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## CROSSLINKING WITH MALONATE BLOCKED ISOCYANATES AND WITH MELAMINE RESINS

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### ABSTRACT

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<sup>1,2</sup>. These coatings contain lower level of melamine crosslinker compared to conventional acrylic/HMMM systems and show excellent acid resistance. We were interested to explore the reaction mechanism of this complex crosslinking system and find explanations for the good chemical resistance properties.

### INTRODUCTION

The environmental acid etch resistance of automotive clearcoats<sup>3</sup> has been one of the major issues in formulating these coatings. This acid etch resistant has become an increasing problem during the last few years, due to the development of higher distinction of image (D.O.I) 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. We have consistently measured at our location<sup>4</sup> in Norwalk CT., which is close to the New York metropolitan area and close to a major highway, a pH of <4.0 during the 1993 measuring period. Most of the factory applied automotive topcoats have been based on melamine resin crosslinked coatings. 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 used about 20-30 % of butylated melamine resins whereas high solids coatings used as much as 40-50% of fully alkylated melamine resins. The high level of melamine resin not only lowered the VOC of the coating but also improved exterior durability and lowered the formulation cost. Unfortunately the higher level of melamine resin had a rather catastrophic effect on the acid resistance of the coating. The basicity of melamine<sup>5</sup> is a function of the degree of substitution. Films prepared with fully alkylated melamine resin initially show a low concentration of NH<sup>6</sup> band in FTIR-ATR. On exposure or overbake, the NH band increases and at the same time the acid resistance as measured by spot tests decreases. The reaction mechanism<sup>7</sup> 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 with water and subsequent selfcondensation reaction. The dominant linkage formed in the crosslinking of polyols with melamine resins is the >N-CH<sub>2</sub>-O-R linkage. Under pH conditions below 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. The films will therefore

start to initially 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<sup>8</sup>, acrylosilane<sup>9</sup> and epoxy/carboxy<sup>10</sup> systems have been described in the literature. In addition to retaining some of the performance and cost advantages of melamine crosslinker, combinations of various crosslinking mechanism<sup>11</sup> 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 endgroup<sup>12</sup> 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<sup>13,14</sup>. In these crosslinked films a more hydrolytically stable linkage -O-C=O-NH-CH<sub>2</sub>-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<sup>15,16</sup> 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. A previous publication showed the reaction of the malonate ester groups of the blocked isocyanate with the acrylic polyol by a transesterification reaction and not by deblocking of the isocyanate<sup>17</sup>. In addition the reaction of the melamine resin with the acrylic polyol was confirmed. But in this publication no consideration was given for a potential reaction of the melamine resin with the acidic CH of the malonate blocked isocyanate. We were interested in investigating if such a reaction is taking place and what the consequences of this reaction on the film properties of the coating would be.

## 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 (sodium nonylphenolate) catalyst and capping the residual isocyanate groups with n-butanol (see Table 1). The residual isocyanate groups were <10% of the starting concentration after malonate reaction as measured by FT-IR. As acrylic resin, a commercially available hydroxyl functional acrylic was used (Table 2). As a melamine resin, we used a commercial version of hexamethoxymethyl melamine (HMMM) with physical properties as given in Table 3. GPC analysis in Figure 1.

**TABLE 1 CHARACTERISTICS OF MALONATE BLOCKED ISOCYANATE TRIMER (MBIT)**

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



**TABLE 2 CHARACTERISTICS OF ACRYLIC RESIN**<sup>18</sup>

Nonvolatile, %	72
Solvent	Methyl amyl ketone
Hydroxy Equivalent Weight, (on solids)	600
Acid Number	~1

**TABLE 3 CHARACTERISTICS OF HMMM**<sup>19</sup>

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

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 5 at 75-80 °C. 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 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. The composition of the model formulation is shown in Table 4.

**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

Formulations were prepared with the MBIT crosslinker and the acrylic resin. The ratio of MBI group to hydroxyl group 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 $\mu$  (1.0 mil) were cast on iron phosphated cold rolled steel panel and cured for 30 minutes at temperatures ranging from 80°C to 140°C. These panels were tested for Pendulum hardness, methylethylketone (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 coating and placed in an oven for 15 minutes. The spot was evaluated for appearance, change in gloss and any other attack.

