

# Crosslinking Kinetics and Network Formation in Organic Coatings Containing Hexamethoxymethylmelamine

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## Synopsis

We have developed a kinetic model of the crosslinking reaction of hydroxy-functional acrylic copolymers with fully alkylated melamines. This model accurately describes the extent of the crosslinking reaction as a function of cure time and melamine concentration in coating films. Using this model, we have determined the effects of acid catalyst concentration and strength and the effects of cure temperature on the rate constant of the crosslinking reaction. The rate constant is proportional to the catalyst concentration and to the square root of the acid constant of the catalyst. The temperature dependence of the rate constant follows an Arrhenius rate law with an activation energy of 12.5 kcal/mol independent of catalyst type. Amine salts of *p*-toluenesulfonic acid have been compared with *p*-toluenesulfonic acid as catalysts in these coatings at different bake temperatures. These kinetic results have been used in a network structure model to calculate the cure response of these coatings as a function of formulation variables.

## INTRODUCTION

Thermoset coatings generally comprise a mixture of resins and crosslinkers that have mutually reactive functional groups. The ultimate properties of the coating depend in large part on the network structure that is formed during cure. This in turn depends not only on the reaction kinetics but also on a variety of other formulation variables including crosslinker and resin composition, resin molecular weight, and resin/crosslinker stoichiometry. In previous studies,<sup>1-3</sup> we have used infrared spectroscopy to measure the extents of the different crosslinking reactions in acrylic copolymer resins crosslinked with melamine formaldehyde-based crosslinkers. We have used these data together with a network structure model based on the work of Macosko and Miller<sup>4,5</sup> to calculate different network structure parameters. In particular, a parameter which we have termed the elastically effective crosslink density<sup>3</sup> has been found to correlate well with such physical measurements of cure as solvent resistance.

The purpose of this work has been to develop general models of cure response in these coatings. In order to do this, it is necessary to have an accurate kinetic model for the crosslinking reactions in melamines. In general, melamine crosslinking kinetics are quite complicated.<sup>6</sup> Melamine crosslinkers undergo both reactions with functional groups on the resin as well as self-condensation depending on the melamine type, the presence of acid catalyst, and the bake conditions.<sup>1,2</sup> Developing a general kinetic scheme for melamine crosslinking which could predict the extents of reaction as a function of formulation variables and bake conditions would be a formidable task. This is particularly true since

we are especially interested in the kinetics at high conversion where optimum properties are generally obtained.

In this report, we have chosen to study the crosslinking kinetics of a single melamine, hexamethoxymethylmelamine (HMMM). This melamine was chosen for a variety of reasons. It has only one type of functional group and thus can be well characterized. Under mild catalyst conditions, it undergoes only one reaction: the reaction of the melamine methoxy group with the hydroxy group on the acrylic copolymer. Using infrared spectroscopy, this reaction can be measured accurately. Since the mechanism of the reaction is known,<sup>6-8</sup> we have a basis for designing our kinetic model. In addition to it being a good model compound, HMMM has important applications to high solids coatings. There is a great deal of practical information concerning coatings crosslinked with HMMM.<sup>9-17</sup> Most of this work has involved developing correlations between physical properties such as hardness and solvent swelling with bake conditions and formulation variables.<sup>9-14</sup> Relatively less work has been done on molecular measurements of the kinetics.<sup>13,15-17</sup> The most complete study to date is that of Biethan and co-workers, who have measured the extent of reaction of HMMM with polyester resins as a function of the methoxy-to-hydroxy ratio and the bake temperature. In most of their studies, they used fairly large amounts of strong acid catalysts, so that competing reactions such as the methoxy self-condensation reaction were important.

In this report, we have chosen to study the methoxy-hydroxy crosslinking reaction under mild catalyst and bake conditions so that competing reactions can be neglected. By following the crosslinking kinetics with time, we can assess different kinetic models. We have developed a model that accurately reproduces the extent of the crosslinking reaction even at high conversion. Using this model, it is possible to determine the effect of different acid catalysts and bake temperatures on the crosslinking rate. Using these results and our network structure model, it is possible to calculate coating cure response as a function of formulation variables.

## EXPERIMENTAL

The acrylic copolymer used in this study was prepared by conventional free radical polymerization and has been described previously.<sup>3</sup> It was composed of 30% hydroxyethyl acrylate, 45% butyl methacrylate, and 25% styrene. A number-average molecular weight of 2300 and a polydispersity ratio  $M_w/M_n$  of 2 were found by gel permeation chromatography. The crosslinker, HMMM, has been characterized previously<sup>1</sup> by <sup>1</sup>H-NMR and was found to have 98% methoxy functionality and 2% methylol functionality. Resin copolymer/melamine mixtures were prepared in the following ratios: 85/15, 80/20, and 75/25. These mixtures had the following values for the ratio of the melamine methoxy group to acrylic hydroxy group: 1.05, 1.49, and 1.98. Five acids were used as catalysts in this study: *p*-toluenesulfonic acid (PTSA), butyl phosphate, hydroxy phosphate,<sup>2</sup> butyl maleate, and hydroxybenzoic acid. The acid strengths and equivalent weights of these acids were determined by titration with 0.1 *N* KOH and are summarized in Table I. The phosphate acids consisted of mixtures of mono- and diacids. The diacid has both a strong and weak acid; the equivalent weights of both the strong and weak acid components are given.

