

## Reactivity of Functional Groups in Surface Coating Polymers. Part I. Hydroxyl Groups in Alkyd Resins

D. H. SOLOMON and J. J. HOPWOOD,\* *Division of Applied Mineralogy, C.S.I.R.O., Melbourne, Australia*

### Synopsis

The factors which can influence the availability of functional groups in polymers are considered. In particular, the importance of hydroxyl groups in the formation and film-forming reactions of alkyd resins is discussed, and evidence is presented to suggest that the number of hydroxyl groups available for chemical reaction is not necessarily equivalent to the theoretical value. Factors which influence the availability of the hydroxyl groups are considered, and some of the properties of the alkyd are related to the available hydroxyl content.

### INTRODUCTION

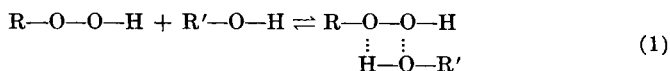
Functional groups are incorporated into polymer molecules for a number of reasons. Their presence may modify the physical properties, such as adhesion to a substrate or solubility in a selected solvent composition, or the functional group may be essential for the polymer-forming reaction or to enable subsequent chemical interaction with other entities. The effectiveness of the functional group in satisfying these requirements will be related to its availability and in this context we have a rather paradoxical situation, as pointed out by Alfrey,<sup>1</sup> since it is necessary to reconcile the theories of equal reactivity irrespective of molecular size with the known differences in the reaction rate of some groups when present in small and large molecules. It is not possible to generalize about the effect of molecular size on the reactivity of a substituent group, since examples of enhanced and reduced activity are known.<sup>1</sup> Satisfactory explanations for some of the above effects have been advanced as a result of detailed studies on the mechanisms operating when a reagent attacks a functional group in a small and large molecule.<sup>1</sup>

The morphology of a polymer can also influence the chemical activity<sup>2</sup> of functional groups by reducing their accessibility, and a similar effect results if the mobility of the attacking species is limited by either physical or chemical factors. For example, it has recently been shown that tolylene diisocyanate cannot react with all the hydroxyl groups of cellulose nitrate,<sup>3</sup> and it has been suggested that, once one of the isocyanate groups reacts, the restricted movement of the second group limits its chances of reaction.

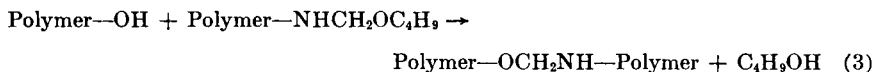
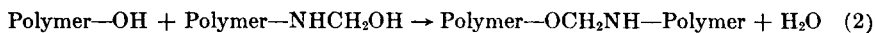
\* Present address: Balm Paints Ltd., Clayton, Victoria, Australia.

A similar situation occurs during the formation of three-dimensional polymers, where it is necessary to have an excess of one reacting species present to allow for the reduced availability of the groups. For example, in the reaction of acid-containing polymers with diepoxides, an excess of the former is used since all the carboxyls are not available.<sup>4</sup>

The film-forming ability of alkyd resins, i.e., fatty acid-modified polyesters, is dependent upon the functional groups present, namely hydroxyl, carboxyl, and, in some cases, carbon-carbon unsaturation. Of these, the hydroxyl group serves a number of most important functions. It is involved in the esterification reaction of the monomeric and low molecular weight entities which leads to polymer formation, and it is from reactions such as these that the concept of equal reactivity of all groups has been developed. This concept is the basis of the kinetic treatments of Flory,<sup>5</sup> Kienle,<sup>6</sup> Carothers,<sup>7</sup> and others.<sup>8-11</sup> Once the polymer has been formed, the presence of the hydroxyl groups is again important in characterization by number-average molecular weight. In polymers designed for use with water as the solvent, hydrophilic groups contribute to the solubility, and it has been claimed by some workers that hydroxyl groups are of even greater importance than ionizable carboxyl groups in conferring water solubility.<sup>12</sup> The function of the hydroxyl group in film formation depends on the conditions of drying and/or the presence of film formers other than the alkyd. Where drying takes place by autoxidation processes involving the formation and decomposition of hydroperoxides, the hydroxyl group can adversely effect the drying rate by complex formation and the consequent stabilization of the hydroperoxide.<sup>13</sup>



In crosslinking reactions with alcohol-modified melamine-formaldehyde condensates, the hydroxyl group is the most reactive center in the alkyd resin and undergoes etherification and ether interchange,<sup>14</sup> as shown in eqs. (2 and 3).



