Degradation of Organic Coatings. I. Hydrolysis of Melamine Formaldehyde/Acrylic Copolymer Films

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Synopsis

The hydrolysis of melamine formaldehyde crosslinked acrylic copolymer films has been studied using infrared spectroscopy. It has been found that during hydrolysis, crosslinks between the acrylic copolymer and the melamine crosslinker are broken and that crosslinks between melamine molecules are formed. The rate of hydrolysis depends on the following: (1) the type of crosslinker used (partially alkylated melamines hydrolyze faster than fully alkylated melamines); (2) the amount and strength of acid catalyst used and whether or not the catalyst can be extracted from the coating during hydrolysis; (3) the initial crosslink density; (4) the hydrolysis temperature. In some formulations, it can be expected that virtually all of the acrylic–melamine crosslinks will be hydrolyzed. However, due to the formation of melamine–melamine crosslinks, the overall crosslink density does not necessarily decrease significantly as a result of this hydrolysis.

INTRODUCTION

Previous reports[1-4] have described the crosslinking chemistry of, and network formation in, melamine formaldehyde crosslinked acrylic copolymer coatings. Using infrared spectroscopy, it has been found that there are two basic crosslinking reactions. One forms acrylic–melamine crosslinks while the other forms melamine–melamine crosslinks. The extent that the different crosslinking reactions occur after a given bake depends on the type of melamine crosslinker (e.g., partially or fully alkylated), the composition of the acrylic copolymer, and the amount and strength of added acid catalyst. The structure of the network is determined by the extent of crosslinking, the acrylic copolymer molecular weight, and by the stoichiometry of the different crosslinking groups. Using a statistical model based on the work of Macosko and Miller,[5,6] it has been determined that a particular network parameter (the elastically effective crosslink density) correlates well with physical measurements of the state of cure in these coatings. These measurements describe the state of cure just after the bake process before any aging of the coating has occurred. There are several processes that can cause the network structure of a coating to change including photodegradation, thermal degradation, and hydrolytic degradation. While there are physical data on the effects of these aging processes, there have been few detailed molecular studies of the changes in the network structure that occur on aging. In particular there

have been no such studies on the effect of hydrolysis on network structures in melamine-crosslinked coatings. In this paper such a study is presented. Using infrared spectroscopy, it has been found that substantial changes in the molecular structure of the coating occur during hydrolysis. The rates of hydrolysis have been determined for a variety of coatings as a function of the type of melamine crosslinker, the presence of acid in the coating, the initial crosslink density, and the hydrolysis temperature.

REACTIONS OF MELAMINE CROSSLINKERS

The reactions of melamine formaldehyde crosslinkers with hydroxy functional compounds have been studied in detail by Blank.[7] The major crosslinking reactions are given in Table I. The mechanism of reaction 1 requires specific acid catalysis. This reaction has been studied in detail[4] as a function of bake time and temperature and of catalyst concentration and strength; it has been found to have activation energy of 12.5 kcal/mol with strong acids (e.g., p-toluene sulfonic acid) being required to achieve cure at moderate bake temperatures. Reaction 2 goes by general acid catalysis and does not require as strong an acid (e.g., acrylic acid) to achieve cure as does reaction 1. Reaction 3 is also catalyzed by general acid catalysis; however, this reaction seems to require a somewhat stronger acid (e.g., phosphate acids) than does reaction 2. In order to determine which reactions are important for a given crosslinker, it is necessary to determine the percentages of the different functional groups on the melamine molecule. Melamine characterization has been reviewed by Christensen.[8] We have used proton NMR to measure the functionalities of different commercial melamine crosslinkers.[1]

By analogy with Table I, the various hydrolysis reactions of a coating cross-linked with melamine are given in Table II. Berge et al. have discussed the degradation of melamine crosslinkers in both acidic and basic environments.[9,10] In particular, they have studied[10] the acid-catalyzed decomposition of melamines and have determined the rates of reactions 3, 4, and 6 (Table II) as a function of pH under aqueous conditions. They find that, above pH 4, the rate of reaction 4 is some 40 times faster than reaction 3, but that, at pH 1, reaction 3 is some six times faster than reaction 4. It is important to note that the product of reactions

