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Study of the Reaction of Resorcinol, Formaldehyde, and Ammonia

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Synopsis

Latex dip adhesives for nylon and rayon tire cords are prepared by reacting resorcinol and formaldehyde in aqueous solution in the presence of a catalyst for a specified time and then adding a butadiene–styrene–vinylpyridine latex. Ammonia improves the stability of the latex and increases the adhesion of rubber to cord. However, a white precipitate forms if ammonia is added before the resorcinol and formaldehyde have reacted sufficiently. This paper is a study of the nature of this precipitate and the conditions for its formation. By measuring the heat of reaction of formaldehyde and ammonia and, subsequently, of mixtures of formaldehyde and resorcinol to which varying amounts of ammonia were added, information on the reaction mechanism has been obtained. Ammonia reacts rapidly with formaldehyde to form an unstable intermediate, presumably trimethylolamine, which then reacts further with resorcinol to form trisdihydroxybenzylamine. This compound is also very reactive and condenses with more ammonia and formaldehyde to give a polymer of low solubility, the composition depending on the amounts of ammonia and formaldehyde available for reaction. Elemental analyses support this concept. Primary and secondary amines react in a manner similar to ammonia.

INTRODUCTION

Resorcinol and formaldehyde have been used in tire cord dip adhesives as far back as 1935[1-3] and are still used extensively for nylon and rayon cord. In the dip process resorcinol and formaldehyde are prereacted in aqueous alkali, and after a certain degree of condensation this solution is added to a vinylpyridine copolymer latex.

Addition of ammonia improves adhesion and dip stability;[4] however, the ammonia must be added after the resorcinol and formaldehyde have reacted sufficiently, otherwise a white precipitate[5] is formed. It is the object of this paper to elucidate the nature of this white precipitate.

FORMATION AND PROPERTIES OF THE WHITE PRECIPITATE

The composition of the resorcinol–formaldehyde solution, hereafter indicated as RF solution, is given in Table I of a previous paper.[6] To a series of bottles containing 50 ml of this solution, 0.5, 1.0, 2.0, ml, etc., of 3N ammonia were added exactly 1 hr after preparation of the RF solution. A thick precipitate was formed in each bottle (see Fig. 1). The experiment was repeated 2, 4, 5, 6, and 7 hr after preparation of the RF solution. The range of ammonia concentrations producing a precipitate diminishes the longer the ammonia addition was postponed. After 7 hr no precipitate was formed with any amount of ammonia. The maximum amount of precipitate is estimated to occur with 2 ml of 3*N* ammonia per 50 ml of RF solution, which corresponds to 6 mmole NH_3/20 mmole resorcinol. All bottles to which 3 ml or more 3*N* ammonia was added contained an excess of ammonia, detectable by means of the blue coloring of moist litmus paper held above the solution.

The precipitate was separated by centrifugation. It was found to dissolve in concentrated ammonia, 1*N* NaOH, and also in acid, which indicates

