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ABSTRACT

AMMONIA-CATALYZED PHENOL-FORMALDEHYDE RESINS

The literature on ammonia-catalyzed phenol-formaldehyde resins is reviewed and critical comparisons are made of the manner in which the ammonia-catalyzed resins differ from both the alkali- and acid-catalyzed resins.

Intermediate products formed during the initial stages of the ammonia-catalyzed phenol-formaldehyde reactions, as reported in the literature, are tabulated and % N contents are calculated.

Experimental determinations of N content of resins with molar ratios of 1:1.25 phenol to formaldehyde with ammonia at 0.2, 0.5, and 1.0 moles per mole of phenol, show that at the 0.2 molar ratio of ammonia, all the N enters into the resin and remains during the curing of the resin. At 0.5 and higher molar ratios of ammonia, only a portion of the N enters the resin. At low bakes (conversion of "A" to "B" stage), the N increases, probably by loss of H₂O or CH₂O from the resin. In the fully-cured resins, N content of all the resins based on 1:1.25 phenol to formaldehyde drops to the same level as in the resin formed using 0.2 moles of ammonia, i.e. (2.75 ± .2% N).

When the formaldehyde ratio is increased to 2.0 moles per mole of phenol, and using 1.0 mole of ammonia, the N content of the fully-cured resin is 4.63%, an increase proportional to the increase in formaldehyde.

AMMONIA CATALYZED PHENOL FORMALDEHYDE RESINS

BY

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Purpose:

The object of this work is to gain a better understanding of the ammonia-catalyzed phenol-formaldehyde resins with respect to the reactions occurring in their formation, and also with respect to the ultimate chemical composition and structure of the resins in their various stages of cure.

Experimental work is based on the preparation of resins with varying molar ratios of ammonia, phenol, and formaldehyde and determining the nitrogen content of the resins at different stages of cure.

General Background of Phenolic Resin Chemistry:

The para and ortho hydrogens of phenols are activated by the OH group and are capable of reaction with formaldehyde under suitable catalytic conditions. Thus, with USP phenol or meta substituted phenols, three points of reactivity are present, and three dimensional polymers are possible, provided sufficient formaldehyde is used. If the para or one of the ortho positions on the phenol structure is occupied by a substituted group (allyl, aryl or halogen, etc.), only linear polymers are possible (at least in theory) since only two reactive hydrogens are present.

Phenol-formaldehyde resins may be divided into three classes according to the type of catalyst used -- acid catalyzed, alkali catalyzed, and ammonia catalyzed.

The acid catalysis of phenol and formaldehyde will result in the uncontrolled production of infusible, insoluble resins if greater than one mole of formaldehyde is used per mole of phenol. When less than six moles of formaldehyde are used per seven moles of phenol, the products are permanently fusible and soluble and are called "novolacs." The structure of the novolacs has been established by several investigators as being linear polymers in which the phenolic nuclei are connected by methylene bridges (3).

The alkali catalysis of phenol and formaldehyde results in markedly different products than those of the acid catalysis. Most investigators are in agreement that the initial reaction product is the addition of methylol groups to the ortho and/or para positions of the phenolic nuclei. These primary reaction products are called "resoles" or "A-Stage Resins." Curing (conversion to insoluble, infusible products) of the resoles occurs through the following reactions:

1. A methylol phenol reacting at the methylol hydroxyl groups with an active hydrogen of another phenolic nucleus with the resultant loss of a molecule of water and the joining of the phenolic nuclei by a methylene bridge.

2. Methylol phenols reacting through the methylol hydroxyls with the loss of a molecule of water and the phenolic nuclei, then being joined by a methylene ether bridge.

3. Methylol phenols reacting through the methylol hydroxyls with the loss of a molecule of water and a molecule of formaldehyde with the phenolic nuclei then being joined by a methylene bridge.

(These are the primary reactions; several additional reactions, not completely understood, also undoubtedly play an important role in the formation of the completely cured resin.)

Since the early history of phenolic resin chemistry, the curing mechanism of the alkali-catalyzed resins has been divided into three phases (3).

A-Stage Resin (resol) - This represents the initial condensation product of phenol and formaldehyde and probably consists mainly of phenol alcohols together with some products of condensation of the phenol alcohols.

B-Stage Resin (resitol) - This represents the second stage of condensation. The resin is no longer soluble in alkalies but is partly or even completely soluble in organic solvents.

The resin is still softened by heat and is plastic while hot, although hard and brittle when cold.

C-stage Resin (resite) - This represents the final stage of polymerization with extensive cross-linkage. The resin is insoluble and infusible.

The ammonia-catalyzed phenol-formaldehyde resins are still very often classified with the alkali-catalyzed resins. It is the writer's opinion that this is incorrect and that the ammonia-catalyzed resins will eventually be recognized as being distinctly different from the alkali-catalyzed types. Characteristics of the ammonia-catalyzed resins, and comparisons with acid- and alkali-catalyzed types, will be expounded on later. It is sufficient to remark here that the ammonia-catalyzed resins go through stages of formation and cure very similarly to the alkali-catalyzed type, and undoubtedly this has been the reason for classifying them together.

Basis for Experimental Work:

The ammonia-catalyzed phenol-formaldehyde resins are a special class of alcohol-soluble, non-oil-soluble resins which, when deposited as thin films from solution and cured at 275° to 400° F. for 5 to 60 minutes, are converted to completely solvent-insoluble, infusible, very resistant, hard films. Widespread use is made of these compositions as tank linings, drum and can linings, electrical insulating varnishes, cartridge case linings, and in many other specialized applications.

