High Temperature Oxidative Degradation of Phenol–Formaldehyde Polycondensates

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Synopsis

The degradation of phenol–formaldehyde polycondensates has been investigated at temperatures as high as 1000°C. By employing infrared spectrophotometric techniques and vapor-phase chromatographic methods, as well as thermogravimetric and x-ray analyses, it has been possible to examine the oxidation chemistry of this resin system. It has been found that the primary degradation route of phenol–formaldehyde polycondensates, regardless of whether the resin is exposed to elevated temperatures in air, argon, or nitrogen, is oxidation. At elevated temperatures, products are observed from thermal pyrolysis in addition to those from the oxidation path. However, throughout the temperature region studied, the oxidative degradation is always more pronounced. The mechanism of oxidation has been found to agree favorably with the proposals formulated earlier by Conley and Bieron. It is also possible to extend this mechanism to include the formation of graphitelike char. This extension is postulated on the simultaneous formation of the char and carbon monoxide. By infrared studies of the intermediate stages in char formation, the postulation that these products arise from quinone-type intermediates is justified. In this study, it was found that phenol–formaldehyde polycondensates of unusual thermal stability could be produced by high temperature postcuring. The comparison of the oxidation rates of the resin cured at low temperature and this material indicates greatly improved oxidative stability, as well as resistance to thermal pyrolysis. This undoubtedly is due to the complete crosslinking of the resin system.

INTRODUCTION

Phenol–formaldehyde polycondensates have been the subject of intensive investigation over the past fifty-year period; however, very little is known concerning the chemistry of this resin system. With the advent of space flight and ballistic missiles, these resins have been used successfully in the ablative heat shields which protect the re-entry vehicle. Since thermal degradation of the polymeric material is part of the process of ablation, a knowledge of the degradation behavior of phenol–formaldehyde polycondensates over a wide range of temperatures would be a valuable aid in the overall understanding of the complex processes that occur during ablation.

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The present program was initiated to investigate the thermally induced reactions of phenol–formaldehyde polycondensates at temperatures as high as 1000°C.

The problem resolves itself into a study of the resin decomposition at elevated temperatures as a function of the heat exposure of the sample. Monitoring chemical changes that occur in the solid phase and compositions studies of the gaseous product mixture seemed the most promising approach to gaining the desired degradation data. Conley and Bieron[1,2] have recently reported the oxidative reactions of phenolic systems at temperatures up to 220°C. In their study, the bulk phase was monitored continuously at the reaction temperature using infrared spectroscopy. This initial study showed that much useful information of both a qualitative[1] and quantitative[2] nature could be gained concerning the changes in polymer structure (i.e., the introduction of new chemical species, etc.). Alternately, Heron[3] has reported that the pyrolytic degradation at elevated temperatures could be studied by using vapor-phase chromatographic techniques.

In addition, thermogravimetric techniques utilized by Heron[3] indicated that the rate of oxidative degradation of phenolic resins increased with increasing oxygen concentration and with decreasing particle size of the initial sample. Heron also observed that the rate decreased as the degradation proceeded. This decreasing rate was attributed to an increase in the stability of the resin. Other studies of a less definitive nature have been reported by Ouchi and Honda,[4] Madorsky and Strauss,[5] and Friedman.[6] In none of these studies[3–6] was a mechanism of degradation accurately established as a function of resin structure. Indeed, the major drawback in almost all previous work has been the complete lack of information concerning the nature of the cured resin system immediately prior to thermal exposure.

In view of this difficulty, it was pertinent to investigate by a variety of techniques the chemistry of the resin system at elevated temperatures. Infrared spectroscopy, vapor-phase chromatography, thermogravimetric analyses, and x-ray diffraction studies were deemed most appropriate for the evaluation of solid- and gas-phase compositions at the various intervals of thermal exposure. It was hoped that this information could be correlated to more conclusively establish the high temperature degradation processes encountered in phenol–formaldehyde polycondensate systems.

EXPERIMENTAL

The resin samples were prepared from reagent grade phenol and formaldehyde by the procedure described by Conley and Bieron[1] for a typical base-catalyzed phenolic resin. The cure time used for the resin samples was generally 3 hr. at 120°C. The curing atmosphere for the resin was: (1) high vacuum (10^{-5} torr), (2) air, and (3) inert atmosphere (argon). The exact method of resin curing varied for a number of samples and will be noted in each of the relevant cases.

Infrared Studies

Resin samples were cured directly on polished salt plates. The cured resins were examined with either a Perkin-Elmer Model 21 infrared spectrophotometer or a Beckman IR-5A infrared spectrophotometer. Both instruments were equipped with sodium chloride optics. After the plates were subjected to various temperatures for a prescribed interval of time, the solid residues on the plates were examined spectrophotometrically. In addition, residues from the pyrolysis studies, involving vapor-phase chromatography studies of volatile product mixtures, were also examined by infrared spectroscopy for functional group changes.

Vapor-Phase Chromatographic Studies

The liquid resin was cured in a 0.035-in. diameter, 0.625-in. long capillary tube at 120°C. in air for 3 hr. The resin was then removed from the capillary, weighed, and inserted into a quartz capillary tube. This tube was inserted into the coiled nichrome ribbon and the whole assembly placed
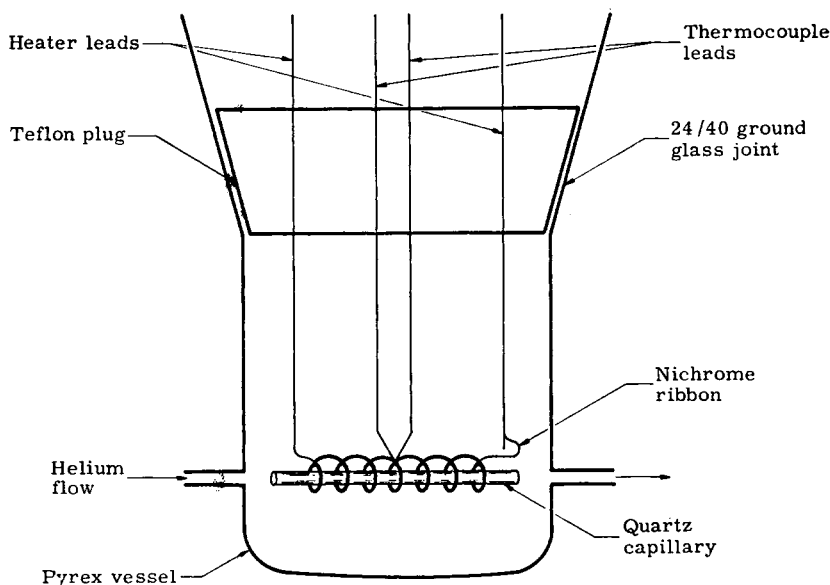

Fig. 1. Pyrolysis chamber.

into the pyrolysis chamber (Fig. 1). The pyrolysis chamber was wrapped with heating tape and allowed to come to thermal equilibrium while being purged with helium. The desired temperature of the run and the heating time were set on the pyrolysis control unit and current was then applied to the ribbon. A F & M Model 500 vapor-phase chromatograph was used to separate the products of degradation. Two columns were used: a Carbowax 1500 column for the condensable products such as benzene, toluene,

and cresols, and a molecular sieve 5A column for the noncondensable products (CH_4, CO, CO_2).

Figure 2 exemplifies, in block diagram form, the complete chromatographic apparatus: the pyrolysis chamber (Fig. 1), the pyrolyzer control, and the inlet heater. The inlet heater was an adaptation of the F & M fraction delivery apparatus. This heater was added to the apparatus to prevent condensation of the reaction products in the inlet line to the chromatograph. The pyrolyzer control unit is unique for studies of this type. A block diagram and the complete schematic of the time–temperature controller are shown in Figures 3 and 4. This unit controlled the temperature of the nichrome sample heater by the use of a feedback circuit. The control
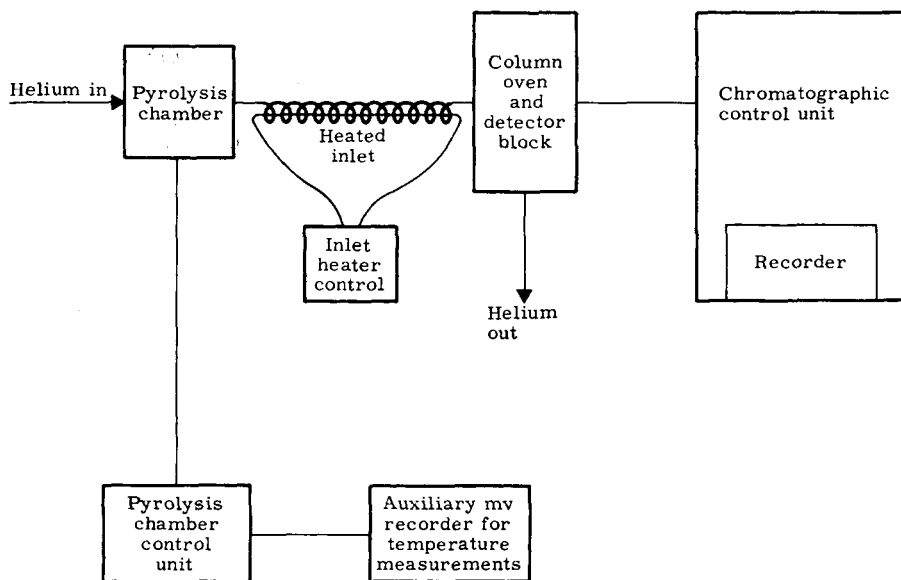

Fig. 2. Chromatographic arrangement.

