NAVWEPS REPORT 7379

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THERMAL DEGRADATION OF PHENOLIC POLYMERS (U)

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U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

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THERMAL DEGRADATION OF PHENOLIC POLYMERS (U)

Prepared by:

Hugh C. Anderson

ABSTRACT: A study has been made of the thermal decomposition of 15 phenolic polymers, using vacuum thermogravimetry as a tool. These polymers included regular phenolics, chlorinated phenolics, and phenolics copolymerized with silane, nylon and phenol-furfural resins. The results are discussed in relationship to the chemistry of phenolic polymers. A high crosslink density and the large concentration of aromatic groups in these polymers are thought to be the causes of their carbonization and slow decomposition characteristics

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WHITE OAK, MARYLAND

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Research reported herein was performed under Task Assignment PR-6. An investigation of the thermal degradation of phenolic polymers, using vacuum thermogravimetry, is described. Although the exact nature of the precursors of these proprietary polymers is not known, the results obtained do lead to some general conclusions that are compatible with the chemistry of phenolic polymers. These conclusions are expected to be useful in the preparation of new more highly heat resistant materials.

W. D. COLEMAN
Captain, USN
Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

ACKNOWLEDGEMENT

The author is indebted to Dr. Mary Aldrich and Mr. Herbert Simmons of the Organic Chemistry Division for making elemental analyses of the polymers.

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ILLUSTRATIONS

REFERENCES

1. Anderson, Hugh C., NAVORD Report 6774 "Thermogravimetric Analysis of the Pyrolysis Characteristics of Polymers," (1960).
2. Anderson, Hugh C., NAVWEPS Report 7335 "Differential Thermogravimetry of the Pyrolysis of Epoxide Polymers," (1960).
3. Gilman, H., "Organic Chemistry - An Advanced Treatise," 731, Wiley, New York, 1947.
4. Fuscon, R. C., "Advanced Organic Chemistry," 12, Wiley, New York, 1956.
5. Ingram, D. J. E., Free Radicals - As Studied by Electron Spin Resonance," 208, Butterworths, London, 1958.
6. Erickson, P. W., Private Communication (Memo to WM Files (available to NOL Staff Members only)), Naval Ordnance Laboratory, White Oak, Md.
7. Madorsky, S. L., WADC Technical Report 59-427 (1960), Conference on High Temperature Polymer and Fluid Research, p. 247.

THERMAL DEGRADATION OF PHENOLIC POLYMERS

INTRODUCTION

1. Reinforced plastics based on glass fibers and phenolic polymers are generally more heat resistant than those employing polyester (Ref. 1) or epoxide (Ref. 2) polymers. However, because of the difficulty in working with phenolic polymers, very little research has been performed on how they thermally decompose. The ever increasing demand of the missile age for materials having better and better heat resistance makes it highly desirable that such research be carried out in an effort to produce such materials.

2. The purpose of this report is to describe work that has been performed as a start toward a better understanding of the thermal degradation of phenolic polymers. Fifteen polymers were studied, using the technique of vacuum thermogravimetry to continuously monitor their decomposition over a temperature range of 25° to 920°C. Elemental analyses were also made on each of the polymers before they were pyrolyzed. The pyrolysis results are discussed in relationship to the general chemistry of phenolic polymers, and suggestions are [illegible] for future work in this area.

THEORETICAL DISCUSSION

3. Regular crosslinked phenolic polymers are generally believed to have chemical structures (Ref. 3) similar to that represented by formula (A) in Figure 1. Their preparation can be shown by equation (B) in Figure 1. When phenol is reacted with formaldehyde, either of the ortho and para positions (activated by the electron releasing hydroxyl group) can add formaldehyde to form hydroxymethyl phenols. The hydroxymethyl groups can in turn condense with the active unsubstituted ortho and para hydrogens of the phenol to form methylene bridges between the phenolic nuclei.

4. Modification of regular phenolics by copolymerization with nylon resins is relatively new, and the chemistry involved has not been established. However, some of the possible reactions are postulated in equations (C) through (F) in Figure 2. Equations (C) and (D) show that formaldehyde could add to the terminal nitrogen group as well as to internal nitrogen groups of the nylon. The terminal carboxyl group could esterify the phenolic hydroxyl group and/or hydroxymethyl group, as shown by equations (E) and (F).

5. Chlorosilanes could react with the hydrogen of the phenolic hydroxyl group and/or that of the hydroxymethyl to form silicon-oxygen bonds, as shown by equations (G) and (H) in Figure 3. The latter reaction would be expected to predominate because aliphatic alcohols are known to be much more reactive than phenols with chlorosilanes.

6. Phenols could theoretically be reacted with any aldehyde to produce various phenol alcohols, but the aldol condensation of aldehydes containing an alpha hydrogen would further complicate the already complex phenol-aldehyde reactions. Therefore, the preparation of phenolic polymers is usually limited to the use of aldehydes not having an alpha hydrogen, e.g., formaldehyde. Furfural, another example of this type of aldehyde, reacted with phenol would give a polymer in which one of the hydrogens of the methylene bridges of a phenol-formaldehyde polymer is replaced by a furan group, as shown by equation (I) in Figure 4.

7. Chloro-phenolic polymers are those in which one or more of the hydrogens in the phenol ring are replaced by chlorine. If two of the active hydrogens are substituted by chlorine, as shown by equation (J) in Figure 5, neither linear nor network polymerization is possible. However, if only one of the active hydrogens are substituted, only linear polymerization is possible through the two hydroxymethyl groups shown by equation (K) and unsubstituted ortho and para positions of the phenol. Crosslinking is possible only when the meta-hydrogens are substituted, leaving the three active positions free, as shown in equation (L). In other words, if two reactants are to polymerize into a crosslinked network, one of them must have a functionality of at least three and the other a functionality of at least two. Formaldehyde has a functionality of two. The effect of the above reactions on the thermal stability of phenolic polymers will be discussed after the experimental data have been presented.

EXPERIMENTAL

8. The polymers studied, were used as received in a powdered form from Ironsides Resins, Inc., Columbus, Ohio, except that they were sieved to give samples passing a 60-mesh screen and stopping on a 100-mesh one. They are described in Table I, and the general reactions involved in their preparation have already been presented in Figures 1 through 5.

9. Apparatus described previously (Ref. 1) was used for the pyrolysis experiments. Samples of approximately 20-milligrams weight were pyrolyzed in vacuo at a heating rate of 3°C/minute. Elemental analyses were made on a portion of each of the unpyrolyzed polymers.

