

Enhanced Reactivity of Melamine–Formaldehyde Resins by Fractionation. Crosslinking at Ambient Temperature

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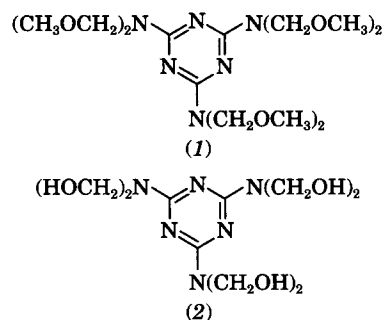
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SYNOPSIS

A commercial hexakis(methoxymethyl)melamine (HMMM) resin was fractionated (1) by crystallization of the hexane-soluble fraction from hexane and (2) by partitioning the hexane-soluble and hexane-insoluble fractions between alumina and various solvents. Crystallization afforded hexakis(methoxymethyl)melamine (1) of 90 to 95% purity. Partitioning afforded 12 fractions with altered proportions of polar and nonpolar species; the least polar fraction was spectroscopically and chromatographically similar to the crystallized material. Relative reactivities of certain fractions were estimated by ¹H NMR studies of the rates of reaction with neopentyl alcohol in the presence of catalytic amounts of *p*-toluenesulfonic acid (*p*-TSA). It was found that the reactivity of fractions, rich in less-polar species, was substantially greater than that of the commercial HMMM resin, whereas reactivity of fractions, rich in polar species, was less. Reactivity was especially enhanced by removal of all active hydrogen species, notably those containing NH groups. A practical consequence of this result was that fully formylated and alkylated melamine resins could crosslink with polyols at substantially lower temperatures than the commercial HMMM resin, which contained NH groups. Therefore, room-temperature crosslinking was feasible.

INTRODUCTION

Melamine–formaldehyde (MF) resins have been widely used for more than 50 years in thermosetting coatings, laminates, and plastics. They are usually used to crosslink polyols, a reaction that is almost invariably effected at elevated temperatures, usually above 100°C. An important type of MF resin is the “monomeric” methylated resins, in which the species hexakis(methoxymethyl)melamine (1) is a major component. Resins of this type are often called HMMM resins. Despite their long history, reactivity of these materials is not completely understood.

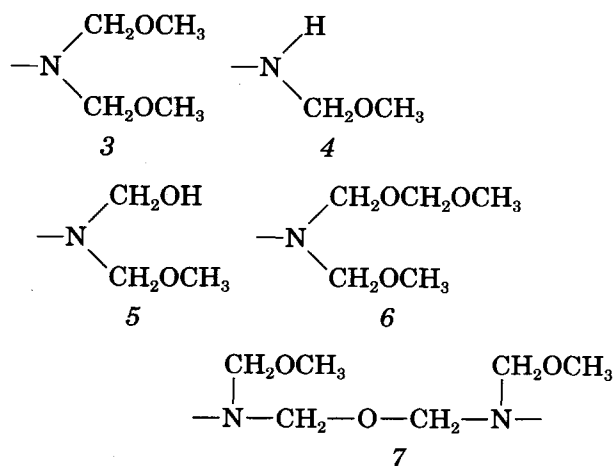


The two-step process for production of HMMM resins has been reviewed.^{1,2} The first step involves formylation of melamine under basic conditions to form methylol melamine derivatives. With excess formaldehyde, the main product is hexakis(methylol)melamine (2), but the product is a statistical mixture, containing both unformylated NH

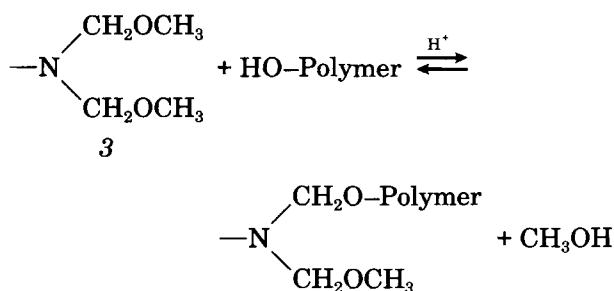
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groups and overformylated $\text{NCH}_2\text{OCH}_2\text{OH}$ groups. In addition, etherification of the reactive hydroxyl groups occurs to form $\text{N}-\text{CH}_2-\text{O}-\text{CH}_2-\text{N}$ groups that bridge two triazine rings. The second step in the synthesis of HMMM resins is acid catalyzed methylation of the methylol group. Again, the reactions (which are readily reversible) do not go to completion, and some NCH_2OH groups are found in the product, along with NH groups carried over from the first step or formed by deformylation and $\text{NCH}_2\text{OCH}_2\text{OCH}_3$ groups. Further, under the acidic conditions employed, more $\text{N}-\text{CH}_2-\text{O}-\text{CH}_2-\text{N}$ bridging groups may form. Formation of a second type of bridging group, $\text{N}-\text{CH}_2-\text{N}$ has been postulated, but has not been confirmed by NMR spectroscopy.²

