Acid Etch Resistance of Automotive Clearcoats. I: Laboratory Test Method Development

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

This paper reports on the development of a laboratory test procedure for the evaluation of the environmental etch resistance of clearcoats. The test evaluates the bulk acid hydrolysis resistance of clearcoats by gravimetrically following material weight loss as a function of exposure time to a sulfuric acid solution, under conditions that simulate outdoor exposure. The bulk hydrolysis resistance of five production clearcoat technologies including acrylic melamine, acrylic melamine-silane, carbamate, acrylic urethane, and epoxy acid were evaluated. Results from the weight loss measurements were consistent with those anticipated based on the coating systems bulk chemistry and inherent hydrolysis resistance, for clearcoat systems processed under nominal processing conditions. The relative rankings from the laboratory test were found to correlate with field etch ratings. The test method is inexpensive, quantitative, and generates repeatable results that are not subject to environmental variations associated with current field etch testing.

INTRODUCTION

Environmental etch is a clearcoat appearance issue associated with the formation of what appears to be non-removable water spotting. The physical damage resulting from etch is associated with the localized loss of material resulting in visible pitting of the clearcoat surface. The etch phenomenon is believed to be primarily the result of crosslink hydrolysis as a result of acid rain exposure.[1-4]

Field exposure testing is commonly employed to evaluate a clearcoat's resistance to acid etch. At present, field testing of automotive coatings for environmental etch normally involves exposure of test panels at outdoor sites, e.g., commonly Jacksonville, FL. Following exposure the panels are evaluated and rated by visual inspection and assigned a number from 1 to 10 which categorizes the severity of the etch into three groups defined as: (1) 0-3, imperceptible to the customer; (2) 4-6, perceptible to the customer but repairable by polishing; and (3) 7-10, perceptible to the customer and repairable by repaint. As would be expected, the evaluation process is subjective, time consuming, and expensive. In addition, from year to year, exposure conditions are neither controllable nor reproducible, adding additional inconsistencies that could lead one to the conclusion that differences in etch performance of a particular coating is more the effect of an episodic event near the exposure site rather than the geographic region where the test is conducted. Partly as a realization of this, attempts have been made by the coatings industry to develop more controllable laboratory tests that simulate field exposure. A number of such laboratory tests have been developed,[3] for example, the Dupont gradient bar test.[3a] However, these tests still rely on a qualitative visual ranking to judge performance. It is apparent that current field evaluations and laboratory tests are complicated by inconsistencies in exposure and subjectivity in etch evaluation. Therefore, the motivation for this work was to develop a controlled laboratory test for etch that is free from the inconsistencies and subjectivity of current field and laboratory testing.

The work presented here summarizes efforts-to-date regarding the development of a laboratory test procedure for evaluating acid etch that is based on the measurement of the relative bulk acid hydrolysis resistance of clearcoat systems. The test procedure relies on exposure of bulk coating to a well controlled acidic environment, and gravimetrically following material weight loss as a function of exposure time. The weight loss experienced by the coating is taken to be a direct indication of its hydrolysis rate and therefore etch resistance. Results are presented verifying the consistency of laboratory and field performance rankings of the etch resistance of a number of current clearcoat technologies.

---

*Ford Research Laboratory, Dearborn, MI 48121-2053.

EXPERIMENTAL

Materials

The automotive clearcoat materials used in this study were 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.

Field Etch Exposure Studies

Field etch exposure studies were conducted during a 16-week time period between May and September of 1994 and 1996. A limited sampling of clearcoats, representing five generic clearcoat technologies (i.e., acrylic melamine, acrylic urethane, epoxy acid, silane-acrylic melamine, and acrylic melamine-carbamate) were evaluated for etch. Identical clearcoat formulations were used over the three-year period for all field and laboratory testing. Panels of clearcoats representing the five generic clearcoats were included in an etch evaluation study conducted at three evaluation sites including Boston, MA; Jacksonville, FL; and Atlanta, GA. A duplicate set of panels, to be utilized for characterization purposes, were exposed at the Jacksonville, FL, site during the same time period. These latter panels were neither washed nor evaluated during the 16-week exposure period. This was done to minimize possible surface contamination of the clearcoats with wash solutions. All other test panels, at all three evaluation sites, were washed and evaluated every four weeks according to normal evaluation process. These panels were rated by visual inspection and assigned a number from 1 to 10 categorizing the severity of the etch observed.

