

## Molecular Weight Distribution in Alkyd Resins. Part III. Presence of Microgel in Alkyd Resins

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### Synopsis

Alkyd resins which have the same overall chemical composition and the same degree of polymerization have been prepared from synthetic mixtures of mono-, di-, and triglycerides of linoleic acid, glycerol, and phthalic anhydride. The properties of these resins differed significantly. Microgel particles are present in all resins, but the quantity and size of the gel particles is a function of the glyceride composition. The concept of microgel is used to explain the solution and film forming properties of these resins. Examination of a range of commercially available alkyd resins has shown that microgel particles are present where the functionality is greater than two.

### INTRODUCTION

Previous papers in this series<sup>1-3</sup> have demonstrated two important principles related to the molecular weight distribution of alkyd resins prepared from a vegetable oil, glycerol, and phthalic anhydride. First, the chemical composition of the vegetable oil-glycerol reaction product has a marked influence on the molecular weight distribution and properties of the alkyd resin, and second, the control tests commonly applied to the vegetable oil-glycerol reaction do not indicate the completeness of the reaction or the attainment of an equilibrium composition.

The above conclusions imply that: (1) for reproducible commercial production of alkyd resins from vegetable oils it is essential to use more reproducible processing conditions than those in present use, and (2) in fundamental studies on alkyd resins, particularly those aimed at molecular weight distribution effects, the chemical composition of the glycerol-oil reaction product must be established unequivocally. Previous studies have not done this, although they have been useful in establishing that differences in molecular weight distribution can arise from variations in the glycerol-oil reaction mixture.

The present study was aimed at producing alkyd resins from fully characterized glycerolysis products and to study the factors which influence the molecular weight distribution and film-forming properties of the resin. At the same time, the opportunity has been taken to extend the preliminary results of previous work to an unsaturated fatty acid, since alkyds prepared

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from the triglycerides of unsaturated fatty acids (linseed oil, soya bean oil, and safflower oil) are the basis of many commercially important paints and enamels.

The composition of the product which results from the reaction of a vegetable oil with glycerol can be varied, within limits, by the choice of reaction conditions (mole ratio of oil to glycerol and the time, temperature, and catalyst used).<sup>1,3</sup> However, while this approach is capable of yielding a number of oil-glycerol reaction mixtures which differ in chemical composition, it suffers from disadvantages in the present context. For example, there is a strong possibility of side reactions taking place; these may occur to a small, but nevertheless significant, extent and result in the formation of polyfunctional compounds which will affect the polyesterification reaction. Also, a natural oil contains a number of fatty acids, and these could be preferentially distributed under some glycerolysis conditions. Furthermore, the composition of the glycerolysis mixture would not be known until a subsequent detailed analysis is carried out. To avoid these difficulties, we have prepared, from linoleic acid, each of the major components found in a glycerolysis mixture; these were then blended to give a number of known compositions which would correspond to those likely to be encountered in practice.

The alkyd formulation chosen for study had a mole ratio of fatty acid/glycerol/phthalic anhydride of 1.0/1.36/1.11, which corresponds to an oil length of 52% and an overall functionality of 2.10. This choice was influenced by a number of factors; such an alkyd formulation is widely known and has been claimed to give optimum properties in air-drying enamels;<sup>4,5</sup> it is a commonly used dispersing aid in pigmented systems even where it is not the major resin used; and it can be used in stoving enamels if blended with a melamine formaldehyde condensate. Therefore, the resin chosen enables a study to be made of distribution effects in both air-drying and stoving enamels and a comparison to be made of a given alkyd distribution under the two conditions of film formation.

## EXPERIMENTAL

The glycerine used contained 99.8% glycerol when analyzed by the periodate method.<sup>6</sup> The acid value of the phthalic anhydride was equivalent to 99.8% purity. Linoleic acid was prepared as described previously<sup>7</sup> from safflower oil fatty acids; analysis of the methyl esters by gas chromatography showed the product to be 98% linoleic acid (*cis,cis*-9,12-octadecadienoic acid). Glyceryl  $\alpha$ -monolinoleate was prepared by the esterification and then scission of isopropylidene glycerol.<sup>7</sup>

### Preparation of Glyceryl Trilinoleate

A mixture of linoleic acid (925 g.), glycerol (86 g.), *p*-toluenesulfonic acid (10 g.), and chloroform (200 g.) was heated under reflux (120°C.) in a 2-liter flask fitted with a stirrer, a Crankcase dilution-type water sep-

arator, and a condenser. A nitrogen atmosphere was maintained throughout the experiment. After 14 hr., 50 ml. of water had separated and the mixture was then cooled, dissolved in *n*-pentane (2 liters) and washed with (a) 500 ml. of 70% ethanol containing potassium hydroxide (20 g.), (b) 500 ml. of 70% ethanol containing potassium hydroxide (5 g.), (c) 70% ethanol (5 times, 750 ml. each) and, (d) water (5 times, 750 ml. each). The solution was dried (anhydrous  $\text{Na}_2\text{SO}_4$ ) and the solvent removed by distillation under reduced pressure in a rotary evaporator at 60°C. The product obtained in 90% yield contained 0.4%  $\alpha$ -monoglyceride and had a hydroxyl value of 1.7 mg. KOH/g. and an acid value of 0.9 mg. KOH/g. There was no band at 3500  $\text{cm}^{-1}$  ( $-\text{OH}$  absorption) in the infrared spectrum of the product. The glyceryl trilinoleate was stored at  $-4^\circ\text{C}$ . under a nitrogen atmosphere.

### Preparation of $\alpha, \alpha'$ -Glyceryl Dilinoleate

Water was removed from oxalic acid by azeotropic distillation with benzene. Oxalyl chloride was made by mixing anhydrous oxalic acid (160 g.), hydrous oxalic acid (2 g.), and phosphorus pentachloride (700 g.). Anhydrous oxalic acid and phosphorus pentachloride did not react; the trace of moisture added as hydrous oxalic was necessary to start the reaction. The mixture was kept in an ice bath (3 hr.) and then at room temperature (4–5 days). The liquid reaction mixture was slowly distilled (12 hr.) and the fraction boiling at 60–100°C. collected. This was refractionated twice to yield oxalyl chloride (158 g., 65%) b.p. 62–64°C., specific gravity 1.480 at 20°C.

Oxalyl chloride (175 g.) was added gradually (1 hr.) to linoleic acid (150 g.). The mixture was cooled in an ice bath; an atmosphere of dry nitrogen was maintained throughout the addition. After keeping the reaction mixture at room temperature (4–5 days) the excess oxalyl chloride was removed by distillation under reduced pressure. *n*-Pentane (1 liter) was added, and the solution was washed with water (5 times, 400 ml.), dried (anhydrous sodium sulfate) and filtered. The *n*-pentane was removed by distillation under a reduced pressure of nitrogen in a rotary evaporator at 60°C. The yield of product, calculated as linoleyl chloride was 75%. The purity of the product, estimated by reaction with methanol and water was 88% fatty acid chloride. A sample of this chloride was hydrolyzed, dried, and the infrared spectrum compared with that of the original linoleic acid. No differences were observed, indicating that the amount and type of unsaturation had not changed during acid chloride formation.

