Mechanism for Environmental Etch of Acrylic Melamine-Based Automotive Clearcoats: Identification of Degradation Products

P.J. Schmitz, J.W. Holubka, and Li-Feng Xu—Ford Motor Company*

This paper focuses on defining the reaction mechanism involved in the environmental etch of acrylic melamine-based automotive clearcoats via an identification of reaction products. This has been accomplished through a comparative study of products formed on acid treatment of neat crosslinkers, and those formed following laboratory acid treatment and field exposure of acrylic melamine clearcoat systems. Bulk elemental, X-ray photoelectron spectroscopy (XPS), and infrared (IR) analyses of sulfuric acid-treated melamine crosslinkers show that acid hydrolysis results primarily in the formation of melamine sulfate. Melamine sulfate formation was also observed following laboratory and field exposure of acrylic melamine clearcoat systems. These results confirm that the primary mode of melamine crosslink decomposition is through hydrolysis of acetal linkages and subsequent formation of melamine sulfates. However, data show that hydrolysis of pendent amino groups on the triazine ring also occurs.

INTRODUCTION

Environmental etch is a clearcoat appearance issue associated with the formation of what appears to be non-removable water spotting. The etch phenomenon is believed to be primarily the result of crosslink hydrolysis as a result of acid rain exposure.[1-4] The physical damage resulting from etch is associated with the localized loss of material resulting in visible pitting of the clearcoat surface.[5] Environmental etching of automotive clearcoats has received considerable attention recently, with studies focused on gaining a more thorough understanding of the chemical mechanism(s) associated with the etch phenomenon.[1-2,6] Understanding the chemical mechanisms responsible for etch degradation not only provides insight into how to prevent etch from a formulation standpoint, but also allows one to design reliable laboratory tests for product evaluation. We have previously described the development of a laboratory test for the evaluation of the acid etch resistance of automotive clearcoats and efforts made to verify the consistency between laboratory and field degradation chemistry.[5-6] Although this work has brought us closer to defining the chemical mechanism(s) associated with environmental etch, there are still unanswered questions. X-ray photoelectron spectroscopy (XPS) results presented in a previous report[6] clearly show that equivalent modification of the melamine crosslinker occurs as a result of both laboratory and field exposure of acrylic melamine-based clearcoat systems. This was evident by the observation of an additional feature in the XPS N 1s spectra occurring at a binding energy of 399.8 eV following laboratory acid treatment or field exposure. Although consistent modification was apparent, a positive identification of the reaction product(s) formed was not pursued. The work contained in this report builds on previous findings and focuses on providing more conclusive evidence of the reaction product(s) formed on laboratory acid treatment and field exposure of acrylic melamine-based systems. This has been accomplished through the study of reaction products formed on acid treatment of neat crosslinkers, and correlation of properties, both chemical and spectroscopic, between these reaction products and those formed following laboratory acid treatment and field exposure of acrylic melamine clearcoat systems. The results presented and conclusions drawn help to more conclusively define the

---

*Ford Research Laboratory, P.O. Box 2053, MD 3083 SRL, Dearborn MI 48121. E-mail: pschmit1@ford.com

