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## Low Temperature Acid Catalyzed Curing of Melamine Resin Systems

**Krister Holmberg**

Berol Kemi AB, Box 851, S-444 01 Stenungsund, Sweden

### SUMMARY

Melamine resins having a high concentration of secondary amino groups (-NH-$CH_2OR$ groups) are able to cure at low temperature under strongly acidic conditions. It is shown by spectroscopic methods that the characteristic curing reaction of this type of resin proceeds via an imino group intermediate. Analogous reactions are proposed for the self-curing of the melamine resin and the co-condensation with hydroxyl containing polymers.

### INTRODUCTION

Melamine resins, which are frequently used as cross-linkers in binder systems are normally not very reactive and need high curing temperatures. When used in paints and lacquers, they are usually combined with alkyds or saturated polyesters with a high concentration of hydroxyl groups.

Certain types of melamine resins are known to be highly responsive to acid catalysts. By using very high amounts of catalyst - up to 25% of the amount of melamine resin - the curing temperature can be kept as low as below 100°C. This enables melamine resin-based systems to be used on heat-sensitive items, such as furniture and window-frames and sills.

It has been observed that secondary amino groups of the type -NH-$CH_2OR$ (where R is lower alkyl) are a necessary condition in order for melamine resins to undergo low-temperature curing under strongly acidic conditions. A number of papers have dealt with this subject (BERGE 1977, BLANK 1979 and 1982, and references cited therein) but no comprehensive understanding of the reactions involved have emerged from the studies. In this paper a mechanism for the acid-catalyzed curing of these systems is presented and spectroscopic data are given as evidence to support the theory.

It should be pointed out that the effect brought about by the acid catalyst on these systems is distinctly different from that exerted on normal alkyd-melamine systems. The usual type of melamine resin used in combination with alkyds is highly methylolated and the concentration of -NH-groups is low. Even if an acid is often used to increase the rate of curing, the effect of the catalyst on these systems is relatively small. The acid-catalyzed curing of the "normal" type of alkyd-melamine systems is believed to be well understood (HOLMBERG 1978, BLANK 1982).

### EXPERIMENTAL AND RESULTS

A model system consisting of a methylated melamine resin with a high concentration of secondary amino groups (about two -NH-$CH_2OR$ per triazine ring), ethylene glycol as hydroxyl-containing component and p-toluene sulphonic acid (pTSA) as catalyst was used. A ratio of melamine resin, ethylene glycol and pTSA of 5:5:1 was used and the pTSA was employed as a 20% solution in ethanol.

The use of a glycol instead of the normal polyol component with higher functionality facilitates the investigation since the curing reactions do not lead to the usual steep increase in viscosity.

The reactions were followed by IR, H-1 NMR and C-13 NMR spectroscopy. As comparison, a curing experiment was also performed in which the melamine resin above was replaced by a highly methylolated one (low concentration of $-NH-CH_2OR$). Finally, a curing reaction was performed in the absence of the acid catalyst. The last two experiments were monitored by IR spectroscopy.

IR analyses were performed at ambient temperature using AgBr windows. Spectra were run on the individual components and on the mixture 4, 10, 30, 60 and 120 min after mixing.

A characteristic band appeared at 1650 $cm^{-1}$ on the spectra of the model system. This band, which is not present in the spectra of any of the starting materials, increases in intensity up to the 30 min recording, then slowly decreases. If the pTSA is omitted, no band is visible at this frequency. When the melamine resin is replaced by a highly methylolated one only a very weak band appears.

The band at 1650 $cm^{-1}$ can be assumed to be due to C=N stretching vibrations of terminal imino groups formed from $-NH-CH_2OR$ groups of the melamine resin. The band is superimposed by the band from in-plane stretching of the triazine ring at 1560 $cm^{-1}$ which is normally the most intense band of a melamine resin. The 1650 $cm^{-1}$ band is comparable in intensity to the characteristic out-of-plane triazine ring vibration at 815 $cm^{-1}$.

H-1 NMR analyses were made at ambient temperature using a 200 MHz apparatus. Spectra were run on the individual components, as well as on the mixture after standing for 3, 12, 40 and 70 min. A new signal, a broad singlet, just downfield of the methylene signals ($=N-CH_2-N=$, $-O-CH_2-O-$ and $=N-CH_2-O-$) of the melamine resin is visible on the 3 min spectrum and grows in intensity up to the 40 min spectrum. Then the signal diminishes. The peak, which is at 5.20 ppm, lies in the region of $CH_2=N$-signals.

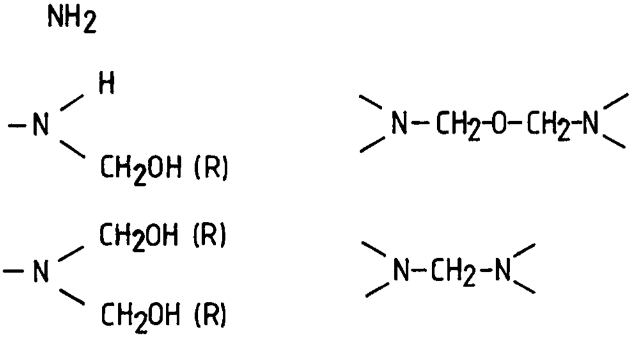

Figure 1. Structures in alkylated melamine resins.

The broad -NH- peak, which is present at 6.80 ppm in the spectrum of the melamine resin, has completely disappeared in the spectra of the mixture. Drawing conclusions from this behaviour is difficult, however, since the rate of exchange of the -NH-proton may decrease in the new environment, giving rise to a peak which is so broad that it is difficult to observe.

