Cooking Schedule of Alkyd Resin Preparation. Part II.   Effect of Cooking Schedule on Molecular Weight Distribution of Alkyd Resin

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Synopsis

The effect of cooking schedule on the molecular weight distribution of an alkyd resin was investigated.   At the molar ratio of 1.03/0.43/1.00 for glycerin, lauric acid, and phthalic anhydride, two kinds of alkyd resin were prepared, one by maintaining the reaction temperature at 170°C for an hour and then raising it up to 230°C (sample I), the other by raising the temperature up to 230°C at a uniform rate of 33°C per 10 min. (sample II).   Sample I and sample II were fractionated into seven or eight fractions by adding n-heptane to 5 wt-% toluene solution at 30°C.   Acid value, hydroxyl value, intrinsic viscosity $[\eta]$, and the number-average molecular weight $\bar{M}_n$ were determined. The result showed that the molecular weight distribution curve obtained from sample I was much narrower than that from sample II.   In addition, a relation was found between $[\eta]$ and $\bar{M}_n$ conforming to the equation $[\eta] = KM^\alpha$, where different values of K and α were obtained for sample I and sample II.   Based on the differences in the molecular weight distribution curves and in the rate constants for the esterification reactions, glycerin/lauric acid and glycerin/phthalic anhydride at 170° and 230°C, the mechanism of condensation reaction of short oil alkyd resin was discussed.

INTRODUCTION

The author reported in the previous paper[1] that the slope C' in the equation $\log \eta = A + C'\bar{M}_n{}^{1/2}$, where η is the viscosity of molten alkyd and $\bar{M}_n$ is the number-average molecular weight, was larger for the alkyd that was prepared by raising the reaction temperature directly up to 230°C than for the alkyd that was prepared by maintaining the temperature at 170°C for 1 hr and then raising it to 230°C.   This suggested that these cooking schedules might result in different molecular weight distributions although in the same formulation.

This paper deals with molecular weight distributions of the alkyd resin prepared by two kinds of cooking schedules.   The purpose of this study is to clarify the significance of maintaining the reaction temperature at 170°C for 1 hr in alkyd synthesis and to discuss some aspects of alkyd kinetics in relation to its molecular weight distributions.

EXPERIMENTAL

Materials

Commercial-grade reagents were used for alkyd synthesis. The phthalic anhydride used had an anhydride content of 98.8% and the glycerin had a glycerol content of 98.5%. The purity of lauric acid was determined by acid value measurement and gas chromatography. The acid content was 98.6%, in which 2.2% of myristic acid and a trace of capric acid were detected.

Preparation of Alkyd Resins

Two kinds of alkyd resins were prepared from glycerin, phthalic anhydride, and lauric acid at a molar ratio of 1.03/1.00/0.43, respectively, by maintaining the reaction temperature at 170°C for 1 hr before raising it to 230°C (sample I) and by raising the temperature directly to 230°C at a uniform rate of 33°C per 10 min (sample II), as shown in Figure 1.

The reactions were carried out in an 1-liter four-necked round-bottom glass flask, fitted with a Dean and Stark water separator, reflux condenser, N₂ gas inlet tube, and thermometer. Solvent cooking (xylol) was em-
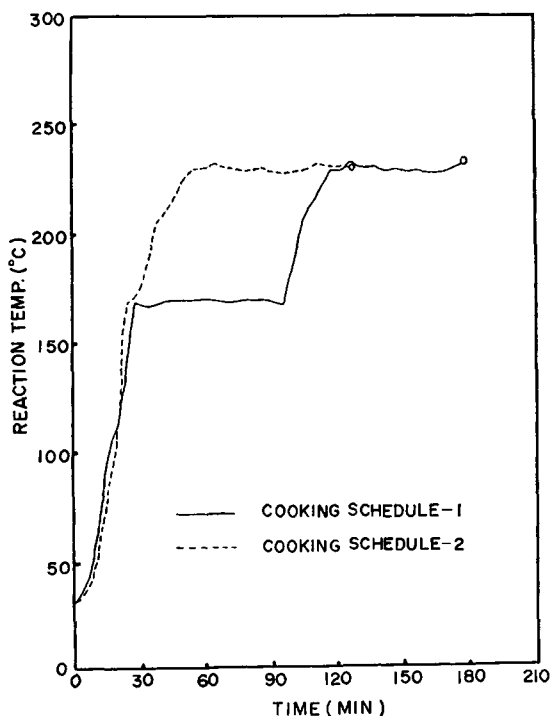

Fig. 1. Cooking schedules of alkyds prepared by a 1-liter four-necked round bottom glass flask. The open circles represent endpoints of the alkyd synthesis.

TABLE I
Data of Unfractionated Samples

	Sample I	Sample II
Acid value, mg KOH/g	11.7	11.6
Hydroxyl value, mg KOH/g	129.3	129.8
$\bar{M}_n$	1170	1250
$[\eta]_{30}°C$, cc/g		
acetone	6.04	7.44
toluene	3.72	4.05
k', 30°C		
acetone	0.94	0.70
toluene	2.48	2.59

ployed and cooking logs were successfully managed by using a C-40 T Minicon (Ohyo Denshi Kohgyo Co. Ltd., Japan).

Samplings were occasionally carried out throughout the reaction to determine acid values and molecular weights. Since the main purpose of this study was to obtain the correlation between molecular weight distribution and cooking schedule, the final acid values of the alkyd resins prepared by cooking schedules I and II were set equal. By obtaining the relation between the acid value and reaction time beforehand, alkyd resins of approximately the same acid values were prepared as shown in Table I. After removing the reflux solvent xylol, distilled toluene was added to the molten resin to obtain a 60% solution.