In polyurethane formation hydroxyl groups are likewise essential and are usually part of an alkyd or similar polyester-type resin.

In all the above considerations, the availability or reactivity of the hydroxyl group will have an important bearing on the formation and film properties of the final coating. While it is often assumed that all hydroxyl groups in an alkyd are equally available, several observations suggest otherwise. Perhaps the most significant of these is that measured hydroxyl contents do not always correspond with the theoretical value, although this difference is usually not commented upon or highlighted.

This paper describes work aimed at clarifying the reactivity of hydroxyl groups in alkyd resins and attempts to relate this to polymer-forming reactions.

### EXPERIMENTAL

Water was removed from glycerine by azeotropic distillation with benzene. The product was 99.8% glycerol as measured by periodate titration.<sup>16</sup> The phthalic anhydride had an anhydride content of 99.8%. *p*-Toluenesulfonic acid (B.D.H. laboratory reagent) contained 1 mole of water and was used without further purification. All solvents were of A.R. quality.

Acid numbers were measured by dissolving a known weight of the resin (approx. 0.3 g.) in a neutralized ethanol-toluene (1:1) mixture and titrating to a phenolphthalein endpoint with 0.1*N* alcoholic potassium hydroxide. The results are expressed as milligrams of KOH per gram solid resin. Hydroxyl numbers are expressed in the same units as the acid numbers and were determined by the method of Wilson and Hughes<sup>16</sup> using acetic anhydride and pyridine and by using phthalic anhydride.<sup>17</sup> The viscosity of the resin samples was determined at 75% solids in toluene by comparison, at 20°C., with Gardner-Holdt standard viscosity tubes. Infrared spectra were run on a Unicam SP-200 spectrophotometer.

To minimize problems associated with the use of mixtures of fatty acids, such as are usually present in the naturally occurring oils, essentially pure linoleic acid was prepared. Safflower oil fatty acids, with the composition 12% saturated acids, 20% oleic acid, and 68% linoleic acid as measured by gas chromatography of the methyl esters,<sup>18</sup> were chosen as starting material since the absence of linolenic acid facilitated purification. Urea (14 kg.) and methanol (38 kg.) were heated to 60°C. under a nitrogen atmosphere and safflower oil fatty acids (15 kg.) preheated to 50°C. added with stirring. The mixture was maintained at 55°C. for 10 min. and then cooled to room temperature (48 hr.). The urea inclusion compound was removed by filtration, water (20 l.) added to the filtrate, and the pH adjusted to 4.5 with hydrochloric acid. The mixture was heated under nitrogen at 50°C. for 1 hr., cooled, and the water layer removed. The fatty acid layer was washed with water (3 × 20 l.) and petroleum ether (7½ l., b.p. 40–60°C.) added. The petroleum ether solution was washed with water (2 × 20 l.), dried (anhydrous Na<sub>2</sub>SO<sub>4</sub>), and the petroleum ether removed by distillation under reduced pressure with the use of a nitrogen bleed, to yield linoleic acid (3300 g., 22%).

Analysis of the methyl esters<sup>18</sup> by gas chromatography showed the product to be at least 98% linoleic acid (*cis,cis*-9,12-octadecadienoic acid). This acid was stored at -4°C. under a nitrogen atmosphere.

#### Preparation of Glycerol $\alpha$ -Monolinoleate

The method used was an adaption of that described by Hartmann<sup>19</sup> for the preparation of glycerol monostearate. Glycerol (500 g.), acetone