Gravimetric Laboratory Test Procedure for Acid Etch Resistance

The detailed procedure for the gravimetric laboratory test for environmental etch involves three major steps: (1) sample preparation; (2) acid exposure; and (3) weight loss measurements.

Sample Preparation: In a typical etch resistance determination, a 25-50 micron clearcoat film is applied to a 10.2 cm × 30.5 cm glass panel with a BYRD applicator. The clearcoat is then crosslinked by heating in an electric convection oven according to the suppliers specified cure schedule. The cured coating is then peeled from the glass panel with the assistance of a razor. This is repeated three times to generate three individual films of a single technology to assure replication. A powder, suitable for acid exposure, is prepared by cryo-grinding the free clearcoat film in a Spex 6700 Freezer/Mill (or equivalent) at liquid nitrogen temperature 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. This is accomplished by heating for two hours at 70°C, followed by equilibration for two hours under conventional ambient laboratory conditions (25°C and 50% RH), and then weighing to .001 g. This drying procedure is repeated until the variation between two consecutive weighings are within ± .001 g. When this has been accomplished, the powder is acceptable for acid exposure.

Acid Exposure: Three samples of the dried clearcoat powder generated from unique clearcoat films are prepared for acid exposure using the following procedure. For each individual sample, about one gram of the dried coating powder is weighed out to an accuracy of 0.001 g (Mettler AE 200 electronic scale) and the material is dispersed in 18 ml of aqueous sulfuric acid of pH = 2.0 ± 0.1 (pH is determined using a pH meter) in a 22 ml glass vial. The vial containing this mixture is sealed using a cap made of an inert material (i.e., teflon or polyolefin) and is placed in a reciprocal water bath shaker (New Brunswick Scientific, R76) with a shaker speed of 100 cycles per minute. The vials are constantly agitated at 60°C, and are removed at specific exposure times for weight loss determinations.

Weight Loss Determinations: The weight loss determination is accomplished by separating the acid exposed powder from the mixture by filtration through a fine fritted filter funnel with a nominal maximum pore size from 4 to 5.5 microns. The filter funnel must be brought to constant weight to ± .001 g prior to filtering. Following the filtering process, the powder is thoroughly washed with DI water and the residual material and filter funnel are dried to constant weight (two hours at 70°C followed by equilibration at ambient laboratory conditions, 25°C and 50% RH for two hours). Consecutive weighings must agree within ± .001 g to be considered at constant weight. The results for the three samples are reported as % weight loss defined by the expression:

$$\% \text{ Weight Loss} = [1 - (\text{weight after exposure} / \text{initial weight})] \times 100$$

RESULTS AND DISCUSSION

Review of the Etch Phenomenon

The first step in the development of a laboratory test for etch involves a physical/chemical characterization of the etch phenomenon. Environmental etch has been studied quite extensively, and a number of significant reports describing the phenomenon and the environmental conditions that contribute to etch have appeared in the literature.[1-7] Results from these investigations suggest that environmental etch is primarily the result of crosslink hydrolysis as a result of acid rain exposure.[3a,6] Based on data from the literature, it has already been fairly well established that the degradation chemistry associated with etch is the result of acid hydrolysis of network crosslinks. Etch degradation (pitting) results when low pH rain or dew condensation forms droplets on the surface of a clearcoat. As evaporation occurs pH decreases and initiates hydrolysis in isolated areas. As hydrolysis progresses, crosslinker-backbone bond cleavage occurs resulting in network fragmentation and subsequent loss of material. As the result of multiple events, droplets preferentially form in depressions left from previous events and etch pits evolve.

Our own independent observations from field panels, as well as from some simple acid drop tests in the laboratory seemed to substantiate reports that the etch phenomenon is the result of localized loss of material resulting from acid exposure, and not a surface staining phenomenon. A photomicrograph of a clearcoat etch crater, representative of the general surface phenomenon observed in degraded areas of field exposed panels, is shown in *Figure* 1. The extent of material removal can be further assessed using laser profilometry and a line scan taken across an etch pit is shown in *Figure* 2. In general, etched areas visible to the customer are consistent with paint removal down to 3-5 microns, as illustrated in *Figure* 2, where the depth of clearcoat removal over a length of about 2 mm area is on the order of 3 microns. However, clearcoat erosion can be in excess of 10-15 microns, and in extremely severe instances, it can go down to the basecoat (30-40 microns). As a result of our initial survey of etch, it was clear that it is associated with erosion of the clearcoat and not just a surface staining (spotting) phenomenon.

