

The Importance of WATER in the Weathering of Automotive Coatings

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Significant efforts have been made over the last decade to improve accelerated weathering of automotive coatings by improving the light sources, filters, and correlation of the light exposure to outdoor conditions.¹ The development of filters has been a continuous process with improvements being made in terms of duplicating the light spectra of actual sunlight. However, only in the last four-to-five years has the coatings industry started to realize the importance of water in the weathering process. In order to understand the role of water in the weathering process, techniques need to be developed that properly measure water levels under field conditions and relate those levels to specific coating film properties and defects.

An automotive clearcoat is a semi-permeable membrane and there are many factors that determine the degree of permeability. These factors include such things as the glass transition temperature of the film (T_g), the degree of crosslinking (crosslink density), and the relative hydrophobic or hydrophilic nature of the coating based on its chemistry type. A study was performed on various automotive clearcoat systems using a Fisher permeability cup (Figure 1). The data is shown in Table 1. The cups are filled with equal weights of water and the films tested are all identical in film thickness. The cups are placed in a desiccator to initiate the water permeation through the film. The desiccator can also be heated to accelerate the process. The clearcoat samples include two-component polyurethane (A), one-component urethanes (B-D), and an acrylic melamine clearcoat (E). The permeability data shown in Table 1 indicates that Clearcoat D is the least permeable prior to temperature exposure while Clearcoat E has the highest level of permeability. Clearcoat A is affected less than Clearcoat D when the apparatus is heated to 140°F. All of the permeability rates increase significantly with the exposure of the cups to elevated temperature.

As water permeates through a film there are potential hydrolysis reactions (aided or started by impurities in the water, i.e., acid rain). The movement/migration of components in the coating, which occurs with water exposure,

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does not occur in a dry climate. Exposure data collected by the coatings industry has indicated that dry exposure (i.e., Arizona) does not cause different failures, but rather the probability of failures is decreased significantly. Therefore, the focus should be directed toward climates and exposure conditions that maximize and present the worst case scenario for water and humidity exposure for testing of automotive exterior coatings. Jacksonville and South Florida are known environments with high levels of condensation and water exposure and are good areas to monitor water exposure levels for coatings.

In an effort to better understand the effects of weathering on automotive coatings, a weather station was set up on the Bayer Material Science test site in Jacksonville, FL (Figure 2). Data was collected every five minutes, 24 hours a day, for a 14-week period each summer between May and August, 2004–2007. This research-grade device measured the rainfall, relative humidity, dew point, solar radiation, ambient temperature, wind direction, and wind speed. Table 2 shows a portion of this data. The test panel surface temperature was monitored on a 10" x 10" cold rolled steel panel coated with a standard automotive black basecoat and a two-component polyurethane clearcoat. Two-component polyurethane clearcoats typically show excellent etch resistance and durability, thus it was the clearcoat chosen for the study. Bayer built and designed a pH meter to measure the pH of the rain. A phone modem connected to the data logger was used to monitor the operation in real time.

A method was needed to measure not only how long the coated panels were wet, but the amount of water to which the coating system was exposed. To accomplish this, a scale was built with a coated panel supported on three strain gauges. The detection limit of the water measurement was 0.44 grams and the scale was capable of measuring events ranging from the formation of light dew to heavy rainfall. Figures 3–5 show the apparatus and examples of condensation (dew) and heavy rainfall on the panel.

The load cell was designed and built to measure the time of wetness and to ascertain the amount of water residing on the test panel during the season. The load cell was calibrated with standard weights and an equation was derived to convert the voltage output from the cell to grams of water. The scale was calibrated at regular intervals during the season and the test panel was cleaned before each calibration. It was found that the data from our setup could be mathematically reproduced.

Figure 6 covers a five-day period when there was dew formation. The random noise in the signal that is prevalent below 10 g scale weight is from the wind hitting the panel. When dew starts to form the wind dies

Figure 1—Fisher permeability cup.



Figure 2—Bayer weather station.



Figure 3—Load cell apparatus.

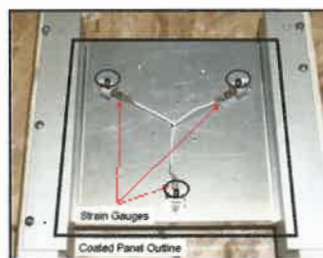


Figure 4—Panel with dew formation.



Figure 5—Panel after heavy rain.



