

Cooking Schedule of Alkyd Resin Preparation. I. Effect of Cooking Schedule on Viscosity-Molecular Weight Relationship

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Synopsis

The two constants in the equation $\log \eta = A + C' \bar{M}_n^{1/2}$ (η is the viscosity of molten alkyd and \bar{M}_n the number average molecular weight) were determined at 110°C for two kinds of alkyd resin prepared with the same formulation but with different cooking schedules. It was found that the magnitude of the slope C' was larger for the alkyd which was prepared by raising the reaction temperature directly up to 230°C, in comparison with that of the alkyd which was prepared by maintaining the temperature at 170°C for an hour and then raising it up to 230°C.

Measurements of η and \bar{M}_n were carried out until the gelation occurred. Both upward and downward breaks were observed in $\log \eta$ vs. $\bar{M}_n^{1/2}$ plot. Based on these viscometric data, the gel point mechanism was discussed. Disagreements between the molecular weight observed and that calculated from the Flory's theoretical equation became more remarkable as the esterification proceeded. This suggested that a large extent of intra-esterification reaction is taking place in alkyd synthesis.

INTRODUCTION

In manufacturing alkyd resins on a plant scale, acid value measurement is usually employed to check the time to arrest the reaction. This method, however, does not appear to be sufficient because an increase in the degree of condensation cannot be tracked continuously during the reaction, thus making it very difficult to accurately control the varnish viscosity. Since the effect of varnish viscosity on paint properties is remarkable, it is desirable to use another better end point determination technique in place of the acid value measurement.

In 1940 Flory found that the simple empirical relationship $\log \eta = A + C' \bar{M}_w^{1/2}$ (η is the viscosity, \bar{M}_w the weight average molecular weight, and A and C' are constants for a specified temperature) can be applied with remarkable accuracy to linear polyesters, polyamides and to certain non-linear polyesters as well.¹ Imoto and Horiuchi confirmed a similar relationship between η and the number average molecular weight \bar{M}_n for fatty acid modified alkyd resins using a specially designed capillary viscometer.² Direct and continuous measurements of the alkyd resin viscosity in condensation reaction would be a good method to control the degree of condensation if the two constants can be determined.

In preparing alkyd resin various cooking schedules would be employed according to the batch size, the heating capacity and the types of raw materials. It has been the long practice of our factory to cook short oil alkyd resins by maintaining the reaction temperature at 170°C for the first one hour in order to lower the varnish viscosity. The viscosity was known to be greatly increased if the temperature is brought directly up to 230°C.³ The chemical significance of maintaining the reaction temperature at 170°C, however, has never been elucidated primarily because of the underestimation of the importance of cooking schedules.

Prior to the application of this method on a plant scale, therefore, the possibility of the dependence of the constants upon cooking schedules has to be confirmed.

EXPERIMENTAL

Materials

At a mole ratio of glycerine, coconut oil fatty acid and phthalic anhydride 1.03/0.43/1.00, two kinds of alkyd resin were prepared; (1) by maintaining the reaction temperature at 170°C for an hour and then raising it up to 230°C, and (2) by raising the temperature directly up to 230°C as shown in Figure 1. Fusion cooking was employed to prepare these resins; glycerine 8.82 Kg, phthalic anhydride 13.52 Kg and coconut oil fatty acid 7.66 Kg were charged into a 36 l stainless-steel kettle. The pilot plant scale kettle was used to make the influence of samplings on the condensation reaction negligible. The agitation was maintained at a constant rate and N₂ gas inlet was adjusted at 0.1 l/min/liter of resin throughout the reaction.

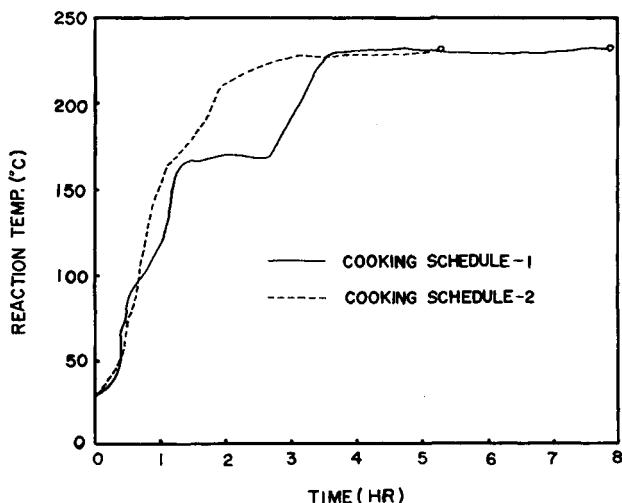


Fig. 1. Cooking schedules of alkyds prepared by a stainless-steel kettle of 36 l capacity. The open circles observed in the figure represent endpoints of the alkyd synthesis.