Glycerol (42 g.) was dissolved in a mixture of dimethylformamide (100 ml.), chloroform (750 ml. alcohol free), and pyridine (250 ml.) in a flask fitted with a dropping funnel, a stirrer, and a drying tube. The flask was purged with dry nitrogen, and then linoleyl chloride (321 g.) was added to the stirred glycerol solution at 0°C. After standing (1 hr.), the mixture was maintained at 15–20°C. (12 hr.) and then cooled to 10°C. Diethyl

ether (1.5 liter) and petroleum ether (1 liter, b.p. 30–40°C.) were added, and the solution washed with 0.5*N* sulfuric acid (2 times, 1 liter), 5% potassium carbonate solution (3 times, 1 liter), and finally water (7 times, 1 liter). The solution was dried (anhydrous sodium sulfate), filtered, and the solvent removed under reduced pressure in a rotary evaporator at 20°C. The product did not react with periodate and was, therefore, free of  $\alpha$ -monoglyceride. The  $\alpha, \alpha'$ -glyceryl dilinoleate (64% yield) was stored under nitrogen at -18°C. The hydroxyl value was 88 mg. KOH/g. (calculated value for diglyceride is 89.6 mg. KOH/g.). The infrared spectrum of the product had no primary hydroxyl band at 1050 cm.<sup>-1</sup>.

### Resin Preparation

The resins prepared all had a mole ratio of fatty acid/glycerol/phthalic anhydride of 1.0/1.36/1.11.

The normal method used for preparing alkyd resins is to add the phthalic anhydride to the preheated glyceride mixture. However, in the present study, this method was not suitable, since it introduced the possibility of alcoholysis and a change in the glyceride distribution before the phthalic anhydride addition. Consequently, an alternative process in which the glyceride mixture was added to the premelted phthalic anhydride was investigated. A mixture of glycerides which corresponded to that expected from the glycerolysis of an oil with a lead catalyst<sup>3</sup> was prepared; it had the composition  $\alpha$ -monoglyceride 41%  $\alpha, \alpha'$ -diglyceride 34%, triglyceride 10%, and glycerol 15%. This mixture (860 g.) was heated to 150°C. and halved. Phthalic anhydride (192 g.), and toluene (40 g.) were added to one half of the glyceride mixture (430 g.) at 150°C. under a nitrogen atmosphere. The mixture was heated to 160°C. (15 min.), and then to 200°C. and maintained at this temperature until the acid value was 9 (approx.). The second half of the glyceride mixture (430 g.) was added to molten phthalic anhydride (192 g.) at 150°C. under an atmosphere of nitrogen (10 min.).

TABLE I  
Influence of the Method of Processing on the Condensation Rate of Alkyds

Time, min.	Water of reaction, ml.	Acid value, mg. KOH/g. resin	Viscosity (Gardner-Holdt)
Resin A (glyceride mixture added to phthalic anhydride)			
22	13.2	51.0	D
49	17.5	27.0	—
87	19.5	16.1	F - 1/4
117	20.5	11.1	H + 1/2
148	21.0	8.7	J - 1/2
Resin B (phthalic anhydride added to glyceride mixture)			
30	13.0	54.0	D
72	18.8	21.8	E
110	20.1	12.8	H - 1/2
140	21.0	8.7	I

TABLE II  
Glyceride Mixtures Used to Prepare Resins 1-6

Resin number	Mono-glyceride, mole	Di-glyceride, mole	Tri-glyceride, mole	Glycerol, mole	Phthalic anhydride, mole
1	6.0	—	—	2.16	6.66
2	3.0	—	1.0	4.16	6.66
3	4.5	—	0.5	3.16	6.66
4	3.0	1.50	—	3.66	6.66
5	4.5	0.75	—	2.91	6.66
6	3.0	0.75	0.5	3.91	6.66

Toluene (40 g.) was added and the mixture condensed at 200°C. Throughout the polymerization, acid values were measured by dissolving samples (approx. 0.3 g.) in a neutralized 1:1 mixture of ethanol and toluene and titrating to a phenolphthalein end point with 0.1*N* alcoholic potassium hydroxide. Viscosities of 75% solutions in toluene were measured at 25°C. in Gardner-Holdt tubes. The results are shown in Table I.

The cloud points of the two resins were measured as a guide to any differences in molecular weight distribution. A 10% solution of the resin in

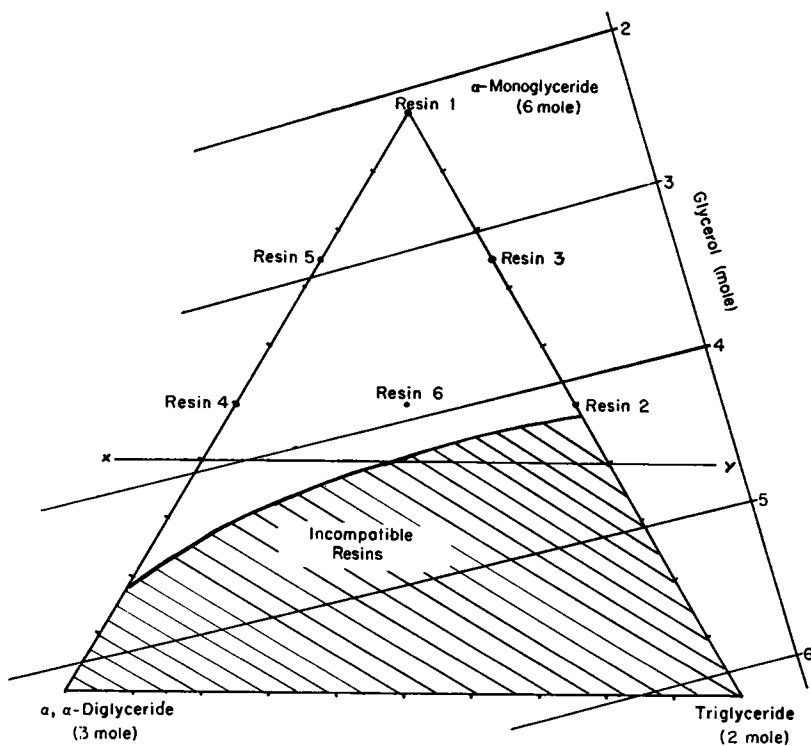


Fig. 1. Compatibility of resins prepared from glyceride mixtures.

TABLE III  
Condensation Rates of Resins 1-6 at 200°C.