(750 ml.), alcohol-free chloroform (1 liter) and *p*-toluene-sulfonic acid (15 g.) were heated under reflux under a nitrogen atmosphere. Water (100 g.) was removed (20 hr.) by fractionation of the vapors and then separation in a Crankcase dilution-type apparatus. Linoleic acid (500 g.) was added and the mixture heated under reflux until the water of reaction (32 g.) had been separated (10 hr.). The acid catalyst was removed by shaking the reaction mixture with powdered sodium acetate (20 g.) and then washing with water ( $3 \times 750$  ml.). The chloroform was removed by distillation under reduced pressure with the use of a nitrogen bleed. The scission of the isopropylidene-glyceryl  $\alpha$ -linoleate was carried out by heating a solution of this compound in 2-methoxyethanol (2 l.) with finely powdered boric acid (1 kg.) on a water bath (3 hr.). The mixture was cooled, dissolved in 1:1 diethyl ether-petroleum (b.p. 30–40°C.) (1200 ml.), washed with water ( $4 \times 1000$  ml.), and dried (anhydrous sodium sulfate). The solution was then diluted with petroleum ether (b.p. 30–40°C.) (3 l.) and cooled to  $-35^\circ\text{C}$ . The separated product (443 g., 70% yield) analyzed for 98.9% glyceryl  $\alpha$ -monolinoleate as determined by periodate titration.<sup>15</sup>

### Resin Preparation

An inert atmosphere was maintained throughout the resin preparation by passing dry nitrogen into the reaction vessel.

Phthalic anhydride (160 g.) was heated to  $160^\circ\text{C}$ . in a flask equipped with a stirrer, dropping funnel, thermometer, sampling device, and nitrogen gas inlet.

A mixture of glycerol (33 g.) and glyceryl  $\alpha$ -monolinoleate (349 g.) was added from the dropping funnel to the molten phthalic anhydride at a rate such that the temperature remained between 160 and  $170^\circ\text{C}$ . (8 min.). Toluene (15 g.) was used to wash out the dropping funnel and was then added to the reaction mixture. The temperature was raised to  $200 \pm 2.0^\circ\text{C}$ . and maintained at this temperature with addition of toluene when necessary, while water was removed in a Dean and Stark water

TABLE I  
Preparation of Linoleic Acid-Modified Glyceryl Phthalate

Time, min.	Water Evolved, ml.	Acid number	Theoret- ical	Hydroxyl number			Viscosity
				Acetic anhy- dride method	Phthalic anhy- dride method	Avail- able fraction <sup>a</sup>	
46	15.9	52.3	147.4	80.0	79.0	0.543	D + $\frac{1}{4}$
78	17.1	31.2	126.3	63.1	59.3	0.499	G + $\frac{1}{2}$
108	18.0	18.9	114.0	47.2	47.0	0.414	K
123	18.3	16.5	111.6	45.0	43.2	0.403	L
163	18.5	12.9	108.0	39.3	38.0	0.364	S
178	18.7	10.7	105.8	35.1	34.6	0.332	T + $\frac{1}{4}$

<sup>a</sup> The available fraction is the ratio of acetic anhydride to theoretical hydroxyl values.

separator. Samples were withdrawn and analyzed for acid number, hydroxy content, and viscosity. Results are given in Table I.

The influence of time of heating under reflux on the hydroxyl value of the alkyd is shown in Table II.

TABLE II  
Effect of Time on the Hydroxyl Value Measurement

Time, hr.	Hydroxyl value
2	35.1
6	36.7
24	38.6
48	39.1

### Commercial Alkyds

Hydroxyl values were also measured by the acetic anhydride-pyridine method for a range of commercial alkyds; the results are given in Table III.

TABLE III  
Hydroxyl Values of a Series of Alkyd Resins

Alkyd composition, molar ratios	Percentage esterifi- cation <sup>a</sup>	Average function- ality <sup>b</sup>	Hydroxyl value	
			Theoretical	Observed
Safflower fatty acids/glycerol/ pentaerythritol/phthalic anhydride = 3.0/1.0/1.49/2.95	87.0	2.12	49.0	48.2
Linseed fatty acids/glycerol/ phthalic anhydride = 3.0/3.0/3.0	95.3	2.00	10.6	10.8
Safflower fatty acids <sup>c</sup> / glycerol/phthalic anhydride = 3.0/4.54/4.50	97.2	2.13	64.2	32.5
Coconut fatty acids/glycerol/ phthalic anhydride = 3.00/5.99/6.09	93.4	2.20	113.0	65.0
Coconut fatty acids/trimethylol propane/benzoic acid/ phthalic anhydride = 3.0/5.76/0.27/5.16	98.3	2.17	102.5	76.0

<sup>a</sup> Carboxyl basis.

