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EXTERIOR DURABILITY OF URETHANE MODIFIED ACRYLIC MELAMINE COATINGS.

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Introduction

Recently, many studies have addressed the degradation mechanism of the outdoor exposure of high solids acrylic polyols crosslinked with melamine-formaldehyde resins¹. High solids coatings are more prone to degradation as compared to low solids coatings, because the network is formed from low molecular weight ingredients, resulting in many linkages that are potentially sensitive to hydrolysis. The crosslinking agent used in most of these coatings is hexamethoxymethylmelamine or a methyl-butyl mixed ether thereof². Hydrolysis of the ether linkage between the acrylic polyol and HMMM is the main cause for degradation of the crosslinked network³. Not only does low pH in combination with water and temperature contribute to hydrolysis, but the hydrolysis is also accelerated in the presence of UV light⁴.

The urethane linkage which is formed in high solids acrylic polyols crosslinked with polyisocyanates has also shown sensitivity to UV radiation. Without a stabilizer⁵ a fast loss of urethane groups⁶ and eventual film failure is observed. The published degradation data on both melamine and urethane crosslinked coatings indicates that these films should fail rapidly after a short exposure time. Degradation of the network should lead to a loss of Tg and eventually a complete loss of film integrity. Most publications indicate additional reactions taking place, leading to crosslinking, and contrary to expectations, to an increase in Tg. For example, increased self-condensation reaction at the expense of crosslinking is cited⁷ as one explanation for the increase in Tg on exposure. This assumption is doubtful considering that for each of the crosslinks lost only half as many self-condensation reactions take place. In addition, the self-condensation reaction contributes less to film hardness than crosslinking.⁸ The overall result is a network with many imperfections. Therefore, to account for the increase in Tg other crosslinking reactions are required. The overall result of exterior exposure of the film is an initial increase in Tg,⁹ shrinkage of the film and subsequent reduction in elongation and loss of flexibility. In pigmented coatings the effect of film degradation is a degradation of the top layer resulting in a reduction in gloss and eventually in chalking. Film failure is usually not catastrophic, but gradual. In automotive clearcoats the UV absorbing effect of the pigment is eliminated, therefore the total film is exposed to UV and to degradation. Failure mode in these coatings is usually not gradual, but is catastrophic. Stress induced failure in these clearcoats leads to checking and cracking; in many instances without previous warning such as reduction in gloss. Additives such as UV absorber and hindered amine light stabilizer improve durability and reduce checking and cracking in these coatings.

In a previous publication we described the improvements in checking and cracking of high solids acrylic/melamine automotive clearcoats modified with a urethane diol¹⁰.

Experimental Part

As a backbone resin for this study a commercially available high solids acrylic resin¹¹ with an average MW of 2500-3000 and a hydroxyl number of 170 was used. This acrylic resin is free of any other aromatic functionality. The acrylic polyol was crosslinked with a commercially available hexamethoxymethylmelamine crosslinker (HMMM). The weight ratio of acrylic resin to HMMM used was 70/30. The formulation was catalyzed with 1% of an amine-blocked dodecylbenzene sulfonic acid¹² (DDBSA) catalyst. As a modifier for the basic formulation 1, 2, 5 and 10 % of an aliphatic urethane diol¹³ was used. The HMMM¹⁴ level was adjusted in these formulations to account for the increase in hydroxyl content of the formulation. For comparison purposes a formulation was also stabilized with a hindered amine light stabilizer¹⁵ (HALS). HALS is an acetylated low pK_b value (>12) compound and does not inhibit the curing reaction of acid catalyzed coatings¹⁶. 1% of HALS was used in the formulation. The clearcoat was applied over a white basecoat and cationic electrocoated zinc phosphated steel panels. Basecoat and clearcoat used the same acrylic/HMMM resin combination. A surface treated grade of exterior durable titanium dioxide rutile¹⁷ was used as the pigment. The formulations were cured at 120°C and 150°C for 20 minutes. Film thickness of the clearcoat was about 1.2 mil. or 30 micron. The coated panels were exposed to QUV, UV-B bulbs and a cycle of 8 hours at 50°C exposure and 4 hours 40°C condensation.

