# Reaction Mechanism of Melamine Resins

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The structure of melamine resins has a significant effect on the mechanism of catalysis. The analysis of the volatile reaction products of amino resins was used as a method to determine the reactions occurring during the cross-linking process. With fully alkylated melamine formaldehyde resins specific acid catalysis was found the dominant cross-linking mechanism. With partially alkylated resins demethylolation and subsequent catalysis by a general acid catalysis mechanism was found to be the cross-linking mechanism, in each case methoxy methyl groups were found to be the reactive site and not methylol groups.

# REACTION MECHANISM OF MELAMINE RESINS

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## INTRODUCTION

Commercially available alkylated amino-formaldehyde resins such as used in coatings are complex mixtures of monomers, dimers, and higher oligomers. Besides being different in molecular weight distribution, these products also vary in molar amounts of formaldehyde and alcohol combined. All these characteristics are interrelated when an amino resin is prepared by a commercial process. The performance of these amino resins in actual application is, therefore, dependent on a rather complex set of structural characteristics, which in the past were not accessible to analytical probing.

Furthermore, a clear understanding of the cross-linking mechanism was made difficult by the presence of catalyst from the manufacture of these resins. The assumption that partially alkylated amino-formaldehyde resins are faster reacting than fully alkylated resins, because of the higher reactivity of methylol groups compared to the alkoxymethyl groups, has been found erroneous. Also, the general belief that strong "acid" conditions are required for good cure has been found wrong.

Some of the conclusions of this work have been expressed in previous work[1], although in my opinion, no comprehensive understanding of the reactions involved emerged from that study.

## COMPOSITION OF MELAMINE-FORMALDEHYDE RESINS

Instead of doing this work with model compounds which are extremely difficult to synthesize, I decided to use commercially available resins whose structure was well defined by analysis. In reacting melamine with formaldehyde, random substitution of the $-NH_2$ groups is observed. Analysis of trimethylolmelamine by NMR technique[2] indicates that mainly the symmetric compound (# 1) is formed and only small amounts of an asymmetric compound (# 2).
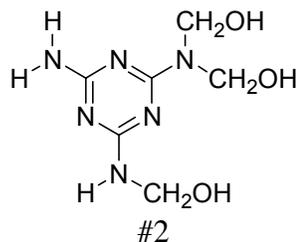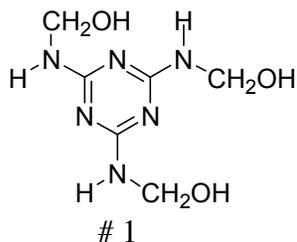
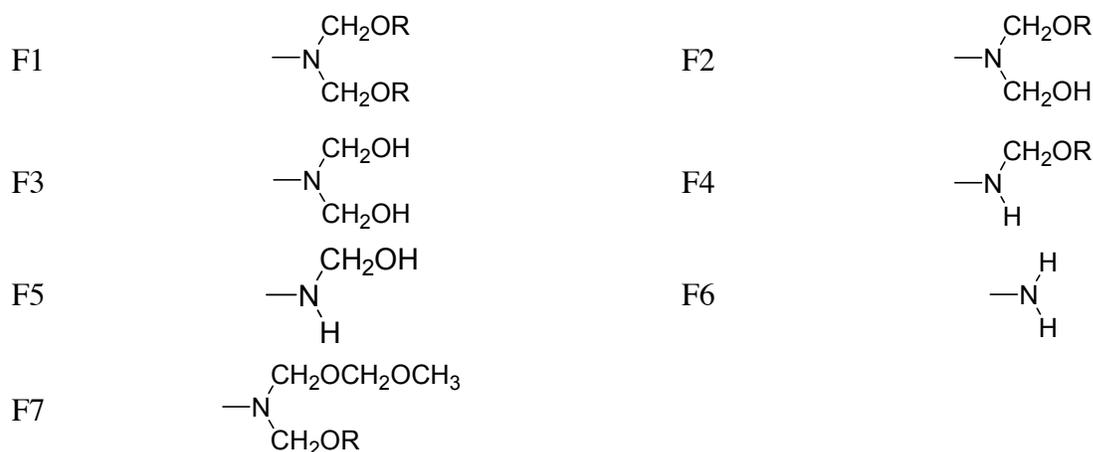We, therefore, can conclude that in a highly monomeric melamine-formaldehyde resin with a melamine-formaldehyde ratio of $> 3$ that most of the unreacted hydrogen on the nitrogen are randomly distributed and either next to a methylol or alkoxy methyl group. Therefore, such a resin will have either $-NHCH_2OR$ or $-NHCH_2OH$ functional sites. The amount of these reactive sites should be equivalent to the -NH content. There is one exception, and that is if the -NH group is located next to a bridge in a polymeric unit of the melamine-formaldehyde resin

$$H\diagdown _N\diagdown _{\overset{H_2}{C}}\diagdown _N\diagup ^{CH_2OCH_3}$$
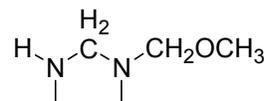
Theoretically at least, the bridge unit could also be a methylene ether group. No analytical tools are available at the present time to prove or disprove the presence of such a unit, but other considerations to be discussed later virtually exclude methylene ether[3] and -NH groups in the same resin. The variety of different possible functional sites on a melamine resin is shown in Table 1.