TABLE I
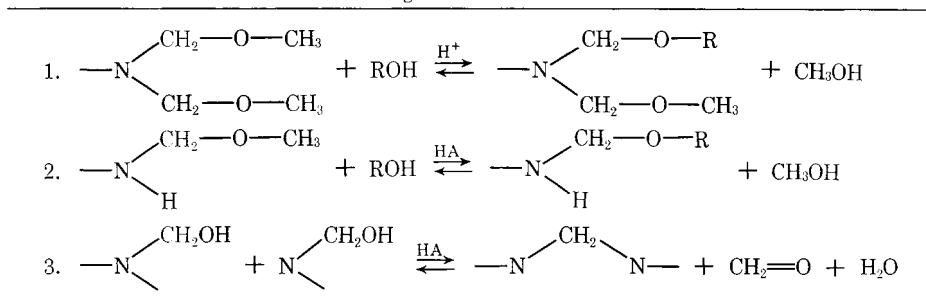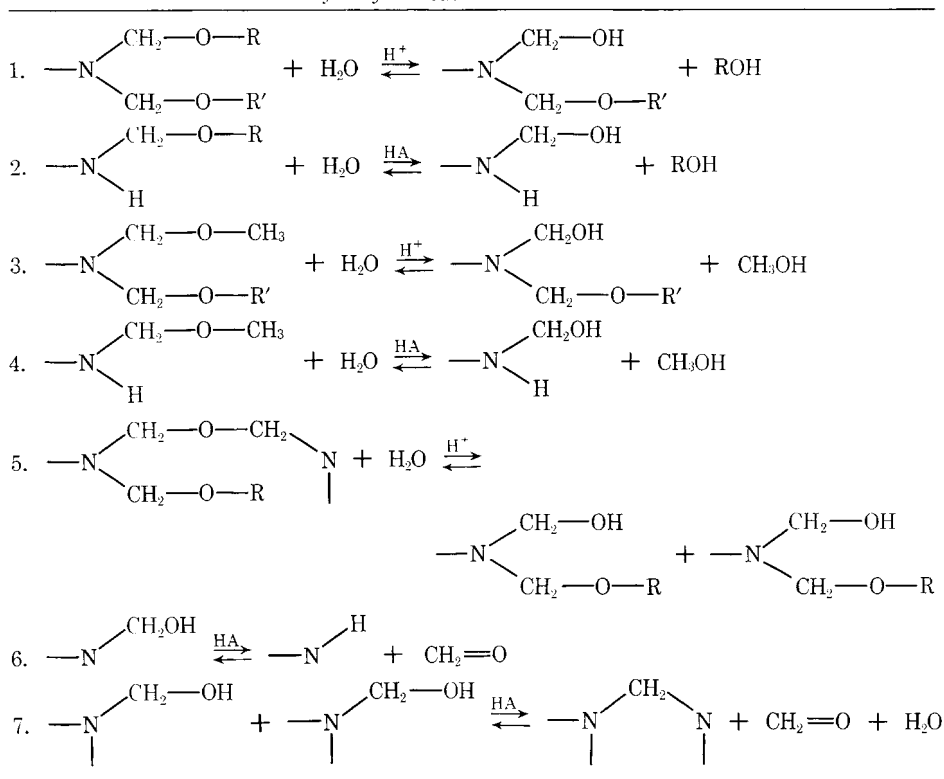Crosslinking Reactions of Melamines

TABLE II
Hydrolysis Reactions of Melamines

1. $-N(CH_2-O-R)(CH_2-O-R') + H_2O \overset{H^+}{\rightleftarrows} -N(CH_2-OH)(CH_2-O-R') + ROH$

2. $-N(CH_2-O-R)(H) + H_2O \overset{HA}{\rightleftarrows} -N(CH_2-OH)(H) + ROH$

3. $-N(CH_2-O-CH_3)(CH_2-O-R') + H_2O \overset{H^+}{\rightleftarrows} -N(CH_2OH)(CH_2-O-R') + CH_3OH$

4. $-N(CH_2-O-CH_3)(H) + H_2O \overset{HA}{\rightleftarrows} -N(CH_2OH)(H) + CH_3OH$

5. $-N(CH_2-O-CH_2-)(CH_2-O-R)\,N\, + H_2O \overset{H^+}{\rightleftarrows}$

$-N(CH_2-OH)(CH_2-O-R) + -N(CH_2-OH)(CH_2-O-R)$

6. $-N(CH_2OH) \overset{HA}{\rightleftarrows} -N(H) + CH_2{=}O$

7. $-N(CH_2-OH) + -N(CH_2-OH) \overset{HA}{\rightleftarrows} -N(CH_2-)N + CH_2{=}O + H_2O$

1–4 is a melamine methylol group. This group does not react with the hydroxy functionality of the copolymer, but can only react with another methylol group or deformylate to give the free amine. Thus hydrolysis is a nonreversible process.