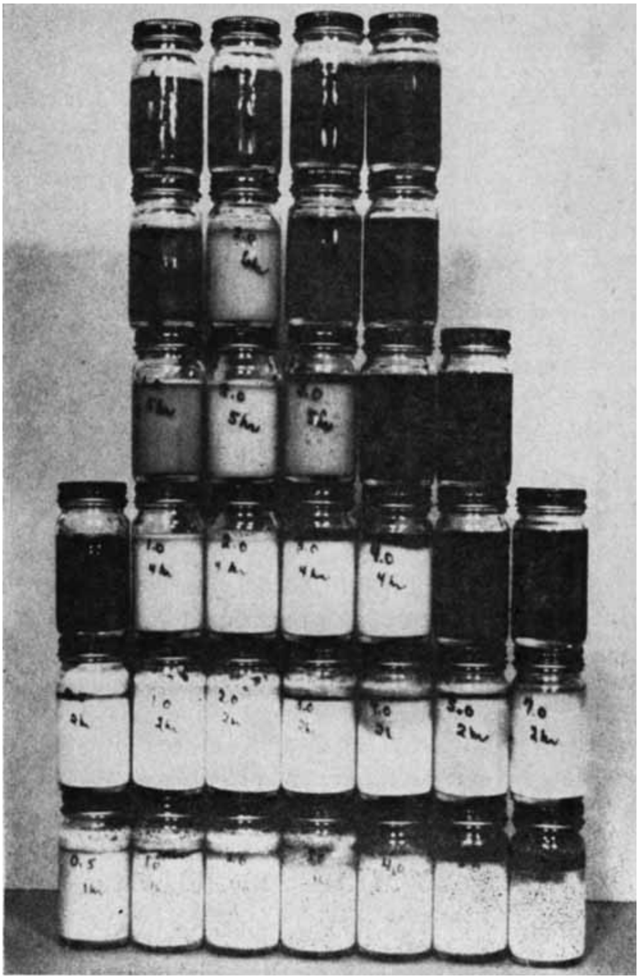


Fig. 1. Addition of ammonia to RF solution at different states of maturity. Picture was taken $^1/_2$ hr after last series of bottles was prepared.

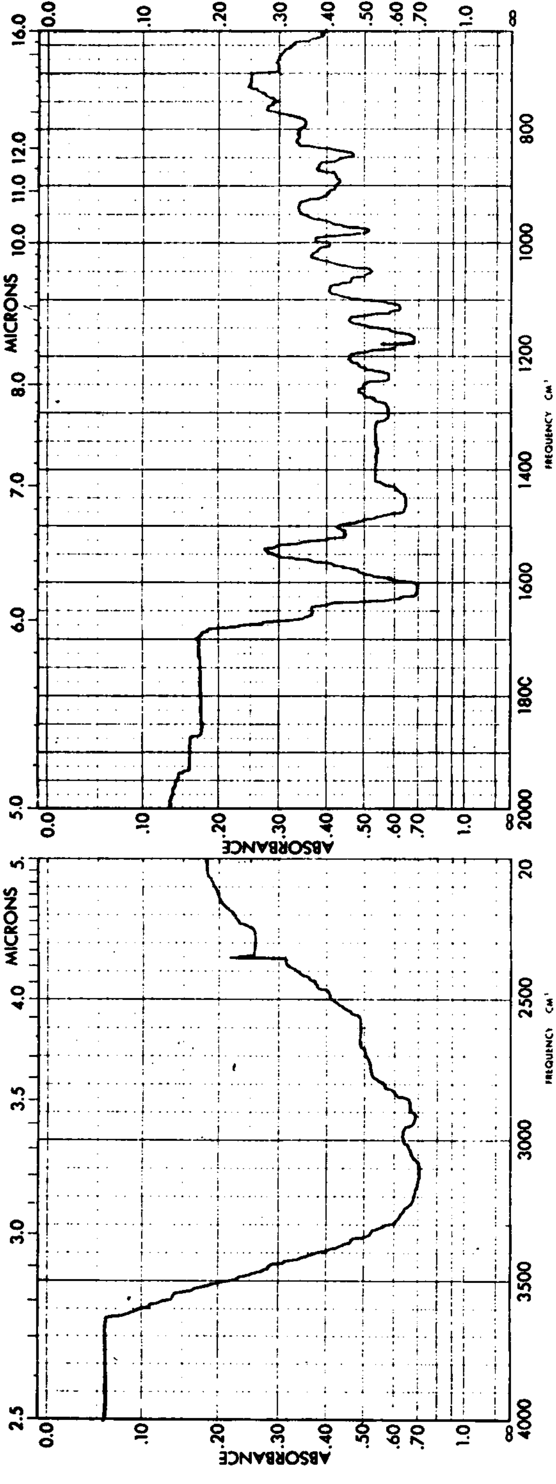


Fig. 2. Infrared Spectrum of white precipitate.