RESULTS

10. Thermogravimetric (TG) curves for the polymers are shown in Figures 6 through 10. A summary of the pyrolysis data is given in Table II, and the elemental analysis data are tabulated in Table III. In general. the polymers decomposed slowly and gradually, rather than catastropically (as is the case for polyester and epoxide crosslinked polymers), leaving carbonaceous residues ranging from 29% for a phenolic resin copolymerized with a nylon

resin to 61% for a chlorinated phenolic resin copolymerized with a silane. The relative thermal stability of polymers is usually represented by the temperatures at which they lose 50% of their weight, based on 100% ultimate weight loss. However, the weight loss for phenolic polymers is generally much less than 100% and may vary greatly for different polymers. Therefore, the above criterion in this case would be somewhat misleading. Consequently, the criterion used for relative thermal stability in this work was taken as the temperature at which 50% of the ultimate percentage weight loss occurred, as shown in Table II. As an example: if the ultimate percentage weight loss were 50, 50% of this would be 25%, the corresponding temperature of which could be obtained from the thermogravimetric curve. On the basis of this criterion, a chlorinated phenolic copolymerized with a silane had the slowest relative rate of decomposition and a regular phenolic copolymerized with a silane had the fastest, as evidenced by corresponding temperatures of 505° and 395°C. Since 395°C was the lowest temperature at which 50% of the ultimate percentage weight loss occurred and 505°C the highest for the group of polymers studied, a temperature (450°C) midway between the two temperatures is taken as another parameter. The percentage weight loss at this temperature is given for each of the polymers in Table II. It is seen that the chlorinated phenolic copolymerized with a silane is rated as the most thermally stable by either of the above three parameters (lowest ultimate percentage weight loss, highest temperature at which 50% of ultimate percentage loss occurs, and lowest percentage weight loss at 450°C).

DISCUSSION OF RESULTS

12. Three of the four regular phenolics decomposed slowly at about the same rate, leaving appreciable carbonaceous residues as shown by the TG curves in Figure 6. There are at least two important reasons for this good thermal stability. One of these is the extreme stability of methylene bridges in the highly crosslinked network. This in turn is due to resonance stabilization of the benzyl group (Ref. 4). The other reason is the high concentration of benzene rings in the crosslinked network. The phenyl radical formed by pyrolysis of the polymer could coalesce into clusters of benzene rings, which would have the high resonance stabilization energy characteristic of condensed ring systems. This is also evidently responsible for the large amounts of carbon remaining after pyrolysis. That this mechanism does occur is suggested by electron spin resonance studies of carbonaceous residues resulting from the pyrolysis of various materials (Ref. 5). No reason is offered for the higher rate of weight loss and the higher ultimate percentage weight loss of the fourth regular phenolic polymer. However, the supplier did indicate that an attempt had been made to produce a polymer having a much higher carbon content than regular phenolics. Table II, however, shows that its carbon content is about the same as that of the other three regular phenolics.

13. Assuming that the same resins in the same proportions were used for each of the two phenolic polymers copolymerized with furfural, the TG curves in Figure 7 show the effect of temperature of cure on the thermal stability. The one cured at the higher temperature was more stable.

14. The TG curves in Figure 8 show that the thermal stabilities of the three phenolic polymers copolymerized with nylon increased with decreasing nitrogen content. The probable reason for this is that either of the reactions (C) through (F) in Figure 2 would upset the idealized crosslinked structure shown by formula (A) in Figure 1. Therefore, varying amounts of the same nylon are copolymerized with a regular phenolic, the above decrease in thermal stability with increasing nitrogen content of the polymer would be anticipated.

15. Relative reates of decomposition and ultimate percentage weight losses for the two phenolic polymers copolymerized with a silane are about equal, as shown in Figure 9 and Table II. Reaction (G) in Figure 3 would deactivate the ortho and para positions of the phenol and phenol alcohols, and consequently forbid or retard formation of the usual methylene bridges through condensation. Reaction (H), the more probable one, would block one of the active positions, making crosslinking impossible. Therefore, phenolic-silane copolymers would be less thermally stable than regular phenolics, as can be seen in Table II.

16. Figure 10 and the temperature column of Table III show that the regular chlorinated phenolic and two of the chlorinated phenolics copolymerized with silane were less thermally stable than the three regular phenolics discussed earlier; the other chlorinated phenolic copolymerized with silane was more stable. Chlorine on the benzene ring can reduce the thermal stability of a regular phenolic by preventing crosslinking when it is in one of the ortho or para positions. Chlorine could also reduce thermal stability when it is on one or both of the meta positions, even though it could not prevent crosslinking. It has been reported (Ref. 6) that some polyphenyl polymers decrease in thermal stability with increasing chlorine substitution. The lower stabilities for the two chlorinated phenolics copolymerized with silane can be attributed to both chlorine and silane substitution, which has already been discussed. No explanation can be offered at present for the comparatively higher stability of the other chlorinated phenolic copolymerized with silane.

CONCLUSIONS

17. The crosslinked phenolic polymers studied here were found to be more thermally stable than polyester and epoxide polymers, as evidence by slower rates of decomposition and lower ultimate percentage weight losses. Temperatures at which 50% of ultimate percentage weight losses occurred

ranged from 395°C for a phenolic copolymerized with silane to 505°C for a chlorinated phenolic copolymerized with silane. It was also found that chemical modification of the regular phenolic crosslinked structure could cause a decrease in thermal stability.

RECOMMENDATIONS

18. From qualitative observations, it appears that a major portion of the weight loss is due to high molecular weight materials which are volatile at the temperature of pyrolysis but not at 25°C in vacuo. Madorsky (Ref. 7) has studied the thermal degradation of one phenolic polymer and reported that 75% of the volatile products was a high molecula weight material; his remaining volatile products were determined by mass spectrometry to be carbon dioxide, acetone, propylene, propanol and butano He did not try to identify the high molecular weight material. It is proposed that molecular distillation be used to collect these high molecular weight materials for infrared study and that the other more volatile materials be identified by gas chromatography. In an effort to obtain more basic information on how phenolic polymers thermally degrade, it is proposed that pyrolysis of the model compounds and polymers shown in Figures 11A, 11B and 11C be investigated.

