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Study Leading to the Development of
HIGH TEMPERATURE RESISTANT ADHESIVES

J. Dickstein
B.D. Halpern

FINAL REPORT

22 June 1960 - 21 June 1961
CONTRACT NO. DA-36-034-ORD-3316-RD
Project No. TB4-002, Task B

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PICATINNY ARSENAL
Dover, New Jersey

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FOREWORD

This progress report covers the work under Contract DA-36-034-ORD-3316-RD, titled, "High Temperature Resistant Adhesives," from June 22, 1960 to June 22, 1961. The work covered in this Report was carried out at the Central Research Laboratory of The Borden Chemical Company by Dr. E. Hoess, Mr. Howard Hoyt, Miss G. Weintrub and the Authors. Analyses were performed by our Analytical Group and Dr. Stephen Nagy, Microchemical Laboratory, Belmont, Massachusetts. Thermogravimetric and X-ray Analyses were performed by the Laboratories of the Picatinny Arsenal, Dover, New Jersey.

J. Dickstein
B. D. Halpern

ABSTRACT

This report presents the results of an investigation towards the synthesis of high temperature resistant metal adhesives.

The following representative phenylene- and triazine-containing polymers were prepared:

- (a) Polyphenylene
- (b) Polyxylenol from 2,6-Xylenol
- (c) Polyxylenol from 4-bromo-2,6-Xylenol
- (d) Polyaryl ethers from o-cresol novolacs
- (e) Melon
- (f) Condensation polymer of cyanuric chloride and benzoguanamine
- (g) Condensation polymer of 2-amino-4,6-diphenoxy triazine.
- (h) Condensation polymer of benzoguanamine and diphenyl carbonate (urea-linked triazine polymer).

Preliminary tests showed good heat stability for all the polymers. The polyxylenols showed no weight loss up to 400°C. by thermogravimetric analysis. Crude adhesion experiments showed excellent affinity of the polyxylenols for stainless steel surfaces. The higher molecular weight polyxylenols proved difficult to mold by conventional techniques although discs prepared from these polymers showed excellent physical properties in regard to strength, hardness and toughness.

Modifications made on the polyxylenols included oxidation to the carboxy derivative, side chain bromination, attachment of quaternary amine side chains, and attachment of tetraalkyl silane side chains. None of the derivatives approached the parent polymers in properties such as temperature resistance and metal adhesion.

Modifications made on the triazine polymers in order to overcome their refractory nature included the reduction of melon to a product called "hydromelon" and amine salt preparation from "hydromelon" and the prepared amino derivative of the urea-linked triazine polymer (h).

As the investigation proceeded, it became increasingly apparent that the combination of good metal-to-metal adhesion and temperature stability dictated that the ideal system should consist of a relatively low melting or liquid polymer capable of thermosetting under the conditions of cure. To this end a number of glycidyoxy-s-triazine compounds were prepared with thermosetting properties. These showed fair metal-to-metal adhesion.

Work in progress consists in the preparation of polyisocyanate derivatives of the lower melting polyxylenols and triazines for "in situ" cure on metallic surfaces. The final phases of this work will be covered in a future report.

INTRODUCTION

A. Purpose of Program:

The objective of this research is the development of a high temperature resistant adhesive for 302 stainless steel which would give a minimum shear strength of 1000 psi at 1000°F. after exposure to 1000°F. in air for a minimum of one hour. The conditions of cure are to be at temperatures no higher than 500°F. and preferably at temperatures near ambient. The impact resistance of the adhesive, when cured, is to be such as to permit a high rate of load as required by missiles in flight or by rough handling.

B. Rationale:

The following factors are believed essential to the success of obtaining a high temperature metal-to-metal adhesive.

- (a) Small molecules must be initially present in either the liquid or low-melting solid form in order to obtain proper wetting and coverage.
- (b) Avoidance of volatile by-products during "curing".
- (c) Proper and accessible groupings on the adhesive.
- (d) Thermosetting structure in the final, cured state.
- (e) Use of mixtures of substances with properties contributing to the ultimate state of the adhesive.
- (f) "Curing" must occur under milder conditions of temperature than that withstood by the least stable component present in the adhesive.

There are two manners of approach that can be followed in producing the desired products. One approach is to start with a polymeric material which gives the desired type of adhesive performance at ordinary temperatures and attempt to modify it so that it will be sufficiently stable at high temperatures. An example of this may be found in various polymers which when chelated with metals show unusual stability. Also the change from an amorphous to a crystalline structure can often improve the temperature resistance.

The second approach is to seek a new polymeric type which has the desired high temperature stability and once this is discovered to modify this fundamental backbone to make the polymer suitable as a durable metal adhesive. This may be illustrated by siliconized epoxy resins. The silicones are relatively heat resistant but do not have sufficient adhesion to be satisfactory. The introduction of the epoxy moiety overcomes this situation.

In this work we decided to pursue the latter course. Therefore we were only concerned with those polymeric systems which we believed to possess back-bone structures with good thermal stability.

C. Work Program:

It is well known that aromatic nuclei are more stable at elevated temperatures than are aliphatic structures and thus polymeric chains rich in aromatic units should show greater heat stability than are shown by the currently available polymeric materials built on carbon chains of an aliphatic nature. In the same manner polymeric chains containing the triazine nucleus should show greater heat stability because of the large resonance energy (greater than 40 k. cal./mole) possessed by this moiety. It is in this area of resonance stabilized ring systems exemplified by phenylene and triazine and their condensed and fused analogs that we decided to do our research for high temperature adhesives.

The phenylene linkage in the backbone of a polymer chain is a very desirable moiety because of the regularity and rigidity imparted to the polymer chain by this repeating unit. As a result of these structure characteristics, polymers containing a significant fraction of phenylene skeletal units are generally crystalline with relatively high melting points. A considerable amount of effort, therefore, has been and is being devoted to the development of polymers based on this structure principally for fiber-formers. In addition to fiber-formation, however, another property inherent in polymers based on phenylene units may well be exceptional toughness as high impact strength in molded plastics may be related to the presence of microcrystallinity.

The resonance energy for the cyanuric nucleus is believed to be about 40 k.cals./mole (R.E. of benzene = 36 k.cals./mole). Some earlier calculations show values as high as 82.5 k.cal./mole (Pauling, L.C., Nat. Acad. Sci, 23, 615, 1937) but this is suspect. Therefore, it may be inferred that with regard to thermal stability, the triazine nucleus may be superior to the benzene nucleus. Thus polymers containing the s-triazine nucleus as the repeating unit may be expected to satisfy the requirements for thermal stability. In addition, it is generally believed that the stability of the linkages, as well as the total resonance energy of the repeating unit, is enhanced if the linkages themselves can take part in the resonance.

A consideration of the electron system of the triazine nucleus shows that a rather high charge exists on the nuclear nitrogen atoms. Therefore the chemical reactivity of triazine and its derivatives is higher than that of the corresponding benzene derivatives. This enables the preparation of a wide variety of monomeric starting materials.

It was decided to divide the experimental work on this project into two phases:

Phase I:

The preparation and evaluation of suitable polymeric backbones, based on phenylene and triazine ring structures. This phase covered the first two months of the project.

Phase II:

The attachment of adhesionable pendant groups to the polymers prepared in Phase I, the study of the extent of adhesion and the heat stability of these modified polymers. This phase covered the remaining ten months of the project.

D. Literature Search:

The first stage in our research progress comprised an extensive survey of the chemical literature on the preparation and properties of phenylene- and triazine-containing polymers. In the field of polyphenyl ether polymers there is very little published information, this development being relatively new^{1,2/}. Among the polymers based on phenylene-containing units investigated in the past, the most outstanding are polyethylene terephthalate and the bisphenol polycarbonates. A number of other polymers have shown interesting properties as a result of this structure including polyphenylene methylene, polyesters of hydroxymethyl benzoic acids, polyphenylene ethylene, polyterephthalic anhydride, polyphenylene phosphites, and polyphenylene itself. Except for the latter, all of these polymers contain two or more atoms between phenylene units, and it is likely that these extraneous units tend to decrease both the thermal and chemical stability of the polymers.

A particular problem in the preparation of polyphenyl compounds has been to develop techniques whereby they could be readily obtained to yield polymers which could be conveniently handled. For the most part, pyrolytic techniques such as hot tube reactions as developed by Szwarc, Price and others have been used. The melting points of the lower p-polyphenyls are quite high and suggest that a high molecular weight p-polyphenyl should be very high melting and quite stable. For example, p-sexiphenyl is reported to melt at 475°C, while p-septiphenyl melts at 545°C.

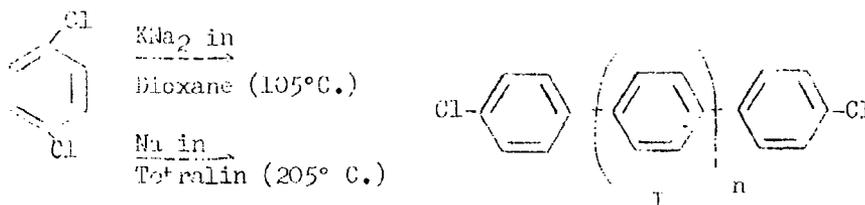
The chemistry of triazines is extensively documented, much of it in the patent literature. However, with relatively few exceptions there is little reference to polymeric materials derived from the triazines. In addition to the patent literature, Chemical Abstracts and the original references abstracted have been studied. Here also relatively few references to polymeric substances exist. An excellent text, "The Chemistry of Heterocyclic Compounds, s-Triazines and Derivatives" by Smolin and Rapaport (Interscience 1959) proved to be useful.

RESULTS AND DISCUSSION

I. Polyphenylene-Containing Polymers

1. Polyphenylene (I)

Polyphenylene, itself, was prepared from p-dichlorobenzene by the following two alternate procedures:

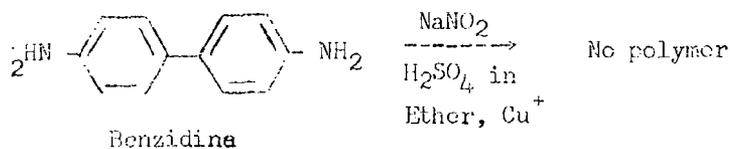


Both polymers had softening points greater than 400°C. and were soluble in benzene and chloroform. The I.R. showed both structures to be identical except for the presence of some quinoid rings in the polyphenylene prepared by the sodium in tetralin procedure. This was confirmed by the ultraviolet absorption spectra which showed greater absorption of this polymer.

Chlorine end group analysis gave the following results:

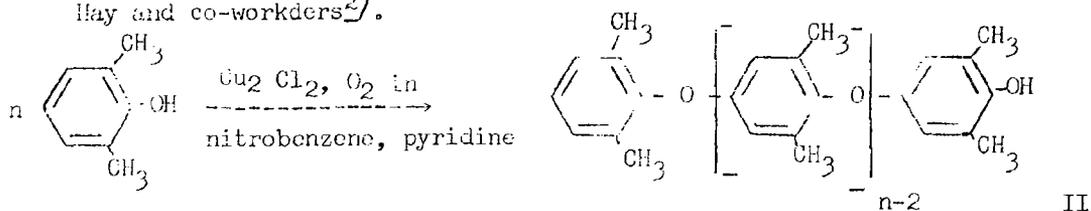
	<u>n</u>	<u>Mol. Wt.</u>
KNa_2 in Dioxane	27	2,000
Na in Tetralin	55	14,200

The preparation of polyphenylene was also attempted by the following diazotization procedure from benzidine.



2. Polymerization of 2,6-Xylenol (II).

The polyether of 2,6-Xylenol was prepared by the method of A. S. Hay and co-workers^{2/}.

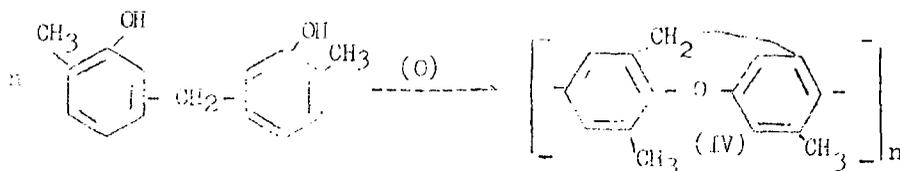


I.R. confirmed the structure

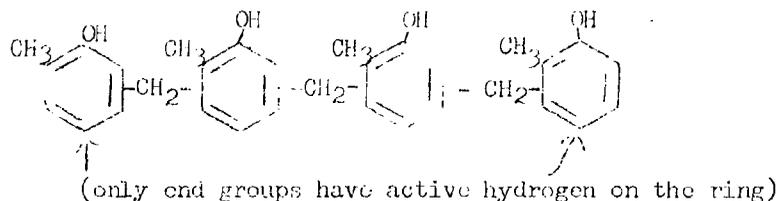
Extensive modifications in the original procedure were made in an effort to arrive at the variables controlling molecular weight. In general, it was found that low temperatures and highly intimate mixing of the benzene and caustic layers led to high molecular weight polymers. The highest melting polymer (over 370°C.) was formed in a one phase system in which methanol was substituted for benzene. The lowest melting polymer 130°C. was obtained when no organic solvent was used. In the latter the polymer fell out of the sodium hydroxide solution as a precipitate as soon as the decrease in hydroxyls limited its solubility as a polymer. In summary, it is believed that for polymer growth, solution is essential.