signal was taken directly from a thermocouple touching the nichrome ribbon. The output of this thermocouple also actuated a millivolt potentiometric recorder so that the temperature of the ribbon could be accurately recorded. The ribbon achieved control temperature within 2 sec. at temperatures up to 800°C. At lower temperatures, there was some overshoot, but a temperature plateau was reached within 3 sec. Figure 5 indicates this temperature rise as a function of time for both a low temperature and a high temperature run. From the linear portion of the high temperature curve, a maximum heating rate of 310°C./sec. was calculated. It can be shown, using the method described by McAdams[7] and known values of the thermal conductivity, density, and specific heat, that the maximum time required for the phenolic to achieve 99.9% of its final temperature is 2 sec. In this calculation, it was assumed that the thermal conductivity was in-
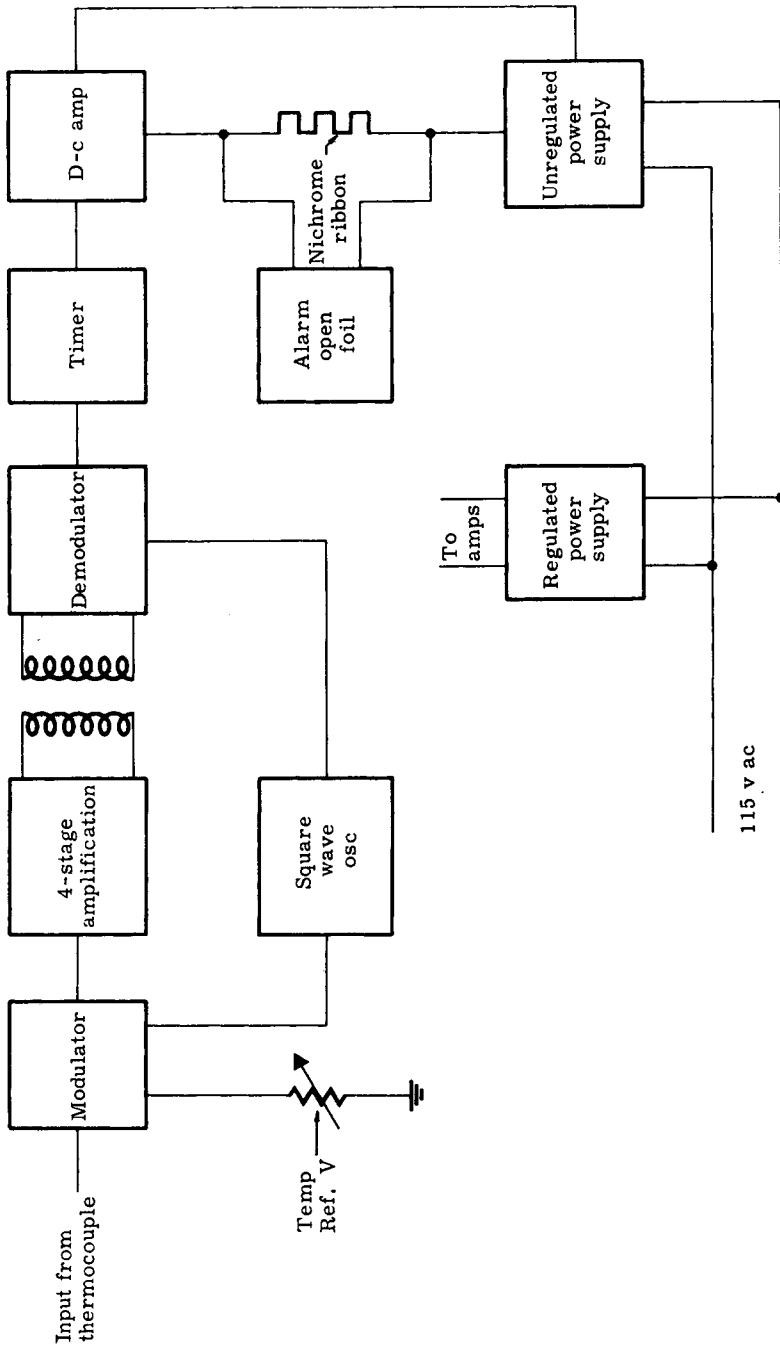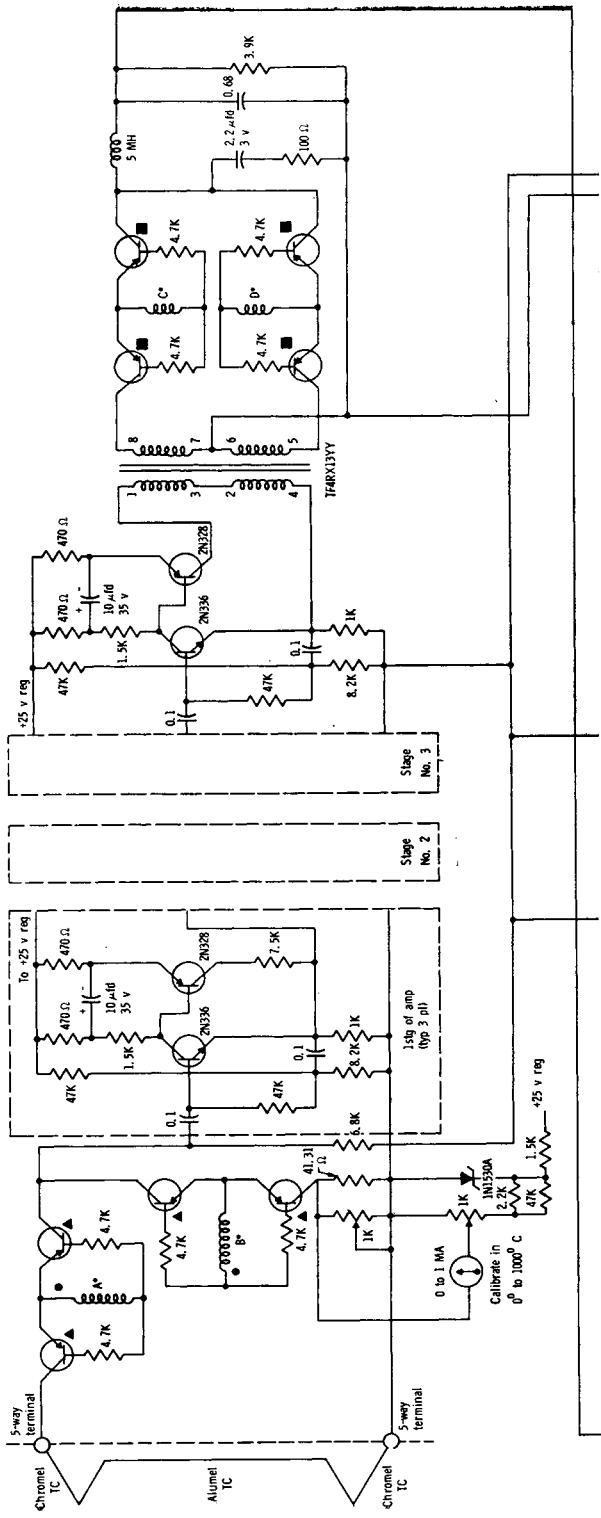
Fig. 3. Time–temperature controller.

Fig. 4. Wiring diagram for time–temperature controller. All capacitors in microfarads unless otherwise noted; all resistors ½ W, 5% unless otherwise noted. (▲), (■) matched 2N527; (*) secondary windings of square wave oscillator transformer.
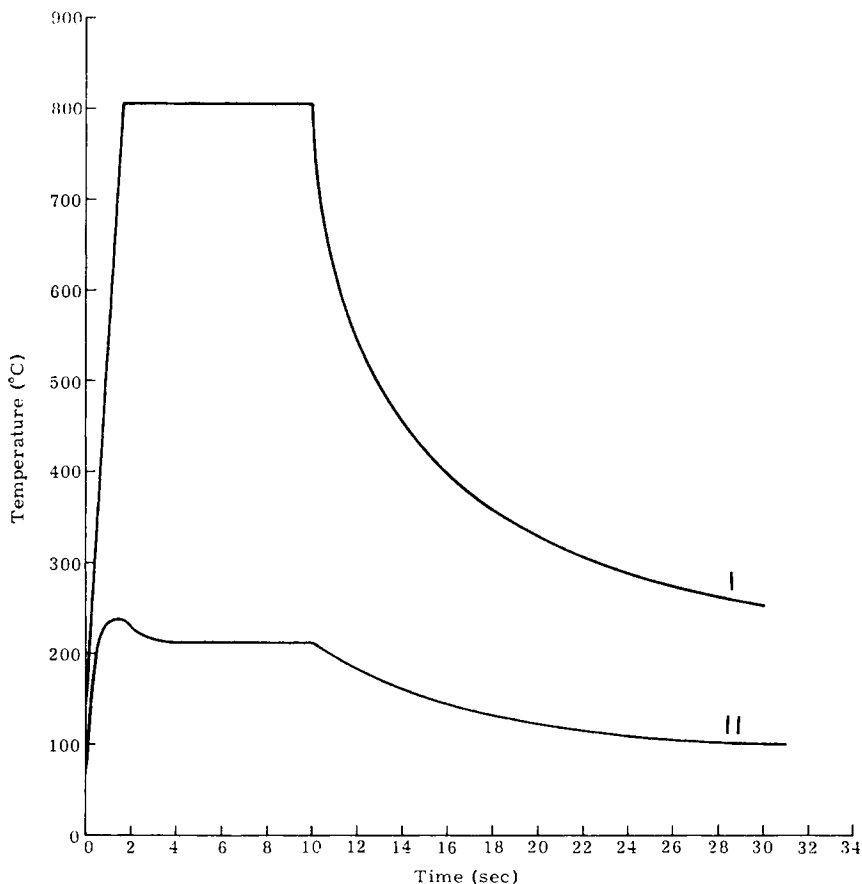
Fig. 5. Temperature of pyrolysis chamber heater versus heating time: (I) high temperature run; (II) low temperature run.

dependent of temperature, whereas, in fact, it increases with increasing temperature. This will tend to make the time even less than 2 sec.