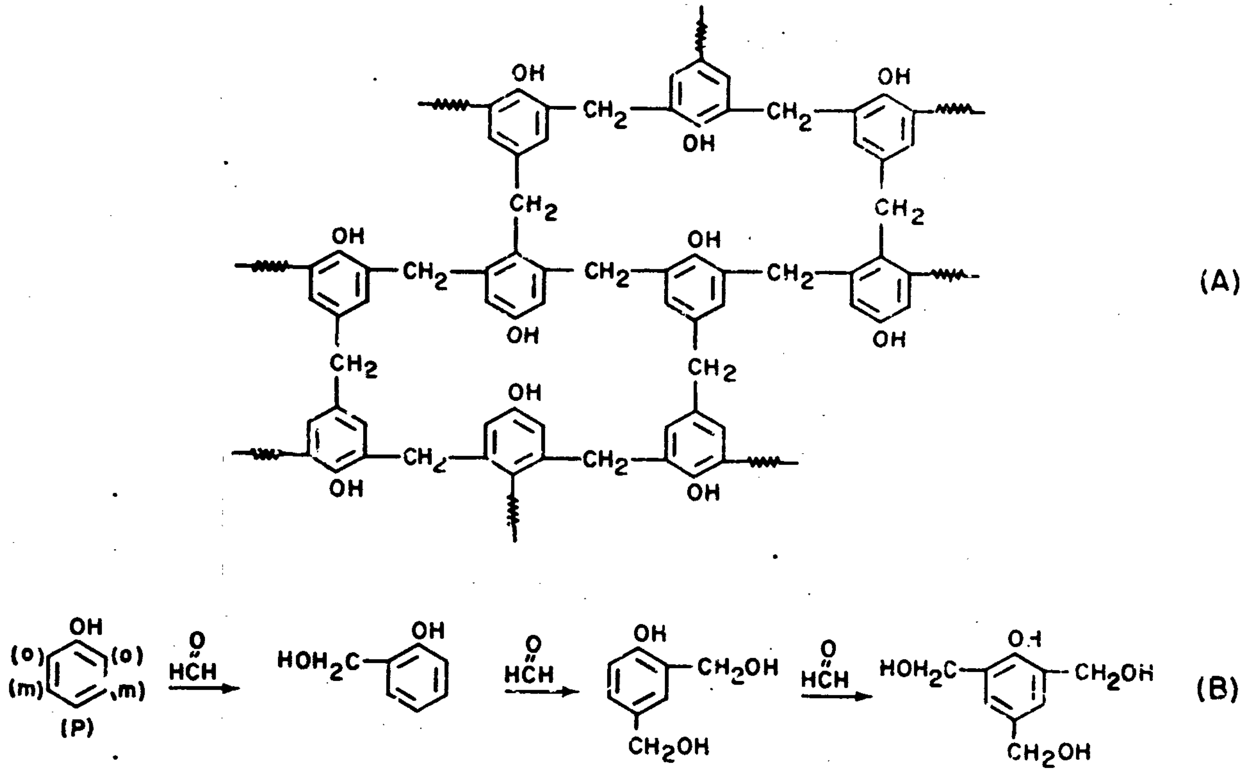


FIG. I CHEMISTRY OF REGULAR PHENOLIC POLYMERS

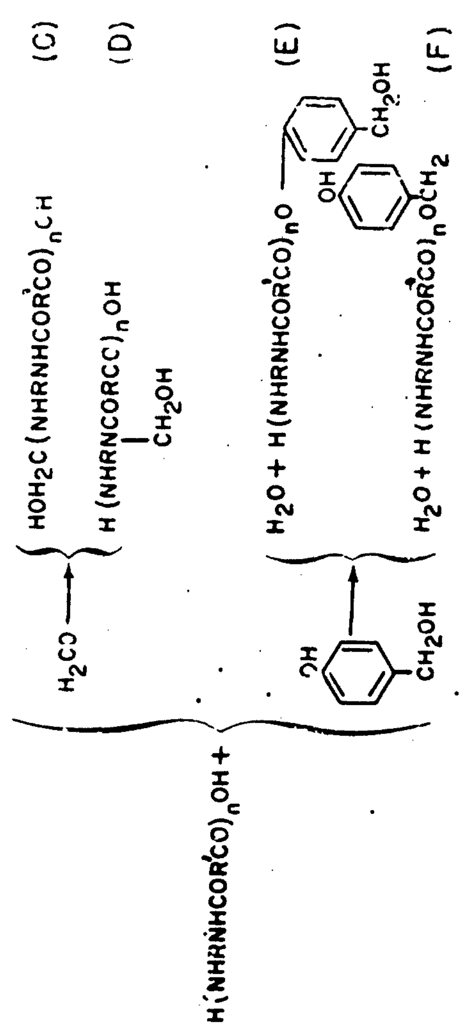


FIG.2 POSSIBLE REACTIONS OF NYLON RESINS WITH FORMALDEHYDE AND HYDROXYMETHYL PHENOLS

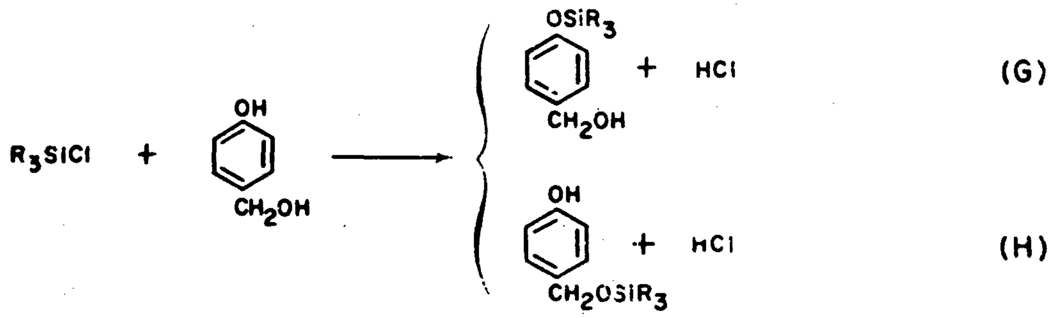
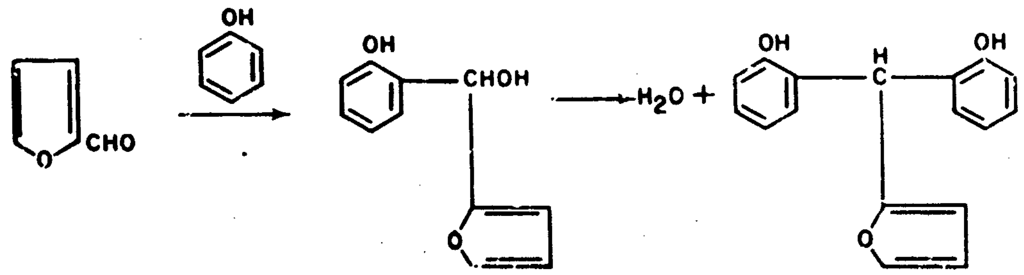


FIG.3 REACTIONS OF CHLOROSILANES WITH HYDROXYMETHYL PHENOLS



(1)