4. Polyaryl Ethers from o-Cresol Novolacs (IV)

A low cost type of raw material of interesting possibilities appeared to be o-cresol novolacs which, like xylenol would be difunctional (OH and ortho or para hydrogen) in respect to the reactions giving polyethers. The first member of this series might in fact be considered a xylenol in which a methyl hydrogen has been replaced by the cresol moiety.



The higher members appeared to offer the possibility of polyethers in which OH groups remained on some of the phenolic nuclei inasmuch as all active hydrogens would be missing from the middle aromatic nuclei and hydroxyls would thus predominate on active hydrogen sites:

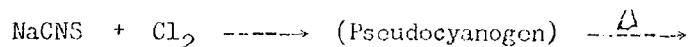


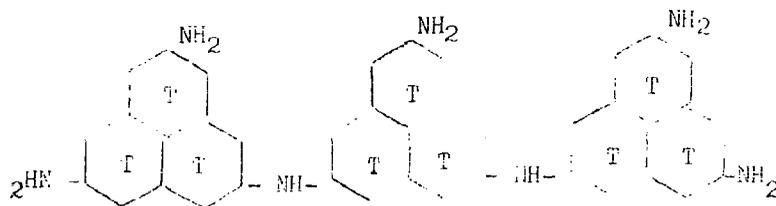
By the oxidation route of Hay infusible products were obtained. By the bromination route, a very low yield of product was obtained, with most of the brominated novolac being recovered unchanged (by acidification of the caustic layer).

B. Triazine-Containing Polymers

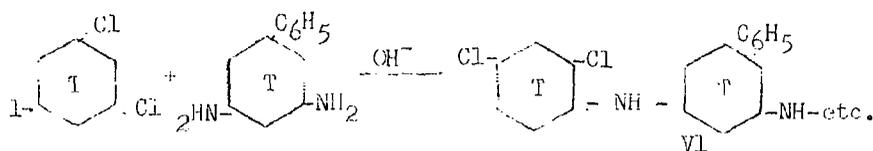
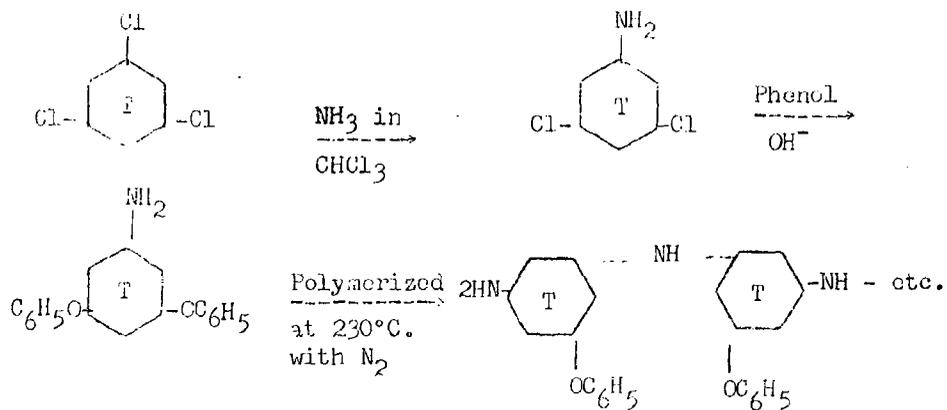
1. Melon (V)

This rather-unique high melting polymer was prepared by the following sequence^{2/}:





Melon (V)

M.Pt. - $> 600^{\circ}\text{C}$.Insoluble in all solvents except hot, concentrated H_2SO_4 .2. Reaction of Cyanuric Chloride With Benzoguanamine (VI)Low yield of Product
believed to be a low polymer.3. Polymerization of 2-Amino-4,6-diphenoxy triazine (VII)

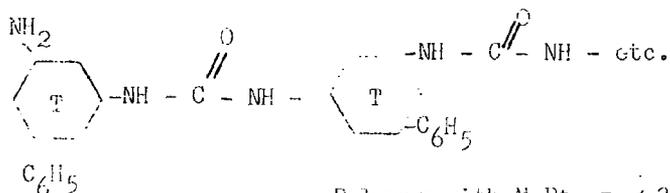
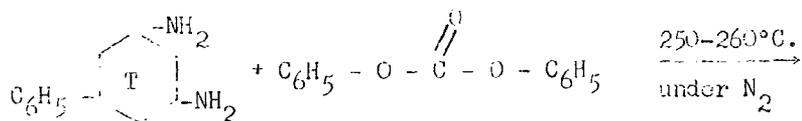
VII

Polymer with M.Pt. = $> 360^{\circ}\text{C}$.

I.R. confirms structure.

4. Reaction of Benzoguanamine and Diphenyl Carbonate (VIII).

The following high melting polymer was prepared in 90% yield.



Polymer with M.Pt. = / 360°C.

I.R. confirms the Urea linkages.

C. Physical Studies on Polymers.

1. Preliminary Heat Stability Studies.

Preliminary heat stability studies were conducted on the more promising polymers prepared in Sections A and B. The procedure used was to subject known weights of polymers to 200° C. heat at 0.5 mm. vacuum for 26 hours. The loss in weight, color changes, and infrared spectra of the polymers were compared after the heat treatment. The results are summarized in Table I.

TABLE I

Effect of Heat (200°C.) and 0.5 mm. Vacuum on Polymers

Polymer System	after 26 hour Exposure		
	% Loss in Wt.	Color Change	I.R. Spectra
Polyphenylene (I)	3.3	None	No change
Poly 2,6-xyleneol (m.pt. = 230°C.) (II)	2.5	"	" "
Poly 2,6-xyleneol (m.pt. = 310° C.) (II)	0.44	"	" "
Poly 2,6-xyleneol (from Bromo-xyleneol) (III)	3.3	"	" "
Melon (V)	3.1	"	" "
Urea-linked triazine polymer (VIII)	9.1	"	" "

With the exception of the urea-linked triazine polymer (9.1%), very little weight loss occurred on the heat treatment. Infrared spectra showed no effect of the heat on the chemical structure of the polymers. Thus it is felt that good heat resistant polymers were available for chemical modification of these polymers into adhesives (Phase II).

2. X-ray Diffraction Patterns.

X-ray diffraction patterns of some of the more promising polymers were determined by the Propellant Research Section of Picatinny Arsenal. The patterns were made using a standard North American Philips Company diffraction unit. The camera had a diameter of 114.6 mm. and allowed rotation of the sample. The samples were ground in an agate mortar and transferred to soft capillaries about 0.3 mm. in diameter. Ten hour exposures using nickel-filtered copper radiation were made with the samples being continuously rotated during exposure. The results are pictured in Figure 1.

The results show that polyphenyl (I) and melon (V) are entirely amorphous, the urea-linked triazine polymer (VIII) is highly crystalline, and both polyxylenols show some well-ordered regions of crystallinity. Polyxylenol III appears more crystalline than the Hay polymer (II).

3. Thermogravimetric Analysis

In order to obtain information regarding the high temperature stability of polyxylenol and its oxidized (carboxy) and bromomethyl derivatives (See Section D), these products were subjected to thermogravimetric analysis by the Plastics and Adhesives Division of Picatinny Arsenal. The polymers were heated at the rate of 3°C. per minute under 100 micron vacuum. The results are reproduced in Figures 2 to 4. The original sample weights were 205 ± 2 mgs. The results show the very good stability of the parent xylenol at temperatures up to 400°C. (Fig. 2). It is interesting to observe the sudden breakdown of this polymer at temperatures greater than 400°C. On the other hand, the carboxy and bromomethyl derivatives show inferior temperature stability as compared to the parent polymer (Figures 3 and 4). Although the volatile breakdown products were not collected and analyzed, the low fractional weight of 0.4 at temperatures in excess of 400°C. shows that carbon-containing compounds (e.g. CO₂) are lost during breakdown (Residue of carbon should have a fractional weight of 0.8).

4. Molding Studies on Polyxylenols

The polyxylenols showed considerable differences in molding temperature, depending on method of preparation and basically on molecular weight. Moldability was determined by calendaring action on 0.1 gram specimens on a controlled surface temperature test plate. Table II represents a selection of typical polyxylenols over the spectrum of molecular weights produced in this work:

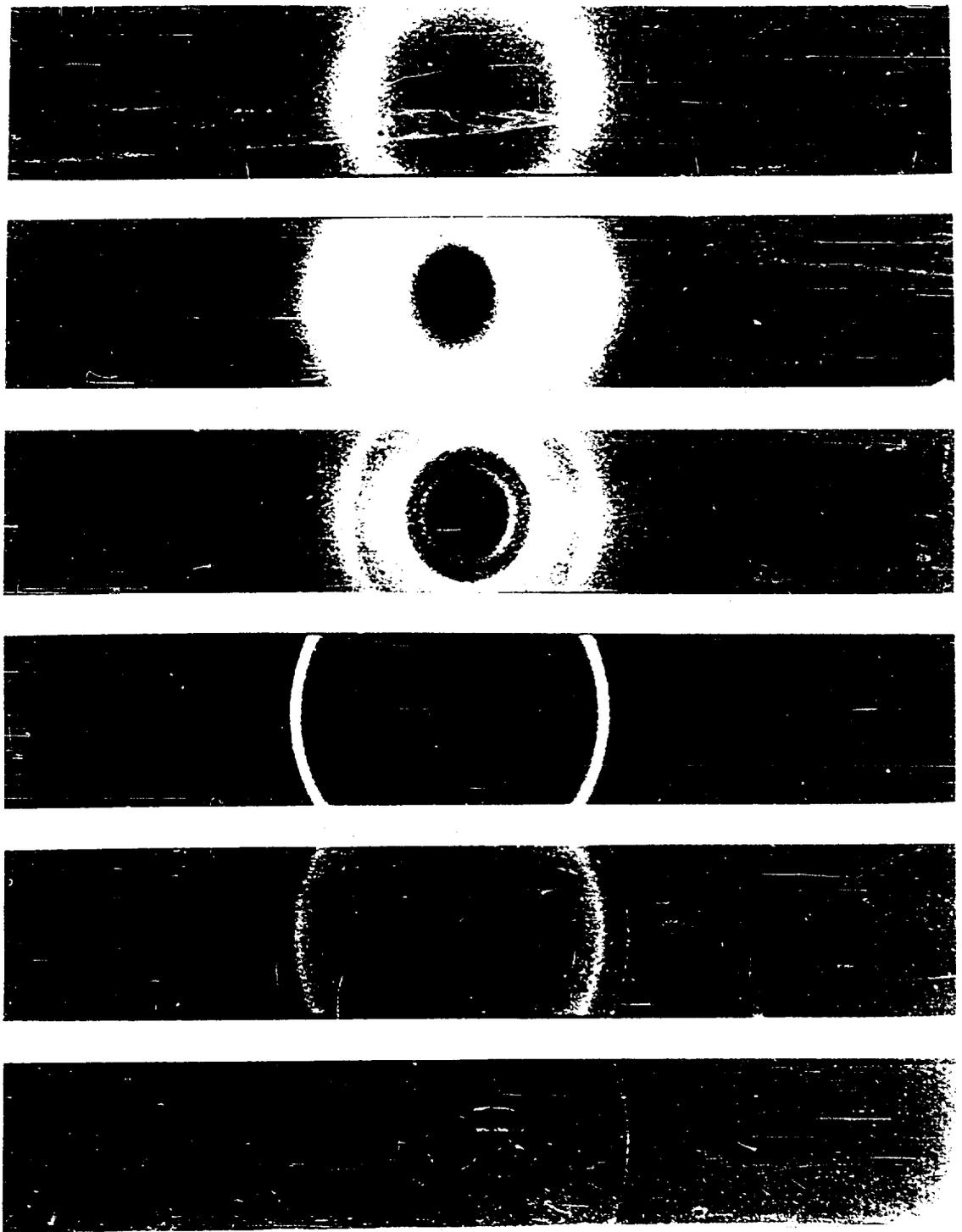
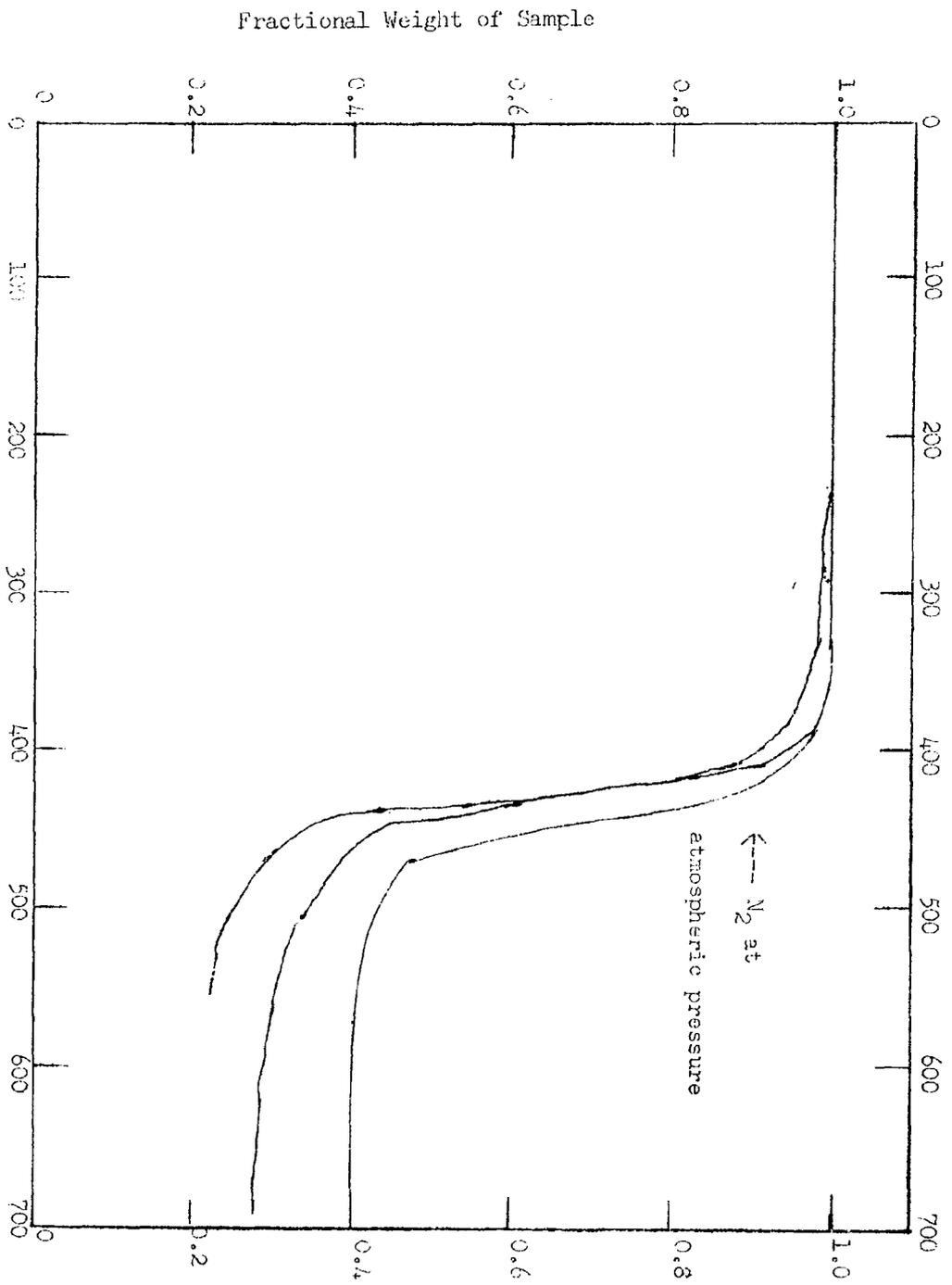


