A Study of the Oxidative Degradation of Phenol-Formaldehyde Polycondensates Using Infrared Spectroscopy[*,†]

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Introduction

The reaction between phenols and aldehydes was first described by Baeyer[1] in 1872. Little attention was given to the reaction which produced nothing but resinous material until Baekeland[2] investigated the condensation products obtained in this reaction. Since Baekeland's findings, phenolic resins have become one of the most prominent and widely used polymers to be produced. In spite of this, the structure of phenolic resins is far from clearly elucidated at the present time. Many hypotheses have been presented to explain the structure of cured phenolic resins, but until recently few of these were based on sound experimental and theoretical basis. Since the cured resin is infusible and insoluble in most solvents, progress in determining structural features has shown almost no progress. It was only after analyses of the uncured resinous condensation products were attempted that some progress was realized in the elucidation of the structural parameters of these resin systems. For example, Traubenberg[3] working with soluble novolak-type resins showed that 4,4'-dihydroxydiphenylmethane and 2,2'-dihydroxydiphenylmethane could be isolated from the product mixture of acid-catalyzed phenol-formaldehyde condensations. Baekeland and Bender,[4] summarizing the existing field of phenolic resin chemistry in 1925, projected the major future avenue for phenolic resin research. The approach used involved the attempted synthesis of phenolic resins from various substituted phenols and alternate condensation methods. Almost all subsequent research has followed similar experimental approaches.

Three major schools of thought arose concerning the structure of phenolic resins. The experimental approach was similar; however, the interpreta-

tion of the resulting data varied markedly. All data were generally obtained by preparing various mono- and disubstituted methylol phenols, heating these monomeric units to hardened resins at various temperatures, and examining the residual and volatile products. Zinke et al.[5] from observations made on heating 2,6-dimethylol-p-cresol concluded that the resin-hardening process occurred in two stages. The first stage resulted in the formation of dibenzyl ethers. The second stage with the evolution of formaldehyde could be explained in a number of ways; the evolved formaldehyde could (a) react with the hydroxyl groups, or else (b) undergo chain splitting to give rise to aldehydes. Subsequently, Zinke and Hanus[6] postulated three possible second-stage hardening routes; (1) reaction of formaldehyde at a reactive ring center, (2) reaction at a hydroxyl group, or (3) reaction with a methylene group. All of these postulations were based on the detection of very small yields of reaction products. Zinke,[7] in 1944, in reviewing resole hardening, summarized their thoughts on the structure of the phenolic resins produced under a wide variety of conditions: (a) resoles obtained by alkaline condensation of phenols and formaldehyde are mixtures of substituted methylol phenols, (b) the primary reaction in the hardening process is the formation of ether bridges with the elimination of water, (c) with further hardening or curing at higher temperatures (170°C.) the ether bridges split to give methylene bridges, and (d) that the initial ether formed partly decomposes with heating to give phenolic aldehydes and methylated phenols.

Von Euler et al.[8] observed results similar to those reported by Zinke and Hanus,[6] however, in a further study[9] using 2,4-dimethyl-6-methylol phenol obtained a dimeric ether. On heating the ether for several hours at 140°C. a quinone methide trimer was isolated. Later, Alder et al.[10] formulated a disproportionation reaction to give as one product the quinone methide trimer during the hardening or curing process.

Lilley,[11] departing from the reaction by functional group species, classified the condensation of phenol and formaldehyde into two parts by reaction type. The first stage was considered to be an ionic reaction while the solvent was present, while the second stage in the solid phase was considered to be free radical in type. In both reaction sequences the primary reaction was considered as the formation of methylene bridges with the ether-forming reaction a possibility to account for a small amount of the functional linkages in the condensate. The formation of ether linkages in either ionic or radical stages was formulated on the basis of previous investigations.[8–10,12,13] It was concluded that ordinary, commercial phenolic resins are for the most part phenol rings connected by methylene bridges and that the ether linkages are of minor consequence.

Another method employed in the determination of resin structure is the complete separation of soluble resins by chromatographic methods. In this manner, Freeman[14] elegantly characterized a number of monomers and dimers. The results of this important investigation support the proposed structural features involving predominantly methylene linkages.[11]

In view of the many suggestions concerning the numerous functional moieties which comprise a phenolic resin system, it was pertinent to investigate the infrared properties of a variety of phenolic resins after the resin had been cured to an infusible mass. It was anticipated that by a detailed study of the thermal degradation reactions, particularly oxidation processes involving specific linkages, using infrared techniques, substantiation or refutation of certain structural moieties postulated as part of the resin system could be accomplished. Several studies of a similar nature have been attempted. Megson[15] has examined the distillates from pyrolysis of phenolic resins *in vacuo*. Recently, Wolfs et al.[16] have studied resin pyrolysis in inert atmospheres. Ouchi and Honda[17] in a comprehensive study of vacuum pyrolysis of phenolic resins propose a mechanism for thermal degradation and carbonization. Oxidative degradation has received very little attention although Hall[18] has reported that the sensitivity of solid phenol novolaks to oxidation as observed by changes in viscosity suggests the methylene linkage as the point of attack. It was therefore of interest to follow the structural changes in these resins, to increase the basic knowledge of the cured resin system, and to elucidate if possible the mode of oxidative thermal degradation.