Melamine resin producers are able to adjust the process to create a broad range of resins with different distributions of functional groups and different properties. All these resins are complex mixtures of chemical species. For example, Hill and Kozlowski reported that a commercial "monomeric" HMMM resin contains 62% monomer, 23% dimer, and 15% trimer and higher oligomers,³ and van Dijk et al.⁴ published chromatographic data showing that the monomeric and oligomeric portions contain appreciable levels of species containing NH and NCH_2OH groups. Thus (1) is the single most populous species in HMMM resins, but its concentration is less than 50% by weight. The balance of the material is a mixture of species containing three pairs, or diads, of the above groups on each triazine ring. In "fully formylated, fully metholylated" resins, the predominant diad is 3; other diads present at substantial levels are 4 through 7, and many others are present in smaller amounts.



HMMM resins are used mainly to crosslink polymeric polyols, the predominant reaction being co-condensation *via* transesterification:



Many other reactions, including self-condensation to form NCH_2N and $\text{NCH}_2\text{OCH}_2\text{N}$ bridges, also play a role in the crosslinking process.^{1,2} Most or all of the crosslinking reactions are reversible.

Reactivities of melamine resins containing various levels of the possible diads have been studied extensively,⁵ although mainly by imprecise methods involving the rate at which network physical properties, such as hardness or solvent resistance, increase. It is often said that resins having high concentrations of the diad 4 are more reactive than those containing high concentrations of diad 3. This generalization is probably based on the observations (1) that reactions of polyols with resins rich in diad 4 can be catalyzed by weak acids, such as carboxylic acids, but reactions of those rich in diad 3 require strong acids, such as *p*-toluenesulfonic acid (*p*-TSA) and (2) that resins rich in diad 4 self-condense more rapidly with any catalyst. However, the actual kinetic situation is far more complex. Some years ago, Blank stated that, under strong acid catalysis, resins rich in diad 4 are actually less reactive toward hydroxyl groups.⁵ Diad 5 is readily esterified and, in addition, is apt to deformylate to form diad 4. Little has been published about the reactivities of overformylated diad 6 and the bridging diad 7, but they are presumably capable of reactions analogous to those of diad 3.

Here we report a study of the effects of the species normally present in HMMM resins on their reactivity. It will be shown that removal of polar chemical species from resins substantially increases reactivity of the nonpolar fraction transesterification. Contrary to conventional wisdom, "pure" HMMM is highly reactive toward alcohols. In fact, it is so reactive that room temperature crosslinking is feasible. Possible explanations will be considered. Independently Cameron and coworkers⁶ have secured a patent on reactive coatings formulations contain-

ing melamine resins said to contain low levels of NH groups.

EXPERIMENTAL SECTION

Materials and Methods

The HMMM resin was Resimine R-747, and the mixed ether melamine resin was Resimine RF-4518 (Monsanto Chemical Company). The structure of RF-4518 is similar to that of R-747, except that isooctyloxy groups have been substituted for roughly $\frac{1}{6}$ of the methoxy groups. Glydexx N-10 is the glycidyl ester of a mixture of branched C-10 monocarboxylic acids. Reagent grade solvents were used. Neutral alumina was Brokman I, standard grade, supplied by Aldrich. Neopentyl alcohol and *p*-toluenesulfonic acid (*p*-TSA) monohydrate were purchased from Aldrich. K-Flex 188, an oligomeric diester diol, was obtained from King Industries, Norwalk, CT. Glydexx N-10, the glycidyl ester of a mixture of branched, ten-carbon, carboxylic acids, was obtained from Exxon Chemical Co. Infrared, ^1H and ^{13}C NMR spectra were obtained using Mattson "Cygnet" FT-IR, Varian EM390 (90 MHz) and JEOL FX-200 (400 MHz) spectrophotometers, respectively. High pressure liquid chromatography was effected using an Isco-2300 pump, coupled to a UA-5 detector, Type-9 optical unit (UV_{254}) with analytical silica gel columns. Solvent evaporation was effected at temperatures not greater than 50°C using a rotary evaporator with a water aspirator.