Figure 1 - X-Ray Diffraction Patterns of Polymers

- | | |
|---|-----------------------|
| (a) Polyphenyl (I) | (c) Melon (V) |
| (f) Urea-linked Triazine Polymer (VIII) | (f) Polyxylenol (III) |
| (e) Polyxylenol (II) | (h) Standard NaCl |



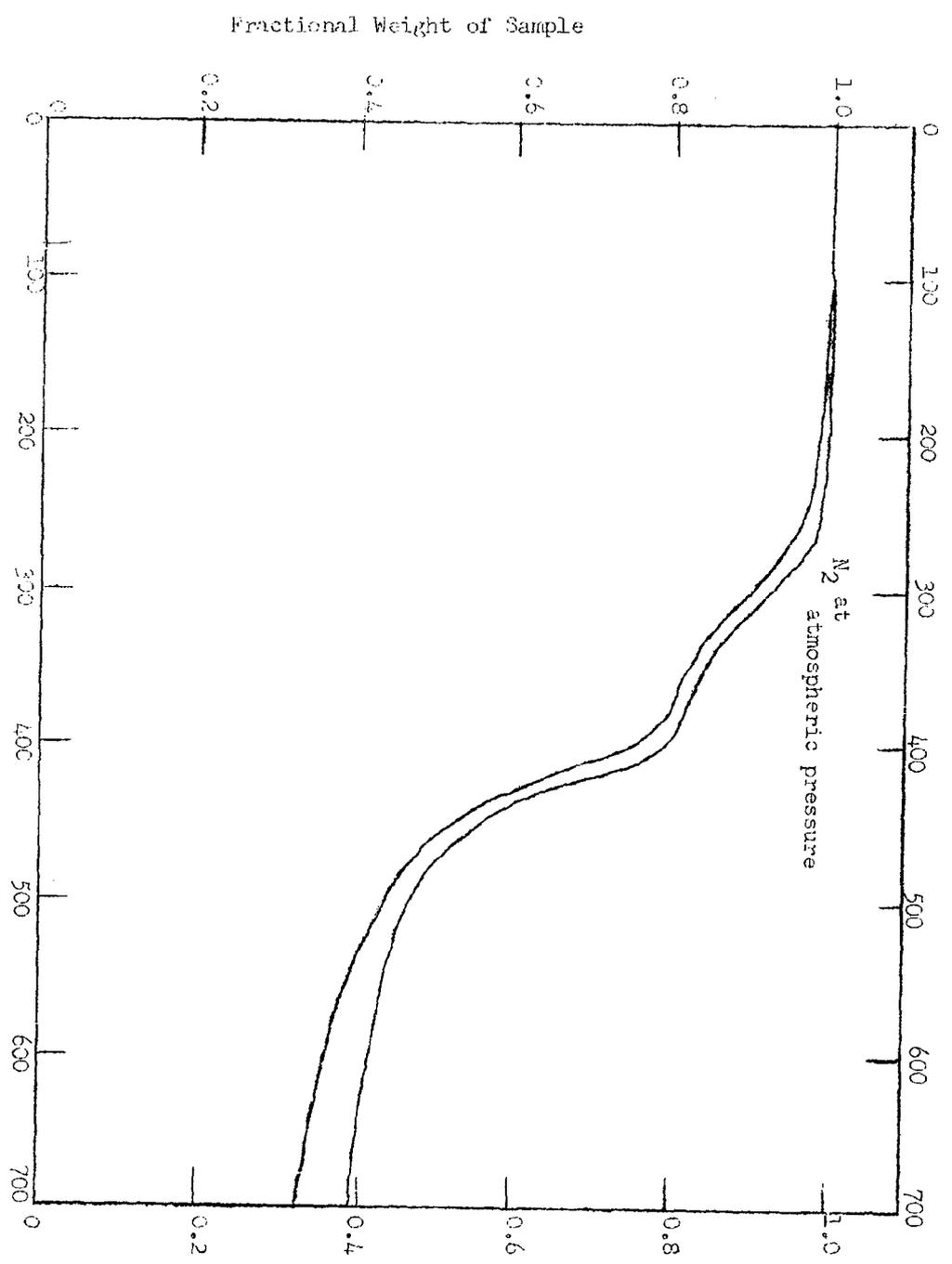


Figure 2 - Thermogravimetric Analysis on Oxidized Polyxylenol

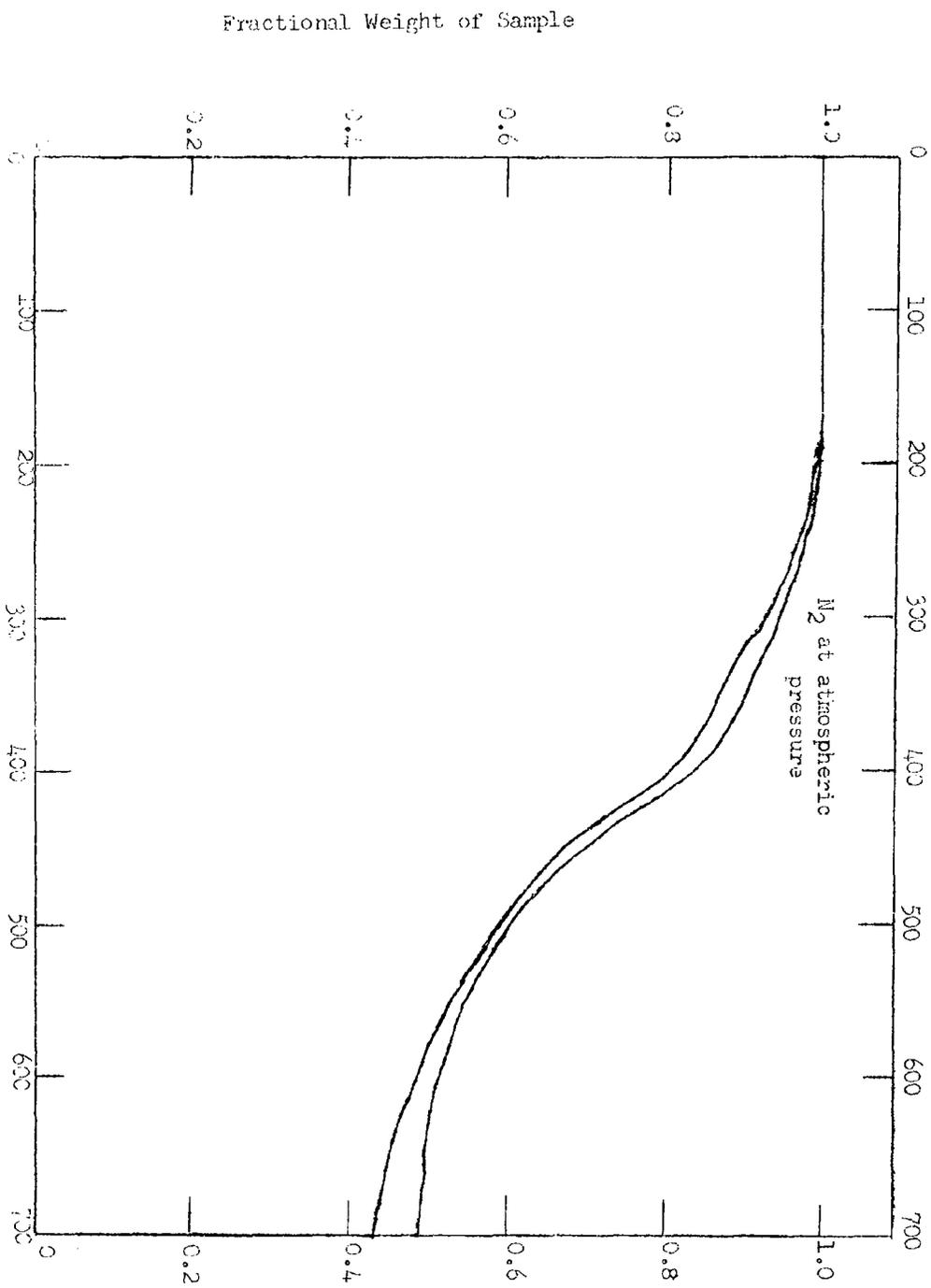


Figure 4 - Thermogravimetric Analysis
on Brominated Polyxylenol

Table II - Variations in Softening Point and Moldability of Polyxylenols

Prepn. No.	Preparative History	MWT	Surface Temperature °F.							
			350	400	450	500	550	600	650	700
248-9	via bromoxylene (Price)	7100	D	S	SM	<u>M</u>	M	M	M	
248-56a	"	7550	D	S	SM	<u>M</u>	M	M	M	
b	"	"		S	SM	<u>M</u>	M	M	M	
c	"	"								
227-82	"	-	D	SM	<u>M</u>	M	M	M	M	
249-101	"	1770	SM	M	<u>M</u>	M	M	M	M	
248-132	"	2880	SH	SM	<u>M</u>	M	M	M	M	
248-130	"	1430	M*	M	M	M	M	M	M	
248-70	via xylenol + O ₂ (Hay)	z		S	SM	SM	SM	M	M	M
248-75	via xylenol + air (Hay)	z	D	D	S	SM	SM	<u>M</u>	M	

Notes: * Molds also at 300°F.
 D = discrete particles
 S = sinters
 SH = semi-moldable

M = moldable
M = initial temperature at which molding is possible.
 z = possibly as high as 20,000

Generally speaking, only those products above molecular weight 4000 gave molded specimens showing of strength and toughness. Below this molecular weight the molds were brittle. We were unable to mold material produced by the Hay method in commercial compression molding equipment.

