

## Molecular Weight Distribution in Alkyd Resins. Part II. Castor Oil and Hydrogenated Castor Oil Alkyds

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### Synopsis

Alkyds prepared from castor and hydrogenated castor oils have been prepared direct from the oil and by first subjecting the oil to a glycerolysis reaction. The molecular weight distributions of the alkyds have been measured in solvent systems designed to separate predominantly on polarity and molecular weight. The properties of the alkyds in stoving enamels have been evaluated. The results are discussed in relation to existing theories relating processing conditions to molecular weight distribution in alkyd resins. Previous suggestions regarding the reactivity of the hydroxyl groups in the oil molecules are not consistent with the results obtained in this study.

### INTRODUCTION

The coatings industry uses alkyd resins (fatty acid modified polyesters) either alone or in conjunction with other film formers, for up to 50% of all paints produced.<sup>1,2</sup> As a consequence of the commercial importance of alkyd resins a tremendous amount of technological development and modification of basic formulations has been carried out. On the other hand, fundamental studies aimed at better prediction and control of alkyd properties and processing are comparatively rare. In fact, some of the basic formulations and manufacturing conditions commonly used for alkyd resins are derived by extrapolation of results obtained on much simpler systems, and not verified in the more complex alkyd structures. For example, Flory's<sup>3</sup> findings regarding the ease and rapidity with which ester interchange-type reactions occur in decamethylene adipates are often assumed to operate in alkyds of the glyceryl phthalate type, whereas Spitzer,<sup>4</sup> Tawn,<sup>5</sup> and we<sup>6,7</sup> have shown they do not always apply. This is a most significant point when considering the preparation of alkyd resins from vegetable oils, where it is necessary to first react the oil with a polyol to ensure compatibility when the phthalic anhydride is added; in the absence of subsequent complete and rapid interchange reactions the final alkyd structure will be governed by the composition of the alcoholysis product (i.e., the amounts of mono-, di-, and triglyceride, and free polyol).

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In Part I<sup>6</sup> of this series we have shown that with an alkyd resin based on glycerol, phthalic anhydride, and coconut oil (a predominantly saturated fatty acid triglyceride) the molecular weight distribution and film-forming properties of the polymer are related to the extent of oil-glycerol reaction as measured by  $\alpha$ -monoglyceride analysis. As an extension of the findings of Part I to alkyds based on other oils, we now report results obtained with castor and hydrogenated castor oil. These oils are predominantly the triglycerides of 12-hydroxyoleic acid (ricinoleic acid) and 12-hydroxystearic acid, respectively. There are a number of reasons why these oils are of interest. First, the presence of a hydroxy group on the fatty acid chain renders the oil miscible with the glycerol-phthalic anhydride mixture, and thus it is not essential to first interchange the oil with glycerol. Consequently, variations in the extent of glycerolysis from 0% to 80% (approx.) are possible. With other oils the range is ca. 25-60%,<sup>6,8</sup> the lower limit is set by compatibility requirements, and the upper limit by the processing conditions and the polyol-to-oil ratio.<sup>6</sup> The greater variation possible in the monoglyceride content suggests that even more significant differences in the molecular weight distribution should result in castor oil and hydrogenated castor oil alkyds than in the systems examined previously. Second, the presence of the hydroxyl groups on the fatty acid chain could lead to competitive reaction with the glycerol hydroxyls and to the possibility of a different molecular structure depending on the extent of alcoholysis. Third and most important, our previous work<sup>6</sup> and preliminary studies by others<sup>9</sup> have indicated that the preferred alkyds are those made from alcoholysis products high in  $\alpha$ -monoglyceride content, whereas current commercial practice with castor and hydrogenated castor oil is to usually prepare the alkyd direct from the oil with no monoglyceride stage.<sup>10</sup>

Therefore, in this paper we report the results of a study of glyceryl phthalate type alkyd resins based on castor and hydrogenated oils, with special reference to the relationship between the degree of glycerolysis of the oil, the molecular weight distribution of the alkyds, and the film properties of coatings prepared from these resins.

### EXPERIMENTAL

The purification and characterization of the solvents, glycerol, and phthalic anhydride has been described previously.<sup>6</sup> The castor oil had a hydroxyl value of 157 mg. KOH/g. which is equivalent to a ricinoleic acid content of 87% of the total fatty acids. The acid value of the oil was 2.84 mg. KOH/g. The hydrogenated castor oil had a hydroxyl value of 152 mg. KOH/g. which is equivalent to a 12-hydroxystearic acid content of 84% of the total fatty acids. The acid value of the oil was 1.62 mg. KOH/g. and the iodine value was less than 5.

Lead naphthenate was used as a solution in mineral spirits equivalent to a lead content of 24%.