In order to attain thermostetting compositions and to insure the reaction of all the phenol present, the ratio of formaldehyde to phenol in these resins is always greater than 1:1. The lowest ratio of formaldehyde to phenol used in this experimental work was 1.25 to 1.0, and this is probably close to commercial practice. The ammonia content was varied from 0.1 to 1.0 mole of ammonia per mole of phenol. Commercial resins are probably based on a relatively low ratio of ammonia to phenol, e.g. 0.1 mole. In this work, the wide range of concentrations was employed in order to study the extent to which the ammonia enters into the resin structure. This is determined by analyzing the resin for nitrogen content.

II. DISCUSSION OF THE LITERATURE

ON

AMMONIA-CATALYZED PHENOL-FORMALDEHYDE RESINS

A. Comparisons Among the Acid-Catalyzed, Alkali-Catalyzed, and Ammonia-Catalyzed Phenol-Formaldehyde Resins:

As mentioned in the introduction, the ammonia-catalyzed resins have often been grouped with the alkali-catalyzed resins. However, a number of research workers have recognized marked differences between the alkali- and ammonia-catalyzed resins.

Recently Hanson (9) wrote: "It is now generally accepted that when the alkali used to catalyze a phenol-formaldehyde reaction is ammonia, some at least of the base becomes "built-in" to the resin, probably in

the form of - NH - bridges between the phenolic nuclei. What may not be so well-known is that the reaction must follow a very different course from that attributed to the corresponding reaction catalyzed by, say sodium hydroxide. Analytical work by D.W.J. Osmond of our research staff on the ammonia-catalyzed reaction between tertiary butyl phenol and formaldehyde has shown that there is a very little build-up of phenolic nuclei into methylene- or oxymethylene-bridged chains in the first stage of reaction, the phenolic intermediates present being phenol di-alcohol and monoalcohol mixed with unreacted phenol. On further reaction at higher temperatures, this intermediate mixture formed low molecular weight methylene-bridged polynuclear products, comparable in structure with the acid-catalyzed "Dovolac" resin. On the other hand, "controls" in which sodium hydroxide replaced ammonia as catalyst, contained 95% of ether-linked polynuclear molecules with a large proportion of methylolated end-groups. The analytical methods used included those for the determination of methylol groups and dibenzyl ether linkages."

More recently Seto and Ozaki (25) reported on the relation between catalyst species and the constitution of the resins formed. They found that ammonia, primary amines, and secondary amines produce nitrogen compounds and hydroxymethyl compounds, while tertiary amines and quaternary amines (Sic) yield no nitrogen compounds.

Goldblum (6) is working on the precipitation point as a tool in the study of the chemistry of phenolic resins, groups catalysts into two classes based on precipitation point: 1) Alkaline catalysts, and 2) ammonia, primary amines and acids. The secondary and tertiary amines are

reported similar to sodium hydroxide in their catalytic activity. In the comparison among resins formed by catalysis with sulfuric acid on the one hand and ammonia on the other, he finds that the sulfuric acid-catalyzed resin grows to a particular size and tends only to build the resin molecule larger very slowly from that point. In contrast, the ammonia-catalyzed resin continues to grow with time and is strongly influenced by temperature, catalyst concentration, and ratio of phenol to formaldehyde.

Martin (19) comments that, because of the rapid loss of water-solubility in ammonia-catalyzed phenol-formaldehyde resins, the formation of phenol alcohols has been much debated. He then shows experimentally that, at least at room temperature, both phenol monoalcohols and phenol dialcohols may be separated from ammonia-catalyzed phenol-formaldehyde reaction products.

Tsuruta and Fukumura (30) on studying varying quantities of ammonia addition to the system phenol-formaldehyde, found that the results indicated that after an induction period of 40 to 60 minutes the reaction proceeded uniformly, and the rate depended only on the quantity of ammonia added, not on the manner in which it was added.

An investigation of heat liberation in phenol-formaldehyde mixtures by Pesin and Khasanov (23) showed the average value of Q to be 150 calories per gram for the condensation of the novolac with hydrochloric acid catalyst, and about 80 calories per gram for the resol resin with ammonia catalyst. For comparison, Manegold and Petzoldt (17) in determining the heat of phenol-formaldehyde reaction at 90° found only small temperature

rises in alkaline solution, with the reaction being slow and the end point difficult to determine. In acid medium they found a rapid exothermic reaction causing pronounced temperature increase. Ammonia catalysis was not mentioned, but on the basis of the previous reference, it can be inferred that the heat liberation with ammonia catalysis is probably midway between that of alkali and acid catalysis.

B. Nitrogen Contents of Ammonia-Catalyzed Phenol-Formaldehyde Resins

In his early work, Turuta (32) suggested that it is fairly probable that in the phenol-formaldehyde-ammonia system an equilibrium state exists expressed by the relation: phenol + formaldehyde + ammonia \rightleftharpoons intermediate, and then the intermediate decomposes with the liberation of ammonia, and the condensation of phenol with formaldehyde takes place in the following irreversible way: intermediate \rightarrow nucleus of resin + ammonia. The nucleus of resin, termed so temporarily is said to probably be a kind of phenol-alcohol.

Zinke, et al (36) on the resinification of phenols with hexamethylenetetramine report that at higher temperatures or in the presence of larger proportions of the phenol, nitrogen is eliminated as ammonia and perhaps amines, so that the overall reaction may under certain conditions give a resin free of nitrogen.

Hanson (9) reported that in phenol-formaldehyde resins about 95% of the nitrogen introduced as ammonia became "fixed" in the resin.