Resin number	Time, min.	Acid value in ethanol-toluene	Acid value in acetone-water	Viscosity (Gardner-Holdt)	
1	46	52.3	56.5	D + 1/4	
	78	31.2	35.8	G + 1/2	
	108	18.4	23.8	K	
	123	16.5	20.3	L	
	137	14.2	19.4	P + 1/4	
	163	12.9	17.6	S	
	178	10.6	15.2	T + 1/4	
	After cooling	10.7	15.0	T + 1/4	
2	49	26.0	31.6	P - 1/4	
	70	16.5	20.6	U - 1/4	
	85	13.0	15.2	V	
	102	9.9	11.5	X + 1/2	
	After cooling	9.4	10.5	X + 1/4	
3	30	47.3	53.4	F	
	60	28.0	31.3	J - 1/4	
	81	17.1	22.6	N + 1/2	
	105	13.0	17.3	T	
	124	10.6	13.4	U	
	138	9.9	12.5	V + 1/2	
	After cooling	9.6	11.0	V + 1/4	
	4	37	48.4	50.2	I + 1/2
67		31.0	32.3	M	
87		25.4	27.3	N + 1/2	
117		20.0	22.5	Q	
137		17.7	19.6	T	
168		14.0	16.4	U - 1/2	
193		13.0	14.3	U + 1/2	
218		11.8	13.5	V	
242		10.3	12.1	V + 1/2	
After cooling		10.6	10.8	W - 1/2	
5		46	42.2	42.8	G
		76	29.5	34.4	H
	106	26.0	27.7	J - 1/4	
	146	18.0	19.4	K	
	176	15.5	17.6	N	
	198	14.4	15.2	R	
	241	11.8	12.8	S	
	261	10.5	11.9	T	
	After cooling	10.0	9.8	T + 1/2	
6	48	38.6	39.4	K	
	73	27.8	29.2	O - 1/4	
	108	17.7	19.3	R	
	123	15.9	16.7	T	
	140	13.0	—	U + 1/4	
	157	11.8	—	U + 1/2	
	177	10.2	11.5	W - 1/4	
	After cooling	10.5	10.4	W + 1/4	

acetone was prepared and titrated with a 70:30 acetone-water mixture. Also, 10% solution of the resin in 40:60 toluene-*n*-pentane was prepared and titrated with *n*-pentane. The cloud points for the acetone-water system were 6.37 and 6.31 ml. for resins A and B, respectively; for the toluene-*n*-pentane system they were 15.08 and 15.23 ml., respectively. On the above evidence, it was concluded that the addition of the glyceride mixture to molten phthalic anhydride was an acceptable method for preparing alkyd resins.

Selected glyceride mixtures were processed into alkyds, by the method described above, to establish compositions which would be compatible (Fig. 1). The method of assessing compatibility was by visual examination after 1 hr. condensation with the phthalic anhydride.

Resins with glyceride compositions chosen to give the maximum cover of the compatible formulation area of Figure 1 were then prepared, in the equipment described previously.<sup>7</sup> The glyceride-glycerol mixture was added to the molten phthalic anhydride in all cases. The initial composition of the resins is shown in Table II and Figure 1. The condensation rates at 200°C. are recorded in Table III. The acid values were measured in ethanol and in acetone-water. The latter gives an indication of the amount of anhydride present since both carboxyls of an anhydride are titrated in acetone-water and only one in ethanol.

To confirm that no alcoholysis reactions had occurred in the glyceride-glycerol mixture prior to addition to the phthalic anhydride, the  $\alpha$ -monoglyceride and glycerol contents of the mixtures were measured by periodate titration. The results are recorded in Table IV.

TABLE IV  
Analysis of Glyceride-Glycerol Mixtures Used in Manufacture  
of Resins 1-6

Resin number	$\alpha$ -Monoglyceride, wt.-%		Glycerol, wt.-%	
	Measured	Calculated	Measured	Calculated
1	91.3	91.4	8.7	8.6
2	45.7	45.5	16.5	16.4
3	68.5	68.5	12.7	12.4
4	45.5	45.5	14.5	14.4
5	68.7	68.5	11.7	11.5
6	45.6	45.5	15.6	15.4

### Resin Characterization

The viscosities of resins 1-6 at a constant solids content are recorded in Table V and the solids content of the resin solutions at a constant viscosity are in Table VI.

**Hydroxyl Values.** The hydroxyl values of the final resins and of the samples withdrawn during the polymerization were measured by acetylation and by phthalylation as described previously.<sup>2,7</sup> The results are recorded in Table VII.

TABLE V  
Viscosities of Resins 1-6 at 55% Solids in White Spirit

Resin number	Viscosity (Gardner-Holdt)
1	F
2	U + 1/2
3	G + 1/4
4	R
5	I + 1/4
6	S - 1/2

TABLE VI  
Solids Contents in White Spirit of Resins  
1-6 That Give a Gardner-Holdt Viscosity of F

Resin number	Solids, wt.-%
1	55.0
2	47.4
3	52.8
4	48.7
5	54.0
6	48.5

TABLE VII  
Hydroxyl Values for Resins 1-6 and for Samples Withdrawn  
during the Polyesterification

Resin number	Acid value	Measured hydroxyl value		Calculated hydroxyl value	Ratio measured/calculated hydroxyl value
		Acetyl-ation	Phthalyl-ation		
1	52.3	80.0		147.4	0.543
	31.2	63.1	59	126.3	0.499
	18.9	47.2		114.0	0.414
	16.5	45.0	43.2	111.6	0.403
	12.9	39.3		108.0	0.364
2	10.7	35.1	34.6	105.8	0.332
	26.0	75.2		121.1	0.621
	9.4	61.5	58.8	104.5	0.589
3	47.3	94.0		142.4	0.660
	17.1	61.3		112.2	0.546
4	9.6	51.0	51.5	104.7	0.487
	48.4	86.0		143.5	0.599
	17.7	54.5		112.8	0.484
5	10.6	47.7	45.9	105.7	0.451
	42.2	73.5		137.3	0.535
	18.0	49.3		113.1	0.436
6	10.0	37.0	36.8	105.1	0.352
	38.6	89.5		133.7	0.660
	15.9	62.8		111.0	0.566
	10.5	54.0	53.2	105.6	0.511



The infrared spectra of resins 1-6 and of the acetylated resins were run as films (deposited from acetone solution) on rock salt plates. A Unicam SP.200 spectrophotometer was used. The results are listed in Table VIII. The band intensities were measured by the base-line method as described by Rao.<sup>8</sup>

TABLE VIII  
Infrared Spectra of Resins 1-6 after Acetylation

Resin number	Absorption intensity		
	3550-3500 cm. <sup>-1</sup> (hydroxyl group) <sup>a</sup>	1100 cm. <sup>-1</sup> (acetate of secondary alcohol) <sup>b</sup>	1025 cm. <sup>-1</sup> (acetate of primary alcohol) <sup>b</sup>
1	0.055 (0.112)	0.508	0.155
2	0.063 (0.180)	0.574	0.260
3	0.057 (0.156)	0.598	0.199
4	0.074 (0.133)	0.544	0.220
5	0.061 (0.124)	0.502	0.208
6	0.059 (0.162)	0.545	0.234

<sup>a</sup> These band intensities were measured at a constant absorption of 0.152 at 1600 cm.<sup>-1</sup>. The figures shown in parentheses are those given by the resins before acetylation.

