

Etch Damage

to Automotive Coatings

by
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BACKGROUND

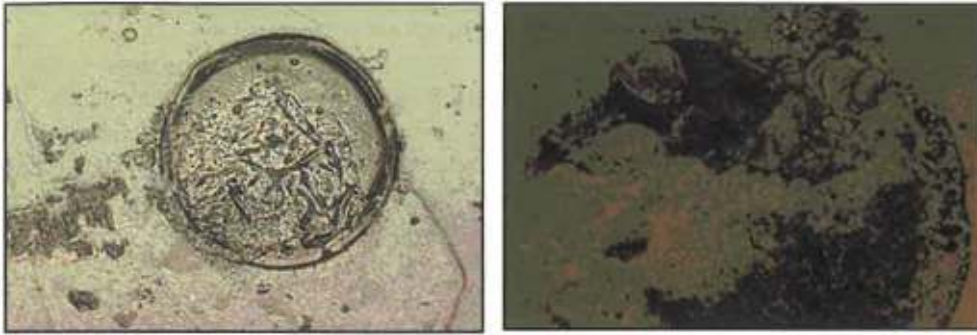
When automobile manufacturers began using clearcoat systems on vehicles in the 1980s, both dealerships and buyers complained about the occurrence of ring, or "water spot," etches on the horizontal surfaces of vehicles. This type of paint damage was found predominately in locations with certain environmental conditions; specifically, locations with more humidity, acid rain, and higher temperatures.

Normal rain is slightly acidic because of dissolved carbon dioxide; however, acid rain is defined differently and is known to cause more severe damage to coatings. Acid rain (acid deposition) occurs in highly industrialized regions of the United States and results when sulfur dioxide (SO_2) and nitrogen oxide (NO_x) gases react in the atmosphere with water and oxygen to form mild solutions of sulfuric and nitric acid. An additional contribution in the South arises from the fact that both sunlight and high temperatures increase the rate of most of these reactions. Both sulfur dioxide and oxides of nitrogen are by-products of transportation and industrial processes such as those used in utility plants and manufacturing. Acid deposition occurs in three forms: (1) wet deposition (dew, rain, snow, sleet, and hail); (2) dry deposition (particles and gases); and (3) vapor deposition (clouds or fog occurring in coastal areas).

It is believed that as a result of acid deposition on the surface of the automotive coating, these etches are formed. Coating material is lost as a result of acid catalyzed hydrolysis of the chemical bonds within the coating. When enough bonds are broken, polymer molecules or fragments become detached from the rest of the coating and are washed away. The lost material is greatest at the edge of water droplets where the acid is concentrated during evaporation. This leads to the familiar ring or "water spot" pattern. These spots cannot be removed by washing (*Figure 1*).

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Figure 1—Examples of water spot and etch defects.



nized scale from 0 (best) to 10 (worst). This rating scale is summarized in *Table 1*.

EXPERIMENTAL

In an effort to determine the specific mechanisms and conditions that cause acid etch damage to automotive coatings, a weather station was designed and set up on the Bayer test site on Blount Island in May of 2004. This

BLOUNT ISLAND EXPOSURES

Blount Island is a major import/export facility for vehicles from many different automotive suppliers and the U.S. military. From 20,000 to 100,000 vehicles could be stored there at various times of the year. Testing of automotive coatings systems began on the island in the mid to late 1980s after significant damage was noted on the stored vehicles.

Blount Island, which is located in Jacksonville, FL, approximately eight miles northeast of downtown Jacksonville and nine miles west of the Atlantic Ocean, provides one of the most severe locations in North America for the summertime conditions that cause environmental etch. The high heat and humidity of the Florida climate, the amount of solar radiation, the nearby coal burning power plant and paper mill, and the close proximity to the coastal area all contribute to the damaging environmental conditions. As a result, this location is the site of numerous annual field tests used to assess the performance of automotive coatings for their etch resistance and for prediction of service life. Varying numbers of hoods, panels, and fascia are placed in Jacksonville each year by the automobile manufacturers and their suppliers. The hoods, panels, and fascia vary in size and shape, but are mostly black to create the worst case scenario for etch testing. These items are exposed in a variety of ways, but typically are tested between 0° and 5° horizontal. The typical testing period is approximately 14 weeks, from late May to August, each year. The test specimens are rated for acid etch damage by professionally experienced raters using a visual method of evaluation at varying intervals throughout the 14-week period.