**Table 1. Functional Groups in Melamine Resin**

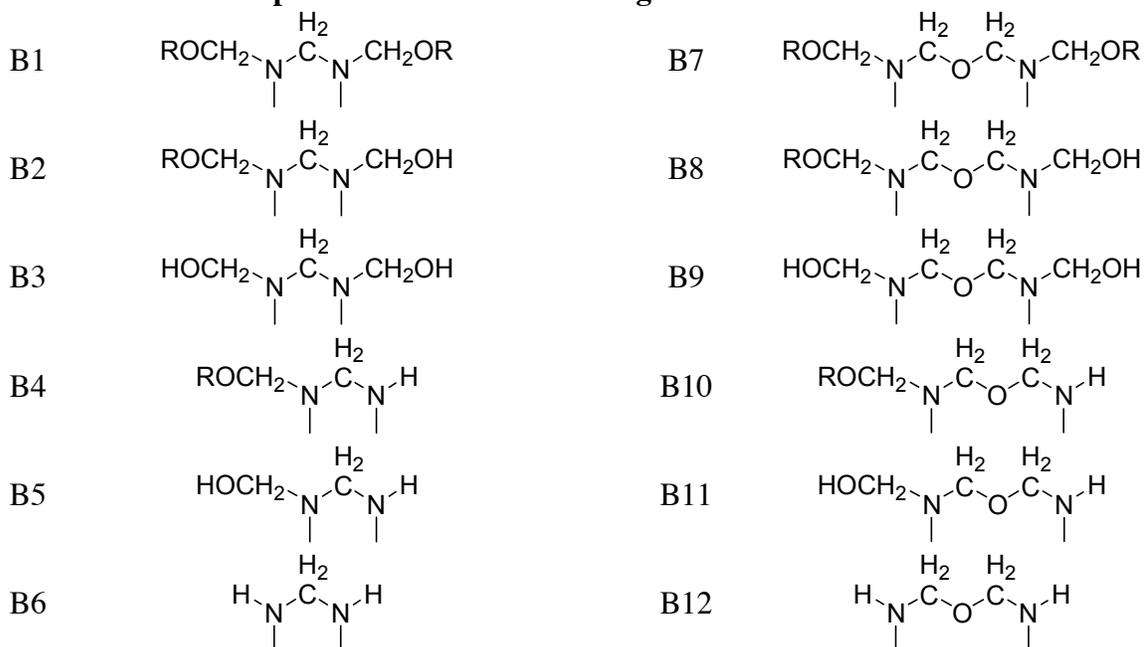| | | | |
|---|---|---|---|
| F1 | $-N\big(^{CH_2OR}_{CH_2OR}$ | F2 | $-N\big(^{CH_2OR}_{CH_2OH}$ |
| F3 | $-N\big(^{CH_2OH}_{CH_2OH}$ | F4 | $-N\big(^{CH_2OR}_{H}$ |
| F5 | $-N\big(^{CH_2OH}_{H}$ | F6 | $-N\big(^{H}_{H}$ |
| F7 | $-N\big(^{CH_2OCH_2OCH_3}_{CH_2OR}$ | | |

Commercial melamine-formaldehyde resins do not contain only one type of functional group, but a combination. The performance characteristics are, therefore, a function of the ratio of these functional groups in the amino resin. In a given amino resin, the process used to make the resin influences this probable distribution of functional groups.

Technically, it is reasonably easy to prepare a monomeric hexakis(alkoxymethyl)melamine with only alkoxymethyl functional sites F1; but It is not technically possible to prepare products with only F2, F3, F4 or F5 (Table 1) functionality. Products made by commercial processes contain a combination of these functional sites. Certain combinations are more frequent in an amino resin, others are, for practical purposes, non-existent. For example, a partially alkylated amino resin could contain F1, F2, and F4 functionality, but no F3, F5, F6, or F7. In a highly alkylated commercial resin, F1, F7, and small levels of F2 are normally present.

All commercial melamine-formaldehyde resins do contain variable levels of higher polymeric materials. All possible combinations of bridging units are shown in Table 2. Again, as in the case of functional groups, the probability for the existence of a certain bridging unit will

vary in different resin types. Methylene bridges (B1-B6) are, for all practical purposes, non-reactive. Methylene ether groups (B7-B12) should undergo the normal reaction of an ether group. Present analytical techniques cannot distinguish between bridging ether groups (B7-B12) and polyether side chains (Table 1, F7). Only circumstantial evidence can indicate the presence of either bridge ether or side chain polyether groups. From an application standpoint. it is not very important to be able to distinguish between either group. Only the presence or amount thereof is of significance.

**Table 2. Functional Groups in Melamine Resin Bridges**

| | | | |
|---|---|---|---|
| B1 | ROCH$_2$–N–C(H$_2$)–N–CH$_2$OR | B7 | ROCH$_2$–N–C(H$_2$)–O–C(H$_2$)–N–CH$_2$OR |
| B2 | ROCH$_2$–N–C(H$_2$)–N–CH$_2$OH | B8 | ROCH$_2$–N–C(H$_2$)–O–C(H$_2$)–N–CH$_2$OH |
| B3 | HOCH$_2$–N–C(H$_2$)–N–CH$_2$OH | B9 | HOCH$_2$–N–C(H$_2$)–O–C(H$_2$)–N–CH$_2$OH |
| B4 | ROCH$_2$–N–C(H$_2$)–N–H | B10 | ROCH$_2$–N–C(H$_2$)–O–C(H$_2$)–N–H |
| B5 | HOCH$_2$–N–C(H$_2$)–N–H | B11 | HOCH$_2$–N–C(H$_2$)–O–C(H$_2$)–N–H |
| B6 | H–N–C(H$_2$)–N–H | B12 | H–N–C(H$_2$)–O–C(H$_2$)–N–H |

For this study, three different types of methylated melamine-formaldehyde resins and one butylated resin were selected. The structure of the methylated resins was clearly established by analysis. More questions remain to be resolved in the case of the butylated resin. Table 3 shows the analysis of these amino resins. The analysis was performed by conventional wet techniques. The alkoxy content was determined by NMR. Amino resin I is a commercial version of a highly methylated melamine-formaldehyde resin. The combined molar ratio of melamine-formaldehyde methanol (MF$_{6.1}$Me$_{5.2}$) Is shown in the first line of the table. The combined amount of 6.1 moles of formaldehyde per melamine Is not an error in the analysis, but an indication that polyether side chains and methylene ether bridging units are present in the resin. Methanol is combined in form of methoxymethyl groups (> N-CH$_2$OCH$_3$ ).

The subsequent number indicates the molar amount of methylol groups per triazine (0.3). The expression of HCHOF, measures the amount free-formaldehyde in moles of HCHO/triazine (0.075). The amount of -CH$_2$OCH$_2$- bridging units and polyether side chains per triazine is shown in the next line (0.9). This number is an approximation not obtained by analysis, but by calculation[4] from molar ratios and degree of polymerization (DP) Information. All analytical errors can be magnified in this calculated "polyether" number; but as long as no reliable analytical tools are available to determine this amount of polyether groups, the calculated number offers important clues about the structure of the resin. The degree of polymerization DP was calculated from gel phase analysis of the resin. Gel phase gives a good separation of

monomer, dimer, and trimer, but falls to give a good separation of higher oligomers. The distribution of higher oligomers can, therefore, be calculated, from the ratio of monomer, dimer, and trimer, assuming a natural distribution of the oligomers. This procedure, although subject to some error, is sufficiently accurate for products high in monomer content, but is not acceptable for highly polymeric products.

Amino resin 2 was a typical commercial partially methylated melamine-formaldehyde resin.

Amino resin 3 was a higher methylated resin with high NH content. The -NH content was determined by NMR.

NH content <l per triazine can also be determined by potentiometric titration. Amino resin 1, as determined by titration, has virtually no NH groups and amino resin 2 has a small amount. Amino resin1 is sold at 99 % solids. Amino resins 2 and 3 are sold as 80 % solids solution in n-butanol.

Amino resin 4 was a conventional butylated melamine-formaldehyde resin, and It was used for comparative purposes. The analysis methods used for the methylated resins were not sufficiently reliable for this resin, therefore, only molar ratio ($MF_5Bu_{2.8}$) and GPC analysis are reported.

