Acid Etch of Automotive Clearcoats II. Comparison of Degradation Chemistry in Laboratory and Field Testing

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A laboratory test procedure was developed to quantitatively evaluate the acid etch resistance of automotive clearcoats. Here we attempt to verify that the conditions used in the laboratory test reproduce the field degradation chemistry to assure that the test is evaluating realistic performance characteristics. In this study we applied X-ray photoelectron spectroscopy (XPS) as a tool to determine if degradation products are observable which can be used to verify the consistency of the field and laboratory degradation processes for acrylic melamine-based clearcoats.

INTRODUCTION

The work described in this report is a continuation of efforts regarding the development of a laboratory test for the evaluation of the acid etch resistance of automotive clearcoats.[1] A primary component of the etch test is a laboratory test method that can be used to correctly and quantitatively evaluate field performance. Acid hydrolysis as a result of acid rain exposure is believed to be primarily responsible for environmental etch degradation.[2-5] Therefore, the laboratory test procedure developed was designed to evaluate the relative bulk acid hydrolysis resistance of clearcoat systems. The test procedure relies on the exposure of bulk coating to a well-controlled acidic environment simulating environmental conditions and gravimetrically following weight loss as a function of exposure time. The rate of weight loss experienced by the coating is taken to be a direct indication of its hydrolysis rate and therefore etch resistance. Results presented clearly indicate that the laboratory test was successful in realistically ranking the field etch performance of current production clearcoat technologies.

Although environmental etch has been studied quite extensively, very limited chemical data has been presented that confirms the mechanism(s) of the degradation process. Most conclusions that have been made are largely based on empirical considerations involving observations that etch is most prevalent in areas having low pH rain, and the results of field etch exposure studies that seem to indicate that the sensitivity of a particular coating to environmental etch is directly associated with the ease of hydrolysis of the crosslink. Although the results of laboratory weight loss measurements were shown to correlate with field etch performance,[1] it could not be concluded from the performance data alone that the laboratory test was correctly simulating the field degradation chemistry. If the laboratory test conditions are considerably different than the field, laboratory testing may result in unnatural degradation chemistry; thus, the results would not reflect realistic performance characteristics. Verification of consistent degradation chemistry is an important consideration, especially if the test method may be used to select clearcoat systems based on their laboratory etch performance. Therefore, to provide more confidence in the laboratory test for etch, it is important to verify that the exposure conditions used in the laboratory etch test are realistically simulating the field degradation phenomenon.

In this study we applied XPS as a tool to examine the surface composition of field exposed panels and compare the results with laboratory treated powders of identical technologies. The goal was to determine if changes are observable which can be used to verify the consistency of the field and laboratory degradation processes. XPS provides both elemental and chemical state information through the acquisition of survey and core level spectra, respectively. Therefore, one can compare the relative elemental surface composition, as well as changes in the core level spectra of elements, to determine if changes found in the field exposed panels are consistent with those resulting from laboratory acid treatment.

EXPERIMENTAL

Materials

The automotive clearcoat materials used in this study were conventional acrylic melamine coatings that were

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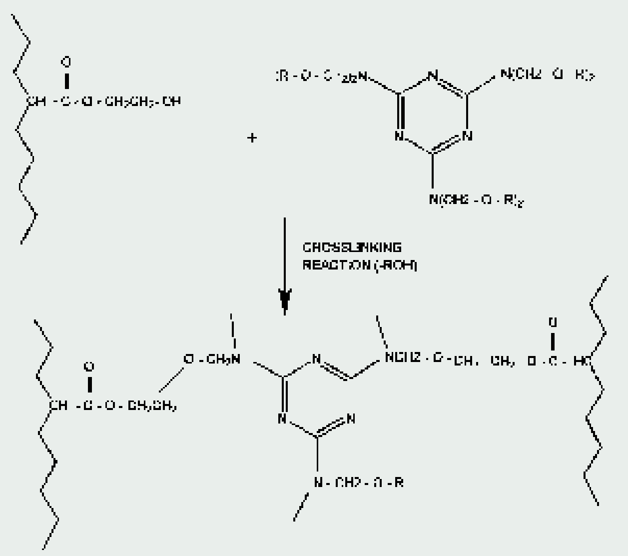

Figure 1—Illustration of crosslinking reaction in acrylic melamine systems. (R = CH_3–, butyl-)

obtained directly from paint suppliers and were cured at nominal schedules defined by the supplier. Panels of the clearcoats used for the field testing were prepared by the individual suppliers. Melamine (1,3,5 Triamino Triazine) and methylated melamine (Resimene 747) reagents were used as standard materials for confirmation of XPS core level spectra and were obtained through Aldrich Chemicals and Solutia, respectively.

Laboratory Etch Test

The procedure for the gravimetric laboratory test for environmental etch involves three major steps: (1) sample preparation; (2) acid exposure; and (3) weight loss measurements. The detailed procedure can be found in a previous report.[1] In brief, a clearcoat film is prepared by applying the coating to a glass panel, and curing it in an electric convection oven according to the suppliers' specified cure schedule. A powder, suitable for acid exposure, is prepared by cryo-grinding the free clearcoat to a powder of about 20-30 microns in diameter. The resulting powder is then placed in a humidity cabinet maintained at 95% relative humidity (RH) and 90°F for 72 hr to assure completion of moisture assisted cure reactions that can occur for some coating chemistries. The powdered clearcoat is then dried to constant weight to assure that all water and residual solvent have been removed. The dried clearcoat powder is dispersed in aqueous sulfuric acid of pH = 2.0 ± 0.1 and is constantly agitated at 60°C and removed at predefined exposure times for weight loss determinations.