SELECTION OF A METRIC FOR ETCH EVALUATION: With the existing data from the literature, it was clear that a test for etch must focus on evaluating the acid hydrolysis resistance of clearcoats. In addition, a quantifiable metric must be used which is directly linked to the field degradation phenomenon. Efforts to quantify etch through spectroscopic means are challenged by a number of issues such as sampling depth (etch being a surface phenomenon), probe size (consistent and representative sampling of surface area), availability of instrumentation, etc. However, the most difficult issue to resolve in the development of a spectroscopic metric associated with crosslink-hydrolysis, is the technique should be applicable to a wide range of clearcoat technologies of significantly different chemistry. Since a spectroscopic based metric, by definition, focuses on following the change in a spectral feature associated with a specific bond or functional group, a tractable feature associated with the hydrolysis process would need to be identified, and would likely be different for each generic clearcoat technology. It was apparent that a spectroscopic approach for quantifying etch would be a complicated endeavor.

Based on previous studies and our own independent survey of clearcoat etch, it was apparent the etch phenomenon, although induced by acid hydrolysis, was also associated with loss of material from the clearcoat surface. It became apparent that weight loss as a result of acid exposure may be a reliable metric that could be used in a simple laboratory test to assess the etch resistance of clearcoat technologies. The measurement of weight loss would be quantitative and the metric would be independent of coating chemistry. In addition, gravimetric analyses could be performed using common equipment (scales and constant temperature shaker baths) that should be available to most analytical laboratories. For these reasons, the development of a gravimetric test which evaluates the bulk hydrolysis resistance of a coating seemed to be a realistic approach to evaluate the etch resistance of clearcoats.

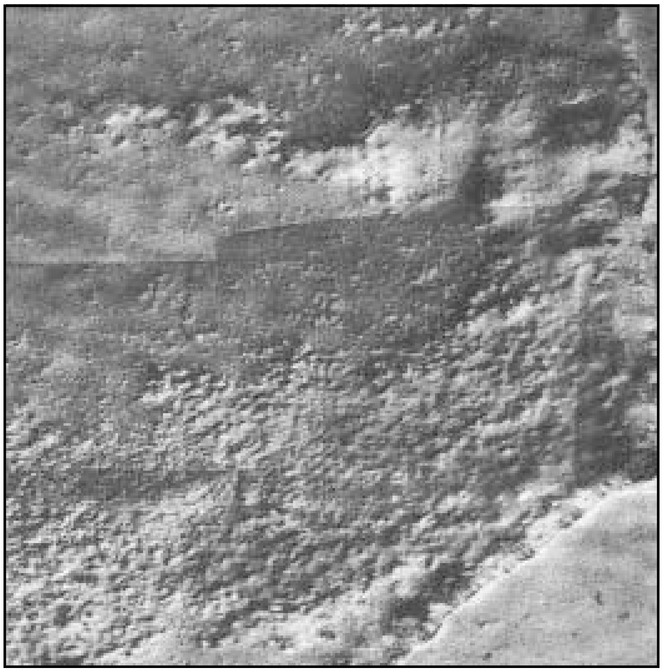

Figure 1—Micrograph of a typical clearcoat etch crater (magnification = 50x).

Gravimetric Test for the Evaluation of Environmental Etch

The laboratory etch test developed for this study involves exposure of a clearcoat material to an aqueous solution of sulfuric acid and follows weight loss as a function of exposure time. Sulfuric acid has been used as the primary component of synthetic acid rain in previous studies[3b,3c,4,5] and was, therefore, chosen for the initial test solution for the gravimetric test. The acid solution is prepared so as to achieve a pH of 2, consistent with other studies indicating the pH level necessary to induce visible surface etching.[1-3] The exposure experi-

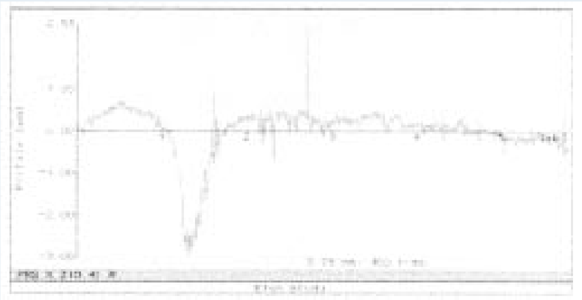

Figure 2—Line scan with a profilometer across an etch crater, indicating etch is associated with the removal of material from the clearcoat surface (abscissa scale in mm, ordinate scale in µm).