Hamard and Jacque (7) have shown that cured phenol-formaldehyde-hexamethylenetetramine resins contain substantial amounts of chemically

bound nitrogen. They found that with up to 25 - 30% hexamethylenetetramine in the resin, the bound nitrogen increased linearly with the amount of hexamethylenetetramine to 7 - 8% nitrogen in the product. With over 25 - 30% hexamethylenetetramine it was found that the bound nitrogen stayed constant but water-extractable nitrogen increased uniformly. Volatilization of an additional amount of nitrogen during curing was reported.

C. Intermediates Formed in the Phenol-Formaldehyde-Ammonia Reaction.

The identification of phenol monoalcohols and phenol dialcohols in the early stages of reaction are reported by several workers (18), (25), (27) and (31).

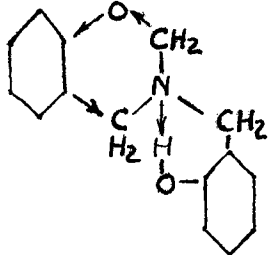
Addition products of phenols and hexamethylenetetramine are reported by a number of investigators (15), (16), (34) and (38). The linkage of phenol and hexamethylenetetramine is shown to consist of a hydrogen bond (15) and (16). These addition compounds probably play no part in resin formation and are only incidental.

The other nitrogen-containing intermediates reported in the literature are tabulated in Table I. The percentage of nitrogen in each has been calculated. Only those based on unsubstituted phenol are tabulated, however, corresponding derivatives from various alkyl-substituted phenols are also reported by several investigators (11), (21), (34), (37), (38), (39), and (40).

Quite recently Shono and Takahashi (29) reported that tris (2 - hydroxybenzyl) amine, obtained from the initial products of phenol, formalin and ammonia, did not react with phenol or formalin, but that

the resin formation between phenol and formalin was catalytically promoted by the tris (2 - hydroxybenzyl) amine.

WEIGHT PERCENTAGE OF NITROGEN PRESENT IN
NITROGEN-CONTAINING INTERMEDIATES FORMED
DURING THE INITIAL STAGES OF THE REACTION
AMONG PHENOL, FORMALDEHYDE, AND AMMONIA,
OR PHENOL AND HEXAMETHYLENETETRAMINE, AS
TAKEN FROM THE LITERATURE.

<u>Name or Structural</u> <u>Formula of Compound</u>	<u>Reference</u> <u>Cited</u>	<u>Empirical</u> <u>Formula</u>	<u>Formula</u> <u>Wt.</u>	<u>Calc'd.</u> <u>% N</u>
(o - HOC ₆ H ₄ CH ₂) ₂ NH *	(12)	C ₁₄ H ₁₅ O ₂ N	229.268	6.11%
(o - HOC ₆ H ₄ CH ₂) ₂ NCH ₂ OH	"	C ₁₅ H ₁₇ O ₃ N	259.294	5.40%
 **	"	C ₁₅ H ₁₅ O ₂ N	241.278	5.81%
α - (3,4 - dihydro - 2H - 1, 3 benzoxazin-3-yl)-o-cresol (29)				
o, o' - dihydroxydibenzylamine * (27)		C ₁₄ H ₁₅ O ₂ N	229.268) 6.11%
bis (2 - hydroxybenzyl) amine * (29),(26)		"	"	
Tris (2-hydroxybenzyl) amine (29),(26)		C ₂₁ H ₂₁ O ₃ N	335.386	4.18%
o, o', o''-trihydroxybenzylamine (28)		"		
2-hydroxybenzylamine	(26)	C ₇ H ₉ O N	123,150	11.37%
4-hydroxybenzylamine	(26)	C ₇ H ₉ O N		
3, 4-dihydro-3-(2-hydroxybenzyl)- 2H - 1,3-benzoxazine **	(26)	C ₁₅ H ₁₅ O ₂ N	241.278	5.81%

* These compounds are the same; ** These compounds are the same.

A. Preparation of Resins

Equipment Used:

2-liter, 2-piece glass reaction flask with top having four necks used in cooks #1-7 inclusive and #10.

500 ml., 3-neck glass flask used in cooks #8 and #9.

Heating mantle controlled by variable transformer.

Motor-driven, stainless-steel agitator.

Water-cooled reflux condenser.

Thermometer 0 - 120°C.

Dropping funnel.

(Fittings on all apparatus were ground glass).

Resin Cook #1:

Molar Ratio:

Phenol: Formaldehyde: Ammonia - 1:1.25:0.2

Material Charges:

6 moles U.S.F. Phenol	564.66 grams	100%
7.5 moles Formaldehyde	602.69 grams	37.37% aqueous
1.2 moles Ammonia	70.22 grams	29.1% aqueous

The phenol and formaldehyde were loaded into the reaction flask and aqueous ammonia was added by means of a dropping funnel. On addition of all the ammonia, an immediate temperature rise of 13.5°C. was observed and then the temperature remained constant. The batch was slowly heated and at 86°C. the cloud point was reached. At 93.5°C. the batch started to reflux and was held at reflux for thirty minutes by which time the temperature had dropped to 96.5°C. The batch separated into a creamy yellow resin layer on the bottom and a milky aqueous layer on top. The top layer was decanted. On cooling the resin, it was found to be hard and only partly soluble in organic solvents.

(It was decided that in order to terminate the resin reaction and facilitate handling, it would be desirable to add solvent. This would result in an aqueous layer which would contain most of the unreacted components and could be separated by decantation. A solvent having a boiling point greater than 100°C., but not so high that it could not be readily evaporated from the resin, was decided on. Other characteristics required of the solvent were low water solubility and good solubility for the resin. No single solvent was found that would meet all these requirements. Therefore, on the basis of screening tests, a combination of 20% n-butanol, 30% xylene and 50% methylisobutyl ketone was selected. The quantity of solvent to be added was arbitrarily set at 2.5 times the weight of phenol used. This resulted in a resin solution having a lower density than that of water, and a reasonably low viscosity.)

