Molecular Weight Distribution in Alkyd Resins.
Part I

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Synopsis

The factors which could affect the molecular weight distribution of a fatty acid modified polyester (alkyd) are discussed. Specific studies on a 33% coconut oil/glycerol/phthalic anhydride polymer are described, and the effect of monoglyceride composition on alkyd distribution and film properties of an automotive baking enamel are considered.

INTRODUCTION

Alkyd resins (fatty acid-modified polyesters) have shown a remarkable ability to maintain their position as one of the major types of vehicles used in the surface coating industry. This has largely been due to the wide range of properties obtainable with these polymers and the possibility of significant modifications by formulation changes.
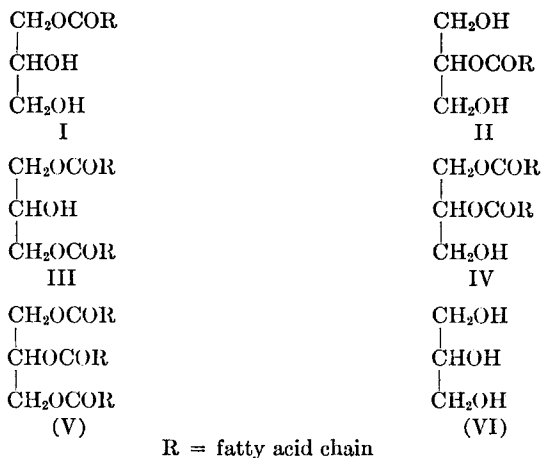
In compositions which "dry" or harden at elevated temperatures, it is usual to rely on reaction of the alkyd with another polymer system.[1] These reactions do not necessarily involve the unsaturation of the fatty acid, and hence, where resistance to discoloration on excessive heating and improved durability are required, alkyds based on the more saturated fatty acids are commonly used. Also, in order to further improve these properties, there has been a tendency to reduce the fatty acid content of alkyds or in other words, to increase the synthetic polyester portion of the polymer.

This trend has helped focus attention on some of the more fundamental properties of alkyds, since as these improvements have been achieved, so the tolerance in batch to batch variation has become less. Also, as the fatty acid content is reduced, the system becomes more highly functional and complex and chemical variations become increasingly likely.
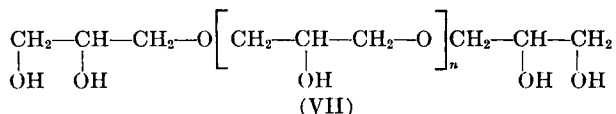
It is informative to consider the chemical reactions, equilibrium compositions, and rate processes which occur when a resin is produced.

Commercially, it is desirable to produce alkyds where possible from the vegetable oils, since these are normally cheaper than the equivalent quantity of fatty acid and glycerol.[2] However, attempts to react the vegetable oil, polyol, and dibasic acid usually lead to incompatibility because of the preferential reaction of the polyol and dibasic acid rather than with the oil.[3] To avoid this, alcoholysis (in some cases acidolysis)
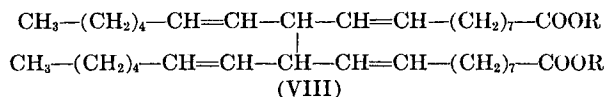
of the oil is carried out prior to the condensation reaction.   When glycerol is used as the polyol, it is theoretically possible to arrive at an alcoholysis product containing α-monoglyceride (I) β-monoglyceride (II), α,α'-diglyceride (III), α,β-diglyceride (IV), triglyceride or oil (V), and glycerol (VI).   This mixture is referred to as a monoglyceride and the procedure of preparing alkyds the monoglyceride process.

$$
\begin{array}{cc}
\text{CH}_2\text{OCOR} & \text{CH}_2\text{OH} \\
| & | \\
\text{CHOH} & \text{CHOCOR} \\
| & | \\
\text{CH}_2\text{OH} & \text{CH}_2\text{OH} \\
\text{I} & \text{II}
\end{array}
$$

$$
\begin{array}{cc}
\text{CH}_2\text{OCOR} & \text{CH}_2\text{OCOR} \\
| & | \\
\text{CHOH} & \text{CHOCOR} \\
| & | \\
\text{CH}_2\text{OCOR} & \text{CH}_2\text{OH} \\
\text{III} & \text{IV}
\end{array}
$$

$$
\begin{array}{cc}
\text{CH}_2\text{OCOR} & \text{CH}_2\text{OH} \\
| & | \\
\text{CHOCOR} & \text{CHOH} \\
| & | \\
\text{CH}_2\text{OCOR} & \text{CH}_2\text{OH} \\
\text{(V)} & \text{(VI)}
\end{array}
$$