<sup>b</sup> These band intensities were measured at a constant absorption of 0.407 at 750 cm.<sup>-1</sup>.

**Measurement of Molecular Weight Distribution.** Two solvent-nonsolvent systems were used to measure the molecular weight distribution of resins 1-6.

A solution of the resin (10% by weight) in acetone was prepared and an aliquot (20 ml.) of this solution placed in a calibrated centrifuge tube with a tapered bottom. The solution was titrated with 70:30 acetone-water (by weight) in a bath at  $27 \pm 0.1^\circ\text{C}$ . until a permanent cloudiness resulted. The volumes required to reach the cloud point are recorded in Table IX. Further additions of the acetone-water mixture were made and the mixture stirred and heated in another bath at  $35-40^\circ\text{C}$ . until a clear solution resulted. The tube was then returned to the bath at  $27 \pm 0.1^\circ\text{C}$ . and allowed to stand (18 hr.). The lower layer was separated and transferred with a Pasteur

TABLE IX  
Cloud Points of Solutions of Resins 1-6

Resin number	Vol. acetone-water, ml.	Vol. <i>n</i> -pentane, ml.
1	4.18	32.50
2	6.72	12.72
3	5.43	23.46
4	5.51	15.76
5	5.14	24.18
6	7.14	14.60

pipet to an aluminum dish. The solids content of the separated fraction was measured by removing the volatile solvents at 35°C. under a reduced pressure of nitrogen (18 hr.). Further additions of nonsolvent were made and the separation procedure repeated until approximately 80% of the

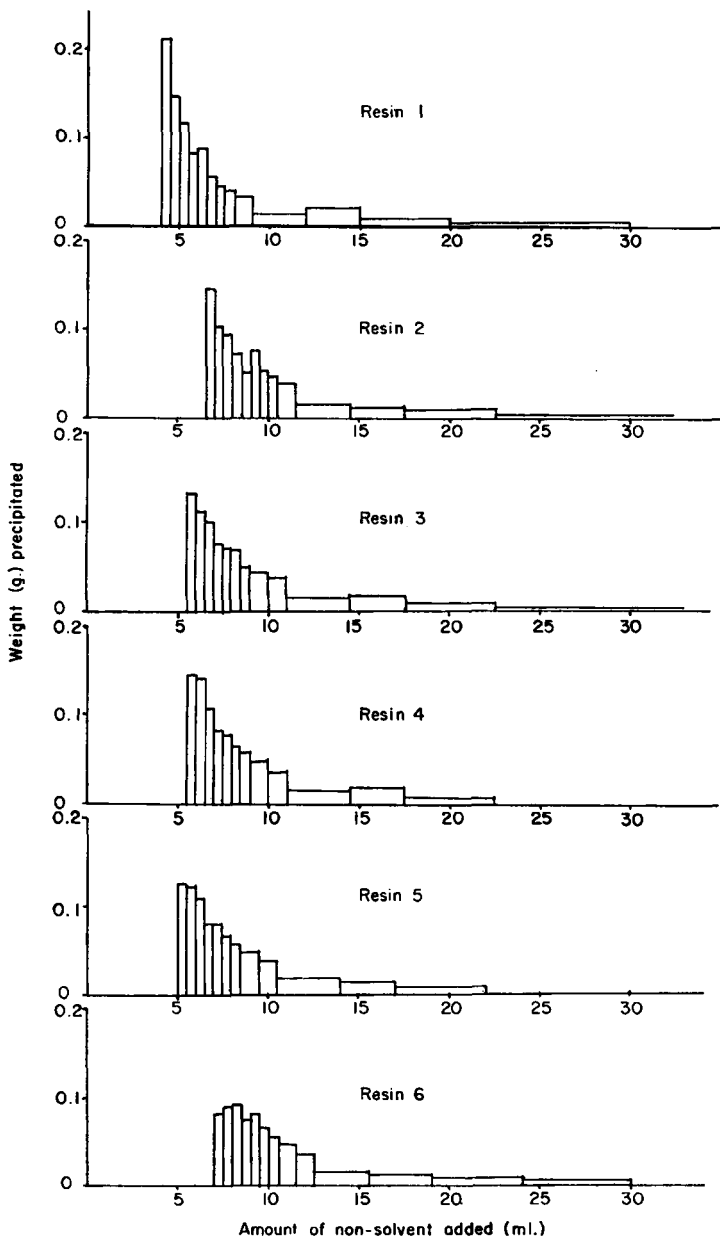


Fig. 2. Molecular weight distribution of resins 1-6 with acetone-water as the solvent-nonsolvent system.

resin solids had been recovered. The remaining soluble fraction was isolated by evaporation of the solvent at 35°C. under nitrogen at reduced pressure (40 hr.). The results of the fractionations are shown in Figure 2.