Fractionation of Alkyd Resin

After removing toluene from the alkyd solution with a rotary evaporator, the alkyd was dried further in a vacuum oven at 75°C for 24 hr. It was confirmed that this drying method does not affect the molecular weight of the resin, as described in the previous paper.[1] The alkyd resins thus obtained were rather sticky because of their small molecular weights and fatty acid modification, sometimes making it difficult to transfer the dried resin from the flask to other vessels. In such a case, the flask was kept in a Dry Ice/methanol mixture for a few minutes before the resin was handled.

Fractionations were carried out as follows. The dried alkyd, 40 g, was dissolved in toluene to prepare 800 g of solution. n-Heptane was first added as a nonsolvent with vigorous agitation until permanent cloudiness developed. The cloudy solution was then heated at an elevated temperature until a clear homogeneous solution was obtained. This was allowed to cool to a constant temperature of 30 ± 0.02°C in a flask with a 10-ml projection at the bottom. Thus precipitation again occurred. After removing the sol to another flask with a siphon, the gel was dissolved in acetone. The acetone solution was dried by using the rotary evaporator and vacuum oven, and the weight of the precipitated resin was measured. The determination of molecular weight, hydroxyl value, acid value, and intrinsic viscosity was carried out for each fraction.

Measurement of Intrinsic Viscosity

The dried sample was dissolved in a solvent to prepare a 2.0 to 2.5 g/100 ml solution and filtered through a fine sintered glass filter to remove traces of suspended materials. Ten milliliters of the solution were pipetted out and transferred to a Ubbelohde dilution-type viscometer to measure the intrinsic viscosity. Another 10 ml of the solution was evaporated to dryness and weighed to determine the exact concentration of the solution by keeping the solution at 75°C under vacuum for 24 hr. The viscosity measurements were carried out in a constant temperature bath maintained at 30 ± 0.01°C. Three dilutions were made in the viscometer allowing efflux time to be measured at concentrations of 2.5, 2.0, 1.7, and 1.3 g/100 ml. Efflux time was recorded to 0.1 sec. Intrinsic viscosities were determined by extrapolation of both the plots of η_{sp}/c against c. The measurements of $[\eta]$ were carried out in acetone and toluene.

Measurement of Acid Value, Hydroxyl Value, and Molecular Weight

Acid values were determined by dissolving the dried resin in an equal volume mixture of benzene and ethanol, and titrating to the phenolphthalein endpoint with standardized base.

Hydroxyl values were determined by the acetic anhydride-pyridine method using perchloric acid as catalyst. Measurements of molecular weight were carried out by the Rast Method as described in the previous paper.[1]

RESULTS AND DISCUSSION

Cooking Schedule and Molecular Weight Distribution of Alkyd Resin

The results of fractionation are given in Tables II and III. The integral and differential weight distribution curves for sample I and sample II are shown in Figures 2 and 3, respectively. An ideal phase separation at a given molecular weight cannot be expected even with linear polymers, much less so with alkyd resins, which are composed of many branches and free carboxyl and hydroxyl groups. Therefore, the information obtained by the precipitation fractionation has to be regarded as comparative. Yet, it is clear that the molecular weight distribution curve of the alkyd prepared by cooking schedule II is broader than that of the alkyd prepared by cooking schedule I. As these differences are important, it seems desirable to search for their theoretical reasons.

As stated in the literature, alkyd resins are formed as a result of several independent reactions which are probably occurring side by side. They are: (1) addition reactions between phthalic anhydride and hydroxyl groups of glycerin, forming half-esters; (2) esterification reactions of the hydroxyls with the carboxyls (fatty acid, phthalic half-ester, or phthalic acid); and (3) dimerization or polymerization reactions at the reactive

TABLE II
Fractionation Result of Sample I

	Fraction[a]							
	F_1-1	F_1-2	F_1-3	F_1-4	F_1-5	F_1-6	F_1-7	F_1-8
Wt ratio of n-heptane/toluene	0.429	0.501	0.584	0.675	0.805	1.236	2.114	—
Wt, g	5.930	3.949	4.195	3.949	3.608	5.548	3.563	8.408
Cumulative wt fraction	0.146	0.288	0.384	0.481	0.570	0.706	0.794	1.000
Acid value, mgKOH/g	11.8	11.9	11.8	11.5	11.1	11.0	10.1	14.1
Hydroxyl value, mgKOH/g	142.4	141.0	140.4	131.4	129.0	124.6	112.0	87.3
$\bar{M}_n$	1370	1240	1120	1030	1020	1000	790	690
$[\eta]_{30°C}$, cc/g								
acetone	8.02	7.35	7.02	6.50	6.21	5.75	4.89	3.38
toluene	4.12	3.98	3.94	3.97	3.90	3.60	2.96	2.74
k', 30°C								
acetone	0.91	0.93	0.81	0.92	0.83	0.78	0.91	1.12
toluene	4.08	3.59	2.86	2.43	2.65	2.79	3.98	3.43

[a] Suffix 1 refers to the fractions of sample I.