Synthesis of Diester Diol

Cyclohexanedicarboxylic acid (85 g, 0.49 mol) was placed in a breakaway flask fitted with a thermometer, a stirrer, a reflux condenser and an addition funnel charged with Glydexx N-10 (242 g, 1 mol) and benzyltriphenylphosphonium chloride (0.5 g, 1.3 mmol). The Glydexx/catalyst solution was slowly added with stirring at 174 to 180°C . The opaque reaction mixture was then stirred at 180° for 4 h to yield transparent, nearly colorless, diester diol. This material was used in crosslinking experiments described below.

Purification of HMMM Resin by Crystallization

R-747 was stirred with about 10 parts by weight of hexane; the soluble portion (about half) was separated and was cooled to -5°C for about 12 h. The crystals were separated by decantation. HPLC in-

dicated the purity of the crystalline material to be 90 to 95%.

Fractionation of R-747 by Partitioning Between Alumina and Solvents

The fractionation scheme is outlined in Figure 1. A mixture of 50 g of Resimine R-747 and 800 mL of hexane was stirred for 3 h using a magnetic stirrer. The turbid mixture was allowed to stand for 3 h at room temperature, and the clear upper layer (hexane solution) was decanted. The hexane insoluble portion (fraction B) weighed 20.7 g. About 7% of the hexane soluble fraction was concentrated, leaving 2 g of residue (fraction A). The remainder was combined with 150 g neutral alumina (Brokman I, standard grade) in a 2-L breakaway flask, fitted with a mechanical stirrer. After stirring for 3 h the hexane layer was decanted and concentrated to give 7.7 g of a low viscosity liquid (fraction C), which solidified

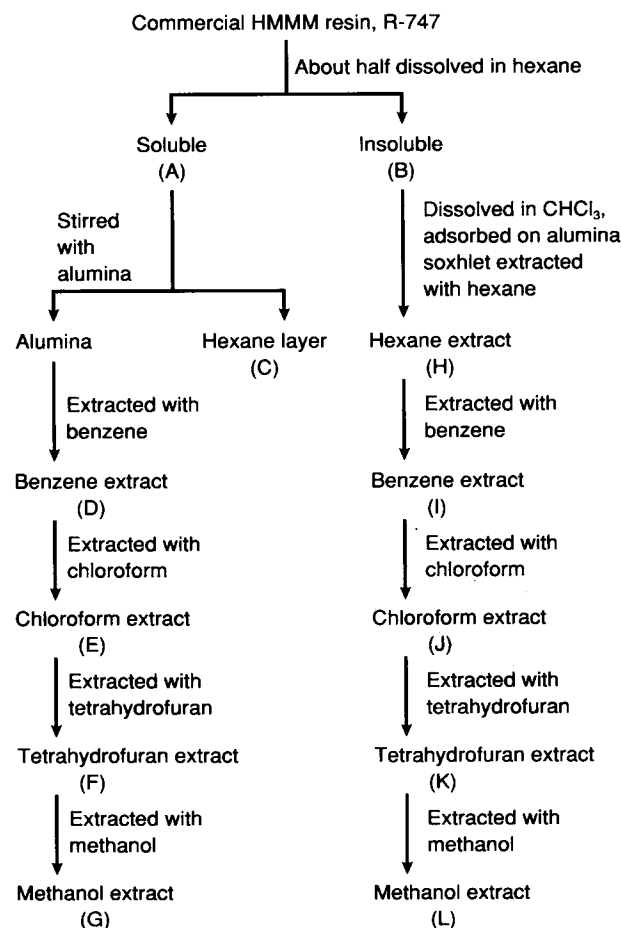


Figure 1 Partitioning of R-747 by adsorption and extraction.

upon standing at room temperature. The alumina was stirred for 1.5 h at 25°C with benzene (400 mL, 1.5 h), chloroform (400 mL, 1.5 h), tetrahydrofuran (400, 1.5 h) and methanol (400 mL, 1.5 h), consecutively. Each solvent fraction was decanted and concentrated to give 6.57 g, 6.49 g, 3.63 g, and 3.7 g of residue respectively (fractions D, E, F, and G).