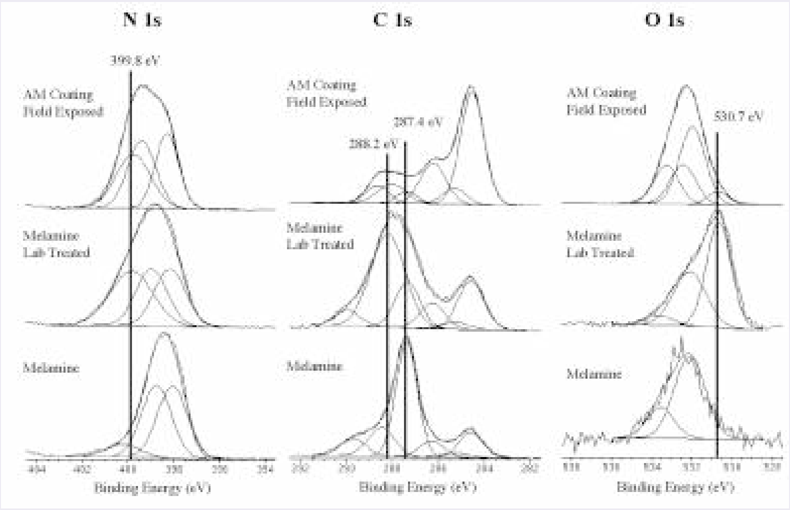

Figure 1—XPS N 1s, C 1s, and O 1s spectra for untreated and laboratory acid-treated melamine and a field acrylic melamine clearcoat system.

mechanism involved in the environmental etch of acrylic melamine clearcoats, and offers an alternative explanation for the origin and contribution of inorganic components often observed on the surface of field exposed coatings.

EXPERIMENTAL

Materials

All materials and reagents for this work were used as received from the supplier. Melamine (1,3,5,-triaminotriazine) was obtained from Aldrich Chemical Company. Hexamethoxymethyl melamine (Resimene 747) was obtained from Solutia. Inorganic materials were obtained from J.T. Baker. De-ionized water was used throughout the study.

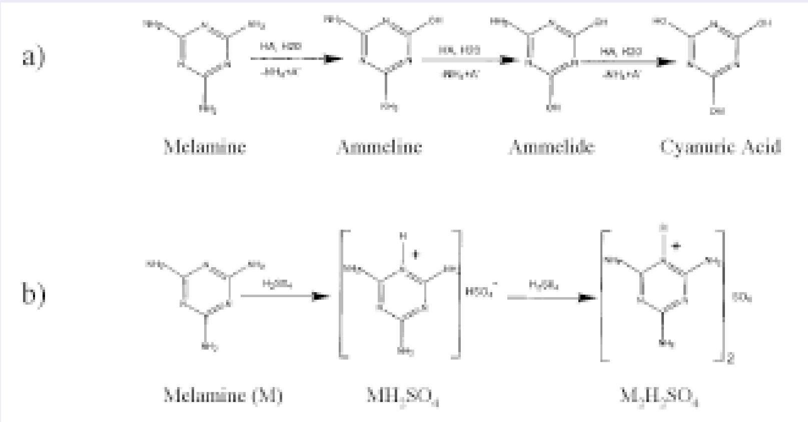

Figure 2—Potential reaction pathways for acid-treated melamine: a) Amino group hydrolysis of melamine, b) melamine salt formation on treatment in dilute acids.

Laboratory Acid Exposure Conditions

The acid exposure conditions used in this study were consistent with conditions defined in previous reports.[5-8] In a typical experiment, the material was exposed to pH 2 sulfuric acid and constantly agitated in a reciprocal water bath shaker maintained at 60°C. After several hours of reaction time, the solid residue was separated from the reaction mixture through filtration, rinsed with de-ionized water, and dried. All base treatments were carried out using a 10% Na_2CO_3 solution at room temperature.

Field Etch Exposure Studies

Field etch exposure studies were conducted during a 16-week time period between May and September of 1996 and 1997. Clearcoat panels were exposed to the environment at a Jacksonville, FL, exposure site. Panels were neither washed nor evaluated during the 16-week exposure period to minimize possible surface contamination of the clearcoats with wash solutions.

Carbon, Hydrogen, and Nitrogen Analyses

The carbon (C), hydrogen (H), and nitrogen (N), bulk analyses were conducted by Galbraith Laboratories, Inc. Compositions were determined by combustion according to ASTM D 5373/ASTM D 5291. Samples submitted for elemental analysis were thoroughly dried in an air circulating oven at 70°C for two hours prior to submission. The compositions were reported as weight percents (wt%). The contributions from other elemental components were determined indirectly by difference.