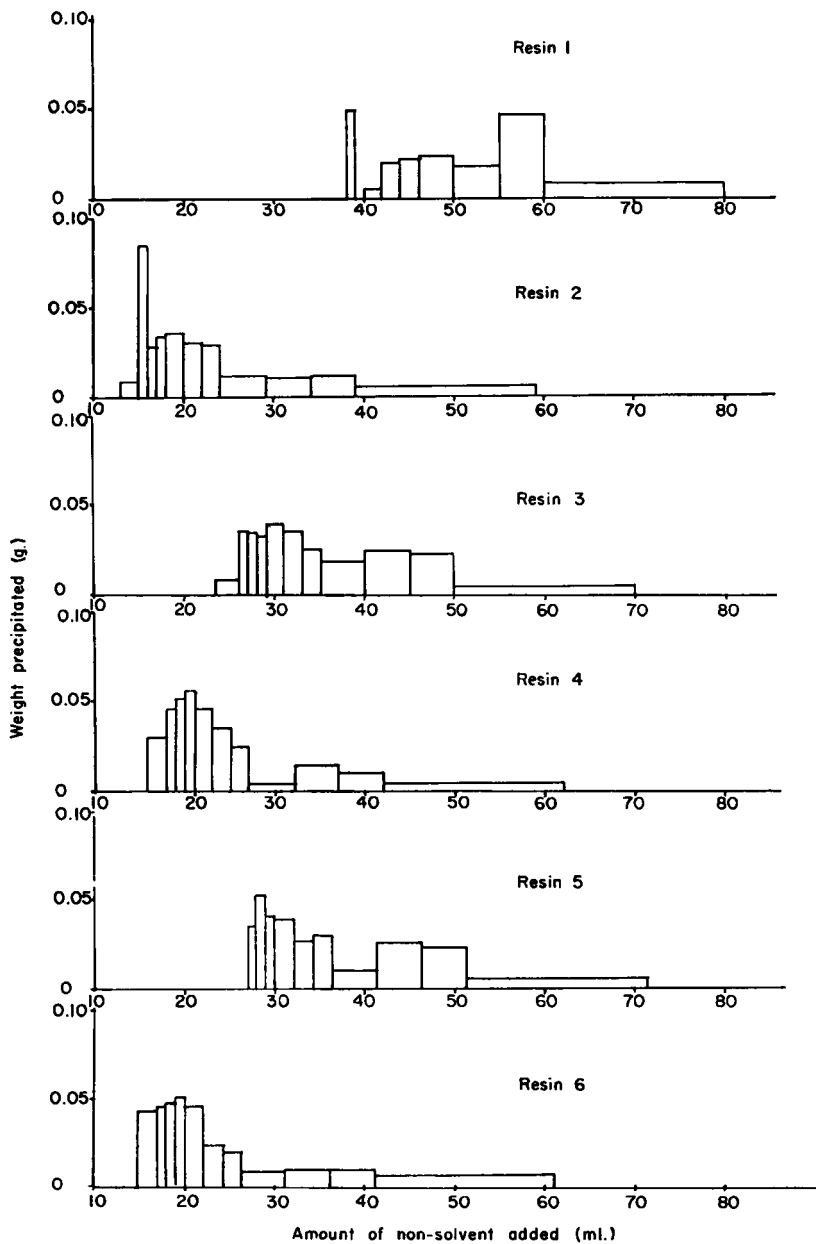
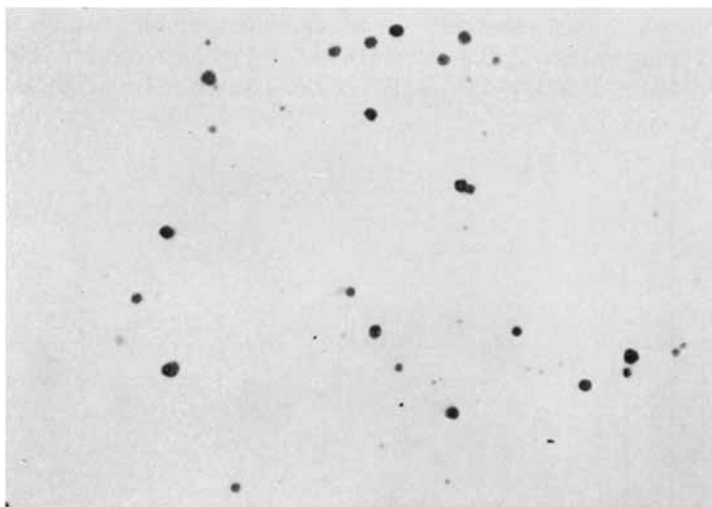
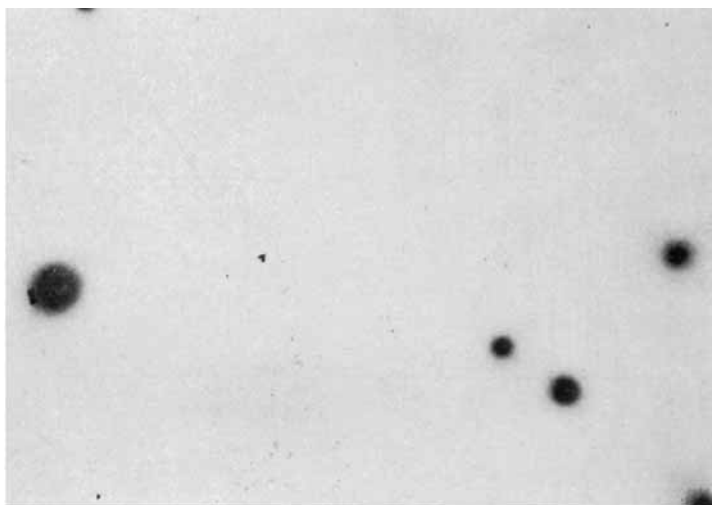


Fig. 3. Molecular weight distribution of resins 1-6 with toluene-*n*-pentane as the solvent-nonsolvent system.



(a)

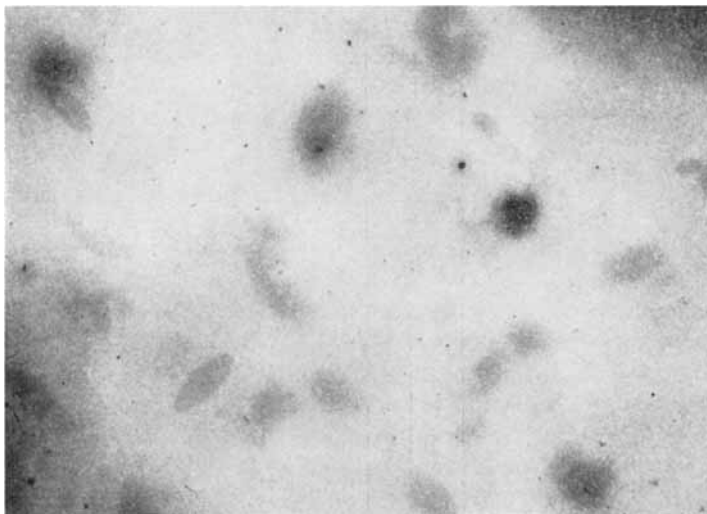


(b)

Figure 4. See caption, p. 1905.

Similarly, the resins were fractionated from a 10% solution in 40:60 toluene-*n*-pentane by titrating with *n*-pentane. The results are shown in Figure 3; cloud point measurements are shown in Table IX.

Infrared spectra were run on all the separated fractions that were soluble in 1,2-dichloroethane. A 4 wt.-% solution in 1,2-dichloroethane was used and the spectra run in a 0.207-mm. cell with the use of a Unicam SP.200 infrared spectrophotometer. The following general observations were noted from the spectra. (1) The presence of a band at  $1160\text{ cm.}^{-1}$  in all resins suggests the presence of some triglyceride. (2) The general trends



(c)

Fig. 4. Electron micrographs of resin samples: (a) resin 1 at acid value 52.3; (b) resin 1 at acid value 10.7; (c) resin 2 at acid value 9.4.

in the acetone-water fractionations were that increasing amounts of non-solvent gave fractions with: (a) decreasing phthalic anhydride contents, (b) increasing fatty acid contents, and (c) variable hydroxyl and acid values. (3) The hydroxyl band peak heights varied in the unfractionated resins 1-6, possibly because of hydrogen bonding or molecular association. The broad nature of the bands at 3500-3600 and 2700-2500  $\text{cm.}^{-1}$  and the presence of a band at 1400  $\text{cm.}^{-1}$ , suggest that hydrogen bonding is occurring.

