

Crosslinking with Malonate Blocked Isocyanates and With Melamine Resins

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INTRODUCTION

The environmental acid etch resistance of automotive clearcoats,³ one of the major issues in formulating these coatings, has become an increasing problem due to the development of higher distinction of image (DOI) basecoat-clearcoat systems and the use of higher-solids coatings. In many industrial nations, acid rain, due to the emission of sulfur dioxide, is a common problem. At our location⁴ in Norwalk, CT, which is close to the New York metropolitan area and a major highway, we have consistently measured a pH of <4.0 over a 12-month period. Melamine resin crosslinked coatings have been widely used in factory applied automotive topcoats for more than three decades. With the development of high-solids coatings based on low molecular weight polyol oligomers, the level of melamine/formaldehyde crosslinker was substantially raised. Conventional low solids automotive topcoats use about 20-30% of butylated melamine resins, whereas high-solids coatings use as much as 35-50% of fully alkylated melamine resins. The high level of melamine resin not only lowers the VOC of the coating but also improves exterior durability and lowers the formulation cost. Unfortunately, the higher level of melamine resin has a rather catastrophic effect on the acid resistance of the coating.

The basicity of melamine⁵ decreases as the degree of substitution increases. Films prepared with fully alkylated melamine resin initially show a low concentration of NH⁶ groups as measured in FTIR-ATR. On exposure, the NH band increases and at the same time the acid resistance, as measured by spot tests, decreases. The basicity of the melamine resins is expected to make a film more sensitive to the penetration and adsorption of an acid.

The reaction mechanism⁷ for both fully and partially alkylated melamine/formaldehyde resins makes it clear that during film formation one of the major side reactions is the hydrolysis of the melamine crosslinkers and subsequent self-condensation. The dominant linkage formed in the crosslinking of polyols with melamine

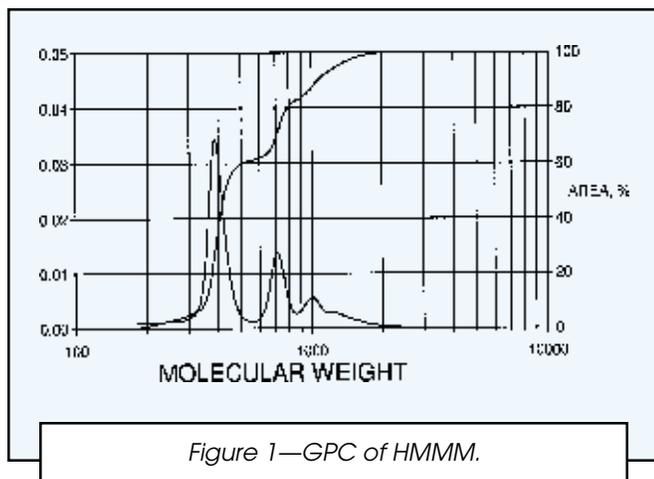
Automotive clearcoats with improved acid etch resistance are being formulated using a combination of a dialkyl malonate blocked polyisocyanate, a melamine crosslinker, and an acrylic polyol.^{1,2} These coatings contain lower levels of melamine crosslinker compared to conventional acrylic/HMMM systems and show excellent acid etch resistance. We explored the reaction mechanism of this complex crosslinking system and found explanations for the good chemical resistance properties.

resins is the >N-CH₂-O-R linkage. At pH conditions less than 6, this ether linkage is subject to hydrolysis, leading to a decrease in crosslink density and to the formation of more basic melamine oligomers which can leach under acidic conditions. Therefore, the films will initially start to show loss of gloss, then turbidity, and eventually lead to pitting of the surface.