TABLE I  
 Acid Strengths and Equivalent Weights

Acid	pK <sub>a</sub> <sup>a</sup>	Equivalent weight <sup>b</sup>		[K <sub>a</sub> /K <sub>a</sub> (PTSA)] <sup>1/2</sup>	Effectiveness
		Total	Strong acid		
<i>p</i> -Toluenesulfonic acid	0.3	172	172	1.0	1.0
Butyl phosphate	1.4	115	182	0.28 ± 0.05	0.22 ± 0.03
Hydroxy phosphate	1.4	215	315	0.28 ± 0.05	0.23 ± 0.03
Butyl maleate	3.0	172	172	0.05 ± 0.01	0.03 ± 0.01
<i>m</i> -Hydroxybenzoic	4.1	138	138	0.015 ± 0.005	0.01 ± 0.02

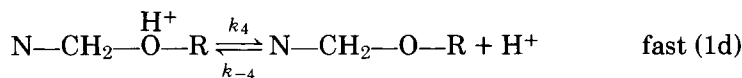
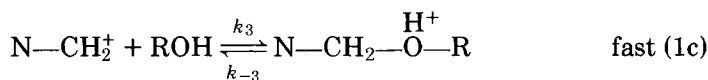
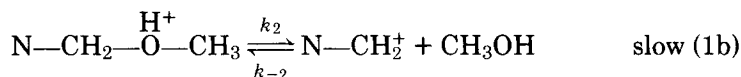
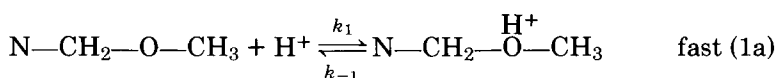
<sup>a</sup> pK<sub>a</sub> of strong acid (±0.1).

<sup>b</sup> Grams catalyst per mole acid.

Films were cast from solution on thin glass slides. The dry film thickness was 25 ± 5 μm. Reaction kinetics were found to be independent of film thickness over this range. The films were cured in an air-circulating oven. Except where otherwise noted, the cure time was 20 min. Bake temperatures ranged from 50 to 190°C. Thermocouple measurements of the glass slide indicated that the sample reached within 5°C of the oven temperature within 2 min of being placed in the oven. Oven temperatures were held to ±0.5°C. The extent of reaction of the acrylic hydroxy group was determined by measuring the disappearance of the acrylic hydroxy band in the infrared spectrum at 3520 cm<sup>-1</sup> relative to that of the styrene band at 3020 cm<sup>-1</sup>. For the uncured acrylic resin, the absorbance of the hydroxy band was 1.55 times that of the styrene band. The absorbance of the small amount of melamine methylol functionality in these formulations was negligible at these frequencies, and the extent of reaction could be measured to ±3%.

### KINETIC MODEL

The mechanism for the crosslinking reaction of HMMM with a hydroxy-functional polymer is generally believed to be given by<sup>6-8</sup>



All the reactions are reversible. The crosslinking reaction is driven to completion by the volatilization of CH<sub>3</sub>OH from the film during the bake. Since the formation of NCH<sub>2</sub><sup>+</sup> is the rate-limiting step, the rate of disappearance of the acrylic hydroxy (ROH) is given by

$$[\text{ROH}] = -k_3[\text{NCH}_2^+][\text{ROH}] + k_{-3}[\text{NCH}_2\text{OR}] \quad (2)$$

Steady-state kinetics can be used to calculate  $[\text{NCH}_2^+]$ :

$$[\text{NCH}_2^+] = \frac{k_2[\text{NCH}_2\text{OCH}_3] + k_{-3}[\text{NCH}_2\text{OR}]^{\text{H}^+}}{k_3[\text{ROH}] + k_{-2}[\text{CH}_3\text{OH}]} \quad (3)$$

Inserting eq. (3) into eq. (2) yields

$$[\text{R}\dot{\text{O}}\text{H}] = -\frac{\left\{k_3k_2[\text{ROH}][\text{NCH}_2\text{OCH}_3]^{\text{H}^+} - k_{-2}k_{-3}[\text{CH}_3\text{OH}][\text{NCH}_2\text{OR}]^{\text{H}^+}\right\}}{k_3[\text{ROH}] + k_{-2}[\text{CH}_3\text{OH}]} \quad (4a)$$