Formulations were also prepared with the MBIT and HMMM. These formulations were catalyzed with dodecylbenzene sulfonic acid (DDBSA) as well as amine and covalent blocked DDBSA. These coatings were also coated onto steel panels at a dry film thickness of 25 $\mu$  (1.0 mil) and cured at temperatures of 80° to 140°C for 30 minutes.

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/NCH<sub>2</sub>OR/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 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 has indeed been recognized as shown in the patent literature. For example, a hydroxybenzoic ester<sup>20</sup> is used as a reactive diluent in melamine resin crosslinked coatings. This material is prepared by reacting hydroxybenzoic acid with an glycidyl ester. This reactive diluent is tri functional 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<sup>21</sup>. 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 Figure 2, 3 and 4. The level of MBI group to OH was varied from 0.7 to 1.8 as demonstrated in Fig. 2 and the cure temperature from 80 to 140°C as shown in Figures 3 and 4. Cure time was kept constant at 30 minutes. 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. Theoretically, assuming all the malonate esters are difunctional, a MBI/OH ratio of 0.5 should give optimum film properties. Apparently steric hindrance gives a functionality for the MBI group close to 1.3. Even under optimum cure conditions the MBIT crosslinked films lack in solvent resistance. The pendulum hardness of the coating reaches a maximum at a cure temperature of 100°C and does not increase at 140°C. Solvent resistance further improves as the cure temperature is raised to 140°C. 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<sup>22</sup>. 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. Surprising is the ease of reaction of the acidic CH group with HMMM. Similar cure studies<sup>23</sup> 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 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 solvent to test the stability of the linkage between MBI 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 MBI. Figure 7 showed a clear decrease of active 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 choose the proton from 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. 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.

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/NCH<sub>2</sub>OR of 1.3/1/1.5 was used. Pendulum and MEK resistance without catalyst, with DDBSA<sup>24</sup>, with a covalent blocked DDBSA<sup>25</sup>, an amine blocked DDBSA<sup>26</sup> were used. All catalyzed formulations contained 0.5% by weight of DDBSA on resin solids. All formulations were cured at 140°C for 30 minutes. Without catalyst the solvent resistance of the formulation is marginal. Hardness is about equal for the catalyzed and the uncatalyzed formulations. Free DDBSA and amine 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 HMMM. Reaction of HMMM with OH and acidic CH of the MBIT appears to proceed at about the same rate.

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

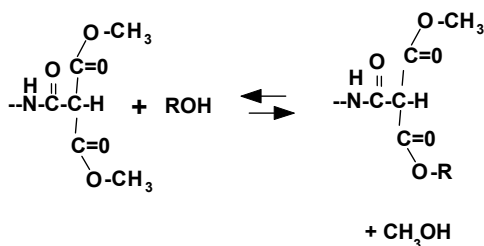
We also performed acid etch tests using 20 % sulfuric acid on the panels. The results are shown in Table 5. The formulation with combined crosslinkers of MBIT and HMMM gave overall best properties of hardness, MEK solvent resistance and acid etch resistance.

**TABLE 5 ACID ETCH TEST ON CURED PANELS**

Components parts by weight			Test results		
<u>ACRYLIC</u>	<u>MBIT</u>	<u>HMMM</u>	<u>Pendulum hardness</u>	<u>MEK, 2X</u>	<u>Acid etch rating</u>
55	45	0	130	65	0
48	40	12	126	200	1
81	0	19	102	200	2
0	73	27	118	200	2

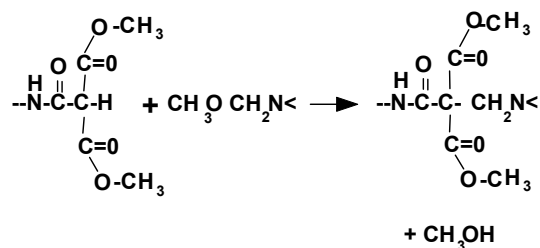
Acid etch rating: 0 no attack, 5 completely destroyed

### Malonate ester exchange



SL2057

### Melamine reaction



SL2056

The network formation of a malonate blocked polyisocyanate with a hydroxyl functional acrylic resin is, in the presence of a melamine resin, much more complex than the separate reaction 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 the acidic CH of substituted malonate groups. Malonate crosslinks with the acrylic resin should not be too stable, these linkages still present activated ester groups and are potentially easy to hydrolyze. After reaction of the CH groups of the malonate with an amino resin, the malonate ester groups are sterically hindered and should be less reactive. The linkage between melamine and malonate is a carbon - carbon linkage and it is more hydrolytically stable than the methylene ether group formed in HMMM/hydroxyl reactions.