Experimental

The synthesis of 4,4'-dihydroxybenzophenone and 2,2'-dihydroxybenzophenone was carried out using the procedures described by Pircard and Kearns[19] and Badder et al.,[20] respectively.

Preparation of Typical Base-Catalyzed Phenolic Resin (Resole)

A mixture of 47 g. of freshly distilled phenol, 80 ml. of 37% aqueous formaldehyde solution, and 100 ml. of 4N sodium hydroxide was left to stand at room temperature for 16 hr. The reaction flask was equipped with a reflux condenser and heated on a steam bath for one hour. The cooled mixture was neutralized to pH 7. The aqueous layer was decanted off, leaving a viscous brown liquid. The wet organic phase was taken up in 500 ml. of acetone, dried over anhydrous magnesium sulfate followed by molecular sieves, then filtered. On evaporation, the resole could be obtained as a water-free light brown syrup. In practice, the acetone solution was used directly after drying in the preparation of film specimens for spectral examination.

Preparation of Typical Acid-Catalyzed Phenolic Resin (Novolak)

A stirred mixture of 188 g. of freshly distilled phenol and 2 ml. of concentrated sulfuric acid was treated with 138 ml. of 37% aqueous formaldehyde solution added in a dropwise manner while maintaining the reaction temperature at 80°C. After the addition was complete, the mixture was refluxed for $1^1/_2$ hr. The water was removed by vacuum distillation, leav-

ing a crude resin contaminated with residual water and unreacted phenol. The resin was thoroughly washed with water to remove unreacted phenol. The wet, solid resin was dissolved and dried as an acetone solution as previously described for the resole resin. The absence of free phenol was checked spectrophotometrically using the 14.6-μ band in the infrared. The resin was isolated as a fine, white powder by vacuum evaporation of the acetone solution.

Thermal Degradation of a Typical Resole Resin in Air

An acetone solution of the base-catalyzed resin was slowly added dropwise to the surface of a polished sodium chloride disc. The acetone was allowed to evaporate in air at room temperature. The deposited film was then cured in dry nitrogen for 3 hr. at 120°C. Samples, in asbestos holders for convenience in handling, were heated in forced-air draft ovens and cooled intermittently for spectral examination. Spectra were taken at successively longer time intervals of heating until no further changes could be detected in the infrared spectra. Aging temperatures used were 100, 150, and 200°C.

Thermal Degradation of a Typical Novolak Resin in Air

A powdered, acid-catalyzed phenolic resin was dissolved in spectral grade acetone and the solution added dropwise to a polished sodium chloride disc. After the acetone had evaporated at room temperature, the sample was heated intermittently as previously described for the resole systems. The only exception being these samples were not cured in an inert atmosphere.

Vacuum Heating of an Uncured Resole

An acetone evaporated film was cured in the usual manner except that it was cured at 150°C. in a sublimation vessel at 0.05 mm. After a short time a white solid was sublimed out of the curing resin and collected on the side of the sublimation tube. The solid was identical in infrared spectrum and melting point, 82–83°C., with o-methylol phenol. Heating of the cured resin remaining on the salt disc and spectral examination showed results identical to those obtained with a nitrogen-cured resin.

Application of the Difference Technique to Phenolic Resins

The difference technique[21] was employed in the spectral examination of phenolic resin systems. A typical example is as follows. Two films of cured resoles were examined spectrally. The films for examination were selected such that an initial linear spectrum was obtained. One film was retained for use in the reference beam of the spectrophotometer. The

other was aged at 200°C. in air for the usual aging cycle. After each heating interval a difference spectrum was recorded. When the intensity of the absorption bands became too great to be observed accurately, the reference sample was degraded for an appropriate time interval slightly shorter than the one desired for examination. By analysis of the changes which occurred, adequate functional changes could be qualitatively ascertained.