$[\text{R}\dot{\text{O}}\text{H}] =$

$$\frac{-[\text{H}^+]K''\{k_3k_2[\text{ROH}][\text{NCH}_2\text{OCH}_3] - k_{-2}k_{-3}[\text{CH}_3\text{OH}]( [\text{ROH}^0] - [\text{ROH}] )\}}{k_3[\text{ROH}] + k_{-2}[\text{CH}_3\text{OH}]} \quad (4b)$$

where  $[\text{ROH}^0]$  denotes the initial concentration of ROH and  $K'' = k_1/k_{-1} = k_{-4}/k_4$ . If the rate of evaporation of methanol is fast,  $[\text{CH}_3\text{OH}] = 0$  and eq. (4b) simplifies to

$$[\text{R}\dot{\text{O}}\text{H}] = -K''k_2[\text{H}^+][\text{NCH}_2\text{OCH}_3] \quad (5)$$

The methoxy concentration is related to the hydroxy concentration by the following expression:

$$[\text{NCH}_2\text{OCH}_3] = [\text{NCH}_2\text{OCH}_3^0] - [\text{ROH}^0] + [\text{ROH}] \quad (6)$$

When eq. (6) is inserted into eq. (5), eq. (5) can be integrated directly. To integrate eq. (4), it is necessary to make an assumption about  $[\text{CH}_3\text{OH}]$ . In the next section, we test some different assumptions about  $[\text{CH}_3\text{OH}]$ . Although eqs. (1) are generally accepted as the mechanism of this reaction, acceptance is not universal. Holmberg,<sup>18</sup> for example, maintains that the rate is given by

$$[\text{R}\dot{\text{O}}\text{H}] = -K[\text{NCH}_2\text{OCH}_3][\text{ROH}] \quad (7)$$

He bases his arguments on the work of Lorimer,<sup>14</sup> who found that the physical properties of alkyd melamine coatings depended on the hydroxy equivalent weight of the alkyd. We<sup>1-3</sup> have shown that measurements of physical properties are not a good criteria for assessing extents of reaction. We show in the next section that eq. (7) is not a good model for kinetics of crosslinking of HMMM. It should be noted that attempts to use solutions to eq. (4) to model the kinetics requires certain assumptions. For example, it is necessary to assume that each methoxy group is equally relative independent of how many methoxy groups on the melamine molecule have already reacted. We also have to assume that the rate constant is independent of the viscosity of the coating film and that the rate is not limited by the rate of diffusion of the reactive species. The validity of these assumptions is discussed below.

## RESULTS AND DISCUSSION

In Figure 1, the extent of reaction of the acrylic hydroxy functionality is presented as a function of bake temperature and concentration of PTSA for a 20-min bake. The extents of reaction increase with increasing bake temperature and

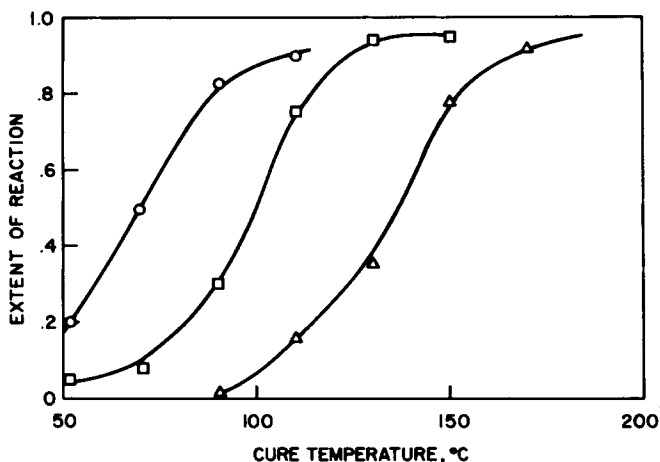


Fig. 1. Extent of reaction of acrylic hydroxy groups vs. bake temperature for different catalyst concentrations:  $2.9 \times 10^{-2}$  M/l PSTA  $\circ$ ;  $5.8 \times 10^{-3}$  M/l PTSA  $\square$ ;  $1.45 \times 10^{-3}$  M/l PTSA  $\triangle$ . The cure time was 20 minutes. The melamine concentration was 20%.

catalyst concentration. As the extent of reaction approaches completion, the rate of increase of the extent of reaction with temperature decreases. The shape of these curves is a complicated function involving integration of eq. (4) with temperature-dependent rate constants. In order to assess what assumptions should be made concerning the methanol concentration in the film, it is more convenient to study the extent of reaction at constant bake temperature as a function of bake time, as shown in Figure 2. For this figure, the methoxy-to-hydroxy ratio was 1.49, the PTSA concentration was  $3.84 \times 10^{-3}$  mol/L, and the bake temperature was 125°C. The assumption that the methanol concentration is zero, i.e., use of eq. (5), is clearly incorrect since it predicts extents of reaction that are too high at long times.

Thus, it appears that the back reactions have to be considered. If we assume that the methanol concentration in the film is constant, we can integrate eq. (4) for different methanol concentrations. A typical example is shown in Figure 2. The approach of the extent of reaction to an equilibrium value also does not agree with the experimental results. In fact, no constant value of the methanol concentration can reproduce the experimental results. Also, it can be noted that calculation of the extent of reaction from integration of eq. (7) does not fit the experimental results. The shape of the extent of reaction curve at low extents of reaction is basically independent of methanol concentration as long as the concentration is reasonably small. The back reactions affect the shape of the curve only at high extents of reaction. Unfortunately, it is at high extent of reaction that the coatings achieve optimum cure. In order to fit the experimental extents of reaction using eq. (4), it is necessary for the methanol concentration to be nonzero for most of the reaction but to decrease to zero at high extent of reaction so that the reaction can go to completion. This decrease is physically reasonable since at high extent of reaction  $[R\dot{O}H]$  decreases. Thus, the amount of methanol produced per unit time decreases, and the concentration of methanol in the film should also decrease.