Many different approaches have been taken to substitute melamine crosslinking with other crosslinking systems. One of the approaches is the complete replacement of melamine resins and the sensitive ether linkage with other crosslinking agents. Blocked isocyanates,⁸ acrylosilane,⁹ and epoxy/carboxy¹⁰ systems have been described in the literature. In addition to retaining some of the performance and cost advantages of melamine crosslinkers, combinations of various crosslinking mechanisms¹¹ with melamine resins are used to improve the acid resistance of coatings. Other approaches have been the replacement of the melamine ether linkage with the polyol with a more acid resistant linkage. Phenolic endgroup¹² containing polyesters based on p-hydroxybenzoic acid can react with melamine resins forming an ortho substituted phenol and a C-C-N< bond which is exceptionally stable to acids. A similar approach is taken by preparing primary carbamate containing polymers.^{13,14} In these crosslinked films a more hydrolyti-

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cally stable linkage, $-O-CO-NH-CH_2-N<$, similar to a melamine methylene bond is formed. These linkages are more stable to hydrolysis under acidic conditions than the ether linkage. Additional approaches to improve the acid resistance have been the preparation of hydrophobic polyurethane polyols,^{15,16} which have no ester linkages.

We were interested to further elucidate the crosslinking mechanism of the combination of a dialkyl malonate blocked polyisocyanate with a melamine resin and an acrylic polyol.^{1,2} A previous publication showed that the reaction of the malonate ester groups of the blocked isocyanate with the acrylic polyol occurred by a transesterification reaction and not by deblocking of the isocyanate.¹⁷ In addition, the reaction of the melamine resin with the acrylic polyol was confirmed,⁷ but no consideration was given for a potential reaction of the melamine resin with the acidic CH of the malonate blocked isocyanate in previous publications. We are interested in investigating if such a reaction is taking place and what the consequences of this reaction would be on the film properties of the coating.

EXPERIMENTAL

A malonate blocked isocyanate trimer (MBIT) was prepared by reacting one mole of a hexamethylene diisocyanate trimer with 3.0 mole diethylmalonate in the presence of a base catalyst (sodium nonylphenolate) and capping the residual isocyanate groups with n-butanol (see Table 1). The residual isocyanate groups were <10% of the starting concentration after reaction with malonate as measured by FTIR. For the binder, a commercially available hydroxyl functional acrylic was used (Table 2). As the melamine crosslinker, we used a commercial version of hexamethoxymethyl melamine (HMMM) with physical properties as given in Table 3, GPC analysis in Figure 1.

Model malonate blocked isocyanate (MMBI) was synthesized from butyl isocyanate and diethyl malonate with sodium methoxide as a catalyst. Its purity was > 94% (by GPC). The MMBI was then reacted with HMMM in a composition shown in Table 4 at 75-80°C.

Table 1—Characteristics of Malonate Blocked Isocyanate Trimer (MBIT)

Nonvolatile, %	46
Xylene %	46
n-butanol %	8
Equivalent weight of polymer, solids basis, acidic CH ^a	356
Equivalent weight of polymer, solids basis, activated ester ^a	178

(a) Calculated

Table 2—Characteristics of Acrylic Resin¹⁸

Nonvolatile, %	72
Solvent	Methyl amyl ketone
Hydroxy equivalent weight, (on solids)	600
Acid number	-1

The reaction was monitored via non-aqueous titration with a Mettler autotitrator by using 0.10 N tetrabutyl ammonium hydroxide in MeOH/isopropanol as a standard solution. Malonate blocked isocyanate is a weak acid and has an end point around pH 13 on the titration curve. The end point was taken from the first derivative of the titration curve ($\Delta E/\Delta V$ vs. V). The acidic CH before and after the reaction was also monitored with a 300 MHz proton NMR spectrometer.

Formulations were prepared with the MBIT crosslinker and the acrylic resin. The ratio of MBI groups to hydroxyl groups was varied from 0.7 to 1.8. One MBI group represents the reaction product of one mole of isocyanate with one mole of diethylmalonate. Films with a dry film thickness of 25 μ (1.0 mil) were cast on iron phosphated cold-rolled steel panels and cured for 30 min at temperatures ranging from 80 to 140°C. These panels were tested for pendulum hardness, methyl ethyl ketone (MEK) solvent resistance, and acid etch resistance. Acid etch resistance was tested with 20% sulfuric acid at 70°C. One drop of 20% sulfuric acid was placed on the cured films and placed in an oven for 15 min. The spot was evaluated for appearance, change in gloss, and any other attacks.