Results

QUV exposure showed checking and cracking of an acrylic/HMMM coating catalyzed with 0.5 % of amine blocked DDBSA. After 2500 hours only formulations with a hindered amine light stabilizer and/or urethane diol modification were free of checks and cracks. (Fig. 1) Gloss retention of the formulation was measured over the 3500 hour exposure time and is reported in Figure 2. Formulations with 6.7, 12.9 and 18.8% of urethane diol and 1 % hindered amine light stabilizer modification showed an improvement in gloss retention over the control. Higher levels of urethane diol (29.5%) result in a decrease in gloss after 2500 hours exposure. The improvement in gloss retention, and especially in checking, was not expected. We reformulated this system using lower levels of urethane diol and compared the performance of the urethane diol with a hindered amine light stabilizer. We also raised the level of DDBSA catalyst from 0.5% to 1.0% to achieve a higher crosslink density and potentially faster checking and cracking. The formulations were exposed to QUV for 4600 hours. Gloss measurements of the 150°C cured panels showed approximately equal gloss for all formulations for 3750 hours. With the exception of the hindered amine light stabilizer formulated coating, all formulations showed sudden loss of gloss after 3750 hours (Fig. 3) . To gain some understanding of the changes in Tg of the cured coating on exposure we measured the Tukon hardness during the first 1600 hours of exposure (Fig.4). We have found reasonable correlation in the measured range between Tukon hardness and Tg¹⁸ in this system. All formulations increase in Tukon hardness for the first 600 hours exposure (120° and 150°C cured), which agrees well with DMA experiments. Surprisingly, the increase in Tukon hardness of about 1.5 unit (or Tg increase of about 8-10°C) is about the same for the control and for the hindered amine stabilized formulation. All the paint systems with 2 to 10 % UD modifications have a higher initial hardness of about 0.5-1.5 Knoop and increase on exposure less (0.5-1.0 Knoop, 3-5°C. Tg) than the hindered amine light stabilized coatings.

Tukon hardness values before and after 4630 hours are shown in Fig. 5. Both the control and the hindered amine light stabilized formulations gain the same amount of hardness during the exposure. The urethane diol modified formulations show little or no change during the exposure (within the experimental error of the method).

Florida exposure of the same formulation gives a slightly different picture. (Fig. 6) On exposure all formulations increase in hardness, the unmodified formulations show more increase in hardness (and Tg) compared to the UD and the hindered amine modified coatings. An increase in Tukon of about 12-35 % is shown. After 48 month period none of the formulations show any checking and cracking and the gloss is the same for all formulations. In a white pigmented formulation some improvement in gloss retention is seen after 36 months of Florida exposure of 6-13 % urethane diol modification; higher levels of UD again give reduced gloss.

Summary.

We have shown that modification of acrylic/HMMM coatings with a low molecular weight urethane diol can under some exposure conditions improve the exterior durability. The improvement is found at a level of approximately 5 % of modification. These formulations show a lesser increase in hardness on exposure than the control or with a hindered amine.

Acknowledgments

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- ¹¹ Elveron 100 acrylic resin, E. I. Dupont, Wilmington Del.
- ¹² NACURE 5543, catalyst, King Industries Inc., Norwalk, CT.
- ¹³ K-FLEX UD-320W Urethane diol, King Industries Inc. Norwalk, CT.
- ¹⁴ Cymel 303 HMMM, Cytek Industries.
- ¹⁵ Tinuvin 440 hindered amine, Ciba-Geigy Corp.
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- ¹⁷ Ti-Pure 960, titanium dioxide, E. I. Dupont, Wilmington, DE
- ¹⁸ L. W. Hill, K. Kozlowski, *J.C.T Vol. 59*, No. 751, (1987) p 63-71.

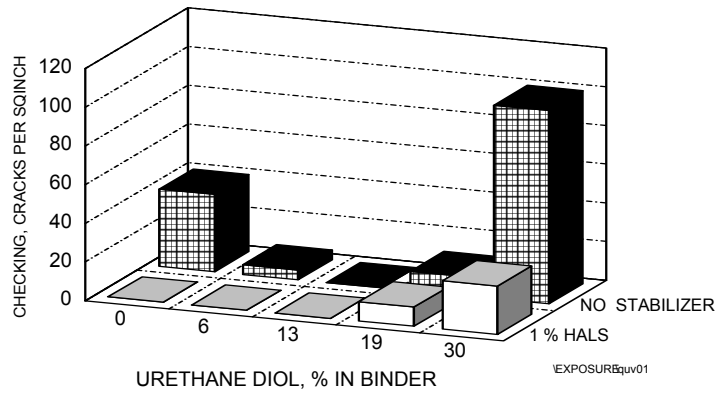


Figure 1. QUV Exposure 2500 hours. Acrylic/HMMM 70/30 Clearcoat, Urethane diol modified, with and without hindered amine light stabilizer. 0.5 % DDBSA catalyst. Cure temperature 20 min. 120°C