Table 1—Permeability Data on Automotive Clearcoats
(Permeability cup weight loss in grams)

Clearcoat	Day 1	Day 2	Day 3	Plus 16 hr, 140°F
A	0.0939	0.1736	0.2682	0.6491
B	0.1185	0.2405	0.3540	0.8985
C	0.1400	0.2782	0.4168	1.1777
D	0.0922	0.1632	0.2444	0.7020
E	0.1400	0.3085	0.4424	1.3503

Table 2—Portion of 2004 Summer Water Data

Date	Avg. Wet Plate Temp	Max. Wet Plate Temp	Avg. Wet Load/Day	Wet Time in Min/Day	Avg. Daylight Wet Load/Day	Daylight Wet Times in Min	Rain Total mm/Day	Avg. Rain pH/day	Min. Rain pH/Day
7/1	21.30	59.27	44.53	865.00	37.24	270.00	4.06	5.99	5.10
7/2	26.71	57.89	35.41	910.00	35.38	305.00	0.00	0.00	0.00
7/3	22.99	30.31	27.72	960.00	36.22	375.00	38.11	5.10	4.61
7/4	26.35	57.98	40.88	1105.00	36.92	520.00	13.21	5.03	4.78
7/5	26.78	47.96	20.30	800.00	29.45	235.00	0.00	0.00	0.00
7/6	26.17	28.31	0.48	585.00	0.96	70.00	0.00	0.00	0.00
7/7	24.03	27.91	17.09	855.00	11.92	235.00	5.33	5.88	5.25
7/8	24.20	51.22	37.37	1190.00	32.82	605.00	3.30	5.87	5.70
7/9	25.71	50.11	26.21	885.00	29.54	295.00	0.00	0.00	0.00
7/10	25.68	31.93	0.12	675.00	0.34	90.00	0.00	0.00	0.00
7/11	24.33	39.67	24.88	1045.00	40.29	440.00	25.15	4.99	4.33
7/12	25.89	55.97	38.56	915.00	29.68	300.00	7.87	4.71	4.15

Table 3—Water and Methylene Iodide Contact Angles with Various Weathering Cycles (Measured in Degrees)

Panel #	As Is		Xenon Arc incl. H ₂ O		SAE J1960	
	H ₂ O	CH ₂ I ₂	H ₂ O	CH ₂ I ₂	H ₂ O	CH ₂ I ₂
11	92	47	72	40	82	42
31	93	34	75	39	81	46
45	91	33	78	40	82	50
67	91	33	76	41	78	43
73	90	35	75	42	80	44
74	92	37	76	40	77	42
Avg	92	36.5	75.3	40.3	80	44.5

down and remains calm during dew formation. Dew formation has a characteristic initial ramp (between A and B). During this period, no rain bucket sensor event occurred that would have indicated a heavy mist or very light rain. One explanation may be water absorbing (3–5 g) into the surface of the panel coating. When dew starts to condense on the panel (between B and C) the wind has stopped. When the sun rises the dew evaporates rapidly (between C and D). When all the dew has evaporated the absorbed water evaporates at a slower rate (between D and E). At point E the sun is at

full exposure and the remaining absorbed water rapidly evaporates.

An important variable in the algorithm for predicting standing water is the maximum amount of water that can reside on the panel, and how that changes with time. As the panel weathers, the surface energy of the coating decreases, the water does not bead up and will flow off the panel easier. Over a 41 day period between June 30 and August 9 in 2006, the maximum amount of water that could reside on the panel decreased at a steady rate. A value of 70 g was used in the

model as the MaxWater constant. In developing the model, to determine the time wet from dew and from rain, any water on the panel after a rain event was considered rain until the panel was fully dry.

Figure 7 provides a detailed look at the water exposure in the summer of 2006. There were more dew events than rain events in the summer of 2006. Also, the derived model was a good match to the actual values for overall water exposure.

The weather station data shows that on most days the coated test panel was wet more than half the time and that most of that time was at night. The maximum temperature when the panel was wet was reached when the panel was heating up in the morning. The largest water weight shown in the data is approximately 40 g. Figure 8 shows what that would look like on a non-oxidized coating surface. Laboratory tests on some oxidized coating surfaces show that it is possible for less than 40 g of water to totally cover the surface. Notice how the 2006 water model shows a decreasing maximum in water weight/volume (Figure 7). This could very well be due to coating oxidation and surface tension changes that occur during exposure. The amount of water required to totally cover a coating surface will depend on the coating chemistry, surfactants used in the formulation, and the extent of surface oxidation. This can be visually noticed in the field as many panels exposed in Florida do change their wetting characteristics in as little as three to six months after exposure. What is important is that some of this water is permeating into the coating layers. This is not only dependent on the clearcoat, but also the type of basecoat used. For example, a waterborne basecoat will absorb more water than a solventborne basecoat.

Figure 9 is the water model for the 2005 season. While there were more rain events in the 2005 season, there are almost twice as many water events related to condensation versus rainfall. The rainfall water volumes are typically higher, meaning that there is probably total surface coverage and significant water uptake during those events.

What effect does water actually have on the coating surface? We know that one effect is acid etch (Figure 10). Data from the weather station has led to a more detailed understanding of the etch phenomena.² It is well known in the coatings industry that acid etch is caused by hydrolysis reactions that occur typically in the top 0.2 mils of the clearcoat film. The reactions are caused by water containing protons (acids) and usually other ions from salts. When high levels of water contact the surface (such as during a heavy rainfall), the water approaches a neutral pH and the reactions are less severe. However, where there are large amounts of water these reactions can take place to a lesser extent but could possibly occur deeper into the coating film. This

Figure 6—2006 dew formation.