Formulations were also prepared with the MBIT and HMMM, but no acrylic polyol. These formulations were catalyzed with dodecylbenzene sulfonic acid (DDBSA) as well as amine blocked and covalent blocked DDBSA. These coatings were also coated onto steel panels at a dry film thickness of 25 μ (1.0 mil) and cured at temperatures of 80 to 140°C for 30 min.

In addition, formulations were prepared with MBIT and HMMM as crosslinker and the acrylic polyol as a resin. These formulations were prepared at different ratios of MBI/NCH₂OR/OH.

EXPERIMENTAL RESULTS AND DISCUSSIONS

In most previous publications on melamine chemistry, only the reaction of HMMM with hydroxyl, carboxyl, and amide groups is discussed. Assuming, as suggested

Table 3—Characteristics of HMMM¹⁹

Nonvolatile, %	98.5
Average degree of polymerization	1.5
Molecular weight average	550
Equivalent weight used in study	130
Theoretical equivalent weight	67
Residual methylol content, %	3

Table 4—Composition of Model Formulation MMBI and HMMM

Component	Parts by weight	Functional group, mole
MMBI	40.7	0.147
HMMM (methoxymethyl)	42.3	0.631
p-TSA 40% in isopropanol	4.0	0.01
MeOH	13.0	0.406

in previous publications, that the reaction of HMMM goes through a carbonium-iminium mechanism, the potential for reacting HMMM with other functional groups is much wider. This indeed has been recognized as shown in the patent literature. For example, a hydroxybenzoic ester²⁰ is used as a reactive diluent in melamine resin crosslinked coatings. This material is prepared by reacting hydroxybenzoic acid with a glycidyl ester. This reactive diluent is trifunctional with melamine resins. In addition to a secondary OH group derived from the reaction of the carboxyl group with the glycidyl groups, it has two reactive CH groups in the ortho position of the phenolic group. The potential for reaction of melamine resins with acidic CH groups of acetoacetates has been shown in the literature.²¹ Although this reaction proceeds readily, it requires a cure temperature of above 140°C and is therefore significantly slower than the reaction of HMMM with hydroxyl functional polymers.

We first duplicated some of the examples reported in the literature and reacted the MBIT with the acrylic resin. The results are shown in Figures 2-4. The level of MBI group to OH was varied from 0.7 to 1.8 as demonstrated in Figure 2 and the cure temperature from 80 to

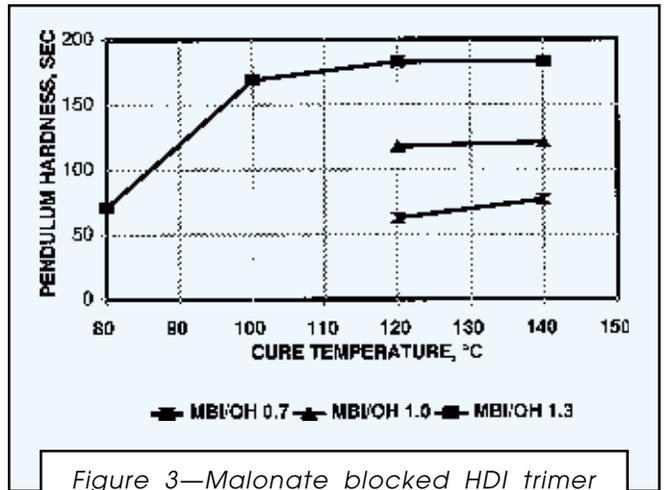


Figure 3—Malonate blocked HDI trimer crosslinking of acrylic polyol. Hardness vs. cure temperature.