Copolymerization of 4,4'-Dihydroxy-
benzophenone into a Phenol-Formaldehyde
Condensate

In an Erlenmeyer flask, 0.5 g of 4,4'-dihydroxybenzophenone, 1 g. of *o*-methylol phenol, 2 ml. of 37% formaldehyde solution, and 50 ml. of 10% sulfuric acid solution were heated for 15 min. on a steam bath. A red, resinous solid was filtered from the reaction mixture, dried *in vacuo* at 50°C. for 2 hr., pulverized, and examined directly in the infrared region as an evaporated film from acetone.

Copolymerization of 2,2'-Dihydroxy-
benzophenone into a Phenol-Formaldehyde
Condensate

A mixture of 0.5 g. of 2,2'-dihydroxybenzophenone and 1 g. of *o*-methylol phenol was heated on a steam bath for 4 hr. A viscous liquid, insoluble in water, was obtained. The liquid was dissolved in acetone and used directly in film preparation. It should be noted that attempts to effect copolymerization by a variety of other techniques failed to yield a polymer.

Results and Discussion

Before a detailed discussion of the experimental results is undertaken it is advantageous to consider the overall process of oxidative degradation, as determined by the infrared method. When a resole condensate is thermal set and hardened in an inert atmosphere such as nitrogen at 120°C. for 3 hr., little or no volatilization of organic materials was detected. Therefore on examining the cured resin, the nonvolatile, solid phase of the polymer system is being monitored. The course of the degradation, exclusive of volatile fragments produced during oxidation, can therefore be detected from changes observed in the functional group bands in the infrared region.

Several observations concerning the structure of cured phenolic resins of this type can be made from initial examination of the infrared spectrum of the resin film sample. If a polymer consisting of phenol rings connected by methylene linkages in the ortho and para positions is assumed, then all the absorption bands appearing in the 2–16-μ region can be assigned to the various vibrational modes expected for a structure of this type. After heating the phenolic resin film *in vacuo* (0.05 mm.) for 50 hr. at temperatures

between 100 and 200°C. no carbonyl bands appeared in the spectrum. Therefore under these conditions of aging, quinone methide structures cannot be supported in the infrared examination of the film specimens. If present, these moieties make up only a small concentration of the resin system.

Similarly, ether linkages are absent in the cured phenolic resin. In order to examine this further a study of the ether linkage and its stability in these systems was undertaken and will be reported separately. Therefore, it appears that the observations made by Lilley[11] are substantially correct. The structures obtained from multisubstituted phenolic rings and formaldehyde cannot be analogously applied to simple phenol-formaldehyde condensation products. In view of these initial facts, the starting material used for the degradation studies was considered to predominantly consist of phenol rings connected by methylene groups substituted at the 2, 4, or 6 positions, or any combination of these according to the formulation shown in Figure 1.
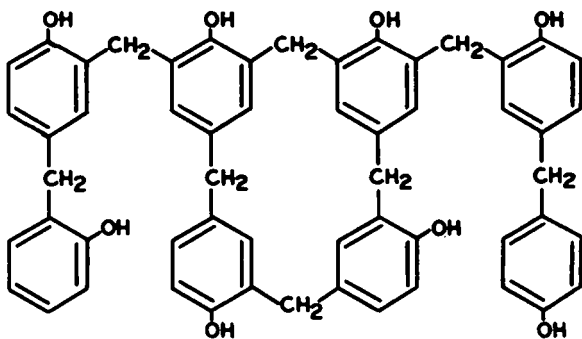

Fig. 1. Structure of typical phenolic resin indicating possible substitution types and major functional groups present in the cured resin.

If the phenolic resin, after it has been cured by heating in nitrogen, is heated further in either nitrogen or vacuum, no apparent degradation occurs, since no changes are observed in the successive infrared spectrum taken to follow any possible chemical change. But, if the resin is heated in air, a number of spectral changes occur. If the air-heated resin is then transferred to an inert atmosphere system for furthe.· degradation, the chemical changes as manifested in changes in the infrared region cease. It can be concluded that the initial degradation is dependent on the presence of oxygen and that the products of degradation are oxygenated species.

When a base-catalyzed phenolic resin is heated at temperatures between 100 and 200°C., a number of changes take place in the polymer system which can be detected by infrared analysis. The overall reaction is basically the same at all three temperatures. Only the rate of oxidation changes with increasing temperature as would be expected from consideration of the Arrhenius equation. By measuring the intensity of the carbonyl

groups produced on oxidation, a general relationship as to the rate of oxidation at different temperatures can be represented in Table I.