ACID ETCH EVALUATION PROCEDURE

The test specimen is washed before each evaluation and the extent of acid damage determined visually. The damage to the coating is rated using an industry recog-

research grade device provided a means of correlating test results in an objective and scientific way by measuring the rainfall, relative humidity, dew point, solar radiation, and ambient temperature. In addition, the surface temperature of two different test panels was measured continuously and a pH meter was built to measure the pH of the rain. These environmental measurements were taken every five minutes, 24 hours a day, throughout the entire season and recorded using a data logger. On occasion, both rainwater samples and water collected from the test panels were analyzed for ion and metal concentration.

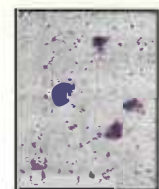
In addition, a load cell was designed and built to measure the time of wetness and to ascertain the amount of water on the test panel during the season. There was also interest in determining when the coating was saturated with water (i.e., during rain events) as well as when droplets were forming, which might cause the etching (i.e., dew formation). The load cell was calibrated with standard weights and an equation was derived to convert the voltage output from the cell to

Table 1—Description of Etch Rating Scale

Rating	Description
0 to 3	Etch is very slight and only noticed by a trained observer
4 to 6	Etch is slight to moderate and, in some cases, noted by a vehicle owner (untrained observer)
7 to 10	Etch is severe enough that many vehicle owners would notice and complain



Etch Rating 3



Etch Rating 10

Note: The blue coloration in the pictures represents an analysis of the surface area that has been affected by etching.

Table 2—Ratings of Systems Used for Correlating Experimental Data

Description	6/11/04 Rating	6/30/04 Rating	7/23/04 Rating	8/9/04 Rating	8/27/04 Rating
Clearcoat 1	2	3	3	5	5
Clearcoat 2	2	6	7	8	9
Clearcoat 3	3	4	5	6	9
Clearcoat 4	2	5	6	6	8

grams of water on the 9 1/2 in. x 9 1/2 in. test panel. Due to total weight restrictions, an aluminum panel was used. All other testing was done using cold rolled steel panels.

DATA ANALYSIS

Four different commercially available automotive clearcoat systems were assessed five times during the season at roughly equal intervals. These clearcoats were applied to electrocoated cold rolled steel panels over different black basecoats. The systems chosen included a two-component coating known to have good etch resistance, as well as a system that has been known to show acid etch failures. All panels were placed flat on

horizontal tables and evaluated for etch damage over the exposure period. The ratings are shown in *Table 2*.

The challenge for data analysis in this study arises from the fact that we have continuous environmental data at five minute intervals that we want to correlate to just five etch evaluation intervals. For this situation, a discriminant statistical analysis was conducted on the environmental data collected during the season

and a correlation was made with the ratings given to the exposed coatings systems. Some classification analysis was also done to compare pH and frequency of dew events for two evaluation intervals, 6/11/04 versus 6/30/04, where the biggest change in ranking occurred.

RESULTS

Panel temperatures have been measured in the past on various Jacksonville test sites but not monitored on a continuous basis. The maximum temperature measurements in this study (174°F) were similar to those recorded on other test sites on the island in previous years. However, the continuous monitoring made obvi-

Figure 2—Fluctuations in panel temperatures due to shifting cloud cover.