Samplings weighing approximately 300 g at a time were occasionally carried on throughout the reaction at 230°C by using a vacuum pump in order to determine viscosities, acid values and molecular weights.

Viscosity Measurements

Immediately after the sampling each molten alkyd resin was transferred into a 300 ml, 4-neck round-bottom flask equipped with a stirrer, thermometer, N₂ gas inlet tube and a Dean-Stark water trap which was connected to a water-cooled condenser. The flask was maintained at a given temperature in the castor oil thermostat, of which temperature was controlled to $\pm 0.05^\circ\text{C}$ by means of a mercury-silicone oil thermoregulator.

The molten alkyd resin in the flask was kept stirred with constant blowing of N₂ gas until the resin reached the desired temperature. Viscosity was then measured at two different levels of the spindle speed by means of a Brookfield Rotary Viscometer which was installed directly into the flask by temporarily removing the stirrer. Although it took about five minutes from the removal of the stirrer to finish the measurements, the desired temperature was successfully maintained by hand agitation.

Brookfield Viscometer was used because of its possible application to a plant scale kettle. Immediately after the viscosity measurement, a small amount of the molten alkyd, weighing 2 to 3 g, was taken out of the flask to determine the acid value and the molecular weight.

Molecular Weight Measurements

Molecular weights of the samples were determined by the Rast method. Dried resin of 20 to 60 mg was melted together with camphor, weighing about 400 mg, in a sealed evacuated glass tube. The solid solution crushed to fine pieces with a microspatula was charged into a capillary, which was then sealed under vacuum. The freezing points of camphor and the solid solution were then determined with a thermometer (150° to 250°C) graduated to 0.1°C.

The number average molecular weight \bar{M}_n was calculated from the following equation by extrapolating W/W_o to zero.

$$\bar{M}_n = \frac{W}{W_o} \times \frac{40,000}{\Delta T} \quad (1)$$

where

W = weight of sample resin

W_o = weight of camphor

ΔT = depression of freezing point ($^\circ\text{C}$)

Three capillaries were prepared for each sample and the freezing point was measured twice on each capillary. ΔT in eq. (1) was calculated by averaging the six data thus obtained. The experimental error was within $\pm 2\%$. It is to be added that the freezing point method gave a better re-

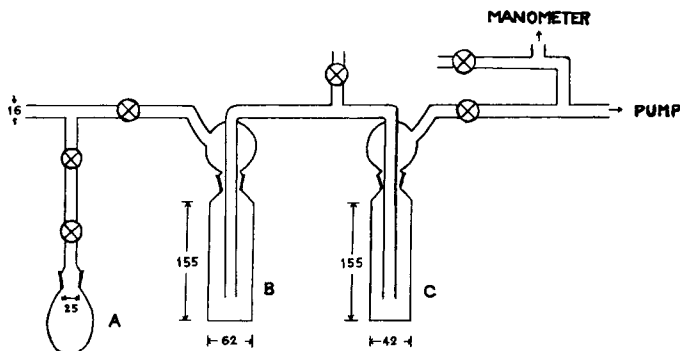


Fig. 2. A device of the freeze-drying technique with benzene. A: round bottom flask of 50 ml capacity. Pyrex glass is used; B and C: traps. (unit: mm).

producibility than the melting point method which showed a considerable dependency on the rate of heating.

Since the presence of trace amounts of water and solvents considerably affects the number average molecular weight, the sample resins were dried to constant weight at 75°C/1–2 mm Hg in a vacuum oven for 24 hr. This was accomplished with ease by spreading a hot resin, weighing only 0.5 to 1.0 g, as thinly as possible on a small flat-bottom beaker.

In determining the drying condition mentioned above, comparisons of the measured molecular weights were made for the alkyd samples dried in the vacuum oven and those dried by the freeze-drying technique with benzene which has been often employed to dry unstable high polymers,^{4,5} since there was no guarantee that \bar{M}_n is not affected by drying at high temperature. Consequently, it was confirmed that the effects of drying time and temperature on the measured molecular weights of the alkyds with various molecular weights became negligible when the samples were dried below 80°C within 30 hr at 1 to 2 mm Hg.

The drying process of the freeze-drying technique with benzene was carried out as follows using a device similar to that used by Yamazaki (Fig. 2).⁶ A 15 wt % benzene solution of an alkyd was transferred into 50 ml flask A, quenched by using dry ice/acetone mixture, and then evacuated to less than 1 mm Hg. Benzene was sublimated by keeping the flask in ice water for 10 hr, and then at room temperature for another 10 hr. The resins thus dried to constant weight were used as the standard samples for molecular weight determination.