Many expressions for the time dependence of  $[CH_3OH]$  could be used. We

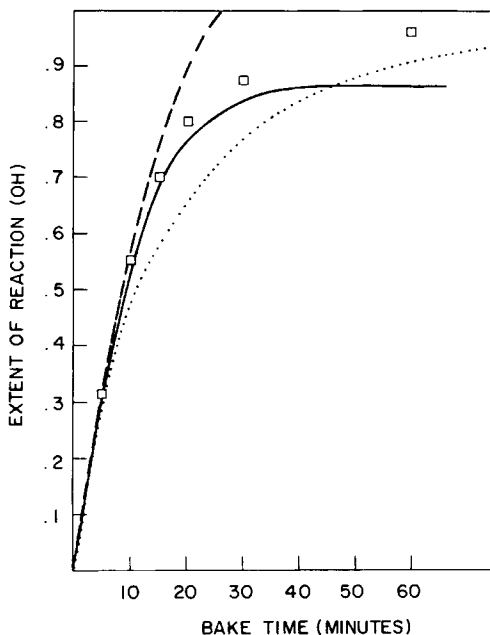


Fig. 2. Extent of reaction vs. bake time at bake temperature equal to 125°C for a methoxy to hydroxy ratio of 1.49 and a PTSA concentration of  $3.8 \times 10^{-3}$  M/l ( $\square$ ). The predictions are those of Eq. 5 (---), Eq. 7 (.....), and Eq. 4 assuming constant methanol concentration (—).

have assumed that the methanol concentration obeys the following relationships: In the initial stage of the reaction,  $[\text{CH}_3\text{OH}] = M$ , a constant; at a certain point in the reaction ( $[\text{ROH}] = M/C$ ),  $[\text{CH}_3\text{OH}] = C[\text{ROH}]$ . Inserting these expressions into eq. (4) yields the following relationship between  $[\text{ROH}']$  and the reaction time for  $[\text{ROH}']$  between 1 and  $M/C$ :

$$\int_1^{[\text{ROH}']} \frac{[\text{ROH}] + M}{[\text{ROH}] + [\text{ROH}](M + A) - M} d[\text{ROH}] = Kt \quad (8a)$$

where  $A = [\text{NCH}_2\text{OCH}_3] - [\text{ROH}^0]$ ;  $[\text{ROH}^0] \equiv 1$ ;  $[\text{ROH}] = 1 - \text{extent of reaction}$ ; and  $K = [\text{H}^+]K''k_2$ . To reduce the number of free parameters, we have also assumed that  $k_2 = k_{-3}$  and  $k_3 = k_{-2}$ . For  $[\text{ROH}']$  less than  $M/C$ , we evaluate eq. (8a) with  $[\text{ROH}']$  equal  $M/C$  and add the following integral:

$$\int_{M/C}^{[\text{ROH}']} \frac{(1 + C)}{(1 + C)[\text{ROH}] + (A - C)} d[\text{ROH}]. \quad (8b)$$

Both expressions can be integrated analytically to yield a relationship between the extent of reaction and  $Kt$ . If  $K$  is a constant, we can predict the time behavior of the extent of reaction.

A comparison of the experimental time dependence of the extent of reaction is compared with eq. (8) in Figure 3 for different methoxy-to-hydroxy ratios. The agreement is excellent over the entire range of extent of reaction. The values of  $M$  and  $C$  may well depend on the coating formulation and the coating thickness. In the fits of Figure 3,  $M$  had a value of 0.15, while  $C$  had the values 0.3, 0.45, and 0.57 for methoxy-to-hydroxy ratios of 1.05, 1.49, and 1.98, respectively.

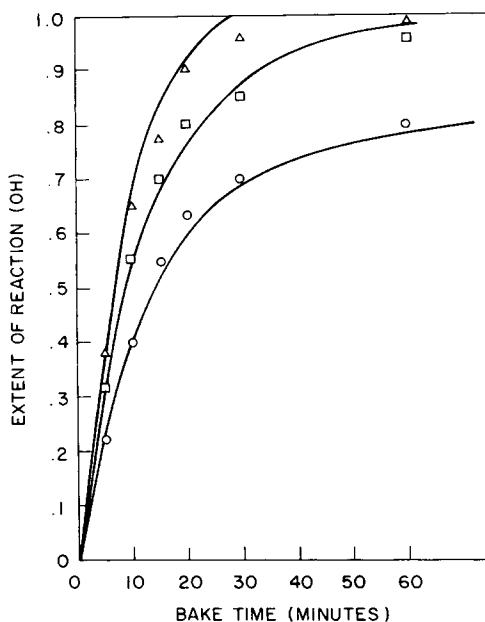


Fig. 3. Extent of reaction vs. bake time for the following methoxy to hydroxy ratios: 1.05 (O), 1.49 (□), and 1.98 (Δ). The bake temperature and catalyst concentrations were identical to those of Figure 2. The lines are the best fit to Eq. 8 (see text).