X-ray Photoelectron Spectroscopy

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 1×10^{-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 leastsquares 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.

Table 1—Carbon, Hydrogen, and Nitrogen Bulk Composition for Untreated and Acid-Treated Melamine

		Composition, wt%		
Compound	Element	Theoretical	Untreated	Acid-Treated
Melamine	C	28.57	28.39	20.54
	H	4.76	4.83	4.67
	N	66.67	67.09	48.44
	Residual	0.00	-0.31	26.35

RESULTS AND DISCUSSION

Review of Laboratory Acid Treatment and Field Exposure of Acrylic Melamine Coatings

As described in previous reports,[5-6] sulfuric acid treatment of melamine crosslinkers results in modifications of the XPS N 1s, C 1s, and O 1s spectra that are consistent with those observed for field exposed acrylic melamine based clearcoat systems (see *Figure* 1). The spectral modifications observed were the appearance of additional features in the N 1s, C 1s, and O 1s spectra at binding energies of 399.8 eV, 288.2 eV, and 530.7 eV, respectively. A more detailed discussion of the assignment of all spectral components, and the approach used to fit the core level spectra can be found elsewhere.[6] These features were not observed in unexposed acrylic melamine coatings and were found not to result from the accumulation of additives (i.e., UVAs or HALS) at the surface following laboratory and field exposure.[6] The consistencies in the core level spectra for the acid treated crosslinker and field exposed coatings strongly suggest that the surface modifications observed for environmentally exposed acrylic melamine systems are the result of the accumulation of an acid hydrolysis reaction product involving the melamine crosslinker.

Although it is clear that 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 are outlined in *Figure* 2. The first, *Figure* 2a, involves the stepwise hydrolysis of the amino groups to form ammeline, ammelide, and cyanuric acid and the subsequent formation of one equivalent of ammonium salt for each amine group removed.[9] This reaction, however, is favored when melamine is exposed to acids at high temperature. Melamine is a strong base and under more mild conditions will form salts with acids. A pathway for salt formation is shown in *Figure* 2b and involves the formation of melamine sulfate on exposure of melamine to dilute sulfuric acid. Melamine functions as a mono-acidic base in most cases, although some salts like sulfate can involve more than one equivalent of acid as shown in *Figure* 2b. Melamine hydrochloride, phosphate, and nitrate have also been prepared by treating melamine with the appropriate dilute mineral acid.[9] Although exposure conditions occurring during environmental exposure, and those used in laboratory testing,[5] would tend to be most consistent with those resulting in the pathway shown in *Figure* 2b, there was experimental evidence that pathway 2a cannot be completely discounted. This is based on the occasional observation of an N 1s spectral feature occurring at a binding energy of 401.6 eV, which is consistent with an ammonium sulfate [$(NH_4)_2SO_4$] product. Since an ammonium sulfate product is water soluble, it would be easily removed from the surface of field and laboratory exposed materials and may account for its occasional observation. Therefore, it is not clear whether the spectral modifications observed for the acid-treated crosslinker and coatings are the result of amino group hydrolysis or melamine salt formation. To more conclusively define the primary reaction product(s) formed on laboratory treatment and field exposure requires a more detailed analysis of the acid-treated crosslinkers. Therefore, fundamental studies were undertaken to more conclusively identify reaction products formed following field and laboratory exposure of acrylic melamine-based clearcoat systems.