Table III - Physical Properties of Molded Polyxylenol

	Polymer Prep.	248-9	248-10	248-56 d	248-70
Tensile at 72° F.	psi	3210	2450	2500	not
Tensile at 392°F.	psi	225	-		
Tensile at 500°F.	psi	failed	failed	failed	mold-
Elastic Modulus at 72°F.	psi	41.5M			able
Rockwell Hardness 72°F.		M 78	M 78		
Impact Strength Notch Izod ft.lbs./in.		.59	.68		
Molecular wt.	appr.	7000	7000	7800	20,000

5. Preliminary Adhesion Studies

Although the molding studies made above on the polyxylenols show the difficulty that is encountered in obtaining flow and wetting of surfaces by high molecular weight species of these polymers, it was still of interest to obtain data on the adhesion of these polymers to metal surfaces.

Preliminary work was done on the initial strengths that could be expected by the use of the polyxylenols and their derivatives as metal adhesives. Lap shear specimens were prepared on degreased aluminum. In all cases a pressure of 200 psi was employed. The results are summarized in Table IV. All strengths were measured at room temperature.

Table IV.- Tensile Shear Tests on Aluminum for Polyxylenols

Description	Temp. of Cure (°F.)	Press Time in Minutes	Shear(1) Strength psi
Polyxylenol	550	5	2046
Polyxylenol	550	2	3440
Videne	300	5	1318
Polyethylene	300	5	592

(1) Average of 5 tests

The above results show that polyxylenol, under the conditions of cure employed, gives better strengths than Videne or polyethylene. The longer time of closed press time may have resulted in slight carbonization, oxidation or other reaction which could account for the lower tensile at the longer time.

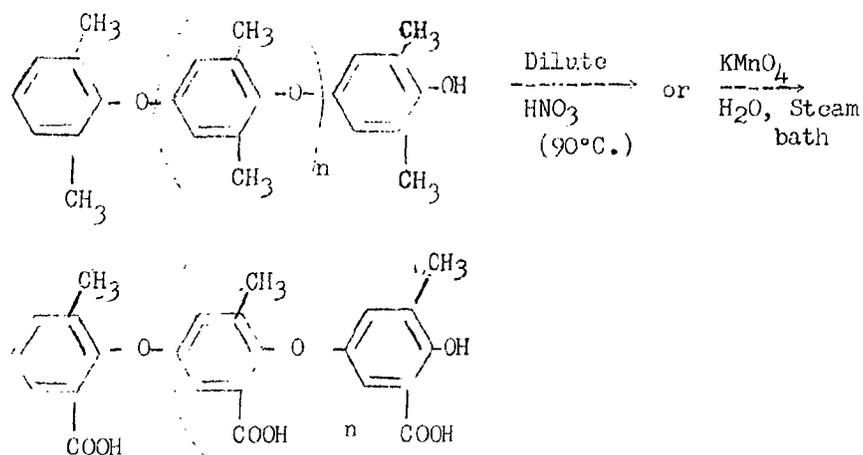
Polyxylenol and some of its derivatives were tested on stainless steel (#302) for tensile shear. The steel specimens were degreased with trichloroethylene and etched with a sulfuric-dichromate mixture. The adhesion results are summarized in Table V. The third column shows the heat treatment employed. All tests were run at room temperature except the last one. This attempt to test the polyxylenol at 500°F. resulted in "no adhesion". The relatively high room temperature strengths obtained, in conjunction with the T.G.A. results (Figure 2), show that the initial adhesion was good but that adhesive failure may have occurred under the conditions used for the strength tests. The physical properties shown in Table III would lead one to expect these poor high temperature results. It is for this reason we have been attempting to get crosslinking.

TABLE V - Tensile Shear Results of Polyxylenol Derivatives on Stainless Steel

No.	Description	Condition	Shear Strength
226-20-2	Parent Polyxylenol	Heated to 550°F. and cooled.	550
226-20-2	" "	Heated to 550°F., held for 2 min. and cooled.	1030
227-29-2	Parent Polyxylenol	Heated to 550°F. and cooled	1512
227-29-2	" "	" " " " "	2550
227-65	Carboxy Derivative of 226-20-2	" " " " "	250
227-65	" "	" " " " "	Broke on removal from jig
227-68	Brominated Derivative of 227-29-2	" " " " "	No adhesion
227-68	" " " "	" " " " "	" "
227-705	Quaternized product of 227-68 with Trimethylamine	" " " " "	" "
227-29-2	Parent Polyxylenol	Heated to 550°F. for 5 minutes and cooled	1930
227-29-2	" "	" " " " "	1930
227-29-2	" "	Heated to 550°F. for 5 mins. and tested at 500°F.	No adhesion

D. Chemical Modification of Parent Polymers1. Incorporation of Carboxyl Groups In Poly 2,6-Xylenol Polymers.

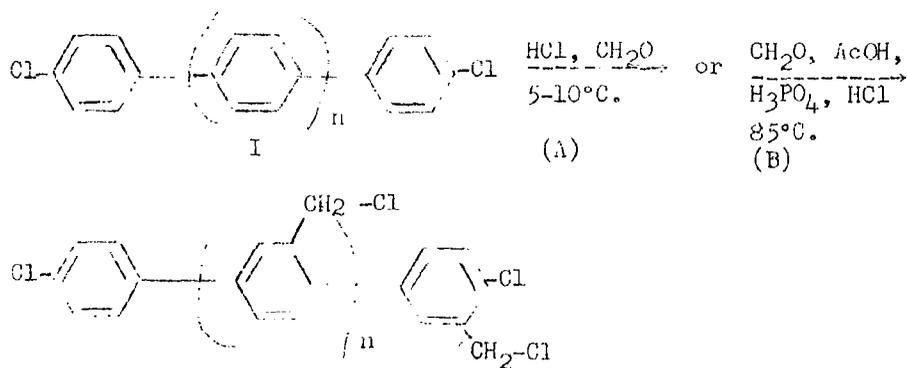
Attempts were made to oxidize some of the methyl groups in poly 2,6-xylenol to the reactive carboxyl groups. Two general procedures were employed:



The permanganate method proved to be the better procedure. The compound was definitely altered by oxidation and originally analyzed to show a high carboxyl content (See Quarterly Report No. 3). However, improved methods of determining acid groups in such polymeric systems showed a maximum of about 3%. I.R. spectra showed no hydroxyl. That the structure was altered in some way by the treatment was evidenced by increased melting point and identification of CO_2 by-product in appreciable amounts. On the other hand, thermogravimetric analysis (Figure 3) and adhesion tests on stainless steel (Table V) gave results which were inferior when compared to the parent polyxylenols.

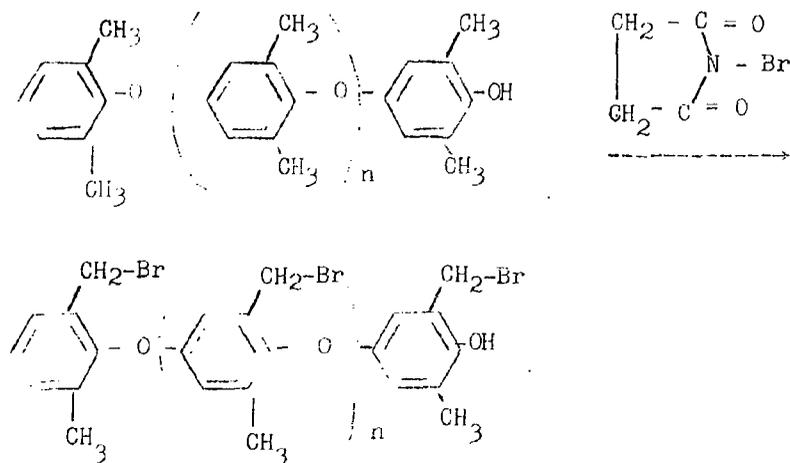
2. Chloromethylation of Polyphenylene

Since it has often been shown that chloromethylation in addition to putting a reactive group on a molecule leads to an increase in the heat stability of the material, the procedure was applied to polyphenylene.



Only procedure (B) was successful (4% chloromethyl groups). No solubility differences between this product and the original polyphenylene could be observed.

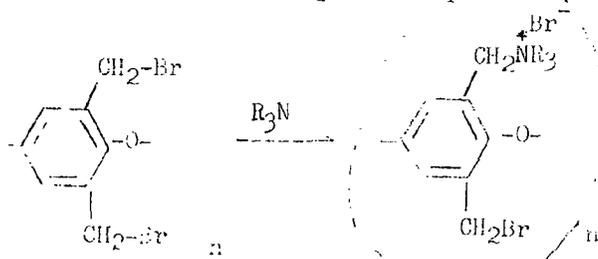
3. Bromination of Side Chains of Poly 2,6-Xylenol Polymers



The above reaction gave a derivative with 22% bromine in good yield. This is equivalent to 0.4 atoms of bromine per repeating unit. The bromo derivative proved inferior to the parent polymer in regard to thermogravimetric analysis (Figure 4) and metal adhesion (Table V).

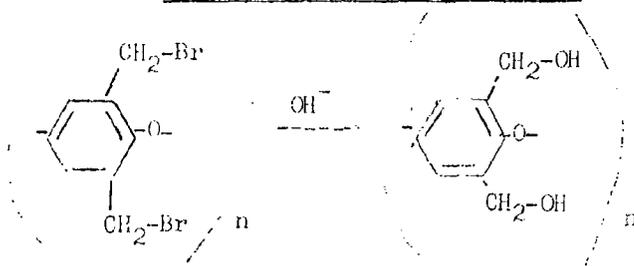
4. Reaction of Polybromoxyleneol With Amines

Polybromoxyleneol could be readily reacted with tertiary amines in benzene solution to give the quaternary bromides.



The quaternaries were high melting, ionic, water soluble products which showed no adhesion to stainless steel (Table V).

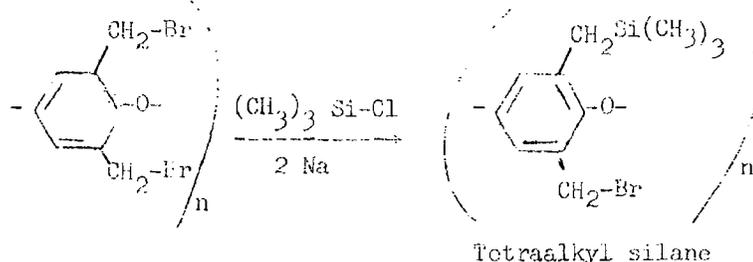
5. Hydrolysis of Polybromoxyleneol



Low melting brominated polyxylenols were reacted with sodium hydroxide and with potassium carbonate, the plan being to produce side chain hydroxyls for thermosetting with polyfunctional materials such as aryl triazinyl diisocyanates. Considering the ease with which benzyl chloride is hydrolyzed to the alcohol, this reaction should proceed readily. In the case of sodium hydroxide an unanticipated result was obtained: the product became insoluble in all solvents tried (although swelling to a gel in solvents normally dissolving the parent substance.) No signs of softening were observed up to 370°C. Analytically, bromine equivalent to that on the side chains was removed yet no hydroxyl groups were found in the product by IR spectra or acetylations. It is believed that a Williamson type reaction may have taken place. Reaction of sodium butylate with the brominated polymer under conditions to force out butanol gave an insoluble, infusible product of similar physical character. Whether or not the suggested mechanism is valid there is little doubt that the reaction with strong bases including amines leads to insoluble high melting polymers. This appears to reinforce the prospect for thermosetting by means of side chain reactions.

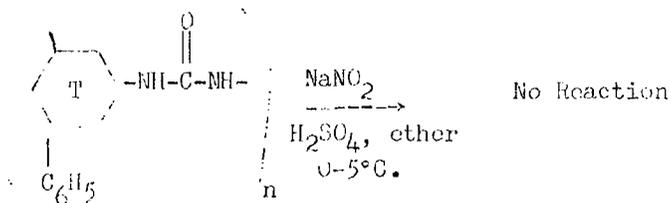
In the hydrolysis by potassium carbonate no removal of side chain bromine occurred.

6. Reaction of Polybromoxylenol And Trimethylchlorosilane



The above transformation was effected in good yield. As expected, the tetraalkyl silane polymer was very high melting. The derivative was undoubtedly cross-linked as it could not be fused or molded. Therefore adhesion tests could not be determined on this derivative.

7. Reaction of Nitrous Acid on Urea-linked Triazine Polymer



8. Reaction of Phosphorous Pentachloride on Urea-linked Triazine Polymer

Phosphorous pentachloride is known to react vigorously with ammonia and urea. The PCl_5 is said to function as a chlorinating agent. However, large amounts of P - N bonds are found in the products.

We have previously found that phosphorous pentachloride reacts vigorously with both benzoguanamine and melamine. Therefore this reaction was applied to our urethane-linked triazine polymer. A high melting product resulted. The product could not be fused and was insoluble in all common solvents. No chlorine was detected in the polymer.