That the value of  $C$  is found to increase with increasing methoxy content is reasonable in view of the fact that as the methoxy-to-hydroxy ratio increases, the reaction rate remains higher at high extents of reaction. Thus, more methanol is produced at high extents of reaction when the methoxy-to-hydroxy ratio is high.

It should not be inferred that the kinetics can be used to determine the methanol concentration in the film. The values of  $M$  and  $C$  are determined assuming a specific form for the variation in methanol concentration. This form was chosen because it was felt to be physically reasonable and because it led to expressions which could be integrated analytically. The good agreement between eq. (8) and the experimental extents of reaction implies that  $K$  is a constant and depends only on the catalyst concentration and type and on the bake temperature. It does not depend on the number of already reacted methoxy groups or on the extent of crosslinking. Thus, we can use experimental measurements of the extent of reaction to determine the variation of the rate constant with catalyst and temperature.

In Figure 4, the rate constant is plotted as a function of catalyst concentration for different catalysts at a single temperature (90°C). Within experimental error, the rate constants are proportional to catalyst concentration. The slopes of the curves indicate the relative effectiveness of the different catalysts in promoting reaction. It can be seen that the catalytic efficiency drops rapidly as the acid strength of the catalyst goes down. PTSA is clearly the most effective catalyst employed in this study.

The relative effectiveness of the other catalysts as determined from the slopes of Figure 4 are given in Table I. The relative effectiveness is very close to the

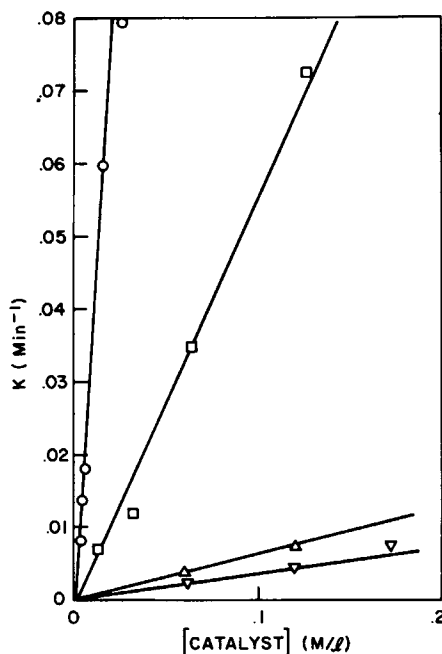


Fig. 4. Rate constant,  $K$ , vs. catalyst concentration for PTSA (O), butyl phosphate (□), butyl maleate (Δ), and *m*-hydroxybenzoic acid (∇). The cure temperature was 90°C.

square root of the ratio of the acid strengths of the catalysts. Of course these acid strengths were determined in an aqueous environment. It is not clear that the ratio of the acid strengths in an aqueous environment are the same as in an organic coating. The rate constant is predicted by eq. (8) to be proportional to  $[H^+]$ . Berge et al.<sup>7</sup> have found that the rate of HMMM decomposition is indeed proportional to  $[H^+]$  in dilute aqueous solution. For a strong acid (completely dissociated),  $[H^+]$  would be proportional to the catalyst concentration but independent of the acid strength. For very weak acid,  $[H^+]$  would be proportional to the square root of the product of the acid strength and the concentration. That our rate constant is apparently proportional to the concentration times the square root of the acid strength is not consistent with either of the above predictions. Apparently, these simple relations are not valid in organic coatings.

In Figure 5, the dependence of the rate constant on PTSA concentration is shown for different bake temperatures. Again, the rate constant is proportional to the catalyst concentration. The slopes of the curve show how the relative rate constant ( $K' = K/[\text{catalyst}]$ ) varies with bake temperature. In Figure 6,  $\log K'$  is plotted vs.  $1/T$  in an Arrhenius plot for the different catalysts. With the exception of butyl maleate at high temperatures, all the plots are straight lines. The deviation for butyl maleate may be due to the evaporation of butyl maleate from the coating at high temperatures. From the slope of the lines, we can calculate an activation energy of 12.5 kcal/mol for the rate-determining step in the reaction. This step is rate determining throughout the entire temperature range. In agreement with the crosslinking mechanism, all the catalysts have the same