EXPERIMENTAL

Sample Characterization

The acrylic copolymers used in this study were prepared by conventional free radical polymerization. The composition and molecular weights as determined by GPC are given in Table III. The first three resins are typical of high solids

TABLE III
Characterization of Resins

Resin	%[a] hydroxy	%[a] acrylic acid	M_n
1	30	0	2300
2	30	2	2300
3	25	4	2200
4	20	0	9500

[a] Percent by weight. For resins 1–3, the hydroxy monomer was hydroxyethylacrylate. For resin 4, the hydroxy monomer was hydroxypropyl methacrylate.

coatings, while the last resin is typical of a low solids conventional coating. The three crosslinkers used in this study have been characterized previously.[1,3] Mel-A is a fully alkylated melamine; Mel-C is a highly polymerized butylated melamine containing very little free amine; and, Mel-D is a partially methylated melamine containing a great deal of free amine.

Hydrolysis of Coatings

Hydrolysis samples were cast on thin glass slides or on AgCl plates and cured in a convection oven at a given bake temperature for 20 min. The cured films were approximately 25 μm in thickness. The samples were suspended horizontally over a hot water bath maintained to within ±0.5°C of the desired hydrolysis temperature. The hydrolysis studies were carried out at 40, 50, and 60°C. The noncondensing humidity samples were placed in a Blue M humidity cabinet maintained at 60°C and 90% relative humidity. Periodically, the samples were removed from the humidity test and dried at 90°C for a few minutes to remove water. Infrared spectra were then obtained.

Infrared Measurements

Typical infrared spectra of cured, uncured, and hydrolyzed coatings are shown in Figure 1. These spectra were obtained from coatings on a AgCl plate using a Perkin-Elmer 165 spectrometer. The particular coating shown was that of resin 2 crosslinked with Mel-D. If Mel-A had been used, the peak at 3370 wavenumbers would not have been present, and the methoxy peak at 915 wavenumbers would have been larger. During the cure the absorbance in the hydroxy region decreases as does the absorbance of the methoxy band. In the partially alkylated melamines such as Mel-D, a relatively weak band indicative of the formation of melamine-melamine crosslinks appears at 1360 wavenumbers. The bands in the hydroxy region are broad and overlap a great deal. A procedure was developed in Ref. 1 to correct for this overlap so that both the decrease in acrylic hydroxy (3520 wavenumbers) and melamine methylol (3370 wavenum-
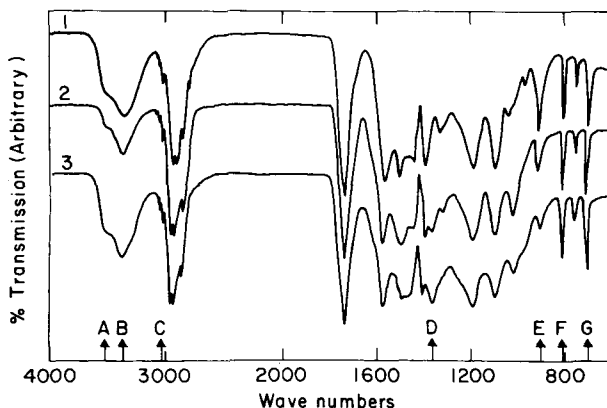

Fig. 1. Infrared spectra of a coating composed of 70% resin 2 and 30% Mel-D: (1) uncured; (2) cured for 20 min at 130°C; (3) hydrolyzed at 50°C for 45 days. The following bands were used for analysis: (A) acrylic hydroxy; (B) melamine methylol and amine; (C) styrene; (D) melamine–melamine bond; (E) melamine methoxy; (F) melamine triazine ring; (G) styrene.

bers) could be determined.   Various bands have been used as internal standards and are so indicated in Figure 1.   The disappearance of acrylic hydroxy during cure correlates well with the disappearance of the melamine methoxy band.   The disappearance of the melamine methylol band during cure correlates well with the appearance of the band at 1360 wavenumbers.   It should be noted that the melamine amine band absorbs at the same wavenumber as the methylol band so that the intensity of this band is a sum of the intensities of the amine and methylol bands.   The relative absorbance of an amine group is only 40% as strong as that of a methylol group.