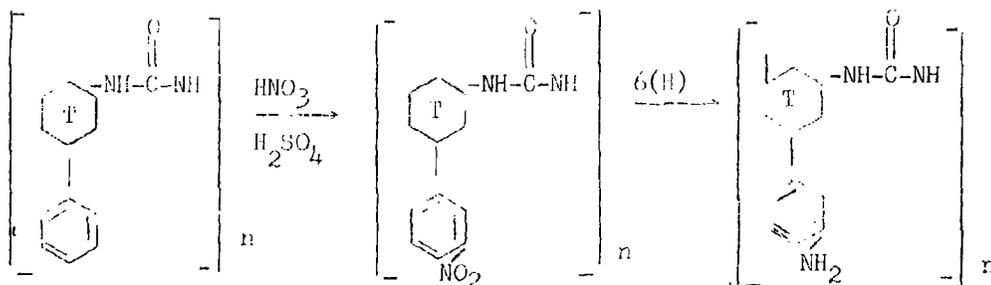
9. Reduction of Melon ("Hydromelon")

The general principle tried from here to section 15 on the highly refractory triazine polymers (melon and urea-linked triazine polymer) was to attach amino groups and consequently form ammonium salts with acids able to etch the stainless steel such as HF , HBF_4 , $\text{H}_2\text{Si}_2\text{F}_7$, NH_4HF_2 and chloromethylphosphonic acid with possible addition of a water-forming hydroxy compound. The intention was to dissociate during cure the ammonium salts forming free concentrated acids and if not successful in an anhydrous medium to add a few

per cent of a polyethylene glycol to form small amounts of water in situ which might help to achieve the etching effect on the stainless steel surface. To achieve this goal, different ways were chosen for both types of triazine systems. Melon is an extremely refractory material and chemical reactions such as nitrations, sulfonations, etc. are almost impossible. However, the compound dissolves in hot concentrated sulfuric acid and this vehicle was chosen to carry out a reduction with a suitable reducing system. At first zinc dust was tried but the zinc salts interfered and reduction went too far (forming water-soluble amines) when the solution was worked up. A better system found was hydrazine sulfate which reduced only at high temperatures as high as 160-170°C. to form an amine which had a very high melting point and was insoluble in all media except dilute aqueous mineral acids. That was exactly what was looked for. However, when an experiment was made to prepare this reduction product, it was found to be sensitive to reoxidation by air, when dried in the drying oven and became insoluble again in dilute aqueous acid and the whole experiment had to be repeated. This time the product was dried in vacuum and therefore remained soluble in dilute acid. The product is called "hydromelon". The greater solubility of this product is believed due to a decrease in the resonance energy of melon by hydrogenation of some of the triazine rings.

10. Amino Derivative of Urea-linked Triazine Polymer

When the benzoguanamine-diphenyl carbonate polymer was subjected to the hydrazine reduction in concentrated sulfuric acid, it was found that the polymer was not stable under these conditions. Decomposition occurred at the amide groupings with the liberation of carbon dioxide. Therefore reduction of the triazine ring in this product was abandoned and the decision was made to attach an amino group to the phenyl group of the benzoguanamine portion in the following manner:



Amino Derivative of a
Polyurea

The above reaction sequence was successfully carried out. Numerous salts were prepared from the amino compound as well as with the above mentioned "hydromelon". These are described in sections 14 and 15.

11. Reaction of Melon with HBF_4 :

Melon was reacted with a solution of fluoboric acid in methanol for 17 hours at 60-70° C. The resulting product contained only 0.82% fluorine.

12. Treatment of Melon with IF_5 :

Melon was reacted with a solution of iodine pentafluoride in chloroform at 60-70° C. The product obtained contained 32.8% iodine and 12.2% fluorine.

13. Treatment of Melon with BrF_3 :

The reaction of melon with bromine trifluoride yielded a product containing 23% bromine and 6.8% fluorine.

14. Salts of "Hydromelon":

"Hydromelon" proved to be a rather weak base since salts could only be formed with strong acids in concentrated solution. However, melon itself does not undergo salt formation under these conditions. On dilution of the "hydromelon" salt solutions, hydrolysis occurs (reprecipitation of "hydromelon"). The following salts were prepared:

- (a) HF salt - contained 8.3% HF
- (b) Fluoboric acid salt - contained 17.3% HBF_4
- (c) Chloromethylphosphonic acid (CMPA) salt - contained 42.8% CMPA.

15. Salts of Amino Derivative of Urea-linked Triazine Polymer:

The following salts were prepared:

- (a) HF salt (2.3% HF)
- (b) HBF_4 salt (17.7% HBF_4)
- (c) Chloromethylphosphonic acid salt (24.6% CMPA)

16. Etching Test:

The ability of the above described amine salts to etch a stainless steel surface was tested as follows:

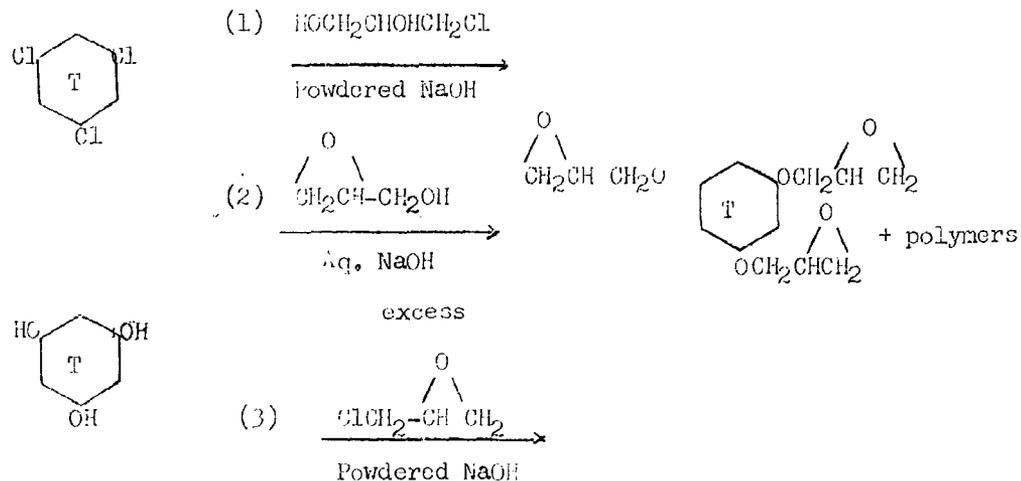
The salts were applied to degreased steel test plates. After sand-wicking the plates together under compression at 300° C., the pressure was released and the extent of etching observed. No noticeable etching (or adhesion) occurred with these salts. In the case of the chloromethylphosphonic acid salts, some slight adhesion was observed upon the addition of small amounts of potassium hydroxide.

In conclusion it was felt that the "etching idea" did not hold promise and therefore was abandoned.

E. Glycidyoxy-s-Triazines:

It was felt that one manner of utilizing the heat resistance imparted by the triazine nucleus and removing the highly refractory nature of compounds of this class would be the attachment of epoxide groupings directly on the nucleus. This should lead to liquids or low melting solids, suitable for proper wetting of a metal surface, which could subsequently be cured "in situ" to hard thermoset products.

In the preparation of these products two routes from cyanuric chloride and one from cyanuric acid were followed in our work:



Route (1) gave clear, viscous, colorless liquids of shelf life from 3 weeks to two months, which analysis indicated to be complex mixtures of base catalyzed polyethers, typical of epoxy compounds. The preparations self polymerized at moderately elevated temperatures to give hard, glossy polymers and cured very rapidly with polyamines at room temperature to give from hard to flexible polymers, depending on amount and type of curing agent. The polymers showed fair heat stability on exposure to temperatures of 500-550°F. but with some embrittlement. It was felt that less highly functional starting materials would give more linear, less brittle products.

Route (3) gave a clear yellow epoxy, remarkably resistant to self polymerization, but readily cured by aliphatic and aromatic diamines and polyamines.

We were unsuccessful with route (2)^{4/} and in the reactions of epichlorohydrin with benzoguanamine in isolating useful products.

The glycidyoxy-s-triazine obtained by route (1) gave "epi" values of 3.65 to 5.2 milliequivalents per gram (theory = 10.1 m.eq./g.). This may be accounted for by the nature of the by-products (all high boiling) and by the fact that step addition polymerization may occur during the preparation. In order to arrive at a less highly functional epoxy resin, cyanuric chloride was first pre-reacted with ammonia to give the mono-amino derivative. The resultant glycidyoxy products, surprisingly, proved to be highly unstable, being difficult to isolate without extensive decomposition. One product was isolated as a glass solid, by stripping at low pressure and temperature. On a 100° C. hot plate surface this material decomposed violently to give a "Pharaoh's Serpent" of foamed plastic with 30% loss in weight and charring in the process.

In order to obtain preliminary information on the adhesion of the glycidyoxy-s-triazines the following crude procedure was used:

Clean stainless steel strips were lapped over thin layers of adhesive, cured under what experiment had indicated to be the optimum curing conditions and broken to determine tensile at break at room temperature. These results

should be regarded as no more than indicative because of the small number tested and in some cases questionable technique in preparing the laps. However, the presence of moderate adhesion was confirmed.

Table VI. - Lap Tensile Tests on Stainless Steel Strips of Glycidylloxy Triazines

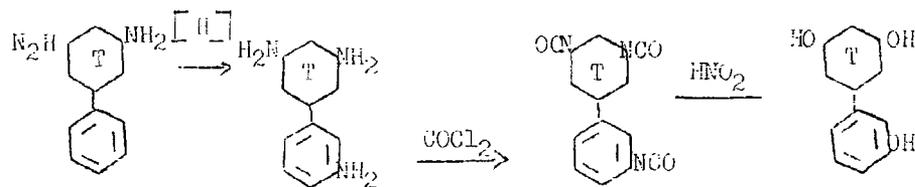
Mix No.	Cure Time Hrs.	Cure Temp. ° F.	Curing Agent	How Lap Made	Tensile psi
125-11	2	200	Versamid 140	500 g. wt.	645
126-2	2	200	Versamid 140	500 g. wt.	1300
127-6a	2	200	Versamid 140	Clamped	470
127-6b	2	200	Versamid 140	500 g. wt.	680
127-4	2	350	none	500 g. wt.	1370
128-2	2	300	none	500 g. wt.	1000

Qualitative observations indicate that holding the strips (Versamid cured) at 525° F. for one hour embrittled and slightly darkened the bond, while possibly improving the adhesion.

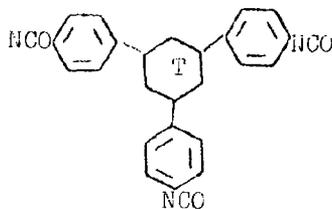
F. Triazine Polyisocyanates:

Commercial isocyanates showed promising behavior in qualitative tests with metal coupons when combined with melamine or benzoguanamine, but the results did not measure up to specified requirements, even when the components were taken in stoichiometric amounts and curing was done under application of much care. Somewhat better results were observed when stoichiometric amounts of phenols were included into these combinations. Phenols applied successfully were: hydroquinone and 1,8-dihydroxyanthraquinone along with benzoguanide. Resorcinol failed under these conditions. The bonds were cured at 250° C. for 20 min. under 150-200 psi pressure in an electrically heated Carver press. Strangely enough the bonds were extremely strong directly after the curing when they were still hot. They could not even be pried apart with pliers under application of brute force and the plates bent off but when they were allowed to cool to room temperature they could be pried loose easily; a strong decrease of tensile strength was very noticeable therefore. It was assumed this behavior stems from brittleness at low temperature (high brittle point).

It was decided to continue synthetic work in the triazine field to obtain more promising base compounds of this class, such as isocyanates and polyphenols. Since aminobenzoguanamine itself did not hold any promise, when combined with commercial triisocyanates it was decided to prepare an isocyanate from it and to convert it into polyhydroxy compounds in the established manner by reaction with nitrous acid (diazotization) and heat conversion into the hydroxy compounds. To achieve this aim more of the base compound, the aminobenzoguanamine had to be prepared in larger amounts. A more successful and economic method of preparation was developed and large quantities are now on hand.



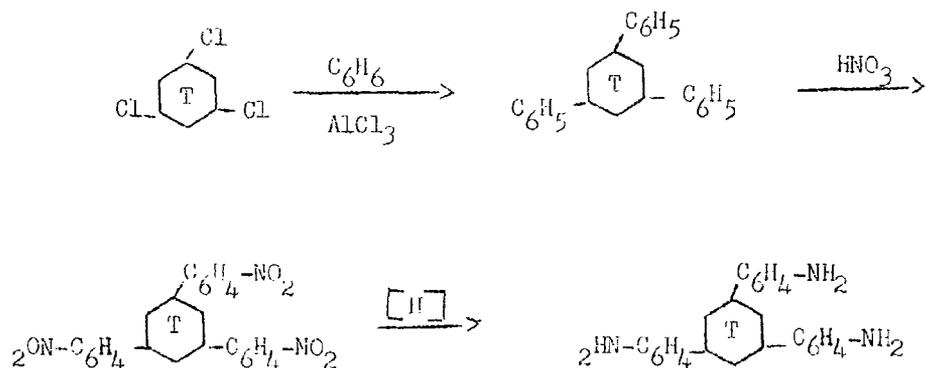
This direction leads to products with only one benzene ring attached to the triazine ring. On the preliminary experiments with commercial isocyanates it was found the triphenylmethane triisocyanate (Desmodur K, Mondur TM) while having good adhesive properties to metal, had a rather poor heat resistance. At 250° C. it carbonized. The triisocyanate seems to be a useful principle, but the attachment of the 3 phenyl rings to a single C atom seems to be the weak spot. It was decided, therefore, to build a similar triisocyanate, with the NCO- carrying phenyl groups attached to the much more heat resistant triazine ring.