The resin was heated and held at a constant temperature for a total time of 10 sec. in the helium gas stream; at the end of this time, the current to the ribbon was cut off. It took approximately 7 sec. for the sample to cool to one-half of the temperature of the flat portion of the heating curve. The residue was then taken out of the capillary tube and weighed.

The products formed during the pyrolysis of the resin were separated on the chromatographic column. Figure 6 shows a typical chromatograph of the noncondensable pyrolysis products. The peaks were identified on the basis of their retention time. Figure 7 shows a typical chromatograph of the condensable products. The first peak in Figure 7 was assigned to the total noncondensable products, since the retention time for this peak represents the dead time of the chromatograph. The second and third peaks were identified as benzene and toluene on the basis of their retention time.
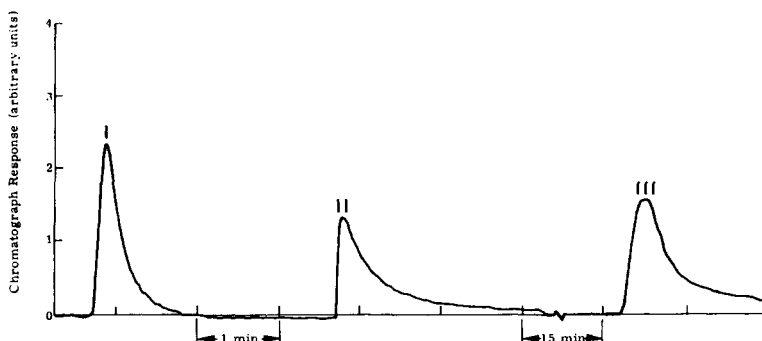
Fig. 6. Chromatograph of a pyrolysis run on a molecular sieve 5A (30/60 mesh) column: (I) CH_4; (II) CO; (III) CO_2. Column conditions: $1/4$-in. diameter $\times$ 12 ft. copper tubing; block temperature 240°C.; injection port temperature 255°C.; initial column temperature 50°C.; chart speed 1 in./min.; helium flow rate, 100 cc./min.; helium back pressure, 55 psi; bridge current 100 ma.; program rate 7.9°C./min.
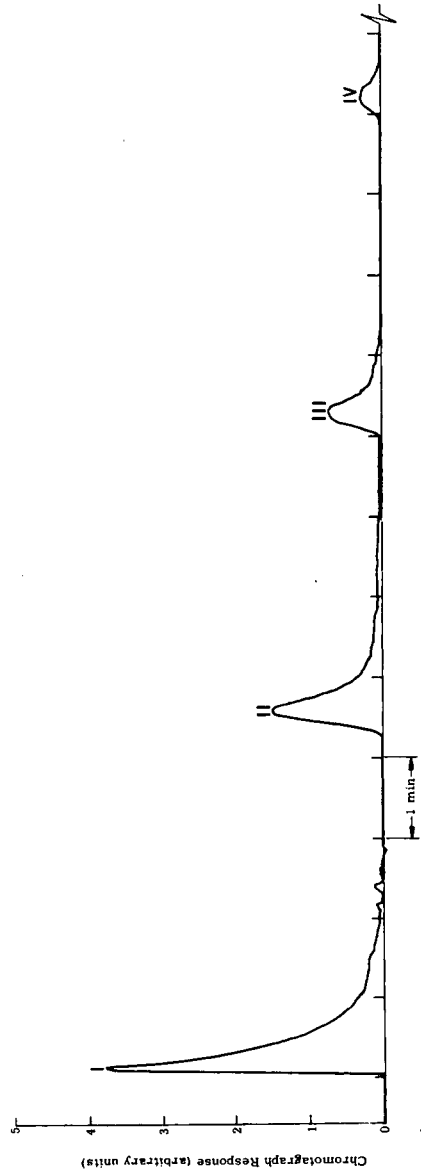
Water and paraformaldehyde were identified both by retention times and by infrared analysis of the trapped material and were associated with the broad peak that exhibits tailing. The peak preceding the o-cresol–phenol peak has not been positively identified because of the inability to trap a sufficient quantity of material for infrared analysis. It is likely that the peak is 2,4-dimethylphenol based on a comparison of retention time with that of an authentic sample. The o-cresol and phenol peak was identified both by infrared analysis and by its retention time when compared with pure phenol and o-cresol samples and various mixtures of these materials. Infrared analysis of the final peak suggested that it was a mixture of p-cresol, and some other cresol or xylenol-type material.

Of the observed weight loss in a sample, 50% could be accounted for on the basis of the total amount of phenol, o-cresol, p-cresol, carbon monoxide, carbon dioxide, methane, benzene, toluene, and benzaldehyde detected. The remaining 50% was due to water and paraformaldehyde and a high molecular weight, nonvolatile residue. The water and paraformaldehyde have been identified qualitatively, but no quantitative measure of their weight has been made. Visual observation of the reaction cell after degradation revealed a yellow nonvolatile residue, confirming that part of the unaccounted weight was due to a high molecular weight nonvolatile residue

RESULTS AND DISCUSSION

Resin Curing and High Temperature Postcuring Studies

Examination of the infrared spectrum of the resin samples deposited on a. salt plate from acetone solution prior to curing is shown in Figure 8. Of particular interest is the absence of absorption bands at 6.03, 5.94, and 5.85 μ; these have been assigned to absorption by benzophenone-type carbonyl linkages, quinone-type carbonyl groups and carboxyl carbonyl species, re-
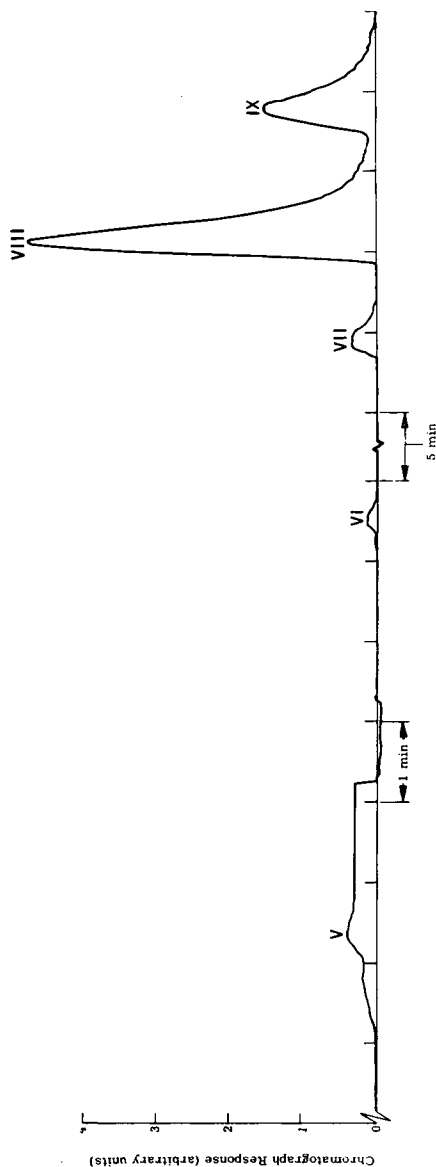
Fig. 7. Chromatograph of a pyrolysis run on a Carbowax 1500–25% by weight Chromosorb P (60/80 mesh) column: (I) noncondensables; (II) benzene; (III) toluene; (IV) unidentified; (V) water and paraformaldehyde; (VI) benzaldehyde; (VII) 2,4-dimethylphenol; (VIII) phenol + o-cresol; (IX) p-cresol. Column conditions: $1/2$ in. diameter × 12 ft. copper tubing; block temperature 230°C.; injection port temperature 222°C.; initial column temperature 50°C.; chart speed 1 in./min.; helium flow rate 100 cc./min.; helium back pressure 55 psi; bridge current 100 ma. Program procedure: hold temperature constant for 6 min. after injection at 50°C. then program at 5.6°C./min. to 200°C. and hold temperature constant until analysis is over.
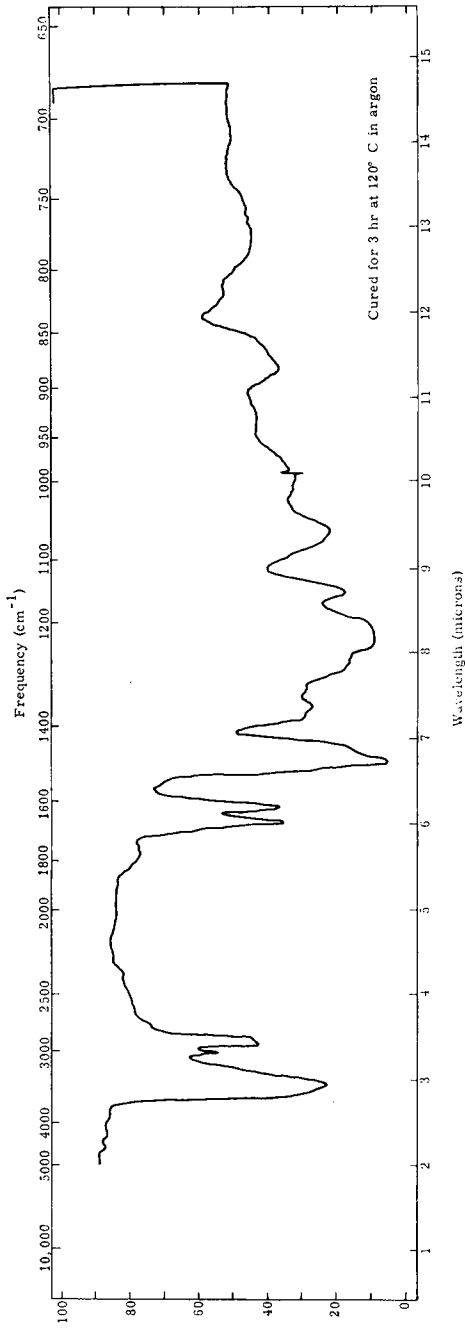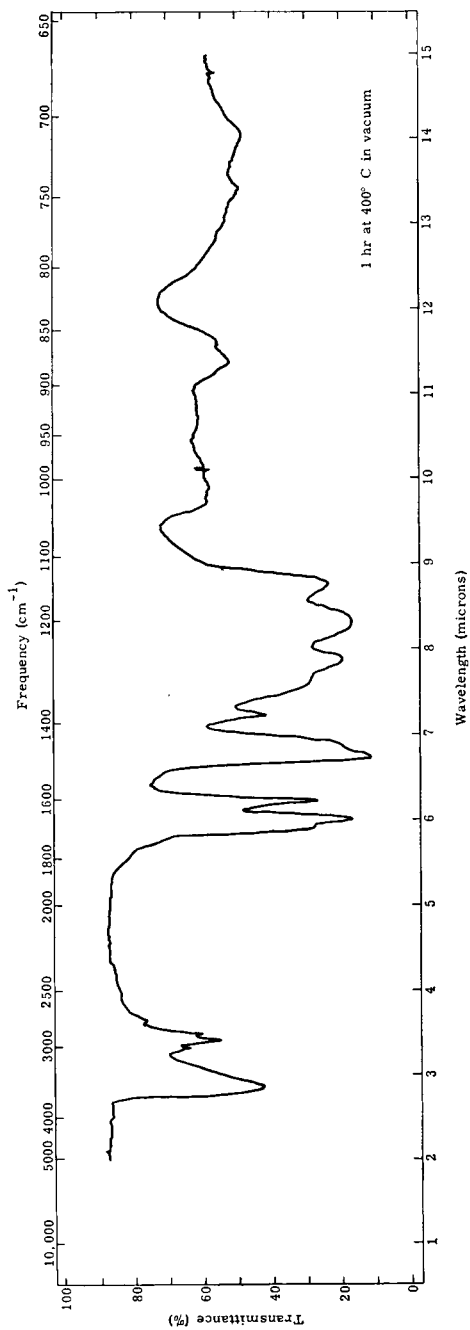
Uncured—3 days at room temperature
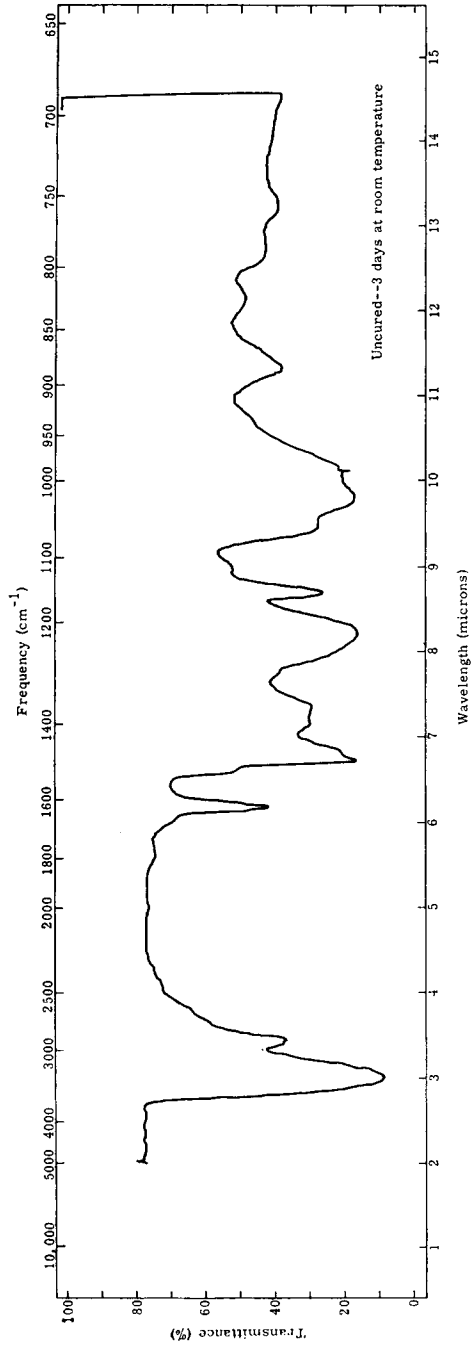
Fig. 8. Infrared spectrum of a typical phenolic resin prior to and after cure.