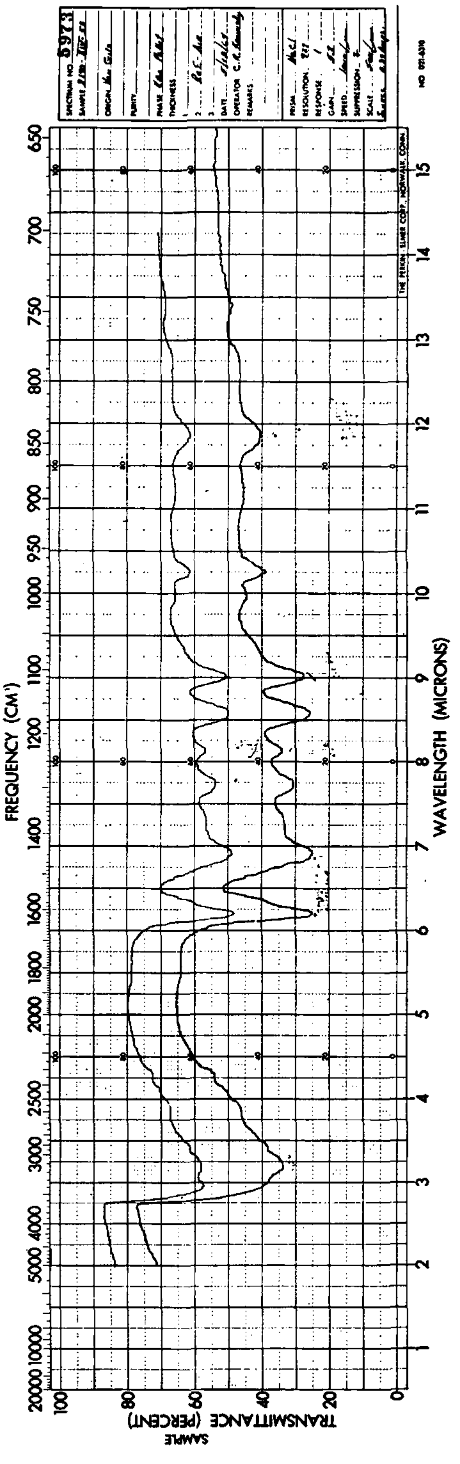


Fig. 3. Infrared spectrum of white precipitate.

its amphoteric nature. It will dissolve in most polar solvents such as DMF, dioxane, THF, and dimethyl sulfoxide but not in benzene, xylene, ethanol, or CCl_4.

The solution in THF was dried by passing through a column filled with Dow 812 resin and cast as a film on a salt flat for infrared spectroscopy (Fig. 2).

On drying in vacuum, the precipitate turned orange to light brown and was no longer soluble in any of the above solvents. An infrared spectrum of this powder in the form of a KBr pellet was made (Fig. 3). On heating the material darkens considerably and releases NH_3 and formaldehyde.

STUDY OF REACTION MECHANISMS

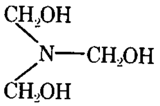
The reaction mechanisms have been studied by calorimetric measurements of the heats of reaction by means of an Aminco-Thermomat made by the American Instrument Company.[7,8] The three components, resorcinol, formaldehyde, and ammonia, have been considered two at a time, and then the addition of the third component was examined.

Resorcinol and Ammonia

These two compounds react with each other as a weak acid with a weak base. On addition of formaldehyde to ammonium resorcinolate, a white precipitate is formed. No calorimetric measurements have been made here.

Formaldehyde and Ammonia

When these two materials are brought together a very fast reaction takes place first, followed by a series of slower reactions. Duden and Scharff in 1895[9a] and more recently Richmond et al.[10] are of the opinion that the first rapidly formed intermediate is cyclotrimethylenetriamine (II). The various subsequent steps in the reaction have not been determined. The ultimate reaction product, however, is undoubtedly hexamethylenetetramine (III).



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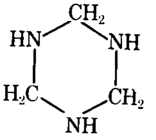
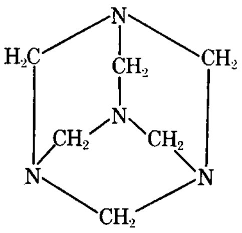


II



III

The experiments described hereafter suggest that trimethylolamine (I), rather than II, is the first intermediate.*

* The concepts in the literature[9a] deviate from ours.