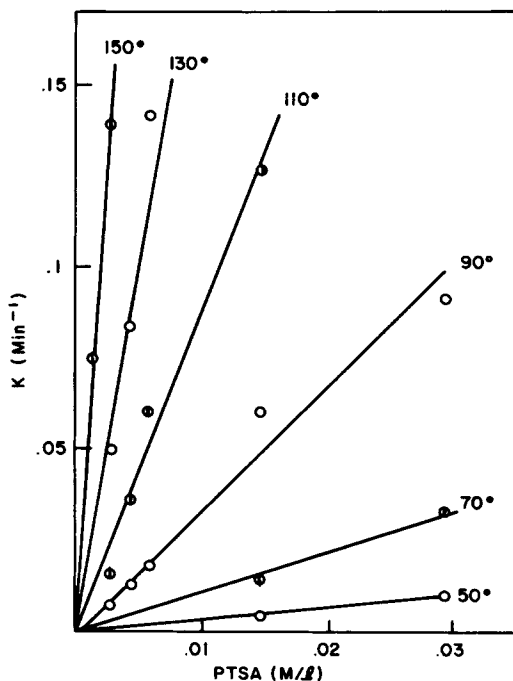


Fig. 5. Rate constant,  $K$ , vs. PTSA concentration for different cure temperatures.

activation energy but a different intercept corresponding to the different relative effectiveness of the catalysts.

The activation energy is an important parameter for practical coatings. It is clear from Figure 2 that if sufficient catalyst is used, the crosslinking reaction can be driven to completion at quite low temperatures. However, another requirement of a practical coating is that it have sufficient shelf stability to be usable over an extended period of time. If the formulation is going to be sprayed, the solution viscosity must remain essentially constant over this period. If too much catalyst is used, the rate of crosslinking will be large even at low temperatures. As crosslinking proceeds, the effective molecular weight of the formulation and thus the viscosity increases. Thus, the amount of a given catalyst can be used is limited by the reactivity of the catalyst at low temperature. This in turn limits the minimum cure temperature of the formulation. The difference between the minimum cure temperature and the maximum storage temperature for which a formulation is stable for a given time is in part determined by the activation energy of the crosslinking reaction. The larger the activation energy, the smaller the temperature difference has to be.

As can be seen from Figure 6, activation energy is independent of catalyst type. For these catalysts, the acid strength is only a weak function of temperature. To increase the activation energy, it is necessary to have an acid whose acid strength is low at low temperature and high at high temperature. One such possibility is a PTSA amine salt. In principle, at low temperatures the amine will neutralize the acidity of the PTSA, and at high temperatures the salt will decompose to yield PTSA and a volatile free amine. We have evaluated the effectiveness of

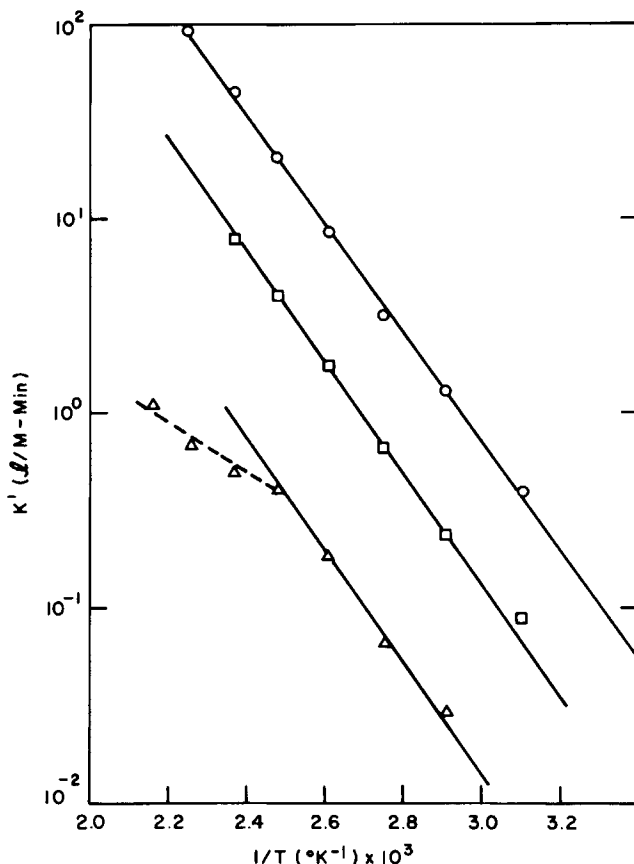


Fig. 6. Log(effective rate constant,  $K'$ ) vs.  $1/\text{temperature}$  for PTSA (O), butyl phosphate (□), and butyl maleate (Δ).

two PTSA amine salts (isopropylamine and triethylamine) as well as mixtures of PTSA and triethylamine where the ratio of PTSA to amine was 2:1 and 1:2.

In Figure 7, the rate constants of the PTSA amine salts relative to those of PTSA are plotted as a function of bake temperature. It can be seen that the PTSA amine salts are less reactive relative to PTSA at low temperatures than at high temperatures. At typical cure temperatures, they are 30–60% as effective as PTSA; while at 60°C, they are only 5–10% as effective. The decomposition of the PTSA amine salt follows an Arrhenius rate law, and the activation energy of the decomposition increases the effective activation energy of the crosslinking reaction from 12.5 kcal/mol to 21 kcal/mol. Underneutralization of the PTSA greatly reduces the gain in viscosity stability, while overneutralization of the acid gives results equivalent to that of the PTSA amine salt.