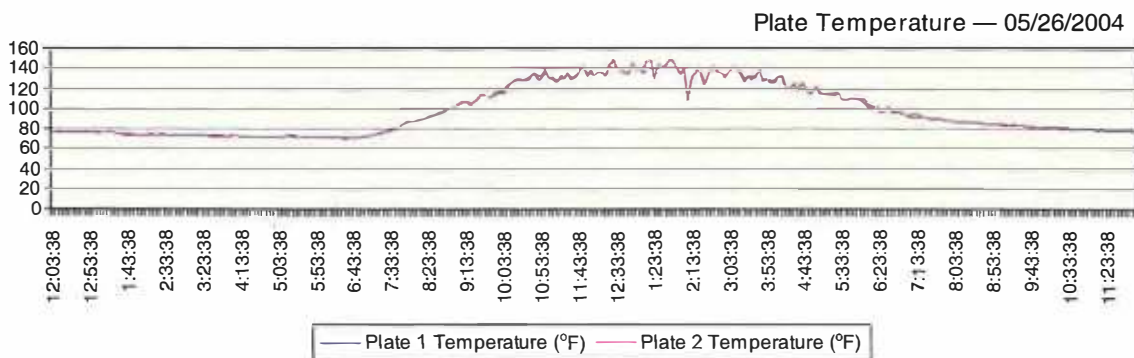


Figure 3—Fluctuations in panel temperature due to rain event.

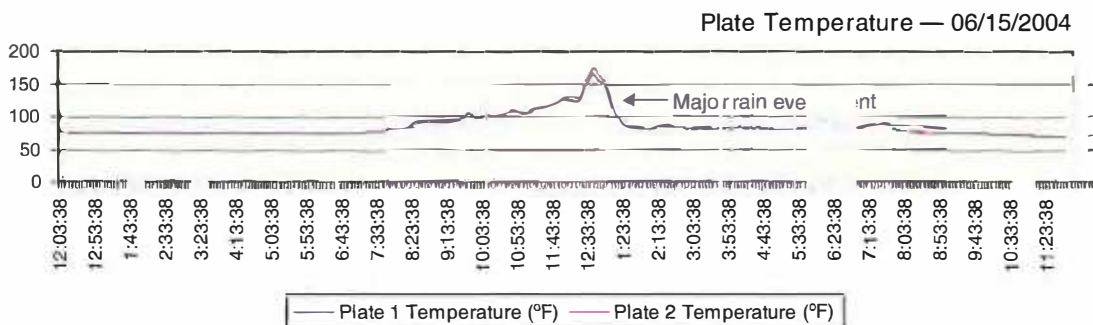


Table 3—Water Composition

2004 Sample Date	Sample Time	Sample	Mg ppb	Zn ppb	Ca ppb	Si ppb	Na ppb	K ppb	Nitrate ppm	Sulfate ppm	Cl ⁻ ppm	pH
6/8	8 a.m.	Wet deposition	506	183	10500	281	1850	1190	9.70	16.4	3.2	6.27
		Rainwater	498	243	2880	164	1810	9550	<1	3.52	10	6.34
6/11	10 a.m.	Wet deposition	836	367	10700	158	1730	476	11.9	22.0	4.9	4.61
6/30	10 a.m.	Rainwater	136	72	528	—	540	1180	<1	1.86	2.03	5.51
7/20	8 a.m.	Wet deposition	158	26	1240	41	880	140	1.80	4.03	1.90	4.07
		Rainwater	259	89	1010	47	830	5700	<1	5.97	4.72	5.84
8/9	11 a.m.	Rainwater	811	70	2580	118	2930	24200	<1	14.3	13.9	—
8/30	8:30 a.m.	Wet deposition	169	—	703	48	309	75	1.5	5.5	1	3.66
		Rainwater	229	85	560	43	521	2120	1.5	5.3	2	4.33

ous some noteworthy temperature stresses that the coatings undergo. For example, fluctuating cloud cover can drop the panel temperature 40° in just 20 min (Figure 2).

Remarkably, on June 15, 2004, a rainstorm brought the temperature down from 174°F to 80°F in a relatively short time period (Figure 3). This will be examined more closely in the discriminant analysis.

Water from a rainwater collection bottle and water removed from test panel surfaces were analyzed for ion concentrations (nitrate, sulfate, and chloride) at the ppm level using a Dionex ion chromatograph, and for elemental composition at the ppb level using an inductively coupled plasma (ICP) technique. The pH was also measured. As seen in Table 3, the most prevalent elemental species from the ICP analysis were calcium, sodium, and potassium. There were small amounts of magnesium, zinc, and silicon. The concentration of the calcium and sodium was higher in the water removed from the test panels (wet deposition) than those measured in the rainwater from the collection bottle. The pH of the water removed from the test panels was more acidic than the rainwater, indicating that as the water evaporates it becomes more acidic.