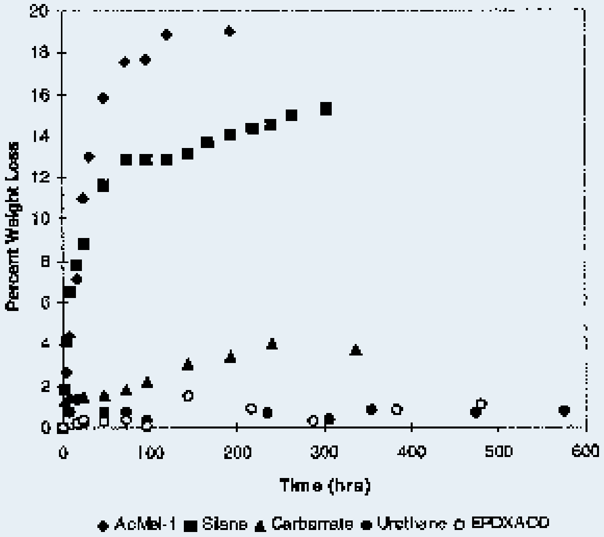

Figure 3—Weight loss as a function of acid exposure time for five production clearcoat technologies including acrylic melamine (AcMel-1), acrylic melamine-silane (silane), acrylic melamine-carbamate (carbamate), acrylic urethane (urethane), epoxy acid (EPOXACD).

ment is conducted at 60°C, which represents the commonly accepted surface temperature of a dark colored vehicle on a typical summer day in Florida. Therefore, the pH and temperature conditions were chosen to represent the harshest conditions likely seen by vehicles in the field.

Etch is a surface phenomenon, however, following weight loss from the surface of a paint film was found to be unfeasible due to the very low weight loss values obtained. More significant and reliable measurements were obtained by increasing the surface area that is exposed to the acidic solution through the use of powdered clearcoat material. Sample preparation requires that the clearcoat be ground to a uniform particle size. This is necessary because the etch hydrolysis reaction on cured paint material is a heterogeneous process, and the surface area of the powdered clearcoat will play a significant role in affecting the rate of removal of material by influencing how much of the clearcoat is available for surface reaction. Controlled mixing during the exposure process is also critical for repeatability of the experiment for similar reasons. The rate of weight loss will be influenced by the efficiency that reaction products (polymer fragments) are removed from the surface of the clearcoat powder during the etch test.

The laboratory etch test is a gravimetric analysis; therefore, accurate and precise weight determinations are critical to the accuracy and precision of the results obtained. Careful attention must be paid to bring all filtering equipment and powdered clearcoat material (reacted and unreacted) to constant weight prior to weight loss determinations and reporting. This requires the powder coating material to be dried and weighed at least twice to assure a constant weight is attained.

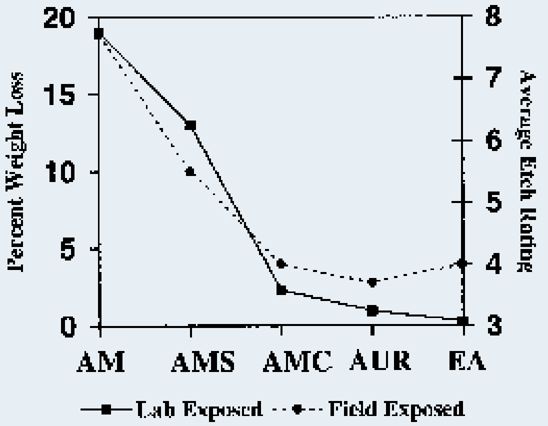

Figure 4—Comparison of etch resistance rankings from lab testing (96 hr exposure time) and field testing. (AM = acrylic melamine, AMS = acrylic melamine-silane, AMC = acrylic melamine-carbamate, AUR = acrylic urethane, EA = epoxy acid.)