Kyaphenine Triisocyanate

In order to obtain the triaminokyaphenine required for the above triisocyanate, many unsuccessful paths were tried. These included (a) Grignard synthesis with cyanuric chloride and p-bromoacetanilide, (b) Ullmann reaction with cyanuric chloride and trichlorobenzene.

The best method of obtaining triaminokyaphenine was found to be as follows:



The details of the above preparation will be described in the first quarterly report of the next contract (No. DA-36-034-ORD-3501-RD).

EXPERIMENTAL

(Unless noted, all temperatures are in °C.)

A. Polyphenylene-Containing Polymers:1. Polyphenylene:

This polymer was prepared by the reaction of p-dichlorobenzene with (1) a potassium-sodium alloy in dioxane, (2) metallic sodium in tetrahydro-naphthalene.

(a) The KNa₂ Method in Dioxane:

The polyphenyl was prepared by the procedure of Edwards and Gold-finger^{5/}.

Metallic sodium (46 g.) and metallic potassium (39 g.) were placed in a 1-liter 3-necked flask containing 100 ml. dry xylene. The mixture was heated to reflux for 34 hrs. to form the liquid alloy.

147 g. p-dichlorobenzene and 250 ml. dioxane were placed in a 1-liter 3-necked flask, equipped with a stirrer, reflux condenser, and a dropping funnel containing the liquid KNa₂ covered with 100 ml. benzene. The flask was heated to 95°, the heat discontinued and the liquid KNa₂ added in small increments over a 2 hour period while maintaining the temperature between 100 and 110°. The mixture was refluxed for 48 hours with vigorous stirring.

The reaction mixture was cooled and water was cautiously added to the flask with nitrogen flooding. Approximately 700 ml. water was employed. The mixture was then heated to reflux overnight.

After cooling, the polymer was filtered, washed with 6 x 200 ml. water, and dried overnight at 85° under vacuum.

The dried solid was suspended in boiling benzene for 24 hours with thorough agitation. The remaining solid was removed by filtration and placed in a Soxhlet Extractor. The polymer was extracted with benzene for 2 days.

The combined benzene extracts were poured into 3 volumes methanol. The precipitated polymer was filtered, washed thoroughly with methanol and dried at 50° under vacuum:

% C	82.02
% H	4.95
% Cl	3.34 (M.Wt. = 2130)

(b) The Sodium in Tetralin Method:

This polymerization was carried out using 147 g. p-dichlorobenzene, 46 g. sodium metal, and 250 ml. tetralin. The reaction temperature was 190-205°.

% C	91.04
% H	5.69
% Cl	1.83 (M.Wt. = 3900).

The elementary analysis showed that a purer, higher molecular weight polymer was obtained by the sodium in tetralin method. Both polymers were soluble in benzene and chloroform.

2. Polymerization of 2,6-Xylenol:

The polymerization was carried out by the method of Hay and associates^{2/}. Modifications were made in the purification and isolation of the polymer.

In a 12-liter 3-necked flask were placed 20.5 g. cuprous chloride, 3.5 liters dry pyridine and 5.5 liters nitrobenzene. Oxygen (2 lbs.) was passed into the solution at a slow rate to oxidize the copper. After the addition of 500 g. 2,6-xylenol, 5 lbs. oxygen was passed in at a slow rate over a 3 hour period. The solution was divided into 700 ml. portions and precipitated by the addition of 3 liters methanol containing 200 ml. concentrated hydrochloric acid. The combined precipitates were collected by filtration and washed with methanolic hydrogen chloride. The polymer was resuspended in a mixture of 1500 ml. methanol and 100 ml. concentrated hydrochloric acid, filtered, washed thoroughly with methanolic hydrogen chloride, and dried at 50° in a vacuum oven.

M. Wt. = 8200 (OH end group analysis).

3. Preparation of 4-Bromo-2,6-xylenol:

2,6-Xylenol (346 g.) was dissolved in 710 ml. glacial acetic acid. The solution was cooled to 7° and, with constant stirring, a solution of 454 g. bromine in 710 ml. glacial acetic acid was rapidly added while maintaining the temperature between 7 and 12° via a dry ice-alcohol bath.

A solution of 37 g. sodium bisulfite in 1700 ml. water was added with stirring. The precipitate was isolated by filtration and washed thoroughly with water. The brominated xylenol was recrystallized from hot hexane to yield 375 g. (66%) of product in the form of long white needles. M.P. = 76-78° (Peilstein gives 79.5°.)

4. Polymerization of 4-Bromo-2,6-xyleneol:

These polymers were prepared from 4-bromo-2,6-xyleneol by a modification of the procedure of Fricke¹. The following illustrates a typical run: Table VII shows the variations in the preparation which were employed in order to obtain products with lower softening points for subsequent "in situ" cross-linking.

4-bromo-2,6-xyleneol (200 g.) was dissolved in 2000 ml. benzene. With stirring a solution of 112 gms. sodium hydroxide in 1 liter water was added. Nitrogen gas was bubbled in for 15 minutes. With continued nitrogen bubbling, a solution of 33 g. potassium ferricyanide in 200 ml. water was rapidly added, while maintaining the temperature below 10°. The reaction mixture was stirred for 1 hour further.

The mixture was transferred to a separatory funnel and the benzene layer removed. The aqueous layer was extracted with 3 x 300 ml. benzene. The combined benzene extracts were washed twice with 5% HCl solution. The benzene solution was evaporated on the steam bath to a volume of 1200 ml. and poured into 4 liters methanol. The precipitated polymer was filtered, washed twice with a dilute methanolic-HCl solution and twice with methanol. The polymer was dried in a vacuum oven at 50° overnight. Yield = 106 gms. (88%).

% C	=	77.23
% H	=	6.40
% Br	=	1.41 (M.wt. = 5700)

Table VII. - Variations in Preparation of Polyxyleneol

	130	132	284 - 133	134	135	136	227- 135
Bromoxyleneol g.	10	10	10	10	10	10	10
12% sodium hydroxide ml	53	53	53	-	53	53	53
40% sodium hydroxide ml	-	-	-	10	-	-	-
K ₃ Fe(CN) ₆ g	1.65	8.3	1.65	1.65	1.65	1.65	1.65
Benzene ml.	-	100	-	40	100	-	100
Methanol ml.	-	-	100	-	-	-	-
Temp. = °C.	29	35	25	45	30	34	10
Agitation	fast	fast	fast	slow	fast	slow	slow
Weight "Yield"							
on bromoxyleneol %	4	30	19	(A)	54	5	47
Bromine in Polymer %	-	-	-	-	35	-	-
Melt Pt. °C. - darkens	130	180	-	-	185	165	200
softens	130	220	-	-	185	165	210
melts	130	-	370+	-	220d	165	280d

Note (A): Could not separate reaction product.

Of the above only those made without organic solvent gave a low, sharp melting point. However, the very low yields obtained precluded use of such a procedure. In all cases where low yields were obtained (below 50%) unchanged bromoxylenol was identified as present. The very high melting point obtained when the product was made in methanol (which gave a one phase rather than a two phase system) is believed to be of theoretical significance. All products melted to give the typical brittle product characteristic of low molecular weight material.

5. Preparation of o-Cresol Novolac:

A low molecular weight o-cresol novolac was prepared according to the procedure of Hegson⁹, using a 4:1 mole ratio of o-cresol to formaldehyde. The molecular weight determined by freezing point lowering in benzene was 582.

Into a 3 liter, 3-necked flask was charged 1296 g. (12M) o-cresol (Pitt Consol 30.5°C. min.), and 245 g. 37.1% formalin containing 5 ml. reagent HCl. The flask was gently heated until an exotherm began at 60° C. at which point cooling was applied sufficient to maintain a temperature of about 80°C. until the exotherm subsided. The reaction mass was then refluxed for two hours. The product was cooled and extracted with 3 x 200 ml. water. It was then stripped of water, and excess cresol at 15 mm pressure to kettle temperature of 252° C. at which point a sharp boiling point rise occurred (to 218° C.). The semi-crystalline mass, weighing 618 grams, was then transferred to a 1 liter distillation flask equipped with a heated condenser. 453 grams of crystalline product were distilled over a 1 mm pressure and boiling point of 212-218°C. This was redistilled under the same conditions to give a middle cut of 250 grams product boiling at 210-222° C. Melting point 109-119°C. Bromine consumption via active hydrogens on the phenolic nuclei was 136.5 g./100 g. Theory for dimer 140, average number of phenolic nuclei 2.1.

A portion of the above novolac was brominated as follows: The product of the above preparation (108 grams) was dissolved in 900 grams glacial acetic acid and the solution cooled to 10°. To this under stirring was added 147 grams bromine dissolved in 500 ml. acetic acid. After 30 minutes 20 grams of sodium bisulfite in 50 ml. water was added. The reaction mixture was poured into 6000 ml. water with stirring. The precipitate was filtered, washed with water, aspirated, then dried under vacuum. Yield 155 grams. m.p. 144-148° C. Bromine 40.4%.

6. Polyaryl Ethers from o-Cresol Novolac:

(a) For the polymerization of the bromo derivative the procedure as described under (4) was followed except in the use of chloroform as solvent. There was substantially no product. When the caustic layer was acidified 85% of the starting material was precipitated unchanged m.p. 120-125° recrystallized from 70-30 ethanol-water.

(b) Via oxidative coupling (Hay method). Essentially the same procedure as described for the polymerization of 2,6-xyleneol was used, except in that twice the proportion of cuprous chloride was required and temperatures of 40-60° C. Yields of about 80% of a polymer were isolated which was insoluble in all solvents tried and which was infusible up to 370° C.

B. Triazine-Containing Polymers:

1. Melon:

This interesting high-melting product was prepared according to the method of Lucas and Redemann^{3/}.

% C	=	21.77
% H	=	1.83
% N	=	42.40

The product was insoluble in all solvents except conc. H₂SO₄.

2. Reaction of Cyanuric Chloride with Benzoguanamine:

Equimolar quantities of the reactants were heated together at 230-250° for 3 hours. After cooling, a tan solid believed to be a low polymer, was isolated.

3. Preparation of 2-Amino-4,6-diphenoxytriazine:

A slurry of 184 g. cyanuric chloride in a mixture of 900 ml. dioxane and 150 ml. chloroform was prepared. With continued stirring, a solution of 34 g. ammonia in 350 ml. ether was added by means of a dropping funnel while maintaining the reaction temperature at 5-10°. The product was stirred for an additional 15 minutes at this temperature. Nitrogen was bubbled in to remove ammonium chloride. Upon cooling, the product crystallized from the filtrate. The product was filtered and used in the next step without drying.

A solution of 60 g. phenol and 28 g. sodium hydroxide in 35 ml. water was prepared and cooled to 10°. The 2-amino-4,6-dichlorotriazine was added and the suspension stirred for 2 hours. The mixture was heated to 95° for 4 hours. After cooling to 50-60°, the product was isolated by filtration, washed 7 times with water and 3 times with ethanol, and dried overnight in a vacuum oven at 50° to yield 37 g. product. M.Pt. = 173°.

% N	=	20.5
% Cl	=	0.84

4. Reaction of Benzoguanamine with Diphenyl Carbonate:

214 g. diphenyl carbonate and 187 g. benzoguanamine were intimately mixed and placed in a 1-liter 3-necked flask equipped with a thermometer, stirrer, heating mantle and a gas inlet tube. With stirring and a slow nitrogen stream, the temperature was gradually raised to 250-260° over a 3 hour period

and then maintained there for 3 additional hours. After cooling the product was removed from the flask, ground fine, and placed in another 1 liter flask with 500 ml. dioxane. With stirring the mixture was refluxed for 3 hours. After cooling, the product was filtered, washed with dioxane and ether, and vacuum dried. Yield = 175 g. M.Pt. = 362°.

I.R. showed NH_2 , amide, carbonyl.

5. Polymerization of 2-Amino-4,6-diphenoxytriazine:

30 g. 2-amino-4,6-diphenoxytriazine was self-polymerized in the same general manner described in (4) above. The melting point of the product was greater than 360°.