Acid Treatment of Melamine

In previous investigations it was found that acid treatment of melamine (1,3,5 triamino triazine) resulted in the appearance of XPS spectral features that were consistent with those observed for laboratory acid-treated and field exposed acrylic melamine clearcoat systems.[6] To gain more insight into the reaction product(s) formed on acid treatment of melamine, the pure material was treated in sulfuric acid solution (pH=2.0, 60°C), rinsed, and dried. The acid-treated melamine was in the form of a white crystalline powder. Transmission infrared spectra clearly indicated that modifications had occurred as a result of acid treatment. Most notable was the loss of

Table 2—Comparison of the Bulk Composition Measured for Acid-Treated Melamine with the Theoretical Bulk Composition of Potential Reaction Products

		Potential Reaction Products				
Element	Melamine Acid-Treated	Ammeline	Ammelide	Cyanuric Acid	MH_2SO_4	$N_2H_2SO_4$
C	20.54	28.35	28.13	27.91	16.07	20.57
H	4.67	3.94	3.13	2.33	3.57	4
N	48.44	55.12	43.75	32.56	37.5	48
Residual	26.35	12.60	25.00	37.21	42.86	27.43

Table 3—Composition of Melamine and Acid-Treated Melamine Reaction Product Determined from Peak Fit Components of XPS Core Level Spectra

	Elemental Composition, Atomic %			
Element	Melamine Experimental	Melamine Theoretical	Melamine Acid-Treated Experimental	$M_2H_2SO_4$ Theoretical
C	33.3	33	30	26.1
N	66.7	67	49	52.2
O	—	—	17	17.4
S	—	—	4	4.4

an absorbance at 815 cm^{-1} that has been assigned to the triazine moiety of these materials.[2,10] To more quantitatively assess the modifications occurring as a result of acid treatment, bulk elemental analyses were obtained. This was accomplished through bulk C, H, and N analysis as described in the Experimental Section. Results from the bulk analysis of untreated- and acid-treated melamine are shown in *Table* 1. The experimentally determined composition (wt%) of the pure melamine material is consistent with the theoretical bulk composition, verifying that the analysis is capable of accurately determining the elemental composition for these systems. Results from the C, H, and N analysis of acid-treated melamine is also shown in *Table* 1. As evident, modification of the relative C, H, and N composition has occurred as a result of acid treatment. Most notable is that the C, H, and N weight fractions account for only ~75% of the treated material. Since the analysis only assesses the weight fraction of the C, H, and N, any additional components (e.g., oxygen, etc.) will be determined by difference and lumped into a residual weight fraction. The residual weight fractions are also summarized in *Table* 1. The observed modification could result from amino group hydrolysis which would remove nitrogen and add oxygen (see *Figure* 2a) or through sulfate formation which would incorporate oxygen and sulfur. To determine if either of these scenarios is consistent with changes in composition measured for the acid-treated melamine, the theoretical compositions for the amino hydrolysis products (ammeline, ammelide, and cyanuric acid), as well as melamine sulfate can be compared to the experimentally measured composition. Summarized in *Table* 2 are the measured C, H, N, and residual weight fractions for the acid-treated melamine, and the theoretical compositions of potential reaction products. It is evident from the data presented in *Table* 2 that rather good agreement is found between the acid-treated melamine and melamine sulfate, $M_2H_2SO_4$. The agreement of the experimental and theoretical compositions of the acid-treated melamine with $M_2H_2SO_4$ are consistent enough that it appears as though the formation of the melamine salt is the primary reaction product. Although the C, H, N weight fractions are consistent with that of $M_2H_2SO_4$, this is not positive verification that the residual weight fraction is associated with sulfate. Further evidence supporting this assumption is obtained from XPS analyses performed on the acid-treated melamine. XPS results revealed that sulfuric acid treatment of melamine resulted in increased oxygen and the incorporation of sulfur. The S 2p binding energy was measured at 168.3 eV, consistent with the sulfur present as a sulfate species. Reconstruction of the composition of the reaction product can also be accomplished through the use of the XPS core level spectra. As was shown in *Figure* 1, additional components were apparent in the N 1s, C 1s, and O 1s spectra following acid treatment. To determine if the concentration of the elements associated with these features are consistent with that for melamine sulfate ($M_2H_2SO_4$), components from the fits were used to construct the relative C, O, N, and S composition of the modified melamine. To verify that it is possible to estimate the composition in this manner, the exercise was completed using the C and N spectra of the untreated melamine. Results, presented as atomic composition, are summarized in *Table* 3. Hydrogen cannot be detected using XPS and therefore is excluded from the composition. For the untreated melamine, the C component at a binding energy of 287.4 eV and the N components at 398.1 and eV 388.8 eV were used to determine the concentrations of C and N associated with melamine. The composition determined in this manner is consistent with the theoretical composition of melamine. Likewise, the elemental concentrations determined using the peak components of the acid-treated melamine (C peak at 288.3 eV, N peak at 399.8eV, O peak at 530.7 eV, S peak at 168.3 eV) are compared in *Table* 3 with the theoretical composition of melamine sulfate ($M_2H_2SO_4$). As is apparent, all the quantitative results are consistent with the formation of $M_2H_2SO_4$ following sulfuric acid treatment of melamine.