Resin Cook #2:

The same molar ratio and charge were used as in Cook #1. The addition of ammonia again resulted in a temperature rise of 13.5°C. The cloud point was reached at 85°C. and reflux started at 98.5°C. After 25 minutes at reflux the temperature was 97°C. and the resin layer had separated as a viscous creamy lower layer. Blended solvents were added and readily dissolved the resin. The entire reduced batch was put in a separatory funnel and after two days had completely separated into a clear, pale amber resin solution as the upper layer, and a clear colorless aqueous layer on the bottom.

A portion of the resin solution was mixed with an equal weight of distilled water, mixed vigorously, and then put into a separatory funnel where it gradually separated as did the original batch.

Resin Cook #3:

The same molar ratio was used as in Cooks #1 and #2, but hexamethylenetetramine was substituted for ammonia.

Material Charge:

6 moles U.S.P. Phenol	564.66 grams	100%
0.3 moles * Hexamethylenetetramine (USP)	42.06 grams	100%
5.7 moles Formaldehyde	458.00 grams	37.37% Aq.

*(This amount of hexamethylenetetramine is equivalent to 1.3 moles of formaldehyde and 1.2 moles of ammonia.)

The hexamethylenetetramine was dissolved in distilled water and added to the phenol and formaldehyde already in the flask. No change in temperature or appearance was noted on addition of the hexamethylenetetramine

solution. The batch was gradually heated to 99°C . at which time refluxing started and the batch clouded suddenly. The reaction became strongly exothermic and remained at reflux without additional heating for 23 minutes at which time the resin had separated as a distinct layer. Blended solvents were added and the resin readily dissolved. It was placed in a separatory funnel, but was lost from the funnel through a leaky stopcock.

Resin Cook #4:

The material charge was the same as in Cook #3.

The batch was slowly heated to 75°C . at which time the heating was discontinued. In 13-1/2 minutes the temperature had reached 90°C . and the batch which was previously clear and colorless became slightly opalescent. One minute later the temperature reached 93.5°C . and the batch suddenly turned milky. Two minutes later the temperature was 98°C . and slight reflux started which slowly became stronger and the batch reached a maximum temperature of 99.5°C . After 12-1/2 minutes from the time refluxing started, the temperature was 99°C ., and refluxing was at a low rate. The batch was quite viscous with some water on top. In 14 minutes the batch was at 94°C . and seemed to be less viscous. Heating was started and a temperature of approximately 94°C . was held for 14 minutes. A yellow resin layer showed considerable separation with a water layer above. Blended solvent was added and the resin slowly dissolved and was placed in a separatory funnel. The batch separated into a clear straw-colored resin solution as the upper layer and a clear colorless water layer below.

Resin Cook #5:

Molar Ratio:

Phenol: Formaldehyde: Ammonia - 1:1.25:0.1

Material Charge:

6 moles U.S.P. Phenol	564.66 grams	100%
7.5 moles Formaldehyde	602.69 grams	33.37% aqueous
0.6 moles Ammonia	35.12 grams	29.1% aqueous

On addition of the ammonia to the phenol and formaldehyde already in the flask, an immediate temperature rise of 9°C. resulted. The batch was gradually heated and began to get hazy at 91°C. At 97.5°C. reflux started and the batch was still only slightly hazy. After 12-1/2 minutes at reflux the temperature was 98°C. and the batch turned milky. After 70-1/2 minutes at reflux the temperature was 96°C. and a fairly viscous resin layer had formed with an upper layer of water. Solvent was added and the resin dissolved. The batch was loaded into a separatory funnel and remained as a milky emulsion. Some clear amber resin solution separated as the upper layer. After a few months, complete separation was still not achieved, but the resin solution layer gelled and was discarded.

Resin Cook #6:

Molar Ratio:

Phenol: Formaldehyde: Ammonia - 1:1.25:0.5

Material Charge:

6 moles U.S.P. Phenol	564.66 grams	(100%)
7.5 moles Formaldehyde	602.69 grams	37.37% aqueous
3.0 moles Ammonia	175.57 grams	29.1% aqueous

The ammonia was added to the mixed phenol and formaldehyde in the flask over a period of 4-1/2 minutes, during which time the temperature rose from 26°C. to 71°C. A minute-and-a-half later the temperature was 72.5°C. and remained steady, with the batch clouding up, and suddenly turning very milky. Heating of the batch was started and reflux began at 96.5°C. In 1-1/2 minutes stronger reflux occurred with the temperature at 97.5°C. and the batch turned yellow. At 3-1/2 minutes from the time of initial reflux, the temperature was 97°C. and the batch was getting viscous with a tendency for water to separate. At 12-1/2 minutes from the start of initial reflux, the temperature was 96.5°C. with moderate reflux and the resin was very viscous. Solvent was added to dissolve the resin and the entire batch was dumped into a separatory funnel. In a few days separation into a lower aqueous clear amber layer and a clear amber resin solution layer above was obtained, with a greenish layer forming at the interface. On removal from the funnel the aqueous layer turned very deep blue-green and had a strong odor of ammonia. The resin solution had a slight odor of ammonia.

Resin Cook #7:

Molar Ratio:

Phenol: Formaldehyde: Ammonia - 1:1.25:1

Material Charge:

6 moles U.S.P. Phenol	564.66 grams	100%
7.5 moles Formaldehyde	602.69 grams	37.37% aqueous
6 moles Ammonia	351.14 grams	29.1% aqueous

(Approx. 395 ml.)