RESULTS

Experimental results of viscosity, acid value and molecular weight measurements are shown in Tables I and II. The viscosity of the samples should have been determined at 230°C, if the viscosity of lower molecular weight samples, e.g. S-1-1, S-2-1 or S-2-2, were measurable at this temperature with a Brookfield Viscometer. Since the major purpose of this ex-

TABLE I
Viscosities, Molecular Weights and Acid Values
of S-1 Series Prepared by Cooking Schedule-1

Samples	Sampling time ^a (min)	Molten viscosity 110°C (centipoise)	Molecular weight (number average)	Acid value (mgKOH/g)
S-1-1	220	617	510	55.6
S-1-2	260	1352	740	37.7
S-1-3	290	3277	970	24.9
S-1-4	320	3885	1290	23.9
S-1-5	410	7075	1370	15.3

^a This represents a time passed through after the initiation of alkyd synthesis.

periment was to obtain information on the relationship between the constants in the Flory's square root equation and cooking schedule, the viscosity was measured at a more convenient temperature, 110°C. Changes in viscosity, acid value and molecular weight during the reaction of S-2-4, however, were followed at 230°C until the gelation occurred.

The reliability of the employed viscometric method was confirmed by determining the viscosity temperature relationship $\log \eta = \alpha + \beta/T$ for HX 791, a commercial coconut-oil fatty acid modified short-oil alkyd varnish. As shown in Figure 3, a straight line was obtained when $\log \eta$ was plotted against $1/T$, making it reasonable to assume the validity of the viscometric method.

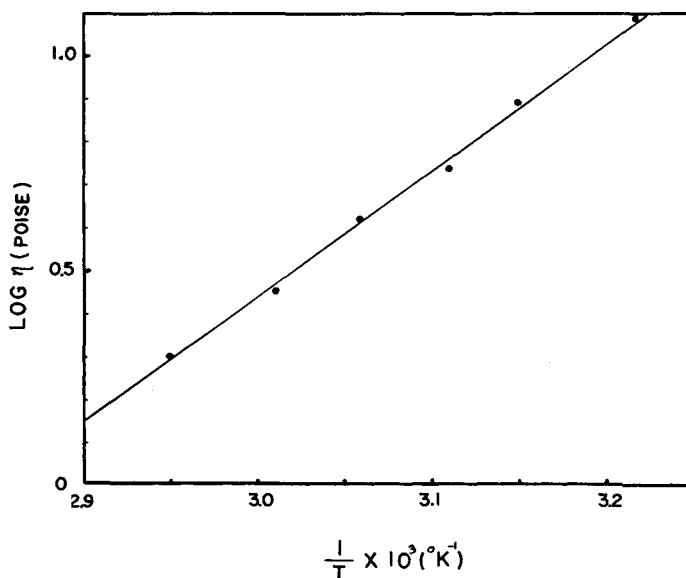


Fig. 3. $\log \eta$ (poise) vs. $1/T$ ($^{\circ}K^{-1}$) for HX 791, a commercial coconut-oil fatty acid modified short-oil alkyd varnish, employing a Brookfield Rotary Viscometer.

TABLE II
Viscosities, Molecular Weights and Acid Values
of S-2 Series Prepared by Cooking Schedule-2

Samples	Sampling time (min)	Molten viscosity 110°C (centipoise)	Molecular weight (number average)	Acid value (mgKOH/g)
S-2-1	105	99	240	162.1
S-2-2	150	553	500	58.2
S-2-3	200	1775	900	29.7
S-2-4	250	3360	1030	17.3
S-2-5	275	5595	1190	13.7

DISCUSSION

Viscosity-Molecular Weight Relationship

Plots of $\log \eta$ vs. $\bar{M}_n^{1/2}$ are shown in Figure 4 for the two kinds of alkyd resin prepared by different cooking schedules. The constants A and C' were calculated by the method of least squares.

$$\begin{aligned} \text{S-1 series: } \log \eta (110^\circ\text{C}) &= -(0.62 \pm 0.18) + (6.52 \pm 0.59) \times 10^{-2} \bar{M}_n^{1/2} \\ \text{S-2 series: } \log \eta (110^\circ\text{C}) &= -(1.32 \pm 0.09) + (9.13 \pm 0.28) \times 10^{-2} \bar{M}_n^{1/2} \quad (3) \end{aligned}$$

where S-1 and S-2 series refer to the alkyd samples prepared by cooking schedules 1 and 2, respectively.