**Table 3. Composition of Amino Resin**

| Amino Resin 1 | $MF_{6.1} Me_{5.2}$ | |
|---|---|---|
| | $-CH_2OH$ | 0.3 |
| | $HCHO_F$ | 0.075 |
| | $-CH_2OCH_2-$ | 0.5 |
| | DP | 1.68 |
| | | |
| Amino Resin 2 | $MF_{5.8} Me_{3.8}$ | |
| | $-CH_2OH$ | 1.0 |
| | $HCHO_F$ | 0.19 |
| | $-CH_2OCH_2-$ | 0.4 |
| | $-CH_2-$ | 0.2 |
| | DP | 2.5 |
| | | |
| Amino Resin 3 | $MF_{4.0} Me_{3.4}$ | |
| | $-CH_2OH$ | 0.57 |
| | $HCHO_F$ | 0.07 |
| | $-CH_2-$ | 0.52 |
| | -NH | 1.48 |
| | DP | 2.5 |
| | | |
| Amino Resin 4 | $MF_{5.0} Bu_{2.8}$ | |
| | GPC Monomer | 16.5 |
| | Dimer | 11.9 |
| | Polymer | 71.6 |

As a backbone polymer for this study, a 100 % solids polyether polyol was selected.  This resin, a reaction product of bisphenol A with 6.5 moles of ethylene oxide, has only primary hydroxyl groups and a very narrow molecular weight distribution.  Therefore, it was very well suited as a model compound.

**Characteristics of Diol**

| | |
|---|---|
| Molecular Weight | 506 |
| Viscosity, Brookfield, 25°C., Pascals | 2.85 |
| MEQ (OH/g.) | 3.95 |

This polymer has no residual acidity, therefore, an acid catalyst had to be used with all coatings formulations.  The acid catalyst used in all experiments, if not otherwise stated, was dodecylbenzene sulfonic acid.

TEST CONDITIONS

Because of the difficulties in analyzing the composition of cross-linked films, I decided to collect the reaction volatiles.  From these volatiles, one can concluded possible reactions and mechanisms of reaction.  For this purpose, coated panels were cured In a flow cell and all reaction volatiles were collected and absorbed In dry n-propanol and analyzed by gas chromatography.

The flow cell (Drawing 1) was constructed of 5 mm window glass and cemented with a silicone rubber adhesive.  The dimensions of the curing chamber are 105 x 100 x 5 mm.

Preheated air enters the mixing chamber at a flow rate of 300 ml./minute.  The air is withdrawn from the main chamber at a lower rate of 100 ml./minute.  A coated and predried panel is inserted into the flow cell.  The chamber does not have to be closed airtight.  Reaction volatiles are drawn from this chamber into the absorption liquid.  The panels were either inserted at the baking temperature into the flow cell or at a lower temperature, and the temperature was raised to the baking temperature within 9-7 minutes. The heat-up rate of a panel in the flow cell and a panel in a forced air oven was about the same and required about 5 minutes to be within 5°C. of the baking temperature.

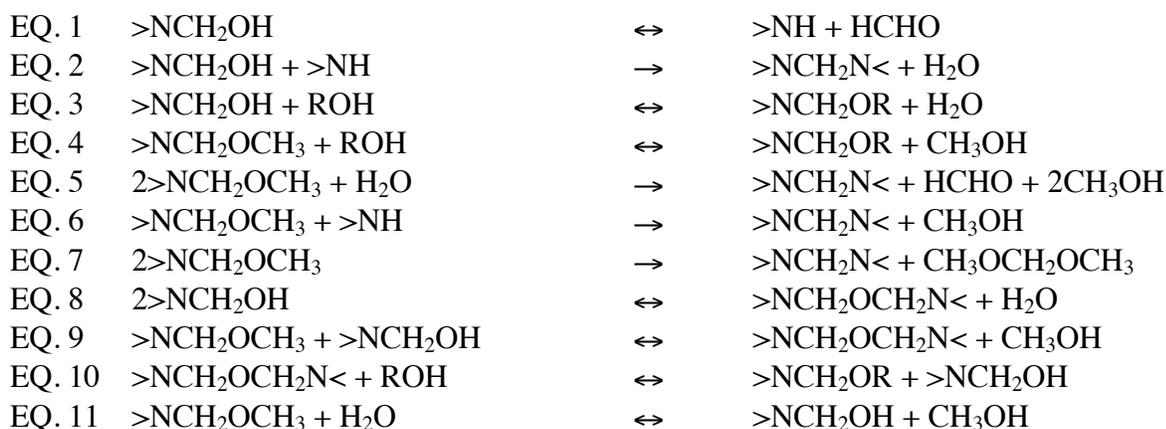**Drawing 1.  Flow Cell for Measuring Volatile Reaction Products**
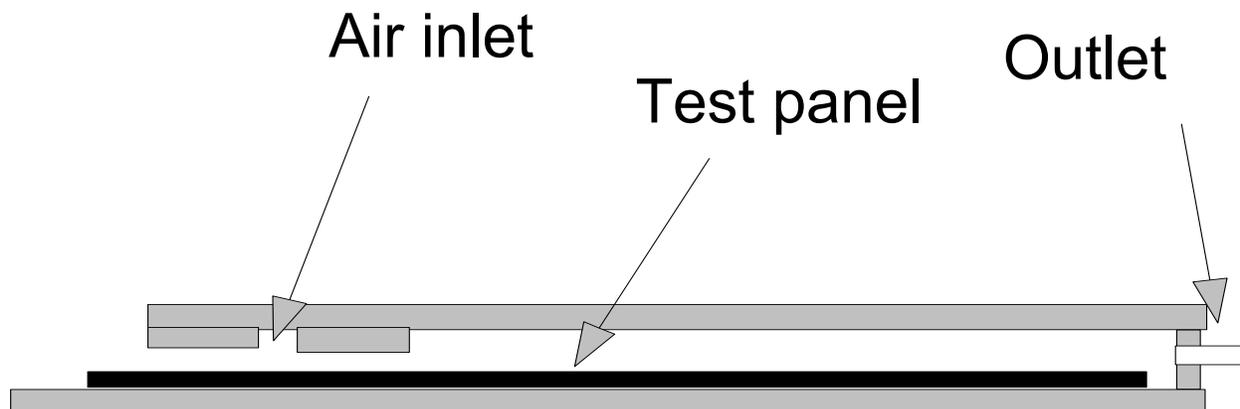
For these experiments, either molecular sieve dried (dry) air or air saturated at room temperature with moisture was used (wet).