TABLE I
Relationship of Temperature and Time to Produce Identical
Spectral Changes in Phenolic Resins

Temp., °C.	Time, hr.
100	1300
150	250
200	8

A number of significant changes take place in the spectra of various resin samples during the course of oxidative aging. A series of bands attributed to the ingrowth of carbonyl groups are observed in the 5.5–6.5-μ region. Concurrent with the ingrowth of these bands a number of other changes appear in these spectra. The overall changes in the polymer structure upon heating in air at 200°C. and detected by infrared spectral analysis are summarized in Table II.

TABLE II
Observed Functional Group Changes in Phenolic Resins
at 200°C.

Frequency, cm.$^{-1}$	Assignment	Change	Time of appearance, hr.
3300	—OH	Decrease	18th
3200	—COOH(OH)	Increase	4th
1650	C=O	Increase	4st
1720	—COOH	Increase	4th
1480	—CH—	Decrease	1st
875,820	1,2,4-tri-substituted aromatic ring	Decrease	18th

A detailed tabulation of the spectral changes at the three temperatures studied are presented in Tables III, IV, and V. The absorbance value A, noted in these tables, is calculated from the relationship, $A = \log I_0/I$, where I_0 is measured by a one point baseline at 5 μ which is constant during the observed course of the degradation and I is the intensity of the absorption band in question as calculated by the method described by Wright.[22] As indicative of the changes which take place spectrum 1 (Fig. 2) is the spectrum of a cured nonoxidized phenolic resin and spectrum 2 (Fig. 2) is the spectrum of the same resin after heating in air for 4 hr. at 200°C.

The course of degradation of an acid-catalyzed phenolic resin (novolak) is essentially the same as that of a base-catalyzed phenolic resin (resole) as evidenced in the changes in the infrared spectrum. The same carbonyl
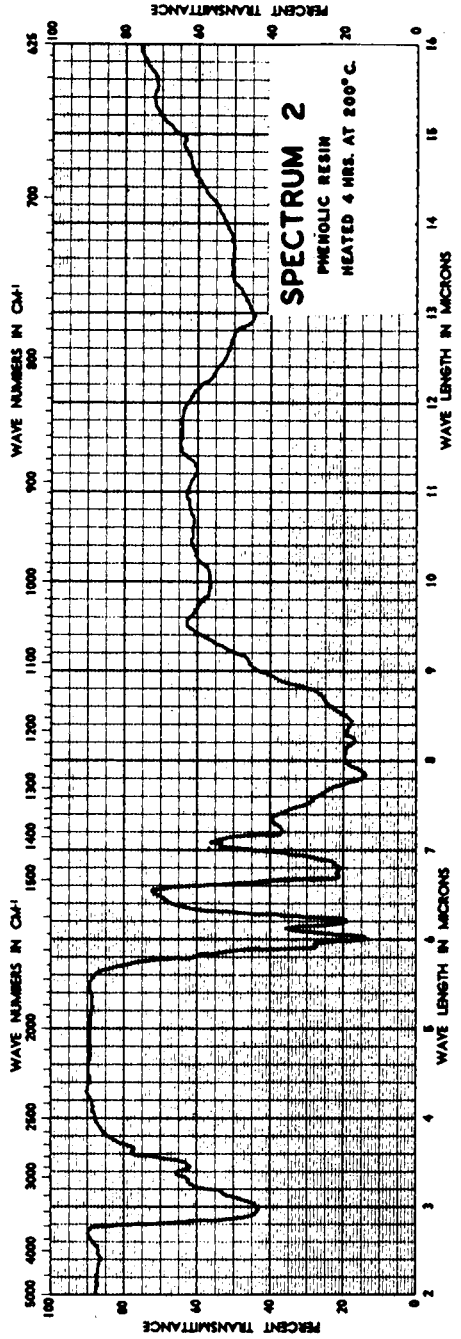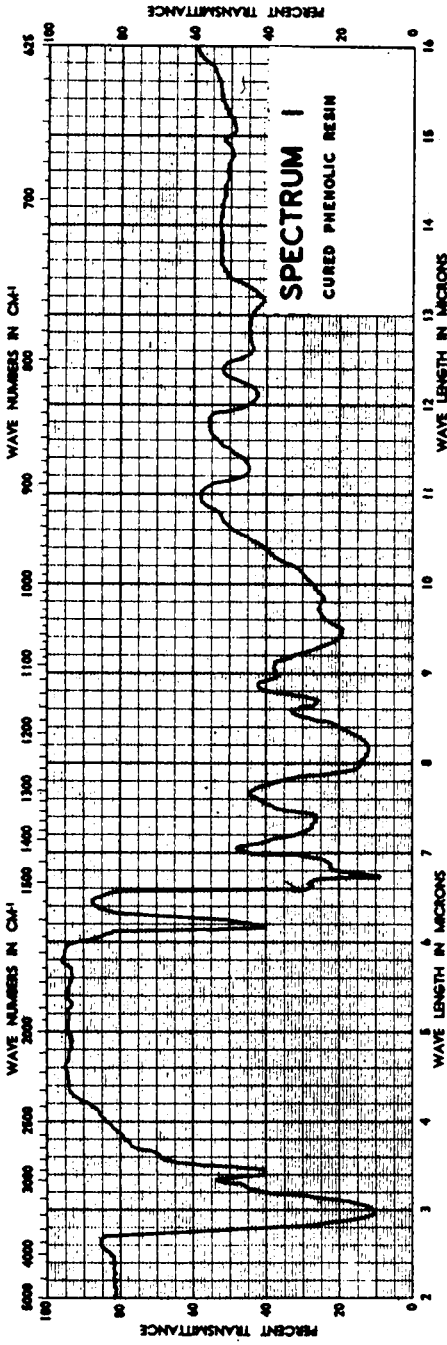
Fig. 2. Typical spectrum before and after air oxidation.