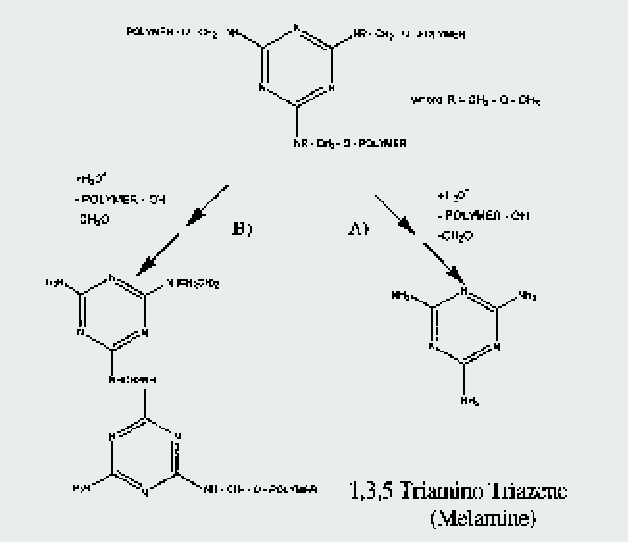

Figure 2—Acid hydrolysis scheme for acrylic melamine crosslinked systems.

Field Etch Exposure Studies

Field etch exposure studies were conducted during a 16-week time period between May and September of 1996 and 1997. Panels of conventional acrylic melamine coatings were prepared by the suppliers and used in the field exposure testing. These panels were neither washed nor evaluated during the 16-week exposure period to minimize possible surface contamination of the clearcoats with wash solutions.

X-ray Photoelectron Spectroscopy (XPS)

All XPS analyses were performed on a Kratos Axis-165 spectrometer, manufactured by Kratos Analytical. The X-ray source provided monochromatic Al K_α radiation (1486.6 eV) and was operated at 300 W. For all acquisitions the area irradiated by the X-ray beam was about 1000 μm in diameter. The analyzer was operated at an 80 eV pass energy for all survey spectra and 20 eV pass energy for the acquisition of all core level spectra. A low energy electron charge neutralizer was utilized to minimize charging effects. The system base pressure was typically 1 x 10^{-9} Torr.

The data system and software routines used were supplied by the instrument manufacturer. Atomic concentrations were obtained by integration of the core level spectra, with appropriate corrections made for photoionization cross-sections and instrument transmission function. High resolution core level spectra were fitted using a least-squares fitting routine to determine core level binding energy positions. A nonlinear Shirley routine, incorporated into the fitting procedure, was used to assure a consistent estimate of the background. All core level binding energies were referenced relative to the C 1s line at 284.6 eV.

RESULTS AND DISCUSSION

Review of Acrylic Melamine Chemistry and Potential Hydrolysis Products

To effectively discuss the experimental results, one must have a general knowledge of melamine crosslinking reactions, proposed hydrolysis degradation pathways, and potential reaction products. In acrylic melamine (AM) systems, the primary crosslinking reaction occurs between the hydroxyl functional groups of the acrylic polymer resin with alkyl-methylol groups on a melamine-formaldehyde-based crosslinker. An illustration of this reaction is shown in *Figure* 1. Crosslinking involves an exchange reaction resulting in the loss of alcohol and the formation of an acetal linkage (N—CH_2—O— Polymer) between the crosslinker and acrylic polymer. For most AM systems, it is commonly accepted that the extent of crosslinking under normal cure conditions results is the reaction of 3-4 of the alkyl methylol groups with the acrylic polymer. The reactivity of the acetal linkage that facilitates the crosslinking is the same that makes these coating systems susceptible to acid hydrolysis. A simple illustration of a proposed hydrolysis mechanism for an AM coating is shown in *Figure* 2. Hydrolysis of the acetal linkage results in replacement of the hydroxyl groups on the acrylic polymer and the melamine crosslinker followed by the loss of formaldehyde from the crosslinker molecule. The loss of formaldehyde results in the conversion of the nitrogen from the acetal linkage to a primary amine. If hydrolysis is extensive, it is possible to hydrolyze all acetal linkages between the crosslinker and acrylic polymer, and if all alkyl-methylol linkages are lost, the crosslinker could be reduced to its root triazine structure, 1,3,5 triamino triazine (melamine), as shown in pathway A in *Figure* 2. In the case of partial hydrolysis, a condensation reaction between two crosslinker molecules is also possible and is illustrated in pathway B of *Figure* 2. The mechanism illustrated suggests that the remaining linkages and potential reaction products present after acid exposure could span the range from crosslinker molecules with 3-4 unperturbed acetal linkages, to those having 1 or 2 remaining linkages to the acrylic polymer, to free melamine. Unfortunately, the scheme shown in *Figure* 2 is likely an oversimplification of the hydrolysis process. In addition to hydrolysis of the acetal linkage described, it is possible that the melamine crosslinker can undergo further reaction, either as a free molecule or while partially linked to the acrylic polymer.