The mixed phenol and formaldehyde were cooled to 6°C . and the ammonia was added from a graduated dropping funnel. The total volume in the dropping funnel at the start was 395 ml. of aqueous ammonia. The effects of ammonia additions were:

<u>Time</u>	<u>Total Ammonia Added</u>	<u>Temperature</u>	<u>Remarks</u>
0	0	$6\text{-}1/2^{\circ}\text{C}$.	Clear solution
1 min.	50 ml.	$19\text{-}1/2^{\circ}\text{C}$.	
2 min.	100 ml.	32°C .	
3 min.	150 ml.	$43\text{-}1/2^{\circ}\text{C}$.	
4 min.	200 ml.	$54\text{-}1/2^{\circ}\text{C}$.	
6 min.	215 ml.	61°C .	Becoming milky rapidly
8-1/2 min.	250 ml.	$67\text{-}1/2^{\circ}\text{C}$.	
10 min.	300 ml.	75°C .	Turning yellow
12 min.	333 ml.	73°C .	
13 min.	395 ml.	71°C .	
16-1/2 min.	395 ml.	70°C .	Fitted on heating mantle

Due to power failure over the next 22 minutes, the temperature dropped to 60°C . In 46 additional minutes the temperature was increased to 90.5°C . and reflux started. Ammonia vapors escaped from the top of the condenser. After 6 minutes at reflux the temperature was 91°C . and the batch separated into a cloudy resin layer on bottom and water on top. Heating was discontinued but the resin was not removed from the flask. After two days the top aqueous layer was greenish amber and the bottom layer was a hard, milky-yellow, solid resin. In one week the upper aqueous layer was fairly clear amber and at the interface between the aqueous and

resin layer an 1/8-inch deposit of reddish-brown slime was present. The water layer was decanted off and had a strong ammoniacal odor. The brownish slime was removed completely with two washings of 100 grams each of blended solvent, 215.1 grams of solution being recovered. The resin, the only material remaining in the flask, was heated, and it melted out readily. A strong odor of ammonia was given off. Blended solvent was added to dissolve the resin and a clear solution of a dark straw color resulted. Seven hundred grams of distilled water were added to the resin solution in a separatory funnel and mixed under violent agitation. Within a few minutes the mix separated into a clear lower water layer and a milky resin solution layer which cleared on standing overnight. The water layer turned pale green on discharge and had a strong odor of ammonia. The resin solution also had an ammoniacal odor.

Eight hundred grams of the resin solution were placed in a separatory funnel and to it were added 209 grams of Reagent Hydrochloric Acid (35-38% HCl) dissolved in 791 grams of distilled water (approx. 2 molar HCl). On addition of the diluted acid, a curd formed instantly and settled to the bottom of the funnel with an aqueous layer above it and a solvent layer on top. The cloudy syrup was removed and the aqueous and solvent layers were discarded. On standing, more solvent and water separated from the syrup and were discarded. The syrup became transparent and ASTM non-volatile (1) was found to be 79.82%. The syrup was insoluble in the blended solvents originally used, in methyl ethyl ketone, in chloroform and in isophorone.

Resin Cook #8:

Molar Ratio:

Phenol: Formaldehyde: Ammonia 1:1.25:0.933

(but using hexamethylenetetramine in place of formaldehyde and ammonia.)

Material Charge:

1-1/3 moles U.S.P. Phenol	125.48 g.
5/18 moles U.S.P. Hexamethylenetetramine	38.94 g.
Distilled water	100.0 g.

The charge was loaded into a 3-neck, 500-ml. glass reaction flask equipped with heating mantle, motor driven stainless steel agitator, condenser, and thermometer. Since the charge was a thick white paste, 50 ml. of distilled water were added to form a thin slurry. This was gradually heated, and at 78°C. a clear, low-viscosity solution existed. On reaching 99°C. the batch rapidly became milky. Slight reflux started with a temperature drop to 98°C. After 10 minutes at reflux the temperature was 97°C., the batch was milky amber, and a slight odor of ammonia was present at the top of the condenser. After 20 minutes at reflux the temperature was 96°C., the batch more viscous, and the odor of ammonia stronger. After 30 minutes at reflux the temperature was 95°C. and there was noticeable separation of resin. After 40 minutes at reflux the temperature was 96°C. and there was very marked separation of resin which was milky yellow, and a clear aqueous layer. The odor of ammonia was less than previously. Solvent was added and the resin dissolved readily. The entire batch was put into a separatory funnel and separated into a clear

amber upper resin solution layer and a lower aqueous layer which was originally colorless but became amber. A green colored band was present at the interface. The aqueous layer had a strong ammoniacal odor and turned green on exposure to air.

Resin Cook #9:

The same ratio and equipment was used as in Cook #8 but it was made non-aqueous.

Material Charge:

125.48 g. U.S.P. Phenol

38.94 g. U.S.P. Hexamethylenetetramine

63 g. Xylol (To moderate reaction should it become too violent)

The batch was heated to 100°C., forming a clear amber solution. It was held at approximately 100°C. and gradually became deeper amber. After 72 minutes, for the first time the odor of ammonia was noticed. After 2 hours at approximately 100°C. the batch was clear amber and of low viscosity. Heating was then discontinued. The following day the product in the flask was observed to be a milky yellow resin which melted readily and evoked a strong odor of ammonia. The resin was dissolved in n-butanol and methyl isobutyl ketone to form a clear yellow solution.

Resin Cook #10:

Molar Ratio:

Phenol: Formaldehyde: Ammonia - 1:2:1

The same apparatus was used as in Cook #1.