TABLE III
Fractionation Result of Sample II

	Fraction[a]						
	F_2-1	F_2-2	F_2-3	F_2-4	F_2-5	F_2-6	F_2-7
Wt ratio of n-heptane/toluene	0.425	0.536	0.665	0.850	1.244	2.127	—
Wt, g	5.374	6.334	6.530	5.119	5.148	3.740	8.583
Cumulative wt fraction	0.130	0.288	0.441	0.564	0.689	0.779	1.000
Acid value, mgKOH/g	9.9	9.8	9.3	9.2	9.0	9.0	17.1
Hydroxyl value, mgKOH/g	148.3	139.7	138.9	132.7	131.3	117.6	88.8
$\bar{M}_n$	2450	1680	1500	1100	990	810	580
$[\eta]_{30°C}$, cc/g							
acetone	12.96	10.47	8.36	7.58	6.66	5.44	3.40
toluene	6.18	5.09	4.56	4.10	3.80	3.62	2.83
k', 30°C							
acetone	0.72	0.61	0.84	0.66	0.60	0.78	1.55
toluene	2.12	2.87	2.48	2.76	2.21	2.14	1.62

[a] Suffix 2 refers to the fractions of sample II.

double bonds of the unsaturated fatty acids or their ester derivatives. Furthermore, ester interchange reactions might take place between different esters (between two fatty acid glycerides or between a fatty acid glyceride and a phthalic glyceride) or between esters and compounds with free hydroxyl or carboxyl groups.

In this experiment, however, it is reasonable to assume that both ester interchange and reversible reactions are negligible since the reaction was carried out below 230°C and the water of reaction was immediately eliminated by means of cooking the solvent xylol. Also, polymerization reactions at the reactive double bonds of the unsaturated fatty acids are considered to be negligible, since lauric acid was used in this experiment. Therefore, discussion on the mechanism of alkyd synthesis may be restricted here to the reactions shown by the following three equations:

$$\text{[phthalic anhydride]} + \text{HO·R} \longrightarrow \text{[benzene with COOR and COOH]} \tag{1}$$

$$R'\text{·COOH} + \text{HO·R} \longrightarrow R'\text{·COO·R} + H_2O \tag{2}$$

$$\text{[benzene with COOR and COOH]} + \text{HO·R} \longrightarrow \text{[benzene with COOR and COOR]} + H_2O \tag{3}$$
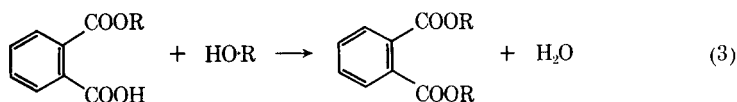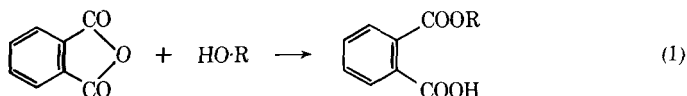
where HO·R and R'COOH refer to the hydroxyl group of glycerin and fatty acid, respectively.

It is well known that the β-hydroxyl group of glycerin is less reactive than α-hydroxyl. This has been shown with fatty acids which form unstable β-glycerides easily converted into α-glycerides as long as α-hydroxyls are available.[2-4] The same is generally assumed for phthalic anhydride. Savard and Diner[5] indicated that the addition of phthalic anhydride at 160°C is extremely rapid with α-hydroxyl. In addition, there are some papers which state that this addition reaction is the most rapid and that it occurs at relatively low temperature (130° to 150°C).[6-8]

TABLE IV
Different Reactivity of Carboxyl Groups with Glycerin as Measured
by Goldsmith[4]

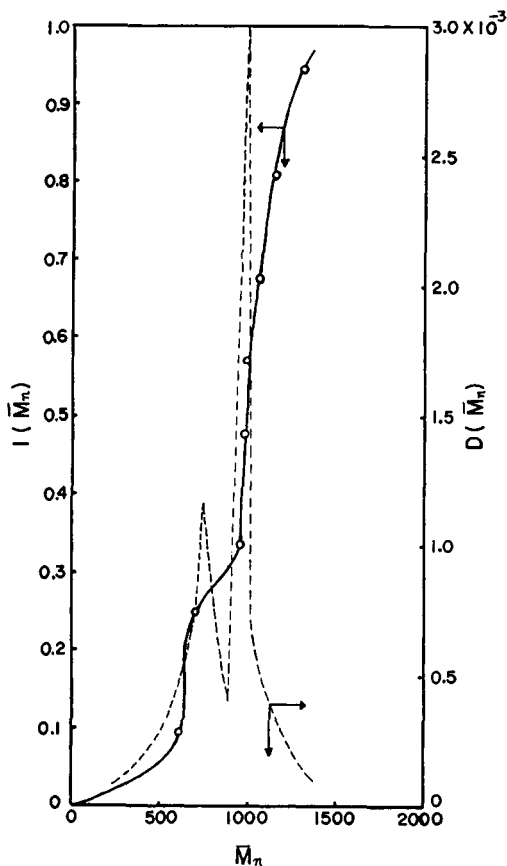| Time above 170°C min	Reacted phthalic half-ester, %	Reacted fatty acids,[a] %	Reacted phthalic anhydride, %
0	0	0	50.0
5	58.5	24.0	79.5
10	71.0	50.0	84.8
15	76.0	62.5	87.8
25	83.0	77.0	91.5
40	—	87.5	—
70	—	95.5	—

[a] Mixture of stearic and palmitic acid.

Fig. 2.   Integral and differential distribution curves of sample I obtained by precipitation fractionation.