groups appear at the same frequencies in the identical order of appearance. Therefore, it is convenient to speak of phenolic resins in general when discussing the course of the degradation, since no differentiation can be made by infrared analysis.

TABLE III

Absorbance Band Changes on Heating a Phenolic Resin
in Air at 100°C.

Time, hr.	Absorbance A				
	1600 cm.$^{-1}$	1650 cm.$^{-1}$	1680 cm.$^{-1}$	1720 cm.$^{-1}$	300 cm.$^{-1}$
1	0.411	0.035			0.937
2	0.398	0.060			0.833
3	0.421	0.076			0.802
4	0.395	0.077			0.770
5	0.406	0.088			0.770
7	0.430	0.105			0.770
9	0.424	0.130			0.770
14	0.413	0.150			0.770
20	0.438	0.213	0.050		0.770
24	0.450	0.239	0.075		0.770
30	0.478	0.273	0.080		0.770
40	0.668	0.538	0.206		0.668
50	0.618	0.668	0.278		0.668
61	0.692	0.823	0.425	0.082	0.594
89.5	0.809	0.876	0.478	0.098	0.594
112.5	0.825	0.876	0.492	0.116	0.594
146	0.841	1.000	0.593	0.128	0.594
249	0.950		0.629	0.164	0.594
349			0.750	0.214	0.522
492			0.750	0.247	0.492
659			0.662	0.265	0.421
822			0.724	0.296	0.457
989			0.808	0.375	0.411
1084			0.918	0.532	0.492
1320			0.980	0.574	0.458

*Effect of Sample Thickness on the Oxida-
tion of Phenolic Resins*

Before examining the oxidative reactions which take place in detail, there remains still one important experimental parameter to be considered. Does oxygen permeate through the entire polymer structure in the films being examined or is the oxidation a surface phenomena? In order to determine this parameter the surface area was maintained at a constant and the sample thickness was varied over a 5-fold range. If the air oxidation is a surface reaction, the amount of oxidation after a certain time interval should

be constant, regardless of the film thickness. But if oxygen attacks the entire polymer species, the amount of oxidized products should vary with the polymer thickness or amount of polymer present. The results obtained by varying the film thickness are shown in Table VI.

The 3.3-μ band in the resin spectrum is indicative of the aromatic carbon-hydrogen content of the resin and is a reliable measure of the resin concentration. The 6-μ band is oxidative in nature and grows in steadily as oxidation continues. If the oxidative process proceeds through

TABLE IV

Absorbance Band Changes on Heating a Phenolic Resin in Air at 150°C.

Time, hr.	Absorbance A				
	1600 cm.$^{-1}$	1650 cm.$^{-1}$	1680 cm.$^{-1}$	1720 cm.$^{-1}$	3300 cm.$^{-1}$
1	0.385	0.056			0.663
2	0.388	0.136			0.632
3	0.398	0.162	0.042		0.612
4	0.412	0.206	0.062		0.612
6	0.450	0.268	0.062		0.612
10	0.506	0.556	0.223		0.493
11	0.492	0.578	0.232		0.472
16	0.632	0.750	0.331	0.068	0.462
20	0.774	0.950	0.518	0.112	0.458
26	0.840		0.632	0.222	0.424
37.5	0.894		0.676	0.238	0.386
48			0.724	0.265	0.386
59			0.724	0.274	0.412
87.5			0.772	0.387	0.423
110.5			0.742	0.414	0.377
144			0.840	0.450	0.435
190				0.505	0.329
347				0.628	0.412
490				0.716	0.442
1082				0.965	0.533

exposure of the entire sample to the aging atmosphere, the ratio of the 3.3–60-μ absorption bands should be constant. However, this should not be the case if the oxidation is a surface phenomena. Regardless of the polymer thicknesss, the amount of oxidized species should remain the same. The results indicate that the oxidation as studied is a surface phenomena since the ratio of the 3.3–6-μ bands varies in an ordered fashion with film thickness.