1 hr at 400° C in vacuum
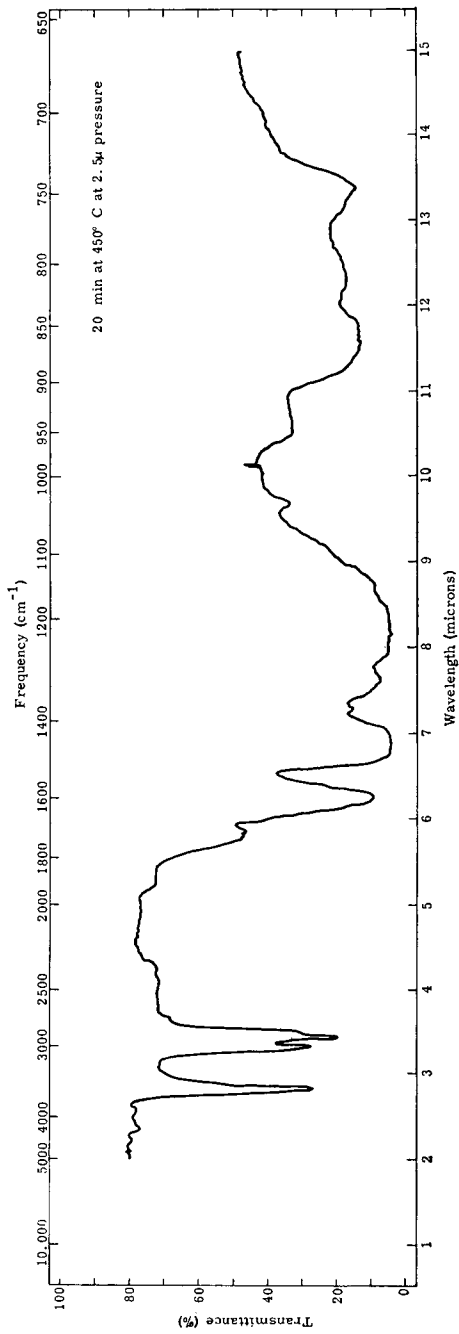
Fig. 9. Infrared spectrum of a typical phenolic resin after high temperature exposure.
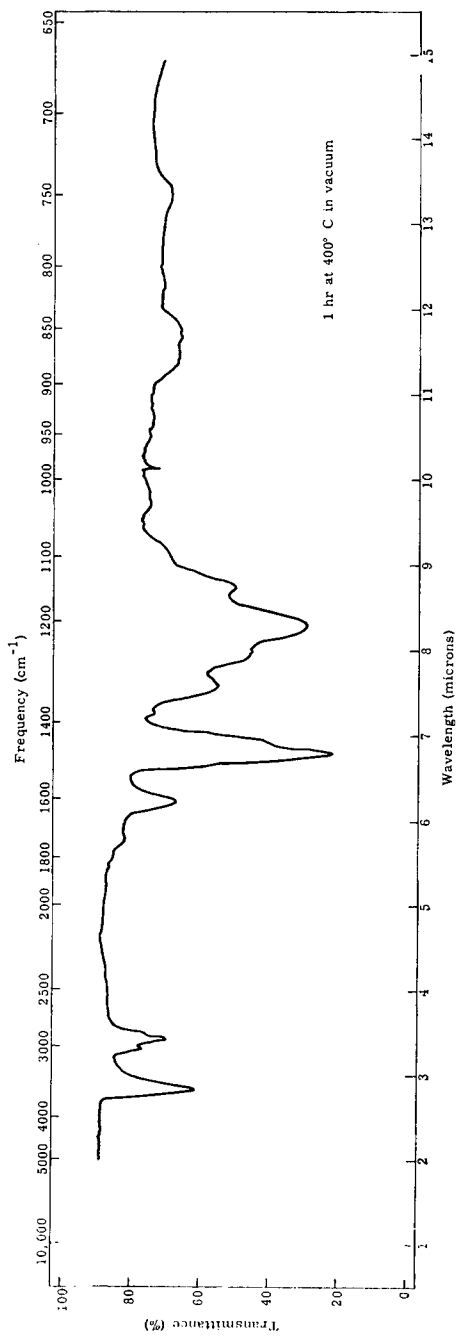
3 hr at 120° C in vacuum
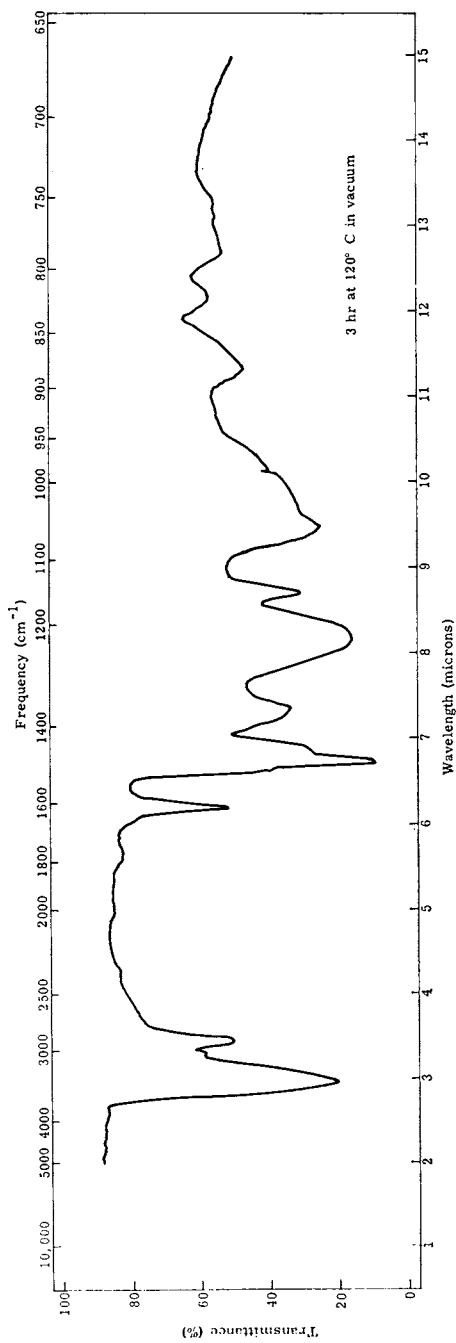
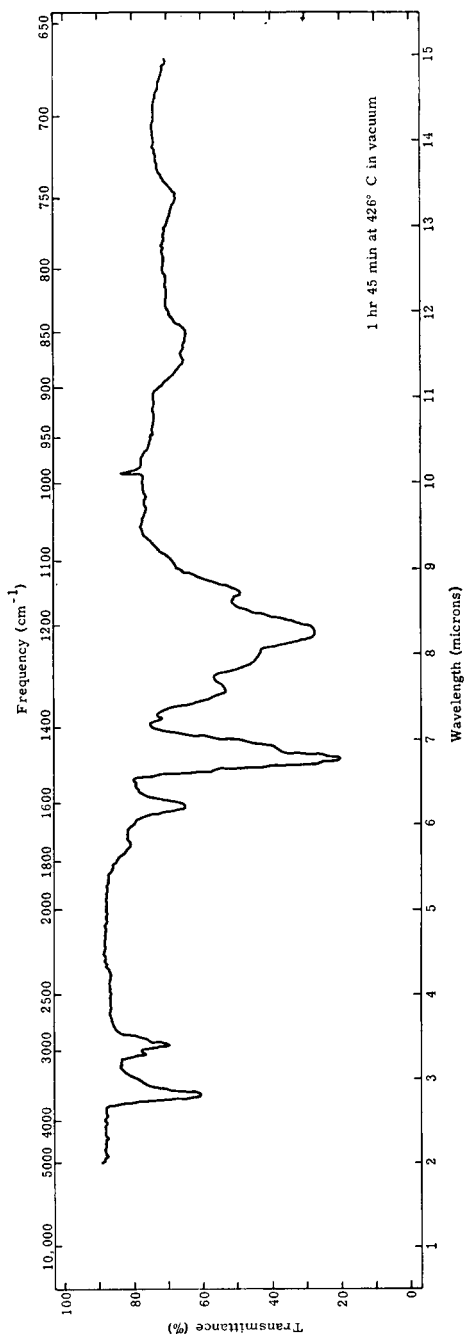Fig. 10. Infrared spectrum of a nonoxidized phenolic resin.