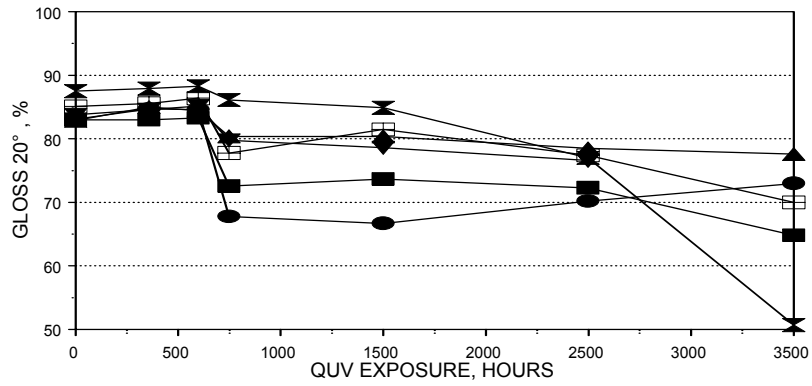


Figure 2. Gloss 20°, 3500 hours QUV exposure, Acrylic/HMMM 70/30 clearcoat, urethane diol modified, with and without hindered amine light stabilizer. 0.5 % DDBSA catalyst,

■ 0 % UD ▲ 6.7 % UD ▼ 12.9 % UD + 18.8 % UD * 29.5 % UD ● 1 % HALS

quv081421B

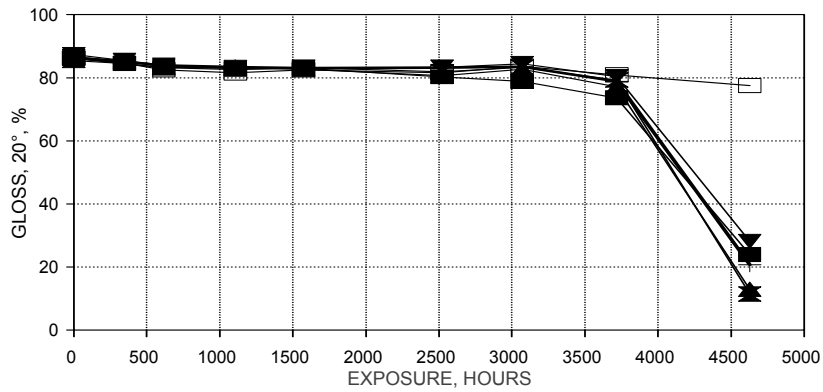


Figure 3.-QUV Exposure 4600 hours. Acrylic/HMMM 70/30 clearcoat, urethane diol modified, with and without HALS. 1.0 % DDBSA. Cure 20 min. 150°C.

■ CONTROL □ 1% HALS ▲ 1% UD + 2% UD × 5% UD QUV0320150bw

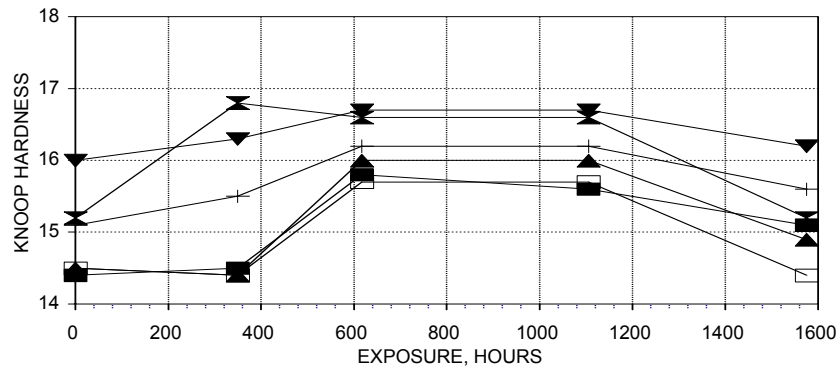


Figure 4.- QUV exposure 1600 hours. Acrylic/HMMM clearcoat, urethane diol modified, with and without HALS. 1.0 % DDBSA. Cure 20 min. 150°C.