Evaluation of Gravimetric Laboratory Test for Etch Resistance

To evaluate the gravimetric laboratory test and its ability to differentiate etch performance of different clearcoat technologies, five generic clearcoats were selected based on an existing knowledge of their bulk chemistry, and their use in commercial applications within the automotive industry. Samples of fully formulated production clearcoats representing acrylic melamine, acrylic melamine-silane, acrylic urethane, acrylic melamine-carbamate, and epoxy acid (listed in order of increasing etch resistance) were prepared and tested according to the experimental procedures described in the Experimental Section of this report. Results obtained for these systems are shown in *Figure* 3, where the percent weight loss exhibited by the coatings are plotted as a function of acid exposure time. From the data, a clear differentiation between the extent of weight loss experienced by the different technologies can be made. Differences are apparent in both the initial slope of the curves, and the apparent "plateau" that is achieved after prolonged exposure time. The epoxy acid coating and the acrylic urethane coatings, which have no hydrolysis prone melamine crosslinks, perform exceptionally well showing minimal weight loss (~1%) even after prolonged exposure up to 600 hr. In contrast, the acrylic melamine system, formulated entirely with a melamine crosslinker and having acetal based crosslinks that are prone to acid hydrolysis, shows nearly 20 times more weight loss. Weight loss measurements were only carried out to 300 hr for this system. When exposure times exceeded 300 hr, depolymerization of the material was so extensive that the residual material was not in a state that was conducive to gravimetric analyses (i.e., clearcoat became gelatinous). Intermediate performance was observed with the silane modified acrylic melamine system. This technology contains reduced concentrations of melamine crosslinker relative to conventional acrylic melamine formulations. The crosslinking chemistry is augmented with additional crosslinking involving silanol-silanol condensation. The carbamate material shows a significantly lower weight loss suggesting better etch performance. Although relying on a melamine-based crosslinker, the carbamate coating contains almost no acetal crosslinks in the final cured film. Instead, crosslink formation is accomplished through reaction of amide functionality on the acrylic polymer with the melamine to form carbamate (urethane) crosslinks which are more acid hydrolysis resistant. What is important to note here is that the general trend in weight loss observed is consistent with that expected based on the material systems bulk chemistry and inherent hydrolysis resistance of the crosslinks.[8]

To determine the reliability of the weight loss data depicted in *Figure* 3, a statistical analysis was conducted. The variance in weight loss was determined for the acrylic melamine, melamine-silane, and urethane systems subjected to 8 hr and 48 hr exposure times. The 95% confidence intervals for all three coatings were found to be ≤8% and ≤9% (of the measured weight loss value) for the 8 hr and 48 hr exposure times, respectively. The data included in this statistical analysis included duplicate results from two independent laboratories. This analysis confirms that differences in weight loss measured for these systems are statistically significant, and that this methodology can be used to evaluate etch performance.

Evaluation of Field Etch and Correlation with Laboratory Results

Although the results from the laboratory test are consistent with expected relative rates of hydrolysis of their coating crosslinks,[3a,8] it was important to correlate laboratory ranking with field etch performance on identical material systems. A correlation with field data would establish that laboratory test results were correctly predicting field performance. In addition, it was important to establish that field and laboratory degradation mechanisms are consistent. In order to accomplish these tasks, field panels exhibiting the etch phenomenon were used for performance ranking as well as physical and chemical characterization.

Field evaluations of these specific automotive clearcoat technologies have been conducted on a yearly basis for several years. As a means of generating test panels for performance ranking and additional characterization, a limited sampling of clearcoats, representing five generic clearcoat technologies, were evaluated at three U.S. sites. The panels to be used for characterization were neither washed nor evaluated during the 16-week exposure cycle. This was done to minimize handling and possible surface contamination of the clearcoats with wash solutions that could interfere with subsequent analyses. At the conclusion of the 16-week exposure period, all panels included in the study were evaluated and assigned an etch rating. A comparative summary of the final etch ratings presented in *Table* 1. As is apparent, the field evaluations of environmental etch can produce a remarkable range in etch performance results that appear to be dependent on both the chemistry of the clearcoat being evaluated and the site of the field exposure. The variance that is observed suggests that the specific location and climate present can strongly influence the apparent results. This is shown by the observation that the etch ratings for all the clearcoats are generally the best in Boston and worse in Atlanta and Jacksonville, even though identical sets of paint panels were sent to all the sites. Climatic data[4,5] shows that differences in pH at these sites are no greater than about 0.5. These results suggest that the acid fallout causing etch is more of a local episodic occurrence rather than a factor characteristic of a specific geographic area. The results from *Table* 1 show that the etch performance increases from top (acrylic melamine) to bottom (acrylic urethane), consistent with the results from the laboratory test. This is displayed graphically in *Figure* 4, where the weight loss observed in laboratory tests, and the average etch rating from the field tests are compared. It is evident that the relative laboratory performance and field etch ratings show very similar trends. A similar plot of the weight loss from laboratory testing versus the average field rating is shown in *Figure* 5. This plot displays the degree of correlation between the laboratory results and the field results for conventional clearcoat systems cured under nominal cure schedules. The correlation observed indicates that the field etch performance is realistically being predicted by the laboratory test method described in this report.

