results of heat treating SVD1781 (pilot plant).

The sharp peak at about 18 mLs elution volume in Figure 14 is a polystyrene marker peak of molecular weight 10^6 Daltons and is not from the resin. The highest peak in the chromatogram is from the analog of linseed oil, with a molecular weight of about 1000 Daltons. The relationship between molecular size, which is the separation parameter in size exclusion chromatography, and molecular weight is non-linear and is different for each chemical species. No simple relationships between the two can be drawn. For that reason, this report uses the term "molecular size" rather than "molecular weight".

Figure 15 shows the result of heat-treating the second alkyd. There is considerably more build-up of high molecular size in that case. (The hump at the left hand side of the chromatogram for the 180°C treatment is an artifact of the column in that some of the material was of too high molecular size to be resolved by the column and hence piled up rather than being spread out.) It is clear that the heat treatment did not extend the SVD material nearly as much as it did the NIST material. Therefore it is expected that heat treatment of the SVD 1781 drum material at BEP will not body the resin successfully.

The corresponding values of the viscosity and acid number for these two cases are shown in Figures 16 and 17. There is a general trend to lower acid number as the heat treatment times increase, as expected if esterification is causing the chain extension, but the change is small and not much more than the experimental error in the determination of the acid number. The viscosity is much more sensitive and better determined, but, being an average value for the resin, gives no quantitative indication of the distribution of molecular sizes. In principle, reactive large molecules (or very reactive small molecules) are necessary for fast setting of the film, and small molecules are necessary to produce a liquid resin of relatively low viscosity. For resistance in the cured film, most or all of these small molecules should be reactive. Use of the viscosity parameter is necessary to provide a mechanically acceptable resin but gives little indication of the relative amounts of high and low molecular size material. The only technique which allows the resin to be characterized in terms of molecular size is size exclusion chromatography.

The goal of this part of the study was to monitor the growth of chain extension (high molecular size) with time and temperature so that (1) a processing temperature more accessible to syntheses carried out in a pilot plant could be selected and (2) the required molecular size could be built up in the first step of the synthesis. Because appreciable chain extension occurs at both 160 and 180°C, a second step temperature of 140°C is indicated. The next section is concerned with adding more diacid in the first step to allow use of the lower temperature in the second step.