## CONCLUSIONS

The crosslinking reaction between acidic CH of malonate blocked isocyanate and HMMM has been confirmed by crosslinking study of coated film as well as model compound investigations. The reaction 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 increases crosslinking density and improves resistance properties of the coated films.

## ACKNOWLEDGMENT

We would like to thank Dr. Ed Hessel for performing the NMR experiments and Dr. Len J. Calbo for his assistance in proof reading the paper and for King Industries Inc., for the opportunity to publish this work.

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<sup>18</sup> Joncryl 906, Acrylic polymer from S.C. Johnson Polymer, Div. of S.C. Johnson & Son, Inc., 1525 Howe St., Racine, WI 53403-5011 USA

<sup>19</sup> Resimine 747 HMMM a product of Solutia Inc., 800 N. Lindbergh Blvd., St. Louis, MO 63167 USA

<sup>20</sup> Exxon Chemical Exx-RD Reactive Diluent, Reaction Product hydroxybenzoic acid with glycidyl ester.

<sup>21</sup> F. D. Rector, W. W. Blount, D. R. Leonard, "Application of Acetoacetyl Functionality in Thermoset Coatings". Preprint "Waterborne and Higher Solids Coatings Symposium", Feb. 3-5, 1988 in New Orleans, 68-93.

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<sup>23</sup> King Industries Inc. Unpublished work showed a cure temperature of 140°C for acetoacetate ester.

<sup>24</sup> NACURE 5076 dodecylbenzene sulfonic acid; A product of King Industries Inc. Norwalk CT. USA.

<sup>25</sup> NACURE 5414 polymeric covalently blocked DDBSA; A product of King Industries Inc. Norwalk CT. USA

<sup>26</sup> NACURE 5225 dodecylbenzene sulfonic acid blocked with an t-amine; A product of King Industries Inc. Norwalk CT. USA; DDBSA BL an experimental t-amine blocked catalyst.

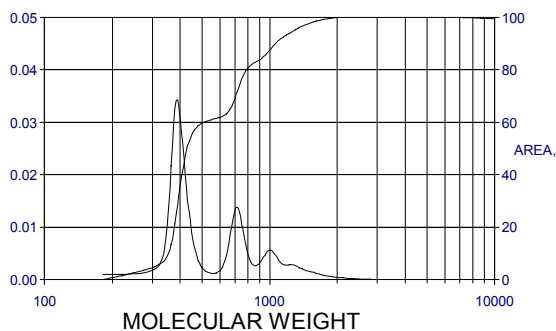


Figure 1. GPC of HMMM

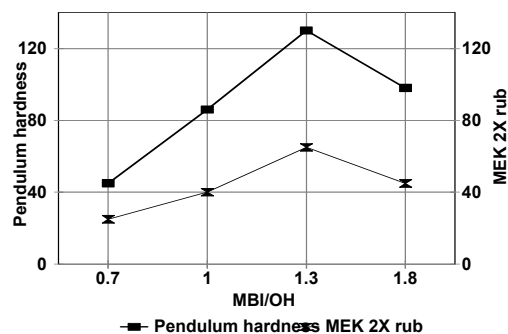


Figure 2. Malonate blocked HDI trimer crosslinking of acrylic polyol, cure response vs. MBI/OH ratio

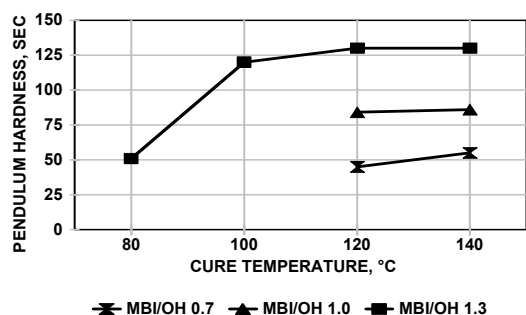


Figure 3. Malonate blocked HDI trimer crosslinking of acrylic polyol, hardness vs. cure temperature.

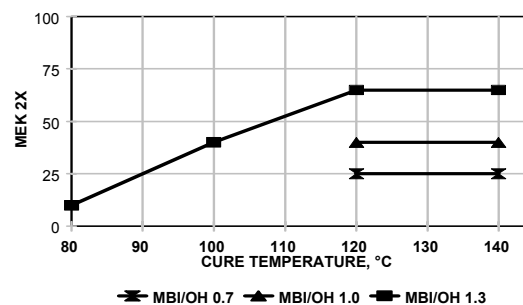


Figure 4. Malonate blocked HDI trimer crosslinking of acrylic polyol, MEK resistance vs. cure temperature.