Taking account of the confidence limits shown in the above equations, it is apparent that slope C' in S-2 series which were prepared by raising the reaction temperature directly up to 230°C is steeper than that of S-1 series, although the experimental data seem to deviate from straight lines. The difference in these constants with cooking schedules would suggest the difference in molecular weight distributions, of which experimental evidence will be reported in the succeeding paper. Since the constants in viscosity-molecular weight relationship depend on cooking schedules, it becomes necessary that cooking schedules be followed accurately to control the molecular weight of alkyd resin by measuring viscosity.

In order to obtain experimental data which can serve to make this end point determination method applicable to a plant scale manufacture, viscosity-molecular weight relationship at 230°C was determined with S-2-4 ($\bar{M}_n = 1030$, $AV = 17.3$) because the degree of condensation of this sample, neither too low nor too high, was considered to be suited for chasing the esterification process up to the gelation. The viscometric measurements and samplings were carried out by the same methods as described before. The results are summarized in Table III. The \bar{M}_n and AV given in the first line of Table III are slightly different from those in the fourth

line of Table II. These disagreements are probably caused primarily by experimental error.

Approximately 10 min after viscosity measurements, of which data are

TABLE III
Changes of Viscosity, Molecular Weight and Acid Value of S-2-4 with Time at 230°C

Reaction time ^a (min)	Molten viscosity 230°C (centipoise)	Molecular weight (number average)	Acid value (mgKOH/g)
0	42.0	1000	16.8
25	60.2	1010	14.6
35	93.9	1270	11.3
45	131.7	1300	10.1
55	171.2	1340	9.73
65	252.8	1410	8.24
70	324.3	1590	8.07
75	584.3	1960	7.65

^a Reaction time = 0 represents the time when the temperature of the alkyd sample S-2-4 reached 230°C.

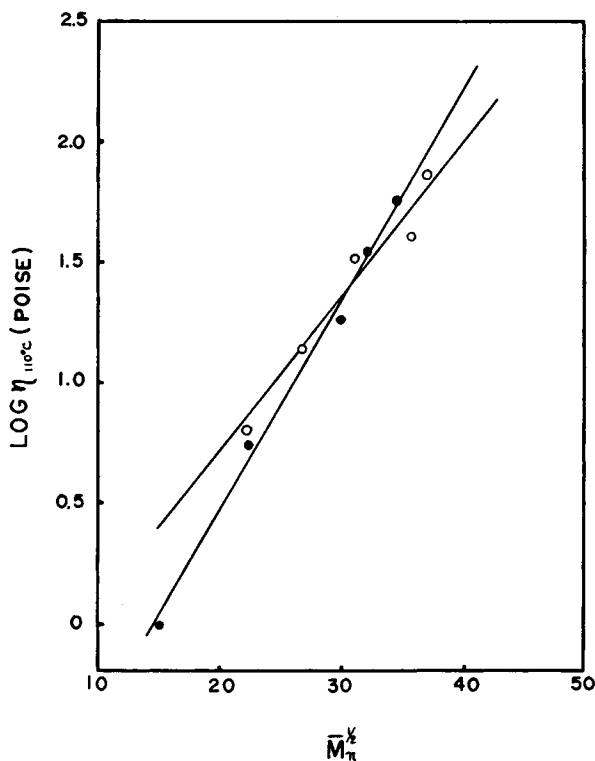


Fig. 4. $\text{Log } \eta_{110^\circ\text{C}}$ (poise) vs. $\bar{M}_n^{1/2}$ for the two kinds of alkyd: (O) S-1 series; (●) S-2 series. S-1 and S-2 series refer to the alkyd samples prepared by cooking schedules 1 and 2, respectively.

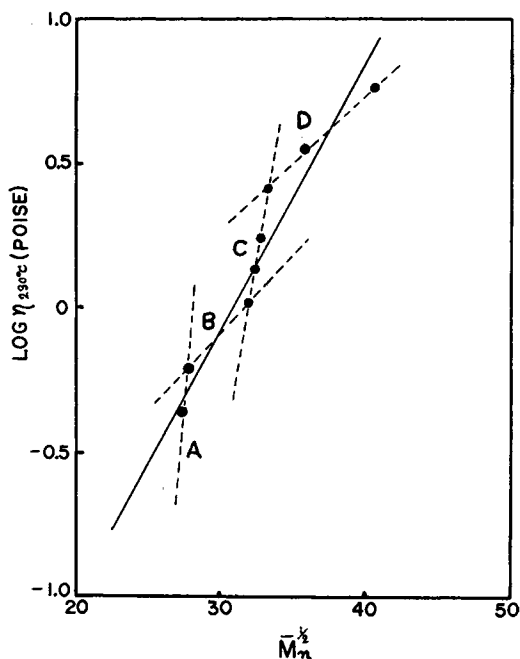


Fig. 5. $\text{Log } \eta_{330c}$ (poise) vs. $\bar{M}_n^{1/2}$ for alkyd sample S-2-4. Both viscometric and molecular weight measurements were carried out for S-2-4 until the gelation occurred.

given in the last line of Table III, the spindle of the viscometer began to be intertwined up with molten alkyd resin, that is, the gelation occurred.