Hydroxyl values were measured by the method of Wilson and Hughes,<sup>11</sup> while solids contents and viscosity were measured as previously described.<sup>6</sup>

### Resin Preparation

Each resin was processed in a 2-liter multineck flask heated by an electric mantle and fitted with a Dean and Stark water separator, reflux condenser, glass stirrer, nitrogen inlet, thermometer, and sample device. Dry nitrogen was used to blanket the contents of the flask during the polymerization.

TABLE I  
Composition of Castor and Hydrogenated Castor Oil Alkyds

Resin number	Composition				Process used
	Oil (1.0 mole)	Glycerol, mole	Phthalic anhydride, mole	Calc. oil length	
1	Castor oil	5.64	6.68	40	Monoglyceride, $\alpha$ -mono content = 78%
2	Castor oil	5.64	6.68	40	No monoglyceride
3	Castor oil	3.39	4.53	50	Monoglyceride, $\alpha$ -mono content = 68%
4	Castor oil	3.39	4.53	50	No monoglyceride
5 <sup>a</sup>	Hydrogenated castor oil	6.54	6.02	40	Monoglyceride, $\alpha$ -mono content = 70%
6 <sup>a</sup>	Hydrogenated castor oil	6.54	6.02	40	No monoglyceride

<sup>a</sup> Attempts to prepare a hydrogenated castor oil alkyd of composition similar to resin 2 failed, since the reaction mixture remained cloudy and gelled at an acid value = 35. The modified formulations were used to lower the acid value at gelation.

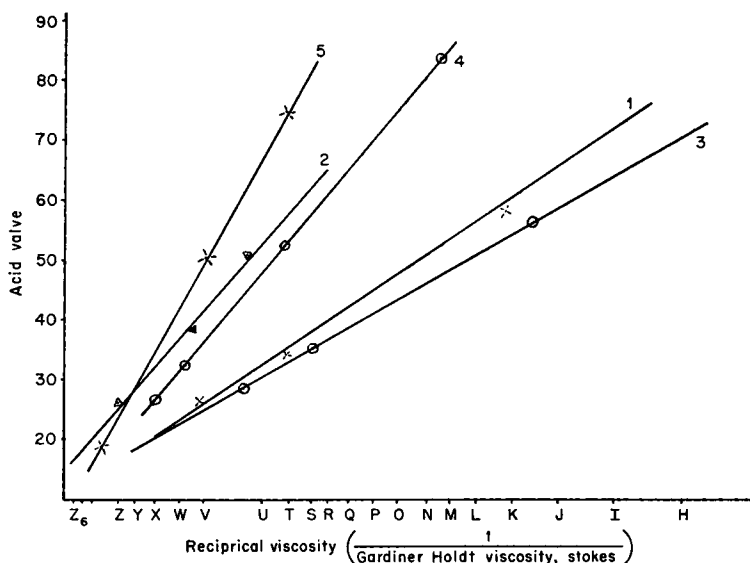


Fig. 1. Relationship between acid value and reciprocal viscosity for resins 1-5.

**Monoglyceride Process.** The oil, glycerol, lead naphthenate solution (3.4 g./450 g. oil), and toluene were heated under reflux at 210°C. for 1 hr. The reaction mixture was cooled (approx. 150°C.), a sample removed for  $\alpha$ -monoglyceride analysis, and then phthalic anhydride added. The polycondensation was carried out at 210°C. and water removed by the Dean and Stark separator. The resin was cooled and thinned in toluene.

**No Monoglyceride or Fusion Process.** Glycerol and phthalic anhydride were heated to 140°C. and a mixture to castor oil, lead naphthenate solution, and toluene added (5 min.). The condensation was carried out at 210°C.

TABLE II  
Condensation Rates for Alkyds

Resin number	Time, min.	Water evolved, ml.	Acid value, mg. KOH/g.	Viscosity at 70 wt.-% solids in toluene <sup>a</sup>	Comments	
1	29	28	87.6	G + 1/2	Clear	
	62	39	57.4	K		
	94	50	34.3	T + 1/4		
	124	52	26.6	V		
	After cooling	—	25.2	V + 1/4		
2	13	17			Reaction mixture cloudy	
	21	24			“ “ “	
	37	40			“ “ “	
	45	42	50.4	U + 1/4		
	71	46	37.5	V + 1/2		
	93	52	26.4	Z		
	After cooling	—	24.9	Z + 1/2		
3	27	27	76.0	G + 1/2	Clear	
	42	35	56.0	J + 1/2		
	66	44	35.0	S		
	95	47	29.0	U + 1/2		
	After cooling	—	28.6	V		
4	15	22			Reaction mixture cloudy	
	22	25	83.0	M		
	45	37	52.0	T		
	70	44	33.0	V + 1/2		
	80	47	27.5	X + 1/2		
	After cooling	—	26.2	Y		
	23	23	80.0			
5	31	29	74.0	T		
	57	41	50.0	V		
	93	47	18.8	Z2		
	After cooling	—	18.5	Z2		
6	5	8			Reaction mixture cloudy	
	29	24				“ “ “
	53	37	46.0			“ “ “
	69	43	31.0			“ “ “
	84	48	18.5			“ “ “
	After cooling	—	18.2			“ “ “

<sup>a</sup> Cardner-Holdt units.