In the case of fatty acid-modified alkyd resins, questions arise regarding the relative reaction velocities of α-hydroxyl with phthalic anhydride, the carboxyls of fatty acid, and phthalic half-esters (cf. eqs. (1), (2), and (3)). To throw some light on this problem, Goldsmith[9] carried out a series of experiments and concluded that the addition of phthalic anhydride to form half-esters is the most rapid and that the reaction of α-hydroxyl with phthalic half-esters is more rapid than its reaction with a mixture of stearic and palmitic acids (Table IV).[9,10]   On the other hand, Yoshida[11] measured the rate constants of esterification reactions of glycerin/lauric acid and glycerin/phthalic half-ester at 170° and 230°C, showing that the former is much larger than the latter (Table V).

Those opposite tendencies obtained from the Goldsmith and Yoshida experiments may be attributed primarily to their different experimental methods, because there are no remarkable differences between C_{11} and C_{15} or C_{17} alkyl groups in electron-donating ability and steric hindrance.   If
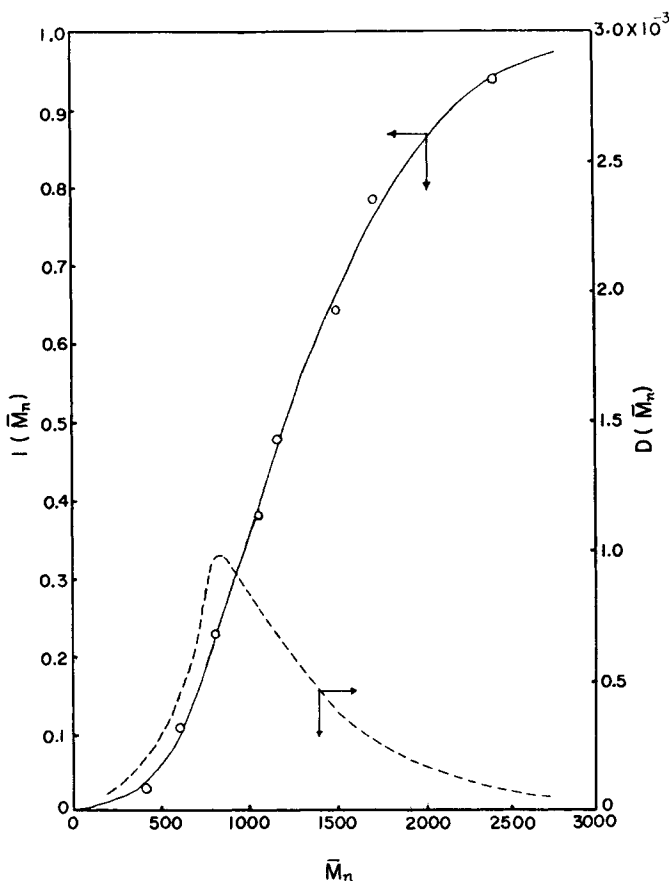
Fig. 3. Integral and differential distribution curves of sample II obtained by precipitation fractionation.

Goldsmith's conclusion is correct, in the alkyd resin preparation, where there is a free-for-all competition among the carboxyl groups (all added at the beginning), the fatty acid carboxyl groups will lag behind in joining α-hydroxyl groups of glycerin and will have to settle for connections with β-hydroxyls. Especially since the molar ratio of phthalic anhydride and lauric acid is 1.00/0.43 in this experiment, the esterification reaction be-

TABLE V

Rate Constants of Esterification Reactions of Glycerin/Lauric Acid and Glycerin/Phthalic Half-Ester at 170°C and 230°C as Measured by Yoshida[11]

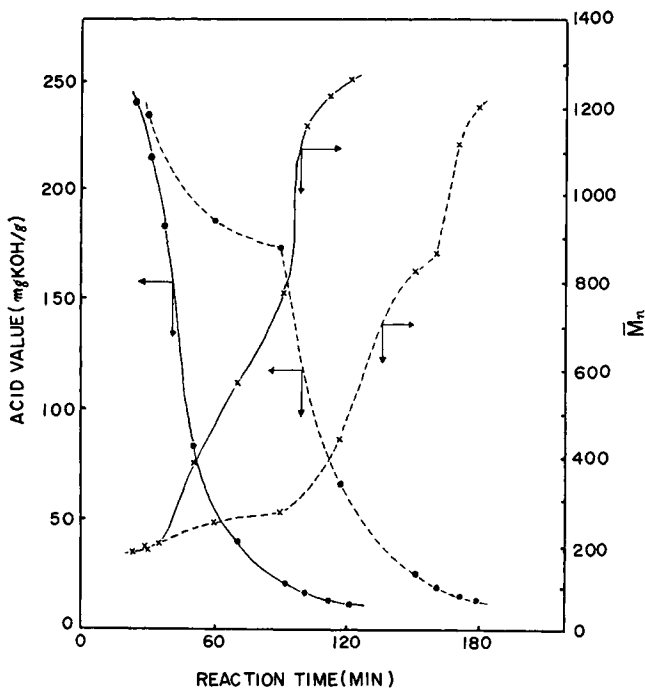|	Rate constant k, min^{-1} (mol/kg)$^{-2}$ or kg^2/mole^2-min	
Reaction temp.	Lauric acid	Phthalic half-ester
170°C	0.546×10^{-3}	0.169×10^{-3}
230°C	9.45×10^{-3}	6.098×10^{-3}

Fig. 4.   Changes of $\bar{M}_n$ and AV (acid value) with reaction time: broken lines, sample I; solid lines, sample II;   (●), AV;   (×), $\bar{M}_n$.

tween carboxyl groups of lauric acid and α-hydroxyls will be quite rare. Suppose Yoshida's conclusion is correct, the fatty acid carboxyl groups will react with α-hydroxyl groups preferentially when the reaction temperature is maintained at 170°C and carboxyl groups of phthalic half ester will be placed at a competitive disadvantage and be forced to settle for a reaction with leftover hydroxyl groups.