One g of the hexane insoluble fraction B (from above) was withheld and the remainder was dissolved in 150 mL of chloroform. Neutral alumina (100 g) was added *slowly* (CAUTION, heat evolved) to this solution. The mixture was concentrated to afford a dry powder of alumina with resin presumably adsorbed. Part of this powder (46.8 g) was placed in an extraction thimble and was then extracted in a soxhlet extractor sequentially with hexane, benzene, chloroform, tetrahydrofuran, and methanol for 10 h, 12 h, 10 h, 10 h, and 24 h, respectively. Each extract was concentrated to leave 1.6 g, 1.4 g, 2.6 g, 0.96 g, and 0.76 g residues, fractions H, I, J, K, and L, respectively. All of these fractions were found to be mixtures of chemical species by chromatography.

Transesterification Rate Experiments

The method of van Dijk et al.⁴ was adapted. In a typical experiment, 0.21 g (2.4 mmol) of neopentylalcohol, and 0.16 g (about 0.41 mmol, assuming a molecular weight of 390) of HMMM, or the fraction to be tested, were mixed in a small vial; 0.1 mL (2 mg, 0.0105 mmol) of a solution of *p*-TSA monohydrate (made by dissolving 20 mg of *p*-TSA monohydrate in 1 mL of CDCl₃ and 2 drops of methanol) was added, screw caps were tightly closed, and the vials were swirled until the solution appeared homogeneous. The reaction mixture was kept at room temperature and the progress of reaction was periodically monitored by ¹H NMR by observing the changes in relative intensity of peaks for the CH₃ of methanol (3.46 ppm), the OCH₃ of HMMM (3.36 ppm), the CH₂ of neopentyl alcohol (3.26 ppm), and the CH₂ of the transesterified product (3.13 ppm), which could be independently integrated to estimate the extent of reaction. Data are reported as percent conversion of the methoxy groups of the resin to free methanol. Two criteria were used to assess relative reactivity: the time required to reach apparent equilibrium and the conversion after 24 h. In this way, the reactivity of all fractions, except K and L which were insoluble, was estimated.

Experiments were also conducted in which certain fractions (e.g., C and J) were mixed to determine deactivating effects. In a similar mixing experiment, the model compound *N*-methoxymethyl-

N',N',N'',N''-tetramethylmelamine was tested as a catalyst deactivator. Synthesis of this material will be described in a subsequent article.⁷

The reactivity of commercial mixed ether melamine resin, Resimene RF-4518, was evaluated similarly. Molecular weight was assumed to be 488, the theoretical molecular weight of monomeric penta(methoxymethyl)isooctyloxy methylmelamine. Molar ratios were similar to those described above. ¹H NMR signals from the isooctyl group present in the resin, and in any isooctanol that may be liberated by reaction, were disregarded, possibly introducing small errors.

Crosslinking Rates of Coatings Made from Fraction C and from R-747 at Ambient Temperature

Fraction C (0.2 g), diester diol made as described above (0.3 g), and *p*-TSA monohydrate (0.3 mL of a solution of 20 mg in 0.6 mL of CHCl₃ and two drops of methanol, 2% of total weight) were mixed in a vial and were diluted with 0.5 mL of *o*-xylene. This solution was cast on a 3 × 9 in. Bonderite 1000 steel panel (Parker) using a No. 26 wire-wound spreading bar. Another formulation was made with same the amounts of materials, except that R-747 was substituted for fraction C. These coatings were left at room temperature and were periodically tested for tackiness by touching them lightly. It was found that the coating made from fraction C was "dry to the touch" (not tacky) after 12 h, while the coating made from R-747 reached this stage only after 5 days.

Crosslinking at Elevated Temperatures

Solutions of K-Flex 188 and R-747 in weight ratios of 1.89 : 0.628 g and 2.15 : 0.375 g (75/25 and 85/15, respectively) in 1.5 g of xylene were prepared. Catalyst (0.5 mL of a solution of 50 mg of *p*-TSA monohydrate in 2 mL of chloroform and 4 drops of methanol, 0.5% of total weight) was added and films were cast on steel panels as described above. Similar formulations were made using Fraction C in place of R-747. Separate panels were heated at temperatures of 50, 60, 70, 80, 90, and 100°C in a forced air oven for 10 min. The 85/15 films did not harden at any temperature, so only the 75/25 films were evaluated (see Results).