The constants were calculated by the method of least squares, and the following equation was obtained.

$$\log \eta (230^\circ\text{C}) = -(3.44 \pm 0.28) + (9.86 \pm 0.77) \times 10^{-2} \bar{M}_n^{1/2} \quad (4)$$

The slope C' coincides with that of the eq. (3) within the experimental error.

By this viscometric measurement it becomes clear that a viscometer is useful to control short oil alkyd synthesis at 230°C ; a viscometer measurable from 1 to 3 poises should be used.

Acid Values and Number Average Molecular Weights

Flory derived the following equation for calculating the number average degree of polymerization of cross-linking system based on the assumptions that all the functional groups are equally reactive and that no intraesterification takes place.⁷

$$\bar{X}_n = \frac{f\left(1 - \rho + \frac{1}{r}\right) + 2\rho}{f\left(1 - \rho + \frac{1}{r} - 2P_A\right) + 2\rho} \quad (5)$$

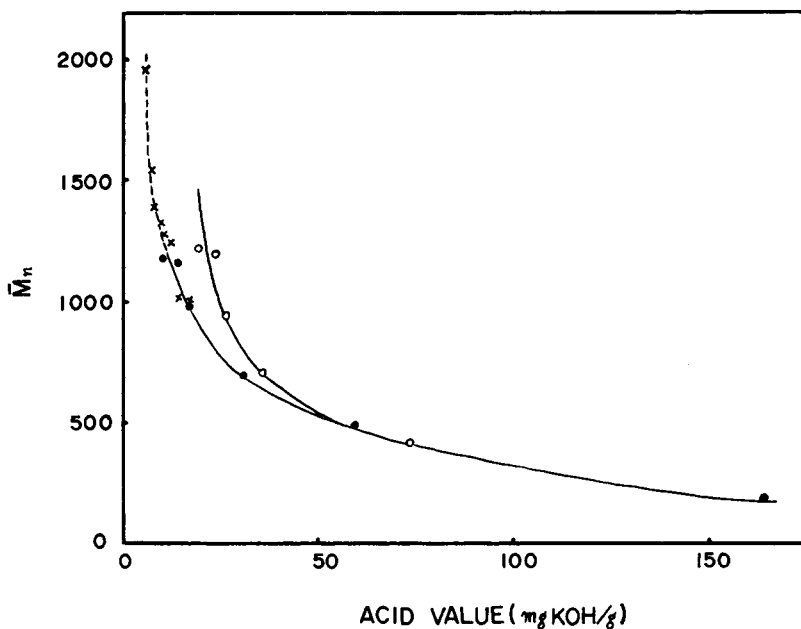


Fig. 6. The number average molecular weight \bar{M}_n vs. acid value for the three kinds of alkyd: (O) S-1 series; (●) S-2 series; (X) S-2-4.

where

\bar{X}_n = number average degree of polymerization,

f = functionality of branching unit A,

ρ = ratio of A belonging to branching unit to total number of A's in mixture,

r = ratio of A to B groups,

P_B = $r \cdot P_A$ supposing A reacts with B only,

P_A, P_B = extent of reaction of A and B, respectively.

Using the same approach as employed by Flory, similar equations have been derived to calculate number average molecular weight of alkyd resins.^{8,9}

It would be of great convenience if the molecular weight of a resin could be obtained by measuring only its acid value. However, plotting acid values vs. the number average molecular weights of the two kinds of alkyd resin, it was found that the relationship between AV and \bar{M}_n depended on cooking schedules (Fig. 6). As the esterification proceeds, the AV vs. \bar{M}_n curve splits into two lines. Since the two kinds of alkyd resin were prepared by the same formulation, it follows that the equality in the extent of esterification does not necessarily mean the equality in the number average molecular weight.