As can be seen from Figure 1, several significant changes occur in the spectrum from hydrolysis of the coating.   The acrylic hydroxy band increases (hydrolysis reactions 1 or 2).   The melamine methoxy band decreases (hydrolysis reactions 3 or 4).   The band at 1360 wavenumbers which is indicative of the formation of melamine–melamine crosslinks increases during hydrolysis (hydrolysis reaction 7).   The intensity of the melamine methylol and amine band at 3370 wavenumbers changes only slightly during the hydrolysis, despite the fact that a great deal of melamine methylol functionality is being produced.   Hydrolysis reaction 7 accounts for some of the consumption of methylol functionality.   Hydrolysis reaction 6 would also cause a decrease in the intensity of this band since the relative absorbance of the amine is less than that of the methylol group.   By determining the extents of reactions 1–4, it is possible to calculate how many melamine methylol groups have been formed at any stage of hydrolysis.   By monitoring the appearance of melamine–melamine crosslinks and the intensity of the melamine methylol and amine band it is possible to calculate the extents of reactions 6 and 7.   There is no convenient way to measure the extent of reaction 5.   It has been assumed that the rate of hydrolysis reaction 5 is the same as that of reactions 1 and 3.   The group in reaction 5 comes from the polymerization of the melamine during its preparation.   Mel-A is monomeric; thus reaction 5 does not occur in coatings with Mel-A.   Mel-D is only slightly polymerized so that reaction 5 is only a small source of hydrolysis in coatings with Mel-D.   Only in coatings containing highly polymerized Mel-C does reaction 5 make a significant contribution to hydrolysis.   The accuracy with which these determinations can be made depends on both the band being analyzed and on the particular system being studied.   In the case of fully alkylated melamines where the melamine methylol band is not present, the amount of unreacted acrylic hydroxy could be determined to ±2%.   For the partially alkylated melamines, band overlap reduced the accuracy to ±5% for both the acrylic hydroxy band and the melamine methylol band.   The amount of residual methoxy functionality can be determined to better than ±5%.   Because the band at 1360 wavenumbers is relatively weak and appears as a shoulder on a stronger band the accuracy of melamine–melamine bond formation could only be determined to ±20%.

RESULTS AND DICUSSION

Acrylic–Melamine Bond Hydrolysis

In order to measure the extent of hydrolysis of acrylic–melamine bonds, it is only necessary to measure the increase in absorbance of the acrylic hydroxy band. From comparisons of this absorbance after hydrolysis with those of the uncured

and cured films, it is possible to determine the fraction of acrylic–melamine bonds hydrolyzed. In Figure 2, plots of the fraction of acrylic–melamine bonds hydrolyzed are shown as a function of hydrolysis time for three different coatings. The hydrolysis temperature was 60°C. The hydrolysis rate of formulations crosslinked with partially alkylated melamines (Mel-C and Mel-D) is much faster than that of formulations crosslinked with a fully alkylated melamine (Mel-A). For the partially alkylated melamines virtually all of the acrylic–melamine bonds are hydrolyzed in about 1 month at 60°C. The hydrolysis rates for the Mel-A and Mel-C formulations seem to be constant with time after an initial rapid hydrolysis for the Mel-A formulation. The hydrolysis rate of the Mel-D formulation decreases with hydrolysis time.

The hydrolysis rate is a strong function of the hydrolysis temperature. In Figure 3 a plot of the hydrolysis of the acrylic–melamine bonds of the Mel-C formulation is shown at three different temperatures. From a plot of the slopes of the hydrolysis curves vs. 1/temperature, an activation energy of 22 kcal/mol was determined. Similar activation energies were found for the Mel-A and Mel-D formulations. This activation energy is roughly equal to the sum of activation energy of crosslinking reaction 1 and of the activation energy for the vaporization of water. This result is consistent with the hydrolysis rate being proportional to the rate of crosslinking and to the concentration of water in the coating, which in turn is proportional to the vapor pressure of water above the coating.