Table 1—Summary of Field Etch Ratings from 1996 Exposure Studies. (Etch Rating Scale: 0 = best (no etch), 10 = worst)

	Field Etch Ratings Exposure Site		
Clearcoat Technology	**Boston**	**Atlanta**	**Jacksonville**
Acrylic melamine	6.0	8.0	9.0
Acrylic melamine-silane	4.0	7.0	5.5
Acrylic melamine-carbamate	1.5	4.5	6.0
Epoxy acid	2.5	4.0	5.5
Acrylic urethane	3.5	2.5	5.0

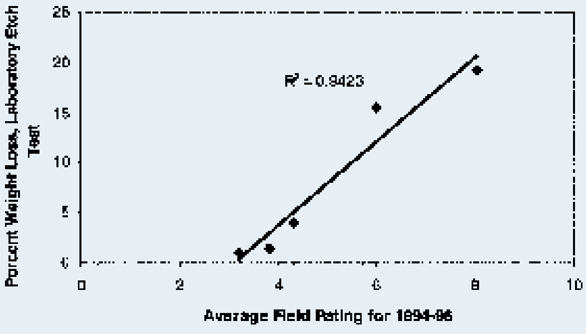

Figure 5—Correlation of lab weight loss results (96 hr exposure) and average field performance for 1994-96, for the five commercial clearcoat technologies.

CONCLUSIONS

This report summarizes efforts-to-date regarding the development of a laboratory test procedure for the evaluation of the acid etch resistance of clearcoats. The test developed is a simple and inexpensive quantitative test that can be performed using common equipment found in most analytical laboratories. The laboratory test for etch evaluates the bulk acid hydrolysis resistance of clearcoats by gravimetrically following material weight loss as a function of exposure time to a sulfuric acid solution. The rate of material weight loss is taken to be a direct indication of the materials hydrolysis resistance. The bulk hydrolysis resistance of five production clearcoat technologies including acrylic melamine, acrylic melamine-silane, acrylic melamine-carbamate, acrylic urethane, and epoxy acid were evaluated using the laboratory test method developed. Results showed that the trend in material weight loss observed for these systems is consistent with that expected based on the material systems bulk chemistry and inherent hydrolysis resistance. In addition, the relative rankings from the lab test were found to correlate with field etch ratings for these systems over the past several years. In addition to verifying a correlation of laboratory and field etch performance, it is equally important to verify that the conditions used in the laboratory test reproduce the same field degradation chemistry to assure that the laboratory test is evaluating realistic performance characteristics. Evidence supporting consistent degradation pathways between laboratory acid exposure and field exposure was obtained through surface analytical measurements. These results will be presented in a subsequent report.

The laboratory etch test described in this report appears to satisfactorily assess the field etch performance of a range of clearcoats of distinctly different chemistry. However, there are potential situations where the test results may not realistically evaluate field etch performance. This can occur in clearcoat systems where modification of the top surface of the coating has occurred, either through post treatment or migration of surface active hydrolysis resistant additives, resulting in surface properties which enhance etch performance. Because the laboratory test evaluates the bulk hydrolysis resistance, these systems may show poor performance in lab testing even though they show increased etch resistance in the field. The effects of these and other issues (cure temperature, catalyst levels, humidity, etc.) will be further addressed in a following report summarizing the effects of process sensitivities on laboratory etch performance, and how to deal with these special situations.

References

(1) Mohnen, V.A., "The Challenge of Acid Rain," *Scientific American*, *259*, 2, 30-38 (1988).

(2) 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).

(3) (a) Gregorovich, B.V. and Hazan, I., *Prog. Org. Coat.*, 245, 131-146, (1994); (b) 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); (c) Wernstahl, 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); (d) Shultz, U. and Trubiroha, P., *Durability Testing of Non-Metallic Materials*, ASTM STP 1294, Herling, R.J. (Ed.), American Society for Testing and Materials, Philadelphia, 1996.

(4) Wiseman, M., *Proc. IBEC '95, Automotive Body Painting*, pp. 15-24, 1995.

(5) 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, 439-457 (1989).

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

(7) Rodgers, 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).

(8) March, J., *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, McGraw-Hill, Inc., 1969.