Reactions of melamine (1,3,5 triamino triazine) are well known and documented in the literature.[6] Exposure of melamine to acids can result in hydrolysis of the amino groups as well as salt formation depending on the conditions of exposure. It has been shown that the amino groups on the triazine ring of melamine are attacked by alkalis and acids under rigorous conditions. Boiling dilute nitric acid hydrolyzes the amino groups in stepwise manner, as shown in *Figure* 3a, producing successively ammeline, ammelide, and cyanuric acid, and one equivalent of the ammonium salt for every amine group removed. It would be reasonable to expect that functional groups associated with the crosslinker in the cured coating network would stabilize hydrolysis intermediates thereby facilitating the hydrolysis of amino groups under the conditions present in the laboratory and field exposures. An alternative and perhaps more apparent pathway for reaction under conditions consistent with those found in field exposure and the laboratory etch test is melamine salt formation. Melamine is a strong base and under more mild conditions will form salts with acids. Melamine hydrochloride, sulfate, phosphate, and nitrate have been prepared by treating melamine with the appropriate dilute mineral acid.[6] Melamine functions as a mono-acidic base in most cases, although some salts involving more than one equivalent of acid are known.[6] The reaction of melamine with sulfuric acid to form melamine sulfate is illustrated in *Figure* 3b. Likewise, reactions could be written for the formation of the hydrochloride, phosphates, and nitrate. Both reaction pathways involving amino group hydrolysis or salt formation could potentially occur with free melamine or melamine anchored to the acrylic polymer. If modification of the melamine occurs while anchored to the acrylic polymer, the modified crosslinker would remain on the clearcoat surface and may be observable using spectroscopic techniques.

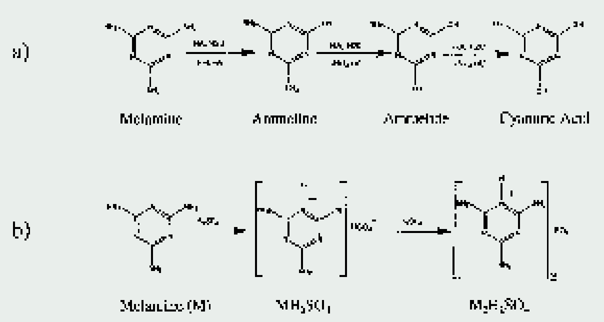

Figure 3—(a) Products formed on amino group hydrolysis of melamine, (b) melamine salt formation on treatment in dilute acids.

Surface Compositions of Field Exposed Films and Laboratory Treated Powders

In this study we have applied XPS as a tool to determine the surface composition of field exposed clearcoat panels and to compare the results with laboratory treated clearcoats of identical technologies. The motivation was to determine if changes are observable which can be used to verify the consistency of the field and laboratory degradation processes. XPS provides both elemental and chemical state information through the acquisition of survey and core level spectra, respectively. Therefore, one can compare the relative elemental surface composition as well as changes in the core level spectra to provide more information about the chemical environment (functional group/oxidation state) of detected elements. It is apparent from the reaction schemes presented, that the potential reaction products formed during acid hydrolysis of an acrylic melamine coating could be quite extensive, and identification of unique reaction products could be difficult. In addition, field exposure could result in the deposition of other extraneous material not associated with the etch phenomenon, further complicating the matter. However, to think in simple terms, it should be feasible to establish whether the crosslinker is removed from the clearcoat surface on laboratory treatment and field exposure by monitoring changes in the surface nitrogen concentration for field exposed and laboratory treated materials. Although it may not be

Table 1—Summary of XPS Elemental Surface Compositions Obtained from Control (Untreated) and Laboratory Acid Treated Acrylic Melamine and Acrylic Melamine-Silane Powdered Clearcoat Systems

Material System	Treatment	Elemental Concentration, Atomic Percent				
		C	O	N	Si	S
Acrylic melamine: Powder	Control (0 hrs)	69.7	20.7	7.6	1.8	0.2
	Lab treated: 10 hrs	72.3	23.1	1.5	2.8	0.3
	Lab treated: 120 hrs	72.9	22.7	1.3	3.0	0.2
Acrylic melamine-silane: Powder	Control (0 hrs)	74.0	21.3	2.8	1.9	0.1
	Lab treated: 4 hrs	74.0	21.6	2.3	1.9	0.2
	Lab treated: 304 hrs	75.1	21.4	1.2	2.2	0.1

possible to make unambiguous assignment of changes in core level spectra, it should be possible to compare changes in the spectra following field exposure and laboratory treatment to establish a consistency or inconsistency in the reaction products formed.

From the results presented in a previous report,[1] it is clear from both field etch ratings and laboratory performance testing that the AM and acrylic melamine-silane (AMS) technologies show the most susceptibility to etch. Therefore, we have focused the XPS studies on these systems since they offer the highest probability in identifying modifications as a result of exposure. To evaluate changes in surface elemental composition following laboratory acid treatment, XPS measurements were acquired on powder clearcoat samples, which were acid treated as part of the gravimetric weight loss measurements. Measurements were made on untreated clearcoat samples and for those treated for periods of time after which significant weight loss had occurred (0 hrs > t < 300 hrs). Summarized in *Table* 1 are the elemental compositions measured for the AM and AMS control and laboratory treated material. Compositions were measured from duplicate areas and were found to be reproducibile to ± 5%. Therefore, for brevity, only results from a single area are reported. Elements observed for the AM and AMS control panels include carbon (C), oxygen (O), nitrogen (N), silicon (Si), and sulfur (S) at concentrations consistent with that expected for these coating technologies. The majority of the C and O observed for both systems is associated with the backbone of the acrylic polymer, while the nitrogen is primarily associated with the melamine crosslinker. However, production coatings also contain other nitrogen containing additives such as UVAs and HALS. Although these additives are present in low concentrations (1-2 wt%), they may contribute to the N observed. The lower N concentration observed for the AMS system (2.8%) relative to the AM (7.6%) is consistent with the substitution of melamine crosslinking by silanol-silanol crosslinking in the AMS coating. The Si observed in the AM system is thought to be associated with a flow control additive and/or inorganic filler (silica). The Si observed for the AMS system is believed to be predominantly associated with the silanol crosslinking. Additional support for the identification of organic versus inorganic Si will be presented when discussing the Si 2p core level spectra. Low concentrations of sulfur (S) were also observed for both systems and are likely associated with a catalyst (p-toluene sulphonic acid) used to cure the coatings.