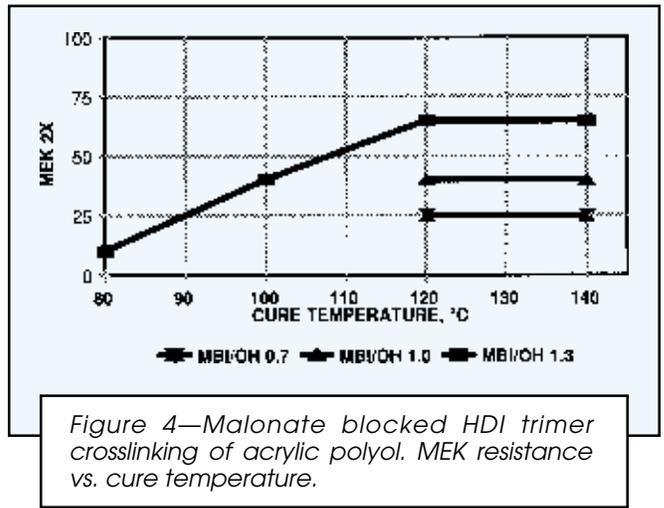


Figure 4—Malonate blocked HDI trimer crosslinking of acrylic polyol. MEK resistance vs. cure temperature.

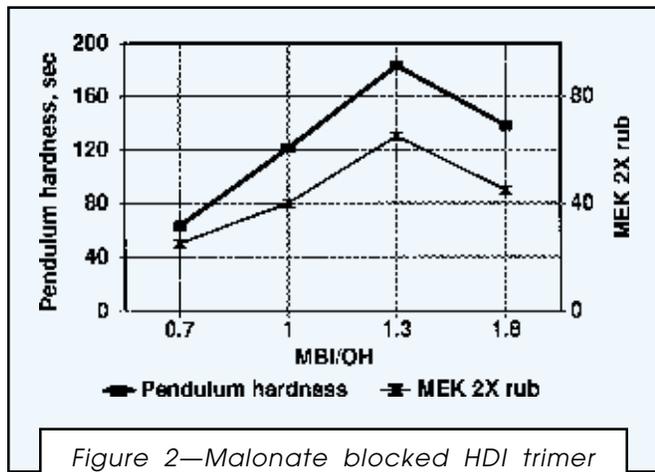


Figure 2—Malonate blocked HDI trimer crosslinking of acrylic polyol. Cure response vs. MBI/OH ratio, cure schedule: 30 min. at 120°C.

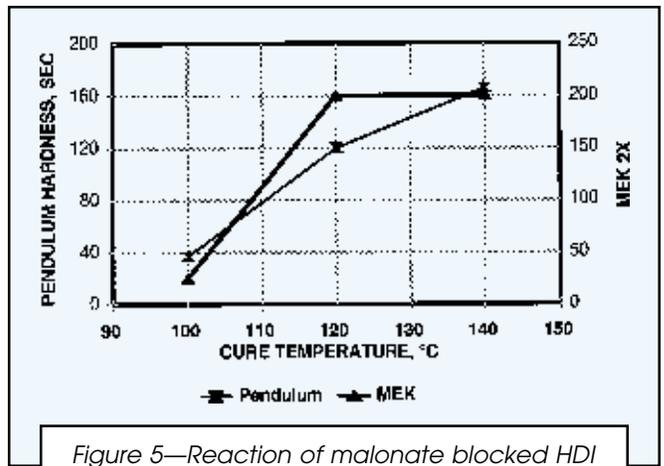


Figure 5—Reaction of malonate blocked HDI trimer and HMMM. MEK resistance vs. cure temperature, acidic CH/>NCH₂OR: 1.0/1.9.