■ CONTROL □ 1% HALS ▲ 1% UD + 2% UD × 5% UD QUV03KNI50BW

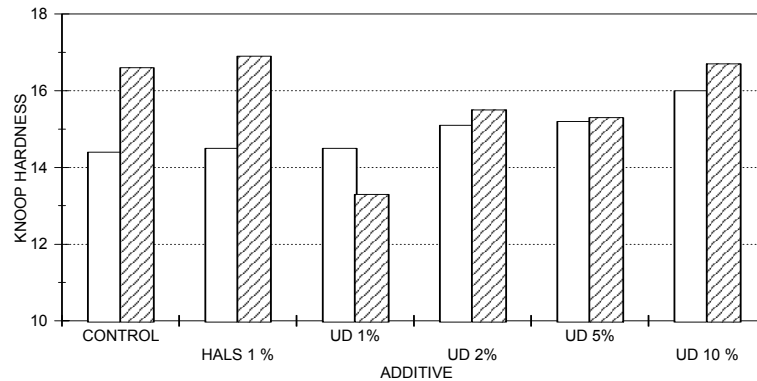


Figure 5.- QUV exposure 4630 hours. Acrylic/HMMM 70/30 clearcoat, urethane diol modified, HALS additive. 1.0 % DDBSA. Cure 20 min. 150°C.

□ UNEXPOSED ▨ EXPOSED

EXP1QUV031KNAGED

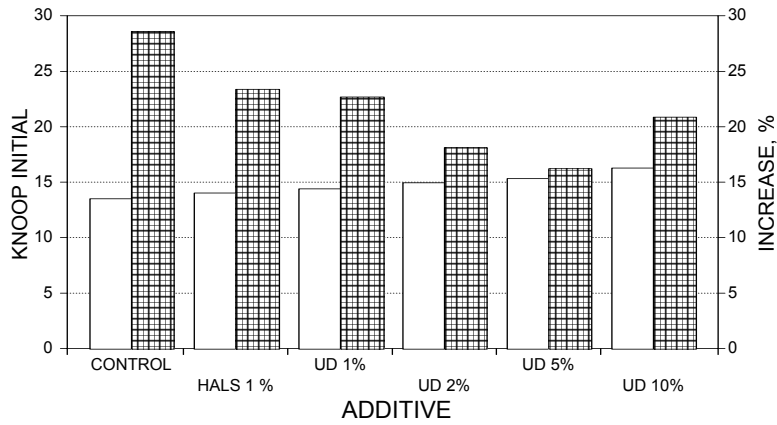


Figure 6.-Florida exposure 36 month, 5° south. Acrylic/HMMM 70/30 clearcoat . 1.0 % DDBSA. Cure 20 min. 150°C.

□ KNOOP ▣ INCREASE FLEXP03SL1648B

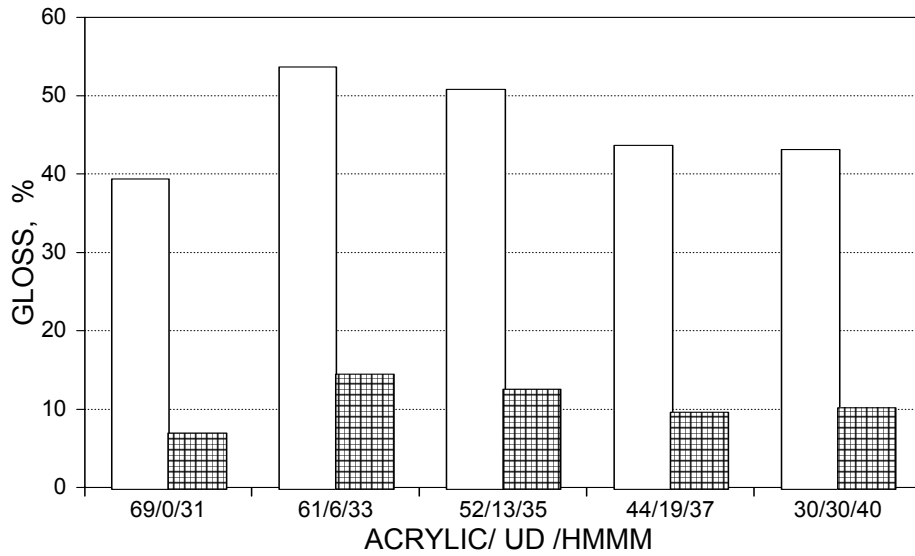


Figure 7.-Florida Exposure, 36 month 5° south, Acrylic/HMMM 70/30, urethane diol modified. Pigment Rutile, Date average of cure 20 min 120° & 150°C.

□ GL60° ▣ GL 20° FORID01/SL1420B