Fig. 11. Infrared spectrum of a nonoxidized phenolic resin after 426°C. exposure.
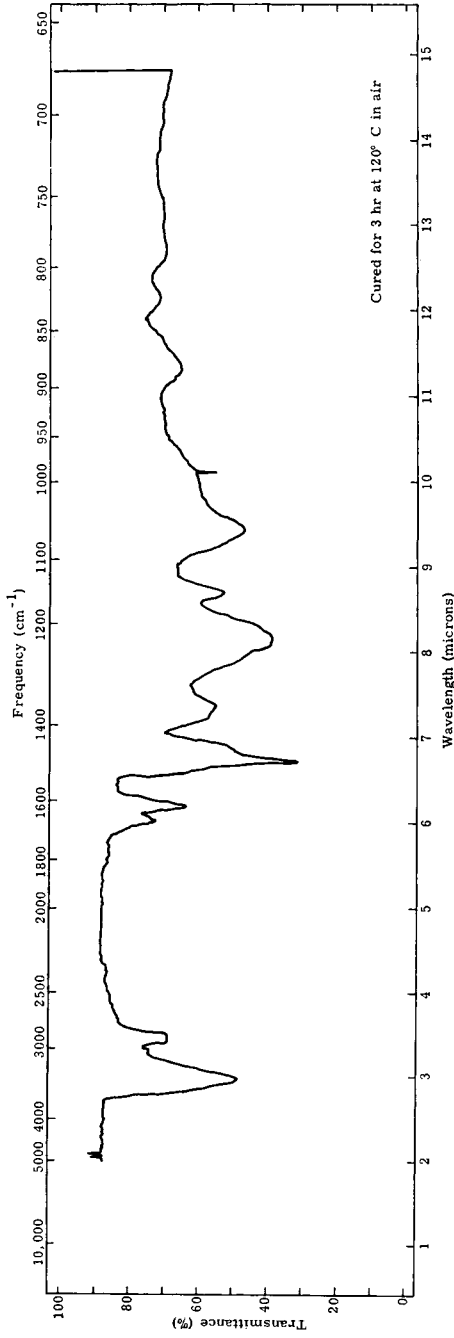
Fig. 12. Infrared spectrum of a typical-air-cured phenolic resin.

spectively.[1] These bands are generally formed from oxidation of the resin, either during its preparation or from exposure to an oxygen-containing atmosphere for extended periods at slightly elevated temperatures. After three days at room temperature in air, no detectable oxidation was evidenced from examination of the infrared spectrum. The absorption band at 9.45 μ, assigned to the hydroxyl group bending mode of the methylol group ($-CH_2OH$), was taken as evidence for the degree of curing the sample had undergone. Complete disappearance of this band would be indicative of the absence of the methylol species, either from extended condensation during the curing cycle, or from oxidation of these groups to carboxyl species during the curing process.

After curing for 3 hr. at 120°C., either in a stream of high purity argon (99.95%) or under high vacuum (10^{-5} torr), oxidation was observed in almost every sample. The spectrum (Fig. 8) showed a rather strong band at 6.03 μ resulting from methylene group ($-CH_2-$) oxidation to benzo-

phenone ($\overset{|}{\underset{|}{C}}=O$). The initial oxidation mechanism prior to carbonyl formation (in the absence of external oxygen) is not known. However, it was established that the presence of water, produced from further condensation during the curing process and the absorption of oxygen and water from the air by predried samples, markedly affects the rate of growth of the ketonic carbonyl group.

Further heating of the resin at higher temperatures in inert atmospheres resulted in condensation (postcuring) and oxidation of the resin. During the postcuring period, the 9.45 μ band due to methylol groups was markedly reduced, as shown in Figure 9. In addition to the condensation step, increased oxidation at the 400°C. temperature has taken place. For example, the quinone-type carbonyl band at 5.94 μ has increased in intensity and a broadening of the 3.0–4.0 μ region, together with a weak shoulder on the 5.94 μ band (indicative of the formation of carboxylic acids), has appeared. These reactions are indicative of extended oxidation from within the resin sample, since oxygen was carefully excluded from the sample during this heating process. Oxygen contamination by absorption at room temperature seems an unjustified explanation of this phenomenon. Treatment of the resin samples at even higher temperatures resulted in a general broadening of the bands from 6 to 14 μ due to scattering of the infrared radiation during the initial stages of char formation. Comparison of the two spectra shown in Figure 9 indicates remarkable differences in the residual solids as the temperature is increased above 400°C. Considerable loss of hydroxylic components, causing a narrowing and sharpening of the hydroxyl frequency, is evident. In the curve obtained by scale expansion of the residual solid, (bottom spectrum, Fig. 9), loss of aliphatic methylene, as compared with aromatic ring carbon-hydrogen vibration, is evident, along with additional amounts of carboxylic acid.

Freshly prepared resin samples, when filmed and cured in vacuum, would

give an occasional nonoxidized resin film, but, in general, these samples were difficult to prepare. In concurrent studies, low temperature curing (below 150°C.) nonoxidized samples, although obtainable routinely in oxygen-free nitrogen atmospheres with the aid of special curing apparatus,[1,2,8] readily oxidized at elevated temperatures (above 200°C.) in the absence of oxygen-containing atmospheres. Figure 10 shows a typical nonoxidized sample which, after postcuring at 400°C. in vacuum, showed no sign of appreciable oxidation. Infrared examination of the volatile components condensed on the walls of the vacuum tube used as the curing oven revealed the presence of oxidized species of relatively high molecular weight (dimers, etc.), indicating that, while oxidation is taking place under all curing conditions, an oxidation-free residual cured resin can, in some instances, be attained. This observation would tend to support the surface oxidation phenomena reported earlier,[2] together with the additional volatilization of fragments under the specific curing conditions employed. Figure 11 indicates even more severe treatment of the nonoxidized sample (1 hr. and 45 min. at 426°C.). The only changes which can be noted in the spectrum are the loss of the methylol group vibration and a decrease in the hydroxyl group vibrations subsequent to treatment at 400°C. for 1 hr. These data tend to point out the remarkable thermal stability of the completely cured, nonoxidized resin. If the initial oxidative reaction could be bypassed or eliminated by appropriate curing and postcuring techniques, the overall thermal stability of the phenolic resins could be improved.

Since oxidative degradation was not consistently prevented, the high temperature degradation studies were carried out on air-cured resins. In all cases, these resins were oxidized on curing to a small extent, as indicated in Figure 12, by the ingrowth of the carbonyl band at 6.03 μ. The phenolic rods used for gas chromatographic studies were cured in air in an identical fashion. Potassium bromide pellets of powdered resin samples were examined spectrally and found to exhibit comparable preoxidation prior to high temperature exposure. It should be noted that previous studies[3-6] have overlooked the initial preoxidation of phenolic resin samples. Indeed, it can be shown (see section on high temperature degradation studies below) that the degradation products differ due to the technique used in resin sample preparation.