FIG.4 SYNTHESIS OF PHENOL-FURFURAL POLYMERS

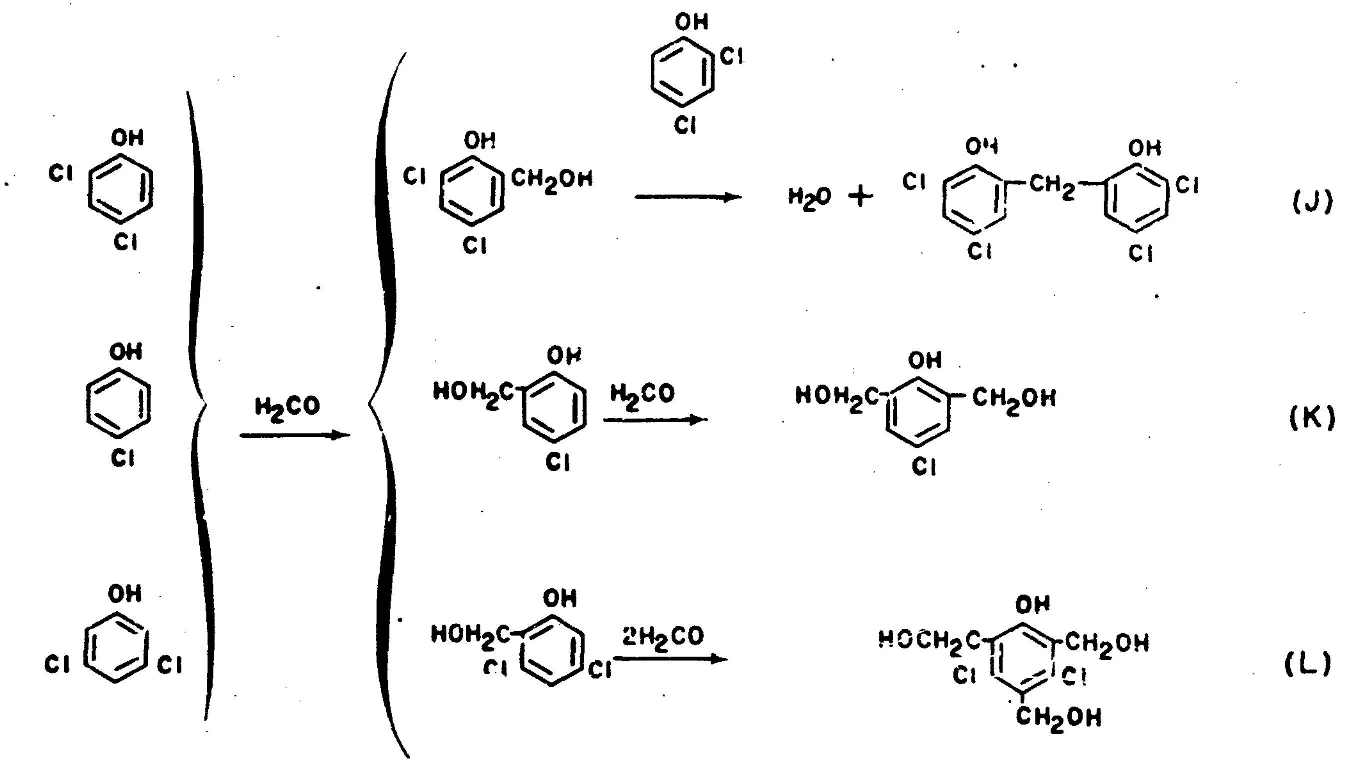


FIG. 5 REACTIONS OF FORMALDEHYDE WITH CHLORO-PHENOLICS

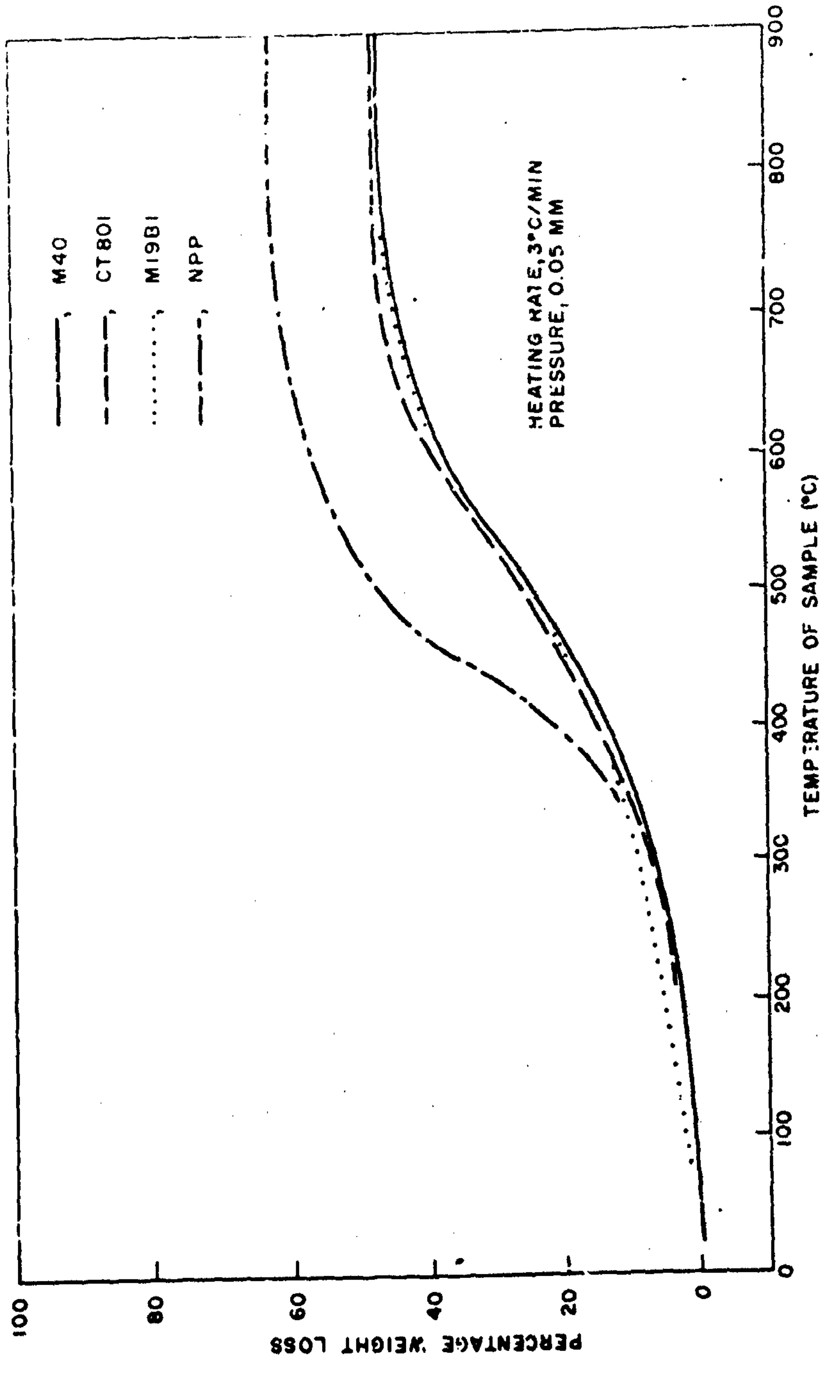