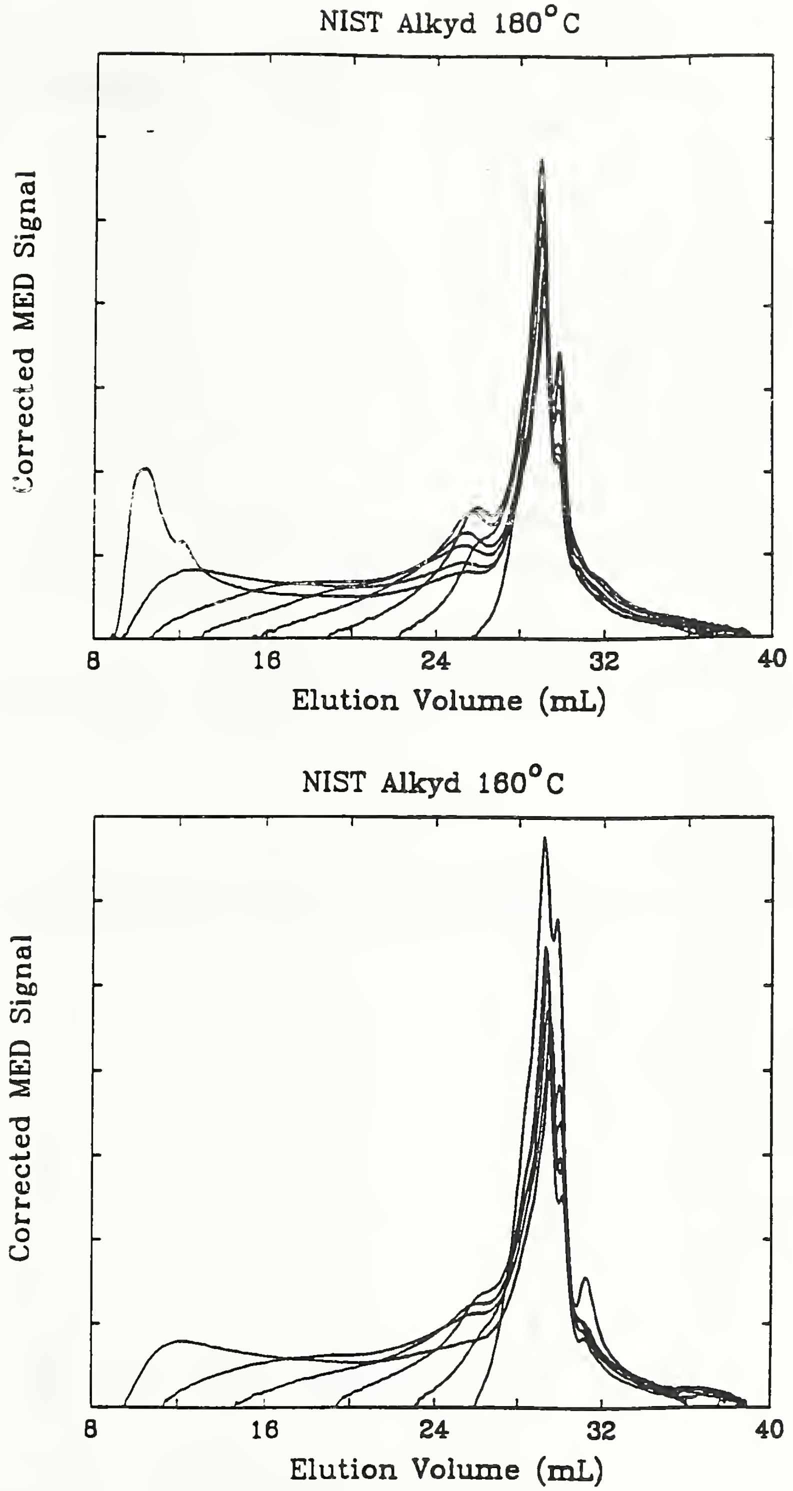
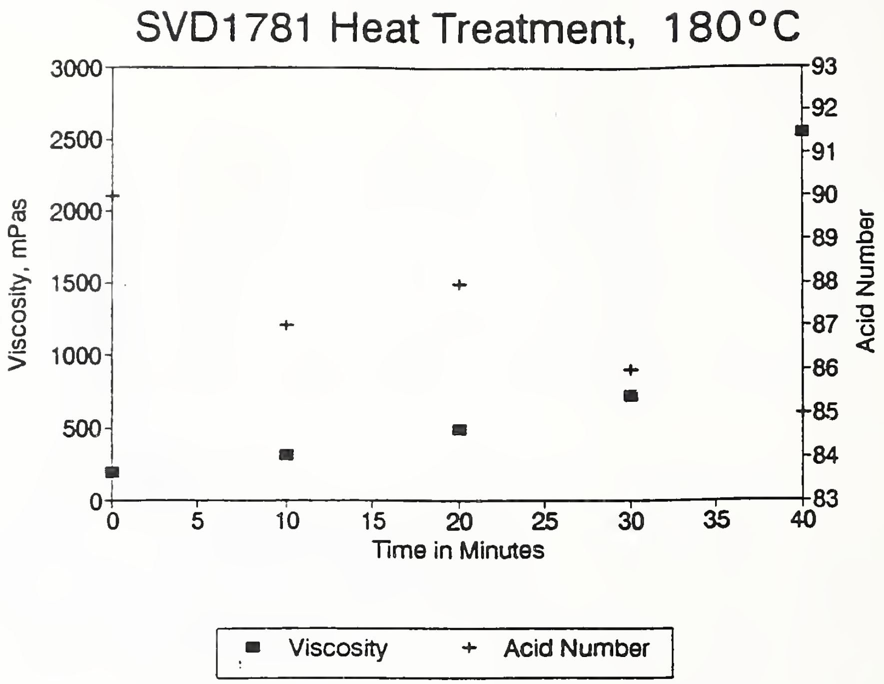


Figure 15: Size exclusion chromatographic examination of heat treatment of a NIST alkyd based on WB27 but with 5% tung oil fatty acids in the recipe.