Material Charge:

4 moles U.S.P. Phenol	376.44 g.	100%
3 moles Formaldehyde	647.37 g. of 37.11% CH ₂ O	
4 moles Ammonia	234.09 g. of 29.1% NH ₃ (aq.)	

The phenol and formaldehyde were loaded into the flask and cooled to 7°C. With all the ammonia added, the temperature of the batch reached 72°C. because of the exothermic reaction, and the batch turned milky. Then the batch was heated to 97°C., and reflux started. The batch was milky yellow and no odor of ammonia was present. After 10 minutes at reflux a slight odor of ammonia was noted, and after 15 minutes the temperature was 96°C. and a strong odor of ammonia was present at the top of the condenser. After 23 minutes at reflux the temperature was 95°C. and the resin separated considerably from the water. Blended solvent was added to the batch and the resin dissolved readily, after which the entire batch was loaded into a separatory funnel. The resin solution separated as a clear amber top layer and the lower aqueous layer was clear pale amber, with a greenish band at the interface. The aqueous layer turned deep green on discharge and exposure to air.

B. Specimens for Nitrogen Analysis:

The samples prepared by evaporating the resin solutions in small aluminum dishes gave erratic results, probably because of entrapped solvent and poor release of volatiles formed during curing. It was finally decided to brush out films of the resin solution on 8" x 12" glass panels at a wet film thickness of approximately one mil. Three different "curing" conditions were used: air dry, three hours at 105°C. (the ASTM (1) time

and temperature used in determining non-volatile matter), and twenty minutes at 400°F. The resin films were scraped from the glass panels with a razor blade, and nitrogen determinations were run on the specimens by a micro Dumas method using a Sargent Micro Combustion Apparatus and a 1.5 ml. micro Nitrometer. This method is described fully by Steyermark in "Quantitative Organic Microanalysis," The Blakiston Co., 1951, Ch. 6, Determination of Nitrogen by the Micro-Dumas Method. Allowable error in these determinations was $\pm 0.2\%$.

The results are shown in Table II.

TABLE II

NITROGEN DETERMINATIONS ON EXPERIMENTAL RESINS

		<u>% N</u>
		<u>Detn.</u>
		<u>Av.</u>
Cook #1	Cast Resin, untreated	2.23%
Cook #2	Resin solution from initial settling - air dried	2.36, 2.92 - 2.89
Cook #2	Water-washed resin solution - air dried	2.95, 2.89 - 2.92
Cook #2	Resin solution from initial settling - 3 hrs. @ 105°C.	2.54, 2.59 - 2.57
Cook #2	Water-washed resin solution - 3 hrs. @ 105°C.	2.91, 2.99 - 2.95
Cook #2	Resin solution from initial settling - 20 min. @ 400°F.	2.52, 2.57 - 2.55
Cook #2	Water-washed resin solution - 20 min. @ 400°F.	2.66, 2.62 - 2.64
Cook #4	Resin solution from initial settling - air dried	3.69, 3.69 - 3.69
Cook #6	Resin solution from initial settling - air dried	4.38, 4.37 - 4.38
Cook #6	" " " " " - 3 hrs. @ 105°C.	5.51, 5.57 - 5.54
Cook #6	" " " " " - 20 min. @ 400°F.	3.00, 2.98 - 2.99
Cook #7	" " " " " - air dried	5.17, 5.09 - 5.13
Cook #7	" " " " " - 3 hrs. @ 105°C.	6.09, 6.05 - 6.07
Cook #7	" " " " " - 20 min. @ 400°F.	2.65, 2.62 - 2.64
Cook #7	HCl washed resin - air dried	5.30, 5.22 - 5.26
Cook #7	HCl washed resin - ASTM N.V.M. ⁽¹⁾	4.91, 4.83 - 4.87
Cook #10	Resin solution from initial settling - air dried	5.12, 5.23 - 5.18
Cook #10	" " " " " - 3 hrs. @ 105°C.	5.44, 5.37 - 5.40
Cook #10	" " " " " - 20 min. @ 400°F.	4.61, 4.65 - 4.63

IV. DISCUSSION OF EXPERIMENTAL

OBSERVATIONS AND RESULTS

From a study of the experimental cooks described in this report (see "Experimental" section), it was observed that on the addition of ammonia to the mixed phenol and formaldehyde, an instantaneous temperature rise occurred which was directly proportional to the quantity of ammonia added. This occurred up to approximately the quantity that would be required to form hexamethylenetetramine from all the formaldehyde present. Ammonia in excess of this quantity resulted in a drop in temperature. The rapidity of "cloud point" and resin formation also increased with the quantity of ammonia added. These observations are shown clearly in the following tabulation which is based on 1.0 mole of phenol and 1.25 moles of formaldehyde.

TABLE III

EFFECT OF AMMONIA CONCENTRATION

ON INITIAL RESIN FORMATION

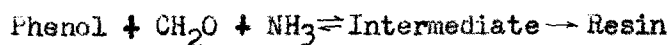
<u>Mole Ratio NH₃ per Mole Phenol</u>	<u>Temp. Rise on Addition of NH₃</u>	<u>Cloud Point</u>	<u>Time at Reflux to complete resin formation</u>	<u>Reference</u>
0.1	9°C.	12½ min. at reflux	70½ min.	Cook #5
0.2	18.5°C.	86°C., 85°C.	25 min.	Cooks #1, #2
0.5	46.5°C.	72.5°C.	12½ min.	Cook #6
1.0	68.5°C. * (max.)	61°C.	Cannot compare	Cook #7

* The maximum temperature rise was reached when approximately

0.75 moles of ammonia had been added. The addition of more ammonia resulted in a drop in temperature. (It would have required 0.833 moles of ammonia to form hexamethylenetetramine with the 1.25 moles of formaldehyde which was present originally. However, as indicated by the cloud point formation, the formaldehyde had partly reacted with the phenol before all of the ammonia was added.)