Details of the resin compositions and condensation rates are given in Tables I and II; Figure 1 is a plot of acid value against reciprocal viscosity.

### Measurement of Molecular Weight Distribution

Molecular weight distributions were measured by precipitating the polymer from a solvent-nonsolvent system. Each fraction was separated,

TABLE III  
Molecular Weight Distribution Measurements of Resins 1-6 with Acetone-Water

Resin	Nonsolvent, ml.	Precipitate, g.	
Resin 1	4.50	Cloud point	
	4.75	0.0652	
	5.00	0.0523	
	5.25	0.0432	
	5.50	0.0180	
	5.75	0.0156	
	6.00	—	
	6.25	—	
	6.50	—	
	7.00	0.1888	
	9.00	0.0027	
	10.00	0.0406	
	14.00	0.0875	
	19.00	0.1176	
	21.50	0.0422	
	24.00	0.0061	
	26.00	0.0007	
	30.00	0.0062	
	40.00	0.0021	
		Soluble fraction	0.1275
	Total	0.8163	
	Wt. of solids in 10 ml. of solution	0.8202	
Resin 2	4.03	Cloud point	
	4.25	0.1442	
	4.50	0.0906	
	4.75	0.0216	
	5.00	0.0281	
	5.25	0.0160	
	5.50	—	
	5.75	0.0207	
	6.50	0.1084	
	9.00	0.0363	
	11.00	0.1005	
	14.00	0.0613	
	16.00	0.0545	
	18.00	0.0132	
		Soluble fraction	0.1151
		Total	0.8105
	Wt. of solids in 10 ml. of solution	0.8188	

(continued)

TABLE III (continued)

Resin	Nonsolvent, ml.	Precipitate, g.
Resin 3	5.0	Cloud point
	6.0	0.143
	7.0	0.095
	8.0	0.097
	9.0	—
	10.0	0.063
	11.0	0.033
	12.0	0.034
	13.0	0.029
	14.0	—
	15.0	—
	16.0	0.052
	17.0	—
	18.0	0.012
	22.0	0.023
	24.0	—
	30.0	0.024
	Soluble fraction	0.201
	Total	0.806
	Wt. of solids in 10 ml. of solution	0.811
Resin 4	5.3	Cloud point
	6.3	0.193
	7.3	0.105
	8.3	0.072
	9.3	0.047
	10.3	0.057
	11.3	0.018
	12.3	0.040
	13.3	0.015
	14.3	0.004
	15.3	0.020
	17.3	0.013
	19.3	0.017
	21.3	0.004
	23.3	—
	Soluble fraction	0.208
	Total	0.813
	Wt. of solids in 10 ml. of solution	0.817

(continued)

dried, and weighed, since the volume separated was not proportional to the weight of the separated polymer. Two solvent-nonsolvent systems were chosen so as to separate molecules predominantly on molecular weight and on polarity. Details of the methods are as follows. A 10% (approx.) solution (w/w) of the polymer in acetone was titrated with a 60:40 mixture of acetone-water in a tapered graduated tube until a permanent cloudiness resulted. The temperature was controlled to  $27 \pm 0.1^\circ\text{C}$ . Further addi-

TABLE III (continued)

Resin	Nonsolvent, ml.	Precipitate, g.
Resin 5	8.34	Cloud point
	9.34	—
	10.34	0.033
	12.34	0.034
	14.89	0.047
	15.89	0.068
	17.89	0.064
	25.89	0.137
	35.89	0.140
	45.89	0.034
	Soluble fraction	0.254
	Total	0.811
Wt. of solids in 10 ml. of solution	0.820	
Resin 6	2.43	Cloud point
	3.43	0.076
	4.43	0.019
	5.43	0.036
	7.43	0.032
	9.93	—
	10.93	0.036
	12.93	—
	18.93	0.088
	28.93	0.132
	Soluble fraction	0.394
	Total	0.813
Wt. of solids in 10 ml. of solution	0.817	

tions of the nonsolvent were made and the tube heated to 35–40°C. until the solution cleared. The tube was then returned to the bath at 27°C. and allowed to come to equilibrium (approx. 18 hr.). The lower layer was transferred by using a pasteur pipet, to a dish, and the solids content determined after drying at 35°C. under nitrogen at reduced pressure. This procedure was repeated until approximately 80% of the resin had been separated. The remaining soluble fraction was recovered by evaporation of the solvent as above. The results are given in Table III and graphed in Figure 2. The above procedure was also carried out with ethyl acetate as the solvent and titrating with petroleum ether (b.p. 40–60°C.). The results of these separations are given in Table IV and graphed in Figure 3.