Another parameter that can affect the hydrolysis rate is the bake temperature of the coating. If the formulation is held constant, varying the bake temperature varies the extent of the crosslinking reaction and thus the state of cure. For example, the state of cure (as measured by the elastically effective crosslink density) of the resin 1–Mel-A formulation has been determined as a function
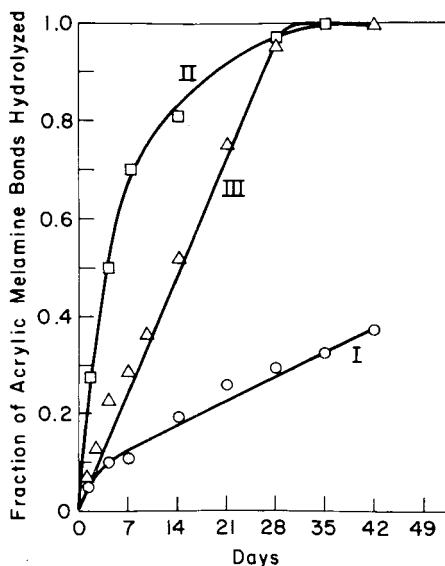

Fig. 2. Acrylic–melamine bond hydrolysis. Hydrolysis temp = 60°C. Coating composition: (I) 80% resin 1, 20% Mel-A (0.08% p-toluene sulfonic acid); (II) 70% resin 2, 30% Mel-D; (III) 70% resin 4, 30% Mel-C.
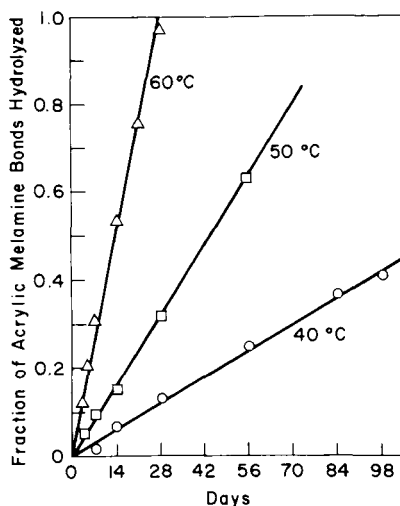
Fig. 3. Temperature dependence of acrylic–melamine bond hydrolysis for coating III of Figure 2.

of bake temperature. The elastically effective crosslink density dropped from 1.6×10^{-3} mol/g at a bake temperature of 140°C to 1.4×10^{-3} at 130°C, to 1.1×10^{-3} at 120°C, and to 0.6×10^{-3} at a bake temperature of 110°C. A plot of the fraction of acrylic–melamine bonds hydrolyzed in this formulation is shown in Figure 4 for the different bake temperatures. The rate of hydrolysis increases with decreasing bake temperature and seems to be roughly inversely proportional to the elastically effective crosslink density. This is understandable since the rate of hydrolysis is proportional to the concentration of water in the coating. As the crosslink density goes down, a larger amount of water can be imbibed by the coating, resulting in an increase in the rate of hydrolysis.

Other formulation variables can also affect the hydrolysis rate. In particular, the amount of acid that is incorporated into the acrylic copolymer or otherwise
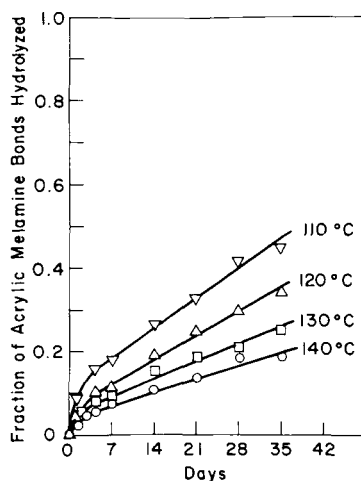

Fig. 4. Acrylic–melamine bond hydrolysis for coating I of Figure 2. Effect of cure temperature.
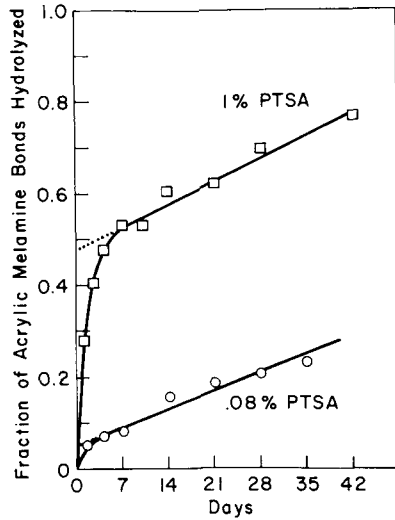
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Fig. 5. Acrylic–melamine bond hydrolysis for coating I of Figure 2. Effect of p-toluene sulfonic acid on hydrolysis. Concentration of p-toluene sulfonic acid: 0.08% (O); 1.0% (□).