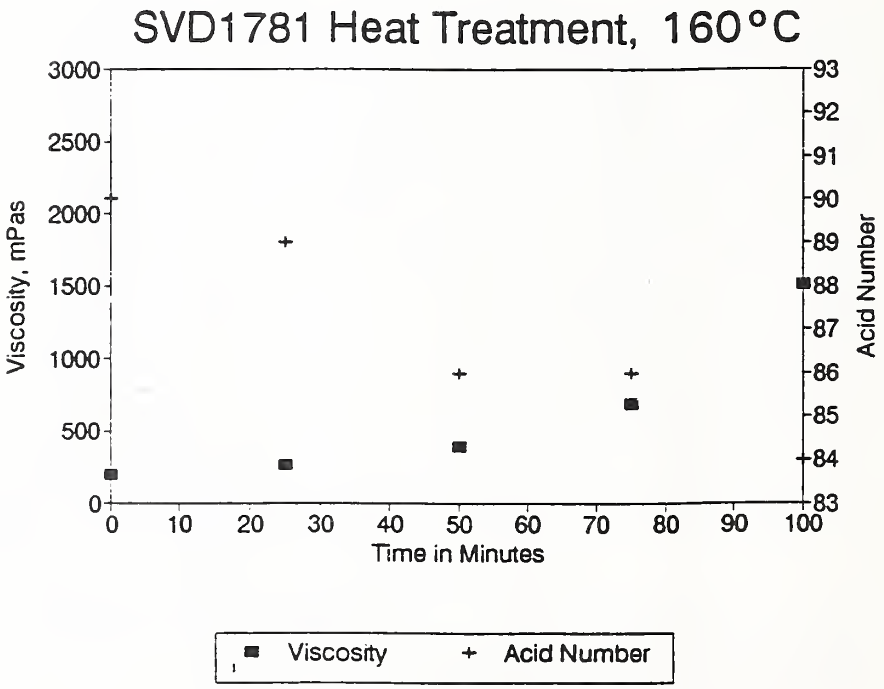
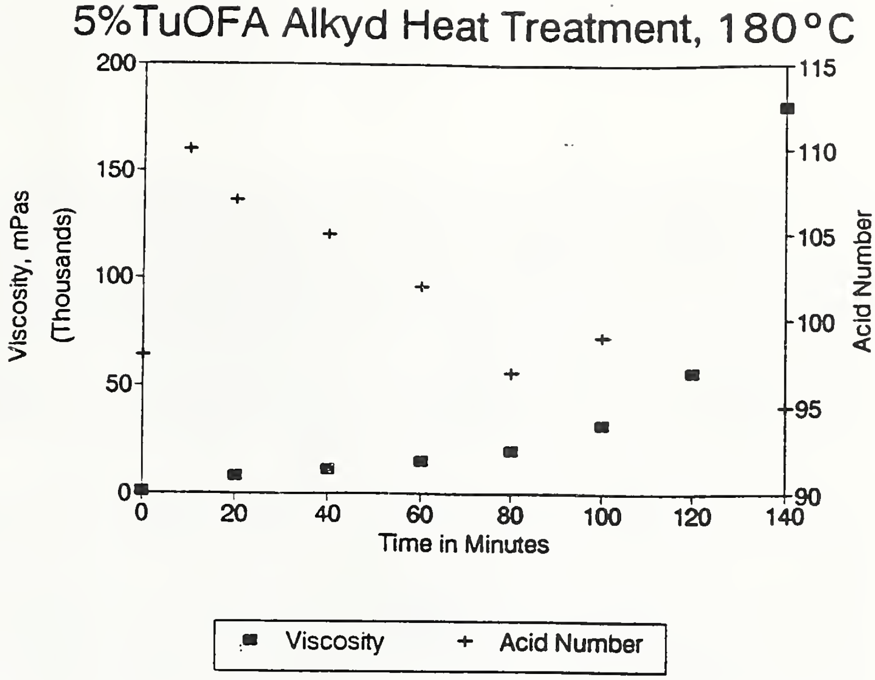


Figure 16: Viscosity and acid number values of heat treated SVD1781 (pilot plant).