C. Chemical Modification of Polymers:

1. Oxidation of Poly-2,6-xylenol:

To a 3 liter 3-necked flask equipped with a stirrer, thermometer and reflux condenser was added 1000 ml. water and 33 grams of potassium permanganate. After solution at 50° C., 25 grams of polyxylenol and 500 ml. benzene were added. The reactants were heated at reflux for two days under good stirring. Five ml. of alcohol were then added to destroy excess permanganate. Five hundred ml. benzene was added to the inseparable gelatinous mass in the flask and the water removed by azeotropic distillation, using a Dean Stark trap.

Toward the end of the distillation 20 ml. of reagent HCl was added. The water-free benzene solution was filtered from inorganic material and precipitated under stirring by pouring slowly into 3 volumes of well-stirred methanol. The fine, non-fibrous precipitate was filtered, washed with methanol and dried. Percent carboxyl by titration was 1.9%. By I.R. spectrum no carboxyl was formed. That oxidation had occurred in some manner was evidenced by permanganate consumption (over 85%), identification of CO_2 by-product, change in physical appearance, elevation of melting point and molding temperature over the original polymer.

This preparation was originally reported to have contained 41.5% carboxyl, but improved analytical techniques now make this figure untenable.

2. Bromination of Side Chains of Poly-2,6-xylenol:

Polyxylenol (25 g.), benzoyl peroxide (0.5 g.), and benzene (150 ml.) were placed in a 500 ml. 3-necked flask equipped with a stirrer, reflux condenser and thermometer. The solution was brought to a boil. An intimate

mixture of 80 g. N-bromosuccinimide and 0.5 g. benzoyl peroxide was added over a 20 minute period. The mixture was refluxed for 30 minutes and filtered. The precipitate was washed several times with benzene. The combined filtrate and washings were dried over anhydrous potassium sulfate and poured into 1 liter methanol. The slightly-brownish product was isolated by filtration, washed with methanol, and dried at 50° under vacuum. Softening pt. = 205°.

% Br = 22.0 (about 0.4 - CH_2 -Br groups per repeating unit).

3. Reaction of Polybromoxylenol with Amines:

(a) The tetraalkyl ammonium salt was prepared on micro scale by the freeze-dry system. 1.063 g. of bromo-(MW 7200) polyxylenol was dissolved in 9 ml. benzene in a 50 ml. round bottom flask. 0.3 grams of triethyl amine was added and the flask contents gently heated to about 50°C. for one half hour. A gelatinous precipitate formed. The contents were cooled in a dry ice bath while rotating to give finely divided crystals, the flask removed from the bath and quickly evaporated at 0.25 mm. until free of all solvent. The hard, horny product analyzed 1.78% nitrogen. It was insoluble in all solvents tried and infusible on a 370° C. surface hot plate.

(b) 0.5 ml. of bromopolyxylenol (prepared from polyxylenol MW 7200) was dissolved in 10 ml. benzene. Three ml. of a benzene solution of trimethyl amine (containing 0.9 gram trimethyl amine) was added under good agitation at room temperature. The immediately produced precipitate was filtered, washed with benzene and dried. The product was insoluble in water, benzene and solvents of intermediate polarity. It did not melt at 700° F.

(c) The following amines intimately mixed at 0.25 to 0.5 parts per 1 part of bromopolyxylenol, then spread on a hot plate at 450° F. (230 °C.) surface temperature set up quickly to give infusible gels: triethylene tetramine, Armour Duomene S (amino propyl Soya amine) Aromene 2HT (secondary O_6 - C_{18})p-diamine. In all cases gelation occurred very fast, before the mixture could completely fuse on the hot plate.

(d) A low molecular weight bromopolyxylenol (prepared from polyxylenol MW 4800) was intimately mixed with p-phenylene diamine in the proportion of 12 parts to 1 by co-dissolving in chloroform and evaporating to dryness under mixing. The dried composition molded on the hot plate, undergoing momentary fluxing to give a stiff rather tough thermoset product.

A. Hydrolysis of Polybromoxyleneol:

A polyxylenol which contained bromine on the phenolic nucleus (1.54% bromine) and bromine on the side chain as $-\text{CH}_2\text{Br}$ (see bromination of side chain) in the amount of 7.2% was used in an attempt to hydrolyze the $-\text{CH}_2\text{Br}$ to CH_2OH .

(a) With NaOH: In a 2-liter 3-necked flask equipped with reflux condenser, stirrer and thermometer 100 grams of the side chain brominated polyxylenol was charged together with 600 ml. benzene and heated to dissolve. Fifty grams of sodium hydroxide in 150 ml. water was added and the mixture heated under reflux with good stirring for seven hours. The gelatinous, inseparable mass was poured slowly into four volumes of hot methanol under good stirring. The precipitated solid was filtered, then reslurried in 5% aqueous HCl, filtered, washed with water and dried. The filter cake was reheated in hot benzene and reprecipitated into 5% HCl in methanol, washed and dried. Yield 96 grams. Melting point over 370°C . % ash 0.37% as Na, Bromine 1.58%, OH by acetylation none, OH by I.R. none. Sodium bromide found in aqueous layer 8.1 grams. The product swelled in hot benzene, hot chloroform, hot dioxane and was totally insoluble in about fifteen other solvents tried. It was infusible up to 370°C .

The desired reaction was obviously not attained and the speculation is offered that a cross-linking reaction of undetermined mechanism occurred.

(b) With K_2CO_3 : Potassium carbonate was substituted for sodium hydroxide in the technique of (a). In this case an easily separable benzene layer was water washed and precipitated into methanol. The dried product contained 0.56% ash as K, 8.38% bromine, no hydroxyl by acetylation and I.R., only 0.1 g. sodium bromide was found in the aqueous layer. The product was soluble in chloroform and benzene and like the starting brominated polymer molded at 500°F . on the hot plate. It must be presumed that no hydrolysis occurred.

(c) With tetraethyl ammonium hydroxide: Reaction was conducted in dioxane-water. The amine reacted to give a gel, which was insoluble and infusible.

5. Reaction of Polybromoxylonol and Trimethyl Chlorosilane:

A solution of 10 g. brominated polyxylonol in 100 ml. toluene was prepared at room temperature. Trimethylchlorosilane (8 g.) was immediately added and the mixture heated to 50° C. Sodium metal (3.2 g.) was added over a 5 minute period. The mixture was slowly brought up to reflux and maintained there for 3 hours. After cooling to room temperature, 200 ml. ethanol was added to destroy the excess sodium. The precipitate was filtered by suction. After drying, the product was slurried in a mixture of 50 ml. benzene and 100 ml. ethanol for 1 hour. The product was filtered, washed with methanol and dried. Yield 12.7 g. On heating the product didn't darken until 270° C. and was completely decomposed at 320° C. The compound was insoluble in all of the common solvents.

6. Reaction of Phosphorous Pentachloride on Urea-Linked Triazine Polymer:

In an evaporating dish 7.5 g. phosphorous pentachloride and 15 g. urea-linked triazine polymer were intimately mixed and warmed gently. No exotherm was observed as is the case with PCl_5 and urea. The mixture was heated to 80° C. with intermittent stirring. The contents were then placed in a vacuum oven overnight at 120°. The final product softened at 360° C. and was insoluble in the common solvents. Analysis showed only 0.3% chlorine. Therefore it was concluded that PCl_5 is without effect on this polymer.

7. Preparation of "Hydromelon":

At first qualitative experiments were attempted to achieve reduction of the melon while dispersed or dissolved in some organic solvent with conventional reducing agents such as Zn dust or NaBH_4 . All of these failed. Complete dissolution could only be achieved in concentrated H_2SO_4 . In this medium Zn dust either reduced the melon completely to water-soluble products or not at all. Hydrazine sulphate finally was found to be an efficient reducing agent at temperatures of 160-170° C. in this medium.

It was found by various experiments that the reduction product ("Hydromelon") was strongly reducing and sensitive against atmospheric oxygen. 100 g. melon were dissolved in 250 ml. concentrated H_2SO_4 at 110° C. and the temperature allowed to rise to 160° C. To this 100 g. hydrazine sulphate was added in portions, and the temperature kept between 160-180° C. for 2 hours with good agitation, under a N_2 blanket. Then the mixture was cooled to room temperature and diluted with ice. Four grams of unreacted melon were recovered after filtration and drying. The solution of the "Hydromelon" was made basic with ammonium hydroxide solution and the precipitated "Hydromelon" filtered, washed and dried under vacuum to prevent reoxidation. This product reduces mercuric salts to metallic mercury. It is readily soluble in moderately conc. aqueous mineral acid under which conditions melon is not soluble. Yield: 74 g. Hydromelon; 48.0% N content found.

B. Amino Derivative of Urea-linked Triazine Polymer:

(a) Nitration of the Substituted Urea Polymer:

After finding this polymer not to withstand temperature of 160°C. in conc. H_2SO_4 as described above under the hydrazine reduction method (CO_2 formation, formation of water-soluble products) a conventional synthesis of an aromatic amine via the nitro compound was started. In qualitative tests the product could be dissolved in concentrated H_2SO_4 at room temperature or below. 38 g. HNO_3 ($d = 1.5$) and 350 g. conc. H_2SO_4 were mixed and cooled to 10° C. and 50 g. of the finely ground urea polymer was gradually added with vigorous agitation and cooling by an external ice bath. The temperature was gradually allowed to rise to 20° C. and the stirring continued for 3 hours until the mixture became a homogeneous yellow mass. Thereupon it was poured into 11 liters of ice water under vigorous agitation and the agitation continued for an additional 30 minutes. Then the slurry was filtered, the residue washed until acid-free and dried. Yield: 59.5 g. (98.2% of theory).

(b) Reduction of the Nitrated Urea Polymer:

After unsuccessful attempts to reduce the nitropolymer with zinc dust, the reduction was carried out under conditions similar to the reduction of nitropolystyrene ($Na_2S_2O_4$ in presence of NH_3). This worked, but the product obtained was of such a fine particle size that it was very difficult to separate from the solution by filtration. Tedious sedimentation techniques had to be applied. The product thus obtained gave a very strong reaction for aromatic primary amine (diazotization and coupling test with alkaline beta naphthol).

75 g. of the nitro product were dispersed in 800 ml. water and 300 g. $Na_2S_2O_4$ were gradually added together with sufficient amounts of ammonium hydroxide solution to keep the media alkaline. The reaction was allowed to proceed under a N_2 blanket for 30 hours at reflux temperature. Then the entire reaction flask was filled with water, the slurry allowed to settle out, the supernatant solution siphoned away. This procedure was repeated several times. After drying in vacuo 60 g. (90% yield) were obtained of a yellow powder which gave a strong reaction for primary aromatic amino groups.

9. Reaction of Melon with Fluoboric Acid:

In qualitative experiments melon proved to be an extremely inert and refractory material. A solution of HBF_4 in MeOH was prepared by freeing it from the water of the 50% commercial grade solution by calcium sulfate treatment. After filtration of the mixture through a coarse sintered glass funnel, it contained 17.7% HBF_4 by weight (sp. gr. = 0.883). When this solution was reacted with melon for 17 hours at $60-70^\circ \text{C}$. in a polyethylene beaker under agitation with a magnetic stirrer, a sample of melon was found to contain, after washing with anhydrous MeOH , only 0.82% F.

10. Treatment of Melon with Iodine Pentafluoride:

2.16 g. melon were dispersed into 50 ml. chloroform (does not react with IF_5) in a nickel beaker. A mixture of 10 g. of IF_5 and 30 ml. CHCl_3 was added in two portions on the hot plate at $60-70^\circ \text{C}$. (at room temperature no reaction occurred) and the solvent allowed to evaporate. 2.03 g. material was recovered after washing with MeOH and drying. The product was slightly darker yellow than the original melon. Analysis: 32.8% I; 37.3% N; and 12.2% F.

11. Treatment of Melon with Bromine Trifluoride:

30 g. of melon were dispersed in 100 g. of Freon 112 (s-tetrachloro-difluoroethane). Under agitation a mixture of 100 g. BrF_3 and 100 g. Freon 112 were added in portions. After each addition, the reaction temperature rose sharply and ultimately reached $70-80^\circ \text{C}$., with external cooling with a dry-ice-Chloroform bath. The solvent again was evaporated after completion of the reaction on the steam bath. The residue was dried in the air oven at 100°C . The product contained 23% Br; 32.2% N (as against 55.5% of the starting material) and 6.75% F.

12. Salts of "hydromelon":

(a) HF Salt:

10 g. "hydromelon" were agitated in a polyethylene beaker with 110 g. of a commercial 60% HF solution for 30 minutes and filtered through a paper filter in a polyethylene funnel and washed with 30 g. HF solution. The HF solution was precipitated by pouring into 1 liter of acetone, filtered, washed with acetone and dried in vacuo at 80°C . Yield 8.5 g. of a white product of the same appearance as the starting hydromelon. HF insolubles: 0.6 g. (reoxidized melon). This dried HF salt hydrolyzes strongly, as a spot test on Congo red paper proved. HF content found: 8.25%, which corresponds to a molecular weight of 485 if 2 HF molecules were bound with the hydromelon. (if HF of melon is ca. 620).