Degradation Reactions as Spectrally Observed

The first new band to appear in the resin spectrum is the carbonyl band at 1650 cm.$^{-1}$ (6.05 μ). Since oxidation at a methylene linkage has been

TABLE V

Absorbance Band Changes on Heating a Phenolic Resin
in Air at 200°C.

Time, hr.	Absorbance A				
	1600 cm.$^{-1}$	1650 cm.$^{-1}$	1680 cm.$^{-1}$	1720 cm.$^{-1}$	3300 cm.$^{-1}$
0.5	0.284	0.272	0.078		0.412
1	0.378	0.500	0.206		0.328
1.5	0.400	0.545	0.236		0.328
2	0.422	0.576	0.284		0.293
3	0.568	0.724	0.390	0.105	0.329
4	0.560	0.650	0.428	0.156	0.293
5	0.576	0.712	0.467	0.185	0.303
6	0.576	0.670	0.474	0.214	0.272
8	0.612	0.670	0.522	0.292	0.262
13	0.725	0.702	0.640	0.422	0.330
18	0.690	0.670	0.630	0.514	0.293
35.5	0.802	0.630	0.650	0.650	0.349
64	0.830	0.630	0.670	0.690	0.358
87 ⎫	0.815	0.612	0.594	0.670	0.333
120 ⎭					
Decomposition from surface					

assumed to be reasonable by Hall,[18] this initial carbonyl absorption was
tentatively assigned to a dihydroxy-substituted benzophenone structure.
It then became necessary to confirm this by independent syntheses of ketone
containing polymers. 2,2′- and 4,4′-Dihydroxybenzophenone were pre-
pared. Both of these ketones exhibited carbonyl frequencies at 1625
cm.$^{-1}$ However, when these ketones were incorporated into the polymer
chain by copolymerization with phenol and formaldehyde, the carbonyl
absorption band was observed at 1650 cm.$^{-1}$ These data confirm the
initial assignment of the primary oxidation band to a carbonyl group arising
from methylene oxidation. The frequency of the monomeric compounds

TABLE VI

Effect of Film Thickness on Oxidation of Phenolic Resin
in Air at 200°C.

Resin, g./cm.^{2} × 10^4	Absorbance		Ratio 3.3/6.0
	3.3	6.0	
11.5	0.149	0.232	0.642
17.3	0.165	0.232	0.712
23.1	0.195	0.244	0.800
28.9	0.206	0.228	0.904
34.6	0.228	0.247	0.924
40.5	0.324	0.273	1.190
52.0	0.344	0.267	1.290

as compared to the polymer might well be expected on the basis of steric considerations in the polymer unit.

This mode of oxidation agrees with previous evidence on the spontaneous oxidation of phenolic resins.[18] Although peroxide intermediates were not detected in the infrared spectrum, their existence was proved by chemical analysis. Therefore the first step in the oxidation of a phenolic resin system can be visualized as shown in Figure 3.
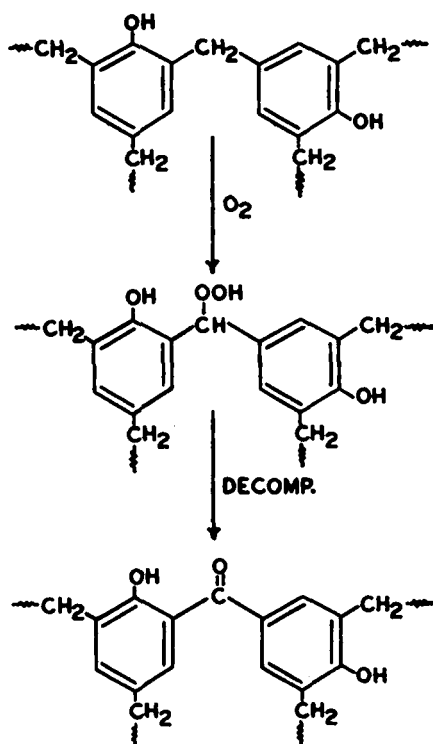

Fig. 3. Primary oxidation route of phenolic resins in which the diphenylmethane unit is converted to benzophenone linkages.