The formaldehyde–ammonia reaction has been studied by measuring the exotherm with a thermometric titrator. Since the temperature is measured with a thermistor in a Wheatstone bridge circuit, change in temperature is measured as voltage change in the recorder. When certain amounts of formaldehyde and ammonia are brought together a small sudden rise of the temperature is observed followed by a gradual rise over a period of time (see Fig. 4).

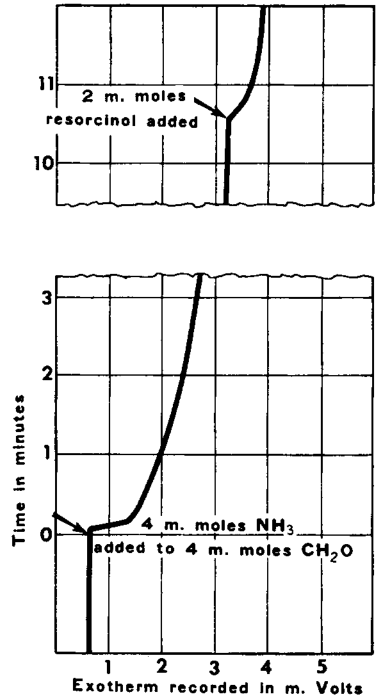


Fig. 4. Time–temperature record of the reaction of 4 mmole NH_3 with 4 mmole CH_2O. Subsequently (after $10^1/_2$ min) 2 mmole resorcinol is added.

We have measured the magnitude of the first temperature rise, which we have called the initial exotherm, at varying formaldehyde–ammonia ratios (Fig. 5).

A sudden break in the curve at 0.33 mole NH_3/mole CH_2O indicates that the initial exotherm is due to the reaction of 1 mole NH_3 with 3 moles CH_2O, presumably forming trimethylolamine in the first step of the reaction. The amount of this compound gradually diminishes due to further reaction. As long as some trimethylolamine is present, addition of resorcinol produces a new temperature rise and causes the formation of a white precipitate (Fig. 4, upper section). The longer the resorcinol addition is postponed, the lower is the second temperature rise, and the smaller the amount of precipitate formed (Fig. 6). After about 30 min no temperature rise and no precipitate formation are observed.

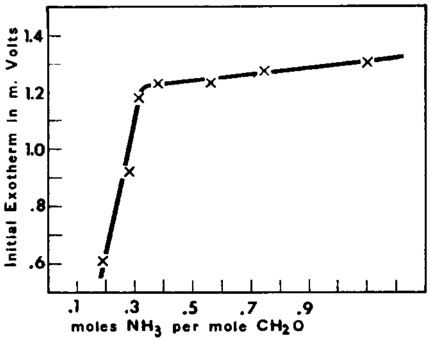


Fig. 5. Initial isotherm at varying formaldehyde–ammonia ratios.

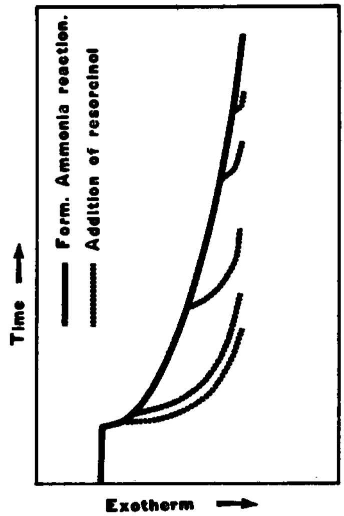


Fig. 6. Effect of the addition of resorcinol after formaldehyde and ammonia have reacted during varying lengths of time.

Addition of resorcinol and formaldehyde to the ammonia or addition of resorcinol immediately after the first exotherm effects the same temperature rise.

Resorcinol and Formaldehyde

In the presence of an alkali, reaction takes place and a number of methylol resorcinols are formed as the first products.[6] When ammonia is added to a mixture of methylol resorcinols, no heat is generated and no precipitate is formed.