As mentioned above, it has become clear from the fractionation that the molecular weight distribution of sample I is narrower and shows a shift to the lower molecular weight region as compared with sample II.   If we adopt Yoshida's conclusion, the most plausible explanation for this would be as follows: Since in cooking schedule I α-hydroxyl groups react with fatty acids preferentially at 170°C, the latter act as stoppers for the growth of the main chain of alkyd resin.   On the other hand, in cooking schedule II, the heterogeneity of the alkyd resin would be accelerated by completely random esterification between glycerin/lauric acid and phthalic half-esters.   Taking the results of molecular weight distribution determination into account, Yoshida's conclusion seems to be more appropriate than Goldsmith's.   However, we must leave this for a future study since it is not valid to draw too many conclusions on such a complex system without clear experimental evidence.

It is interesting to note that the molecular weight distribution curve of sample I has two peaks, as shown in Figure 2. The appearance of the peak in the lower molecular weight region might be attributed to the preferential reaction between glycerin and lauric acid at 170°C. That is, this group might be formed by such alkyd species in which the ends of the main chain are sealed with fatty acids. However, since the same type of curve as shown in Figure 2 is often observed when separation is poor, it is desirable to confirm the existence of two peaks in the molecular weight distribution curve of sample I by means of another methods, e.g., the Diffusion Method[12] or Gel Permeation Chromatography.[13]

It has become clear from Figure 4 that $\bar{M}_n$ does not exceed 250, in spite of the continued decrease in acid value (AV), while the reaction temperature is kept at 170°C. This would mean that the growth of the main chain of alkyd polymer does not take place at this temperature. The number-average molecular weight of the prepolymer, $\bar{M}_{ncal} = 300$, calculated from the molar ratio of glycerin, Iduric acid, and phthalic anhydride, is in a reasonable agreement with $\bar{M}_{nobs} = 250$. During the process of raising the reaction temperature from 170° to 230°C, $\bar{M}_n$ increases rapidly as AV decreases, as shown in Figure 4, indicating that the growth of the main chain of alkyd, i.e., the reaction between glycerin and free carboxyl groups of the phthalic half-esters, is remarkable.

Chemical Analysis of Alkyd Fractions

The most familiar model structure of alkyd resin is illustrated by Figure 5. It can be seen that the number of free hydroxyl groups per alkyd molecule (OH/mole) will depend on the molecular weight of the alkyd resin. Since
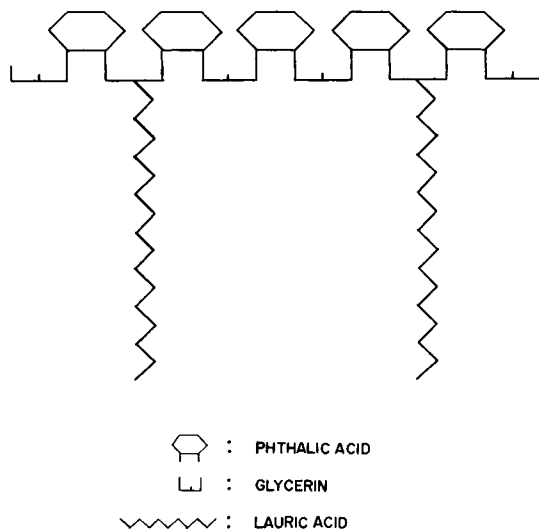

⬡ : PHTHALIC ACID

⊔ : GLYCERIN

〰 : LAURIC ACID

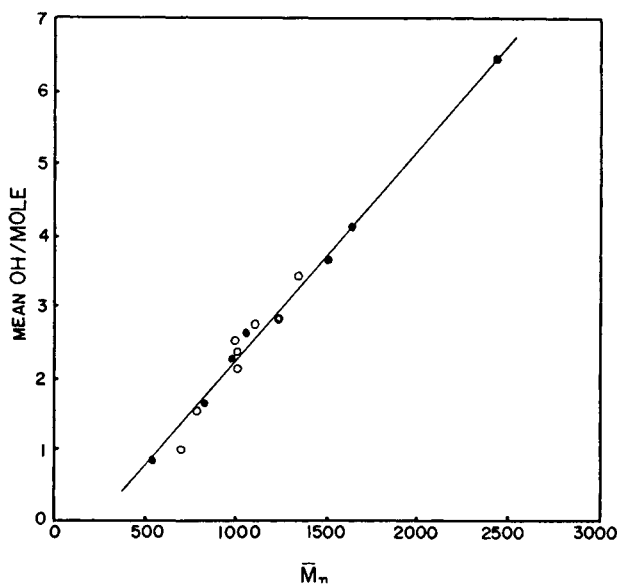Fig. 5. A model structure of alkyd resin.