Elemental compositions measured for the laboratory treated materials are also summarized in *Table* 1. The changes observed as a result of laboratory acid treatment do not appear to be extensive for either the AM or AMS systems. For the AM system a small increase in the C, O, and Si concentrations are observed, together with a decrease in the N concentration. For the AMS system, virtually no change was observed in the C and O oxygen concentrations, and only a small decrease in the N concentration was observed. The loss of N, together with the small increased in C, O, and Si is consistent with the loss of the melamine crosslinker from the clearcoat surface. Loss of acrylic monomer fragments may also occur. However, since the coating is dominated by the acrylic resin the loss of monomer would not significantly affect the residual C and O concentrations.

To evaluate whether consistent changes in the surface elemental composition occur as a result of field exposure relative to laboratory acid treatment, XPS measurements were performed on field exposed AM and AMS systems. Field exposed panels and complimentary control panels, prepared and exposed as part of testing at the Jacksonville, FL, site, were utilized for the XPS studies. Etched areas were clearly visible on the exposed panels. Heavily etched areas, along with areas from the same panels that showed no visible signs of etch, were cut from the panels and prepared for analysis. Elemental

Table 2—Summary of XPS Elemental Surface Compositions Obtained from Control Panels and Field Exposed Films for Both the Acrylic Melamine and Acrylic Melamine-Silane Systems

Material System	Treatment	Elemental Concentration, Atomic Percent							
		C	O	N	Si	S	Al	Na	Ca
Acrylic melamine	Control	70.7	21.0	7.0	1.2	0.2	—	—	—
	Field exposed, visible etch	53.5	32.1	10.1	3.6	0.3	0.3	0.2	—
	Field exposed, no visible etch	53.7	32.6	9.5	3.3	0.3	0.3	0.2	—
Acrylic melamine-silane	Control	71.6	24.0	2.5	1.6	0.3	—	—	—
	Field exposed, visible etch	71.4	23.6	3.1	1.1	0.2	0.4	0.2	0.1
	Field exposed, no visible etch	71.5	23.6	2.9	1.2	0.2	0.4	0.1	0.2

compositions measured for the field exposed films and corresponding control (untreated) films, for both the acrylic melamine and acrylic melamine-silane systems are summarized in *Table* 2. Compositions were measured from duplicate areas. However, due to the consistency of the results, only those from a single area are reported.

The elements observed for the AM and AMS control panels include C, O, N, Si, and S at concentrations very similar to those reported in *Table* 1 for control clearcoat compositions. The association of these elements with coating components is the same as stated previously. XPS analyses from the field exposed coatings are also summarized in *Table* 2. In addition to the C, O, N, Si, and S observed for the control films, the exposed panel surfaces for both systems also contain low levels of elements such as aluminum (Al), sodium (Na), and calcium (Ca). The presence of these elements has been reported in previous studies of environmental etch.[3] As will be discussed later, these are thought to be primarily associated with inorganic compounds (silicates) from atmospheric particulates. In addition to the observation of Al, Na, and Ca on the exposed panel surfaces, it is apparent that significant differences in the C, O, N, and Si concentrations are observed for the AM system on field exposure. The C concentration has decreased, and the O, N, Si, and S concentrations have increased following field exposure. No difference was observed between heavily etched and visibly unetched areas suggesting that similar chemical changes have occurred at the surface, even in areas showing significant differences in the extent of physical damage. For the AMS system, only a small increase in the nitrogen concentration was observed in addition to the appearance of the Al, Na, and Ca following field exposure.

To compare the relative changes in crosslinker concentration following field exposure and laboratory acid treatment one can look at changes in the N/C atomic ratio. Shown graphically in *Figure* 4 are the N/C atomic ratios for the control, field exposed films, and laboratory acid treated powders. The N/C ratio for the AM and AMS after laboratory acid treatment both show a decrease consistent with a loss of N due to removal of the melamine crosslinker. Conversely, for the AM and AMS field exposed film, an increase in the relative N/C ratio is observed. The increase in the N/C ratio as a result of field exposure and decrease in this ratio on laboratory treatment are consistent for both the AM and AMS systems. An enhancement of the N concentration on field exposure suggests that some N containing component from the coating is accumulating at the surface as a result of field exposure and may reflect an accumulation of crosslinker associated reaction products. An explanation for the differences in surface nitrogen concentrations following laboratory acid treatment and field exposure may lie in the differences of the exposure processes. A discussion of this will be deferred until after the presentation of the core level spectra.

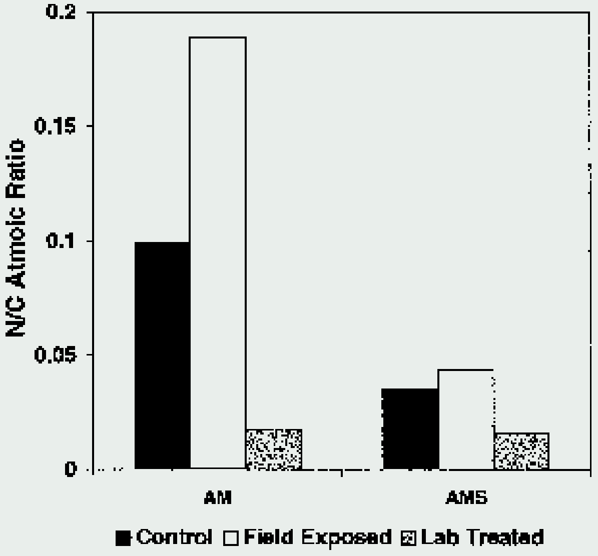

Figure 4—Comparison of elemental atomic ratios for the control film, field exposed film, and laboratory acid treated powder for the acrylic melamine system.