Hydrogenated castor oil was extracted from resin 6 as follows.

Resin 6 (30 g. of solid) was heated with acetone (500 g.) for 10 min., and the mixture allowed to stand (16 hr. at 25°C.). The white precipitate which formed was removed by filtration, washed with acetone (50 g.), and dried under reduced pressure (16 hr. at 40°C.). Water (75 g.) was added to the filtrate, and the precipitate which separated after standing (16 hr. at 25°C.) isolated as above, and combined with the initial precipitate. The

total yield was 0.92 g. This material had an infrared spectrum similar to that of hydrogenated castor oil, a hydroxyl value of 160 mg. KOH/g., and a saponification value of 182 mg. KOH/g. From these results we have concluded that the precipitate is hydrogenated castor oil.

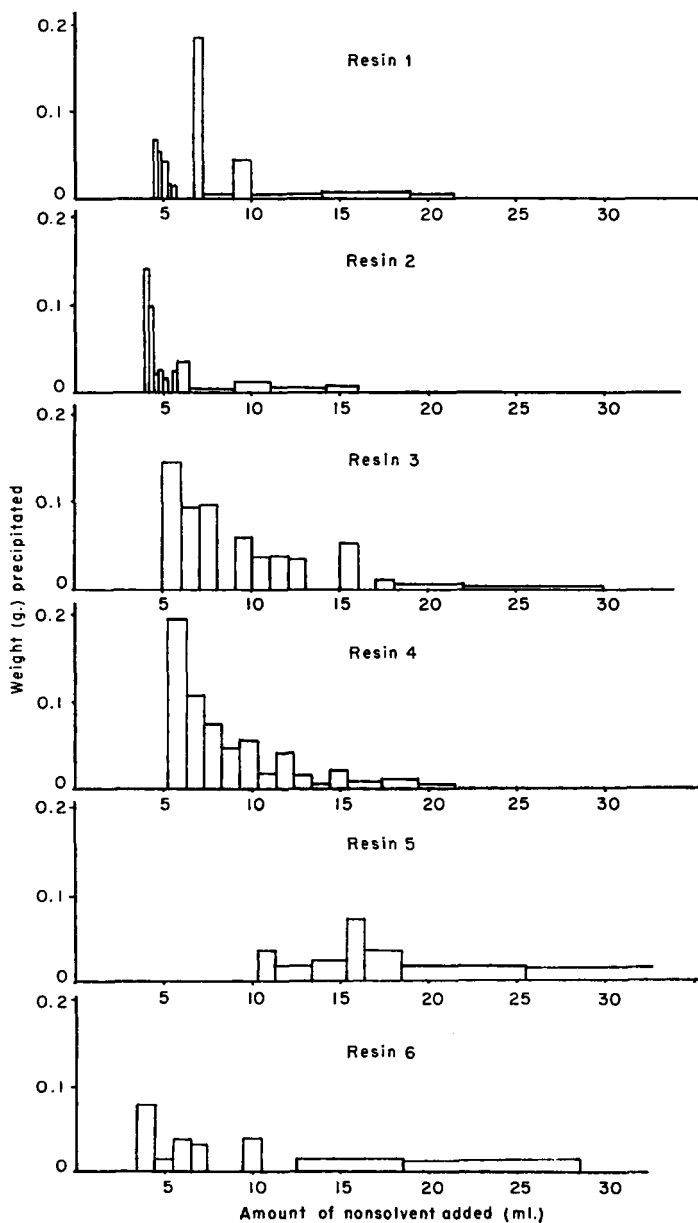


Fig. 2. Molecular weight distribution of alkyds with acetone-water as the solvent-nonsolvent system.