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Fig. 6. Correlation of the number of free hydroxyl group per alkyd molecule with $\bar{M}_n$: (O), sample I; (●), sample II.

hydroxyl value (HV) is defined as the mg of KOH necessary to neutralize 1 g of a resin, the mean OH/mole value of a fraction is given as $(\bar{M}_n \times HV \times 10^{-3})/56.11$. Expectedly, plots of the mean OH/mole values versus $\bar{M}_n$ gave a straight line for both sample I and sample II, as shown in Figure 6. This indicates that glycerin is an important component for the
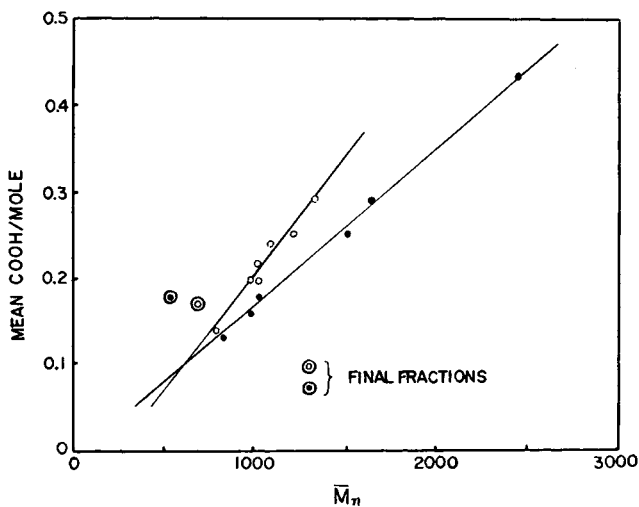

Fig. 7. Correlation of the number of free carboxyl groups per alkyd molecule with $\bar{M}_n$: (O), sample I; (●), sample II.
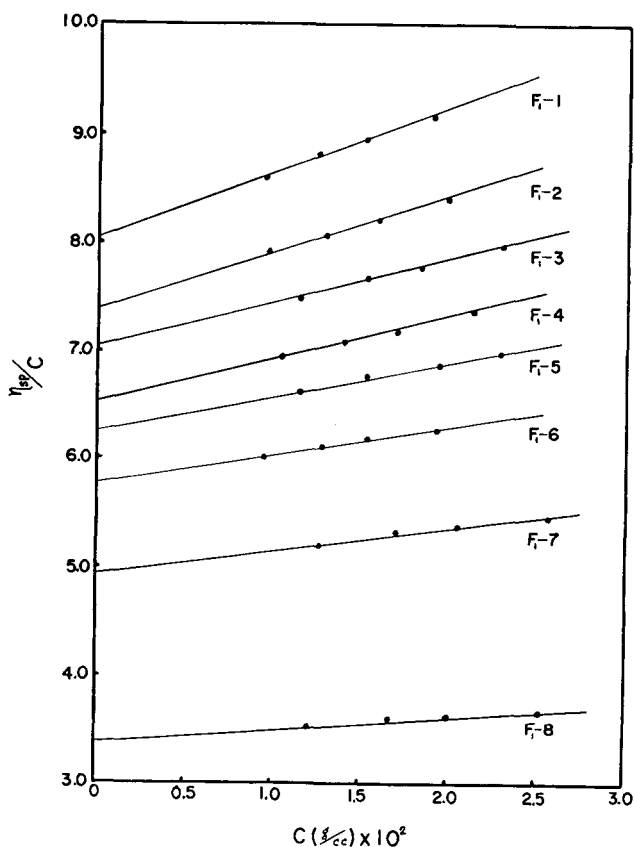
Fig. 8. Plots of η_{sp}/c vs. c for acetone solutions of the fractions of sample I: measurement temperature $30 \pm 0.01°C$.

main chain of alkyd resin and that the model structure of alkyd resin as shown in Figure 5 is an appropriate one.

Free carboxyl groups, on the other hand, will exist only at the ends of alkyd polymers and the number of free carboxyl groups per alkyd molecule (COOH/mole), therefore, is not expected to depend on its molecular weight. Plots of the mean COOH/mole values versus $\bar{M}_n$, however, gave straight lines, as shown in Figure 7. Here all the mean COOH/mole values obtained are given as decimals. This means that free carboxyl groups do not exist along the main chain of alkyd polymer. The author is of the opinion that Figure 7 shows that the alkyd resins were fractionated by polarity as well as by molecular weight. Since the first fraction obtained by the addition of n-heptane contains various alkyd molecules of high polarity, the mean COOH/mole value became the largest. It is reasonable that the last fractions of sample I and sample II, which contain low molecular
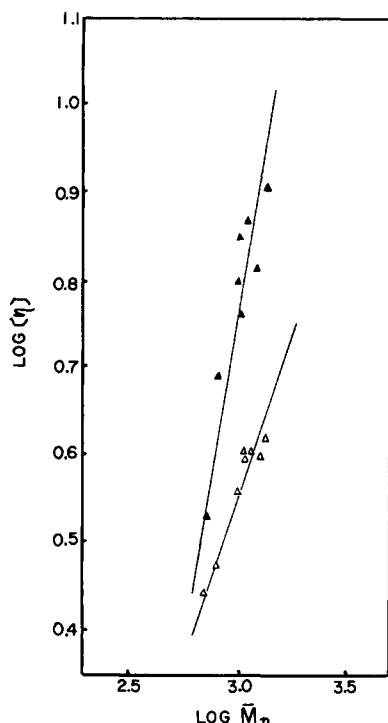
Fig. 9.   Log [η] vs. log $\bar{M}_n$ plots for sample I: (▲), acetone₉ (△), toluene.

weight alkyd species with free carboxyl groups, have a little higher mean COOH/mole values.

It is interesting to find that both sample I and sample II are on the same line of the plot of mean OH/mole versus $\bar{M}_n$. as shown in Figure 6, while the plot of mean COOH/mole versus $\bar{M}_n$ gives two straight lines, one for sample I and another for sample II.   This is attributable to the fact that the distribution of free carboxyl groups is affected by the cooking schedules.