Table 4—Reversibility of Bulk Composition of Acid-Treated Melamine on Treatment with Weak Base

	Experimental wt%		
Element	Untreated	Acid-Treated	Acid + Base Treated
C	28.39	20.54	28.51
H	4.83	4.67	4.86
N	67.09	48.44	66.47
Residual	-0.31	26.35	0.16

For further verification that the acid treatment results in salt formation, one can look at the reversibility of the acid-base reaction. If melamine sulfate is being produced on acid exposure, reaction of the salt with weak base (Na_2CO_3) should result in conversion back to melamine. This would not be the case if acid treatment resulted in amino group hydrolysis. Bulk C, H, and N analysis of Na_2CO_3 treated reaction product yielded the results summarized in *Table* 4. These data show that following base treatment, the composition reverts back to that consistent with untreated melamine. These data are completely consistent with salt formation on acid treatment, which is reversible on reaction in base. XPS measurements were also carried out on untreated, acid-treated, and acid-treated and base neutralized materials. All XPS quantitative results were completely consistent with the conversion of the salt back to melamine following treatment in base. In addition, it was found that modifications observed in the XPS N1s, C 1s, and O 1s spectra of melamine following acid treatment were removed after reaction in Na_2CO_3 solution. This is illustrated in the spectra of *Figure* 3. Additional infrared measurements of the acid- and base-treated melamine (data not shown) also illustrated the reversibility of this process. The bulk quantitative results and the base reversibility of the acid-treated melamine conclusively demonstrate that exposure of melamine to sulfuric acid under the conditions used in this work results primarily in the formation of melamine sulfate. It should be noted that the same series of experiments were carried out on hexamethoxymethyl melamine [$C_3N_6(CH_3OCH_2)_6$], a functionalized melamine-based crosslinker which models more closely the crosslinker in an acrylic melamine coating. Complete hydrolysis of the methylol groups resulting in conversion to the root melamine was not obtained during acid treatment. This was evident from bulk elemental analysis, XPS, and IR results. Although complete hydrolysis was not observed, XPS results were consistent with partial hydrolysis of the methylol groups and formation of the sulfate. As was found for the acid treatment of melamine, the features attributable to the melamine salt were reversible following base treatment.

All results presented demonstrate that exposure of melamine to sulfuric acid under the conditions used in laboratory testing result in the formation of melamine sulfate. Data was also presented showing the consistency in XPS spectral changes observed for field exposed clearcoat films which implies that melamine sulfate is also formed following field exposure. As a final verification that the spectral changes observed for field exposed films are the result of melamine salt formation, the intact clearcoat films were base treated under the same conditions as the melamine crosslinkers to see if this would result in the removal of the spectral features associated with a melamine salt. The N 1s, C 1s, and O 1s spectra obtained for untreated, field exposed, and field exposed base-treated films are summarized in *Figure* 4. It is apparent that the spectral features associated with the melamine sulfate are indeed removed following base treatment of the field exposed films. This could result from the reaction of the salt or removal of the reaction product from the surface during the treatment procedure. However, also listed in *Figure* 5 beside each N 1s spectrum, are the N/C atomic ratios for the untreated, field exposed, and field exposed based-treated materials. As is evident, only a slight decrease in the relative N concentration is observed following base treatment, and is not large enough to account for the complete loss of the sulfate related N 1s spectral component. Therefore, the results are most consistent with conversion of melamine sulfate back to melamine during base treatment. The consistency in the formation of a melamine sulfate on both field exposure and laboratory acid treatment strongly suggests that the reaction pathway illustrated in *Figure* 2b occurs, and is likely the dominant reaction pathway.