FIG.6 TG CURVES OF REGULAR PHENOLIC POLYMERS

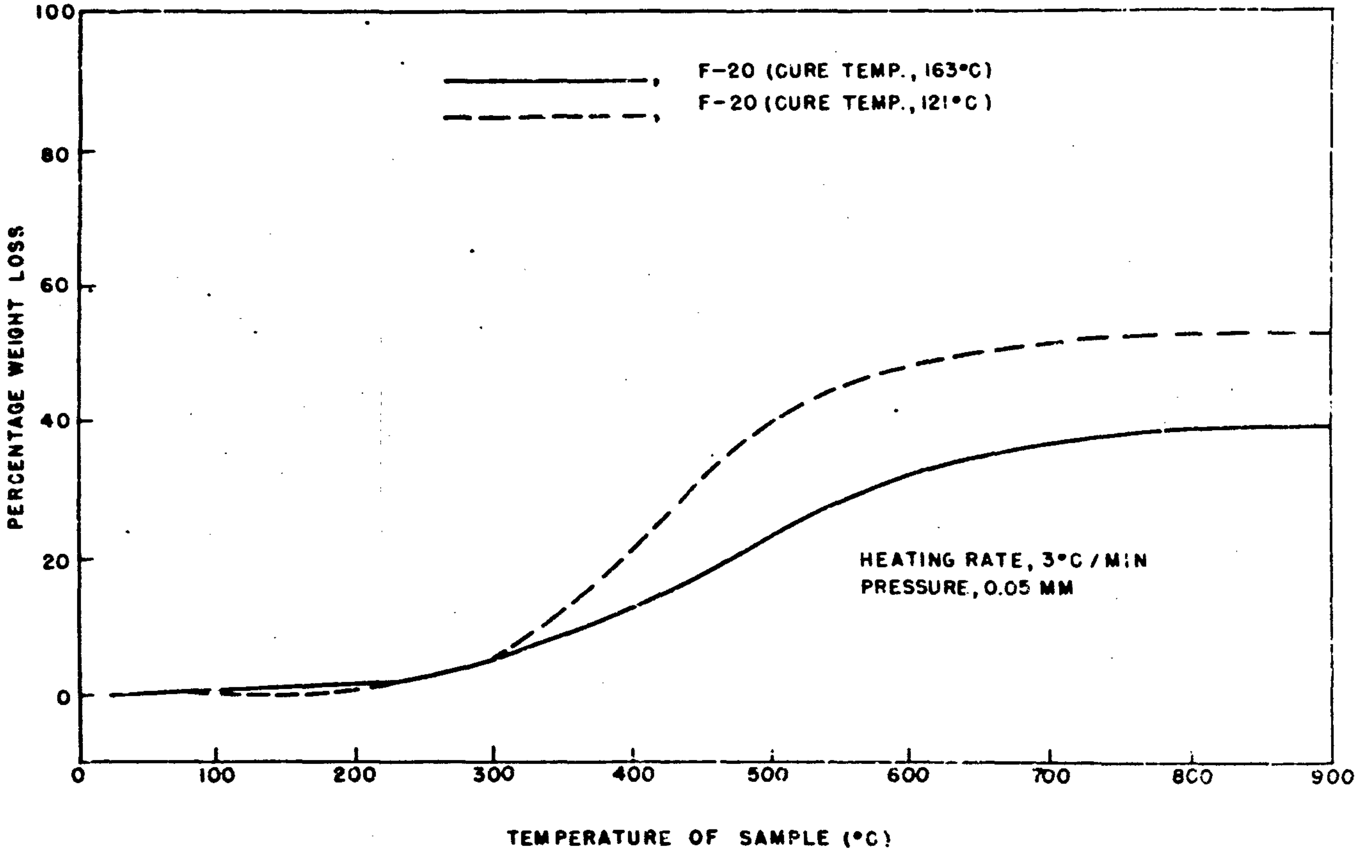


FIG.7 TG CURVES OF PHENOLIC-FURFURAL POLYMERS