XPS High Resolution Core Level Spectra

In addition to the measurement of the elemental composition of the control, field exposed, and laboratory treated materials, high resolution core level spectra were also acquired. The core level spectra provide more information on the chemical environment (functional group/oxidation state) of detected elements, and, therefore, could be useful in further comparing similarities and differences between field exposed and laboratory treated materials. Core level C 1s, N 1s, O 1s, Si 2p, and S 2p spectra were acquired for the laboratory treated and field exposed AM and AMS systems. From the hydrolysis scheme presented in *Figure* 2, it is apparent that the primary reaction products would involve some modification of the melamine crosslinker. Since the nitrogen in the system is dominated by that associated with the melamine crosslinker, modification of the crosslinker would be most apparent through changes in the N 1s spectra. Therefore, our initial discussion will focus on the presentation of the N 1s core level spectra.

The N 1s core level spectra acquired from untreated, field exposed, and laboratory treated AM and AMS materials are summarized in *Figure* 5. The spectra for the untreated materials were fit by three components at binding energies of 398.3 eV, 399.4 eV, and 400.4 eV. The two lower binding energy components are associated with the ring and pendant nitrogen of the melamine crosslinker, respectively (see *Figure* 1). These assignments have been confirmed through the acquisition of spectra from melamine and hexamethoxymethyl melamine standards. The component at 400.4 eV has not been assigned, but was also observed in the spectra of the melamine standards, indicating that it may not be due to a unique N species but to some peak asymmetry. However, production coatings also contain other low concentration N containing additives, and contributions from these additives cannot be precluded. The N 1s spectra from the field exposed films are also displayed in *Figure* 5. The spectra from both the AM and AMS systems show a

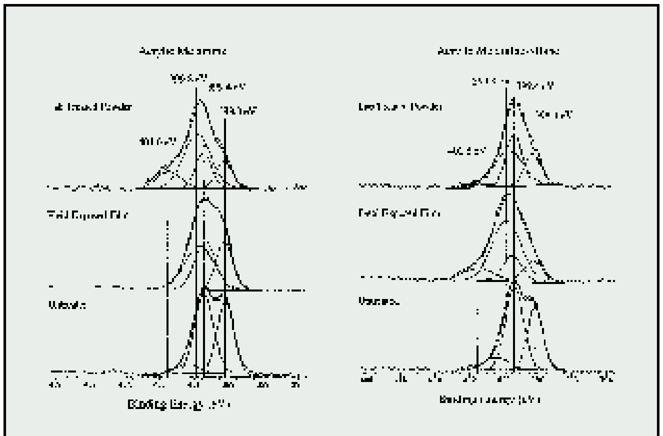

Figure 5—XPS N 1s spectra of untreated, field exposed films, and laboratory acid treated powders for the acrylic melamine and melamine-silane systems.

broadening on the high binding energy side of the spectral envelope, relative to the untreated materials, indicating that changes have occurred as a result of field exposure. These spectra were fit by constraining the position, widths, and relative intensities of the crosslinker components from the untreated spectra, while adding additional components necessary to fit the residual area in the spectral envelope. For the AM system, this was accomplished with a single component at a binding energy of 399.8 eV, while the AMS system required components at 399.8 eV and 401.6 eV. The N 1s spectra for the laboratory treated powders, *Figure* 5, also showed very similar broadening on the high binding energy side of the spectral envelope, and likewise were fit by additional components at binding energies of 399.8 eV and 401.6 eV. The component at a binding energy of 399.8 eV is a prominent component of the N spectra and is consistently observed for both material systems following both field exposure and laboratory treatment. At present, this component cannot be unambiguously assigned, but it is important to note that the change in the spectral envelope necessitating the addition of this component is consistently observed for both the field exposed and laboratory treated materials, suggesting that a similar modification has occurred as a result of each treatment. Further discussion of the assignment of this peak will be deferred until later. The component at 401.6 eV is observed for both material systems, although was not consistently observed for both field exposure and laboratory acid treatment. The binding energy position of this feature is consistent with that of an ammonium salt.[7] Ammonium salts can form on amino group hydrolysis of melamine as shown in *Figure* 3. For the laboratory treated materials, the salt formed would be ammonium sulfate. XPS N 1s spectra acquired from an ammonium sulfate standard indicated the position of the N 1s peak at 401.3 eV, similar to that observed for the laboratory treated and field exposed materials. The apparent inconsistency in the presence of this component likely results from the solubility of a sulfate species and the history of the treated material.

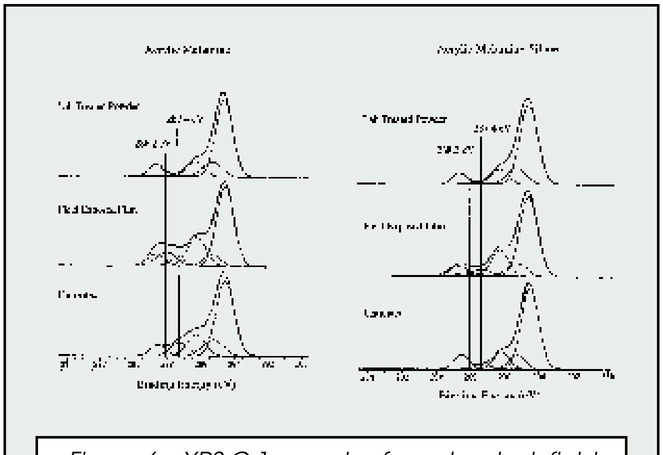

Figure 6—XPS C 1s spectra for untreated, field exposed films, and laboratory acid treated powders for the acrylic melamine and melamine-silane systems.