In the absence of catalyst and at room temperature no reaction takes place within the time of the experiment. The addition of ammonia now effects a temperature rise, which increases with increasing amounts of ammonia, until a plateau is obtained. The results are represented in Figure 7

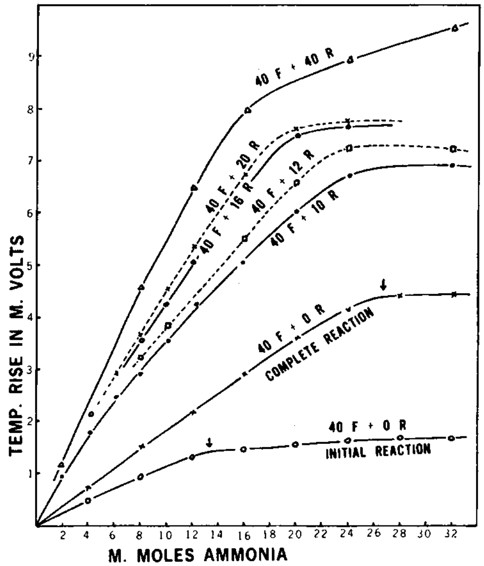


Fig. 7. Temperature rise obtained on addition of ammonia to mixtures of resorcinol and formaldehyde.

In this particular experiment we kept the amount of formaldehyde constant at 40 mmole. The amount of resorcinol varied from 0 to 40 mmole.

For the reaction of formaldehyde with ammonia (no resorcinol), both the initial and the complete temperature rise are indicated. In Table I we have estimated the amounts of NH_3 where the plateau in the curves is reached.

TABLE I
Amount of NH_3 Producing Break in Curve

Resorcinol, mole/mole formaldehyde	Ammonia, mole
0	0.33 (initial reaction)
1	0.375
0.5	0.475
0.4	0.525
0.3	0.575
0.25	0.60
0	0.67 (complete reaction)

These results suggest that when enough resorcinol is present the reaction is similar to the "initial" ammonia–formaldehyde reaction, but with less resorcinol the reaction shifts to the "complete" type.

The same reaction was also studied by measuring the pH and determining the amount of precipitate by centrifuging and drying. The results on the series of experiments with 12 mmole formaldehyde, 10 mmole resorcinol, and varying amounts of ammonia are described in Table II.

TABLE II

Results of Mixing 5 ml Resorcinol (2*N*), 6 ml Formaldehyde (2*N*) and Varying Amounts of Ammonia (1.94*N*)

Water	Volume of ml ammonia, 1.94*N*	pH	Weight of precipitate, g	Color of liquid
38	1	6.8	0.396	Colorless
$37^1/_2$	1.5	6.85	0.5833	Colorless
37	2	7.1	0.770[a]	Yellowish
36	3	8.3	0.326	Light green
35	4	8.95	0.017	Green
34	5	9.25	0.007	Green

[a] Maximum precipitate.

The results obtained on all series are given in Figure 8. Each curve represents a certain ratio of formaldehyde to resorcinol.

In all series the maximum formation of precipitate is reached at pH of about 7. The liquid obtained after centrifugation of the precipitate is colorless at pH's lower than this point and light green beyond the maximum. The number of moles of ammonia to reach pH 7 is exactly $^1/_3$ of the number of moles of formaldehyde, up to 18 moles.

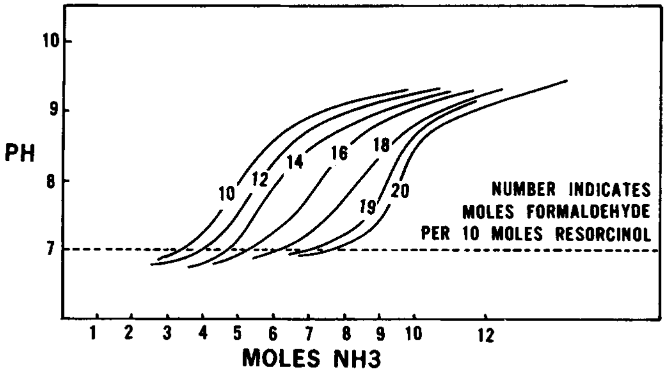
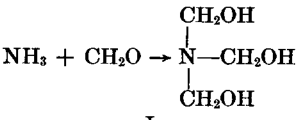


Fig. 8. pH change on addition of ammonia to resorcinol–formaldehyde mixtures.