High Temperature Degradation Studies

In screening the techniques available for gaining information as to the extent of degradation to volatile products, it was of interest to compare the weight loss determined by thermogravimetric analysis (TGA) and that loss in weight which occurred under the high heating rates (310°C./sec.) described in the experimental section for the vapor phase chromatographic analyses. As can be seen in Figure 13, these curves vary considerably. At the low temperature portion of these curves (0 to 250°C.), the weight loss for the 310°C./sec. heating rate is considerably lower than for the corre-
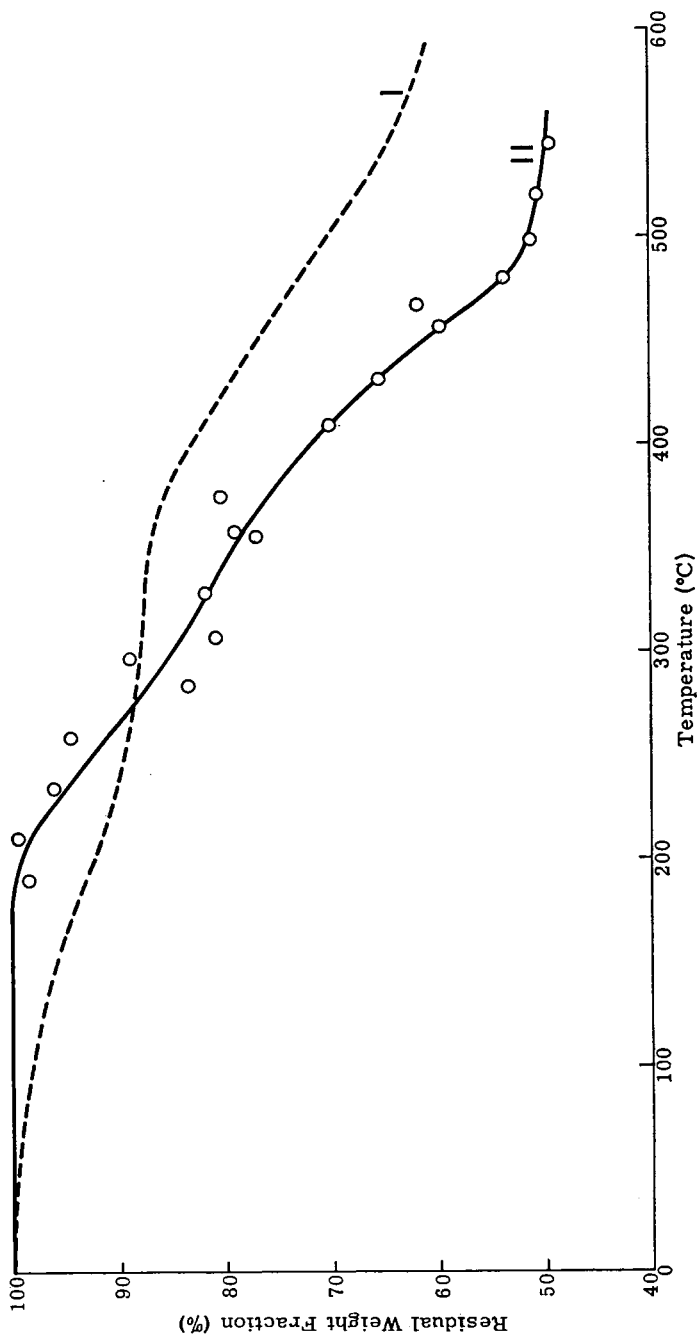
Fig. 13. Weight loss curves for phenolic resin in inert atmosphere: (*I*) heating rate = 0.05°C./sec. (thermogravimetric analysis); (*II*) heating rate ≈ 300°C./sec. to indicated temperature and held at temperature for a total exposure of 10 sec.; (○) determined by weighing the residue at end of run.
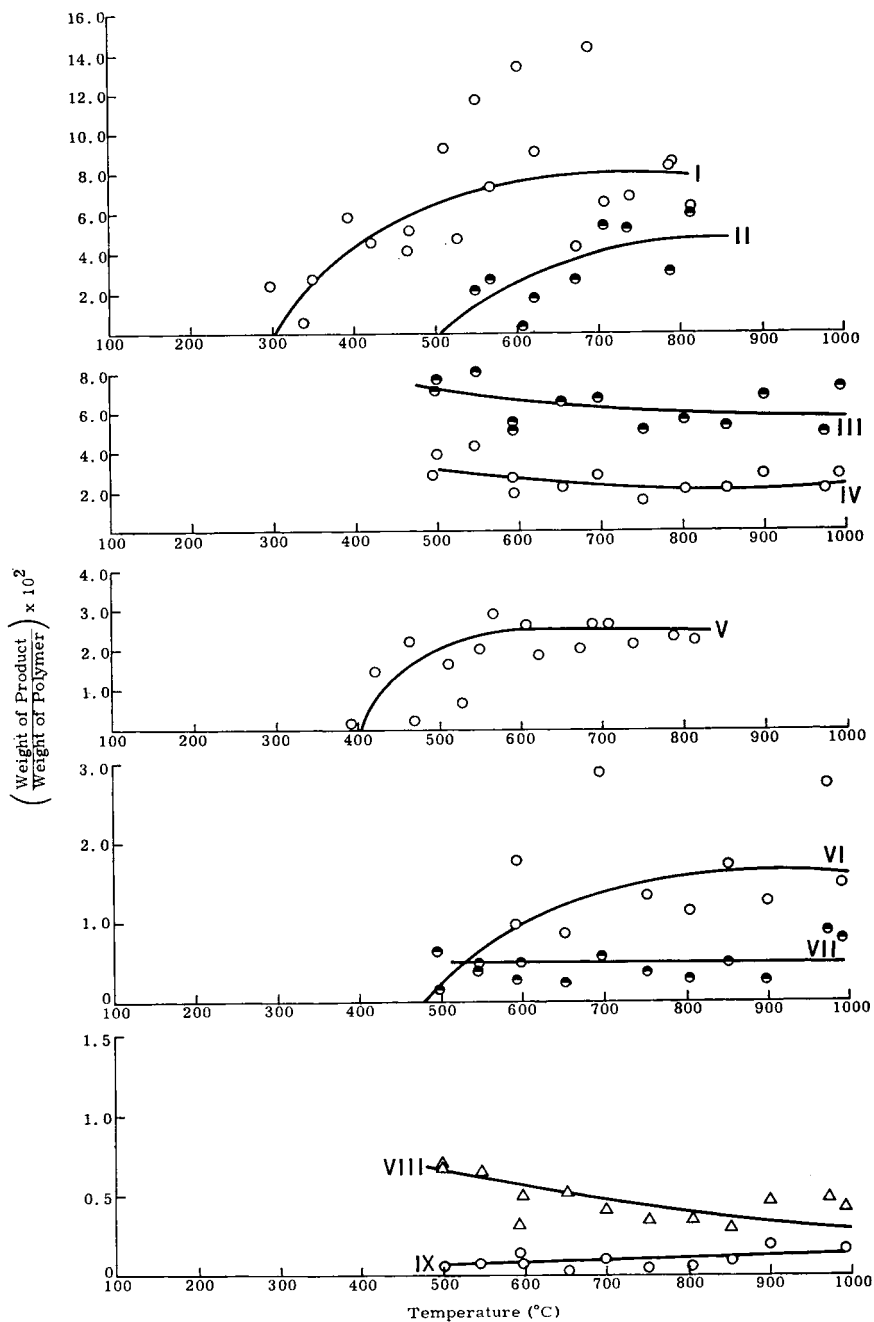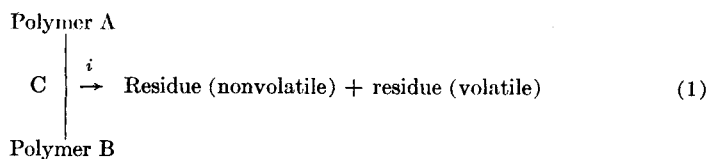
Fig. 14. Variation in pyrolysis product formation with pyrolysis temperature: (*I*) CO_2; (*II*) CO; (*III*) phenol + *o*-cresol: (*IV*) *p*-cresol; (*V*) CH_4 ; (*VI*) benzene; (*VII*) toluene; (*VIII*) 2,4-dimethylphenol; (*IX*) benzaldehyde.

sponding TGA curve.   This is consistent with a generalized mechanism for weight loss which can be depicted as shown in eq. (1):

Polymer A

$$C \quad \overset{i}{\to} \quad \text{Residue (nonvolatile)} + \text{residue (volatile)} \tag{1}$$

Polymer B

where polymer A is the starting cured resin, polymer B is the postcured material, i is the number of reaction steps required to produce the residue products and determined by the temperature and molecular weight of the polymer, and C is extended condensation (postcuring).   Weight loss at low heating rates would be expected to be greater than that observed at higher heating rates if diffusion of material of high volatility (low molecular weight) is the mechanism controlling weight loss.   At higher heating rates, the volatile species would be expected to undergo thermally induced postcuring reactions (C) since they would not have time to diffuse out of the solid matrix.   At high temperatures (300–600°C.) and high heating rates, more of the residue from polymer A is volatilized as it degrades thermally, hence, a larger overall weight loss.   The high heating rate weight loss curve was terminated at 600°C. because internal stresses occurring above this temperature caused powdering of the sample.   This, in turn, led to large errors in the determination of the weight losses.   It should be noted here that the TGA measurements of total weight loss, when compared with the high heating rate situations (such as encountered in re-entry problems) give residues of a higher weight.