The test panels used were 100 x 300 mm aluminum panels. These panels were dried and stored in a desiccator before use. Drawdowns were prepared in the open air, weighed immediately, and stored in the desiccator before use. When a solvent containing formulation was tested, the panels were dried at 45°C for 45 minutes In a forced air oven after drawdown. They were then weighed and stored In the desiccator. Even with these precautions, It was not possible to completely exclude moisture from the reaction chamber. Even the very short handling in the air was sufficient for small amounts of water to be absorbed In the coating. Therefore, analysis for water as a reaction product was abandoned. Accurate measurements of the amount of water volatilized would have been of Interest, but the required effort was not justified by the results expected from this work. Therefore, the efforts were mainly aimed at analyzing for formaldehyde, alcohol, and other volatile reaction products.

REACTION VOIATILES

Wohnsiedler[5] has shown in his work on an alkyd melamine resin system, that a variety of reactions can take place. Possible reaction schemes are shown In Table 4. He did not mention the influence of water on the self-condensation reaction (Eq.5 ) and he did not consider demethylolation (EQ. 1) as major reaction steps required for crosslinking of melamine resins.

**Table 4 Reaction Volatiles**

EQ. 1   $>NCH_2OH$ $\leftrightarrow$ $>NH + HCHO$
EQ. 2   $>NCH_2OH + >NH$ $\rightarrow$ $>NCH_2N< + H_2O$
EQ. 3   $>NCH_2OH + ROH$ $\leftrightarrow$ $>NCH_2OR + H_2O$
EQ. 4   $>NCH_2OCH_3 + ROH$ $\leftrightarrow$ $>NCH_2OR + CH_3OH$
EQ. 5   $2>NCH_2OCH_3 + H_2O$ $\rightarrow$ $>NCH_2N< + HCHO + 2CH_3OH$
EQ. 6   $>NCH_2OCH_3 + >NH$ $\rightarrow$ $>NCH_2N< + CH_3OH$
EQ. 7   $2>NCH_2OCH_3$ $\rightarrow$ $>NCH_2N< + CH_3OCH_2OCH_3$
EQ. 8   $2>NCH_2OH$ $\leftrightarrow$ $>NCH_2OCH_2N< + H_2O$
EQ. 9   $>NCH_2OCH_3 + >NCH_2OH$ $\leftrightarrow$ $>NCH_2OCH_2N< + CH_3OH$
EQ. 10   $>NCH_2OCH_2N< + ROH$ $\leftrightarrow$ $>NCH_2OR + >NCH_2OH$
EQ. 11   $>NCH_2OCH_3 + H_2O$ $\leftrightarrow$ $>NCH_2OH + CH_3OH$

In Table 5, the reaction volatiles of amino resin I with the polyol were studied at different ratios of polyol to amino resin, 75/25, 62.5/37.5, and 50/50 at a baking schedule of 20 minutes at 120°C. The reaction was catalyzed with 0.84 % of dodecylbenzene sulfonic acid (DDBSA) based on the total binder. The 100 % solids resin blend was low enough in viscosity to be applied by draw down without any dilution. Immediately after draw down, the coating weight was determined. The dry film thickness of the coating was 25 µm.

**Table 5. Volatiles**

Amino Resins 1 Composition: $MF_{6.1}$ $Me_{5.2}$, $-CH_2OH_{0.3}$, $HCHO_{F\ 0.075}$, $-CH_2OCH_{2-0.5}$, DP 1.68
Baking Conditions: 20 minutes 150°C, (302°F), Film thickness 25 µm; Catalyst DDBSA 0.84 %

| Polyol/Amino Resin | 75/25 | 62.5/37.5 | 50/50 |
|---|---|---|---|
| OH/Triazine | 4.48/1 | 2.49/1 | 1.49/1 |
| Mol Volatiles/Triazine | | | |
| HCHO | 0.2 | 0.52 | 0.33 |
| MeOH | 5.0 | 3.07 | 2.4 |
| Methylal | --- | --- | 0.09 |
| $H_2O$ | 1.02 | 0.72 | 0.5 |

  Assuming only reaction between the methoxy and the hydroxyl groups of the polymer (Table 4, Eq. 4), the molar amount of methanol should be equivalent to the molar amount of hydroxyl groups in the polymer. Any excess of methanol has to come from self-condensation or hydrolysis of the melamine resin (Table 4, Eq. 5, 11).

  IR analysis of -the cured film did not show any evidence of increased HN<levels, therefore, self-condensation of melamine according to Eq. 5 must be taking place. The level of formaldehyde found in the reaction volatiles also indicates a demethylolation reaction. The resulting -NH groups, from the demethylolation reaction, react either with some remaining methylol or methoxy groups. There is obviously no way to account for the amount of water collected In the trap. All reaction water has to be derived from the reaction of methylol groups (Table 4, Eq. 2, 3, 8). Assuming that some of the water hydrolyzes the melamine resin, we arrive at the following equation for the reaction water:

$$H_2O \text{ Volatiles} = Eq.2 + Eq.3 + Eq.8 - Eq.5$$

  The larger amount of water formed in the collector, therefore, has to come from water absorption of the uncured film and the panel. Therefore, in subsequent work, the amount of water collected was measured, but not reported.

  Raising the level of amino resin I from 25 to 37.5 % or a ratio of hydroxyl/triazine of 2.49/1 again produces higher than calculated levels of MeOH. At the 50/50 ratio of polyol/melamine resin, some traces of methylal were formed in the reaction mixture. This was the only occasion where we ever observed the formation of methylal. The overall reaction responsible for formation of methylal Is shown in Table 4, Eq.7. Again, significantly higher levels of methanol volatiles compared to the theoretical level were observed. J. N. Koral and coworkers[6] found in their work formation of methylal as self-condensation product of hexakis (methoxymethyl) melamine and concluded that methylal is the only reaction product of self-condensation. Their experiments were done under dry nitrogen.

  The fact that methanol is the reaction product of the self condensation reaction and not methylal led to the concept that not only water in the film, but possibly the humidity of the air could have an influence on hydrolysis and self-condensation reaction of a fully alkylated melamine resin.

Therefore, air was saturated at room temperature with moisture and introduced into the flow cell. This air will be identified In the experiments as "wet". Calculations show that at 150°C the relative humidity of such wet air is about 1 %.

The experiments in Table 5 at the 62.5/37.5 polyol/melamine level were repeated with slight modifications. Panels were inserted into the oven at 100°C. and heated within 8 minutes to 150°C. This slower heatup rate gave more reproducible results. The tests were farther run with dried and wet air. The results are shown In Table 6. Surprisingly, a significant increase In HCHO (0.8 moles) and methanol (3.5 moles) volatiles was found, which shows that diffusion of moisture in the air into the film can have a substantial impact on hydrolysis, demethylolation, and self-condensation reactions.