The C 1s spectra for the two production clearcoat systems are summarized in *Figure* 6. Focusing on the spectra for the untreated materials, the peak envelopes were fit with five components. The peak components occurring at binding energies of 284.6 eV, 285.3 eV, 286.2 eV, and 288.6 eV are assigned to the aliphatic (—CH$_2$—), carbon at an α-position from a carboxyl carbon ($\underline{\text{C}}$—CO$_2$—R), ether/hydroxyl ($\underline{\text{C}}$—O—C, $\underline{\text{C}}$—OH), and ester/carboxyl ($\underline{\text{C}}$O$_2$—R) carbon, respectively. Each of these carbon components are predominantly associated with the acrylic polymer resin (see *Figure* 2). The spectral component at a binding energy of 284.7 eV is associated with the ring carbon of the melamine crosslinker. The assignment of this component is supported by our own independent measurement of melamine and hexamethoxymethyl melamine standards. The lower relative intensity of the melamine crosslinker component (287.4 eV) observed for the AMS system is consistent with the lower melamine concentration of this formulation. Spectra for the field exposed panels are also shown in *Figure* 6 and were fit by constraining the peak positions and widths of the five spectral components of the acrylic resin described previously. The peak envelope, however, was not fit well in the region between the components at 287.4 eV and 288.6 eV. A sixth component, at a binding energy of 288.2 eV, was necessary to fit the additional area under the spectral envelope for the field exposed material. This was necessary for both material systems, however, is more apparent for the AM system. The spectra for the laboratory treated materials were fit in a similar manner using the constrained peaks from the untreated spectra. As is apparent, the peak component at 287.4 eV associated with the melamine crosslinker has decreased in intensity following laboratory treatment, consistent with the loss of melamine from both systems with acid treatment. Because of the very low spectral intensity in the region between 287.4 eV to 288.6 eV it was not possible to assess the necessity of a peak at 288.2 eV to fit the spectral envelope. This does not preclude the possibility of a very low concentration of this species for the laboratory treated material.

The O 1s and Si 2p core level spectra acquired for the two clearcoat systems are shown in *Figures* 7 and 8, respectively. The O 1s spectra of the untreated and labo-

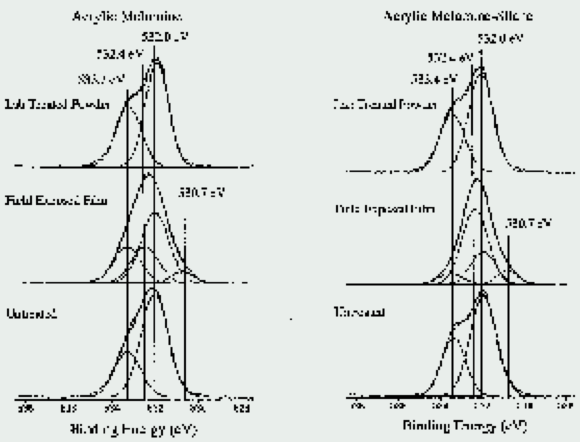

Figure 7—XPS O 1s spectra for untreated, field exposed film, and laboratory acid treated powders for the AM and AMS systems.

ratory treated AM and AMS systems were best fit with two peaks at binding energies of 532.0 eV and 533.4 eV. These peaks are assigned to the ether/hydroxyl and ester carbonyl oxygen from the acrylic resin. The field exposed spectra for both systems, in addition to the components described earlier, were best fit by the addition of two peaks at binding energies of 530.7 eV and 532.4 eV. The peak at 530.7 eV occurs at a binding energy consistent with metal oxides. Assignment of the component at 532.4 eV is not as straightforward. However, some insight is gained from the Si 2p spectra shown in *Figure* 8. The Si 2p spectra for the untreated material from both systems could be fit by two peaks at binding energies of 101.8 eV and 103.2 eV, representing organic and inorganic silicon, respectively. The untreated and lab-treated spectra for both material systems are dominated by the organic components, while the field exposed materials are dominated by the inorganic component. The domination of the inorganic component for the field exposed films likely accounts for the feature observed in the field exposed O 1s spectra. Independent measurements from SiO_2 (quartz) indicate an O 1s binding energy of 532.5 eV, consistent with that used to fit the field exposed O 1s spectra of *Figure* 7. The presence of the inorganic silicon, together with the cations (Ca, Al, Na) observed on the field exposed films suggests that they may be the result of the deposition of silica and/or silicates from atmospheric particulates. However, silica is often used in production systems to control rheological properties of the coating, and the observation of inorganic silicon at the surface following field exposure may be the result of a bulk silica filler. Core level spectra were also acquired for the S 2p region. In all instances where S was detected, the S 2p binding energy was found to be 168.4 eV, consistent with S in a sulfate species.

It is apparent that changes are observable in the core level spectra as a result of laboratory treatment and field exposure. In the case of the N 1s spectra, additional peak components at binding energies of 399.8 eV and 401.6 eV were observed for both the lab treated and field exposed materials. The feature at 401.6 eV is consistent with N in an ammonium species, possibly ammonium sulfate. The formation of ammonium sulfate through the hydrolysis of melamine amine groups is plausible as shown in *Figure* 3. The peak component at 399.8 eV may be the result of an additional hydrolysis reaction product. However, UVA and HALS additives present in the coatings also contain N, and it is possible that these additives concentrate on the surface as a result of laboratory and field exposure and contribute to the changes observed in the N 1s spectra. As an attempt to rule out contributions from production additives, laboratory acid treatment was carried out on a simple model AM system produced by crosslinking an acrylic monomer with hexamethoxymethyl melamine. The model coating had no nitrogen containing additives such as UVA or HALS commonly found in production systems. Core level N 1s spectra acquired from the acid treated model system also showed a consistent broadening on the high binding energy side of the spectral envelope and could be fit by using an additional peak at a binding energy of 399.8 eV consistent with that used for the laboratory and field exposed production systems. As was found for the laboratory treated production systems, no other changes in the C 1s and O 1s spectra were observed following acid treatment aside from a loss in the carbon component associated with the melamine crosslinker. The ability to reproduce the N 1s spectral feature at 399.8 eV on acid treatment of a model coating strongly suggests that the additional component observed in the sulfuric acid treated model and production materials, as well as the field exposed production material, is the result of a hydrolysis product involving the melamine crosslinker and not the result of an additive contribution.