<sup>b</sup> Average functionality is the ratio of total equivalents to total moles.

<sup>c</sup> Contains fatty acid derived from bodied safflower oil of viscosity 5 poise.

### Resin Evaluation

The linoleic acid-modified glyceryl phthalate was evaluated in typical surface coating formulations.

Acetylated alkyd was prepared by heating the resin (4-5 g.) with the acetylating reagent (50 ml.) for 2 hr. After cooling, toluene (200 ml.)

was added and the solution washed with water ( $4 \times 200$  ml.) and the toluene removed under reduced nitrogen pressure at  $35^\circ\text{C}$ .

The infrared spectrum of the acetylated resin had the hydroxyl band at a lower wave number,  $3500\text{ cm.}^{-1}$ , than the alkyd, and the presence of both primary and secondary acetates was indicated by the bands at  $1025$  and  $1100\text{ cm.}^{-1}$ .<sup>20</sup>

**Reaction with a Melamine-Formaldehyde Condensate.** Hexakis(methoxy methyl)melamine (Cymel 300, marketed by American Cyanamid Company) (0.081 g.), alkyd resin (1.269 of 100% solids) and *p*-toluene-sulfonic acid (0.015 g.) were mixed until a homogeneous solution resulted. A thin film of this mixture on a NaCl disk was heated under nitrogen at reduced pressure at  $150^\circ\text{C}$ . The reaction was followed by measuring the intensity of the infrared absorption at  $3500\text{--}3550\text{ cm.}^{-1}$  (hydroxyl) and  $2880\text{ cm.}^{-1}$  (methylene) by the base line method as described by Rao.<sup>21</sup> Results are shown in Table IV.

TABLE IV  
Reaction of the Alkyd with a Melamine-Formaldehyde Resin

Time, min.	$3500\text{ cm.}^{-1}$	$2880\text{ cm.}^{-1}$	$3500/2800\text{ cm.}^{-1}$
30	0.152	0.782	0.195
75	0.147	0.746	0.197

The band ratio for the peaks at  $3550$  and  $2880\text{ cm.}^{-1}$  for a blend of the alkyd and melamine formaldehyde without catalyst was 0.219.

Similar treatment of the acetylated alkyd gave the results shown in Table V.

TABLE V  
Reaction of the Acetylated Alkyd with a Melamine-Formaldehyde Resin

Time, min.	$3500\text{ cm.}^{-1}$	$2880\text{ cm.}^{-1}$	$3500/2880\text{ cm.}^{-1}$
30	0.056	0.441	0.127
70	0.054	0.422	0.128

The band ratios for the peaks at  $3500$  and  $2880\text{ cm.}^{-1}$  for a blend of the acetylated alkyd and melamine formaldehyde without catalyst was 0.128.

**Reaction with Phenyl Isocyanate.** To a solution of the alkyd (4 g. of a 4% weight/weight solution in 1:2 dichloroethane) was added freshly distilled phenyl isocyanate (0.082 g.) and the infrared absorption spectrum run in a 0.207 mm. cell. The results are shown in Table VI where the peak heights have been adjusted to a constant methylene adsorption ( $2880\text{ cm.}^{-1}$ ) and the zero time bands were obtained from the alkyd solution run in the same cell. There was always a large excess of isocyanate, as shown by the strong band at  $2300\text{ cm.}^{-1}$ .

Similar treatment of the acetylated resin with phenyl isocyanate showed no loss of the hydroxyl adsorption at  $3500\text{ cm.}^{-1}$ .

TABLE VI  
Reaction of the Alkyd Solution with Phenyl Isocyanate

Time after isocyanate addition, min.	3500-3550 cm. <sup>-1</sup> absorption
0	0.068
20	0.059
60	0.059
180	0.059

### Autoxidation of the Alkyd

Autoxidation catalysts (driers) were added to the alkyd and acetylated alkyd and the solutions allowed to stand for 24 hr. Drying times were determined on 0.0056-in. thick films at 25°C. and a relative humidity of 50% (Table VII).