SUGGESTED REACTION MECHANISM

Based on the experimental results the reaction mechanism of eq. (1) is suggested.



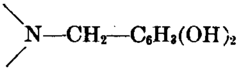
$$NH_3 + CH_2O \rightarrow \underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_2OH}{|}}{N}}—CH_2OH \qquad (1)$$

I

Each methylol group can potentially react (a) with ammonia to form IV

IV

or (b) with resorcinol to form V.



V

When no resorcinol is present, the reaction will follow route (a), ultimately leading to the formation of hexamethylenetetramine. When resorcinol is present, route (b) is preferred, leading to the formation of trisdihydroxybenzylamine (VI)

$$N[CH_2—C_6H_3(OH)_2]_3$$

VI

Since resorcinol has more than one reactive site, compound I can also form bridges between molecules of VI, thus leading to the formation of large molecules. The lower the ratio of resorcinol to formaldehyde, the higher is the probability that route (a) will occur simultaneously. The ultimate product formed would thus contain more formaldehyde and ammonia than VI. For reasons discussed later, the reactants would most likely be taken up in the ratio, 6 formaldehyde to 4 NH_3, as in hexamethylenetetramine. This assumption is supported by the results of an experiment in which 50 mmole resorcinol was reacted with 100 mmole formaldehyde and 50 mmole ammonia in 250 ml water. The resulting precipitate was centrifuged, dried under vacuum to constant weight and analyzed for carbon, hydrogen, oxygen and nitrogen. A computer analysis was made in which it was assumed that the product is composed of $x(C_{21}H_{21}O_6N) + y[3(CH_2O) + (NH_3)]$.

It was found that agreement with the elemental analysis is the closest when $x = 8$ and $y = 3$, as is shown in Table III.

TABLE III

	Found by analysis	Calculated composition
C, %	61.9	61.82
H, %	6.0	5.94
O, %	26.2	26.54
N, %	5.9	5.70

In a triangular diagram (Fig. 9), the composition of the indicated product obtained is denoted by a point (▲) located on a line connecting the trisdihydroxybenzylamine composition with the point representing hexamethylenetetramine.

The circles in Figure 9 represent compositions corresponding with the breaks in the curves in Figure 7. It is significant that these points are also located on the aforementioned line.

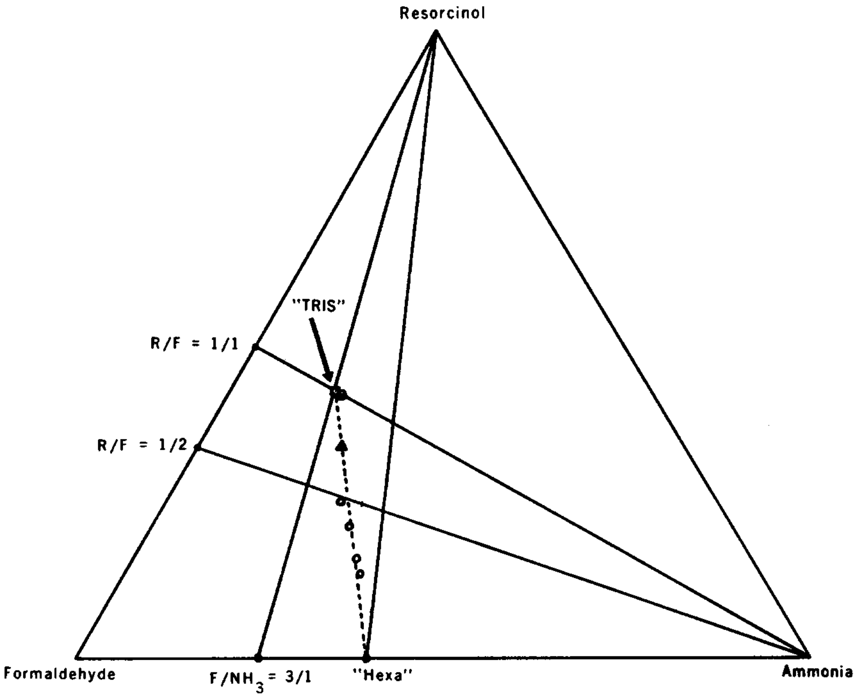


Fig. 9. Composition of the white precipitate in relation to the components: Resorcinol, Formaldehyde, and Ammonia