Chemical Mechanism for Environmental Etch of Acrylic Melamine Clearcoats

All the experimental data presented here and in previous reports[5-6] are consistent with the environmental etch of acrylic melamine clearcoats resulting from acid hydrolysis. The exposure of clearcoats to moisture, reduced in pH due to the incorporation of industrial pollutants containing sulfur oxides (SO_x), results in hydrolysis of acetal linkages as illustrated in *Figure* 5. As the hydrolysis progresses, crosslinker backbone cleavage occurs resulting in network fragmentation and subsequent loss of material. Results from this investigation indicate that the degradation products observed are consistent with a melamine sulfate species. Melamine is known to form salts with mineral acids.[9] It is not entirely clear whether the melamine, which is complexed with the sulfate, is free melamine or that which is still an-

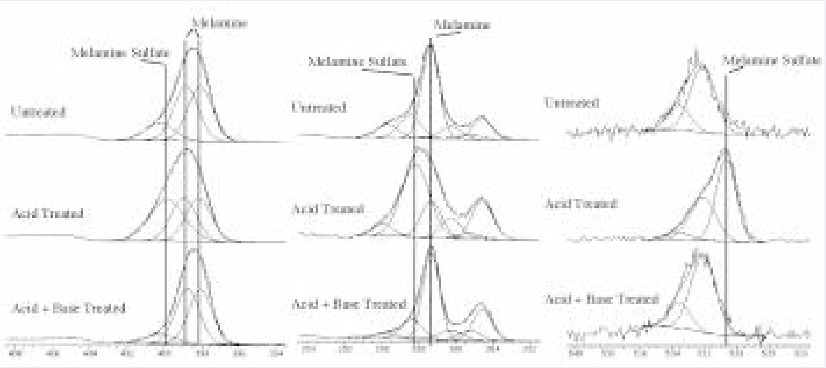

Figure 3—XPS N 1s, C 1s, and O 1s core level spectra for untreated, acid-treated, and acid + base treated melamine.

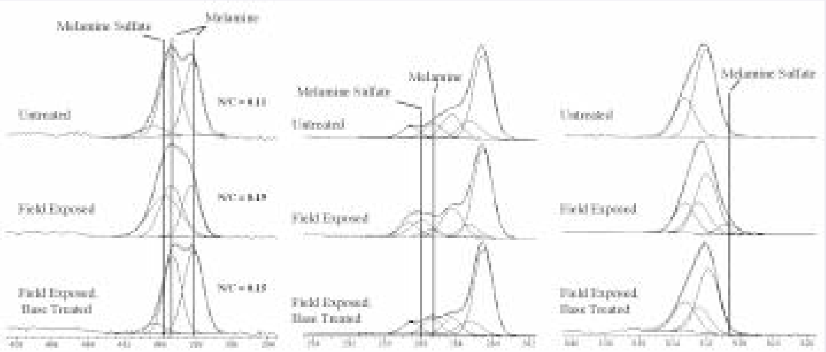

Figure 4—XPS N 1s, C 1s, and O 1s core level spectra for untreated, field exposed, and field exposed and base-treated acrylic melamine clearcoat film.