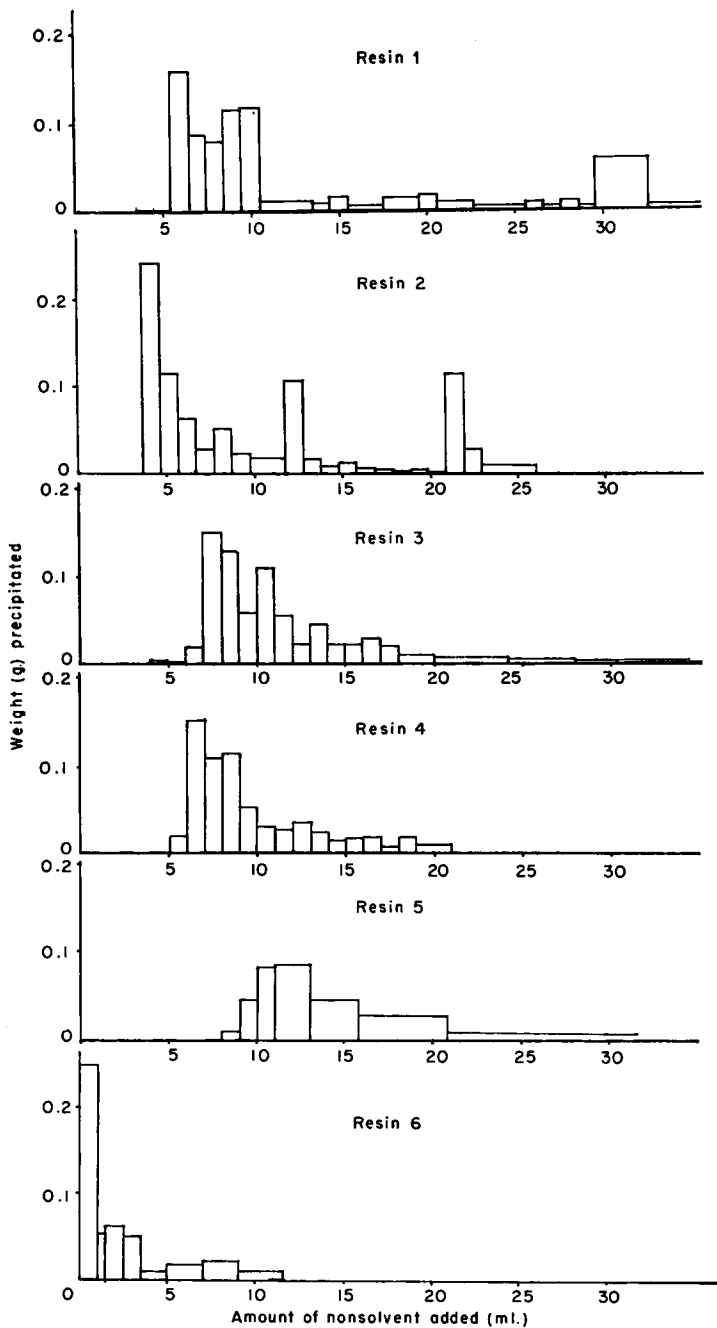


Fig. 3. Molecular weight distribution of alkyds with ethyl acetate-petroleum ether as the solvent-nonsolvent system.

TABLE IV  
Molecular Weight Distribution Measurements of Resins 1-6 with Ethyl Acetate-  
Petroleum Ether

Resin	Nonsolvent, ml.	Precipitate, g.
Resin 1	3.33	Cloud point
	4.33	—
	5.33	0.1577
	6.33	0.0853
	7.33	0.0791
	8.33	0.1172
	9.33	0.1184
	10.33	0.0200
	11.33	—
	12.33	0.0094
	13.33	0.0132
	14.33	—
	15.33	0.0046
	16.33	0.0011
	17.33	0.0269
	18.33	0.0164
	19.33	0.0081
	20.33	0.0067
	23.33	0.0077
	24.33	0.0069
25.33	0.0016	
26.33	0.0078	
27.33	0.0027	
31.33	0.1328	
35.33	0.0213	
63.33	0.0203	
	Soluble fraction	0.0390
	Total	0.9042
	Wt. of solids in 10 ml. of solution	0.9168

(continued)

The infrared spectra were run on a Unicam SP-200 infrared spectrophotometer. The fractions separated in the molecular weight distribution studies were dissolved in toluene, cast as a film on a rock salt plate, and dried at 35°C. under a reduced nitrogen atmosphere (3 hr.).

The band intensities were measured by the method described by Rao.<sup>12</sup> The results are in Table V.

### Evaluation of the Alkyd Resins in Industrial Baking Enamels

Each resin was processed into an enamel-based or r-titania (Austiox-R.C.R.) at a pigment/binder ratio of 100/100 by grinding the pigment in a partially butylated melamine-formaldehyde condensate (BE-615 as marketed by Monsanto Australia Ltd.), and then adding the alkyd resin to this mill-base. The 40% oil alkyds were evaluated at an alkyd/melamine-formaldehyde ratio of 77.5/22.5 and the 50% alkyds at a ratio of 74.5/25.5.