In the presence of a sufficient excess of methoxymethyl groups, these groups will be hydrolyzed, on extensive overbake; after loss of most of the methanol, hydrolysis of the melamine/polymer backbone linkages could take place. Indeed some evidence for this has been found in some coil coatings; which can lose solvent resistance on overbake. Under most normal baking conditions, sufficient moisture is in the air to cause self-condensation of a hexa(alkoxymethyl)melamine resin. The release of formaldehyde from this reaction cannot be eliminated. Therefore, a reduction In residual methylol content of a hexa(methoxymethyl)-melamine resin to reduce loss of HCHO by demethylolation during cure is, under normal humid conditions, not sufficient.

**Table 6. Volatiles   Dry-Wet**

Amino Resins 1 Composition: $MF_{6.1}$ $Me_{5.2,}$ -$CH_2OH_{0.3,}$ $HCHO_{F\,0.075}$, -$CH_2OCH_{2\text{-}0.5}$, DP 1.68
Baking Conditions: 20 minutes 100 → 150°C, (212→302°F), Film thickness 25 μm;
Catalyst DDBSA 0.84 %

| Polyol/Amino Resin | 62.5/37.5 | |
|---|---|---|
| OH/Triazine | 2.49/1 | |
| Air flow | Dry | Wet |
| Mol Volatiles/Triazine | | |
| HCHO | 0.35 | 0.83 |
| MeOH | 2.64 | 3.5 |

In Table 7, the volatile loss at increased baking temperatures is shown. Indeed as expected, raising the temperature from 125°C. to 200°C. increases the level of self-condensation reaction and about doubles the loss of HCHO.

**Table 7. Volatiles   Temperature**
Amino Resins 1 Composition: $MF_{6.1}$ $Me_{5.2,}$ -$CH_2OH_{0.3,}$ $HCHO_{F\,0.075}$, -$CH_2OCH_{2\text{-}0.5}$, DP 1.68
Film thickness 25 μm; Catalyst DDBSA 0.84 %

| Polyol/Amino Resin | 62.5/37.5 | | | |
|---|---|---|---|---|
| OH/Triazine | 2.49/1 | | | |
| Baking Temperature, 20 min. °C | 125 | 150 | 175 | 200 |
| Mol Volatiles/Triazine | | | | |
| HCHO | 0.35 | 0.5 | 0.65 | 0.8 |
| MeOH | 2.6 | 3.1 | 3.6 | 4.3 |

Table 8 gives the volatiles as a function of catalyst level at dry and wet conditions. At 100° C. cure temperature in a dry atmosphere, Amino Resin 1 does not self-condense even in the presence of large levels of acid catalyst. Increased moisture in the air again significantly increases self-condensation. At a catalyst level higher than 1.75 %, no further increase in self-condensation is found up to a level of 3.5 %.

**Table 8. Volatiles     Catalyst Level   Dry (Wet)**
Amino Resins 1 Composition: $MF_{6.1}$ $Me_{5.2,}$ $-CH_2OH_{0.3,}$ $HCHO_{F\,0.075}$, $-CH_2OCH_{2\text{-}0.5}$, DP 1.68
Baking Temperature 20 min. 100°C; Film thickness 25 μm; Catalyst DDBSA 0.84 %

| Polyol/Amino Resin | 62.5/37.5 | | | |
| OH/Triazine | 2.49/1 | | | |
| Catalyst, DDBSA, % | 0.88 | 1.75 | 2.625 | 3.5 |
| Mol Volatiles/Triazine | | | | |
| HCHO | 0.35 (0.19) | 0.38 ().48) | 0.34 (0.39) | 0.39 (0.54) |
| MeOH | 2.6 (3.0) | 2.5 (3.43) | 2.35 (3.43) | 2.5 (3.4) |

These data show that higher temperature and higher humidity in the air are mainly responsible for the self-condensation reaction of a fully alkylated melamine resin, but that increased acid catalyst levels are not. Therefore, decrease in performance of highly catalyzed coatings is probably not caused by a different extent of self-condensation reaction of the melamine resin, but rather by Interaction of the acid catalyst with the substrate interface or by a change in migration rate of ions and water through the film.
Increasing -the baking temperature from 100°C. to 120°C. (Table 9) brings the expected increase in methanol and formaldehyde evolution, but otherwise, no change in the already observed pattern occurs.

**Table 9. Volatiles     Catalyst Level   Dry (Wet)**
Amino Resins 1 Composition: $MF_{6.1}$ $Me_{5.2,}$ $-CH_2OH_{0.3,}$ $HCHO_{F\,0.075}$, $-CH_2OCH_{2\text{-}0.5}$, DP 1.68
Baking Temperature 20 min. 120°C; Film thickness 25 μm; Catalyst DDBSA 0.84 %

| Polyol/Amino Resin | 62.5/37.5 | | | |
| OH/Triazine | 2.49/1 | | | |
| Catalyst, DDBSA, % | 0.88 | 1.75 | 2.625 | 3.5 |
| Mol Volatiles/Triazine | | | | |
| HCHO | 0.4 (.54) | 0.45 (.56) | 0.48 (0.7) | 0.6 (0.84) |
| MeOH | 2.56 (3.64) | 2.85 (3.93) | 2.77 (3.78) | 2.93 (3.92) |

In another set of experiments, the partially methylated melamine-formaldehyde resin, amino resin 2, was selected as a cross-linker (Table 10). This cross-linking agent has methylol and methoxy groups as potential functional sites. The films were predried for 45 minutes at 45°C, to remove the n-butanol solvent after drawdown. Using a 0.38 % catalyst level and a baking schedule of 20 minutes at 125°C 0.85 mole of HCHO Is released during cure. This amount of HCHO is partially derived from free-formaldehyde (0.189) and partially from a demethylolation reaction (0.66). This would indicate that under the reaction conditions described demethylolation and formation of $-NHCH_2OCH_3$ groups (Table 1, F4) is a major reaction step. The molar amounts of methanol evolved are about equivalent to the moles of hydroxyl groups in the polyol used. This would indicate that methoxymethyl groups are the

reactive site. Higher humidity also increases the HCHO and methanol volatiles. The difference between dry and wet conditions is smaller than for amino resin 1, although the absolute level of HCHO volatilized is higher. Therefore, demethylolation is a major reaction step in the cure of a partially alkylated resin.

The rather high formaldehyde content in the volatiles of methylated melamine-formaldehyde resins is of concern, so we, decided to use a conventional solvent soluble butylated melamine-Formaldehyde resin for comparison. This resin is typical of the majority of melamine resins used in coatings.