R = fatty acid chain

Because oils are mixed glycerides of the various chain length fatty acids,[4] further possibilities arise regarding the distribution of these acids.   However since alcoholysis is an equilibrium reaction,[5] a reproducible composition should be reached provided sufficient time is allowed and there are no competing side reactions.   In practice, the reaction is usually only followed by measuring the tolerance of the mixture to anhydrous methanol or ethanol but it has been shown by Mort[6] and others[7] that markedly different compositions will pass this test; thus this does not therefore indicate attainment of equilibrium.   Extending the reaction time to allow the mixture to reach equilibrium is complicated by the possibility of non-reversible competing reactions involving fatty acids and polyol taking place.   Under basic catalysis (used to promote alcoholysis) glycerol undergoes etherification[8] to form polyglycerols of the type (VII), and since it is conventional to azeotropically remove water during monoglyceride formation, this reaction will not be reversible.

$$
\underset{\underset{\text{OH}}{|}}{\text{CH}_2}-\underset{\underset{\text{OH}}{|}}{\text{CH}}-\text{CH}_2-\text{O}\left[\text{CH}_2-\underset{\underset{\text{OH}}{|}}{\text{CH}}-\text{CH}_2-\text{O}\right]_n \text{CH}_2-\underset{\underset{\text{OH}}{|}}{\text{CH}}-\underset{\underset{\text{OH}}{|}}{\text{CH}_2}
$$

(VII)

Similarly, unsaturated fatty acid esters may oxidize or polymerize to give products of the type (VIII) (or isomers),

$$
\text{CH}_3-(\text{CH}_2)_4-\text{CH}=\text{CH}-\underset{|}{\text{CH}}-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{COOR}
$$
$$
\text{CH}_3-(\text{CH}_2)_4-\text{CH}=\text{CH}-\text{CH}-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{COOR}
$$

(VIII)

where R is a fully or partially esterified glycerol or polyglycerol. If the above products (VII–VIII) interchange with compounds (I–VI), the chemical possibilities are increased enormously. Similarly, if polyols other than glycerol (e.g. trimethylol ethane, trimethylol propane, pentaerythritol) are used, the reaction product is further complicated, since two polyols are now present (glycerol from the oil).

Because of the possibilities of competing side reactions and the distribution of the chemical components it would seem unlikely that the alcoholysis stage is reproducible when regarded from the viewpoint of chemical composition.

The addition of the dibasic phthalic anhydride (the usual acid used) provides further opportunity for competitive reactions.

A half ester (IX) forms by opening of the anhydride ring, and this takes place more readily with primary than with secondary hydroxyl groups.[9]

(IX)
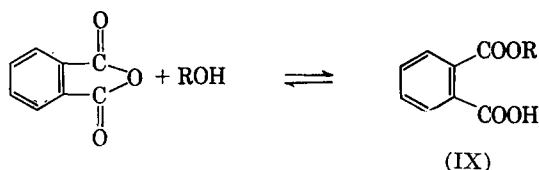
Also, the esterification of the acid-phthalate (IX) is more rapid with primary than with secondary hydroxyls,[9] and because water is removed from the reaction vessel, this reaction, in contrast to the half ester formation, is not reversible.
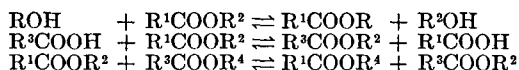

Thus, the composition of the monoglyceride stage vitally influences the rate of condensation.

Etherification (acid catalyst) is also possible with some systems and further complicates polymerization.[10]

The usual control procedures used to follow esterification are related to the rate of reaction and it is therefore reasonable to assume that alkyds made from the same chemical formulation could vary in molecular weight distribution (the term is used here to include distribution of functional groups also) particularly if the monoglyceride compositions are different.