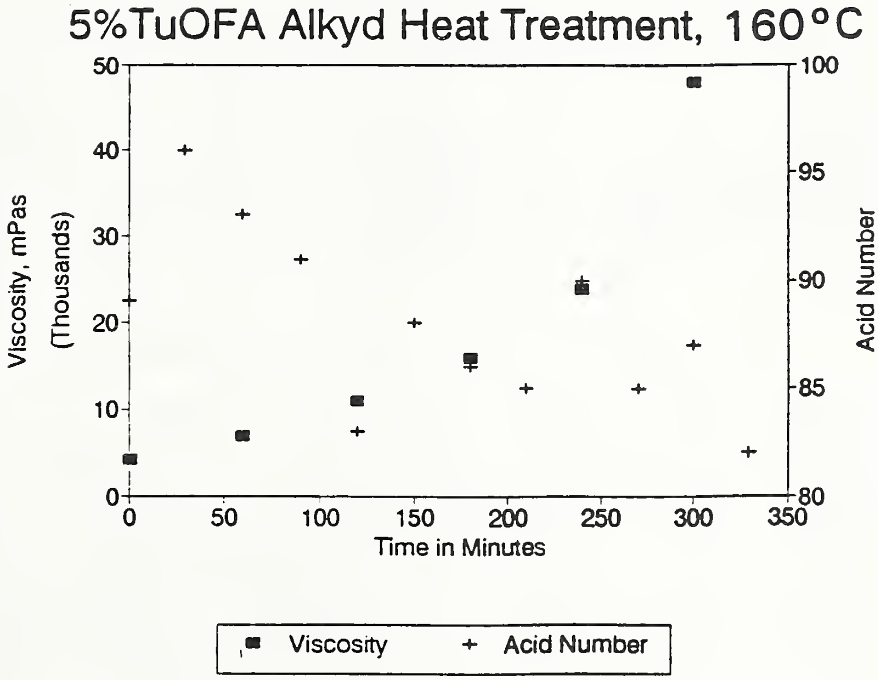


Figure 17: Viscosity and acid number values of a heat treated NIST alkyd based on WB27 but with 5% tung oil fatty acids in the recipe.

5.2: Increasing the Amount of Diacid in the First Step

Increasing the level of di-acid in the first step of the synthesis gives more chain extension by esterification in the first step. Also, carrying out the reaction of succinic anhydride in the second step at 140°C minimizes the amount of chain extension by further esterification. Previously, WB 27 had been synthesized at 180°C in the second step. At 180°C, a considerable amount of further esterification takes place.

Another important variable is the acid number to which the first step is taken. The lower the acid number, the greater the degree of esterification and hence chain extension in the first step. In these investigations of the effect of the amount of diacid, about half the material was removed from the first step at an acid number of 30 mg KOH/g resin and the remainder was further reacted to an acid number of about 10. Both parts of the resin were then acidified by reacting them separately with succinic anhydride.

Several syntheses, codes RL1 to RL6, were carried out with various levels of diacid in the first step as shown in Table 14.

Table 14: Formulae and codes for resins, quantities in moles

Resin:	WB 27	RL1	RL2	RL3	RL4	RL5	RL6
LOFA	1.40	1.40	1.27	1.22	1.05	0.97	1.01
Sebacic acid	0.40	0.50	0.55	0.61	0.75	0.83	0.80
Pentaerythritol	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Succinic anhydride	1.35	1.35	1.23	1.17	1.02	0.93	0.98

Code	Acid Numbers		viscosity, Pa s		Resistance*, 24h soak in 2% aq. NaOH
	1st step	2nd step	1st step	2nd step	
RL1/30	25	110	0.7	5.5	failed
RL1/10	8.5	122	1.3	14	failed
RL2/30	33	126	0.7	7	failed
RL2/10	12	99	1.6	9.5	passed
RL3/30	34	139	0.55	6	failed
RL3/10	11	98	1.8	10	marginally failed
RL4/30	33	119	1.4	15	passed
RL4/10	10	88	4.3	55	too viscous
RL5/30	26	115	2.5	25	passed
RL5/10	10	89	9.0	120	too viscous
RL6/30	27	114	3.0	42	too viscous
RL6/10	10	gelled in first step			

* Inks made and tested by John Moynihan at BEP.

Resin viscosities ranged from 0.55 to 120 Pa s, where 1 Pa s = 10 poise. All inks made from these resins emulsified satisfactorily in Dalmar solution. The resins which were found to be satisfactory had viscosities in the range 9 to 25 Pa s. Thus, control of resin viscosity is essential.