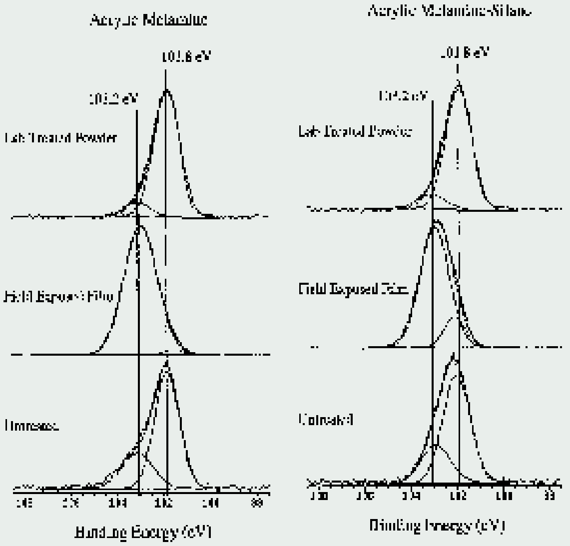

Figure 8—XPS Si 2p spectra for untreated, field exposed film, and laboratory acid treated powders for the AM and AMS systems.

The association of the additional features in the core level spectra with a hydrolysis product involving the melamine crosslinker is further supported by the XPS results obtained from acid treated melamine and

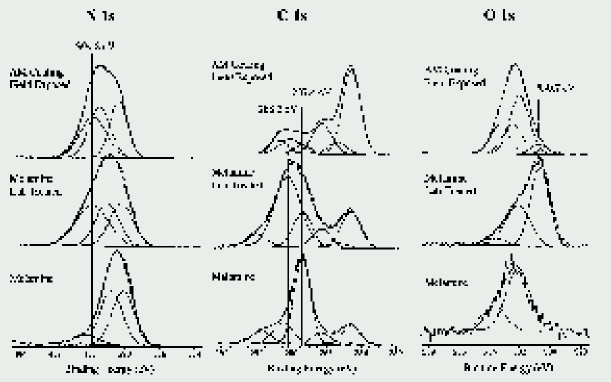

Figure 9—XPS N 1s, C 1s and O ls spectra for untreated and laboratory acid treated melamine and field exposed AM systems.

hexamethoxymethyl melamine standard materials. Commercially available melamine and hexamethoxymethyl melamine were treated in sulfuric acid under conditions consistent with that of the laboratory acid treatment (pH = 2.0, 60°C). The treated materials were analyzed using XPS to determine if changes in the core level spectra following acid treatment are consistent with those observed on laboratory and field exposure of the production and model coating systems. The N 1s, C 1s, and O 1s core level spectra from untreated and acid treated melamine as well as the field exposed production coating are shown in *Figure* 9. The N 1s spectra for the untreated melamine is composed of three components. The two lower binding energy components of equal intensity are due to the ring and pendent N of the melamine. Following acid treatment, the spectral envelope shows a broadening to higher binding energy and was fit with an additional component at 399.8 eV consistent with the field exposed and laboratory treated production materials. The C 1s spectra for the untreated melamine is dominated by the component at 287.4 eV and is assigned to the C in the triazine ring. The other low concentration C components are likely the result of residual carbon contamination. Following acid treatment, a broadening to higher binding energy is also observed and was fit with an additional component at 288.2 eV consistent with that observed for the field exposed production material. Melamine should be oxygen free, however, some low concentration oxygen containing species were observed at binding energies consistent with organic contamination. After acid treatment a prominent low binding energy peak appeared at 530.7 eV, consistent with a feature observed in the field exposed production system. The acid treatment of hexamethoxymethyl melamine was also studied and resulted in equivalent changes in the N 1s, C 1s, and O 1s spectra.

The results presented for the acid treatment of the neat crosslinkers strongly suggest that the modifications observed in the N 1s, C 1s, and O 1s for the field exposed materials are the result of the presence of a melamine hydrolysis product. Changes observed in the N 1s spectra on laboratory treatment suggest that similar modification of the crosslinker is occurring under the conditions of the laboratory test. Similar changes were not observed in the C 1s and O 1s spectra on laboratory treatment, likely due to the dramatic decrease in the crosslinker concentration resulting in a low concentration of residual modified melamine. The loss of the crosslinker reduces the crosslinker C concentration to the extent that the spectra is dominated by the acrylic resin carbon, making it extremely difficult to detect low concentrations of the reaction product. Similar arguments can be made for the domination of the O 1s spectra by the acrylic polymer components. Changes are observable in the N spectra because it is dominated by the contributions from the melamine crosslinker. This is further supported by the changes observed in the surface elemental composition following laboratory treatment and field exposure. As described previously, the N/C ratio for the AM and AMS systems after laboratory acid treatment both show a decrease consistent with a loss of N due to removal of the melamine crosslinker. Conversely, for the AM and AMS field exposed films, an increase in the relative N/C ratio is observed. The increase in the N/C ratio as a result of field exposure and the decrease in this ratio on laboratory treatment are consistent for both the AM and AMS systems. An explanation for the differences in surface nitrogen concentrations following laboratory acid treatment and field exposure may lie in the differences of the exposure processes.