TABLE IV (continued)

Resin	Nonsolvent, ml.	Precipitate, g.
Resin 2	2.75	Cloud point
	3.75	0.2399
	4.75	0.1163
	5.75	0.0631
	6.75	0.0282
	7.75	0.0495
	8.75	0.0245
	10.75	0.0311
	11.75	0.1056
	12.75	0.0141
	13.75	0.0085
	14.75	0.0099
	15.75	0.0043
	16.75	0.0033
	17.75	0.0021
	18.75	0.0041
	19.75	0.0005
	20.75	0.1132
	21.75	0.0209
	24.75	0.0219
	Soluble fraction	0.0465
	Total	0.9075
	Wt. of solids in 10 ml. of solution	0.9155
Resin 3	4.0	Cloud point
	5.0	0.002
	6.0	—
	7.0	0.018
	8.0	0.150
	9.0	0.130
	10.0	0.059
	11.0	0.110
	12.0	0.056
	13.0	0.023
	14.0	0.048
	16.0	0.042
	17.0	0.027
	18.0	0.020
	20.0	0.020
	24.0	0.034
	28.0	0.030
	40.0	0.024
	Soluble fraction	0.108
	Total	0.901
	Wt. of solids in 10 ml. of solution	0.905

(continued)

TABLE IV (continued)

Resin	Nonsolvent, ml.	Precipitate, g.	
Resin 4	2.95	Cloud point	
	4.00	—	
	5.00	—	
	6.00	0.019	
	7.00	0.151	
	8.00	0.110	
	9.00	0.114	
	10.00	0.052	
	11.00	0.031	
	12.00	0.028	
	13.00	0.035	
	14.00	0.024	
	15.00	0.014	
	16.00	0.016	
	17.00	0.018	
	18.00	0.008	
	19.00	0.018	
	21.00	0.020	
	23.00	—	
	25.00	—	
	Soluble fraction	0.242	
	Total	0.900	
	Wt. of solids in 10 ml. of solution	0.903	
Resin 5	6.93	Cloud point	
	7.43	—	
	8.43	0.011	
	9.43	0.045	
	10.93	0.085	
	12.93	0.165	
	15.93	0.113	
	20.93	0.140	
	35.93	0.113	
		Soluble fraction	0.326
		Total	0.998
		Wt. of solids in 10 ml. of solution	0.910
	Resin 6	0.00	0.246
0.50		0.052	
1.50		0.063	
2.50		0.050	
4.00		0.024	
6.00		0.031	
8.50		0.032	
13.50		—	
28.50		—	
		Soluble fraction	0.410
	Total	0.908	
	Wt. of solids in 10 ml. of solution	0.915	

TABLE V  
Infrared Spectra of Resin Fractions Separated by Ethyl Acetate-Petroleum Ether

Resin	Precipitate increment, wt.-%	Ratio of band intensities	
		3550 cm. <sup>-1</sup>	750 cm. <sup>-1</sup>
		2950 cm. <sup>-1</sup>	2950 cm. <sup>-1</sup>
Resin 1	17.2	0.46	0.80
	9.3	0.43	0.74
	21.5	0.40	0.65
	13.0	0.52	0.72
	4.7	0.35	0.61
	7.0	0.31	0.56
	27.3	0.42	0.45
Resin 2	Unfractionated alkyd	0.44	0.64
	38.0	0.50	0.89
	15.3	0.48	0.79
	6.1	0.55	0.63
	13.1	0.40	0.61
	16.0	0.42	0.49
	11.5	0.34	0.24
Resin 3	Unfractionated alkyd	0.40	0.63
	18.7	0.38	0.63
	20.8	0.29	0.57
	30.7	0.26	0.51
	11.1	0.28	0.46
	5.9	0.31	0.44
	12.8	0.19	0.24
Resin 4	Unfractionated alkyd	0.26	0.48
	18.9	0.39	0.67
	12.2	0.37	0.60
	12.7	0.30	0.58
	9.2	0.28	0.54
	11.2	0.29	0.54
	8.9	0.26	—
26.9	0.18	0.23	
	Unfractionated alkyd	0.26	0.49

TABLE VI  
Gloss (60° Gardner Glossmeter) of Enamels Prepared from Resins 1-5

Resin composition	Gloss
Resin 1/MF = 77.5/22.5	75
Resin 2/MF = 77.5/22.5	79
Resin 3/MF = 74.5/25.5	74
Resin 4/MF = 74.5/25.5	82
Resin 5/MF = 77.5/22.5 <sup>a</sup>	80

<sup>a</sup> Resin 5 gave an enamel which was satisfactory for all properties, including durability after 1500 hr. accelerated weathering (Marr Weatherometer).

Resin 6 was incompatible with melamine resin and was, therefore, not evaluated further.