Resin Cooks #3 and #4 were based on the same ratio of phenol, formaldehyde and ammonia as Cooks #1 and #2 except that an equivalent charge of hexamethylenetetramine was used in place of ammonia, and the formaldehyde charge was reduced by the amount of methylene equivalents in the hexamethylenetetramine, e.g. (1 mole of hexamethylenetetramine is equivalent to 4 moles of ammonia and 6 moles of formaldehyde.) If the initial reaction product of ammonia, when added to mixed phenol and formaldehyde, is hexamethylenetetramine, then when all of the ammonia had been added, Cooks #1 and #2 should have followed the same reaction pattern as Cooks #3 and #4. However, once all of the ammonia had been added in Cooks #1 and #2, and the initial heat evolution had occurred, considerable heat input was required to raise the batches to reflux and to hold them at reflux. But in Cook #4 (in which hexamethylenetetramine is used) heating was stopped at 75°C., and without further heating the temperature rose, first gradually, and then more rapidly to 99.5°C. Then the batch remained at reflux for over 20 minutes without external heating! It must be assumed then, that ammonia does not simply react with the formaldehyde to form hexamethylenetetramine, but that an intermediate compound or complex is formed.

S. Turuta (32) postulates in this connection the formation of an equilibrium system expressed by the relation:



Another possibility is the formation of a compound other than hexamethylenetetramine by the reaction of ammonia and formaldehyde, e.g. trimethylenetriamine. Walker (33) reports that freshly prepared solutions containing equimolar proportions of formaldehyde and ammonia do not behave like aqueous hexamethylenetetramine.

In Cook #7, based on a ratio of 1 mole of ammonia, 1 mole of phenol, and 1.25 moles of formaldehyde, it was noted that as soon as reflux temperature was reached, ammonia vapors were released from the condenser. However, Cook #10, based on a ratio of 1 mole of ammonia, 1 mole of phenol, and 2 moles of formaldehyde, did not release ammonia until the later stages of reaction. With Cook #6, containing 0.5 moles of ammonia, no odor of ammonia was noted coming from the top of the condenser, but the odor of ammonia was present in the water separated from the resin, indicating that a small proportion, at least, of the ammonia, was not bound in the resin. With the lower ratios of ammonia catalyst, no odor of ammonia was present during or at the end of the cooks. In each case where the odor of ammonia was present, the water separated from the resin solution on exposure to air turned a deep blue-green color. This observation is merely an interesting sidelight but is mentioned because no reference was found in the literature to any such color formation.

Cooks #8 and #9 were the same, containing only phenol and hexamethylenetetramine as the reactants. Cook #8, which had water present, appeared to

react more rapidly than Cook #9 which was run under anhydrous conditions. An interesting aspect of Cook #9 is that there was no possibility for methylol groups to form during any stage of reaction, yet resin formation occurred.

The films that were deposited on glass from the resin solutions were quite similar in physical properties regardless of the particular resin cook involved. Resin films formed by air-drying or by baking at 105°C. for 3 hours were quite friable and were easily scraped from the glass panels. Films baked 20 minutes at 400°F., however, were hard and relatively tough, forming ribbons when scraped from the panels.

The nitrogen contents of the various resins at various stages of cure (Table IV) show some very significant results. With the resins based on 1 mole ratio of phenol to 1.25 of formaldehyde, when 0.2 mole of ammonia is used, the nitrogen content of the resin remains fairly constant regardless of cure, i.e. approximately $2.75 \pm 0.2\%$ nitrogen. This value is higher than that calculated for the resin based on the materials reacted. However, it could be accounted for if all of the formaldehyde did not enter the reaction. With 0.5 moles of ammonia the nitrogen content of the resin was slightly less than that calculated, which is not surprising, considering the odor of ammonia which was present at the end of the resin formation. With 1.0 moles of ammonia the N content of the resin is only slightly greater than when 0.5 moles of ammonia are used. It is interesting to note that with the resins based on both 0.5 and 1.0 mole of ammonia, the N content of the resin films which were baked 3 hours at 105°C. was approximately 1% higher than that of the air dried films. These results indicate a loss of water or

formaldehyde, or both, on heating without commensurate loss of ammonia, and could be considered as the transition from the resol to the resitol stage. The most significant results, however, were shown by the fully cured films (resites). In all cases those based on 1.25 moles of formaldehyde to one mole of ammonia reached a final content of approximately $2.75 \pm .2\%$ nitrogen. It is difficult to relate the nitrogen content of the fully cured films (approximately 1 mole of Nitrogen to 5 moles of phenolic nuclei) to any concept of resin structure.

In Cook #10 where the ratio of formaldehyde was increased to 2 moles per mole of phenol, and 1.0 mole of ammonia was used, the nitrogen content of the resin did not change significantly from when 1.25 moles of formaldehyde were used, but the nitrogen content of the fully-cured resin increased in proportion to the increase in formaldehyde.

In Table IV, following, a comparison is made of the determined nitrogen contents of the resins and the nitrogen content that would be expected if there were no loss of ammonia. Calculations are made (1) assuming no loss of any kind during resin formation, and (2) assuming loss of one mole of water per mole of formaldehyde and one atom of hydrogen per mole of ammonia. In an actual resin cook, if there were no loss of nitrogen and all of the reactants were combined in the resin, the actual nitrogen content should be expected to lie somewhere between that calculated by method (1) and (2).