added to the formulation greatly affects the hydrolysis rate, as shown in Figures 5 and 6. In Figure 5 the effect of varying the amount of p-toluenesulfonic acid catalyst on the hydrolysis of the Mel-A formulation is shown. In Figure 6 the effect of varying the amount of acrylic acid in the acrylic copolymer on the hydrolysis of the Mel-D formulation is shown. The coatings were baked at different bake temperatures to achieve approximately the same state of cure. The effect of increasing the amount of p-toluenesulfonic acid is to increase the amount of hydrolysis that occurs initially but not to change the hydrolysis rate after the initial period. This can be explained as follows: Hydrolysis in the presence of p-toluenesulfonic acid is very rapid; however, p-toluenesulfonic acid is soluble
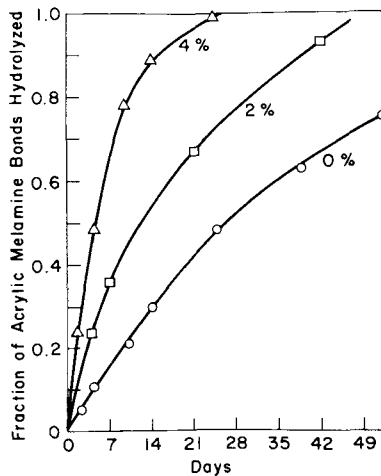

Fig. 6. Acrylic–melamine bond hydrolysis. Effect of acrylic acid on hydrolysis of coatings crosslinked with 30% Mel-D. The percent acrylic acid in the resin is as follows: 0% (O); 2% (□); 4% (△). The bake temperature were adjusted so that the same crosslink density was achieved in all three coatings.

in water and thus can be leached out of the coating. This happens in the space of a few days, increasing the pH and slowing the hydrolysis rate to that value which would occur in the absence of any p-toluenesulfonic acid. This hypothesis was tested by determining the hydrolysis rate under noncondensing humidity conditions. Since in noncondensing humidity there is no liquid water present, no acid can be extracted. Thus the hydrolysis rate of a Mel-A formulation which contains p-toluenesulfonic acid should remain very rapid under noncondensing humidity conditions. This is exactly what is observed. When 1% p-toluenesulfonic acid is used, all of the acrylic–melamine bonds are hydrolyzed in 3 days of noncondensing humidity at 60°C. Similar, though not as dramatic, effects are observed when strong acids such as p-toluenesulfonic acid or phenyl acid phosphate are incorporated into the Mel-C or Mel-D formulations. Thus noncondensing humidity is a much more severe test of hydrolysis of coatings containing leachable acid catalysts than is condensing humdity. The hydrolysis temperature in a condensing humidity test also affects the amount of hydrolysis that occurs when a leachable acid is present. Decreasing the hydrolysis temperature decreases the amount of hydrolysis due to the strong acid. In the 1% p-toluenesulfonic acid Mel-A formulation, 48% of the acrylic–melamine bonds are hydrolyzed by the strong acid at a hydrolysis temperature of 60°C. This value drops to 18% when the hydrolysis temperature is 40°C. The acrylic acid incorporated into the acrylic copolymer is not leachable from the coating. As shown in Figure 6, increasing the acrylic acid content increases the rate of acrylic–melamine bond hydrolysis over the whole hydrolysis period.