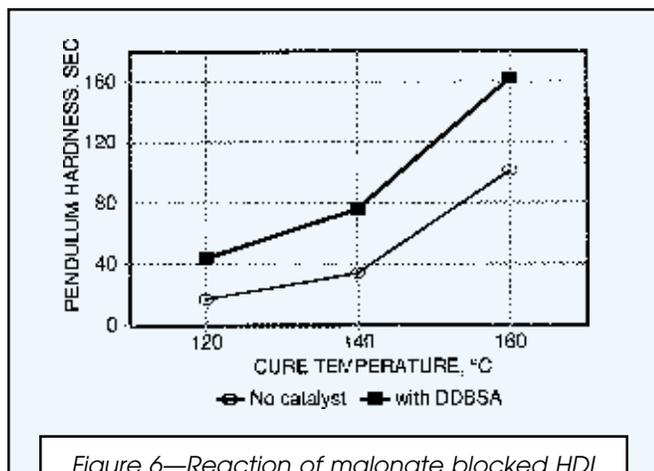


Figure 6—Reaction of malonate blocked HDI trimer and high NH melamine. Hardness vs. cure temperature.

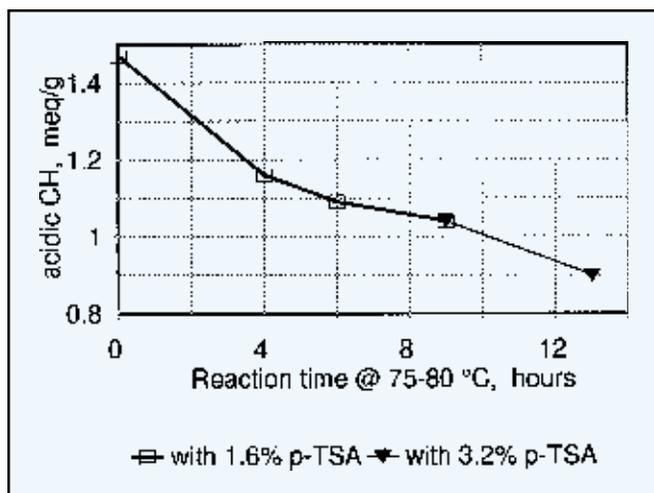


Figure 7—Acidic CH concentration vs. reaction time.

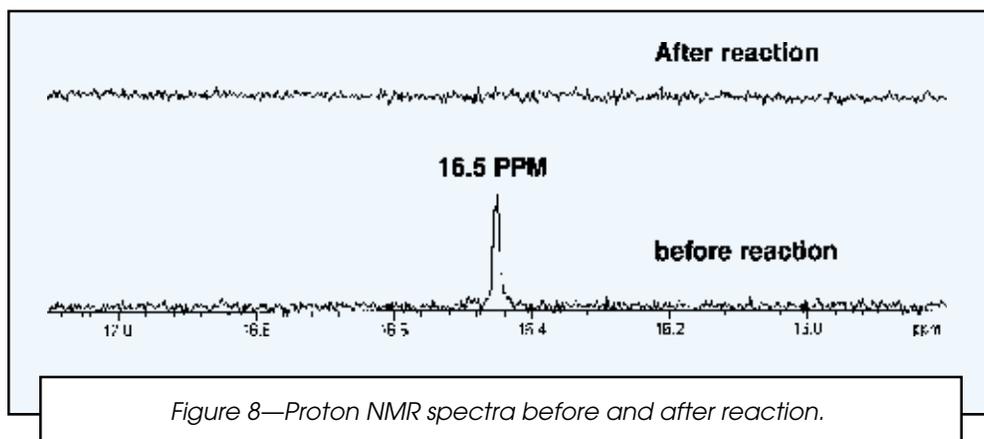


Figure 8—Proton NMR spectra before and after reaction.

140°C as shown in Figures 3 and 4. Cure time was kept constant at 30 min. Increased levels of malonate ester groups beyond the theoretical amount improve the film hardness and solvent resistance. The 1.3/1 MBI level gives the best results. Assuming all the malonate esters are difunctional, an MBI/OH ratio of 0.5 should give optimum film properties theoretically. Apparently steric hindrance and other side reactions give a functionality for the MBI group close to 1.3. The pendulum hardness of the coating reaches a maximum at a cure temperature of 100°C and does not increase at 140°C (Figure 3). Solvent resistance further improves as the cure temperature is raised to 140°C (Figure 4). Even after complete cure, the solvent resistance of the MBI crosslinked film is insufficient.