TABLE VII  
Drying Times of Alkyd and Acetylated Alkyd

Drier composition, % metal on wt. resin	Resin	Drying time, min. <sup>a</sup>
0.2% Co, 1.5% Pb	Alkyd	6
0.2% Co, 1.5% Pb	Acetylated alkyd	1½
0.2% Ca, 0.08% Co	Alkyd	42
0.2% Ca, 0.08% Co	Acetylated alkyd	10

<sup>a</sup> Drying times were measured on a Beck-Koller type Drying Machine.

### Water Solubility of an Alkyd

In order to gain water solubility it was necessary to limit the degree of condensation of an alkyd of similar composition to that used above, so as to have a lower molecular weight and higher concentration of hydrophilic groups. A resin of acid number 26 was, therefore, used. The alkyd (1.0 g.) was dissolved in butyl cellosolve (Union Carbide Chemicals Company) (0.54 g.) and sufficient triethanolamine added to raise the pH to 7. The mixture was infinitely dilutable with water.

When the alkyd was acetylated, the mixture would not tolerate any water. The acetyl value was 50 and the calculated figure 121.1.

### DISCUSSION

Initial studies were made on an alkyd prepared from fatty acid, glycerol, and phthalic anhydride in the mole ratio of 1.0/1.36/1.11, corresponding to an overall functionality of 2.10 and an oil length of 52%. The alkyd was processed from glyceryl  $\alpha$ -monolinoleate, glycerol, and phthalic anhydride so that the phthalic anhydride and phthalate half ester would be the only acid entities involved in the polyesterification. This type of alkyd is widely used in air drying enamels, as a dispersing aid for pigments, and

occasionally in stoving enamels. During the course of the polyesterification, the hydroxyl content was measured by the generally accepted acetic anhydride-pyridine method described by Wilson and Hughes.<sup>16</sup> As shown in Table II, substantial increases in the time for the acetylation reaction did not markedly increase the values obtained. The results in Table I show that the measured hydroxyl values are considerably less than the calculated figures, and the difference between these values increases with the molecular weight and complexity of the polymer molecule. The possibility that the hydroxyl groups were lost by side reactions, such as etherification, was discounted, since the water of reaction in the polyesterification corresponded only to that required to account for esterification of the reacted carboxyl groups. Also, the acetylated resin showed a considerable hydroxyl band at 3500  $\text{cm.}^{-1}$  in the infrared. This hydroxyl band occurs at a slightly lower wave number than in the untreated alkyd; this is consistent with the unavailable groups being more strongly bonded.<sup>20</sup> The absorption bands at 1025 and 1100  $\text{cm.}^{-1}$  in the acetylated alkyd indicate that both primary and secondary hydroxyl groups<sup>20</sup> are available for acetylation. Examination of a number of alkyds, with formulations typical of the range in common use, showed that the measured hydroxyl value corresponded to the theoretical figure only when the system had a functionality of two or the percentage of the carboxyl groups esterified was low (Table III). In the other polymers, the measured values were considerably less than the theoretical. All the polymers reported in Table III are amorphous, but in crystalline poly(ethylene succinate), where the overall functionality was slightly less than two, Carothers and Dorough<sup>22</sup> were unable to react the hydroxyl groups with phenyl or naphthyl isocyanates or acetic anhydride. Our results, taken in conjunction with those of Carothers and Dorough, suggest that the degree of crystallinity, the overall functionality and the degree of polymerization all play an important role in determining the availability of the hydroxyl groups. In explaining their results, Carothers and Dorough<sup>22</sup> stated that "these failures appear to be due to a reluctance of the hydroxyl groups to react, and they are not altogether surprising in view of the diminished reactivity which is frequently associated with increased molecular size." Subsequently, Flory<sup>5</sup> has stated that "at all stages of the polymerization the reactivity of every like functional group is the same." We suggest that an intermediate situation exists in amorphous polymers which are capable of forming branched or three-dimensional structures. In such polymers, the lack of reactivity of some of the hydroxyl groups may be related to their changed environment as the polymer molecule increases in complexity.