Table 14 shows that, even at a temperature of 140°C in the second step, the viscosities increased by a factor of about 10 during the addition of succinic anhydride to the reaction mixture. Figure 18 shows the increase in molecular size during step 2 of a typical alkyd synthesis. This shows that further esterification is occurring to an appreciable extent even at 140°C.

It seems that the reaction temperature during the anhydride addition can not be reduced much more. Use of such a low temperature as 140°C is possible because the acid anhydride used, succinic anhydride, melts at about 122°C. The reaction of the anhydride with the hydroxyl groups on the alkyd is carried out most satisfactorily when the anhydride is in intimate contact with the alkyd, i.e., when it melts or dissolves in the resin. In the syntheses carried out here, the anhydride does not dissolve in the resin, so a low-melting anhydride is necessary. The conclusion is that tight control and careful monitoring of the reaction during the second step will always be necessary.

The effect of adding more diacid in the first step is shown in Figure 19. The first step was taken to an acid number of about 30 mg KOH/ gram resin for these resins. The final effect of the diacid on molecular size is shown in Figure 20. Similar plots are given in Figures 21 and 22 for the case where the first step was taken to an acid number of about 10.

5.3: Viscosity vs. Molecular Size

An alkyd analogous to WB 27 was made with much higher viscosity than WB 27. This was achieved by using the aromatic diacid isophthalic acid instead of sebacic acid in the first step of the alkyd synthesis. The resultant resin was made into an ink by John Moynihan at BEP but failed the resistance test. This suggests that high molecular size in the resin is essential for good solvent resistance in the cured film. Our use of exclusively aliphatic ingredients allows us to prepare alkyds which have very large molecular dimensions but which are relatively non-viscous.