RESULTS

Fraction C of HMMM resin R-747 was estimated by size exclusion chromatography (SEC) to be 95%

monomer and 5% dimer; comparison to polystyrene standards indicated a molecular weight of 392. HPLC and thin layer chromatography indicated that over 90% of this material is a single compound. ^1H NMR, ^{13}C NMR, and FT-IR spectra were consistent with hexakis(methoxymethyl)melamine (1) of 90 to 95% purity. The ^1H NMR (DMSO- d_6 , 400 MHz) shows two peaks at 5.02 and 3.24 ppm, plus other small peaks, and the ^{13}C NMR spectrum in DMSO- d_6 shows peaks at 166.31, 76.60, and 55.30 ppm, and other small peaks. The values for the triazine, methoxy, and methylene carbons agree well with those reported by Tomita and Ono⁸ (166.2, 77.4, and 55.3 ppm, respectively, in DMSO- d_6) and Bauer² (165.4–165.8, 76.8, 55.4 ppm), and not as well with those reported by Schindlbauer and Anderer⁹ (167–168, 78.9, and 57.5 ppm, DMSO- d_6). NMR spectra in benzene- d_6 had slightly different chemical shifts in the ^1H NMR (5.20, 3.38 ppm) and in the ^{13}C NMR (167.28, 76.79, 55.64 ppm), indicating some sensitivity to the medium. Our values are judged definitive for compound 1 under the conditions used. Two of the small peaks noted above were at 94.39 and 72.67 ppm, assignable to $\text{N}-\text{CH}_2\text{O}-\text{CH}_2-\text{OCH}_3$ and $\text{N}(\text{H})\text{CH}_2-\text{OCH}_3$, respectively, in agreement with Tomita and Ono.⁸ FT-IR of fraction C showed no peaks between 3100 and 4000 cm^{-1} , indicating that $\text{N}-\text{H}$ or $\text{O}-\text{H}$ are virtually absent. In contrast, R-747 shows weak absorptions at 3300–3600 cm^{-1} .

Crystallization of the hexane soluble fraction of HMMM resin R-747 yields a solid and it is chromatographically similar to the crystallized material described above. The ^1H and ^{13}C NMR were nearly identical to that of fraction C; however, the IR spectrum had an absorption at 3449 cm^{-1} , indicating the presence of an OH group.

None of the fractions obtained in the partitioning experiments (Chart I) appeared to be pure compounds. For example, SEC of fraction J indicated a mixture of one or more trimers, at least two types of dimers, and one or more monomer. The IR of the fraction J shows a strong unsplit absorption at 3342 cm^{-1} , indicating the presence of a high population of $\text{N}-\text{H}$ groups. The ^{13}C NMR of this fraction was complex, with several peaks centered around 76 ppm, indicating different methylene ether bridging diads (type 7), and four peaks at 73 ppm, attributable to different diads of type 4. ^1H NMR shows two large, unresolved groups of peaks at 3.3 and 5.1 ppm, attributable to $\text{N}-\text{CH}_2\text{OCH}_3$ groups, along with small, broad peaks at about 5 ppm. It was noted that chemical changes of the more polar fractions apparently occur during fractionation.

The reactivity of all the fractions was assessed

by the rate of transesterification with neopentyl alcohol, as described in the Experimental section. This coreactant was chosen mainly because of its simple ^1H NMR spectrum and also because of its resemblance to the end groups of widely-used polyols, many of which are based on neopentyl glycol. Reactivity of fraction C was the highest of any fraction; it reached equilibrium (about 40% conversion of the neopentyl alcohol) within 3 h. The other fractions were evaluated after 24 h, the extents of reaction being: (A) 17%, (B) 9%, (C) 40%, (D) 30%, (E) 8%, (F) 9%, (G) 9%, (H) 17%, (I) 10%, (J) 7%. Fractions K and L were not soluble in the reaction medium. Resimene R-747 showed 15% reaction after 24 h and 30% reaction after 5 days. Reactivity of commercial resin RF-4518 was similar to that of fraction C: about 42% reaction in 3 h; however, the precision of this experiment was low because of partial interference with the isooctyl group of the resin.

Crystallized R-747 was compared with fraction C in the transesterification rate experiment with neopentyl alcohol. After 3 h, the recrystallized sample showed 28% reaction while fraction C had reached equilibrium at 40% reaction. This indicates that purification by adsorption of contaminants with alumina yields a more reactive product, consistent with the observation that FT-IR indicates traces of active hydrogen material in the recrystallized material and no traces in fraction C.