The rate of acrylic–melamine bond hydrolysis has been found to be determined by the type of acrylic–melamine bond being hydrolyzed (i.e., hydrolysis reaction 1 or 2), by the pH of the coating (as determined by the amount and strength of acid catalyst), and by the concentration of water in the coating (which is determined by the hydrolysis temperature and the coating crosslink density). These results are consistent with the results of Berge et al.[10] for the hydrolysis of melamine compounds in aqueous solution. Coatings crosslinked with Mel-A can only hydrolyze by reaction 1. In the absence of strong acid catalyst in the coating, this reaction is very slow. Coatings crosslinked with Mel-D can hydrolyze both by reaction 1 and 2. Since the crosslinking reaction 2 is more facile under the bake conditions used here, most but not all of the acrylic melamine bonds in this coating will be crosslinked by reaction 2. These bonds will also be more easily hydrolyzed than those produced by crosslinking reaction 1. As the hydrolysis proceeds, those bonds which can be hydrolyed by reaction 2 will be depleted relative to those which are hydrolyzed by reaction 1. Eventually, only bonds which can be hydrolyzed by reaction 1 are left in the film, and the hydrolysis rate decreases. This accounts for the curvature in the hydrolysis of the Mel-D coatings. The initial rate of hydrolysis of the Mel-D coating should be characteristic of the hydrolysis rate of reaction 2. Berge et al. found that the ratio of hydrolysis rates of reaction 4 and 3 (in the absence of strong acid) was around 40:1. It is expected that the ratio of rates of reactions 2 and 1 should be similar. Comparison of the initial hydrolysis rate of the Mel-D-Resin coating yields a ratio of 30:1, in good agreement with the result of Berge et al.[10] The effect of acid on the different hydrolysis rates is also consistent with Berge et al. They find that the rate of reaction 4 increases with decreasing pH to a plateau value at pH 2.5, while the rate of reaction 3 increases steadily wtih decreasing pH eventually

becoming larger than that of reaction 4. We find that the rate of hydrolysis of Mel-A coatings is much more sensitive to the presence of strong acid than is the rate of the Mel-D coatings. The rate of hydrolysis of a Mel-A coating containing 1% p-toluene sulfonic acid is some 80 times faster than the rate with no acid. The increase in the hydrolysis rate for a Mel-D coating under similar conditions is only a factor of 5.

From the measured activation energy it can be estimated that 1 month of condensing humidity at 50°C is equivalent to 2 years of 75% relative humidity at 25°C. Assuming that the strong acid catalyst is leached out of the coating, hydrolysis of coatings crosslinked with fully alkylated melamines should be small under typical conditions. Hydrolysis of coatings crosslinked with partially alkylated melamines under typical conditions can be significant, however. In fact, it can be expected that most of the acrylic–melamine crosslinks will be broken during the lifetime of the coating. The effect of this hydrolysis on some of the physical properties of the coating will be discussed below.

Hydrolysis of Melamine Methoxy Groups

The mechanism of hydrolysis reactions 1 and 3 are the same and the rate of these reactions should be expected to be similar. In fact, the fraction of malamine methoxy groups in Mel-A coatings that have been hydrolyzed after a given time is the same within experimental error as the fraction of acrylic–melamine bonds that have been hydrolyzed. Thus, all of the results that were determined for acrylic–melamine bond hydrolysis for the Mel-A coatings also apply to Mel-A methoxy hydrolysis. Methoxy group hydrolysis in Mel-D crosslinked coatings is somewhat more complicated. Plots of the fraction of methoxy groups and acrylic–melamine bonds hydrolyzed as a function of time are shown in Figure 7. The methoxy functionality hydrolyzes much more slowly. Before crosslinking, Mel-D contains both types of methoxy groups. During the cure, crosslinking reaction 2 dominates. Thus most of the groups which are easily
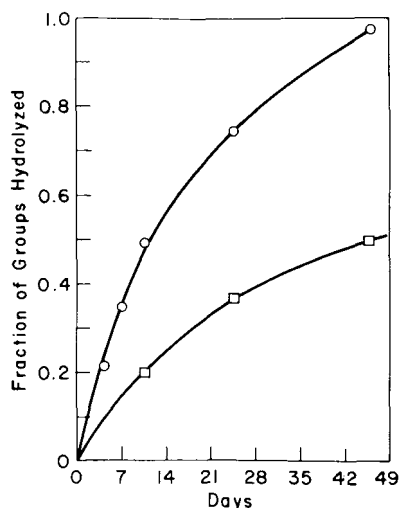

Fig. 7. Comparison of acrylic–melamine bond (O) hydrolysis with melamine methoxy group (□) hydrolysis for coating II of Figure 1.

hydrolyzed have reacted to form acrylic–melamine bonds. Most of the unreacted methoxy groups can only hydrolyze by reaction 1. Thus, it should not be surprising that the unreacted methoxy functionality should hydrolyze more slowly than the acrylic–melamine bonds formed by Mel-D. It is not possible to measure the hydrolysis rate of the unreacted butoxy groups in the Mel-C coating by infrared spectroscopy. Since this melamine does not contain much free amine, it is likely that the rate of butoxy group hydrolysis is the same as the hydrolysis rate of acrylic–melamine bonds in this coating.