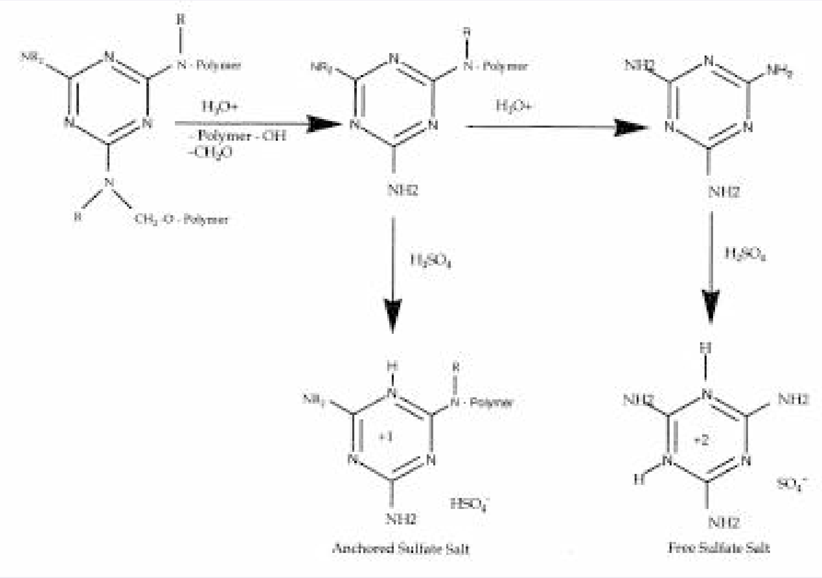

Figure 5—Acid hydrolysis scheme for acrylic melamine crosslinked systems.

chored to the polymer through intact acetal linkages. Depending on the extent of hydrolysis, hydrolysis products could span the range from loss of a single acetal linkage to loss of all acetal linkages between the crosslinker and acrylic polymer. The extent of reaction cannot be assessed directly from the data obtained here. Data presented in a previous report[6] indicated that field exposed materials showed an accumulation of a nitrogen containing species on the surface which we believe is associated with melamine sulfate. An accentuation of a crosslinker (the primary nitrogen containing component) reaction product could occur either through the residual anchoring of the crosslinker with preferential loss of the surrounding polymer matrix, or through accumulation of insoluble reaction products (see *Figure* 5). Either is plausible since melamine sulfate has been reported to have limited water solubility (0.19 g/100 g of H_2O at 20°C) and therefore could accumulate on the clearcoat surface.[9] In either case it is clear that the primary reaction product is that of a melamine sulfate, confirming an acid hydrolysis mechanism for environmental etch.

The majority of the experimental data points to a reaction pathway consistent with salt formation. However, the occasional observation of ammonium sulfate for both field and laboratory exposed materials implies that a second competing pathway can occur.[6] The laboratory exposure conditions are much less aggressive than those described in the literature for amino group hydrolysis.[9] However, for the field exposed materials, the temperature conditions experienced for dark colored vehicles in Florida could approach those described in the literature for amino group hydrolysis.[9] Also, since ammonium species were never observed for the laboratory acid-treated neat melamine crosslinkers, this raises the question of the influence of the acetal linkages present on the crosslinked melamine systems on the kinetics of the reaction pathway. In a crosslinked system for example, the amino hydrolysis intermediate may be stabilized through electron pushing characteristics of the R groups present resulting in some ammonium sulfate formation. Although there is evidence of reactions occurring along both pathways, it is presumed that formation of the melamine salt is the dominant pathway. In either case both pathways are consistent with acid hydrolysis.