The kinetic model we have developed makes it possible to predict the extent of reaction as a function of bake conditions and formulation variables. This data, together with a network structure model developed previously,<sup>3</sup> can be used to calculate the cure response in these coatings. Optimum cure (as defined by

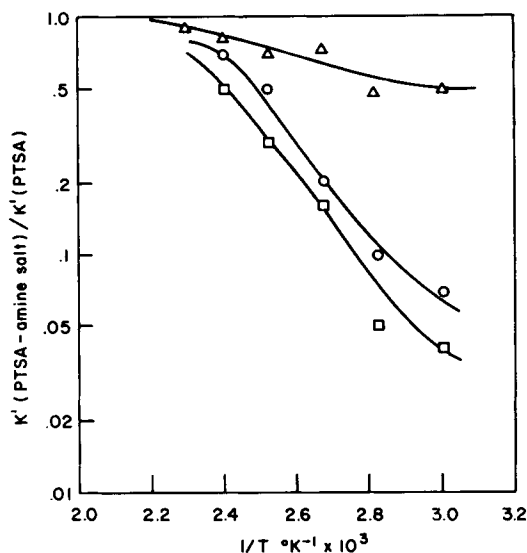


Fig. 7. Ratio of rate constant for PTSA and that for PTSA amine salts vs. bake temperature: (O) PTSA isopropylamine salt; ( $\square$ ) PTSA triethylamine salt; ( $\Delta$ ) one part PTSA, one half part triethylamine.

solvent resistance) is achieved when the value of the elasticity effective crosslink density is  $1.0 \times 10^{-3}$  mol crosslinks/g coating.<sup>3</sup> This parameter, together with the kinetic model, can be used to determine formulations that give the most rapid cure. For example, if the catalyst level, the bake temperature, and the acrylic hydroxy equivalent weight are held constant, we can calculate the bake time needed to achieve the optimum crosslink density as a function of the ratio of methoxy to hydroxy. As can be seen from Figure 8, the fastest cure response is achieved with a methoxy-to-hydroxy ratio of around 2.

Another important factor is the shape of the cure response curve with bake conditions. We have found<sup>19</sup> that around the optimum crosslink density, there exists a range of elastically effective crosslink density for which acceptable properties are generally achieved. The size of this range depends on the criteria that are used to determine coating acceptability. Using solvent resistance and humidity sensitivity to determine the underbake limit and intercoat adhesion measurements to determine the overbake limit, we find that the range of crosslink density for our coatings lies between  $0.8$  and  $1.25 \times 10^{-3}$  mol/g. Again, we can use the kinetic and network structure models to predict the formulations that will have acceptable properties over the widest range of bake conditions (i.e., the coatings that have the widest cure window). For the purpose of this calculation, we keep the bake time constant at 20 min. The catalyst level is fixed at that value which yields an extent of reaction of 0.85 at a bake temperature of  $130^\circ\text{C}$  for the formulation with a methoxy-to-hydroxy ratio of 1.5.

The acrylic hydroxy equivalent weight is adjusted so that the optimum crosslink density is reached at  $130^\circ\text{C}$  for all the formulations. As can be seen from Figure 9, the higher the ratio of methoxy to hydroxy, the flatter the cure response with bake temperature and the wider the cure window. This is due

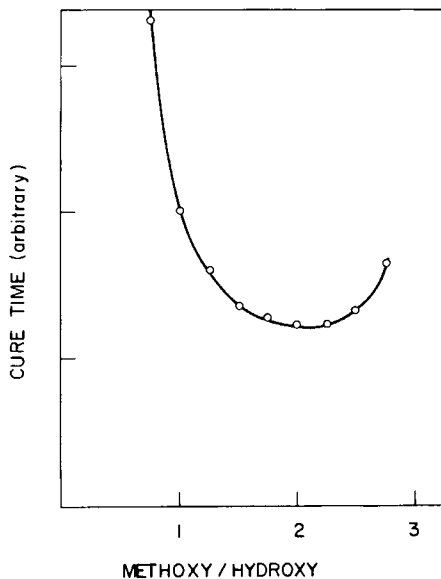


Fig. 8. Bake time necessary to achieve an elastically effective crosslink density of  $1.0 \times 10^{-3}$  mol/g vs. methoxy-to-hydroxy ratio. The catalyst level and acrylic hydroxy equivalent weight were held constant.

to the fact that the higher the methoxy-to-hydroxy ratio, the higher is the extent of hydroxy reaction under constant bake conditions. The higher the extent of the hydroxy reaction, the less sensitive the extent of reaction becomes to bake