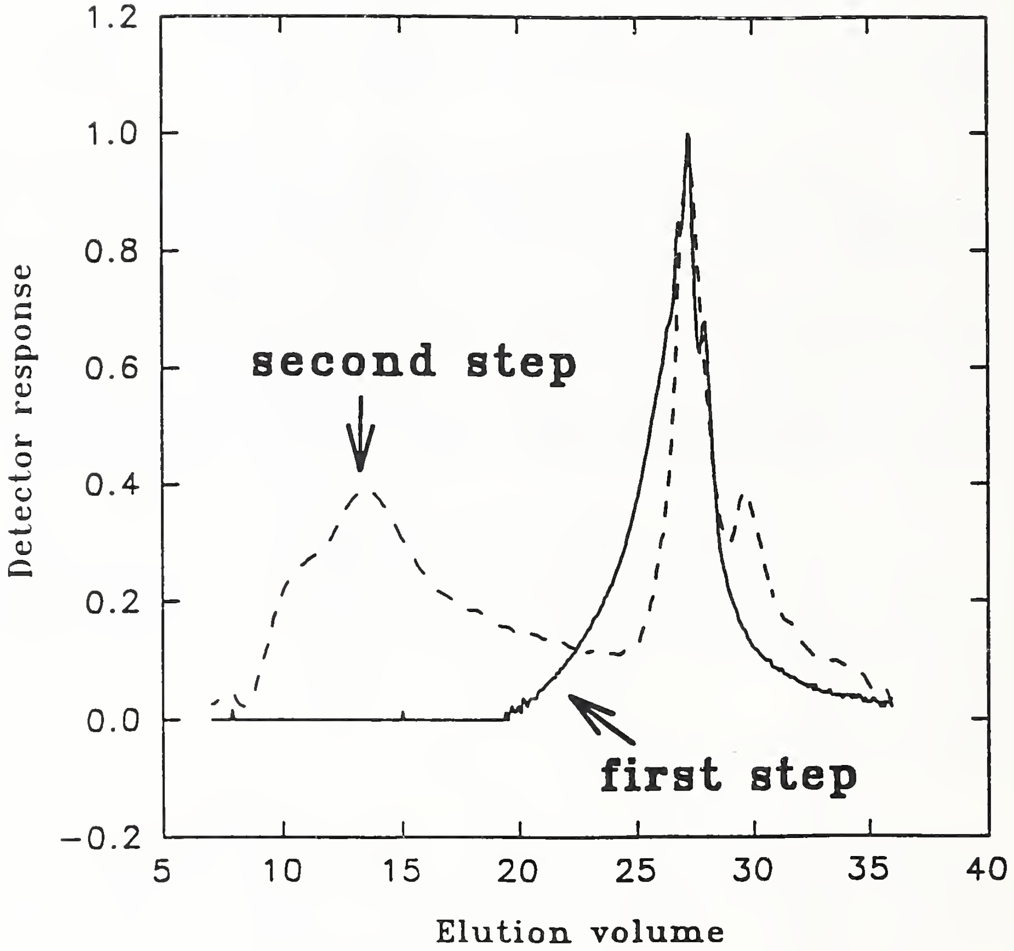


Figure 18: Effect of carrying out the acidification of the alkyds (second step of the synthesis) on molecular size, as shown by size exclusion chromatography. First step of reaction carried out to acid number of 30 (mg KOH/ gram resin).

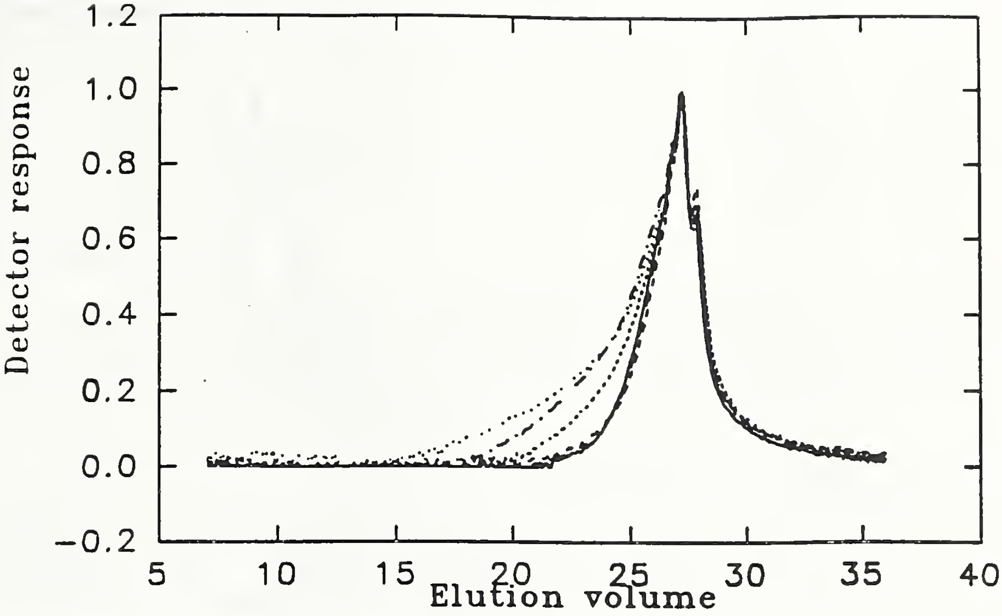


Figure 19: Effect on molecular size of adding more diacid in the first step of the synthesis, as shown by size exclusion chromatography: result at end of first step, acid number = 30.