Most studies detailed in the literature agree that environmental etch is a chemical degradation process resulting from acid hydrolysis of the coating. However, some studies have concluded that the etch phenomenon is the result of a physical disruption of the surface by the incorporation of inorganic material. These reports have focused on observations of metal containing moieties on the surface of field exposed coatings. Most notably, calcium sulfate has been reported.[11] They suggest that environmental etch is to a large extent due to the physical deposition of inorganic materials on the surface that embed themselves into the coating as it softens under high temperature excursions encountered on sunny summer days. We have also observed low levels of certain elements including calcium, sodium, and aluminum on field exposed panels exhibiting etch.[6] Attempts within this laboratory to produce surface spotting by depositing inorganic sulfates on the surface followed by anneals to simulate field conditions have failed. As we discussed in a previous report,[6] the metals observed could be from atmospheric particulate contamination in the form of silicates, which were introduced from rain and dew exposure. However, it is also plausible that the crosslinker sulfate species could undergo cation exchange leading to the formation of other inorganic sulfates. The inorganic materials observed are not believed to contribute to the chemical or physical degradation that is responsible for the surface spotting associated with etch. Rather, the etch phenomenon is associated with a localized loss of material resulting from crosslink hydrolysis following acid rain exposure.

CONCLUSIONS

All the experimental data presented here and in previous reports,[5-6] are consistent with the environmental etch of acrylic melamine clearcoats resulting from acid hydrolysis. Inorganic deposits, although present on field exposed coatings, are not believed to significantly contribute to the etch phenomenon. Control studies from acid-treated melamine crosslinkers have shown that hydrolysis of melamine results in the formation of melamine sulfate moieties. All data from field exposed acrylic melamine systems are consistent with the formation of similar sulfate species involving the melamine crosslinker. Although the primary mode of melamine crosslink decomposition is through hydrolysis of acetal linkages and subsequent formation of melamine sulfates, data show that amino group hydrolysis may also occur.

References

(1) Gregorovich, B.V. and Hazan, I., *Prog. Org. Coat.*, 245, 131-146 (1994).

(2) Rogers, W.R., Garner, D.P., and Cheever, G.D., "Study of the Attack of Acidic Solutions on Melamine-Acrylic Basecoat/Clearcoat Paint Systems," JOURNAL OF COATINGS TECHNOLOGY, *70*, No. 877, 83 (1998).

(3) Wernståhl, K.M. and Carlsson, B., "Durability Assessment of Automotive Coatings—Design and Evaluation of Accelerated Tests," JOURNAL OF COATINGS TECHNOLOGY, *69*, No. 865, 69 (1997).

(4) Shultz, U. and Trubiroha, P., ASTM STP 1294, Herling, R.J. (Ed.), American Society for Testing and Materials, Philadelphia, 1996.

(5) Holubka, J.W., Schmitz, P.J., and Xu, L., "Acid Etch Resistance of Automotive Clearcoat. I: Laboratory Test Method Development," JOURNAL OF COATINGS TECHNOLOGY, *72*, No. 901, 77 (2000).

(6) Schmitz, P.J., Holubka, J.W., and Xu, L., "Acid Etch of Automotive Clearcoats II: Comparision of Degradation Chemistry in Laboratory and Field Testing," JOURNAL OF COATINGS TECHNOLOGY, *72*, No. 902, 53 (2000).

(7) Edney, E.O., Cheek, S.F., Corse, E.W., Spence, J.W., and Haynie, F.H., *J. Environ. Sci. Health Part A*, *24*, No. 5, pp. 439-457 (1989).

(8) Edney, E.O., Cheek, S.F., Stiles, D.C., Corse, E.W., and Wheeler, M.L., *Mater. Perform.*, *27*, No. 3, pp. 47-50 (1988).

(9) Smolin, E.M. and Rapoport, L., *The Chemistry of Heterocyclic Compounds, S. Triazines and Derivatives*, Interscience Publishers Inc., New York, 1959.

(10) Bauer, D.R., "Chemical Criteria for Durable Automotive Topcoats," JOURNAL OF COATINGS TECHNOLOGY, *66*, No. 835, 57 (1994).

(11) Wolff, G.T., Rogers, W.R., Collins, D.C., Verma, M.H., and Wong C.A., *J. Air Waste Manage. Assoc.*, *40*, 1638-1648 (1990).