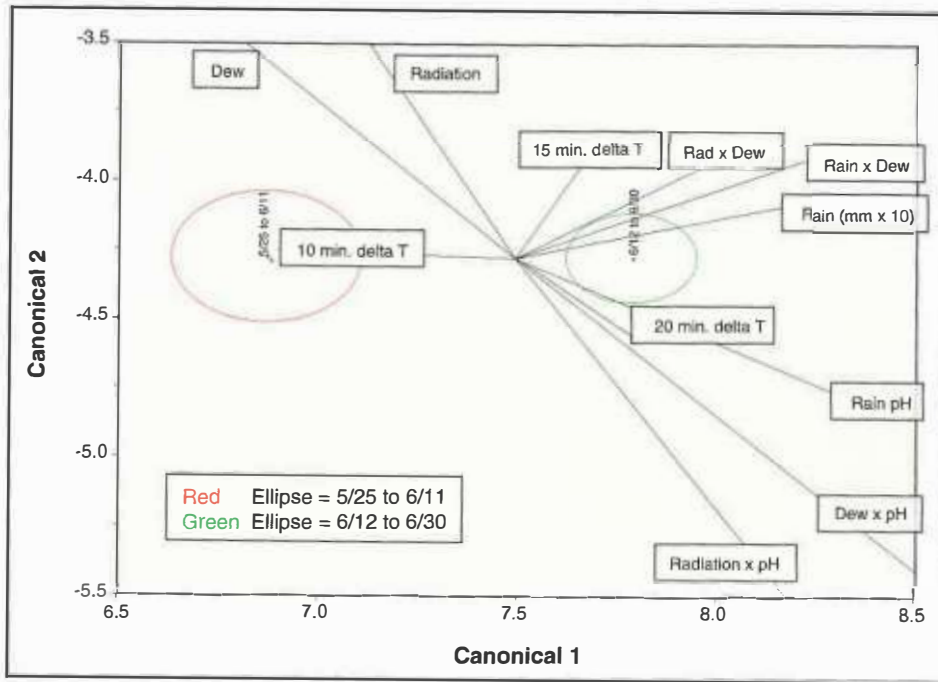
As explained earlier, acid rain is formed when sulfur dioxide and nitrogen oxide react with water and oxygen. This is indicated by the presence of sulfate and nitrate ions. The close proximity of the Atlantic Ocean may account for the presence of sodium, magnesium, potassium, and chloride ions (from sea salt). In general, the ions collected from wet deposition on the panel are greater than the ions measured from water in the rainwater bottle. This suggests that the ions build up on the test panel due to water evaporation. As the water evaporates the acid becomes more concentrated in concentric circles, producing the characteristic ring, or water spot, damage to the coating. If a heavy rain occurs, the acid could be diluted and washed from the surface. If this is true, the effect of solar radiation and dew formation should be more important than rain events.

The amount of water on the panel (dew + rain) was measured using a load cell. Early in the trial period, however, the strain gauge was bent, possibly by a bird, and caused a drift in the baseline readings of the load cell. This problem was repaired and a deterrent shield installed in July. The damage to the load cell obviated any direct measure of the amount of water on the panel in the first half of the study, but at least the presence of dew was able to be calculated by assuming that, when the plate temperature falls below the dew point, moisture will precipitate on the panel. Dew events calculated in this way were compared to similar events later in the study, when the load cell was repaired, and were found to be in good agreement. The resultant data, therefore, contains information about when dew, rain, or both were present on the panel even though the amount is not known. A second issue is that the pH of the dew was not constantly measured. For this analysis, we assumed that the dew was the same pH as the last rain event. From Table 3, we see that this is a very conservative estimate and that the dew is likely to be more acidic than the rain.

Although the panels were rated five times during the study, only one interval showed a change in etching of more than one point. For example, the initial interval, from 5/25 to 6/11, showed a one-point change while in some cases the second interval, from 6/12 to 6/30, showed as much as a four-point change. All of the later intervals showed a much smaller change. For this data, then, a discriminant analysis was conducted. This method compares probable differences in environmental conditions, measured at five minute increments, among the five intervals. However, because the only significant ratings change occurred between the first and second intervals, these two were used as the grouping variable for the analysis.