Effect of Hydrolysis on Network Structure

It has been shown that coatings crosslinked with partially alkylated melamines can be expected to undergo significant hydrolysis during their expected service life. So far, only reactions 1–5 have been considered. All of these reactions produce melamine methylol groups. These groups are not stable in the coating and undergo further reaction (hydrolysis reactions 6 and 7). In order to characterize the molecular structure of the hydrolyzed coating, it is necessary to determine the extent of these reactions. It is particularly important to determine the extent to which the methylol groups react to form melamine–melamine bonds since these crosslinks can compensate for the acrylic–melamine crosslinks that are broken during hydrolysis. By measuring the increase in acrylic hydroxy absorbance (reactions 1 and 2) and by measuring the decrease in melamine methoxy absorbance (reactions 3 and 4), it is possible to determine how many melamine methylol groups are produced at any given stage of hydrolysis. From the increase in absorbance of the band at 1360 wavenumbers, we can determine how many of the methylol groups have reacted to form melamine–melamine bonds. By comparing the melamine methylol and amine band (3370 wavenumbers) absorbance with that expected from the amount of methylol produced by hydrolysis and consumed by reaction 7, we can estimate the fraction of methylol groups that have deformylated to yield free amine. From this data and our statistical model,[3] it is possible to calculate the elastically effective crosslink density for the hydrolyzed coatings. Since this quantity depends to a large extent on our determination of the amount of melamine–melamine bond formation which can only be determined to ±20%, the values of the crosslink density for the hydrolyzed coating are only accurate to ±20%. The data and the calculations are shown in Table IV for the coating composed of 70% resin 2 and 30% Mel-D as a function of hydrolysis time. As the hydrolysis proceeds, nearly all of the acrylic–melamine bonds are broken and 50% of the methoxy groups are hydrolyzed. In spite of the large amounts of melamine methylol groups that are being produced, the melamine band at 3370 wavenumbers increases only slightly. This is because 55% of the methylol groups react to form melamine–melamine crosslinks and 40% undergo deformylation to the free amine. Hydrolysis of this formulation initially causes a decrease in crosslink density; however, as hydrolysis proceeds, the crosslink density remains virtually constant. Similar behavior is observed with the solvent resistance of the coating as determined by MEK rubs. Despite vast chemical changes in the molecular structure of the coating during hydrolysis, only a relatively small change in elastically effective crosslink density results. It is likely that these chemical changes affect other physical properties to a greater extent than they do the crosslink density. Work investigating these possible effects is in progress.

TABLE IV
Hydrolysis and Network Structure[a]

Time (days)	0	10	24	45
% Acrylic–melamine bonds hydrolyzed	0	49	76	98
% Methoxy hydrolyzed	0	20	37	50
Intensity of 3370 band[b]	0.85	0.92	1.00	1.08
Total methylol[c]	0.16	0.72	1.10	1.41
Methylol reacted[c]	0.36	0.63	0.75	0.95
% Methylol reacted	69	58	51	54
% Methylol deformylated	0	34	45	40
Elastically effective crosslink density $\times 10^{-3}$ (mol/g)	1.08	0.7	0.8	0.75
MEK rubs	100	40	45	50

[a] Coatings composition: 70% resin 2, 30% Mel-D. Baker temperature 130°C for 20 min. Hydrolysis temperature 50°C.

[b] Relative to the amount of acrylic hydroxy functionality before cure.

[c] Methylol unreacted during cure plus that produced by hydrolysis.

CONCLUSION

It has been found that hydrolysis causes significant changes in the molecular structure of melamine formaldehyde crosslinked acrylic copolymer coatings. Acrylic–melamine crosslinks are broken and melamine–melamine crosslinks are formed during the hydrolysis process. The rate of hydrolysis is determined by the type of melamine crosslinker used, by the presence of acid in the coating, by the crosslink density of the coating, and by the hydrolysis temperature. The rate of hydrolysis of fully alklated melamines is significantly slower than that of partially alkylated melamines. Under normal service life, it can be expected that virtually all of the acrylic–melamine bonds in a partially alkylated melamine formulation will be hydrolyzed. The formation of melamine–melamine bonds compensates for this hydrolysis, and the crosslink densities of hydrolyzed coatings need not be significantly different from the unhydrolyzed coating.

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