The laboratory test procedure relies on the exposure of a bulk coating to a well-controlled acidic environment and gravimetrically following weight loss as a function of exposure time. Although exposure conditions such as pH and temperature were chosen to simulate field conditions, other details of the exposure process were altered as a necessary requirement of the weight loss measurements. Because it was not feasible to conduct weight loss measurement on free films, the laboratory test relies on performing the test on clearcoat powders, which are ground to a uniform particle size to increase the surface area in a controlled manner. In addition, during the exposure process, the powdered clearcoat is dispersed in an acidic solution that is continuously agitated. The solution is purposely agitated so that unbound fragments, released as a result of crosslink hydrolysis, are removed from the clearcoat surface and lost into solution. The rate of weight loss associated with the removal of unbound material is what allows for an assessment of the relative acid hydrolysis resistance. Therefore, the decrease in N concentration for the AM and AMS systems on laboratory acid treatments is the result of hydrolysis of acetal linkages and removal of the melamine crosslinker from the powdered clearcoat surface. Details of the environmental exposure process will be understandably different. First of all, field exposure is conducted on a free film. However, this would not solely explain the differences observed in the surface composition. We believe that the primary difference lies in the laboratory and field exposure processes. Field degradation is thought to occur as a result of acid hydrolysis resulting from exposure to acid rain and dew condensation which forms droplets on the surface of the clearcoat. As the water evaporates, pH increases, and hydrolysis occurs in isolated areas on the panel surface. In this scenario, reaction products that are formed as a result of hydrolysis go into solution (depending on their solubility), however, as evaporation progresses the reaction products are redeposited in the etched areas. As the result of multiple events, reaction products are carried away leading to the evolution of etch pits. However, the reaction products may not be removed as efficiently as those formed in the laboratory test, thus leading to an accumulation on the surface. Therefore, we believe the differences observed in the surface concentration of the modified crosslinker lie in the differences in the removal of degradation products from the clearcoat surface.

Although it is clear that laboratory treatment and field exposure results in the formation of a reaction product involving the melamine crosslinker, there are a number of potential products that could be formed. The two reaction pathways that have been documented for the reaction of melamine in an acidic medium were outlined in *Figures* 2 and 3. The first involves the cleavage of the acetal linkage resulting in the removal of melamine from the system (*Figure* 2). The formation of free melamine would not result in the changes observed in the N 1s core level spectra. Additional reactions of melamine are outlined in *Figure* 3 and involve the hydrolysis of amino groups to form ammeline, ammelide, and cyanuric acid and subsequent formation of the ammonium salt. A component in the N 1s spectra was found at a binding energy consistent with ammonium sulfate suggesting that some amino group hydrolysis does occur. This reaction, however, is favored when melamine is exposed to acids at high temperature.[6] A second pathway is shown in *Figure* 3b and involves the formation of melamine salts on exposure of melamine to dilute acids. To more conclusively define the primary reaction product formed on laboratory treatment and field exposure would necessitate a more detailed study of the product formed on laboratory acid treatment the neat crosslinkers. Work in this area has been completed using bulk quantitative elemental, XPS, and infrared analyses of the acid-treated melamine crosslinkers. Results are consistent with the formation of a melamine salt (melamine sulfate) on acid treatment of the crosslinkers as well as laboratory and field exposure of the production coating systems. Details of this work and results obtained will be presented in a subsequent report. What is most important to note at this point is that the degradation products that form on acid treatment of pure melamine as well as laboratory and field exposure of production systems show strong similarities, suggesting that the conditions used in the laboratory test are realistically reproducing the field degradation chemistry.

CONCLUSIONS

In this study, we have applied XPS as a tool to verify that the exposure conditions used in the laboratory gravimetric etch test realistically simulate field degradation pathways. XPS was used to look at the elemental surface compositions and high resolution core level spectra of laboratory treated powders and field exposed panels to determine if similar chemical trends were observable. The elemental surface compositions observed for the laboratory treated powders and field exposed panel surfaces showed inconsistencies in the residual crosslinker concentrations. For the laboratory treated materials, a reduction in N was observed, consistent with the acid hydrolysis of the acetal linkage and subsequent removal of the melamine crosslinker. However, the surface nitrogen concentration was observed to increase for the field exposed panels suggesting that there may be an accumulation of N containing material on the panel surfaces. The differences observed are not believed to be the result of inconsistencies in exposure conditions but more likely differences in the exposure processes for the lab testing and environmental exposure.

High resolution core level spectra obtained support the idea of consistent exposure conditions and similar degradation pathways. Changes in the N 1s, C 1s, and O 1s core level spectra were observed following field exposure. Consistent changes in the N 1s spectra were observed for the laboratory treated materials. The changes were shown to be consistent with modification of the melamine crosslinker on acid treatment. Results to be presented in a subsequent report indicate that the modifications observed are predominantly the result of melamine salt formation, most likely melamine sulfate. However, the occasional observation of ammonium sulfate indicates that amino group hydrolysis also occurs. The consistency in the formation of a melamine salt and ammonium sulfate on both field exposure and laboratory acid treatment strongly suggests that the laboratory treatment conditions realistically simulate the field exposure conditions. These results give credence to an acid hydrolysis mechanism for environmental etch resulting from acid rain exposure. The consistency in the lab and field results lends additional confidence that the conditions used in the laboratory realistically reflect the field exposure conditions.

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