However, many workers in this field argue that interchange reactions (alcoholysis, acidolysis, and ester interchange) occur during the condensation stage and these tend to even out the possible differences,[11] e.g.,

$$ROH \quad + R^1COOR^2 \rightleftharpoons R^1COOR \ + R^2OH$$
$$R^3COOH + R^1COOR^2 \rightleftharpoons R^3COOR^2 + R^1COOH$$
$$R^1COOR^2 + R^3COOR^4 \rightleftharpoons R^1COOR^4 + R^3COOR^2$$

The extent of this evening out will depend on the relative rates of the interchange processes and the condensation or polymerization reactions.

The comparison of the monoglyceride and fatty acid methods for pre-

paring alkyd resins should provide evidence pertaining to the above arguments. Using this latter process, fatty acids, polyol, and dibasic acid are reacted simultaneously and the reactions are different from those involving monoglyceride and discussed above. Here, the fatty acids undergo esterification (compared to alcoholysis in the monoglyceride method) and thus compete with the phthalic anhydride and phthalic acid half ester for available hydroxyl groups. The relative rates of these reactions have been discussed by Goldsmith[9] and are such that a different molecular weight distribution in the final product would be expected provided interchange reactions are comparatively slow. A number of workers have claimed different properties from alkyds prepared by the monoglyceride and fatty acid processes and explain these differences in terms of molecular weight distribution.[12,13] These findings support the contention that interchange reactions are, in some cases, at least, comparatively slow.

Kraft[14] has provided further evidence of interchange reactions being slower than esterification and has developed a high polymer technique utilizing this fact. In this process the monobasic acid is added at intervals to the polymerizing polyol–dibasic acid mixture, thereby reducing chain-stopping reactions and favoring the formation of high molecular weight polymers   Alkyds prepared by this method have different molecular weight distributions and film properties to those manufactured by the normal fatty acid process.

Previous attempts have been made to relate the processing conditions including monoglyceride composition with molecular weight distribution and final film properties.[11] However, most of these studies have been carried out on alkyds which dry by autoxidation and contain 50–70% of a drying oil, and hence fatty acid polymerization during processing has been a competing and complicating reaction. Nevertheless, these investigations have resulted in the development of a number of very useful techniques for characterizing molecular weight distribution of alkyds, and these have been ably reviewed by Tawn.[15] In an attempt to simplify work in this field, Tawn[15] and Bobaleck et al.[16] have investigated alkyds based on saturated fatty acids but have not related the molecular weight distribution to final film properties.

From the above discussion it is reasonable to expect that processing, as it affects the various stages of alkyd preparation, could lead to effects on film properties.

The present study therefore attempts to relate monoglyceride composition to molecular weight distribution and final film properties of an alkyd resin containing saturated fatty acids.

EXPERIMENTAL

The coconut oil used had an acid value of less than 0.5, while the glycerine analyzed for 98.3% glycerol. The phthalic anhydride had an

anhydride content of 99.7%. The catalyst solution consisted of sodium hydroxide (16.2 g.), in water (13.8 g.) and glycerine (70 g.). Xylene was used as the solvent.

Each alkyd was processed in a 10-liter, three-necked, round-bottom flask, heated by an electric mantle, and fitted with a Dean and Stark water separator, reflux condenser, glass stirrer, nitrogen inlet, and thermometer.

The solid contents were determined by heating approximately 1.0 g. of resin solution in a 3-in. diameter aluminum dish at 105°C. for 3 hr. Viscosity was measured at 55% solids in xylene at 25°C. using the Gardner-Holdt scale.

Resin Preparation

All resins were made by the following general procedure using the monoglyceride process. Coconut oil (1733 g.) and glycerine (485 g.) were heated under a nitrogen blanket and with stirring to 115°C. The catalyst solution (34 g.) was added and heating continued. The α-monoglyceride content was varied by controlling the temperature and time as follows.