**Table 10. Volatiles    Catalyst Level  Dry (Wet)**
Amino Resins 2 Composition: $MF_{6.1}$ $Me_{5.8}$, $-CH_2OH_1$, $HCHO_{F\,0.189}$, $-CH_2OCH_{2^-0.4}$, DP 2.5
Baking Temperature 20 min. 100→120°C; Film thickness 25 μm; Catalyst DDBSA 0.385 %

| Polyol/Amino Resin | 56.5.5/43.5 | |
|---|---|---|
| OH/Triazine | 1.74/1 | |
| Mol Volatiles/Triazine | DRY | WET |
| HCHO | 0.85 | 0.96 |
| MeOH | 1.71 | 1.97 |

Amino resin 4, as shown In Table 3, is a polymeric resin. Approximate methylol content is 5-7% weight. This resin is supplied as a 75 % solution in n-butanol. Most butylated resins are catalyzed with carboxylic acid. Therefore, 2 % maleic acid (MA) was used as a catalyst.

Table 11 shows the volatile composition. The amount of formaldehyde released during lure is larger than that of the methylated resins tested. The n-butanol released is also of the same order as the hydroxyl groups In the blend. Increased humidity raises the formaldehyde to a very high level. There is some discrepancy in the amount of n-butanol released under wet conditions, which remains to be resolved.

**Table 11. Volatiles**
Amino Resins 2 Composition: $MF_5$ $Bu_{2.8}$,
Baking Temperature 20 min. 100→150°C; Film thickness 25 μm; Catalyst MA 2.0 %

| Polyol/Amino Resin | 56.5.5/43.5 | |
|---|---|---|
| OH/Triazine | 2.14/1 | |
| Mol Volatiles/Triazine | DRY | WET |
| HCHO | 0.96 | 1.43 |
| MeOH | 2.1 | 1.9 |

The reaction volatiles for all partially alkylated melamine-formaldehyde resins indicate that demethylolation is a major reaction step (Table 4, Eq. 1). Therefore, if it is not the methylol, but the $-NHCH_2OR$ group, which is the reaction site, significant reduction in formaldehyde, could be achieved by preparing such a resin.
Amino resin 3, which is a higher alkylated, high NH resin, fits the description for such a product. Indeed this resin gives reduced formaldehyde emission under dry and wet conditions (Table 12). The Increase In formaldehyde volatiles under wet cure conditions is still observable, but not nearly as pronounced as In a highly alkylated resin. (Amino Resin 1)

Using a weaker acid catalyst such as a partial ester of pyrophosphoric acid (DMAPP) gives excellent cure with amino resin 3. Increased levels of catalyst at a baking temperature of

100°C produce a very low level of formaldehyde.  The higher level of acid does not increase the formaldehyde loss (Table 13).

**Table 12. Volatiles    Dry-Wet**
Amino Resins 3 Composition: $MF_4$ $Me_{3.4,}$ $-CH_2OH_{0.57,}$ $HCHO_{F\,0.07}$, $-NH_{1.48}$, DP 2.1
Baking Temperature 20 min. 100→150°C; Film thickness 25 μm; Catalyst DDBSA 0.385 %

| Polyol/Amino Resin | 56.5.5/43.5 | |
| OH/Triazine | 1.46/1 | |
| Mol Volatiles/Triazine | DRY | WET |
| HCHO | 0.24 | 0.32 |
| MeOH | 1.68 | 1.91 |

**Table 13. Volatiles    Catalyst Level**
Amino Resins 3 Composition: $MF_4$ $Me_{3.4,}$ $-CH_2OH_{0.57,}$ $HCHO_{F\,0.07}$, $-NH_{1.48}$, DP 2.1
Baking Temperature 20 minutes 100°C; Film thickness 25 μm;

| Polyol/Amino Resin | 56.5.5/43.5 | | | |
| OH/Triazine | 1.46/1 | | | |
| Catalyst DMAPP, % | 1 | 1.5 | 2 | 2.5 |
| Mol Volatiles/Triazine | | | | |
| HCHO | 0.2 | 0.15 | 0.17 | 0.15 |
| MeOH | 1.36 | 1.3 | 1.3 | 1.36 |

MECHANISM OF CROSS-LINKING

Fully alkylated melamine-formaldehyde resins (amino resin 1) have been studied extensively by Koral, et.al[6].  The need for a strong acid catalyst, such as pTSA, is described. Weaker or undissociated acids do not effectively catalyze the reaction.  Therefore, it can be assume that specific acid catalysis is the catalyzing mechanism for fully alkylated melamine-formaldehyde resins[7],[8]. A proposed reaction pathway is shown In Table 14.

TABLE 14. Reaction Pathway (Specific Acid Catalysis)
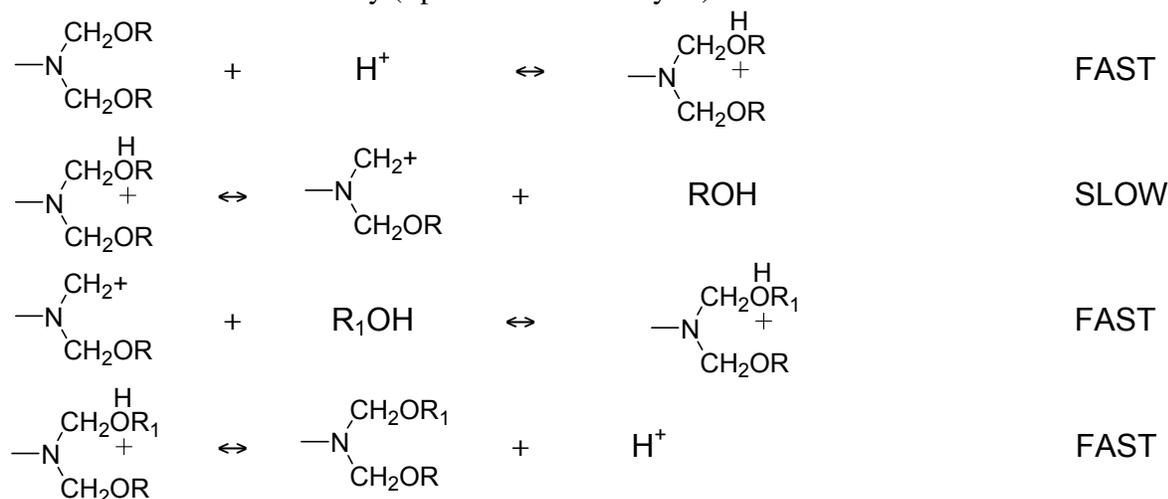
The formation of the carbonium ion determines the maximum rate, which can be obtained. The carbonium ion can recombine with the split off alcohol or it can react with the functional groups on a polymer, such as hydroxyl, carboxyl, amide, or mercapto.

The overall rate of cross-linking will be determined by the reaction rates of all reaction steps. Indeed different rates of reaction have been observed for hydroxyl, carboxyl, and amide groups by Koral, et. al[6]. So for an example, an already formed crosslink between polymer and cross-linking agent can be reprotonated and form a carbonium ion, which then in turn can react with the alcohol, which has been split off from another alkoxymethyl group. Therefore, bonds are formed and broken continuously during the cross-linking process. The loss of the alcohol by diffusion and evaporation has, therefore, a significant influence on the reaction rate. Absolute rate measurements in a coating film are, therefore, virtually impossible. The rate of formation of the carbonium ion can be approximately measured if a mercaptan is used to scavenge the carbonium ion. The mercapto/melamine resin ($-NCH_2SR$) linkage cannot be reprotonated and, therefore, is the end product of the reaction.