The mathematical objective of discriminant analysis is to weigh and linearly combine the discriminating variables in some fashion so that the groups are forced to be as statistically distinct as possible. The model is

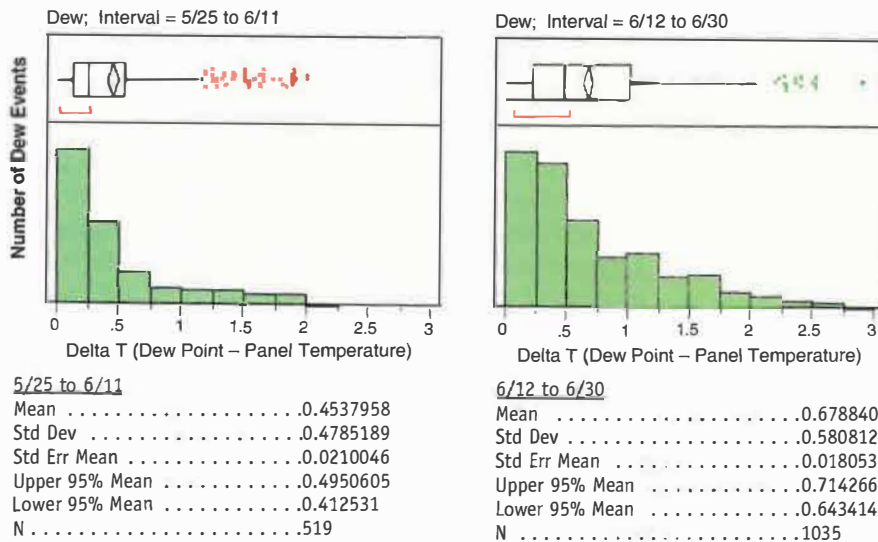
Figure 4— Canonical plot for first and second intervals.



built based on a set of observations for which the classes are known. This set of observations is sometimes referred to as the training set. Based on the training set, the technique constructs a set of linear functions of the predictors, known as discriminant functions, such that:

$$L = b_1x_1 + b_2x_2 + \dots + b_nx_n + c,$$

Figure 5—Comparison of dew frequency and extent.



where b is discriminant coefficients, x is the input variables or predictors and c is a constant. A canonical correlation is the correlation of two latent variables, one representing a set of independent variables, the other a set of dependent variables. Each set may be considered a latent variable based on measured indicator variables in its set. The canonical correlation is optimized such that the linear correlation between the two latent variables is maximized. The purpose of canonical correlation is to explain the relation of the two sets of variables, not to model the individual variables. For a more detailed description of this analysis technique, see reference 3.

As can be seen in Figure 4, the two intervals, "5/25 to 6/11" versus "6/12 to 6/30," can be effectively discriminated by certain environmental parameters.

The interpretation of Figure 4 is as follows:

(1) The two intervals are well discriminated; "5/25 to 6/11" is the left red ellipse and "6/12 to 6/30" is the right green ellipse. The actual data points are also shown in their respective colors.

(2) The black lines, called rays, indicate the probable differences of the environmental parameters between the two intervals. The boundary between these two intervals is clearly marked by the rays for solar radiation, dew, and the interaction of these parameters with pH. Because of the sign, or direction, of these rays, the conclusion is that the greatest effects on etching are due to acidic dew which formed on subsequently sunny days.

(3) The smaller rays pointing right toward the green ellipse, 6/12 to 6/30, are:

- (a) Rain pH
- (b) Rain x dew interaction
- (c) Rainfall
- (d) Radiation x dew interaction
- (e) Delta 10°C change in a 20-min time span

- (f) Delta 10°C change in a 15-min time span

These effects further support the contribution of acidic moisture, in this case rain pH, to the etching problem. The fact that actual rainfall has such a low contribution may be taken as support for the theory that rain washes away accumulated residue and thereby reduces the rate of etching. The last two effects, (e) and (f), give some indication that a thermal shock to the panel may also contribute to etching.