#### Electron Microscopy of Resins 1-6

The resins were dispersed in toluene by an ultrasonic vibrator. Standard copper grids with a carbon support film were dipped into the resin solution, dried (5 min.) under nitrogen, and then examined in a Hitachi Model 11A electron microscope fitted with a cooling stage.

The samples were examined at a magnification of 7,500. The results are recorded below, and selected electron-micrographs are reproduced in Figure 4.

**Resin 1.** Micro gel particles were present in sample 1 (A.V. 52.3) as shown in Figure 4. The amount of microgel, and the size of the largest particles increased as the degree of polymerization increased. The final sample (A.V. = 10.7) is shown in Figure 4.

**Resin 2.** Microgel was present in all samples but the particle size was small (compared to resin 1), and the particles had a swollen diffuse lay around the small nucleus (Fig. 4).

TABLE X  
Microgel in Commercially Available Alkyd Resins

Alkyd type	Uses	Average functionality	Esterification, %	Hydroxyl Value		Appearance under electron microscope at 7,500X
				Theoretical	Measured	
Long oil length linseed oil pentaerythritol phthalate alkyd	Air-drying enamels	2.00	95.3	25.0	24.6	No microgel particles
Medium oil length coconut oil alkyd	Plasticizing alkyd for nitrocellulose and melamine formaldehyde resins	2.05	97.6	68.2	67.1	Trace quantities of microgel particles only
Medium oil length dehydrated castor oil alkyd <sup>a</sup>	General industrial stoving enamels	2.21	96.2	165	46	Large amounts of microgel particles of 0.75 $\mu$ diameter
Short oil length linseed oil glyceryl phthalate alkyd	Fast air-drying finishes and baking finishes	2.10	85.2	52.5	21.4	Large quantities of particles of 0.75 $\mu$ diameter were present
Medium oil length tung oil/linseed oil glyceryl phthalate alkyd	Fast air-drying finishes	2.12	97.6	73.2	37.0	Some particles of 0.75 $\mu$ diameter

Short oil length coconut oil glyceryl phthalate alkyd	High quality automotive enamels (with a mel-amine resin)	2.20	93.4	113	65	Particles 0.5-0.75 $\mu$ in diameter
Short oil length coconut oil/trimethylol propane/benzoic acid/glycerol/phthalate alkyd	High quality baking enamels	2.17	98.3	102.5	76	Fine microgel particles, ca. 0.25 $\mu$ diameter
Medium oil length safflower oil/bodied safflower oil/glyceryl phthalate alkyd	Air-drying low gloss finishes	2.13	97.2	64.2	32.5	Particles 0.25-0.5 $\mu$ diameter
Short oil length linseed oil rosin-modified glyceryl phthalate alkyd	Fast air-drying enamels and baking finishes	2.10	85.6	84.5	62.0	Fine microgel particles, ca. 0.25 $\mu$ diameter
Short oil length linseed oil phenolic-modified alkyd	Fast air-drying and baking finishes	2.21 <sup>b</sup>	92.5	90.4 <sup>b</sup>	37.5	Large quantities of microgel particles, ca. 1.0 $\mu$ diameter

<sup>a</sup> Solutions of these resins in toluene were filtered through a 0.45- $\mu$  millipore filter. The filtered solutions did not contain significant quantities of microgel particles. The hydroxyl values of the solution before and after filtering were comparable.

<sup>b</sup> The functionality has been calculated assuming the modifying resin has a zero functionality. The values shown for average functionality and the theoretical hydroxyl values, therefore, represent the minimum possible values.

**Resin 3.** A considerable quantity of very fine particles was present. Between A.V. 17.1 and A.V. 13.0, there was a noticeable change; there were more particles and they were of a larger size than earlier samples.

**Resin 4.** Isolated large particles were present in early samples (A.V. greater than 20). Between A.V. 17.7 and A.V. 11.8 there was a significant increase in the amount of microgel.

**Resin 5.** A small number of large particles was present. Between A.V. 26.0 and A.V. 11.8 there was a significant increase in the amount of microgel.

**Resin 6.** There was a large number of very fine microgel particles present, even at A.V. 38.6. Between A.V. 17.7 and A.V. 11.8 there was a significant increase in the amount of microgel.

A range of commercial alkyd resins was examined for microgel content and hydroxyl values. The results are shown in Table X.

### Resin Evaluation

The resins were evaluated in air-drying enamels, baking enamels, and for water solubility. Where possible, the resins were compared at the same solids content, rather than at the same viscosity, so as to minimize variations in film thickness.

**Air-Drying Enamels.** Autoxidation catalysts (driers) were added to the resins and the solutions allowed to stand (24 hr.) at 25°C. Drying times with a Beck-Koller type drying machine were recorded on 0.0056-in. films at 25°C. and 50% R.H. The results are recorded in Table XI.

TABLE XI  
Air-Drying Times of Resins 1-6

Resin number	Drier composition	Drying time, min.
1	0.2% Co, 1.5% Pb	6
2	"	24
3	"	18
4	"	42
5	"	30
6	"	54
1	0.08% Co, 0.2% Ca	42
2	"	93
3	"	45
4	"	90
5	"	69
6	"	87

A similar ranking was obtained when the resins were pigmented with titanium dioxide.

**Baking Enamels.** Baking enamels were prepared from the resins by the addition of driers or by blending with a melamine formaldehyde resin.

Driers (0.35% lead, 0.05% manganese) were added to the resins, and after standing (24 hr.) 0.0056-in. films were baked (30 min. at 120°C.) on



glass panels. Resin 1 gave by far the hardest film. The variation between the remaining resins was small.

Baking enamels were also prepared by blending the resins with a butylated melamine-formaldehyde<sup>1</sup> (80% alkyd solids, 20% melamine solids). Once again, the major difference was between resin 1 and the other resins. Resin 1 was incompatible with the melamine resin as shown by visual examination, thixotropic index (resin 1 = 3.54, resins 2-6 gave results from 1.06 up to 1.17), and the gloss of films baked 1/2 hr. at 120°C. (resin 1 gave a 60° gloss of 36, the values for the other resins were 85-90).

**Water Solubility of Resins.** The water solubility of samples removed during the preparation of resins 1-6 was evaluated as follows. The resin sample (1.0 g.) in butyl Cellosolve (0.54 g.) (Union Carbide Chemicals Co.), was mixed with triethanolamine (sufficient to neutralize the acid groups), and the mixture titrated with distilled water to a permanent cloud point. The results are recorded in Table XII.