The enamels were evaluated on phosphated steel panels, after baking for  $1/2$  hr. at  $120^{\circ}\text{C}$ ., for solvent resistance (xylene and acetone), impact resistance (60 in.-lb. reverse), flexibility (Mandrel bend test Conical,  $1/4$ - $1\ 1/2$  in.; this test was also done on untreated steel panels), hardness (coin scratch and Tukon), salt spray resistance (400 hr.), and viscosity stability (at  $40^{\circ}\text{C}$ .). In all of these tests the monoglyceride and no-monoglyceride process resins were equivalent and satisfactory. The humidity resistance (400 hr. at  $40^{\circ}\text{C}$ .) of formulations in resins 2 and 4 was slightly better than those on resins 1 and 3. Overbake discoloration (extra bake of 1 hr. at  $120^{\circ}\text{C}$ .) was satisfactory on all enamels. The gloss of the enamels is given in Table VI.

### Oil/Phthalic Anhydride Equilibrium

Oil (59 g.) and phthalic anhydride (27.2 g.) were heated for 30 min. at  $160^{\circ}\text{C}$ . in a 250-ml. multineck flask fitted with a stirrer, thermometer, air condenser, and nitrogen gas inlet. Acid value was measured in acetone-water, to determine total carboxyls, since the standard method with toluene-ethanol as a solvent only titrates one carboxyl of the anhydride group. The results are given in Table VII.

When glycerol, in the same proportion as used to prepare resins 2 and 6, was added to the above reaction mixtures and the condensation carried out

TABLE VII  
Reaction of Phthalic Anhydride with Castor, and Hydrogenated Castor Oil

Oil type	Acid value in ethanol	Acid value in water	Free phthalic anhydride in reaction mixture, % <sup>a</sup>	Phthalic anhydride present as half ester, % <sup>a</sup>
Hydrogenated castor oil <sup>b</sup>	94	139	33.2	52.3
Castor oil	106.5	115	7.4	89.4

<sup>a</sup> Based on the original weight of phthalic anhydride.

<sup>b</sup> Considerably more phthalic anhydride sublimed onto the inside of the flask than in the castor oil experiment.

TABLE VIII  
Hydroxyl Values of Alkyd Resins

Resin	Measured hydroxyl value, mg. KOH/g.	Theoretical hydroxyl value, mg. KOH/g.
1	131.4, 132.0	169.2
2	138.0, 139.0	168.9
3	102.0, 102.5	139.6
4	103.4, 104.0	137.2
5	229.0, 228.3	273.5
6	204.5, 201.0	273.2

at 200°C., the hydrogenated castor oil system became increasingly cloudy, while the castor oil system remained clear.

### Hydroxyl Values of Alkyds

The hydroxyl value of each alkyd was measured by the method of Wilson and Hughes,<sup>11</sup> and the results are given in Table VIII.

### DISCUSSION

Castor oil fatty acids have one double bond per molecule, whereas hydrogenated castor oil fatty acids are saturated; consequently, the oils, or alkyds derived from them, are not film-forming under autoxidation conditions. However, alkyds prepared from these oils are widely used as polymeric plasticizers for other film-forming resins; the two most important types are cellulose nitrate and melamine-formaldehyde condensates. The alkyds used with cellulose nitrate usually contain 55-70% by weight of oil and are of comparatively low molecular weight; there is no chemical combination of the alkyd and cellulose entities during film formation. On the other hand, with the melamine-formaldehyde system, where chemical interaction is the basis of film formation, the alkyd has less oil (40-50%), and is of a higher molecular weight. In order to study molecular weight distribution effects, formulations suitable for use with melamine-formaldehyde condensates were chosen, since the shorter oil length results in a more highly complex glyceryl-phthalate component, and the higher molecular weight would be expected to accentuate differences in the molecular weight distribution of the resins.<sup>6</sup>

From the results in Figure 1 and Table II it can be seen that the ratio of the acid number (number-average molecular weight) to viscosity (approaching a weight-average figure) in 40% and 50% castor oil alkyds depends on the method of processing (or in other words on the degree of alcoholysis of the oil); this suggests a difference in molecular weight distribution\* in the resins. Evidence substantiating the differences in molecular weight distribution is given by the fractionation studies, recorded in Tables III and IV and graphed in Figures 2 and 3. The infrared spectra of the fractions separated by ethyl acetate-petroleum ether further support the differences in molecular weight distribution of the alkyds (Table V); the differences are more apparent in the more complex short oil alkyds.

Pigmented industrial enamels prepared from the castor oil alkyds were different, particularly for gloss and humidity resistance; the alkyds prepared direct from the oil gave the better properties.

There is also a distinct and significant difference between the processing of alkyds prepared from castor oil and hydrogenated castor oil; with hydrogenated castor oil it is essential to carry out a prior glycerolysis of the oil to obtain a satisfactory resin (Table VI) for use in industrial enamels, whereas the converse applies to castor oil.