Most of the methanol collected as volatiles can be accounted for as a product of the crosslinking reaction. Assuming complete reaction of the functional groups of -the backbone resin with the fully alkylated melamine-formaldehyde resin, for each mole of functional groups, one mole of methanol has been formed in the volatiles. Any excess methanol has to come from hydrolysis of the melamine resin (Table 4, Eq. 5). This finding is also confirmed by the tests conducted under dry and wet conditions, which show significant increase in methanol and formaldehyde levels in the volatiles.

At the lower baking temperature especially, this appears to be the only mechanism, which causes self-condensation of the fully alkylated melamine resin. It is rather surprising that water can, during the baking process, diffuse into the film and hydrolyze the amino resin. One would assume that the reaction volatiles such as methanol or formaldehyde would prevent any diffusion into the coating film. Calculations show that about 10 % of the water contained in the air flawing through the cell participates in the hydrolysis of the melamine resin.

The reaction of partially alkylated melamine-formaldehyde resins with hydroxyl functional polymers proceeds readily in absence of strong acid catalyst. The assumption that no catalyst is required is wrong. Completely neutral, salt-free systems will not react with a partially alkylated resin. For example, amino resins 2 and 3 will not react with the polyol used in this study at 150°C. baking temperature. Kinetic hydrolysis studies by Berge et. al.[7,8] of methylated trimethylol melamine and hexakis(methoxymethyl) melamine clearly show a different mechanism, indicating that general acid catalysis is involved In $-NHCH_2OR$ functional amino resins. Therefore, any undissociated acid, salt, or weak acid should be a good catalyst. These studies by Berge et. al.[7,8] do not clarify the reaction mechanism of a partially alkylated melamine-formaldehyde resin. Such a resin with $-N(CH_2OCH_3)CH_2OH$ as a functional site should react by a mechanism similar to a fully alkylated product; but the actual performance of a partially alkylated melamine-formaldehyde indicates a general acid catalysis mechanism.

Our work with a partially alkylated melamine-formaldehyde resin (amino resin 2) shows that demethylolation (Table 14, Eq.1) is a major reaction step in a partially alkylated melamine-formaldehyde resin. Therefore, the behavior of a partially alkylated and a fully alkylated, high NH melamine-formaldehyde resin is very similar in a coating formulation. This is not surprising because after demethylolation of the partially alkylated melamine-formaldehyde resin, a fully alkylated, high NH melamine-formaldehyde resin is formed. Table 15 shows the reaction path.

In this mechanism, possibly a Schiff base intermediate is formed and not a carbonium ion. The resulting Schiff base is reactive with hydroxyl, amide, and other -NH groups of the melamine, but not very reactive with carboxyl groups.

**TABLE 15.  Reaction Pathway (General Acid Catalysis)**



In most coating systems, one can, of course, observe an overlap of specific or general acid catalysis. Table 16 gives the reaction products of a partially alkylated melamine-formaldehyde resin under specific and general acid catalysis conditions. Volatile tests have indeed shown that reduction in formaldehyde can be observed using increased levels of a strong acid catalyst ($H^{+s}$).

**Table 16.  Reaction of Partially Alkylated Melamine Resins**



With highly alkylated, high NH melamine-(amino resin 3) formaldehyde resin, the cure response is significantly better with a weaker acid than a stronger acid. Therefore, only a weak

acid is an acceptable catalyst. Figure 1 gives a comparison of a hydroxyl functional acrylic resin cross-linked with amino resin 3 and catalyzed with an alkyl acid pyrophosphate and p-toluene sulfonic acid catalyst. At equal MEQ of acid in the system, the stronger acid is a poorer catalyst. This effect can be explained by the increased basicity[9] of the triazine ring of a highly alkylated, high NH melamine-formaldehyde resin leading to a protonation of the ring and reduction in reactivity.

**Figure 1. ACRYLIC/AMINO RESIN 3**

Arcylic  OH, COOH; Arylic/Amino 65/35; Baking Conditions 20 min. 93°C,
Film thickness 25μm; Substrate cold rolled steel
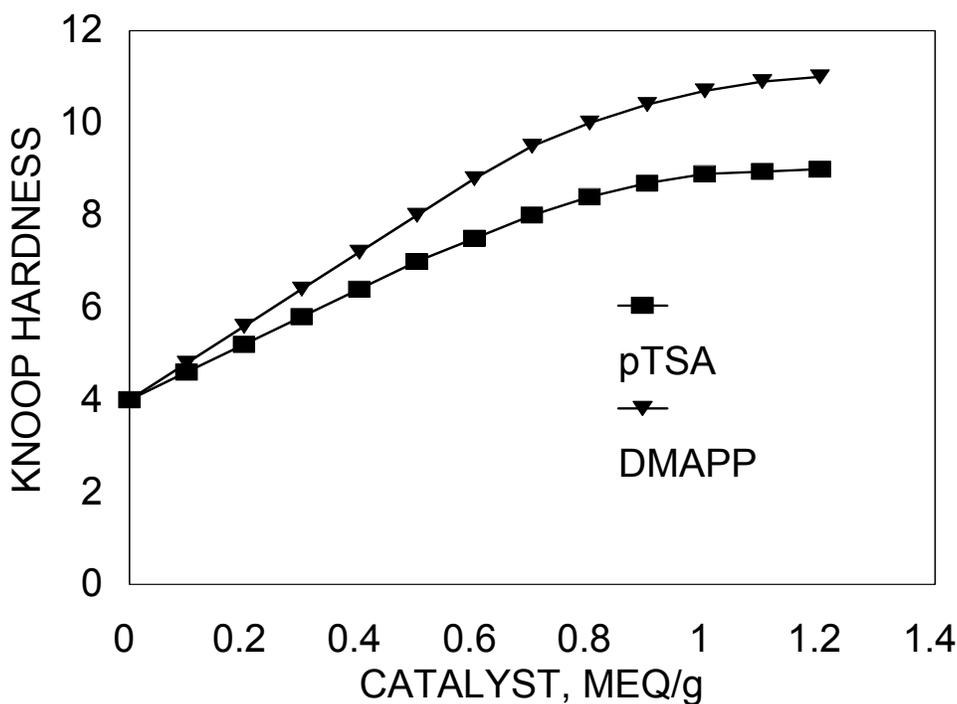


Comparing the cure response of amino resins 2 and 3 in a coating system (Table 17), we find that the highly alkylated, high HH amino resin is faster reacting than the partially alkylated resin at lower cure temperatures (120°C.). The demethylolation step, which is quite fast at higher temperatures, slows considerably at temperatures below 120°C.