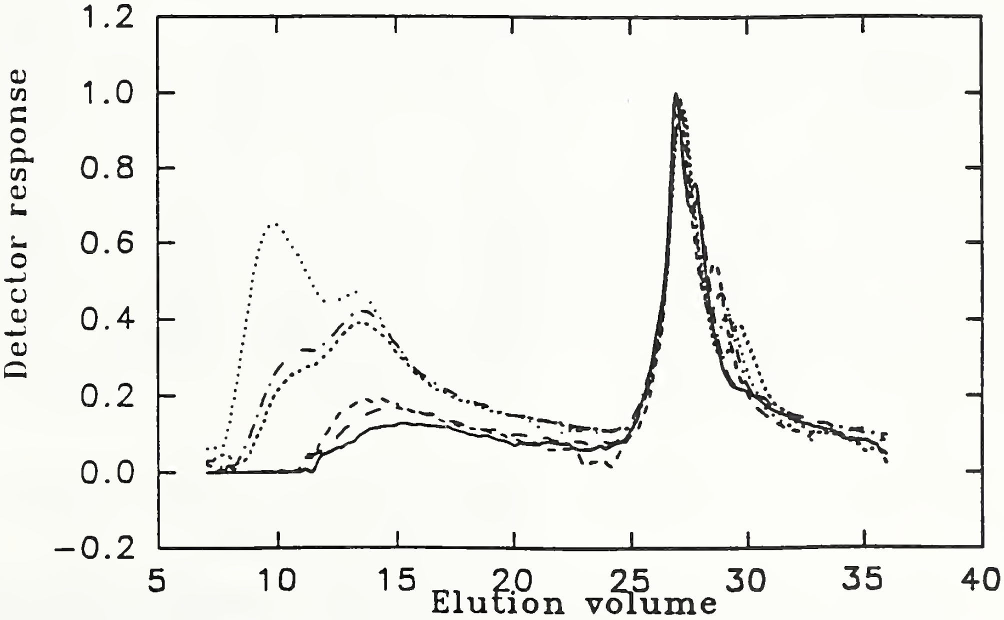


Figure 20: Effect on molecular size of adding more diacid in the first step of the synthesis, as shown by size exclusion chromatography: result at end of second step (first step taken to acid number of 30). Peak at left hand side of figure is artifact of molecular size being too big for chromatographic column to resolve.

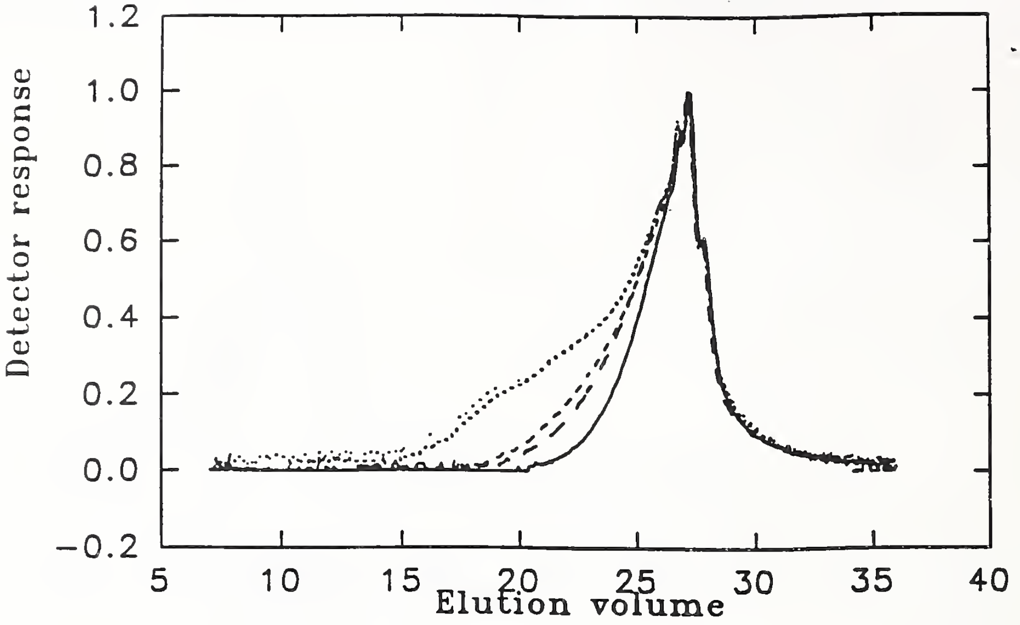


Figure 21: Effect on molecular size of adding more diacid in the first step of the synthesis, as shown by size exclusion chromatography: result at end of first step. First step of reaction carried out to acid number of 10 (mg KOH/ gram resin).