Upon further oxidation, a shoulder on the initial carbonyl band grows in at a frequency of 1680 cm.$^{-1}$ A consideration of the chemistry of this system led to the general deduction that only two further chemical processes are possible which would lead to the further formation of carbonyl-containing fragments. One is the cleavage to acid fragments and the second is rearrangement to quinoid-type structures. The band at 1680 cm.$^{-1}$ is far too low in frequency to be assigned to an acid moiety.[23] Therefore, it is postulated as due to the formation of quinone-type structures. Examination of a large number of quinones has shown that the general region in which these systems exhibit absorption is from 1660–1690 cm.$^{-1}$[23] which is in good agreement with the observed frequency for the second carbonyl

frequency appearing on oxidation. Previous chemical evidence also favors an interpretation of this type. It has been reported[24] that sterically hindered phenols are oxidized to quinone-type structures. It has also been reported[25] that quinone-type structures were not formed if hydrogens were located alpha to the aromatic ring. Once the carbonyl structure is formed from the methylene group, the conditions of steric hindrance and the absence of alpha hydrogens are fulfilled, thus lending support to quinoid intermediates in the secondary oxidative processes.

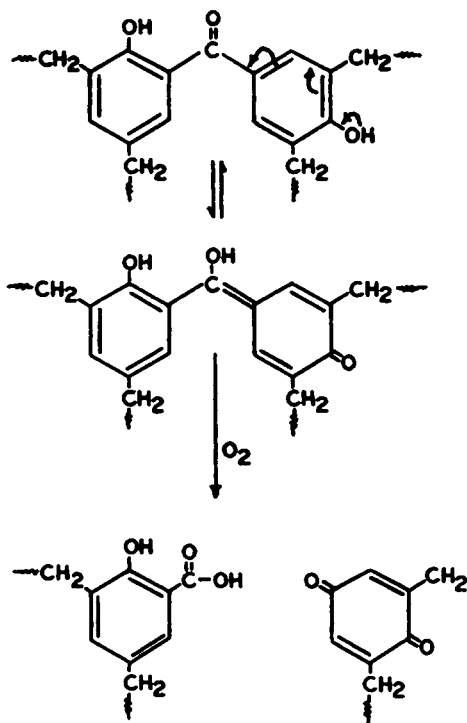Oxidative degradation does not stop at this stage, but proceeds further.

Fig. 4. Secondary oxidation involving chain scission through quinoid linkages to give quinone and acid fragments.

A third absorption band grows in at 1720 cm.$^{-1}$ and is accompanied by a broad band at 3100 to 3300 cm.$^{-1}$ (3 μ region). Using the difference spectrum technique,[21] it is possible to partially resolve this band. The changes occurring indicate that the phenolic hydroxyl band is decreasing and an acid hydroxyl is appearing. Therefore, the final stage of the secondary oxidative degradation can be formulated as show in Figure 4.

After the appearance of acid fragments, no further chemical changes occur which are detectable by infrared analysis. After many hours of further heating the spectrum slowly diminishes to a few broad bands which are of no real analytical value. Sufficient data were obtained, however, to

postulate and experimentally substantiate a sound working hypothesis for degradation in phenolic resin systems. Further work concerning the finer details of this mechanism is in progress using other analytical techniques and will be reported in the near future.

References

1. Baeyer, A., *Ber. deut. chem. Ges.*, **25**, 280 (1872).
2. Baekeland, L. H., *Ind. Eng. Chem.*, **1**, 149 (1909).
3. Traubenberg, J. K., *Angew. Chem.*, **36**, 515 (1923).
4. Baekeland, L. H., and H. L. Bender, *Ind. Eng. Chem.*, **17**, 225 (1925).
5. Zinke, A., F. Hanus, and E. Ziegler, *J. prakt. Chem.*, **152**, 126 (1939).
6. Zinke, A., and F. Hanus, *Ber. deut. chem. Ges.*, **74**, 205 (1941).
7. Zinke, A., *Chemikerztg*, **47**, 151 (1944).
8. von Euler, H., E. Alder, and J. Bergstrom, *Arkiv. Kemi, Mineral. Geol.*, **14B**, No. 25 (1941).
9. von Euler, H., E. Alder, and J. O. Cedwall, *Arkiv. Kemi, Mineral. Geol.*, **14A**, No. 14 (1941)
10. Alder, E., H. von Euler, and J. O. Cedwall, *Arkiv. Kemi, Mineral. Geol.*, **25A**, No. 7 (1941).
11. Lilley, H. S., *J. Soc. Chem. Ind. (London)*, **67**, 196 (1948).
12. Ziegler, E., *Ber. deut. chem. Ges.*, **74**, 841 (1941).
13. Hiltzsch, K., *Kunststoffe*, **32**, 69 (1942).
14. Freeman, J. H., *Anal. Chem.*, **24**, 955 (1952).
15. Megson, N. J. L., *J. Soc. Chem. Ind. (London)*, **58**, 131 (1939).
16. Wolfs, P. M. J., D. W. van Krevelen, and H. I. Waterman, *Fuel*, **39**, 25 (1960).
17. Ouchi, K., and H. Honda, *Fuel*, **38**, 429 (1959).
18. Hall, R. Q., *Chem. & Ind. (London)*, **1952**, 693.
19. Pircard, J. P., and C. W. Kearns, *Can. J. Research*, **B28**, 56 (1950).
20. Badder, F. G., L. S. El-Assol, and V. B. Baghos, *J. Chem. Soc.*, **1955**, 1714.
21. Conley, R. T., and J. F. Bieron, *J. Appl. Polymer Sci.*, in press.
22. Wright, N., *Ind. Eng. Chem., Anal. Ed.*, **13**, 1 (1941).
23. Bellemy, L. J., *The Infrared Spectra of Complex Molecules*, 2nd ed., Wiley, New York, 1958.
24. Kharasch, M. S., and B. S. Joshi, *J. Org. Chem.*, **22**, 1439 (1957).
25. Cook, C. D., D. A. Kuhn, and P. Fianu, *J. Am. Chem. Soc.*, **78**, 2002 (1956).