The difference in cure mechanism between fully alkylated and partially alkylated, fully alkylated, high NH melamine-formaldehyde resins have significant implications from a formulation standpoint.

**Table 17.  Low Temperature Cure White Gloss Enamel**

Binder Alkyd/amino 65/35, Pigment $TiO_2$ 44 %,
Solvent Xylene/n-Butanol 75/25, Nonvolatile 60 %
Film thickness 25μm,

| Amino Resin | 2 | | 3 | | 4 | |
|---|---|---|---|---|---|---|
| Catalyst, DMAPP % of resin | 0 | 0.8 | 0 | 0.8 | 0 | 0.8 |
| | | | | | | |
| Cure 20 minutes 93°C | | | | | | |
| Hardness Knoop, $KHN_{25}$ | 1.0 | 5.0 | 2.5 | 9.0 | 2.0 | 6.0 |
| Hardness Pencil | 5B+ | B-HB | B-2B | HB-F | 5B+ | B-BH |
| MEK Resistance 2X Rubs | 5 | 50 | 5 | 125 | 10 | 75 |
| | | | | | | |
| Cure 20 minutes 121°C | | | | | | |
| Hardness Knoop, $KHN_{25}$ | 11.0 | | 15.0 | | 11.5 | |
| Hardness Pencil | H-2H | | H-2H | | H-2H | |
| MEK Resistance 2X Rubs | >200 | | >200 | | >200 | |

Fully alkylated melamine-formaldehyde resins give good cure response only in the presence of a strong acid catalyst; and amines and pigments with reactive surfaces can significantly inhibit the cure response.  Contrary to the common opinion, fully alkylated melamine-formaldehyde resins are not slower curing than partially alkylated resins if properly catalyzed. Partially alkylated and fully alkylated, high NH melamine-formaldehyde resins are, with respect to catalysis, much more forgiving. Amines will reduce the cure response, but not inhibit the reaction, pigments will have no or only a slight effect on the cure rate.  Stability on the other hand is not as good as that of fully alkylated resins, even in absence of a strong acid catalyst.

In water-borne coatings, the amine salts of the carboxyl groups are an excellent catalyst for partially alkylated or high NH resins, regardless of the pH of the system.  Therefore, stability of fully alkylated resins in water systems is superior to partially alkylated resins. The only way to improve stability in a water system would be to choose resins with very low acid number, thus, reducing the level of catalyst In the system.  This improved stability can indeed be observed in emulsions, which give excellent stability with partially alkylated melamine resins.

It is also a fallacy to expect improved stability in an amine neutralized, water-borne coating if the strong acid catalyst, such as pTSA, is omitted from the formulation.

On baking, most of a strongly basic -t-amine will have to leave the film before a fully alkylated melamine-formaldehyde resin will start to react.  This temperature is usually above 135°C.  Addition of larger levels of acid catalyst will not enhance the cure response at lower temperatures.  A partially alkylated or a high HH melamine-formaldehyde resin will react in the presence of the amine, or at about 110-120° C.; this can result in poorer water-resistance and increased blister tendency.

Cross-linking agents responding to two different mechanism of catalysis should not be blended in a formulation if low temperature cure is desired (Table 18).  The increased basicity of the partially alkylated or the high NH melamine resin is sufficient to neutralize portions of the

strong acid catalyst and, therefore, reduce the acidity of the system. The weak acid catalyst on the other hand will not catalyze the fully alkylated resin. This effect of cure inhibition is only observable at lower cure temperature, but not at temperatures above 150°C.

**Table 18. Low Temperature Cure of Combination of Amino Resins**

Unpigmented system; Cure 20 min. schedule 93°C; Substrate cold rolled steel zinc phosphated

| System | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Alkyd           solids weight, % | 70 | 70 | 70 | 70 | 70 |
| Amino 1         solids weight, % | 15 | 15 | 15 | --- | 30 |
| Amino 3         solids weight, % | 15 | 15 | 15 | 30 | --- |
| Catalyst  DMAPP, % on TRS | 0.5 | --- | 1.0 | 1.0 | --- |
| Catalyst  DDBSA, % on TRS | 0.84 | 1.68 | --- | --- | 1.68 |
| | | | | | |
| Dry film thickness, μm | 21 | 21 | 21 | 21 | 22 |
| Hardness Knoop, KHN25 | 2.2 | 1.7 | 2.3 | 8.0 | 7.0 |
| MEK resistance double rubs | 25 | 20 | 25 | 100 | >200 |

CONCLUSION

Understanding the mechanism of catalysis of amino resins is essential to predict the behavior of a cross-linking agent in a complex paint system. General acid and specific acid mechanism are responsible for catalysis of different amino resins. A. Berge[1] distinguishes between primary ($-NHCH_2OCH_3$) and secondary ($-N(CH_2OCH_3)_2$) ether in melamine resins, kinetic hydrolysis studies show that primary ether groups are catalyzed by a general acid catalysis mechanism and secondary ether by a specific acid mechanism. Unfortunately, existing commercial partially alkylated amino resins, which are known by experience to be catalyzed by weak acidic catalyst or by a general acid catalysis mechanism, not to contain a sufficient amount of primary ether groups to account for such a mechanism. Our work has shown that demethylolation of partially alkylated melamine formaldehyde resins and the formation of primary ether groups is a major reaction step. The thus formed primary ether functionality is then catalyzed by a general acid catalysis mechanism. Highly alkylated high NH resins low in methylol content also have shown to be reactive by the same weak acid catalyst, which confirms A. Berge's proposed mechanism.

Fully alkylated only secondary alkoxy group containing melamine resins require a strong acid catalyst for cure, which agrees with A. Berge's mechanism. In previous publications[6] formation of methylal was claimed as the reaction product of the self-condensation reaction. Under practical conditions in presence of small amounts of moisture no formation of methylal was observed, but we found that hydrolysis and demethylolation is the actual mechanism of self condensation of hexa(methoxymethyl)melamine. This work also shows that the composition of the volatile reaction products depends to a large extend on the composition of the amino resin, catalyst used and application conditions. Conventionally used partially butylated and methylated melamine formaldehyde resins emit the largest level of formaldehyde during cure, fully methylated melamine formaldehyde resins emit less and highly methylated high NH resins do emit .the least formaldehyde. Increased moisture in the baking oven has significant effect on

increasing formaldehyde emission and self-condensation.  A similar trend is seen with increased baking temperature.  Higher catalyst levels surprisingly have only a small effect on the level of formaldehyde emitted and higher levels of catalyst combined with a reduction in baking temperature can actually reduce formaldehyde emission.

## ACKNOWLEDGMENT

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