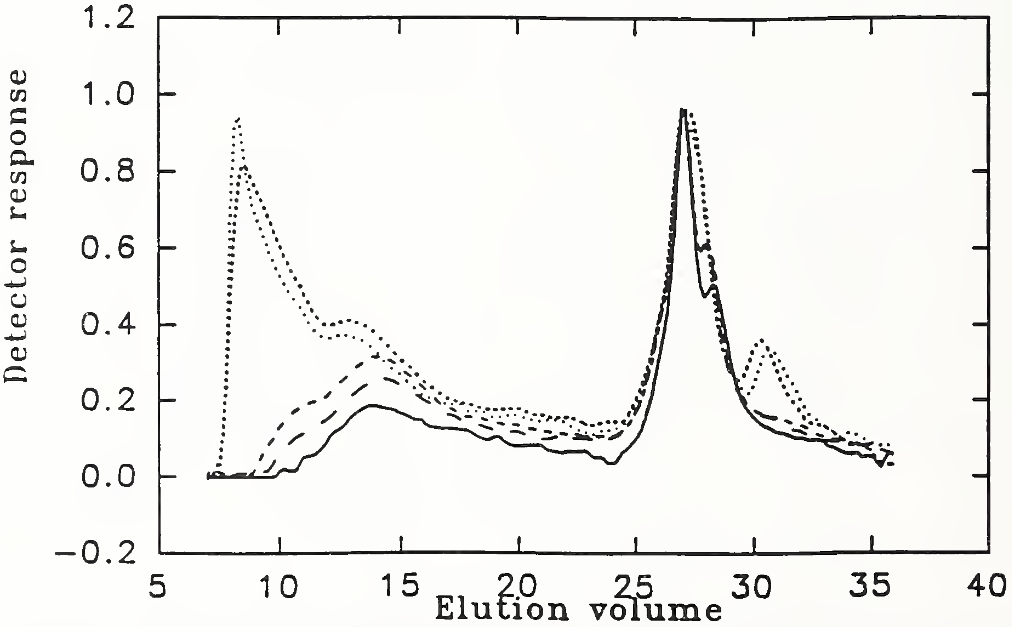


Figure 22: Effect on molecular size of adding more diacid in the first step of the synthesis, as shown by size exclusion chromatography: result at end of second step (first step taken to acid number of 10). Peaks at left hand side of figure are artifacts of molecular size being too big for chromatographic column to resolve.

6: CONCLUSIONS

From tests of various ink formulations performed at BEP, it is clear that the details of the formulation strongly influence a wide range of ink properties. Several formulations should be tried before a resin is rejected.

Ink formulators typically blend several resins when making an ink. The resins described here were made in one reaction sequence. No blending of resins was necessary. Thus, the work described here shows that it is possible to make resins that allow successful intaglio inks to be made even when the resin is not blended.

The viscosity of resins increases with increasing molecular size of the resin molecules. To obtain resins which contained molecules with a suitably large range of molecular size but with workable viscosity, aliphatic ingredients were used so that the resin backbones would be flexible. By using aliphatic components in the resin syntheses, we have been able to make high molecular weight resins that do not require solvents when formulated into intaglio inks. These resins should allow BEP to comply with Air Pollution Regulations for the foreseeable future.

Alkyd resins contain a range of molecular sizes even when they are made in one reaction. The molecular size distributions of our most successful resins include very large molecular sizes. Since resins containing even larger molecules were too viscous to be formulated into successful intaglio inks, there is an optimum range of molecular size.

Several candidate resins which passed BEP's preliminary tests were synthesized. The principles of designing intaglio ink resins have been established. The influence of temperature in the second step of the alkyd synthesis was shown to be very important in determining the final molecular size range of the resins. Appropriate temperatures and reaction procedures for the synthesis of air-dry intaglio ink resins have been documented.

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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.)

Tung oil fatty acids were used in alkyd syntheses to improve the rate and extent of air-dry cure of inks made from these alkyd resins so that the resistance to aqueous alkali solutions would be improved to the point of becoming satisfactory. Because tung oil fatty acids are not commercially available, the synthesis procedure was more involved than the relatively simple synthesis of alkyds based on linseed oil fatty acids. Moreover, the tung oil fatty acid-containing resins were not better than the linseed oil containing alkyd resins.

Linseed oil fatty acid-containing alkyd resins which passed laboratory tests for washing (ability to emulsify in Dalmar solution) and chemical resistance were successfully designed and synthesized. The key was to increase the average molecular size of the alkyd resin molecules. To accomplish this without increasing the viscosity beyond the usable range of about 10 to 15 Pa s, aliphatic ingredients were used. Most alkyd resins are made from at least some aromatic ingredients. At least three of these resins produced inks which are promising candidates for production intaglio inks.

Because of acid numbers of the resins are designed to be about 100 (mg KOH per gram resin), no solubilizing amines are needed. Because of the designed viscosity of the resins, no solvent is needed. Therefore, the resins should meet the requirements of air polution regulations for the foreseeable future.

12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)
air-dry; alkyd resins; intaglio ink resins; molecular size distributions; synthesis; water-dispersibility

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