REACTIONS WITH AMINES

It was observed that, in addition to ammonia, the following amines formed precipitates when mixed with unmatured RF solution: dimethylamine, propylamine, *tert*-butylamine, *n*-hexylamine, 1,6-hexanediamine,

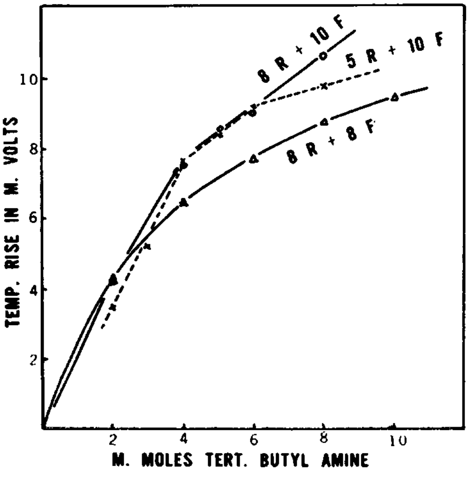


Fig. 10. Addition of *tert*-butylamine to resorcinol–formaldehyde mixtures.

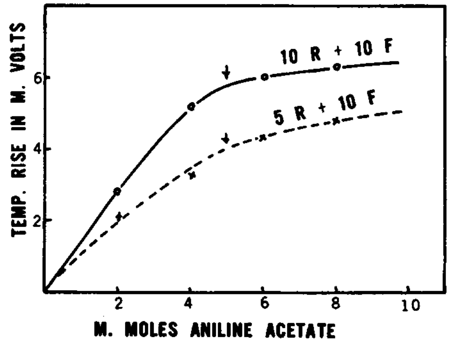


Fig. 11. Addition of aniline acetate to resorcinol–formaldehyde mixtures.

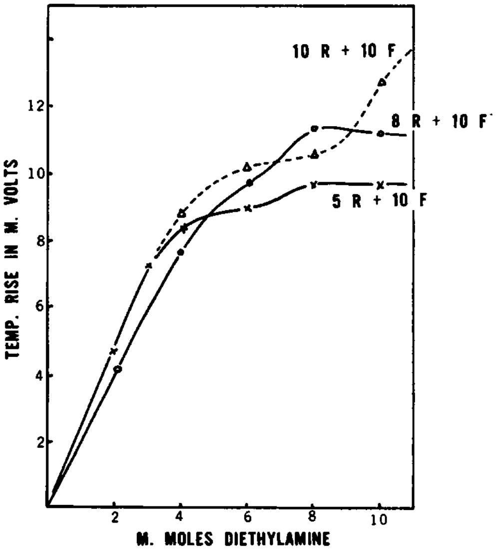


Fig. 12. Addition of diethylamine to resorcinol–formaldehyde mixtures.

TABLE IV
Significant Stoichiometric Ratios

	Resorcinol, mole	Formaldehyde, mole	Amine, mole
tert-Butylamine	10	10	5
	10	12.5	6.25
	10	20	10
Aniline	10	10	5
	10	20	10
Diethylamine	10	10	5
(first bend)	10	12.5	6.25
	10	20	8
Diethylamine	10	10	10
(second bend)	10	12.5	10
	10	20	16

monoethanolamine, monoisopropylamine, *N*-phenylethanolamine, *N*-ethylethanolamine, and methylethanolamine. Each of these precipitates was soluble in an excess of the amine. No precipitate was formed with diethanolamine, although heat was generated on mixing. No reaction occurred with tertiary amines.

Reaction exotherms have been measured with *tert*-butylamine, aniline acetate, and diethylamine. The results are shown in Figures 10, 11, and 12. From the breaks in the curves (in some cases determined rather arbitrarily) the stoichiometric ratios in Table IV were derived.