Resin 1. The monoglyceride was prepared at 200°C. (approx. 140 min.) and contained 37% α-monoglyceride when analyzed by the method of Pohle and Mehlenbacker.[17] For the purpose of comparison with resins 2 and 3 below this figure corresponds to 28.3% α-monoglyceride, since in these latter resins the analysis is carried out after the second glycerine addition. Phthalic anhydride (2495 g.), glycerine (770 g.), and xylene were then added. The free glycerol content (i.e., the total of that present in the initial stage together with the second glycerol addition) was 34.4% when analyzed by periodic acid oxidation.[17]

Resin 2. The monoglyceride was prepared at 240°C. (approx. 10 min.), further glycerine (770 g.) was added and the mixture heated for 5 min. Analysis showed the presence of 41.4% α-monoglyceride and 29.5% free glycerol. Xylene and phthalic anhydride (2495 g.) were then added.

Resin 3. The monoglyceride was prepared as in resin 2, but the time after the second glycerine addition was extended to 60 min. Analysis showed 47.0% α-monoglyceride and 28.7% free glycerol. Xylene and phthalic anhydride (2495 g.) were then added.

All monoglycerides gave clear solutions when diluted with two parts of anhydrous methanol at 25°C.

The resins were condensed at 200°C., and the constants are given in Table I.

Measurement of Molecular Weight Distribution

The procedure used to measure the molecular weight distribution of the resins was basically that described by Robson and Wilson.[11]

The solids content was adjusted to 10% by the addition of acetone and then a 50 ml. aliquot placed in a calibrated centrifuge tube. The contents were titrated with distilled water (drop-wise addition) until a permanent cloudiness resulted.

TABLE I
Condensation Rates for Alkyds

Time, min.	Water evolved, ml.	Acid value	Viscosity
Resin 1			
20	100		
43	137		
55	160		
88	200		
95	212	67.7	T + $^1/_2$
125	240	52.0	U + $^1/_2$
155	262	39.3	W
180	280	—	—
After			Y + $^1/_4$ (on 54.2%
overnight	—	30.4	solids)
standing			
Resin 2			
25	50		
52	115		
75	165		
103	200	68.9	P
137	230	56.0	Q
163	243	46.3	T + $^1/_2$
200	258	34.4	V + $^1/_2$
245	268	—	—
After			X + $^1/_2$ (at 55.0%
overnight	—	27.1	solids)
standing			
Resin 3			
35	100		
60	136		
79	160		
112	200		
127	212	63.9	J
157	235	52.6	P + $^1/_2$
187	252	41.0	R
217	265	36.5	U + $^1/_2$
247	278	27.5	W + $^1/_2$
272	282	—	—
After			Y + $^1/_4$ (at 54.2%
overnight	—	23.7	solids)
standing			

Further additions of 0.25 ml. were then made, the solution thoroughly mixed and allowed to stand to approach equilibrium and the volume of the separated layer measured. This procedure was repeated until no further separation occurred on the addition of 0.25 ml. of water. Results are recorded in Table II are graphed in Figure 1.

Attempts to Interconvert Resins 1, 2, and 3

The resin (1500 g.) was heated in a three-liter flask and xylene removed in order to reach a reflux temperature of 200°C. (about 80% solid resin).
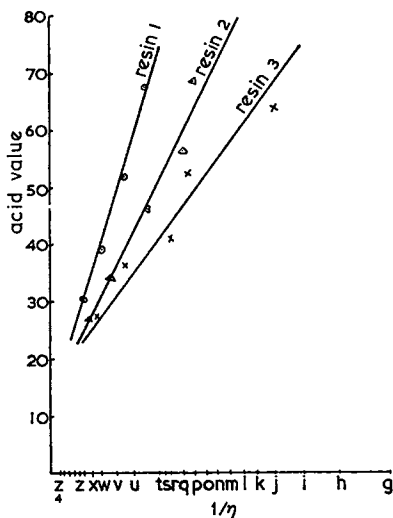
Fig. 1. The relationship between acid value and viscosity of resins 1, 2, and 3.

Samples were removed at intervals and the distribution measured as above. Results are shown in Table II.

Evaluation of Resins in an Automotive Baking Enamel

Each resin was processed into an enamel based on r-titania (Austiox-R.CR) at a pigment-to-binder ratio of 80:100. A partially butylated melamine formaldehyde condensate, type similar to BE615 as marketed by Monsanto (Australia) Pty. Ltd., was added as the crosslinking agent, such that the ratio of alkyd to melamine formaldehyde condensate was 80:20 on a solids basis.