Difficulties encountered in the kinetic analysis of the formation of alkyd resins could also be related, at least in part, to the availability of the hydroxyl group. For example, Kienle et al.<sup>6</sup> could not explain the glycerol-phthalic anhydride reaction by simple second- or third-order equations, whereas in fatty acid-modified polyesters Wekua and Klausch<sup>11</sup> and Berryman<sup>23</sup> claim second-order kinetics to apply. However, Tawn<sup>10</sup> favors third-



order kinetics, but only where the degree of reaction is 70–80%. If these reactions were simple polyesterifications in which all functional groups had equal reactivity irrespective of molecular size, then third-order kinetics could be expected on the basis of Flory's predictions.<sup>5</sup>

The formation of the 52% oil length alkyd described above does not follow either second- or third-order kinetics on the basis of either the measured or theoretical hydroxyl values shown in Table I. Of the possible explanations for this observation the three most likely would appear to be: (a) fractional kinetics apply, possibly because of the difficulty associated with the removal of the water of reaction at the high viscosities encountered;<sup>24</sup> (b) under esterification conditions, more hydroxyl groups are available than is indicated by acetylation; (c) some of the carboxyl groups are also not available for reaction.

We do not yet have sufficient evidence to decide between these alternatives, but it is worth noting that phthalylation, which should closely parallel the conditions operating during polyesterification, gave substantially the same hydroxyl values as acetylation (Table I). Also, no evidence has been found for gross errors in the carboxyl estimations, a finding supported by experiments carried out by Carothers and Dorough,<sup>22</sup> who treated neutral poly(ethylene succinate), in which the hydroxyl groups are not reactive under normal conditions, with succinic anhydride under forcing conditions and were able quantitatively to estimate the resultant carboxyl group.

The lack of availability of the hydroxyl groups in these polyesters could also partially explain the divergence between calculated and observed gel points.

The significance to film-forming reactions of the available, rather than the theoretical, hydroxyl values, is demonstrated by the following studies on typical crosslinking reactions. When the alkyd, a melamine-formaldehyde condensate, and an acid catalyst were heated together, free hydroxyl groups remained even after 75 min. at 150°C., as shown by absorption at 3500  $\text{cm.}^{-1}$  in the infrared spectrum (Table IV). In a similar experiment with the acetylated alkyd, no change in the infrared spectrum occurred (Table V), indicating that the hydroxyls involved in the condensation with the melamine-formaldehyde resins are those which react with acetic anhydride. Likewise, reaction of the alkyd with excess phenyl isocyanate indicated that some hydroxyl groups were not attacked (Table VI) and, since the acetylated resin did not show any change in hydroxyl intensities when treated with the isocyanate, it is concluded that the same hydroxyl groups react with both acetic anhydride and the isocyanate. Therefore, measurement of the available hydroxyl groups by acetylation offers a method of predicting the potential reactivity of the alkyd resin in thermosetting film-forming reactions.

It is much more difficult to demonstrate unambiguously the effect of available hydroxyl groups on the rate of air drying of the alkyd and on the solubility of a similar polymer in water, since in removing the active or

available hydroxyl groups by acetylation, the total hydroxyl value is naturally decreased. However, the acetylated alkyd formed a dry film in one-quarter of the time required by the alkyd (Table VII), and the magnitude of this improvement warrants further studies to determine the relative importance of available and total hydroxyl contents on the rate of autoxidation and film formation. An alkyd of a lower degree of condensation and soluble in a butyl cellosolve-amine-water mixture had its water tolerance reduced from infinity to zero by the acetylation of one-third (approximately) of its total hydroxyl groups, and once again the magnitude of this change suggests that available hydroxyl groups could be of vital importance in conferring water solubility on the polymer.

It is hoped to report shortly a much more detailed investigation aimed at relating chemical composition, average functionality and the degree of polymerization of a wide range of alkyd formulations to the availability of the hydroxyl groups.

### CONCLUSIONS

The behavior of the hydroxyl groups in alkyd resins does not necessarily accord with the theory of equal reactivity irrespective of molecular size. The availability of these groups is limited particularly in highly condensed systems with an average functionality greater than two. The film-forming ability of the alkyd is shown to depend on the available, rather than the total, hydroxyl content.

The authors wish to thank the Research Director of Balm Paints Ltd., Mr. J. N. Graves, for permission to publish this work. The helpful suggestions of Dr. D. Willis are gratefully appreciated.