The extraction scheme shown in Figure 1 was carried out in the hope of isolating from the commercial melamine resin a single species that is responsible for reduced reactivity. Single compounds were not isolated, at least partly because chromatography on silica and, quite possibly, adsorption on alumina cause chemical reactions of some of the species present in HMMM resins. However, it was demonstrated that fractions containing large populations of NH groups are catalyst poisons. For example, it was found that fraction J strongly inhibits transesterification when mixed in varying proportions with Fraction C. One part of fraction J was sufficient to lengthen the equilibration time of 16 parts of Fraction C from 3 h to 5 days, making its reactivity similar to that of the commercial HMMM resin, R-747. Looking at it another way, about 10 mg of fraction J appears capable of deactivating about 2 mg of *p*-TSA to that level.

It was also of interest to probe how much of *p*-TSA must be added to resin R-747 in order to increase its reactivity to the level of fraction C. When transesterification reactions were carried out with varying amounts of *p*-TSA and R-747, it was found that 12 mg of *p*-TSA catalyzed the reaction of R-

747 at about the same rate as 2 mg of *p*-TSA catalyzed fraction C.

In a subsequent article we will describe the synthesis of *N*-methoxymethyl-*N'*,*N'*,*N''*,*N''*-tetramethylmelamine.⁷ This new compound is a model for melamine resins, which contains only a single reactive diad, 4. Only 5 mg of this compound was needed to slow the transesterification fraction C from 3 h to 5 days, indicating its catalyst poisoning effect is twice that of Fraction J on a weight basis.

The question arises as to how the enhanced reactivity of fraction C, observed with neopentyl alcohol, relates to reactivity in formation of a crosslinked network when the purified melamine resins react with a polyol. As described in the Experimental section, a heavily catalyzed (about 2% of the total weight of binder) formulation of a polyester diol, and Fraction C, crosslinks to a "dry to touch" state in 12 h at ambient temperature. This diol has secondary hydroxyl groups, and even faster reaction might be anticipated with a diol with unhindered primary hydroxyl groups. This result is consistent with results reported by Cameron, et al.⁶ Further, 75/25 formulations of *K*-Flex 188 diol and fraction C (catalyst level, 0.5% of the total weight of binder) crosslinked to a hard film within 10 min at 60°C; in contrast, R-747 films required 80°C. Hill and Kozlowski previously described crosslinking of *K*-Flex diol,³ which has relatively reactive primary hydroxyl groups. Preliminary studies indicated films made with Fraction C have better impact resistance than comparable films made with R-747, while the hardness of the films is similar.

DISCUSSION

In this study, two procedures were demonstrated for enriching the fully alkoxyated part of a commercial HMMM resin, removing all or almost all of the species that contain active hydrogens. Both procedures involve extraction of the commercial resin with hexane, the proportion being that roughly half of the material is soluble. Further fractionation is then accomplished by crystallization from hexane or by treatment with alumina. The products are solids of ill-defined crystallinity, which are judged to be over 90% pure hexakis(methoxymethyl)melamine (1). Absence of IR absorptions in the 3100 to 4000 cm⁻¹ region of the alumina-treated material (fraction C) indicates that almost all species bearing NH or OH groups have been removed, while the FT-IR spectrum of the crystallized materials indicates traces of OH groups. Whereas fraction C contains 5 to 10%

of dimers, and presumably traces of higher oligomers, it appears to be essentially fully methoxylated.

It was shown that these fully methoxylated materials are considerably more reactive than commercial HMMM resins, such as Resimene 747. The increase in reactivity is such that fraction C can crosslink a model polyol to form a good film within 10 min at 60°C with about 0.5% (of the weight of binder) of strong acid catalyst. Today's coatings, based on HMMM resin crosslinkers, generally contain 0.1 to 0.5% (of the weight of the binder) of catalyst, and are cured at temperatures in the range 110 to 140°C. Coatings that could be crosslinked at temperatures of 70°C or lower are attractive in many industrial applications, not only because of energy savings, but also because plastic items that are distorted at 110°C are unaffected at 70°C, and because these temperatures are attainable with steam heated ovens. Curing temperatures can be reduced to the vicinity of 70°C by the expedient of adding high levels (up to 5 wt %) of strong acid catalyst, but large amounts of residual catalyst substantially harm the coatings' resistance to moisture and weather. For example, Bauer¹⁰ showed that increasing the *p*-TSA catalyst concentration from 0.08% to 1% increases the rate of hydrolysis of acrylic-melamine coatings tenfold. The results described here suggest a new, alternative way to increase reactivity: the use of highly reactive crosslinkers, such as fraction C with moderate catalyst levels. Of course, it is possible that more reactive crosslinkers might form more reactive films that would be vulnerable to moisture and weather. It remains to be seen which method is more advantageous.