   The most significant portion of this study resulted from the study of the volatile degradation products summarized in Figure 14 as a function of temperature and amount of pyrolysis product produced.   The products, as expected for the extended oxidation of the resin, consisted chiefly of carbon dioxide and carbon monoxide.   Water, paraformaldehyde, methane, and aromatic products were also formed, although all of the weight loss cannot be accounted for by the products listed.   Residues which were volatilized from the sample as a result of the degradation were detectable in the walls of the pyrolysis vessel and in the heated lines to the chromatograph.   Products reported by Heron,[3] Ouchi and Honda,[4] Madorsky and Strauss,[5] and Friedman[6] included propanol, propylene, ethane, and ethylene.   Vapor-phase chromatographic attempts to detect these products, as well as the presence of hydrogen, as reported by Ouchi and Honda,[4] failed even after extended work under conditions which normally detect such materials.   It is likely that these investigators worked with phenolic resins from commercial sources which contain propanol as a solvent.   The thermal decomposition of entrapped solvent would adequately account for the observed differences in degradation products.   Since the resins prepared in this study were cured under carefully controlled conditions to remove all solvents and ex-

amined thoroughly by spectrophotometric methods for contamination, this conclusion seems reasonable.

Water and paraformaldehyde were among the major products formed on heating the phenolic resin to 400°C. Quantitative data were not obtainable, due to difficulties encountered in peak resolution and calibration of the chromatograph. It is estimated that these products were present in the same order of magnitude as the 2,4-dimethylphenol (Fig. 14). In order to correlate these results to earlier work,[1] it should be pointed out that neither of these products appeared in significant quantities below 400°C. Therefore, they are products of high temperature resin reactions and are not present as impurities in the resin sample. The infrared studies discussed in the previous section indicated they result from the loss of methylol groups in this temperature range. It is consistent to propose the reaction sequence shown in eq. (2) to account for the formation of these products.


$$(2)$$
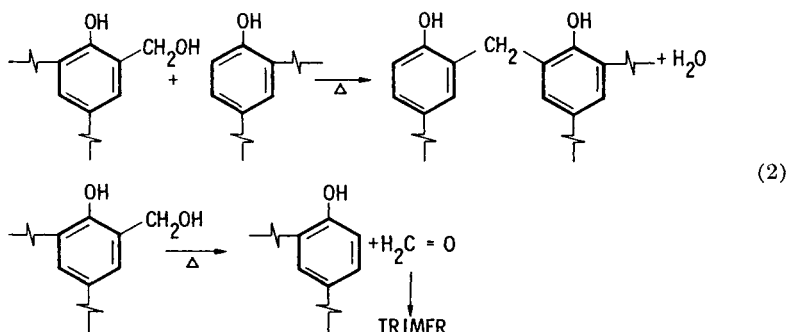
This mechanism is in contrast to the mechanism proposed by Ouchi and Honda,[4] shown in eq. (3), for which we have been able to gain no experimental verification. The present proposal has the advantage of consistency with the observed loss of methylol groups and the lack of detectable diphenylether linkages in the infrared spectra in both this study and in the initial lower temperature degradation studies.[1,2]

$$(3)$$
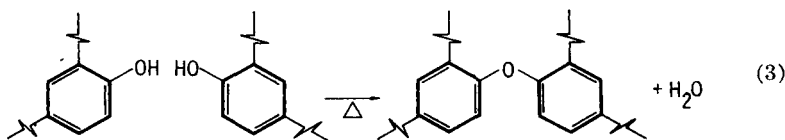
If one considers the possible modes of production of products from the data summarized in Figure 14, two processes are seemingly in competition as the temperature is increased. In all cases, oxidation, as evidenced by the production of carbon dioxide and carbon monoxide, is the predominant reaction route. It is known from the infrared data that the initial cured resin contains methylene linkages, appreciable amounts of residual methylol groups, and dihydroxybenzophenone linkages from oxidation during curing. The variations in the relative amounts of these species, together with the

additional amounts of dihydroxybenzophenone linkages from further methylene oxidation and substituted salicylic acid moieties from methylol oxidation, as shown in eqs. (4) and (5), would tend to account for the large degree of scatter observed in the data reported for carbon dioxide and carbon monoxide formation.   Since the number of reactions producing these products becomes increasingly complex as the temperature is increased and adequate experimental control of the individual concentration of each species is nearly impossible, more accurate results, at the present, seem to present an insurmountable task in analysis of this resin system.

$$(4)$$

$$(5)$$
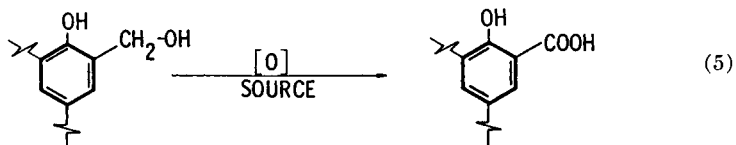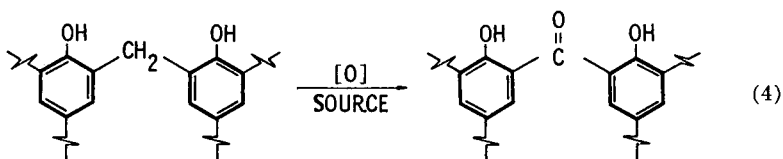
Despite the difficulties encountered in the analysis of carbon dioxide and carbon monoxide, the formation of aromatic products, which presumably arise from a radical bond rupture reaction sequence, shows much less scatter in the individual data points.   Since these products are produced in smaller amounts, and the concentration of the initial reactants is more constant (since these species comprise the bulk of the resin sample) the observed deviations might be expected to be decreased considerably.   A comparison of the data obtained indicates that only benzene and toluene show significant scattering in their respective product yield determinations.

The additional reactions proposed to account for the formation of the observed products are indicated in Figure 15.

From the initial oxidation reactions of eqs. (4) and (5), supported by the infrared data and previous work,[1,2] it is possible to extend the degradation reaction sequence to account for all of the observable products.   Route I, Figure 15, summarizes the oxidative degradation processes in generalized form.   Particular substitutions of methylene and hydroxyl are not indicated. This is done for reasons of simplicity and because the choice between the various substituted species, insofar as degradation differences are concerned, has not been possible.   The second route (route II, Fig. 15) indicates the formation of phenol, cresol, and other methyl-substituted species, together with methane.   It should be noted that the formation of methane occurs in increasing amounts above 400°C., whereas the other species of a cresol and xylenol type are generally found in relatively constant amounts or even in slightly decreasing amounts, as the temperature increases.   Ben-

I

II

CH$_3$· $\xrightarrow{\quad\text{CH}_2\quad}$ CH$_4$ + CH·

III

OR HIGHER
HOMOLOGS

Route I   Oxidative Degradation Processes
Route II   Fragmentation Reactions
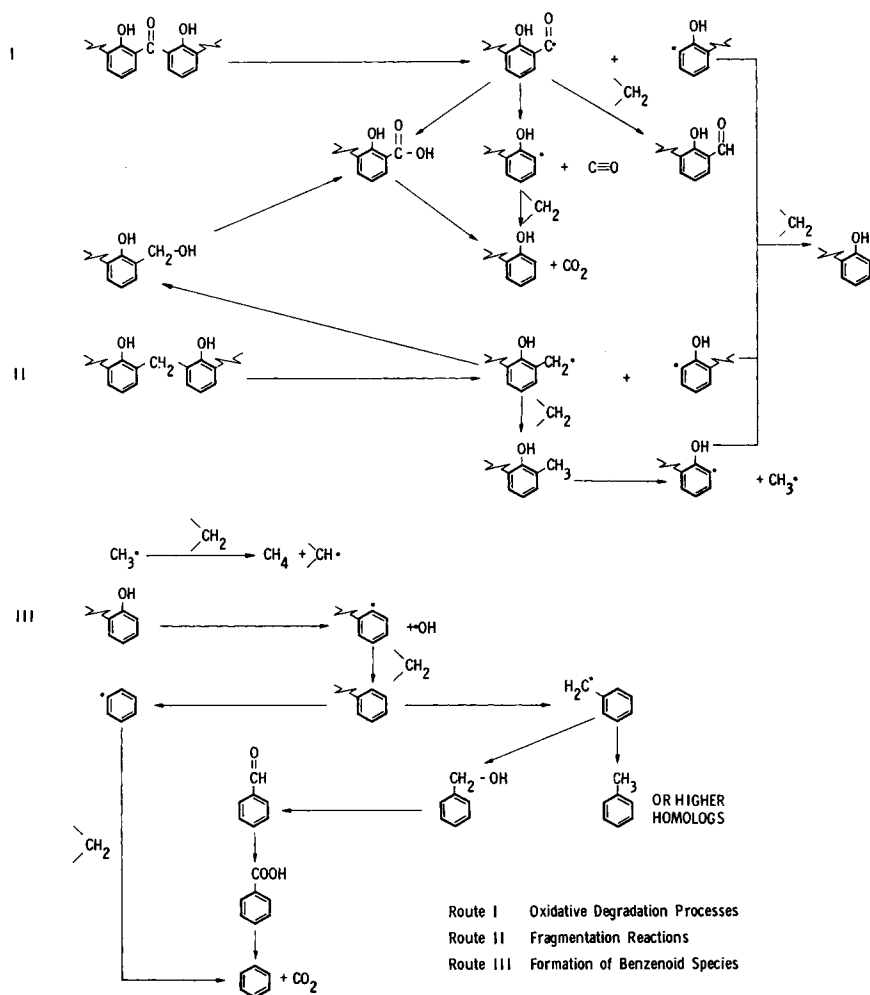Route III Formation of Benzenoid Species

Fig. 15. Typical reactions proposed for resin decomposition at elevated temperatures. (Route I) oxidative degradation processes; (Route II) fragmentation reactions; (Route III) formation of benzenoid species.

zene, toluene, and benzaldehyde are of particular interest in this respect, since the loss of hydroxyl from the aromatic ring is a necessary requirement for the formation of these materials (route III, Fig. 15).   The hydroxyl radical, in turn, would represent a source of oxygen for further oxidation reactions and, as well, a source of water through hydrogen extraction from any available methylene linkage.   In none of these reactions does the hydrogen atom become significantly available for combination to form the hydrogen molecule.   Therefore, it seems unlikely that the hydrogen observed in previous work[4] was produced from the phenolic resin system.   Further substantiation of this seems to be borne out in the observation of methane,

which is apparently formed via a hydrogen abstraction process by methyl radicals. The radical concentration is never high enough to recombine to form ethane. The oxidation reactions shown in Figure 15 are consistent with the formation of the two initial reactants proposed in eqs. (4) and (5). The decarboxylation and decarbonylation to form carbon dioxide and carbon monoxide are consistent with the respective temperatures at which each product begins to appear. The remaining reactions are generalized to show the formation of phenol, cresols and higher phenolic species. Since these materials are produced at the lower temperatures in appreciable amounts, it is doubtful that they arise from the nonoxidized, postcured resin. Most likely these products are formed from dihydroxydiphenylmethane and slightly higher homologs (low polymer which has been terminated) entrapped in the cured resin system.