The enamels were evaluated on phosphated steel panels using an Epon ester-based undercoat. The top coat was baked $1/2$ hr. at 120°C. and then evaluated for flexibility (mandrel $1/8$ in. at small end), hardness (Tukon), chip resistance, water soak (distilled water at 32°C.), and impact resistance (20 in. lb.).

Under all these tests, the enamels gave equivalent results. Gloss (60° Gardner glossmeter) was measured after various baking schedules; the results are given in Table III.

These baking schedules were selected since they cover the conditions likely to be experienced in practice in automobile painting.

The above enamels used for gloss measurements, were prepared by grinding the pigment in the melamine formaldehyde condensate so as to use one common base for all enamels.

The above results for both resin manufacture and evaluation were reproduced within experimental error on two batches of each resin.

TABLE II
Molecular Weight Distribution of Alkyd Resins

H₂O addition	Precipitate	Precipitate increment
Resin 1, sample 1 (taken immediately on reaching reaction temp.)		
7.95	Cloud point	...
8.20	0.10	0.10
8.45	0.60	0.50
8.70	2.10	1.50
8.95	2.95	0.85
9.20	3.60	0.65
9.45	4.25	0.65
9.70	4.80	0.55
9.95	5.15	0.35
10.20	5.40	0.25
10.50	5.80	0.40
10.75	6.00	0.20
11.25	6.25	0.25
11.75	7.00	0.75
12.25	7.10	0.10
Resin 2, sample 1		
6.25	Cloud point	...
6.50	0.75	0.75
6.75	2.80	2.05
7.00	3.95	1.15
7.25	4.65	0.70
7.50	5.00	0.35
7.75	5.45	0.45
8.00	5.85	0.40
8.25	5.95	0.10
8.50	6.05	0.10
8.75	6.20	0.15
9.00	6.35	0.15
9.25	6.50	0.15
Resin 3, sample 1		
6.70	Cloud point	...
6.95	0.40	0.40
7.20	2.15	1.75
7.45	3.10	0.95
7.70	4.05	0.95
7.95	4.50	0.45
8.20	5.00	0.50
8.45	5.50	0.50
8.70	5.70	0.20
8.95	6.00	0.30
9.20	6.10	0.10
9.70	6.40	0.30
10.20	6.70	0.30
Resin 1, sample 2 (after 135 min. at 200°C., A.V. = 20.0)		
7.25	Cloud point	...
7.50	0.65	0.65

TABLE II (*continued*)

H₂O addition	Precipitate	Precipitate increment
	Had to wait 17 min. to settle precipitate	
7.75	2.25	1.60
8.00	3.15	0.90
8.25	4.25	1.10
8.50	5.00	0.75
8.75	5.35	0.35
9.00	5.75	0.40
9.25	5.90	0.15
9.50	6.10	0.20
10.00	6.40	0.30
10.50	6.55	0.15
11.00	6.50	0.00
11.50	6.80	0.30
12.00	6.90	0.10
Resin 2, sample 2 (A.V. = 11.6)		
5.85	Cloud point	...
6.10	2.50	2.50
6.35	4.50	2.00
6.60	5.15	0.65
6.85	5.60	0.45
7.10	5.95	0.35
7.35	6.10	0.15
7.60	6.20	0.10
7.85	6.40	0.20
8.10	6.55	0.15
8.35	6.60	0.05
8.60	6.60	0.00
8.85	6.65	0.05
Resin 3, sample 2 (A.V. = 14.4)		
5.95	Cloud point	...
6.20	3.70	3.70
6.45	4.60	0.90
6.70	5.30	0.70
6.95	5.80	0.50
7.20	6.05	0.25
7.45	6.15	0.10
7.70	6.40	0.25
7.95	6.60	0.20
8.20	6.60	0.00
8.70	6.80	0.20
9.20	6.90	0.10
9.70	6.80	0.00

DISCUSSION

A formulation based on glycerine, phthalic anhydride, and a low percentage (33%) of a saturated vegetable oil (coconut) was chosen for study because these alkyds are of commercial importance for use in automotive baking enamels. Also the low fatty acid content results in a molar ratio

TABLE III

Resin	Gloss (60° Gardner glossmeter)		
	Baked ¹/₂ hr. at 121°C.	Baked ¹/₂ hr. at 121°C. followed by ¹/₂ hr. 138°C.	Baked ¹/₂ hr. at 160°C.
Resin 1	83	74	61
Resin 2	85	77	68
Resin 3	86	79	71

of glycerine/oil of 5/1 (approximately) and this allows for significant variation in the chemical structure of the monoglyceride.