The water solubility of resin mixtures was measured on some of the higher acid value samples taken during the preparation of the resins. A mixture

TABLE XII  
Water Solubilization of Resin Samples

Resin preparations from which sample taken	Acid value of sample prior to neutralization	Cloud point, ml.	Storage stability after 3 months at 25°C.*
1	52.3	1.05	—
	31.2	0.75	—
	18.9	<0.20	—
2	26.0	0.45	—
	16.5	0.25	—
	13.0	<0.20	—
3	47.3	0.50	—
	28.0	0.35	—
	17.1	<0.20	—
4	48.4	1.55	—
	31.0	1.15	—
	25.4	0.90	—
	20.0	0.55	—
5	17.7	<0.20	—
	42.2	∞	Clear
	29.5	∞	Clear
	26.0	∞	Clear
	18.0	15.0	Clear
	15.5	5.05	Slight haze
6	14.4	3.10	Cloud
	38.6	2.55	Clear
	27.8	2.15	Cloudy
	17.7	1.05	—
	15.9	0.65	—
	13.0	0.35	—

\* Measured on a sample which contained 2.0 g. water/g. resin.

of resin sample (1.0 g.), butyl cellosolve (0.54 g.), and triethanolamine (sufficient to neutralize the acid groups) was mixed with water (2.0 g.). Blends (1:1) of these solutions were made and titrated to a cloud point with water. The results are recorded in Table XIII.

TABLE XIII  
Water Solubility of Selected Blends of Resin Samples

Resin preparation from which sample taken	Acid value of sample prior to neutralization	Appearance of resin solution	Appearance of blend	Water tolerance of blend	Storage stability after 3 months at 25°C.*
1	52.3	Cloudy	Cloudy	—	—
2	26.0	Cloudy	Cloudy	—	—
1	52.3	Cloudy	Clear	∞	Clear
4	48.4	Cloudy	Clear	∞	Clear
1	52.3	Cloudy	Clear	∞	Clear
5	42.2	Clear	Clear	∞	Clear
1	52.3	Cloudy	Clear	∞	Clear
6	38.6	Clear	Clear	∞	Clear
2	26.0	Cloudy	Clear	∞	Clear
4	48.4	Cloudy	Clear	∞	Clear
2	26.0	Cloudy	Clear	∞	Clear
5	42.2	Clear	Clear	∞	Clear
3	47.3	Cloudy	Clear	∞	Clear
4	48.4	Cloudy	Clear	∞	Clear
4	48.4	Cloudy	Cloudy	—	—
5	42.2	Clear	Clear	∞	Clear

\* Measured on a sample which contained 2.0 g. of water/g. resin.

## DISCUSSION

The glycerolysis mixtures which would yield compatible alkyd resins when condensed with phthalic anhydride were established (Fig. 1) and then six glyceride mixtures, which were so chosen as to give the maximum variation in the glyceride composition and yet to give a compatible resin (mixtures 1-6, Figure 1), were processed into alkyd resins. These glyceride mixtures gave alkyd resins (resins 1-6) which at the same number-average molecular weight, showed the following major, and highly significant, differences: (1) the time to attain a given degree of esterification varied considerably (Table III); (2) the ratio of the number-average to viscosity-average molecular weights varied, and in agreement with this observation, the molecular weight distributions were markedly different (Figs. 2 and 3); (3) the viscosities of the polymer solutions at a constant solids content and the solids content at a constant viscosity varied (Tables V and VI); (4) in no resin did the measured hydroxyl value approach the calculated value, and even more significant, the measured hydroxyl values varied between the resins by a factor of two (approx.) (Table VII); and, (5) the neutralized

resins showed a wide variation in water tolerance and water solubility (Tables XII and XIII).

These differences in solution properties are reflected in the film-forming properties when the resins are crosslinked by autoxidation or by reaction with a melamine formaldehyde resin. Many of these differences in properties are not consistent with the generally accepted theories on polyester formation<sup>9</sup> and the properties expected from solutions of polyesters. For example, it is generally agreed that the higher the solution viscosity of an alkyd resin, the higher will be the molecular weight and the shorter the time required for a dry film to form by autoxidation. However, the results reported here are the complete opposite to this: resin 1 with the lowest solution viscosity gave a dry film in the shortest time (Table XI).

Electron microscopy shows that all of these resins have microgel particles dispersed in a continuous phase of soluble polymer. Highly significant differences between the resins exist in the degree of condensation at which significant quantities of microgel form, and in the amount and size of the microgel particles. For example, resin 1 has significant amounts of relatively large microgel particles, even in the early stages of condensation (Fig. 4), whereas resin 2 has only small swollen particles even at the end of the polyesterification. The presence of microgel particles has also been noted by Bobalek et al.<sup>10</sup> in a recent study of concepts of the gel point in alkyd resins.

The presence of the microgel particles in these resins enables rational explanations to be put forward for the apparently contradictory properties noted above. Since these alkyd resins are not true solutions they cannot be treated by the theories of polyesterification and ester interchange advanced by Flory;<sup>9</sup> one of Flory's basic stipulations is that the polymer should be in solution.<sup>9</sup> Thus the polyesterification does not follow simple third-order kinetics for any of the resin formulations 1-6; this is understandable since microgel forms early in the reaction and removes some groups from the reaction phase (see below). Furthermore, the available hydroxyl groups do not correspond to the calculated value even early in the reaction and the percentage of available groups decreases with increasing degrees of polymerization and amounts of microgel (Table VII). The unreactive hydroxyl groups are those present in the microgel as shown by separating the gel fraction by filtration through a micropore filter; the soluble polymer gave a hydroxyl value equivalent to the original resin (Table X). This finding is in agreement with the infrared spectra which show that the unavailable groups are more strongly bonded than the reactive groups (Table VIII). The number of unavailable hydroxyl groups is approximately proportional to the microgel content of the resins. Both primary and secondary hydroxyl groups are available for acetylation, as shown by the infrared spectra of the acetylated resins (Table VIII).

The molecular weight distribution of the resin is related to the individual chemical components of the starting composition; consequently, ester interchange and the other related reactions are not occurring rapidly com-

pared with microgel formation. Once microgel forms, it would not be expected to enter exchange reactions. Some interchange does occur in the solution phase, as would be predicted by the theories developed for linear polymers in solution. This is shown by the presence of triglycerides in resins 1, 5, and 4, which were prepared from  $\alpha, \alpha'$ -di-glyceride and/or  $\alpha$ -monoglyceride. The fractionation studies have confirmed the differences in molecular weight distribution and also given some indication of the nature of the microgel. With the acetone-water solvent-nonsolvent system, which would be expected to separate on a molecular weight basis, the molecular weight distributions are as expected from the microgel contents; resin 1 (highest microgel) precipitates at the lowest nonsolvent content, while resin 2 (lowest microgel) requires the highest amount of nonsolvent. The other resins are between these two extremes (Fig. 2). On the other hand, with toluene-*n*-pentane as the solvent-nonsolvent system, which separates on a polarity basis, more nonsolvent is required to precipitate resin 1 than resin 2 (Fig. 3). These results suggest that the microgel has a nonpolar surface with its polar groups buried in the interior of the particle. This hypothesis is in agreement with the infrared data which show that hydroxyl groups are bonded and presumably "buried" inside the microgel particle.