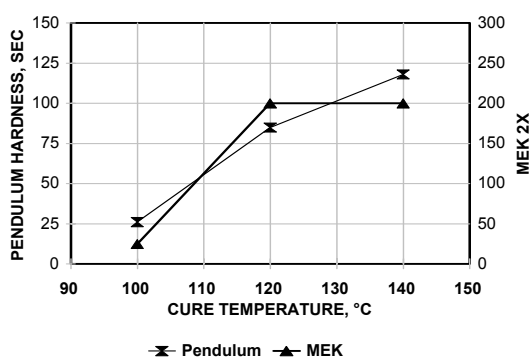


Figure 5. Reaction of malonate blocked HDI trimer and HMMM, MEK resistance vs. cure temperature, active CH/>NCH<sub>2</sub>OR: 1.0/1.9.

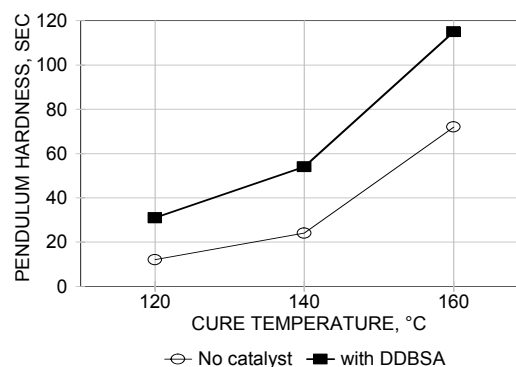


Figure 6. Reaction of malonate blocked HDI trimer and high NH melamine, hardness vs. cure temperature.

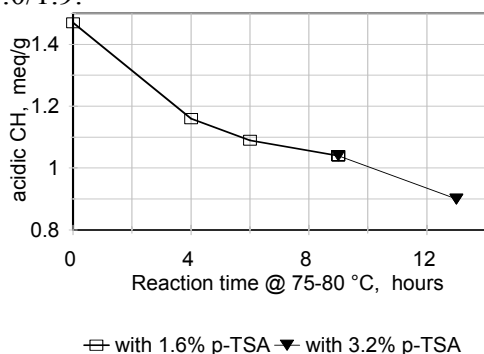


Figure 7. Acidic CH concentration vs. reaction time

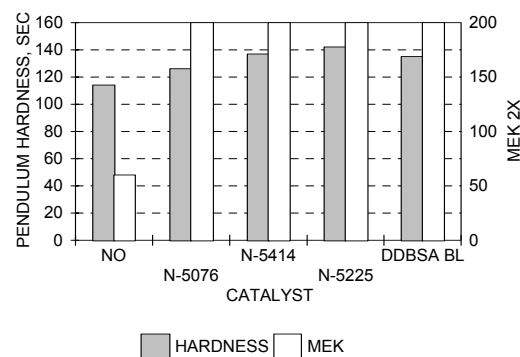


Figure 9. Cure response vs. catalyst types, active CH/OH/>NCH<sub>2</sub>OR: 1.3/1.0/1.5.

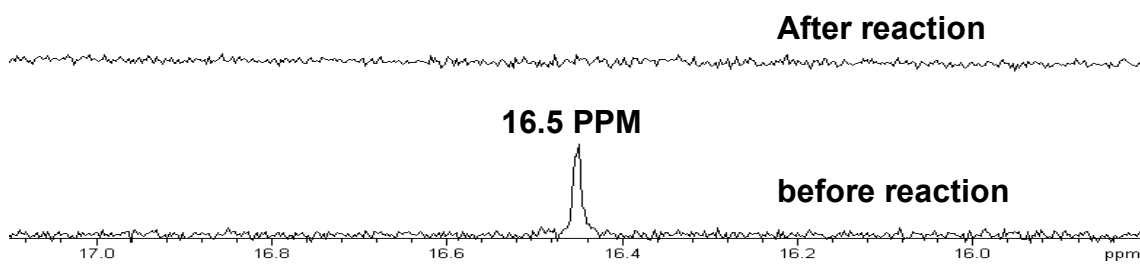


Figure 8. Proton NMR spectra before and after reaction