Previous work in these laboratories has shown that at molar ratios of glycerine/oil from 2/1 to 5/1 it is possible to vary the free glycerol and α-monoglyceride contents of the monoglyceride by changes in reaction conditions.[18]   Thus, at 200°C. and a molar ratio of glycerine/oil = 2/1 the α-monoglyceride content is comparatively low and the free glycerol high, while at higher temperatures (240°C.) and increased glycerine/oil ratios (5/1) a higher α-monoglyceride and a lower free glycerol content results.

Based on these principles, three monoglycerides were prepared and these contained 28.3, 41.4, and 47.0% α-monoglyceride and 34.4, 29.5, 28.7% free glycerol, respectively.   When these were processed into alkyds by condensation with phthalic anhydride vastly different rates of reaction were observed, and these are recorded in Table I.   The very much faster decrease in acid value shown by resin 1 (34.4% free glycerol) can be attributed to the greater percentage of primary hydroxyls available initially. Resin 3 (28.7% free glycerol) with the lowest number of such groups gave the slowest reaction rate, while resin 2 occupied an intermediate position. Major differences were also shown in the relationship of acid value to viscosity (Fig. 1), and this indirectly suggests possible differences in molecular weight distribution since the former constant is a measure of number-average molecular weight while the latter approaches a weight-average figure.   The ratio of these two average molecular weights is generally accepted as a measure of the molecular weight distribution.[19]   Thus, at a given acid value, resin 1 is always considerably more viscous than resin 2, while this, in turn, is slightly higher in viscosity than resin 3.   In the absence of complete interchange reactions these results are to be expected since the highest viscosity system will tend to be more heterogeneous, (closer to incompatibility) and consist of free coconut oil and polyester. These findings are in agreement with those of Robson and Wilson,[11] who studied a 67% drying oil alkyd, but conflict with the findings of Mort,[6] who investigated a 52% drying oil alkyd.   Other variables would be present (i.e., polyol/dibasic acid ratio), but it would seem likely that each system requires a separate study and that general conclusion relating monoglyceride structure to acid value and viscosity could be misleading.
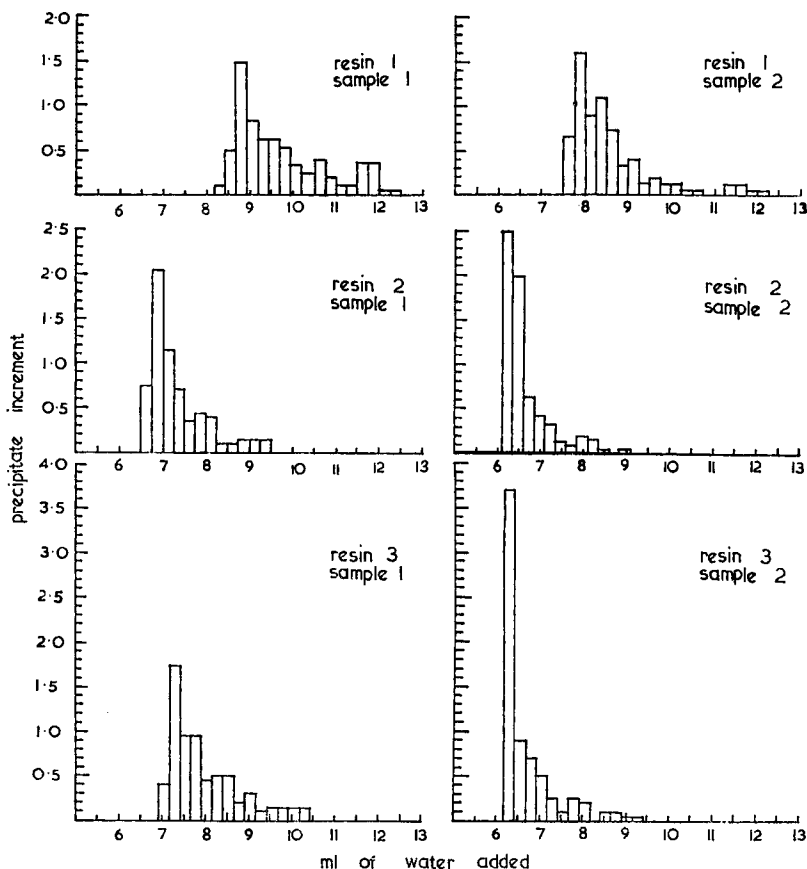
Fig. 2. The molecular weight distribution of resins before and after heating.