The solubility in water of the resins, and of samples taken during the resin preparation at low degrees of polymerization, varied considerably (Table XII). It is difficult to clearly relate this property to the microgel content alone, since the interaction of the other molecules in the system with the microgel will contribute to solubility. This is shown by the blending of selected samples (Table XIII); two insoluble (cloudy) mixtures can give rise to clear solutions with good storage stability.

The film-forming properties of the resins are directly related to the microgel content. Resin 1 formed a tack-free film when autoxidized at room temperature more rapidly than the other resins (Table XI). There are probably a number of factors which contribute to the rapid drying of resin 1; first, it contains more microgel than the other resins, second, the molecular weight of the microgel is higher than in the other resins, third, the free-radical processes involved in autoxidation proceed more rapidly in the microgel particles, since chain-terminating reactions involving dimerization are kept to a minimum,<sup>10</sup> and fourth, the hydroperoxides formed in the solution polymer would decompose more rapidly when the hydroxyl value is low.<sup>7</sup> At elevated temperatures, the more rapid autoxidation of resin 1 is again apparent. Therefore, the low viscosity and rapid air-drying properties of resin 1 are not contradictory, since the high molecular weight microgel fraction is not solution and does not contribute significantly to solution viscosity.

Enamels prepared by blending the resins with a butylated melamine-formaldehyde resin showed marked differences, particularly between resin 1 and resins 2-6. Resin 1 was incompatible with the melamine resin and gave films with a low gloss. The other resins were compatible and gave

acceptable films. The reactions which take place between an alkyd resin and a melamine formaldehyde condensate on heating involve the hydroxyl groups of the alkyd resin.<sup>11</sup> Consequently, resin 1 with the lowest available hydroxyl value would be expected to give the least chemical interaction; the large microgel particles would also emphasize any nonhomogeneity in the film or solution, whereas the smaller microgel particles (e.g., resin 5), would be less obvious.

These evaluations in systems which cure by autoxidation and by chemical interaction with a melamine resin, show clearly that there is no one preferred molecular weight distribution for an alkyd resin; it is essential to relate the distribution to the end use of the polymer.

The compatibility region of Figure 1 also highlights the dangers of using only an  $\alpha$ -monoglyceride analysis to characterize the product resulting from the glycerolysis of an oil. The line XY (Fig. 1) which corresponds to an  $\alpha$ -monoglyceride content of 40% passes through compatible and incompatible regions. The present work, therefore, confirms the conclusions reached in a study of the linseed oil-glycerol reaction.<sup>3</sup>

The presence of a microgel fraction in the alkyd resin is of considerable theoretical and technological importance. The more theoretical aspects related to the formation of microgel, the conditions necessary for microgel formation, and the significance of these observations to the basic theories of polyesterification will be discussed in a following paper. However, the technological development of alkyds can now be approached more scientifically once the concept of microgel is accepted. For example, in the development of a fast air-drying resin, one of the laboratory control tests, and a guide to resin performance, should be examination of the microgel fraction.

Examination of a selected range of commercially produced alkyd resins has shown that microgel fractions are present, to various extents, in all resins except those which are linear (Table X). The presence of microgel is also directly related to the available hydroxyl groups; only alkyds where all the hydroxyl groups could be acetylated were devoid of microgel. Therefore, there is a direct relationship between the functionality of the system, the molecular weight distribution, the available hydroxyl groups, and the amount of microgel in the polymer.

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### References

1. J. R. Fletcher, L. Polgar, and D. H. Solomon, *J. Appl. Polymer Sci.*, **8**, 659 (1964).
2. D. H. Solomon and J. J. Hopwood, *J. Appl. Polymer Sci.*, **10**, 993 (1966).
3. D. H. Solomon and Jean D. Swift, *J. Oil Colour Chemists' Assoc.*, in press.
4. T. C. Patton, *Alkyd Resin Technology*, Interscience, New York, 1962, p. 176.
5. D. W. Berryman, *J. Oil Colour Chemists' Assoc.*, **42**, 393 (1959).
6. W. D. Pohle and V. C. Mehlenbacher, *J. Am. Oil Chemists Soc.*, **27**, 54 (1950).

7. D. H. Solomon and J. J. Hopwood, *J. Appl. Polymer Sci.*, **10**, 981 (1966).
8. C. N. R. Rao, *Chemical Applications of Infrared Spectroscopy*, Academic Press, New York, 1963.
9. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953.
10. E. G. Bobalek, E. R. Moore, S. S. Levy, and C. C. Lee, *J. Appl. Polymer Sci.*, **8**, 625 (1964).
11. D. H. Solomon, *Rev. Pure Appl. Chem.*, **13**, 171 (1963).

### Résumé

Des résines alkydes qui avaient la même composition chimique globale et le même degré de polymérisation ont été préparées au départ de mélanges synthétiques de mono-, di-, et triglycérides d'acide linoléique, de glycérol, et d'anhydride phthalique. Les propriétés de ces résines différaient de façon significative. Les particules de micro-gel étaient présentes dans toutes les résines, mais la quantité et la grandeur des particules de gel étaient une fonction de la composition du glycéride. La notion de micro-gel était utilisée pour expliquer les propriétés des solutions et filmogènes de ces résines. L'examen d'une gamme de résines alkydes disponibles dans le commerce a montré que les particules de micro-gel sont présentes lorsque la fonctionnalité est plus élevée que deux.

### Zusammenfassung

Alkydharze mit der gleichen chemischen Bruttozusammensetzung und dem gleichen Polymerisationsgrad wurden aus synthetischen Mischungen von Linolsäuremono-, -di- und -triglyceriden, Glycerin und Phthalsäureanhydrid dargestellt. Die Eigenschaften dieser Harze zeigten wesentliche Unterschiede. Alle Harze enthalten Mikrogeleilchen, die Menge und Grösse der Geleilchen ist aber von der Glyceridzusammensetzung abhängig. Das Mikrogeleilchenkonzept wird zur Erklärung der Lösungs- und Filmbildungseigenschaften dieser Harze herangezogen. Die Untersuchung einer Anzahl handelsüblicher Alkydharze zeigte, dass bei einer Funktionalität grösser als zwei Mikrogeleilchen auftreten.

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