DISCUSSION

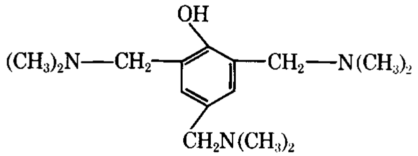
When discussing the reaction of formaldehyde and ammonia, we postulated the formation of an unstable trimethylolamine based on the sharp bend in the exotherm curve. When amines are reacted, the methylolamines formed are not unstable. Henry prepared in 1894 methylolamines from mono- and dialkylamines. The products were colorless, viscous liquids which decomposed on heating.[9b] The reactions (2) and (3) are suggested.

$$CH_3NH_2 + CH_2O\ (aq) \rightarrow CH_3NHCH_2OH \qquad (2)$$

$$(CH_3)_2NH + CH_2O\ (aq) \rightarrow (CH_3)_2NCH_2OH \qquad (3)$$

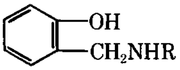
We have prepared dimethylmethylolamine in aqueous solution. On addition of an equimolar amount of resorcinol, heat was generated. The amount of heat was the same for a freshly prepared methylolamine solution as for one that was 3 hr old.

Bruson and MacMullen[11] prepared phenolic triamines (VII) by reacting phenol (or cresol) with excess formaldehyde and 3 mole of a strongly basic nonaromatic amine.

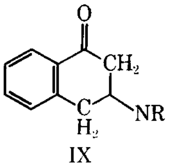


VII

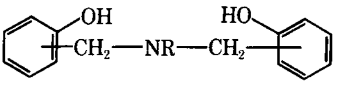
Burke, et al.[12] studied the reaction of phenol with $RN(CH_2OH)_2$ and obtained as products VIII, IX, or X, depending on the ratio of constituents.



VIII



IX



X

When a solution of phenol in water is mixed with ammonia and formaldehyde and then the water evaporated, a crystalline product is obtained which, however, is not a compound but a molecular complex of 3 molecules of phenol with one molecule of hexamethylenetetramine.[9c] During the condensation of phenol with formaldehyde, when ammonia is used as catalyst, many products are formed. Shono[13] identified one of these as bis(2-hydroxybenzyl)amine, $(HOC_6H_4CH_2)_2NH$. (Later work was done by Imoto.[14] This compound was prepared by Paal and Senniger[15] by heating *o*-hydroxybenzyl-alcohol with alcoholic ammonia. A tris(2-hydroxybenzyl)amine has been synthesized by Zemplen and Kunz[16] by heating tris-[2-(tetraacetyl-*d*-glucosidohydroxy)-benzyl]amine with 5% HCl. The hydrochloride is reported to be crystalline, soluble in alcohol and acetone, difficultly soluble in water, insoluble in benzene and chloroform, and to decompose at 110°C.

RESORCINOL–FORMALDEHYDE–AMINE COMPOUND IN CORD DIP ADHESIVES

It was stated in the introduction that premature addition of ammonia to a latex containing resorcinol and formaldehyde is undesirable because of formation of precipitate. It is interesting however, that when we go to the other extreme and add ammonia to the latex before any reaction between resorcinol and formaldehyde has taken place, a very stable dip with good adhesive properties to nylon and rayon is obtained.[17]

For instance the following recipe can be used: water, 350 parts (by weight); resorcinol, 350 parts; formaldehyde (37%), 16.2 parts; sodium hydroxide, 0.6 part; Gen-Tac (41%) (a vinylpyridine copolymer latex made by The General Tire & Rubber Company), 250 parts; ammonia (28%), 6 parts.

The water has to be used to make solutions of resorcinol and NaOH and to dilute the formaldehyde and ammonia. The sequences of addition in rapid succession is: resorcinol, formaldehyde, latex, NaOH, and ammonia. The dip can be used immediately but higher adhesions are obtained after one or two days. The high adhesion is retained for months, dropping off at the end of one year. Storage at temperatures up to 158°F does not change the adhesive properties of the dip, but the useful life of the dip is shortened. This is quite in contrast with regular ammoniated resorcinol formaldehyde latex dip, which loses its adhesive properties after a couple of weeks.

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