Measurement of the molecular weight distribution by a method similar to that described by Robson and Wilson[11] further indicated differences between the three resins. The distributions are recorded in Table II and graphed in Figure 2. This method uses acetone/water as the solvent/nonsolvent mixture and would be expected to separate more on molecular weight than polarity.

In an attempt to interconvert the three resins and ultimately arrive at the equilibrium state, each resin was heated under reflux at 200°C. so as to minimize further polymerization but favor interchange processes. From the limited study carried out, only small changes in the shape of the distribution curves took place (Fig. 2). The general displacement of the graphs can be explained by the further polymerization which occurred as is evidenced by the fall in acid value. This took place despite attempts to minimize the removal of water from the system.

Automotive enamels based on the three alkyds and using a melamine formaldehyde condensate as the crosslinking resins were prepared and evalu-

ated for the normal working properties.   While the enamels gave equivalent results for flexibility, hardness, chip resistance, water soak, and impact resistance, marked differences were observed in the initial gloss development and gloss retention when subjected to excessive heating.   Resin 2 and resin 3 gave enamels which were commercially acceptable, whereas resin 1 gave a lower initial gloss and a greater loss of gloss on overbake. Preliminary studies[20] have shown that the gloss differences result from variation in the state of pigment dispersion which can be effected by adsorption of components of the resin on the pigment surface.   Resin 3, which gave acceptable enamels, produced a dispersed system, whereas in resin 1 the pigment was flocculated.   Differences in the reaction of the resins with the melamine formaldehyde condensate[1] could also be expected to produce greater film shrinkage or heterogeneity which could lead to the gloss characteristics observed.   Durability on exterior exposure, is being checked.

Further work is in hand to characterize the various fractions contributing to the molecular weight distribution of each resin and their individual effects on film properties.

This study, which must be regarded as preliminary in this general field has considered the change in molecular weight distribution obtained by processing changes with a system prepared from a vegetable oil and the effect of these on the properties of the polymer.   However, it should be realized that this is only one approach to this problem, and solvent fractionation can also be used to alter the distribution and properties.   It is hoped to report on work of this type in the near future.

CONCLUSIONS

1.   The molecular weight distribution of a 33% coconut oil/glycerol/ phthalate alkyd has an important bearing on the gloss and gloss retention on overbake of an automotive baking enamel based on this alkyd and a melamine formaldehyde condensate.

2.   The composition of the monoglyceride stage is related to the final alkyd distribution.

3.   In the alkyd studied, interchange reactions were slow compared to esterification.

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Résumé

On discute les facteurs qui peuvent influencer la distribution des poids moléculaires d'un polyester (alkyde) modifié d'acide gras. On décrit des études spécifiques sur un polymère à 33% en huile de noix de coco/glycérine/anhydride phthalique et on considère l'effet de la composition en "monoglycéride" sur la distribution alkyde et les propriétés des films d'un vernis par étuvage.

Zusammenfassung

Die Faktoren, welche Einfluss auf die Molekulargewichtsverteilung eines fettsäuremodifizierten Polyesters (Alkyd) haben können, werden diskutiert. Untersuchungen an einem Glycerin-Phthalsäureanhydrid-polymeren mit 33% Kokosnussöl werden beschrieben und der Einfluss der "Monoglycerid"-Zusammensetzung auf die Alkyd-Verteilung und Filmeigenschaften eines Auto-Einbrennlackes erörtert.