Now let us compare the molecular weights observed with those calculated. Since the mole ratio of glycerine, phthalic acid anhydride and fatty acid is

1.03:1.00:0.45; thus $f = 3$, $\rho = 0.68$ and $r = 1.33$. The theoretical monomer unit becomes 124. Thus, the number average molecular weight can be calculated from the following equation.

$$\bar{M}_{ncal.} = 124\bar{X}_n \quad (6)$$

\bar{X}_n for each alkyd sample is obtained substituting $f = 3$, $\rho = 0.68$, $r = 1.33$ and the extent of reaction of acid groups into eq. (5). The results are shown in Table IV. $\bar{M}_{ncal.}$ coincides with $\bar{M}_{nobs.}$ in the early stage of reaction, whereas the former becomes approximately twice as large as the latter as the esterification proceeds. In addition, Table IV shows that the ratio $\bar{M}_{ncal.}/\bar{M}_{nobs.}$ of S-2 series increases as the reaction proceeds. This undoubtedly suggests that a greater extent of intraesterification is taking place. Judging from the results of Figure 6 and Table IV, intraesterification seems to occur to a greater extent with the cooking schedule 2.

TABLE IV
Comparison of \bar{M}_n Determined by The Rast
Method and \bar{M}_n Calculated by Acid Value

Samples	$\bar{M}_{nobs.}$	$\bar{M}_{ncal.}$	$\bar{M}_{ncal.}/\bar{M}_{nobs.}$
S-1-1	510	780	1.53
S-1-2	740	1160	1.57
S-1-3	970	1640	1.69
S-1-4	1290	1670	1.30
S-1-5	1370	2430	1.78
S-2-1	240	210	0.87
S-2-2	500	790	1.58
S-2-3	900	1400	1.56
S-2-4	1030	2210	2.14
S-2-5	1190	2640	2.22

One more interesting fact is that the \bar{M}_n vs. AV curve of S-2-4 which was cooked at 230°C until the gelation traces precisely the curve of S-2 series as shown in Figure 6. This would suggest that S-1 and S-2 series have different molecular compositions.

Gel Point Mechanism of Alkyd Resin

Numerous authors, including in particular Flory¹⁰ and Stockmayer,¹¹ have made important predictions of the gelation point of polyfunctional polymers. Kahn, for instance, derived an equation showing gel point of such polycondensation polymers as consisting of two kinds of polybasic acids and polyhydric alcohols.¹² Imoto and Horiuchi had expressed the gel point in terms of degree of reaction for the condensation reaction between glycerine and a mixture of mono- and dibasic acid.¹³ They observed that variations of R , the ratio of rate constants of esterification of α -OH and β -OH groups of glycerine, did not considerably affect the extent of reaction at the gel point and suggested that the gelation of alkyd resin

would occur at a given extent of reaction regardless of the process of chain growth.

In the case of systems containing mono functional components like this, however, terminating effect on chains or branches of mono functional components must be taken into consideration. Although Case derived the gel point equation for alkyd resin, this terminating effect of fatty acid was not taken into account.¹⁴ It is Yoshida that this effect was first taken into account to predict the gel point of phthalic acid anhydride-fatty acid-polyhydric alcohol systems.¹⁵

$$r \rho_2 P_{2A} P_{2B} \left[\frac{s \rho_2 (P_{2A} + P_{2B})}{2P} + \sigma_2 \right] = 1 \quad (7)$$

where

- r = mole ratio of total carboxyl and hydroxyl groups, COOH/OH
- ρ_2 = fraction of COOH that belongs to dibasic acid anhydride of all COOH groups
- P_{2A} = extent of reaction of the 1st COOH of dibasic acid anhydride
- P_{2B} = extent of reaction of the 2nd COOH of dibasic acid anhydride
- P = extent of total acid reaction
- σ_2 = fraction of OH that belongs to diol of all OH
- $s = \Sigma(n - 1)\sigma_n$
- σ_n = fraction of OH that belongs to n -functional polyol of all OH

Since the variables r , ρ_1 (fraction of COOH that belongs to fatty acid in all COOH groups), ρ_2 , s and σ_2 are dependent on an alkyd formulation and P_{2A} and P_1 (extent of reaction of fatty acid) are considered to be unity at the gel point, P can be obtained from the eq. (7) and (8).

$$P = \rho_1 P_1 + \frac{\rho_2}{2} (P_{2A} + P_{2B}) \quad (8)$$

Yoshida's gel point equation is probably the most advanced one among many equations which have been derived so far by numerous authors. Nevertheless, the agreement between actual and theoretical values obtained from eq. (7) is still unsatisfactory for control work.

One of the most reliable reasons for this is considered to be due to ring formation or intraesterification in growing polymer chains. Judging from the disagreement between $\bar{M}_{\text{cal.}}$ and $\bar{M}_{\text{obs.}}$ and the experimental fact that the same extent of reaction does not always mean the same number average molecular weight as shown in Figure 6, we may conclude that the assumption that no intraesterification reaction takes place in alkyd synthesis is no longer acceptable. Apart from the ring formation hypothesis, we must perceive that these equations have been derived based on the premise that the gelation of polyfunctional polymers occurs only by infinitely consecutive branchings. The application of this premise to alkyds without any revision is considered to be one of the reasons why the gel point equations are nearly of no practical use.