\* This term is used in the broad sense to indicate a difference in molecular weight and/or polarity of the molecules.

The differences noted above between alkyds prepared from castor oil and hydrogenated castor oil are somewhat unexpected and conflict with the conclusions drawn by Fry<sup>13</sup> for similar resins. Fry has concluded that in alkyd manufacture the hydroxyl groups of either oil are considerably more reactive than those of glycerol; the free hydroxyl groups of the alkyd are mainly present on glycerol residues. Fry has further concluded that the hydroxyl groups on hydrogenated castor oil are more reactive than those on castor oil (95% and 77% esterified, respectively). If Fry's conclusions are correct we would expect the alkyds prepared directly from the oil to become more compatible as the esterification proceeds as a result of the oil and glyceryl phthalate entities combining chemically. Furthermore, the hydrogenated castor oil alkyd should become compatible more readily than the castor oil resin. Our observations are not consistent with these predictions; the castor oil alkyds become more compatible with increasing degree of esterification whereas the hydrogenated castor oil resins become incompatible. Brett<sup>14</sup> has also noted the improved compatibility of castor oil alkyds as esterification proceeds. The incompatibility of hydrogenated castor oil alkyds prepared directly from the oil suggests that the hydrogen-castor oil is not being combined chemically into the resin structure. This suggestion is substantiated by the separation from the polymer mixture of unchanged hydrogenated castor oil. Further support for our findings on these alkyds is given by a study of the reaction of phthalic anhydride with the oils. More phthalate half ester forms from castor oil than from hydrogenated castor oil (Table VII). This suggests that the castor oil hydroxyl groups are the more reactive, or that the castor oil half ester is the more stable; in either case there should be more likelihood of compatibility with castor oil alkyds, as confirmed by our experiments. A possible reason for the difference in our conclusions and those of Fry is that Fry used hydroxyl values measured by chemical methods in calculating the relative amounts of oil and polyol hydroxyl groups esterified. These values are not always quantitative and can be misleading.<sup>15</sup> This is particularly relevant to the alkyds under discussion; our measured hydroxyl values are 16-27% lower than the calculated values (Table VIII).

The results reported in this paper have considerable significance to the commercial production of alkyd resins from hydrogenated castor oil. Alkyds prepared direct from the oil with no glycerolysis stage are usually processed only to a low degree of condensation (high acid value) and then thinned in strong solvents such as Cellosolve acetate (Union Carbide Corp.). These limitations are necessary if the resin is to give a clear solution. However, they also result in poor film properties, particularly exterior durability.<sup>16</sup> The glycerolysis of the oil prior to adding the dibasic acid removes these limitations.

The results are also of importance in relation to the extent of oil-glycerol reaction which gives the best alkyd from a given formulation. Examples are now recorded where the maximum glycerolysis of the oil gives the more desirable resin (hydrogenated castor oil, coconut oil) and where no reaction



between the oil and glycerol is preferable (castor oil). With the present state of knowledge in this field it is not yet possible to generalize regarding the extent of glycerolysis for a given formulation and use.

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### Résumé

Des résines alkydes préparées au départ d'huile de ricin, et d'huile de ricin hydrogénée ont été préparées directement au départ de l'huile et en soumettant, au préalable, l'huile à une réaction de glycérolyse. Les distributions de poids moléculaire des résines alkydes ont été mesurées dans un système solvant choisi pour séparer de façon prédominante suivant la polarité et le poids moléculaire. Les propriétés de ces alkydes dans des émaux à l'étuve ont été évaluées. Les résultats sont discutés en rapport avec les théories existantes qui relient les conditions de processing à la distribution des poids moléculaires des résines alkydes. Les suggestions antérieures concernant la réactivité des groupes hydroxyles dans les molécules d'huile ne sont pas en accord avec les résultats obtenus dans cette étude ci.

### Zusammenfassung

Aus Ricinusöl und hydriertem Ricinusöl wurden Alkydharze direkt aus dem Öl und nach vorhergehender Glycerolyse des Öls dargestellt. Die Molekulargewichtsverteilung der Aldehydharze wurde in Lösungsmittelsystemen gemessen, die vorwiegend nach der Polarität und nach dem Molekulargewicht auf trennten. Die Eigenschaften der Aldehydharze in Ofenemail wurden bestimmt. Die Ergebnisse wurden an Hand der bekannten Theorien für die Beziehung zwischen Verarbeitungsbedingungen und Molekulargewichtsverteilung bei Alkydharzen diskutiert. Frühere Vorschläge bezüglich der Reaktivität der Hydroxylgruppen in den Ölmolekülen sind mit den hier erhaltenen Ergebnissen nicht vereinbar.

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