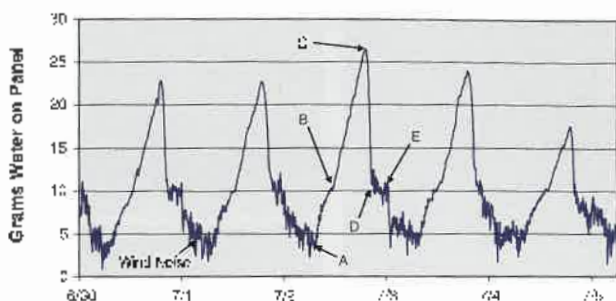


Figure 7—2006 rain and dew/scale versus model.

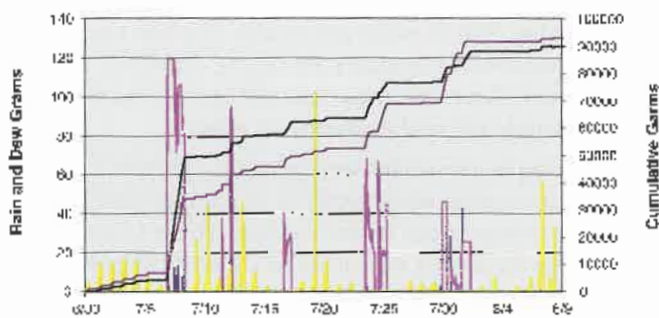


Figure 8—Test panel with 40 g of water on the surface.

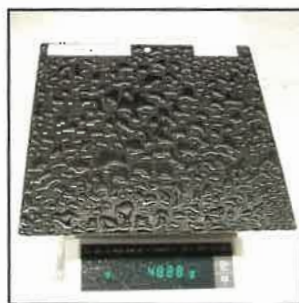


Figure 9—2005 rain and dew/scale versus model.

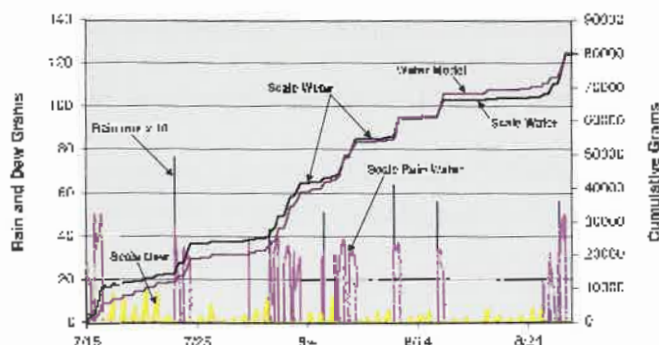
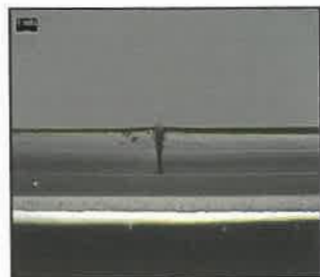


Figure 10—Elch defect.



Figure 11—Cracking defect.



could lead to gloss loss and delamination. Another effect of water exposure is humidity related effects such as whitening. When water penetrates into the coating surface, water-soluble materials can be dissolved into an aqueous phase and these microscopic pockets of soluble materials cause the whitening effect.

Blistering is caused by large pockets of water formation in the coating when water is in contact with hydrophilic components in the coating. These blisters can cause large areas that will actually cause localized stress in the coating and can lead to cracking (Figure 11).

Water exposure causes a loss of materials in the coating, resulting in surface energy changes. When water penetrates the coating film, the water-soluble materials and other components not reacted into the crosslinked network of the film migrate throughout the film. These materials include acids, surfactants, UV absorbers, light stabilizers, etc. One way to observe this effect is by measuring the contact angle or surface energy. The data in Table 3 shows water and methylene iodide contact angle measurements with six different panels (different basecoat and clearcoat compositions). The amount of UV exposure in the Xenon Arc exposure using an increased water amount versus the UV exposure in the SAEJ1960 method is the same (same total kJ and light filter). Since the contact angles will also change with different light filters and irradiance, any experiment should be well controlled to ensure that the differences observed are due to only a different water exposure level.

This article illustrates the methodology in which to determine the effects of water and how to correlate them to actual field results. This information will be valuable in determining how to properly implement the amount of water needed in an accelerated weathering test. An earlier publication addressed the measurement of water uptake in accelerated weathering tests.³ Using all these tools, it should now be possible to control the wetting aspect of weathering to the same extent as the light portion of the test.

In conclusion, it has been shown that water does permeate through coating films in different amounts and rates depending on the exposure conditions and the coating chemistry. A mathematical water model can be generated for a specific time period and location with use of the proper outdoor monitoring devices. When exposing coatings to a controlled water exposure, a number of film changes and defects can be created. These changes and defects can be seen visually but also can be measured analytically depending on the test criteria.

A high level of activity is in progress in the coatings industry to improve correlation of accelerated tests to outdoor exposure. With a clearer understanding of water and its role in the weathering process, developments of improved accelerated weathering methods are possible.

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