TABLE V
Chemical and Physical Characteristics of The Fractions Determined by Seavell¹⁶

Fraction	Temp. (°C) of Separation	Wt %	A.V.	OH V.	\bar{M}_n	\bar{M}_w
A	+4	18.0	11	Gelled ^a	Gelled ^a	39,000
B	-12	21.0	11	42	3,700	—
C	-30	21.0	11	29	2,500	38,000
D	-65	17.6	14	25	1,500	—
E	Soluble at -65°C	22.4	25	30	1,200	1,700

^a Gelled prior to determination.

Note: The experimental methods of \bar{M}_n and \bar{M}_w determination are not reported in this paper.

Before discussing what the gelation of alkyds really means, a few papers will be reviewed. Seavell dissolved an alkyd resin in acetone and fractionated it into a number of fractions by the low temperature phase separation method, and the chemical and physical characteristics of each fraction, i.e., acid value, hydroxyl value, \bar{M}_n and \bar{M}_w were determined.¹⁶ The results are shown in Table V. It is interesting to note that the fraction of $\bar{M}_w = 39,000$ gelled while it was left at room temperature for the determination of OH value and \bar{M}_n . Bobalek et al. observed that the apparent molecular weights of alkyd resins obtained by extrapolation of the light scattering data were greatly influenced by the kinds of solvent (Table VI).¹⁷ If the high value of \bar{M}_w (71,000) in cyclohexane was regarded as being caused by the association of alkyd polymers and a complete dissociation was assumed in MEK ($\bar{M}_w = 2000$), then clusters consisting of about 35 molecules per unit had to be present. Brett treated an alkyd with diazomethane to reduce the number of free carboxyl or free hydroxyl groups and found that the melt viscosity was considerably reduced demonstrating the very significant effect of hydrogen bonding on the melt viscosity of alkyd resins.¹⁸ Berryman extracted an alkyd reacted close to gelation with alcohol and obtained approximately 4 wt % of alcohol soluble material

TABLE VI
Light Scattering Data for Dilute Solutions of Alkyds Determined by Bobalek et al.¹⁷

Types of Alkyd	Linseed-glycerol		Soya-PE		Coconut-glycerol
	LG-1	LG-2	SP-1	SP-2	CG-1
Resin No.					
Limit Hc/τ at $c = 0 \times 10^4$ in:					
C ₆ H ₁₂	0.17	0.11	0.10	0.0402	0.14
MEK	0.475	0.29	0.404	0.150	5.0
Apparent \bar{M}_w in:					
C ₆ H ₁₂	59,000	91,000	100,000	250,000	71,000
MEK	21,000	35,000	25,000	67,000	2,000
$[q] = I_{45^\circ}/I_{135^\circ} - 1$ at $c = 0$ in:					
C ₆ H ₁₂	0.17	0.05	0.19	0.11	0.04
MEK	1.08	0.18	0.25	0.08	0.17

from the total resin.¹⁹ He concluded from this experimental result that even at the gelation threshold was still a significant proportion of low molecular weight material present.

When we consider the process of gelation of alkyds taking into account all the experimental results described so far, it seems to be contradictory that \bar{M}_w instead of \bar{M}_n as Christensen recently reemphasizes²⁰ goes to infinity at the gel point. Although it is theoretically true that the \bar{M}_w goes to infinity when gelation or net work is brought to completion, we must notice here that gel point is not always equal to gelation. Gel point should rather be regarded as the point of initiation of gelation. It is at this gel point when the molten resin begins to intertwine a stirrer, in other words, when it begins to show structural viscosity. If this structural viscosity is due to the net works formed by chemical bondings between alkyd molecules, one cannot explain the Brett's results. In reality, if we treat a molten alkyd with an amine such as triethylamine immediately after the gel point and then add such a good solvent as ethylacetate with vigorous agitation, a homogeneous viscous solution can usually be obtained. The amine treatment becomes less effective as the gelation proceeds. This would suggest that a greater portion of the net works at the gel point is formed by intermolecular associations, and not by chemical bondings. The time interval from the gel point to the complete gelation seems to be dependent on the reaction temperature and the alkyd formulation, especially on its oil length and excess OH concentration.