Attempts to prepare the H_2SiF_6 salt were unsuccessful.

(b) Preparation of the Fluoborate:

In this case no acetone could be taken for the precipitation step, since the salt was acetone-soluble, but isopropanol precipitated the salt. 10 g. hydromelon were dissolved in 100 g. of hot commercial grade 50% HBF_4 solution until white fumes appeared. This solution was filtered quickly and precipitated with 250 ml. isopropanol, filtered, washed and dried in vacuo. Yield 12 g., F content 14.8%, which corresponds to 17.3% HBF_4 . This corresponds to a μ / of 508. The product molded readily on the hot plate but left discrete particles.

(c) Preparation of Salts of Chloromethylphosphonic Acid (CMPA):

20 g. crystallized CMPA (Victor Chemical Works, Chicago) were dissolved into 10 ml. hot water and 5 g. hydromelon were added with stirring and replacement of lost water. The solution was precipitated with 500 ml. acetone, filtered again, washed and dried. Yield: 4.5 g.; Cl content 2.83%; P content 1.98% which corresponds to 8.35% CMPA.

Better CMPA binding was found to take place if ethylene glycol were substituted for the water as a solvent for CMPA.

When 20 g. CMPA were dissolved into 20 g. of hot ethylene glycol and 5 g. of "hydromelon" added it took temperatures up to 150° C. to achieve complete dissolution. However, at this temperature, gas formation occurred after 1-2 minutes and the product was precipitated again. This product was mixed with 300 ml. acetone, filtered, washed and dried. Cl content found 7.02%; P content 10.15%, which corresponds to 42.8% CMPA. Yield 4.5 g.

When 30 g. CMPA were dissolved in 20 g. of the glycol, 5 g. of the "hydromelon" could be dissolved at 100° C. without any gas formation or re-precipitation. Yield: 4.5 g.; Cl content, 9.5%; CMPA content 37.9%. Both products became plastic on the hot plate.

13. Salts of Amino Derivative of Urea-Linked Triazine Polymers:

The HF salt contained only 2.28% HF. The H_2SiF_6 salt contained 9.4% H_2SiF_6 which was far short of stoichiometric requirements. The HBF_4 salt prepared from the aqueous slurry of the amine contained 15.3% F or 17.7% HBF_4 .

(a) Preparation of the GMPA Salt:

It was found that dissolution of the amino polymer did not occur in aqueous conc. GMPA. Therefore glycol had to be used. 20 g. GMPA were dissolved in 20 g. glycol and 5 g. of the amino polymer was added with heating until dissolved. The product was precipitated with 300 ml. acetone, filtered, washed and dried in vacuo. Yield 4.5 g; color: brown. The salt softens on heating on the hot plate. Cl content 7.42%; GMPA content 24.6%.

D. Glycidyoxy-s-Triazines:1. Epoxy Triazine from Cyanuric Chloride and 3-Chloro 1,2-Propanediol:

In a two liter three neck flask equipped with a stirrer, thermometer and powder funnel 480 ml. dioxane, 132.2 gms. 3-chloro-1,2-propanediol and 73.5 gms. of cyanuric chloride were added. Over a period of two hours, 96 gms. of powdered NaOH was added in 8 g. portions every 10 min., using a cold water bath to keep temperature at 25° C. during the additions. Then stirred vigorously at 30-35° C. for five hours, cooled, filtered precipitate and washed with dioxane. Dried in a 120° F. oven overnight and then put in a desiccator with H₂SO₄ under vacuum for 18 hours. Final yield was 170 gms. containing 1.44 gms. of free NaOH.

The pH of the filtrate was adjusted to 3.3 by the addition of 1 cc of formic acid and was then vacuum distilled to a temperature of 51° C. at 1 mm. pressure. Yield was 91 gms. of a pale yellow viscous material. The epoxide value averaged 3.35 Meq/gram and the chlorine was 4.2%. The viscosity gradually increased from 16" at 72° F. over 2 Gardner to 240" in thirty-seven days.

One gram of this material mixed at room temperature with 0.3 gms. triethylenetetramine thermoset with an exotherm in 25 min. at room temperature. A small sample on a 150° F. hot plate remained unchanged after one hour. When the temperature was raised to 200° F. it solidified in 1/2 hour.

2. Epoxy Triazine from Cyanuric Acid and Epichlorohydrin^{8/}:

In a two liter three neck flask, equipped with reflux condenser, stirrer and thermometer combined 1388 gms. of Epichlorohydrin plus 129 gms. cyanuric acid plus 5 gms. triethylamine. Cautiously brought up to reflux (exotherm), cooling in the initial stage, to dissolve cyanuric acid and complete reaction, which was continued under reflux for four hours. Cooled to room temperature and added 123 gms. of powdered caustic soda over a period of 1-1/2 hrs. The temperature range during this addition was 25-65° C. Stirred for 3 hours, and then filtered and washed with epichlorohydrin. Vacuum distilled approximately 300 ml. solvent, then transferred to a beaker and adjusted the pH from 9.55 to 4.8 by adding a total of 7.0 cc. of formic acid. Then continued vacuum distillation to a temperature of 100° C. at

1 mm. pressure. Yield was 359 gms. of a viscous, yellow liquid. Epoxy value was 3.15 milliequivalents of epoxide group/gram.

3. 2-Amino-4,6-Dichloro Triazine Preparation:

300 ml. of chloroform was cooled to about -40° C. and liquid ammonia added to a net weight increase of 30 grams. To a 2 liter 3-neck flask, equipped with stirrer, thermometer and reflux condenser, 155 g. cyanuric chloride was added (Eastman Practical), 760 ml. dioxane and 126 ml. chloroform. The contents were cooled to 3° C. and under stirring the chloroform solution of ammonia was added. The temperature arose to and was maintained at 10° for 1 hour. After standing overnight, nitrogen was bubbled through for $1/2$ hour. The flask was heated to 95° , the contents filtered to remove ammonium chloride, the cake washed with chloroform. The mother liquor was cooled to give a crystal crop of 70 grams of white crystals which melted at 235° with decomposition. % Cl 50.9, m.p. 235° d. This preparation was used to react with 3-chloro-1,2-propanediol to form the epoxy derivative.

4. Epoxy Derivative of 2-Amino-4,6-Dichloro Triazine:

To a 2 liter 3-neck flask equipped with stirrer, reflux condenser and thermometer, 124 grams of the above preparation was charged together with 168 grams of 3-chloro-1,2-propanediol, in 916 ml. dioxane as solvent. While maintaining a temperature of $32-38^{\circ}$ C., 126 grams of powdered sodium hydroxide was added portionwise over a two hour period. The contents were maintained for an additional five hours at $30-35^{\circ}$ C. 5.7% of the sodium hydroxide remained unreacted. The reaction product was filtered free of inorganic materials, washed with dioxane. The filter cake after air drying was further dried to constant weight at room temperature under vacuum over concentrated sulfuric acid. The filtrate was adjusted from a pH of 9 to 4.4 by the addition of 0.4 ml. of formic acid. It was then stripped at 1 mm. pressure to a kettle temperature of 62° C. A resinous solid weighing 112 grams was obtained.

A four gram sample placed in a foil dish on a hot plate surface of 200° F. semi-melted, then exothermed violently to give a Pharoah's Serpent of rigid foamed plastic, charring slightly in the process and losing 30% of its original weight.

E. Triazine Polyisocyanates:

1. Reaction of Commercial Polyisocyanates and Triazine Amines:

(a) Into a small beaker were weighed 1.26 g. melamine (0.01M) and added from a buret 13.9 ml. Mondur TM solution. Assay of the latter ($d = 1.32$) approx. 20% - this corresponds to 18.35 g. solution or 3.67 g. (0.01 M) (equimol parts) triphenylmethane triisocyanate dissolved in methylene chloride. Added were finally 0.2 g. triethylamine as a catalyst. Curing was done in the electrically heated Carver press at 350° C. on stainless steel plates, four by one inches and 1/16" thickness which were degreased with C_2Cl_4 and etched with a mixture of HNO_3 and HF (1:1) (HNO_3 65% assay and HF 60%) but the latter did not show a marked increase in bonding strength. In later experiments it was omitted therefore, since they were qualitative and orientating in character only.

This experiment brought almost no bonding strength at all.

(b) Under the same conditions were taken this time 0.84 g. Melamine (0.0066 M) and the same amount of Mondur; again complete failure.

(c) Mondur alone; same failure.

(d) 1.23 g. Benzoguanamide (0.0066 M) and same amount of Mondur TM; same failure.

(e) 1.23 g. isocyanate and benzoguanamine (with approx. 1 NCO group), same amount of Mondur TM; same failure.

(f) 2.03 g. (0.01 M) aminobenzoguanamine, same amount of Mondur TM; same failure.

2. Reaction of Commercial Polyisocyanates and Phenols:

(a) 1.90 g. (0.01 M) of cyanuric chloride, 1.1 g. (0.01 M) hydroquinone, 2.4 g. (0.01 M) Mulltrathane M (diphenyl methanediisocyanate) 3.67 g. (0.01) Mondur TM dry (i.e., 13.9 ml. solution) 0.3 g. quinoline as a catalyst. This cure had good bonding strength, when it was still hot fresh from the press; allowed to cool, however, the strength was rather poor.

(b) Same amounts of isocyanates and catalyst as with (a) 1.1 g. hydroquinone (0.01 M) and 1.9 g. benzoguanide (0.01 M) brought a very good bonding strength when hot; cold again it was poor.

(c) Same amounts of isocyanates and catalyst 1.9 g. benzoguanide, 1.1 g. resorcinol (0.01 M) brought a poor bonding strength, even when freshly cured.

(d) Same amounts of isocyanates, catalyst and hydroquinone as in (b), 0.005 M, 1.8 dihydroxyantraquinone brought very good results when freshly cured and hot, and the strength after cooling was markedly better than with the foredescribed experiments.

3. Reaction of Cyanuric Chloride and p-Bromoacetanilide:

(a) Fittig-type reaction between cyanuric chloride and p-bromoacetanilide in hot toluene:

64.2 g. of p-bromoacetanilide (0.3 M) were dissolved into 300 ml. of toluene under reflux. After complete dissolution were dissolved also 19 g. of cyanuric chloride and added were gradually 15 g. sodium metal in strips under reflux, vigorous agitation and N_2 blanket. The reaction was allowed to proceed for 2 hrs. and was thereupon stopped by cooling and cautious additions of water at 10° C. under the N_2 blanket to destroy the last remnants of unreacted sodium metal. The layers were carefully separated and the aqueous layer analyzed by titration for content on ionogenic halogens. 0.379 moles of halogen ions were found by titration. To be expected were 0.6 m. This would correspond to an overall conversion of 62%, but under the conditions of the experiment in the subsequent hydrolysis cleavage of cyanuric chloride occurs anyway to Cl ions, so 50% from foresaid 62% have to be deducted which leaves only 12% for the Br ions formed in the reaction or 26% of the total Br applied as p-bromoacetanilide. This was considered to be a failure.

In another experiment of the same size with a large excess of sodium metal (50 g.) and 6 hrs. reaction time, only 40% Br-conversion was achieved.

(b) Above reaction with dioxane as a solvent:

Into 60 ml. of refluxing absolute dioxane were added 19 g. (0.09 M) of p-bromoacetanilide and allowed to dissolve completely; thereafter were added 5.5 g. of cyanuric chloride (0.03 M) dispersed into 40 more ml. of absolute dioxane and allowed to dissolve in the hot reaction mixture. Thereupon were added gradually 7 g. sodium metal (excess) in

strips under a N_2 blanket and vigorous agitation. After ca. 30 min. almost no Na was left and the solution darkened considerably. The reaction was stopped by cooling and drowning. The aqueous phase again was collected, brought to 1 liter and titrated. 0.146 M of halogen ions were formed in the reaction. As expected, this time 0.18 M which corresponds to an overall conversion of 90% of the Br applied had reacted.

4. Attempt to Prepare Benzoguanamine-diisocyanate:

50 g. of benzoguanamine hydrochloride (prepared by combining benzoguanamine and conc. hydrochloric acid and drying of the product) were finely ground and suspended into 100 ml. of dry chlorobenzene as a dispersant. Phosgene was introduced in a slow stream at room temperature for one hour and thereupon the temperature allowed to rise slowly to the reflux of the chlorobenzene (130° C.). At this temperature the mixture was allowed to remain for 6 hours. Even in this long time the benzoguanamine did not dissolve in the solvent. Formation of HCl had ceased by this time. After cooling to room temperature, the insoluble product was filtered under completely dry conditions, washed with dry methylene chloride, and dried at 70° C. in vacuum. Yield 55 g.; NCO content found 12.8% (theoretical for one NCO group 19.7%). The NCO content did not even reach one NCO group for one benzoguanamine. Apparently the solubility of the product in the solvent was too poor during the reaction with phosgene.

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