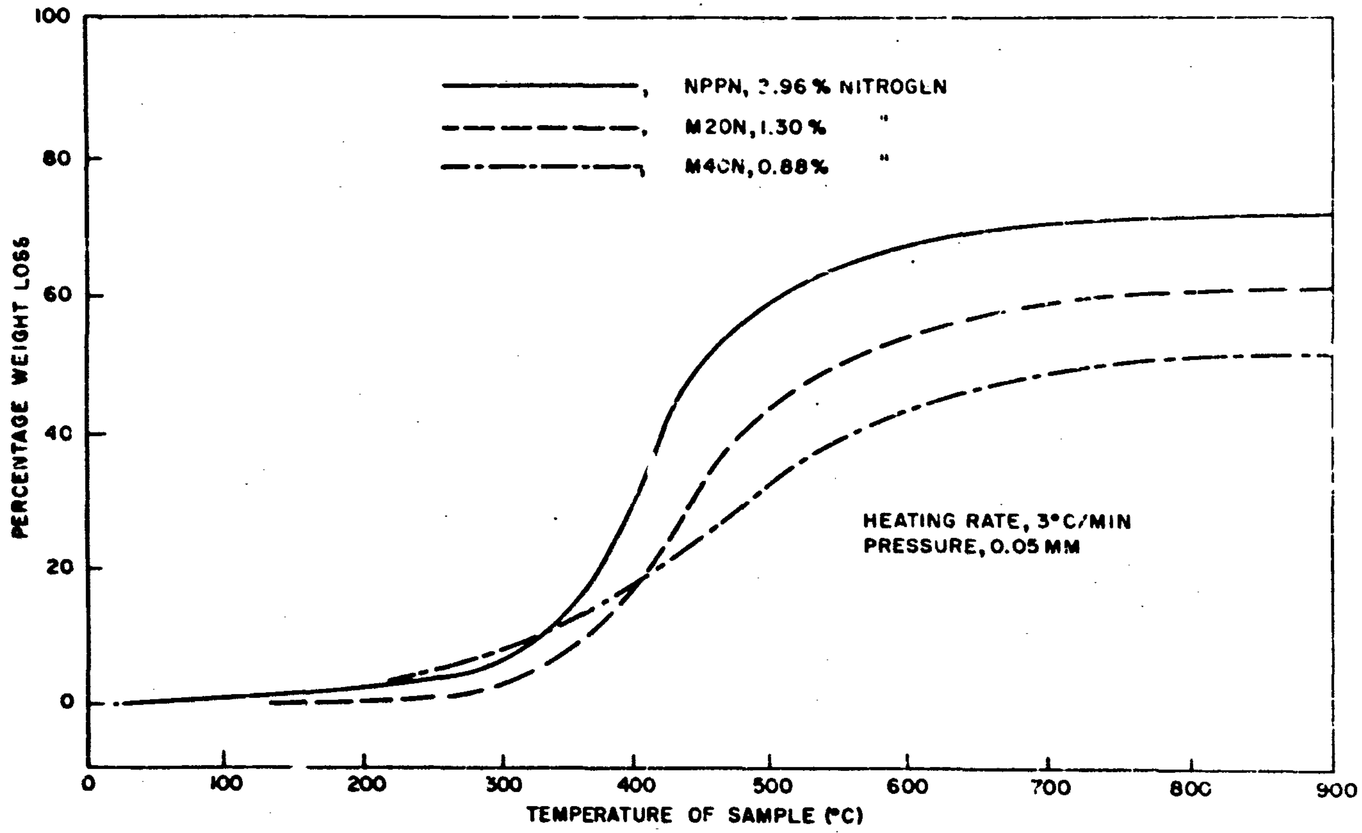


FIG.8 TG CURVES OF PHENOLIC-NYLON POLYMERS

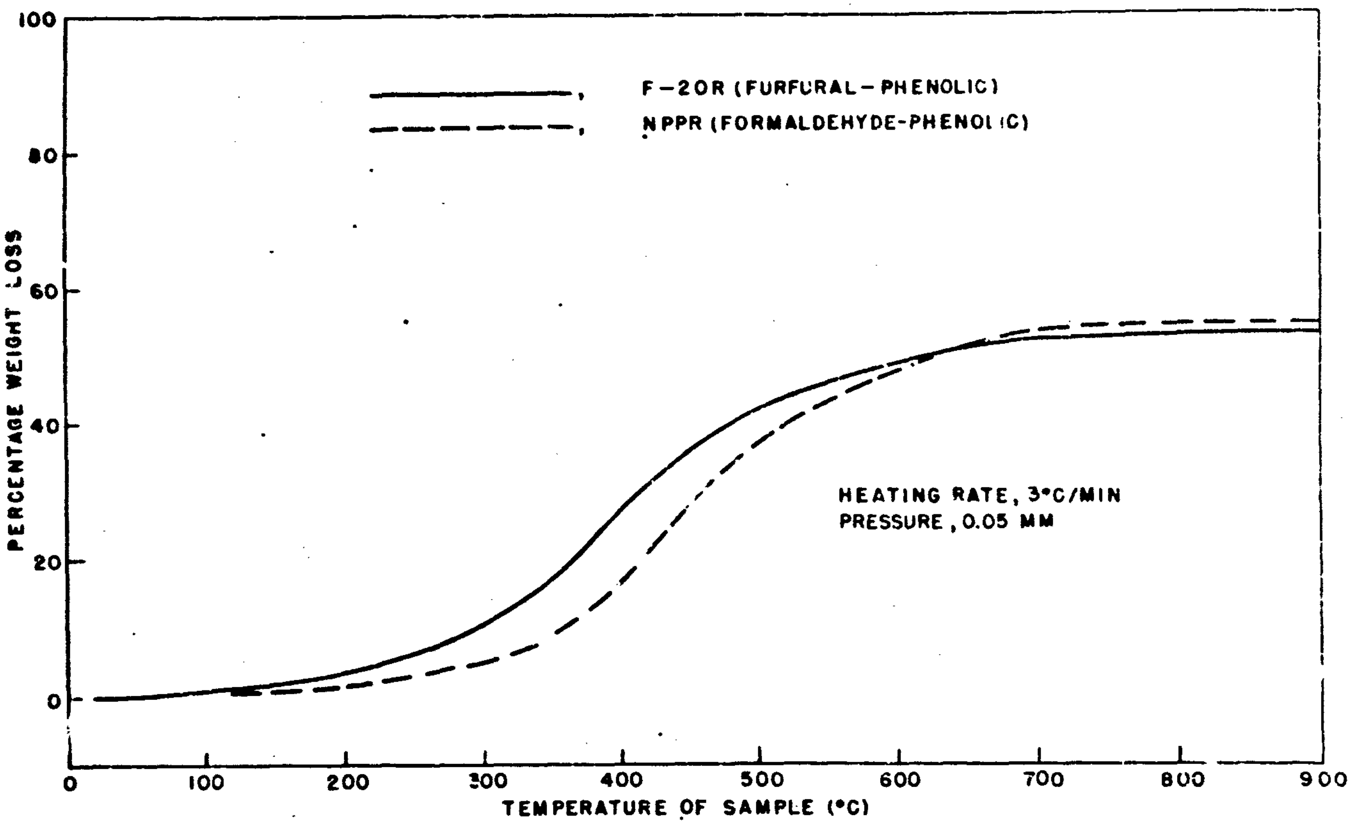


FIG. 9 TG CURVES OF PHENOLIC-SILANE POLYMERS