Judging from the characteristics of alkyd resin gelation mentioned so far, the present author proposes the following *two-step mechanism* theory for the process of alkyd gelation. During the course of gelation, two kinds of essentially different phenomena are occurring alternately in the polymer bulk. One is intermolecular associations or physical entanglements and another is intermolecular condensations. Repeating these processes, alkyd molecules grow to a variety of bulky clusters which differ in either sizes or configurations, which gradually begin to occupy the polymer bulk. It is these bulky clusters that play an important role in alkyd gelation. When a net work is formed among these clusters by either intermolecular associations or physical entanglements, the molten alkyd would begin to show structural viscosity and to intertwine a stirrer up. This is what we call the gel point. The gelation will be brought to completion by intermolecular condensations between associated clusters.

The results shown in Figure 5 can be explained by this theory. The line is composed of several upward and downward breaks, though $\log \eta$ (230°C) is approximately a linear function of $\bar{M}_n^{1/2}$. Since the increase in intermolecular associations do not contribute appreciably to the increase in molecular weight of the resin as compared to its contribution to viscosity, the slope C' of the function between $\log \eta$ and $\bar{M}_n^{1/2}$ will be steeper (see lines A and C in Fig. 5). When chemical bondings are being formed among associated molecules, the molecular weight is remarkably increased, but not the melt viscosity. Accordingly, the slope is less steep during

this period (see lines B and D in Fig. 5). It is considered that a break appears in the transition state where intermolecular condensations take place.

In order to verify this proposed mechanism, the relation between melt viscosity and \bar{M}_w instead of \bar{M}_n should be chased until the gelation sets in. Unfortunately, however, the determination of \bar{M}_w of alkyds by the light scattering method is encountered by various technical problems. One of them is the great influence of solvent on \bar{M}_w as reported by Bobalek et al.¹⁷ Another is the problem of resin purification. This would be formidable, since perfection demands a process which removes all particulate matters greater in size than the prepolymer molecule. Thus in order to obtain the absolute molecular weight of an alkyd by the light scattering method, it is necessary to search a proper solvent, an optimum concentration of the solution for the measurement, the method of preparation of the solution and so on, as Maron and Lou did in their work with sucrose.²¹

The two-step mechanism can be verified if one can follow the relation between melt viscosity and \bar{M}_w up to gelation, although \bar{M}_w of an alkyd just before the gel point seems to be unexpectedly small.¹⁶

Recently, Bobalek and his co-workers proposed a hypothesis on gel point mechanism.⁸ According to their hypothesis it is the gel point where the microgel particles react with one another after the flocculation set in just like the case of gelation of latex dispersions. The present author believes, however, that the hypothesis of microgel particles is not applicable to the alkyd system simply because the heterogeneity of alkyd resin, including

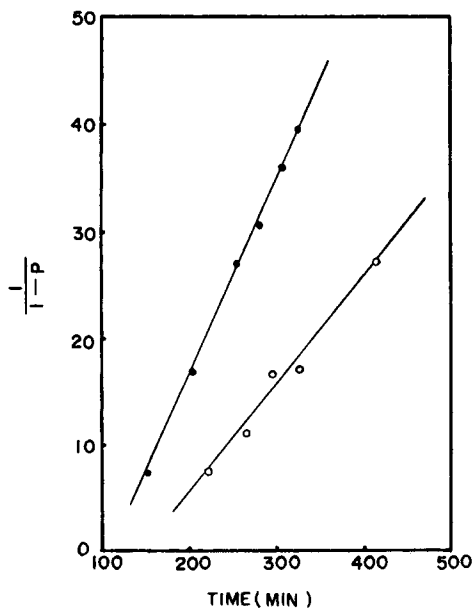


Fig. 7. $1/1 - P$ vs. T (min) plots for the alkyds: (○) S-1 series; (●) S-2 series.

both in molecular size and configuration, should become so remarkable at the gel point that the flocculation of mirogels will not result in sphere particles of the same size.

Cooking Schedule and The Order of Reaction

Since the dependence of viscosity-molecular weight and acid value-molecular weight relationships on cooking schedules has become clear, the

TABLE VII
Effect of Diazomethane Treatment on The Viscosity
of An Alkyd Resin Measured by Brett¹⁸

Sam- ple	AV (mg- KOH/g)	OH V. (mg- KOH/g)	Melt viscosity (poise at 25°C)		Ratio of melt vis- cosities	Intrinsic viscosity (g ⁻¹ cc)	
			before treatment	after treatment		before treatment	after treatment
1	44.2	44.0	209	60	3.5	3.42	3.44
2	30.5	29.7	481	176	2.7	3.95	3.95
3	20.5	21.6	814	460	1.8	4.43	4.48
4	10.3	11.1	1710	857	2.0	5.65	5.59

correlation between the order of reaction and cooking schedules were examined. Straight lines were obtained by plotting $1/1 - P$ vs. T , where P is the extent of esterification and T the reaction time, for the two cooking schedules (Fig. 7). This shows that the reactions are second order.

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