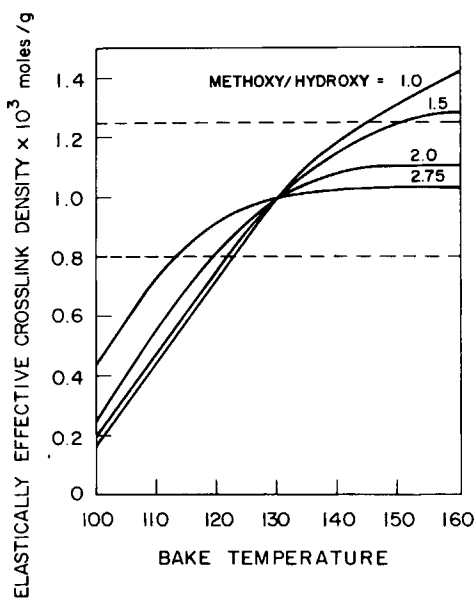


Fig. 9. Elasticity effective crosslink density vs. bake temperature for different methoxy-to-hydroxy ratios. Bake time was 20 min. Catalyst level was held constant, and acrylic hydroxy equivalent weight was adjusted so that a crosslink density of  $1.0 \times 10^{-3}$  mol/g was achieved for all formulations at  $130^\circ\text{C}$ .

conditions. There are practical limits to how high the methoxy-to-hydroxy ratio can be. For example, when the methoxy-to-hydroxy ratio is 2.75, the optimum crosslink density is achieved at near complete conversion. Any batch-to-batch variation in formulation which reduces the crosslink density at complete conversion would have serious effects on the performance of this coating. It should be noted that this calculation ignores the possibility of other reactions. It is possible that the methoxy self-condensation reaction could become important at high bake temperatures. This would increase the crosslink density at high bake temperatures, especially for the coatings with high methoxy-to-hydroxy ratios.

In general, it appears that optimum cure response will be achieved with a methoxy-to-hydroxy ratio of around 2. This is generally found to be the case in practical coatings.<sup>6</sup> The shape of the cure response curve is independent of catalyst type since the activation energies are independent of catalyst type. However, if a catalyst is volatilized from the coating as appears to be the case with butyl maleate, the over bake cure window will be wider.

## CONCLUSIONS

Using the known mechanism of the crosslinking reaction, we have developed a kinetic model for crosslinking of fully alkylated melamines which accurately predicts the observed dependence of the extent of reaction on bake time and melamine concentration. Using the model and the extents of reaction, a rate constant for the crosslinking reaction can be determined. The rate constant has been found to be proportional to catalyst concentration and to be proportional to the square root of the acid strength of the catalyst. The rate constant follows an Arrhenius rate law with an activation energy of 12.5 kcal/mol independent of catalyst acid strength. We have also used this model to evaluate *p*-toluenesulfonic acid amine salts as catalysts for these coatings. We have found that the acid amine salts should provide some improvement in low-temperature stability over the simple acids. Using the kinetic model together with a network structure model, we have found that optimum cure response is achieved when the methoxy-to-hydroxy ratio is around 2.

## References

1. D. R. Bauer and R. A. Dickie, *J. Polym. Sci. Polym. Phys.*, **18**, 1997 (1980).
2. D. R. Bauer and R. A. Dickie, *J. Polym. Sci. Polym. Phys.*, **18**, 2015 (1980).
3. D. R. Bauer and G. F. Budde, *Ind. Eng. Chem. Prod. Res. Devel.*, **20**, 674 (1981).
4. C. W. Macosko and D. R. Miller, *Macromolecules*, **9**, 199 (1976).
5. D. R. Miller and C. W. Macosko, *Macromolecules*, **9**, 206 (1976).
6. W. J. Blank, *J. Coat. Tech.*, **51**(656), 61 (1979).
7. A. Berge, B. Kvaeven, and J. Ugelstad, *Eur. Polym. J.*, **5**, 171 (1969).
8. A. Berge, S. Gudmundsen, and J. Ugelstad, *Eur. Polym. J.*, **6**, 981 (1970).
9. S. E. Stromberg, *ACS Div. Org. Coat. Plast.*, **29**(2), 321 (1969).
10. J. V. Zuylen, *J. Oil Col. Chem. Assoc.*, **52**, 861 (1969).
11. R. Seidler and H. G. Stolzenbach, *Farbe und Lacke*, **81**, 281 (1975).
12. R. Saxon and J. H. Daniel, Jr., *J. Appl. Polym. Sci.*, **8**, 325 (1964).
13. R. Saxon and F. C. Lestienne, *J. Appl. Polym. Sci.*, **8**, 475 (1964).
14. J. W. Lorimer, *J. Paint Tech.*, **40**, 586 (1968).

15. J. Dorffel and U. Biethan, *Farbe und Lacke*, **82**, 1017 (1976).
16. K. H. Hornung and U. Biethan, *Farbe und Lacke*, **76**, 461 (1970).
17. U. Biethan, K. H. Hornung, and G. Peitscher, *Chem. Zeitung*, **96**, 208 (1972).
18. K. Holmberg, *Proceedings of the 4th International Conference in Organic Coatings Science and Technology*, G. D. Parfit and A. V. Patsis, Eds., Technonic Pub. Westport, CT, 1980, p. 76.
19. D. R. Bauer and R. A. Dickie, *J. Coat. Tech.* **54**(685), 57 (1982).

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