### References

1. Alfrey, T., in *Chemical Reactions of Polymers*, E. M. Fettes, Ed., Interscience, New York, 1964, p. 1.
2. Segal, L., in *Chemical Reactions of Polymers*, E. M. Fettes, Ed., Interscience, New York, 1964, p. 44.
3. Woodman, A. L., and A. Adicoff, *Ind. Eng. Chem. Prod. Res. Develop.*, **1**, 278 (1962).
4. Murdoch, J. D., and G. H. Segall, *Off. Dig. Federation Soc. Paint Technol.*, **33**, 709 (1961).
5. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953.
6. Kienle, R. H., P. A. Van Der Meulen, and F. E. Petke, *J. Am. Chem. Soc.*, **61**, 2258 (1939).
7. Carothers, W. H., *Trans. Faraday Soc.*, **32**, 39 (1936).
8. Vaughan, C. L. P., and F. E. Schmitt, *Off. Dig. Federation Soc. Paint Technol.*, **30**, 1131 (1958).
9. Johnston, C. W., *Off. Dig. Federation Soc. Paint Technol.*, **32**, 1327 (1960).
10. Tawn, A. R. H., *J. Oil Colour Chemists Assoc.*, **39**, 223 (1956).
11. Wekua, K., and W. Klausch, *Farbe Lack*, **59**, 85 (1953).
12. Tawn, A. R. H., *J. Oil Colour Chemists Assoc.*, **47**, 794 (1964).
13. Khan, N. A., *Pakistan J. Sci.*, **12**, No. 2, 95 (1960).
14. Solomon, D. H., *Rev. Pure Appl. Chem.*, **13**, 171 (1963).

15. Pohle, W. D., and V. C. Mehlenbacher, *J. Am. Oil Chemists Soc.*, **27**, 54 (1950).
16. Wilson, H. N., and W. C. Hughes, *J. Soc. Chem. Ind.*, **58**, 74 (1939).
17. Mehlenbacher, V. C., in *Organic Analysis*, Vol. 1, Interscience, New York, 1953, p. 35.
18. Medcalfe, L. D., and A. A. Schmitz, *Anal. Chem.*, **33**, 363 (1961).
19. Hartmann, L., *Chem. Ind. (London)*, **1960**, 711.
20. Colthup, N. B., L. H. Daly, and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, 1946.
21. Rao, C. N. R., *Chemical Applications of Infrared Spectroscopy*, Academic Press, New York, 1963.
22. Carothers, W. H., and G. L. Dorough, *J. Am. Chem. Soc.*, **52**, 711 (1930).
23. Berryman, D. W., *J. Oil Colour Chemists Assoc.*, **42**, 393 (1959).
24. Marvel, C. S., *An Introduction to the Organic Chemistry of High Polymers*, Wiley, New York, 1959.

### Résumé

Les facteurs qui peuvent influencer la disponibilité des groupes fonctionnels dans les polymères sont considérés. En particulier, l'importance des groupes hydroxyles dans la formation et dans les réactions filmogènes de résines alkydes est discutée; on démontre que le nombre de groupes hydroxyles disponibles pour la réaction chimique n'est pas nécessairement équivalent à la valeur théorique. Les facteurs qui influencent la disponibilité en groupes hydroxyles sont considérés et certaines propriétés des résines alkydes sont liées à cette teneur en hydroxyle disponible.

### Zusammenfassung

Die Faktoren, welche die Zugänglichkeit funktioneller Gruppen in Polymeren beeinflussen können, werden untersucht. Im besonderen wird die Bedeutung der Hydroxylgruppen für die Bildung und die filmbildenden Reaktionen von Alkydharzen diskutiert und Hinweise angeführt, welche zeigen, dass die Zahl der für die chemische Reaktion verfügbaren Hydroxylgruppen dem theoretischen Wert nicht notwendigerweise äquivalent ist. Faktoren, welche die Zugänglichkeit der Hydroxylgruppen beeinflussen, werden untersucht und gewisse Eigenschaften des Alkydharzes werden zum Gehalt an zugänglichen Hydroxylgruppen in Beziehung gesetzt.

Received August 20, 1965

Prod. No. 1275