Reactions of malonate ester blocked isocyanates with melamine resins have not been reported in the literature. It is known that malonate esters react with formaldehyde to form methylene derivatives.²² As shown in Figure 5, MBIT starts to react with HMMM in the presence of a catalyst at 100°C. Close to full cure is achieved at 120°C, as measured in solvent resistance and in hardness development. The ease of reaction of the substituted malonate group with HMMM is surprising. Similar cure studies^{21,23} with acetoacetate functional polymers give much slower curing coatings. Reaction of MBIT with a high imino group containing methylated melamine resin (NH-MEL) is shown in Figure 6. Although the reaction proceeds without a catalyst, catalysis improves the hardness development. Cure, however, is not as good as with a fully alkylated melamine resin.

To study the reaction site of MBI and HMMM further, a model MBI compound, synthesized from butyl isocyanate and diethyl malonate, was reacted with HMMM. Methanol was used as a solvent to test the stability of the linkage between MMBI and HMMM. The reaction mixture was refluxed at 75-80°C, and the degree of reaction was monitored by titration of the acidic CH groups in MMBI. Figure 7 shows a clear decrease of acidic CH concentration as the reaction proceeds. Even with the presence of a large amount of methanol this linkage is formed, indicating improved stability versus the ether linkage. The reaction is relatively slow due to the low reaction temperature and large amount of methanol. Addition of more acid catalyst or removal of methanol will speed up the reaction.

The reaction of acidic CH with HMMM was further confirmed with the proton NMR spectra of the model compound reaction mixture before and after reaction. We selected the proton from the enolized tautomer of malonate blocked isocyanate (around 16.5 ppm) as a monitor for the reaction because it is free of interference from any other protons. Since the acidic CH form of malonate blocked

Table 5—Acid Etch Test on Cured Panels

Components Parts by Weight			Test results		
Acrylic	MBIT	HMMM	Pendulum Hardness, sec	MEK, 2X	Acid Etch Rating
55	45	0	183	65	0
48	40	12	177	200	1
81	0	19	144	200	2
0	73	27	166	200	2

Acid etch rating: 0 no attack, 5 completely destroyed

isocyanate is in equilibrium with its enolized tautomer, the concentration of acidic CH is equal to the concentration of enolized proton times a constant. As shown in Figure 8, the mixture before reaction showed a distinctive enolized proton peak around 16.5 ppm. After complete reaction (methanol was removed via distillation), no peak around 16.5 ppm was found. This is a clear indication of the participation of acidic CH in the reaction.

The cure response of a completely formulated coating consisting of MBIT, HMMM, and the acrylic resin is shown in Figure 9. In this formulation a ratio of functional groups of MBI/OH/NCH₂OR of 1.3/1/1.5 was used. Pendulum hardness and MEK resistance without catalyst, with DDBSA,²⁴ with a covalent blocked DDBSA,²⁵ and an amine blocked DDBSA²⁶ were measured. All catalyzed formulations contained 0.5% by weight of DDBSA on resin solids. All formulations were cured at 140°C for 30 min. Without catalyst the solvent resistance of the formulation is marginal. Hardness is about equal for the catalyzed and the uncatalyzed formulations. Free DDBSA, amine blocked, or covalent blocked DDBSA give about the same hardness. Solvent resistance is more than 200 MEK rubs for all the catalyzed formulations.

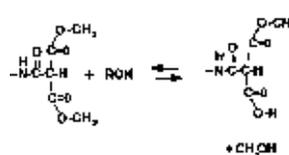
Based on the rate of cure of both the MBIT crosslinker and HMMM, it appears that the ester interchange reaction of MBIT is a faster reaction at temperatures below 120°C compared to the reaction of HMMM with MBIT. This reaction starts at temperatures above 80°C without

the need of any catalysts. Reactions of HMMM with OH and acidic CH of MBIT appear to proceed at about the same rate (both reactions start at temperatures around 100°C).