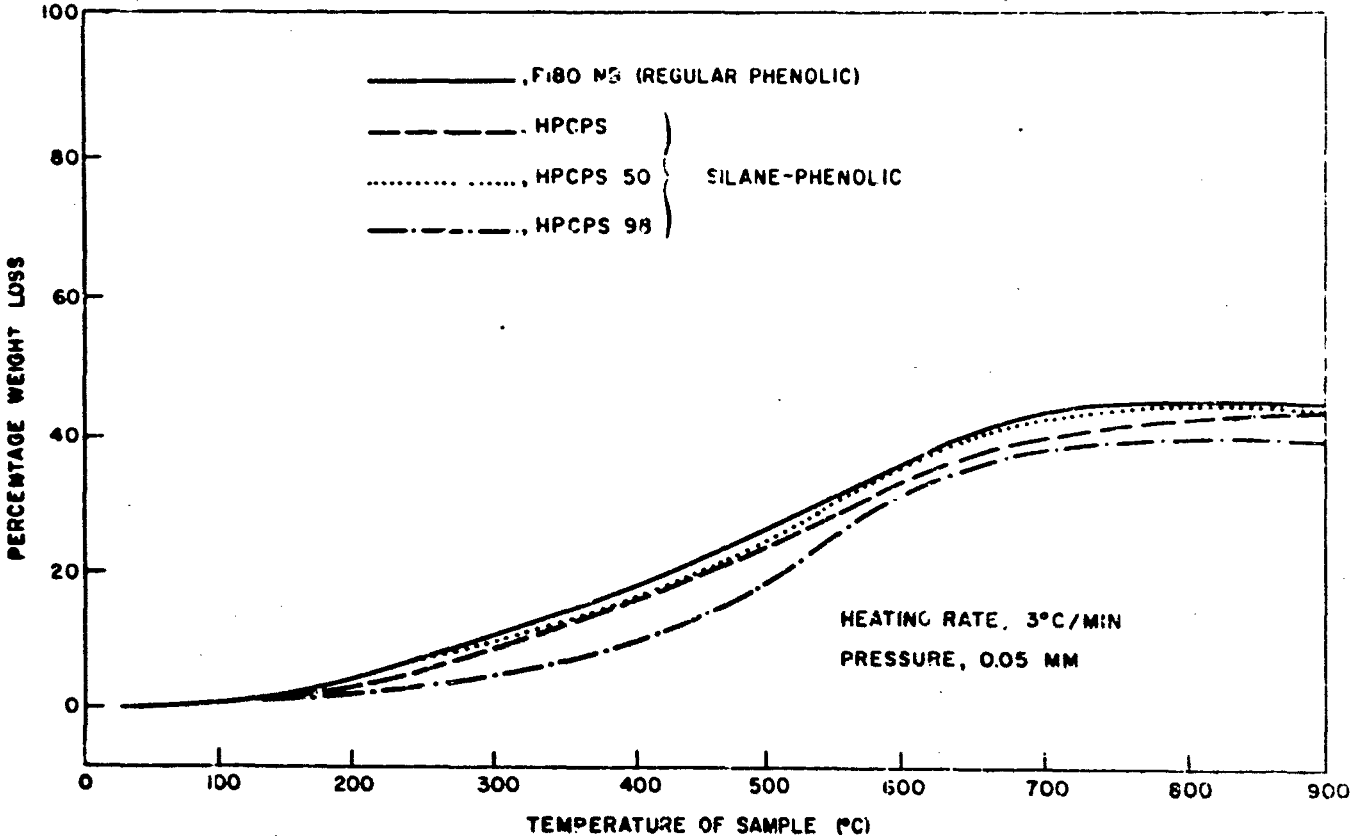


FIG. 10 TG CURVES OF CHLORINATED PHENOLIC POLYMERS

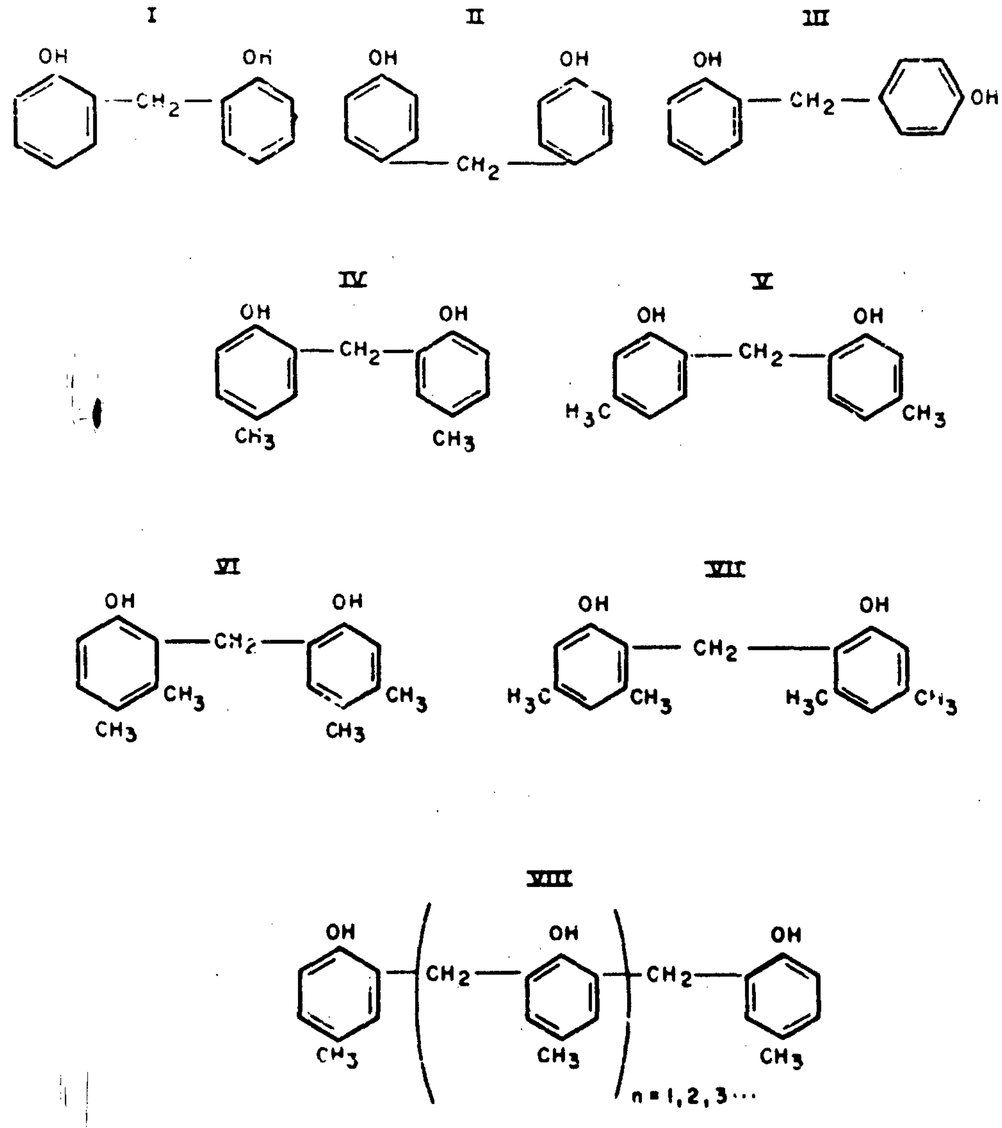
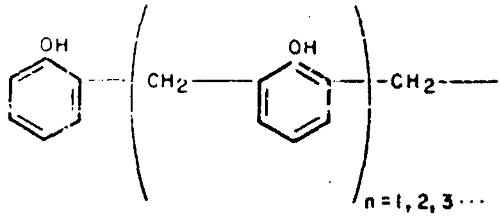