TABLE IV

CALCULATED AND DETERMINED NITROGEN CONTENTS OF
AMMONIA-CATALYZED PHENOL-FORMALDEHYDE RESINS

<u>Resin Composition</u> <u>Molar Ratio - Phenol:</u> <u>Formaldehyde: Ammonia</u>	<u>Identification of</u> <u>Resin</u> <u>and Treatment</u>	<u>Cure of</u> <u>Resin</u>	<u>Remarks</u>	<u>Wt.</u> <u>% N</u>
1:1.25:0.2	Cook 1 - Cast Resin	Initial Cast Resin		2.23%
" "	Cook 2 - Initial ^{Settling}	Air Dry		2.89%
" "	" "	3 hrs. @ 105°C.		2.57%
" "	" "	20 min. @ 400°F.		2.55%
" "	" Water Washed	Air Dry		2.92%
" "	" " "	3 hrs. @ 105°C.		2.95%
" "	" " "	20 min. @ 400°F.		2.64%
" "	Cook 4 - Initial ^{Settling}	Air Dry	Ammonia and equiv. moles of CH ₂ O replaced by Hexa.	3.69%
" "	Calculated		Basis of no loss	2.07%
" "	Calculated		Basis of 1 mole H ₂ O lost per mole CH ₂ O and mole H per mole NH ₃ .	2.49%
<hr/>				
1:1.25:0.5	Cook 6 - Initial ^{Settling}	Air Dry		4.38%
" "	" "	3 hrs. @ 105°C.		5.54%
" "	" "	20 min. @ 400°F.		2.99%
" "	Calculated		Basis of no loss	5.00%
" "	Calculated		Basis of 1 mole H ₂ O per mole CH ₂ O and mole H per mole NH ₃ .	5.98%
<hr/>				
1:1.25:1.0	Cook 7 - Initial ^{Settling}	Air Dry		5.43%
" "	" "	3 hrs. @ 105°C.		6.07%
" "	" "	20 min. @ 400°F.		2.64%
" "	Calculated		Basis of no loss	9.1
" "	Calculated		Basis of 1 mole H ₂ O per mole	

"	"	"	Water Washed	Air Dry		2.92%
"	"	"	"	"	3 hrs. @ 105°C.	2.95%
"	"	"	"	"	20 min. @ 400°F.	2.64%
"	"	"	Cook 4 - Initial	Settling Air Dry		Ammonia and equiv. moles of CH ₂ O replaced by Hexa. 3.69%
"	"	"	Calculated			Basis of no loss 2.07%
"	"	"	Calculated			Basis of 1 mole H ₂ O lost per mole CH ₂ O and mole H per mole NH ₃ . 2.49%
<hr/>						
1:1.25:0.5	"	"	Cook 6 - Initial	Settling Air Dry		4.38%
"	"	"	"	"	3 hrs. @ 105°C.	5.54%
"	"	"	"	"	20 min. @ 400°F.	2.99%
"	"	"	Calculated			Basis of no loss 5.00%
"	"	"	Calculated			Basis of 1 mole H ₂ O per mole CH ₂ O and mole H per mole NH ₃ . 5.98%
<hr/>						
1:1.25:1.0	"	"	Cook 7 - Initial	Settling Air Dry		5.13%
"	"	"	"	"	3 hrs. @ 105°C.	6.07%
"	"	"	"	"	20 min. @ 400°F.	2.64%
"	"	"	Calculated			Basis of no loss 9.1
"	"	"	Calculated			Basis of 1 mole H ₂ O per mole CH ₂ O and mole H per mole NH ₃ . 11.19%
<hr/>						
1:2:1.0	"	"	Cook 10 - Initial	Settling Air Dry		5.18%
"	"	"	"	"	3 hrs. @ 105°C.	5.40%
"	"	"	"	"	20 min. @ 400°F.	4.63%
"	"	"	Calculated			Basis of no loss 8.18%
"	"	"	Calculated			Basis of 1 mole H ₂ O per mole CH ₂ O and mole H per mole NH ₃ . 9.27%

V. CONCLUSIONS

Ammonia-catalyzed phenol-formaldehyde resins are a distinct class in themselves, differing quite markedly from either the alkali-catalyzed or acid-catalyzed resins. The mechanism of reaction apparently lies between that of alkali- and acid-catalyzed resins. Also, in alkali- or acid-catalyzed resins, the catalyst can be readily removed from the resin, but with the ammonia catalyzed resins the ammonia enters into, and becomes a part of the resin.

In resins based on a molar ratio of 1 mole phenol to 1.25 moles of formaldehyde, if .2 moles of ammonia are used, all of the nitrogen enters into the resin and is firmly bound and remains so during all stages of curing. With .5 moles or greater of ammonia, only a portion of the nitrogen enters into the resin. However, on heating at temperatures below those required to fully cure the resin, (e.g. 3 hours @ 105°C.), the resin converts from "A" stage to "B" stage and nitrogen content of the resin increases, probably due to the loss of water and/or formaldehyde without commensurate loss of nitrogen. At higher bakes (20 minutes @ 400°F.) the resin is completely cured to the "C" stage, and a quantity of nitrogen, probably in the form of ammonia or amines, is split off from the resin and the nitrogen content of the resin drops to the same level as the resin based on .2 moles of ammonia (approximately 2.75% N). This is equivalent to approximately 1 mole nitrogen to 5 moles of phenol or 6 moles of formaldehyde. Nothing known of the structure of cured phenol-formaldehyde resins would account for these ratios.

When the ratio of formaldehyde to phenol is increased, it is indicated that a correspondingly greater amount of nitrogen remains in the fully cured resin.

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