C-13 NMR spectra were recorded with the same apparatus at 20 and 40°C using deuterated acetone as solvent. Spectra were run 20, 60 and 90 min after mixing the components. A peak at 140 ppm, not present in the spectra of the individual starting materials, appears with about equal intensity in the first two recordings and is somewhat smaller in the 90 min spectrum. The signal lies in the region where $CH_2=N-$ signals appear.

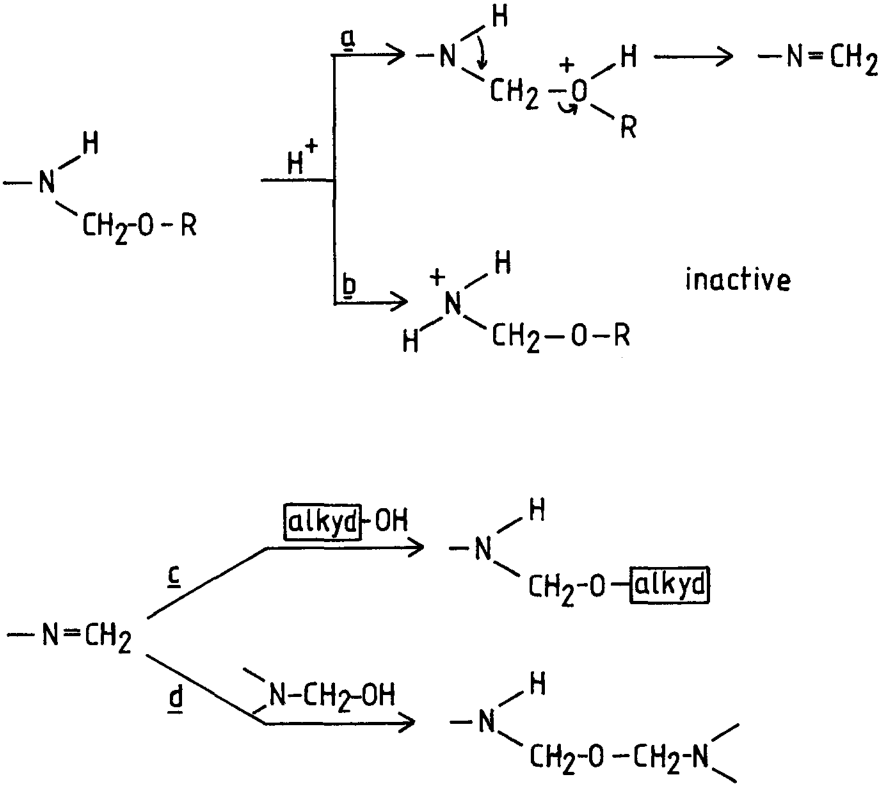

Figure 2. Curing reactions of melamine resins containing a high concentration of secondary amino groups.

## DISCUSSION

The main functional groups present in melamine resins are shown in Fig. 1. As mentioned above, it has been empirically found that a high concentration of $-NH-CH_2OR$ groups in the amino resin is a necessary condition in order for acid-catalyzed curing to take place at low temperatures. It is, therefore, reasonable to assume that this group plays a vital role in the curing mechanism.

Under strongly acidic conditions, elimination of alcohol from the alkoxymethylamino group is feasible, leading to imino groups. The reaction, which is shown in Fig. 2, path a, is an elimination which could either proceed by a concerted (E2 type) or a stepwise (E1 type) mechanism (SAUNDERS and COCKERILL 1973). The E1 mechanism would involve a primary carbonium ion which normally is very unstable. In this case, however, the carbonium ion would be resonance-stabilized by the free electron pair on the adjacent nitrogen atom.

A protonation of the ether oxygen rather than of the amino nitrogen atom is a prerequisite of a -elimination reaction, regardless of whether the mechanism is of the E1 or E2 type. In alkoxymethylamino groups the nitrogen atom would normally be expected to be far more basic than the oxygen, and the protonation would, therefore, lead to an inactive ammonium ion (Fig. 2, path b). In this case, however, the basicity of the nitrogen atom is considerably reduced since it is linked to the heteroaromatic triazine ring. Hence, protonation according to path a should be able to compete favourably with that of path b. (A competing protonation of a nitrogen atom in the triazine ring is also conceivable; this, however, would represent a deactivation (BERGE 1977).)

The formation of imino groups is reversible and addition of an alcohol would give back an alkoxymethylamino group. Since the curing is usually performed at a temperature above the boiling point of the alcohol of the melamine resin (normally methanol or butanol), addition would either take place to hydroxyl groups of the alkyd or to hydroxymethylamino groups of another melamine resin molecule. The reactions, leading to co-condensation of the two polymers and self-curing of the melamine resin, respectively, are illustrated by pathways c and d of Fig. 2.

As is shown in the preceding section, spectroscopic data strongly support the theory of curing via formation of imino groups. This, of course, does not exclude other curing mechanisms to be operative as well. The curing of normal alkyd-melamine resin systems where the melamine resin is highly methylolated and, thus, unable to undergo -elimination is believed to be a substitution of alkoxyl groups of the alkyd by a $S_N2$ mechanism (HOLMBERG 1978, SANTER and ANDERSON 1980). This reaction is difficult to study by spectroscopic methods and may well contribute to the curing also of the type of system used in this work. The present work only implies that the characteristic feature of melamine resins with a high concentration of secondary amino groups is their ability to react with hydroxyl-containing compounds in the presence of an acid catalyst via formation of imino groups. This curing reaction seems to be the reason behind the ability of these resins to cure at low temperatures.

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