Intrinsic Viscosity Data of Alkyd Resins

The equation $[\eta] = K\bar{M}^\alpha$, where $[\eta]$ is intrinsic viscosity, $\bar{M}$ molecular weight, K and α are characteristic constants of a given polymer, solvent, and temperature, has been found to apply for a number of high molecular weight polymers.[14,15]   For alkyd resin, Bobalek et al.[16] used this expression to correlate $[\eta]$ with the number-average degree of polymerization, $\bar{X}_n$, determined by end group analysis.   In discussing the validity of this expression, they observed that $[\eta]$ followed the equation $[\eta] = K\bar{X}_n^\alpha$ fairly well up to $\bar{X}_n$ of 30, from where a sharp upward deviation started.   They suggested that this sharp deviation was attributable to the presence of a "nucleation phase," which was defined as the formation of a more complicated molecular species of greatly increased hydrodynamic volume.   It is
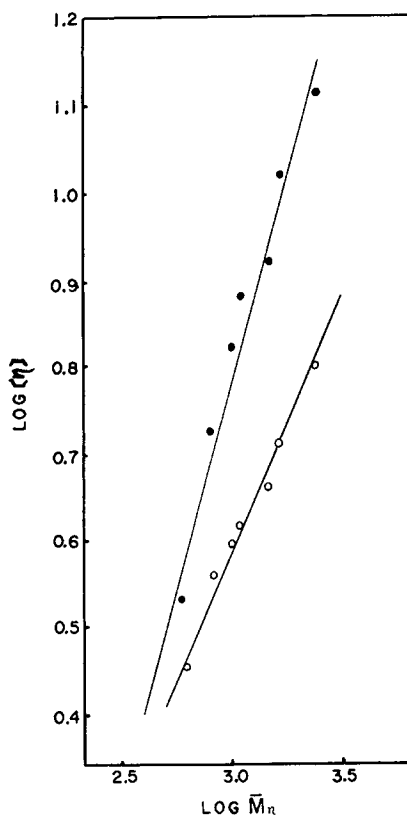
Fig. 10. Log [η] vs. log $\bar{M}_n$ plots for sample II: ($\bullet$), acetone ($\circ$), toluene.

believed, however, that this deviation is attributable to the fact that they measured [η] at a considerably high concentration and used the number-average degree of polymerization, $\bar{x}_n$, calculated by acid value instead of observed $\bar{M}_n$. In the present study, the measurements of [η] were carried out at a sufficiently low concentration for each fraction of sample I and sample II using acetone and toluene as solvents at 30°C. The plots of η_{sp}/c versus c for acetone solutions of the fractions of sample I are illustrated in Figure 8. The data of [η] are given in Tables II and III. Linear functions were observed here between log [η] and log $\bar{M}_n$ determined by the Rast Method as shown in Figures 9 and 10. The constants K and α were calculated by the method of least squares (cf. Table VI). It is to be noted that the two constants are different for the two cooking schedules. As shown in Table VI, the K value of sample II is much larger than that of sample I for both acetone and toluene solutions. This indicates that sample II is more heterogeneous than sample I as verified by fractionation.

The Flory-Fox theory predicts that α approaches 0.8 in a good solvent and 0.5 in a poor solvent.[17,18] It is known that the value of α usually lies
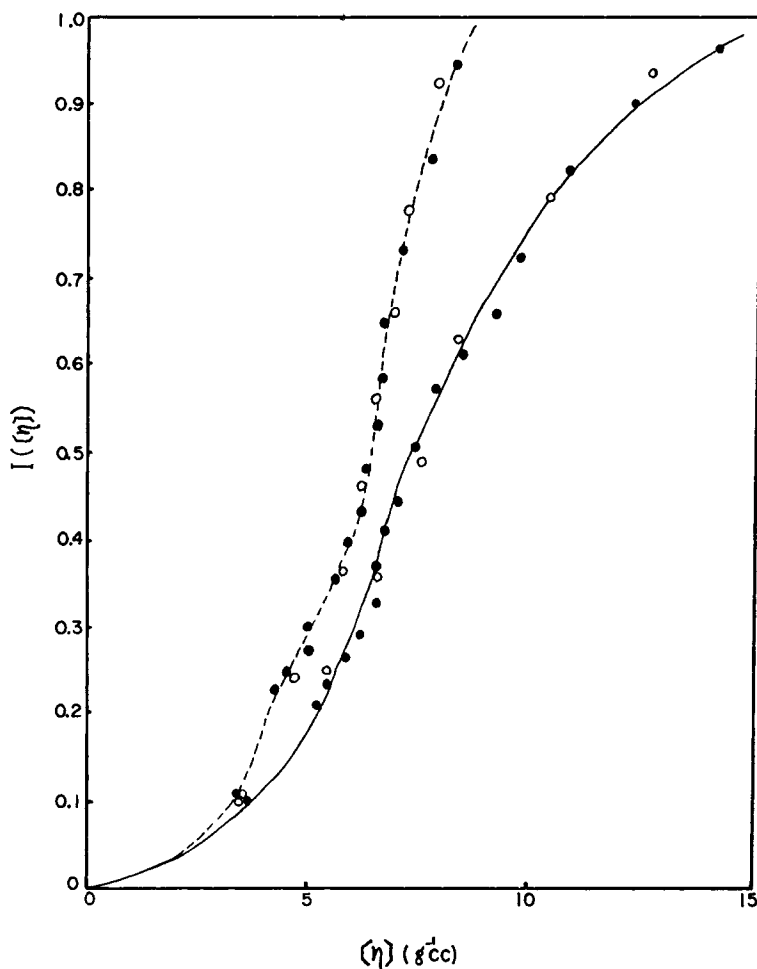
Fig. 11.   Reproducibility of precipitation fractionation of alkyds: broken line, sample I
solid line, sample II; (O), rough fractionation; (●), fine fractionation.