FIG. 11A MODEL COMPOUNDS AND POLYMERS FOR FUTURE STUDY

IX



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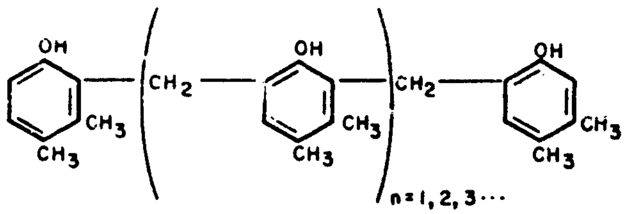


XI

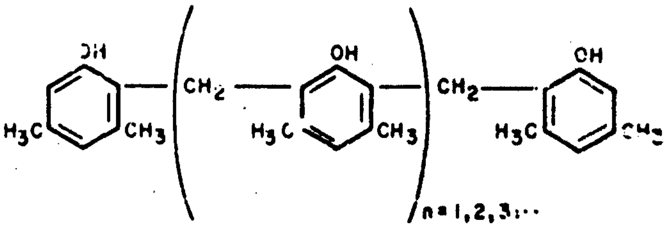
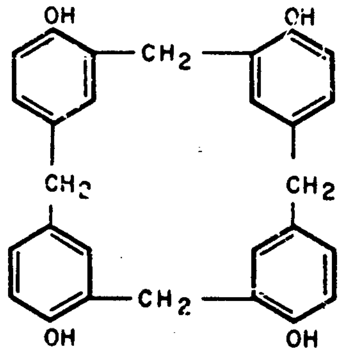


FIG. 11B MODEL COMPOUNDS AND POLYMERS FOR FUTURE STUDY

XII



XIII

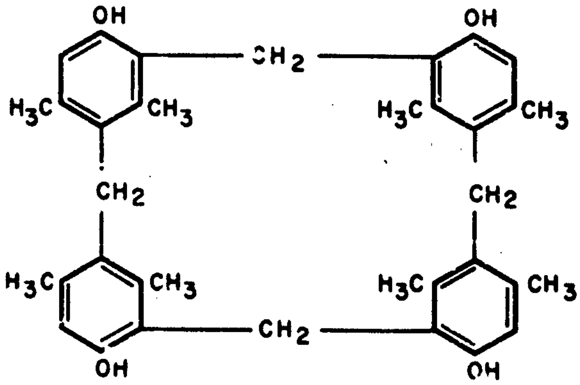


FIG. 11C MODEL COMPOUNDS AND POLYMERS FOR FUTURE STUDY

TABLE I

IDENTIFICATION OF PHENOLIC POLYMERS

Designation(1)	Description
M19B1	Regular Phenolic
M40	Regular Phenolic
CT 801	Regular Phenolic
NPP	Regular Phenolic
F-20	Phenolic copolymerized with furfural
FA-20	Phenolic copolymerized with furfural
M40N	Phenolic copolymerized with nylon resin
M20N	Phenolic copolymerized with nylon resin
NPPN	Phenolic copolymerized with nylon resin
F-20R	Phenolic copolymerized with silane and furfural
NPPR	Phenolic copolymerized with a silane
HPCPS-98	Chlorinated phenolic copolymerized with a silane
HPCPS-50	Chlorinated phenolic copolymerized with a silane
HPCPS	Chlorinated phenolic copolymerized with a silane
P180MB	Chlorinated regular phenolic

(1) All 15 polymers, in powdered form, were furnished gratis by Ironsides Resins, Inc., Columbus, Ohio. The above designation is the Ironsides code. M40, NPPN and HPCP-98 polymers were polymerized in thin sheets for one-half hour under a pressure of 400 p.s.i. and at a temperature of 205°C. FA-20 polymer (catalyzed with a small amount of maleic anhydride) was polymerized for one-half hour at 400 p.s.i. and 121°C. All of the other polymers were polymerized at 400 p.s.i. and 163°C.

TABLE II

SUMMARY OF PYROLYSIS DATA FOR PHENOLIC POLYMERS

Polymer(1)	Ultimate percent weight Loss up to 920°C	Temperature at 50% of Ultimate percentage Weight Loss, °C	Percentage Weight Loss up to 450°C
M19B1	45.6	490	19
M40	46.3	490	18
CT801	47.2	480	20
NPP	59.0	430	36
F-20	55.9	475	17
FA-20	53.2	430	32
M40N	51.1	460	24
M20N	60.8	445	32
NPPN	71.3	410	50
F-20R	53.4	400	36
NPPR	54.3	395	28
HPCPS-98	39.3	505	14
HPCPS-50	43.0	455	21
HPCPS	43.1	465	20
P180NB	45.3	445	23

(1) See Table I for description of Polymers.

TABLE III

ELEMENTAL ANALYSIS DATA(1) ON PHENOLIC POLYMERS

Polymer(2)	% Carbon	% Hydrogen	% Chlorine	% Silicon	% Nitrogen
M19B1	74.6	5.98	-	-	-
M40	76.5	5.41	-	-	-
CT801	76.0	5.54	-	-	-
NPP	77.0	8.13	-	-	-
F-20	71.6	4.72	-	-	-
FA-20	70.4	5.19	-	-	-
M40N	73.6	5.96	-	-	0.88
M20N	75.0	7.19	-	-	1.30
NPPN	74.9	7.66	-	-	2.96
F-20R	64.3	5.34	-	6.91	-
NPPR	71.9	6.94	-	6.22	-
HPCPS-98	71.0	5.46	0.80	4.32	-
HPCPS-50	67.2	5.56	7.44	2.41	-
HPCPS	62.6	4.92	12.13	4.60	-
P180NB	63.1	5.04	16.58	-	-

(1) Each value is an average of at least two determinations.

(2) See Table I for description of polymers.

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(NAVWEPS report 7379)
THERMAL DEGRADATION OF PHENOLIC POLYMERS (U), by Hugh C. Anderson. 23 Jan. 1961. 5p. charts, tables, diagrs. Project PR-6.
Unclassified

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Abstract card is unclassified

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2. Silane
3. Nylon
4. Phenol-furfural
I. Title
II. Anderson, Hugh C.
III. Project

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1. Phenols, Chlorinated
2. Silane
3. Nylon
4. Phenol-furfural
I. Title
II. Anderson, Hugh C.
III. Project