Synopsis

An infrared spectrophotometric examination of the oxidative degradation of acid- and base-catalyzed phenol-formaldehyde polycondensates, novolaks and resoles, respectively, has been carried out in the temperature range form 100–200°C. The existence of structural moieties such as quinone methides and dibenzyl ethers in the cured phenolic resin systems could not be substantiated. The oxidation of phenolic resins was shown to be a stepwise degradation. Attack of oxygen, a surface reaction, was shown to be at the doubly activated methylene bridge linkage to form a substituted dihydroxybenzophenone system. This species was substantiated by the synthesis of polymers containing the ketonic linkage and their spectral identity to the degrading resin. The initial oxidation was shown to continue through the formation of quinone structures and secondary oxidation at these functional linkages to produce carboxylic acids as one of the fragments during chain scission. This degradation mechanism is in good agreement with other supporting experimental data concerning phenolic resin degradation.

Résumé

Un examen spectrophotométrique infra-rouge de la dégradation oxydante de polycondensate phénol-formaldéhyde formés en présence de catalyseurs acides ou basiques,

de novolaques et de résoles, a été réalisé sur une gamme de température de 100 à 200°C. L'existence d'unités structurales telles que des méthides quinoniques ou des éthers dibenzyliques dans les résines phénoliques cuites n'a être prouvée. L'oxydation des résines phénoliques est une dégradation graduelle. L'attaque de l'oxygène qui est en fait une réaction de surface a leiu au pont méthylène doublement activé et forme un système dihydroxybenzophénone substitué. Cette hypothèse a été confirmée par la synthése de polymères contenant la lien cétonique, et dont le spectra est identique à celui de la résine dégradée. L'oxydation initiale continue par la formation de structures quinoniques et parune oxydation secondaire de ces groupes fonctionnels, pour aboutir à la formation d'acides carboxyliques, comme étant un des fragments durant la scission de chaîne. Ce mécanisme de dégradation est en accord avec les autres données expérimentales concernant la dégradation des résines phénoliques.

Zusammenfassung

Eine Untersuchung des oxydativen Abbaus von säure- und basenkatalysierten Phenol-Formaldehyd-Polykondensaten, Novolaken, bzw. Resolen wurde mittels Infrarotspektrophotometrie im Temperaturebereich von loo bis 200°C durchgeführt. Das Vorhandensein von Cinonmethiden und Dibenzyläthern als Struktureinheiten in den gehärteten Phenolharzsystemen konnte nicht sichergestellt werden. Es wurde gezeigt, dass die Oxydation von Phenolharzen ein stufenweiser Abbau ist. Der Sauerstoffangriff, eine Oberflächenreaktion, erfolgte an einer doppelt aktivierten Methylengruppe unter Bildung eines substituierten Dihydroxybenzophenonsystems. Diese Gruppierung wurde durch die Syntheses der Polymeren mit Ketonbindung und deren spektrale Identität mit dem abgebauten Harz nachgeweisen. Es wurde gezeigt, dass die primäre Oxydation unter Bildung von Chinonstrukturen weiterschreitet und dass an diesen funktionellen Bindungen eine sekundäre Oxydation unter Bildung von Carbonsäuren als eines der Bruchstücke einsetzt. Dieser Abbaumechanismus stimmt mit anderen Versuchsergebnissen beim Abbau von Phenolharzen gut überein.