Char Formation

The char-forming reaction shown in eq. (6) is best explained through the initial formation of a quinone-type linkage. The production of this linkage during degradations of phenolic systems is known from infrared studies.[1] At temperatures above 450°C., decomposition to produce char and carbon

$$(6)$$
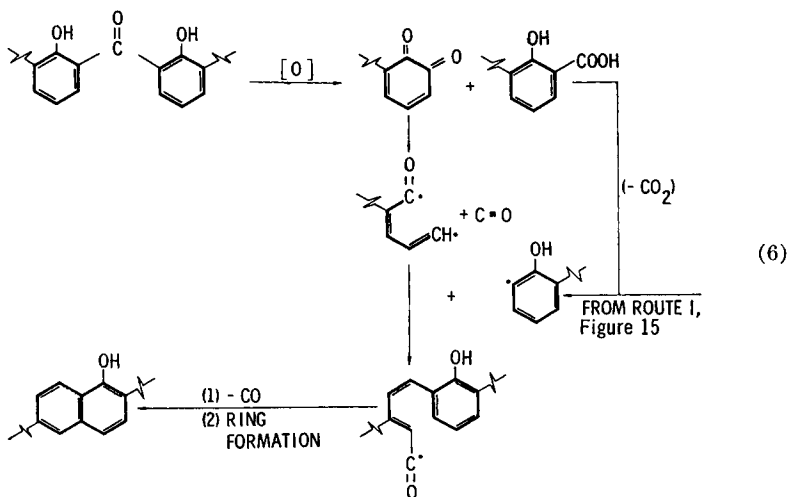
monoxide, via ring scission, is rapid. This is supported by the observation that the carbon monoxide expected from this degradation does not appear at lower temperatures. Further, in this temperature range, carbon char is found in the residual products of the degradation. The char formation is first detected visually and substantiated for materials heated to higher temperatures (600°C.) by the presence of a graphite-like line in the x-ray pattern of the residues. This reaction also accounts for the observation of hydroxyl and carbonyl groups at 700°C. in the charred material.

An interesting aspect of the present work is that, at no point up to temperatures of least 500°C. is it necessary to invoke thermal nonoxidative degradation of the completely cured, nonoxidized, crosslinked polymer (post-cured polymer).   This is consistent with the observed fact that the post-cured polymer shows no change in its infrared spectrum after prolonged heating to 450°C. in vacuum.   The postcured polymer has been shown to have a higher oxidative stability than the nonpostcured, partially oxidized resin.   For example, it has been shown previously[2] that the rate constants, as determined by infrared spectrophotometric monitoring of the ingrowth of benzophenone carbonyl groups, are quite large.   In contrast, rate constants obtained on nonoxidized samples from this study (using the same method), cured at 450°C. in high vacuum, are considerably smaller (a factor of roughly 33).   This comparison is summarized in Table I.   For the non-oxidized samples of this study cured at 450°C., a plot of $-\log K$ versus the reciprocal of the absolute temperature gives a straight line whose slope, when multiplied by $2.303R$, gives an activation energy of approximately 16.7 kcal.   This value corresponds favorably with the value for the same oxidation reaction obtained earlier[2] on the resins cured at 120°C.   It is also interesting to mention here that the rate constants obtained on the post-cured resin (450°C.) and the activation energy determined are almost identical with those obtained in a study of the oxidative degradation of poly-benzyl.[9]

TABLE I

Comparison of Rate Constants Obtained for the Initial Oxidation Reaction of Phenolic Resins as a Function of Resin Curing Temperature

Temperature, °C.	$1/T$, °K.$^{-1}$ × 10^{-3}	Rate constant, min.$^{-1}$ × 10^{-2}	
		Curing temp. = 120°C.	Curing temp. = 450°C.
180	2.21	6.88	0.22
		7.67	0.28
200	2.12	17.5	0.61
		17.8	0.56
220	2.03	37.6	1.12
			1.44

The phenolic resin normally employed for high temperature thermal protection systems (ablators) is very different chemically from a pure non-oxidized, crosslinked phenolic polymer.   The crosslinked, nonoxidized polymer has been shown to have a high stability toward thermal fragmentation and oxidation.   However, of the two degradation mechanisms, the oxidative mechanism is faster than the fragmentation reaction in the temperature range of the present study (to 1000°C.).

The char is apparently formed by the decomposition of the oxidized resin through a quinone-type intermediate.   This accounts for the occurrence of char formation simultaneously with the appearance of carbon monoxide.

References

1. Conley, R. T., and J. F. Bieron, *J. Appl. Polymer Sci.*, **7**, 103 (1963).

2. Conley, R. T., and J. F. Bieron, *J. Appl. Polymer Sci.*, **7**, 171 (1963).

3. Heron, G. F., *Conference on High Temperature Resistance and Thermal Degradation of Polymers, Monograph 13*, Plastics and Polymer Group, Society of Chemical Industry, London, 1961, p. 475.

4. Ouchi, K., and H. Honda, *Fuel*, **38**, 429 (1959).

5. Madorsky, S., and S. Strauss, WADC Technical Report 59–64, June 1959.

6. Friedman, H. L., Tech Information Series, No. R60SD380 and R61SD145, GE Space System Laboratory.

7. McAdams, W., *Heat Transmission*, McGraw-Hill, New York, p. 31.

8. Conley, R. T., *J. Appl. Polymer Sci.*, **7**, 1757 (1963).

9. Conley, R. T., unpublished data.

Résumé

La dégradation des polycondensats de phénol-formaldéhyde a été examinée à des températures allant jusqu'à 1000°C. En employant la spectrophotométrie infrarouge et la chromatographie en phase vapeur de même que la thermogravimétrie et les rayons X, il a été possible d'examiner la chimie de l'oxidation de ces systèmes de résines. On a trouvé que la première voie de dégradation des polycondensats de phénol-formaldéhyde est l'oxydation, sans tenir compte du fait que la résine est exposée à des températures élevées dans l'air, l'argon, ou l'azote. A des températures élevées on observe des produits provenant de la pyrolyse thermique en plus de ceux provenant de l'oxydation. Néanmoins, la dégradation oxydante est toujours plus prononcée dans la région de température étudiée. On a trouvé que le mécanisme d'oxydation s'accorde bien avec les propositions formulées antérieurement par Conley et Bieron. Il est également possible d'étendre ce mécanisme pour y inclure une carbonisation avec une formation semblable au graphite. Cette extension est proposée pour la formation simultanée de produit carbonisé et monoxyde de carbone. En étudiant par infra-rouge les étapes intermédiaires dans la formation de produit carbonisé, le postulat suivant lequel ces produits proviennent d'intermédiaires du type quinone, est justifié. Dans cette éture, on a trouvé que des polycondensats de phénol–formaldehyde d'une stabilité thermique inattendue pouvaient être produits par post-traitement à température élevée. La comparaison entre les vitesses d'oxydation de la résine traitée à basse température et cette matière, indique une stabilité améliorée vis à vis de l'oxydation de même qu'une résistance à la pyrolyse thermique. Ceci est dû sans aucun doute au pontage complet du système de résine.

Zusammenfassung

Der Abbau von Phenol-Formaldehydpolykondensaten wurde bei Temperaturen bis zu 1000°C. untersucht. Mittels infrarotspektrophotometrischer Verfahren und gaschromatographischer Methoden zusammen mit thermogravimetrischen und Röntgenstrahlanalysen war es möglich die Oxydationschemie dieses Harzsystems zu erforschen. Es zeigte sich, dass die primäre Abbauroute von Phenol-Formaldehydpolykondensaten, unabhängig davon ob die Hitzebehandlung in Luft, Argon oder Stickstoff erfolgt, immer Oxydation ist. Bei erhöhten Temperaturen treten zusätzlich zu den Oxydationsproduk

ten auch solche der thermischen Pyrolyse auf.   Im ganzen untersuchten Temperatur-
bereich hat aber immer der oxydative Abbau das Übergewicht.   Der Oxydationsmech-
anismus zeigt eine befriedigende Übereinstimmung mit den schon früher von Conley und
Bieron formulierten Annahmen.   Dieser Mechanismus lässt sich auch soweit erweitern,
dass er die Bildung von graphitartigen Verkohlungsprodukten erklären kann.   Diese
Erweiterung sieht eine gleichzeitige Bildung von Verkohlungsprodukten und Kohlen-
monoxyd vor.   Infrarotuntersuchungen der Zwischenstufen bei der Verkohlung recht-
fertigen die Annahme einer Entstehung dieser Produkte über chinonartige Zwischen-
körper.   In der vorliegenden Untersuchung konnten Phenol-Formaldehydpolykonden-
sate von ungewöhnlicher thermischer Stabilität durch eine Hochtemperatur-Nachhärtung
gewonnen werden.   Ein Vergleich der Oxydationsgeschwindigkeit des bei niedriger
Temperatur gehärteten Harzes und dieses Produkts zeigt seine stark verbesserte Oxyda-
tionsbeständigkeit und auch Beständigkeit gegen thermische Pyrolyse.   Unzweifelhaft
ist dieses Verhalten auf die vollständige Vernetzung des Harzsystems zurückzuführen.