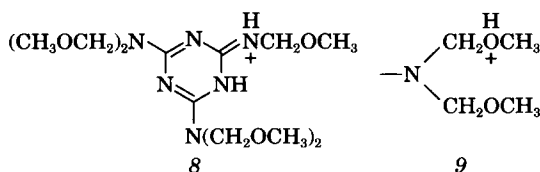
The high reactivities of fraction C and of R-4518 raise the question of whether crosslinking at ambient temperatures is feasible. The potential importance of such a development is evident; it is impractical to bake many objects to be coated. Ambient cure formulations have been described previously, for example by Koral and Petropoulos,¹¹ but high catalyst levels (5 wt % on total resin solids of 37% HCl or 10 wt % on HMMM of *p*-TSA) were required. High catalyst levels are likely to be deleterious to coating durability. Our results indicate that ambient temperature curing of coatings, made with fully alkoxyated melamine resins, may be feasible using less extreme catalyst levels: 2 wt % on total resin solids in this case. Properties of the coatings made in this study were not evaluated. They are probably not good because of the use of coreactants that were not optimized. However, it may be possible to make good ambient-temperature coatings if the optimum coreactant polyols are developed for the purpose.

Most present-day coreactants are designed to take advantage of the fact that melamine resins self-condense at elevated temperatures, as well as cocondense with the polyol.¹² Virtually no self-condensation of totally alkylated melamine resins would be expected at ambient temperature.

Our results are consistent with those of Cameron et al.,⁶ who reported low-temperature and room-temperature curing formulations based on three melamine crosslinkers, all having IR spectra with low absorption in the 3100 to 4000 cm^{-1} region, and all described as being free of NH groups. Two of these crosslinkers were of unspecified origin; the third was Resimine RF-4518, the commercially available material studied here. It is a "mixed ether" resin, whose alkyl groups are methyl and isooctyl in about a 5 : 1 mol ratio. The resin is almost completely alkylated and, as demonstrated by Cameron, and independently by us, and it is highly reactive. Its reactivity was similar to that of Fraction C in our transesterification experiment.

The reasons for the enhanced reactivity of fully alkylated HMMM resins are not, at this stage, proven. It appears likely that one or more species present at the time of crosslinking deactivate the strong acid catalyst. Cameron et al. suggest that the secondary amine functionality is directly responsible. Their explanation is consistent with the fact that high reactivity is associated with a low population of NH groups, and it is supported by our demonstration that fraction J, with its high level of NH, is an efficient catalyst poison, as is the model compound containing diad 4.

A possible explanation for the enhanced reactivity can be found in an early study by Dixon et al.,¹³ who found that partly substituted melamines are considerably stronger bases than fully substituted melamines. Dixon et al. postulated that ring nitrogens are more basic when they are adjacent to a nitrogen that has a hydrogen on it, because of the formation of tautomeric forms, such as 8.



The mechanism of transesterification is thought to involve intermediates, such as protonated diad 9, with the proton from the *p*-TSA catalyst associated with the ether oxygen.^{1,2} Such species will exist in equilibrium with other species, in which the proton

is associated with other basic sites, such as the various nitrogens. Kinetic theory predicts that the rate of transesterification is directly proportional to the concentration of reactive species 9. It is possible that the concentration of species 9 is low, since the oxygen must compete for a limited supply of protons with all other basic sites in the system. Assuming that Dixon's conclusions about the strong basicity of melamine resins containing NH groups are correct, it can be visualized how removal these species could substantially increase the concentration of reactive intermediate 9, and proportionately increase the rate of transesterification.

Other explanations, involving bases other than amino resins with NH groups, cannot be ruled out. For example, it could be postulated that some strongly basic species are present in small amounts in commercial melamine-formaldehyde resins, or are formed by some reaction when the resin is exposed to strong acid. However efforts to isolate such a species by the extraction scheme shown in Figure 1 were fruitless.

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