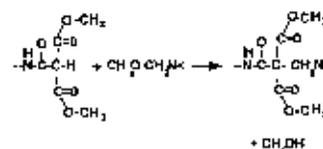
The effect of DDBSA catalyst on the MBIT reaction with hydroxyl groups was also investigated in this study and no increase in reaction rate was found.

We also performed acid etch tests using 20% sulfuric acid on the panels. The results are shown in Table 5. Although the formulation without melamine resin gives the best acid etch resistance, it lacks solvent resistance. The formulation with combined crosslinkers of MBIT and HMMM gives the best combination of properties based on hardness, MEK solvent resistance, and acid etch resistance.

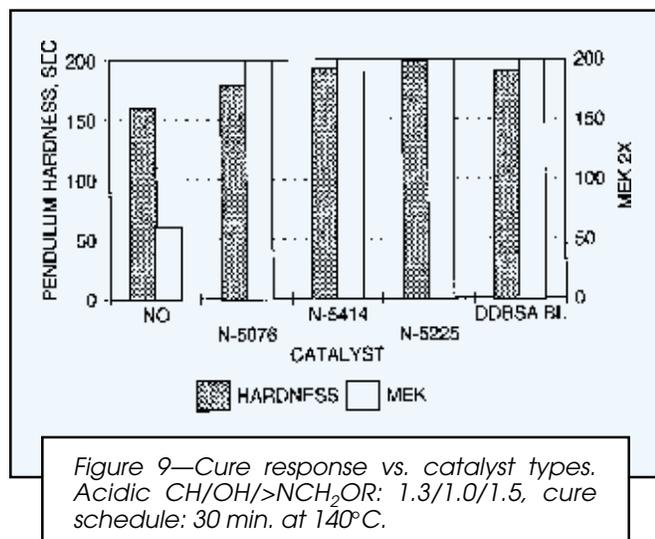
Malonate ester exchange



Melamine reaction



The network formation of a malonate blocked polyisocyanate with a hydroxyl functional acrylic resin, in the presence of a melamine resin, is much more complex than the separate reactions of malonate ester groups and amino resin with the hydroxyl groups because there is a three way crosslinking reaction taking place. In addition to the reactions of both malonate and the amino resin with the hydroxyl functional groups of the acrylic resin, there is an additional crosslinking mechanism which is the reaction of the melamine resin with substituted malonate groups. The titration and proton NMR studies of model compound reaction have confirmed the participation of acidic CH of malonate groups in this reaction. The reaction progresses even in the presence of large excess of methanol (excess methanol to malonate mole ratio of 2.8 in Table 4), which indicates that the newly formed bond is more stable than the regular ether linkage in melamine resin/acrylic reaction. This result favors a carbon - carbon linkage between melamine resin and malonate (shown above), although it is also possible to form an ether linkage through the reaction of melamine resin with the OH of enol form of the malonate ester. ¹³C NMR and FTIR studies of the similar reaction between melamine



crosslinker and acetoacetylated resin found no evidence of ether linkage formation in that system.²³

It is believed that this additional crosslinking reaction between the melamine resin and the malonate ester will increase the crosslinking density and improve the resistance properties of the films. This reaction should also impose additional steric hindrance on the ester linkage between malonate blocked isocyanate and acrylic resins, which could further strengthen the crosslinked network.

CONCLUSIONS

The crosslinking reaction between acidic CH of malonate blocked isocyanate and HMMM has been confirmed by a crosslinking study of coated film as well as model compound investigations. The rate of this crosslinking reaction is comparable to that of HMMM/hydroxyl reaction. The crosslinking between malonate blocked isocyanate and HMMM in an acrylic/HMMM/malonate blocked isocyanate formulation improves resistance properties of the coated films.

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