(4) The ray pointing left toward the red ellipse, 5/25 to 6/11, is for a 10°C temperature change in a 10-min time span. Because this actually occurred in the interval with no significant etching, we conclude that such short temperature changes had no significant effect. The conclusion seems to be that the critical time frame for thermal shock is between 15–20 min.

These results strongly support the hypothesis that evaporating acidic moisture, especially dew, could be responsible for the etching because the results suggest that the actual pH of the dew is even lower than our conservative estimate.

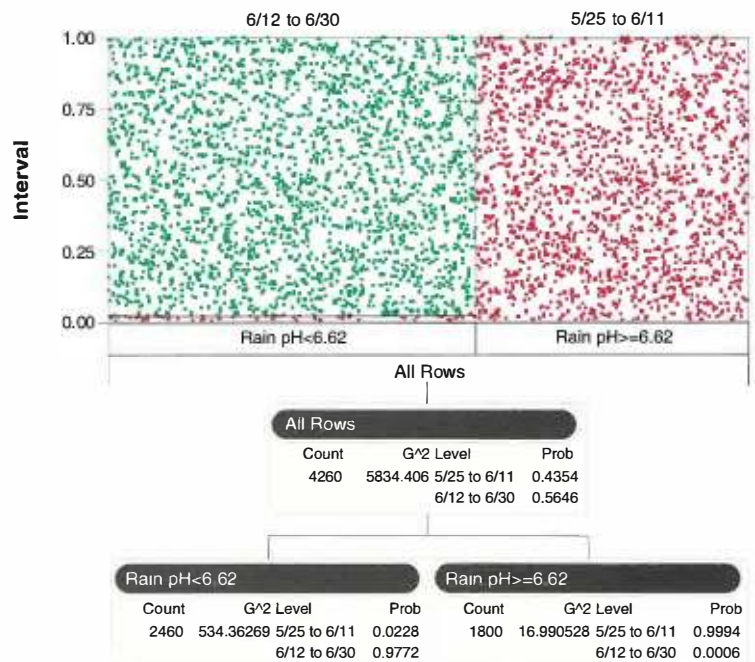
Because of the apparent strong correlation between dew and pH to the increased etching between "5/25 to 6/11" and "6/12 to 6/30," a classification analysis was also conducted for these two parameters. In *Figure 5*, the histograms show the frequency of dew events at different temperatures below the dew point temperature. The X axis is the delta T between the panel and the dew point temperatures. The interval "6/12 to 6/30" had about twice the number of dew events—1035 versus 519—as interval "5/25 to 6/11." Also, "6/12 to 6/30" had many dew events that were colder—by 2°–3°—which may indicate greater amounts of dew.

The final classification was for Rain pH and the partition function is shown in *Figure 6*. The color of the dots in the graph is consistent with our previous color scheme—"5/25 to 6/11" data points are red and "6/12 to 6/30" data points are green. There is virtually no overlap between the two intervals partitioned at pH = 6.62. Thus, the interval "6/12 to 6/30" had the majority of pH values more acidic than 6.62 (probability >0.97), which is again consistent with the hypothesis that lower pH produces a greater degree of etching.


CONCLUSIONS

The influence of exposure conditions on paint damage due to etch is a complex problem. The general assumption is that acid moisture evaporates on the surface, concentrating acidity, thereby decomposing the coating and leaving a nonreversible ring, or water spot,

Figure 6—Partition for rain pH.



on the surface. This study provides statistical evidence that this assumption is valid. Further, it appears that evaporating dew is a much more significant contributor to etching than rain. In fact, there is some evidence that the rain may even mitigate the etching problem by washing the residue from the panel's surface. There is also some evidence that thermal shocks of 10°C in a 15–20 minute interval may also contribute to etching. All of these conclusions could be strengthened by evaluations of the panels at shorter intervals. In this study, there were really only two intervals that provided useful data for comparisons.

The severity of the climatic conditions in Jacksonville varies from year to year. 2004 was regarded by the industry as a very severe season. This study will continue in the 2005 etch season with some upgrades. A more rugged load cell has been designed with more sensitivity. The wind speed and direction will be measured. Also, the frequency of etch evaluations and collection of moisture from the panels will be increased. 

References

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