between 0.6 and 0.8 for normal dilute polymer solutions.   However, re-
markably large values of α were obtained for acetone solutions of sample I
and sample II as shown in Table VI, which can be attributed to the low
molecular weight and high degree of branching of alkyd resin.   Studies on
the constant α for various polymer/solvent systems have been carried out
extensively, and there is a paper reporting that a value of α over 1.0 is
possible.[19]   It is seen from Table VI that acetone is a good solvent for
alkyd resin, while toluene is a rather poor solvent.

It is known that k' of Huggin's which is a constant for a given polymer,
solvent, and temperature, is independent of the molecular weight of poly-
mers and that it decreases as the solvent improves.[20-23]   As shown in
Tables II and III, the values of k' obtained for toluene solutions of each

TABLE VI
Constants K and α Calculated by the Method of Least Squares

Solvent	K	α
Sample I		
acetone	9.55×10^{-4}	1.26
toluene	2.95×10^{-2}	0.70
Sample II		
acetone	1.02×10^{-2}	0.93
toluene	6.61×10^{-2}	0.59

fraction are much larger than those for acetone solutions. This indicates that toluene is a poor solvent for alkyd compared with acetone. On examination of Tables II and III, it is apparent that k' of each fraction does not show any regularity with respect to the order of precipitation. Although the physical meanings of k' has not been clarified yet, it is of interest to note that k' of toluene solutions of alkyds is unusually large. This might suggest that k' depends on the configuration of the resin as well as on the interaction between resin and solvent.

Reproducibility of Fractionation of Alkyds

Since a polymer should be fractionated, strictly speaking, at least into 15 to 16 fractions in order to obtain a molecular weight distribution curve, additional fine fractionations were carried out with sample I and sample II to verify the validity of the molecular weight distribution curves obtained by the rough fractionations as described before. Instead of $\bar{M}_n$ deter-

TABLE VII
Fine Fractionation Result of Sample I

Fraction	Wt ratio of n-heptane/ toluene	Wt, g	Cumulative wt fraction	$[\eta]_{30°C}$, cc/g acetone	k', 30°C
F_1-1	0.398	3.870	0.100	8.33	0.69
F_1-2	0.467	4.564	0.218	7.80	0.60
F_1-3	0.530	3.729	0.315	7.13	0.67
F_1-4	0.562	2.526	0.380	6.68	0.93
F_1-5	0.632	2.231	0.438	6.62	0.80
F_1-6	0.698	2.153	0.494	6.53	0.65
F_1-7	0.773	1.705	0.538	6.30	0.75
F_1-8	0.832	1.916	0.588	6.20	0.80
F_1-9	0.996	0.906	0.611	5.84	0.92
F_1-10	1.082	1.281	0.644	5.58	1.11
F_1-11	1.272	1.281	0.654	5.28	1.21
F_1-12	1.447	1.360	0.679	5.28	0.82
F_1-13	1.692	1.086	0.707	5.01	0.84
F_1-14	2.156	0.862	0.730	4.56	1.13
F_1-15	2.390	0.608	0.779	4.22	1.52
F_1-16	—	8.525	1.000	3.44	1.31

TABLE VIII
Fine Fractionation Results of Sample II

Fraction	Wt ratio of n-heptane/ toluene	Wt, g	Cumulative wt fraction	$[\eta]_{30°C}$, cc/g acetone	k', 30°C
F_2-1	0.407	2.881	0.072	14.26	0.75
F_2-2	0.440	1.990	0.122	12.40	0.61
F_2-3	0.504	4.195	0.227	10.88	0.62
F_2-4	0.570	3.651	0.318	9.79	0.59
F_2-5	0.613	2.022	0.369	9.25	0.68
F_2-6	0.642	1.110	0.396	8.40	0.84
F_2-7	0.701	2.306	0.454	7.88	0.72
F_2-8	0.810	3.305	0.534	7.33	0.84
F_2-9	0.894	1.688	0.576	6.98	0.85
F_2-10	0.969	1.114	0.604	6.66	0.95
F_2-11	1.097	1.853	0.651	6.55	0.69
F_2-12	1.265	1.605	0.691	6.55	0.43
F_2-13	1.428	1.212	0.721	6.10	0.76
F_2-14	1.653	1.021	0.746	5.73	0.85
F_2-15	1.968	1.035	0.772	5.37	0.98
F_2-16	2.517	1.106	0.800	5.07	0.73
F_2-17	—	7.998	1.000	3.54	0.89

mination, $[\eta]$ of acetone solution was determined at 30°C for each fraction. Comparison was made for the integral distribution curves of $[\eta]$ obtained by the rough and the fine fractionations. The coinciding of the results obtained from these fractionations provides some assurance that the molecular weight distribution curve of an alkyd can be obtained by fractionating the alkyd into ten fractions (Figure 11).

CONCLUSIONS

In alkyd resin preparation, the quality of the resin is usually controlled by acid value, molten viscosity, and color number measurements. Since none of these gives any information of the molecular weight distribution, exact establishment of a cooking schedule is indispensable for the manufacture of alkyd resins of uniform quality.

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