Correlations Between Xenon Arc Accelerated Weathering Tests and Outdoor Weathering

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Abstract

The ability to predict the long-term outdoor weathering of coatings and printed graphics is essential to many industries. However, this is a difficult task. Rates of photo-oxidation and hydrolysis for different materials often do not increase by the same factors in accelerated weathering tests, primarily because of differences between the spectral power distributions of sunlight and artificial light sources. For some materials, accelerated testing results correspond poorly to phenomena observed in outdoor exposures. Because of these difficulties, few correlation studies have been published. This paper describes a correlation study between a Xenon Arc Weather-Ometer and Milwaukee outdoor weathering. Color changes of signs and printed ink jet media were measured with colorimeters and optical densitometers. Correlations were determined for both individual materials and overall data sets. The merits of measuring color changes with colorimeters and optical densitometers will be discussed. The efficacy of the ASTM G26 and SAE J1960 testing cycles will also be considered.

Introduction

Just think about the number of times you hear the questions: "How long will this product last outdoors?" or "This sample failed after X hours in the accelerated weathering test - how many years is that outdoors?" Unfortunately, there is no simple answer to these questions. There is no universal correlation that relates outdoor weathering to time spent in an accelerated weathering chamber.

Intuitively this makes sense. Outdoor weathering varies from year to year and site to site. There are currently no light source and filter combinations that can exactly reproduce the spectrum of sunlight. Accelerated weathering instruments use three factors to test materials: light, temperature, and water exposure. Each of these factors will affect materials differently by activating one or more degradation pathways. There is no way to ensure that the scale factors relating the rates of these degradation mechanisms in the weathering chamber and outdoors will be the same for all mechanisms. Consequently, it is really only possible to develop weathering correlations for a single material tested with one standard test cycle rather than a universal correlation for all possible materials. It should also be noted that even for one material, the correlations for color changes, gloss changes, and changes in mechanical properties may all be different.

Forecasts of material or product performance in outdoor environments have long been sought. A fast, accurate predictive weathering test would be invaluable. However, no such universal test method has been established. Efforts to mimic the spectrum of sunlight with artificial light sources have continued since early in the 20th century.

The spectrum of sunlight is heavily weighted toward the visible and infrared. However, it is the small fraction (6.0%) of ultraviolet (UV) light that is responsible for most of the damage to polymers and colorants. In particular, it is the UVC (100 – 290 nm) that is the most destructive. It is critical to filter out all UVC radiation in an accelerated test, or else the results are likely to be nonphysical, because the earth's ozone layer filters out all UV radiation below 295 nm.

There are many types of accelerated weather testing instruments. Their usefulness may be characterized by two parameters: correlation, and acceleration factor. Correlation is the degree to which data obtained in the testing chamber agrees with data obtained outdoors. The acceleration factor is the ratio of failure time outdoors to failure time in the test instrument. For example, an acceleration factor of 12 means that a one-month accelerated weathering test corresponds to one year outdoors. Of course, acceleration factors will vary with the choice of the outdoor site. The most cited outdoor weathering facility is that of the South Florida Test Service, a subsidiary of Atlas Electric Devices, Inc.

The primary determinant of the degree of correlation for a weather-testing instrument is the degree to which the artificial light source approximates the spectral power distribution of sunlight[1]. Xenon arc lamps provide the best available match to sunlight. Indeed, in a comprehensive study of the accelerated weathering of polyester gel coats, Crump[2] found that xenon arc weathering gave higher correlation coefficients than methods employing carbon arcs or fluorescent light source. However, most of the comprehensive comparisons of various types of weathering tests in the literature do not include correlation data. It may be assumed that many proprietary correlations have been developed but not published.

Materials and Methods

Test Samples

A variety of sign and graphics materials were tested in order to include several different classes of polymers. All ink and substrate colorants were pigments rather than dyes.

1. Vinyl ink jet graphics materials with polyamide-silica top coats were printed with process color blocks on a Brady ColorPix ® Pro 36 ink jet printer; some of these graphics were covered with acrylic or two-pack urethanes clear coats.
2. Two types of high-impact polystyrene (HIPS) signs were tested: one printed with an acrylic UV curable ink, the other printed with a wax-based ink and protected by a 1.0 mil polyester overlaminate.
3. Aluminum signs coated with a white polyester enamel were printed with a wax-based ink and protected by a 1.0 mil polyester overlaminate.
4. Polyester (PET) film printed with a UV curable ink was protected with a 1.0 mil poly(vinyl fluoride) (PVF) film.
5. Pigmented vinyl films were printed with UV curable inks.

Outdoor Testing

Small (4 cm x 4 cm) samples were cut, adhered to large aluminum plates, and then placed on a weathering rack in Milwaukee. The panels were oriented to face south at an inclination of 45°. Each panel stayed out on the rack until the end of its weather exposure, and was then brought inside for colorimeter and densitometer testing. Panels were weathered for 1, 2, 3, 6, 9, 12, 18, and 24 months. Due to variations in weathering throughout the year, only data for 0, 12, and 24 months were used in calculations of correlation coefficients.

Atlas Weather-Ometer Tests

Accelerated weathering was conducted in a Ci5000 Xenon Arc Weather-Ometer from Atlas Electric Devices, Inc. The filter combination and environmental conditions were taken from the following two test standards:

The **ASTM G26** standard[3] employs Borosilicate inner and outer filters for the xenon arc lamp. The light cycle has two parts:

1. Irradiance for 102 min with a set point of 0.35 ± 0.01 W/m^2 at 340 nm, a black panel temperature of 63 ± 3°C, and 50% relative humidity.
2. Front water spray for 18 min; same irradiance as (1).

The **SAEJ1960** standard[4] calls for a Quartz inner filter and a Borosilicate outer filter for the xenon arc lamp. The cycle has four stages:

1. Irradiance for 40 min with a set point of 0.55 ± 0.01 W/m^2 at 340 nm, 50% relative humidity, and a black panel temperature of 70 ± 2°C.
2. Front water spray for 20 min; same irradiance as (1).
3. Same conditions as (1) for 60 min.
4. Dark cycle for 60 min at 38 ± 2°C dry bulb temperature 95 ± 5% relative humidity with back water spray.

Reflected optical density and color values were measured after approximately every 200 hr of exposure out to 3000 hr. Two SAE J1960 Weather-Ometer samples were tested for each material and color, while only one was run with the ASTM G 26 method.

Color Measurements

Reflected optical densities were measured with a Gretag Macbeth RD-1200 or RD-1255 densitometer. For the process primary colors only one color was measured. For red samples, magenta and yellow were measured; for green samples, cyan and yellow were measured; only cyan was measured for blue samples. Each data point was taken as the average of five measurements – the four corners and center point of the rectangular color patch.

A Hunter Ultrascan colorimeter was used for color difference measurements in *L,a,b* space. The small area aperture (1/4") was used for all samples. The colorimeter was configured for a D65 light source, a 10° angle of view, and specular reflections included. All data points were taken as the average of five measurements – the four corners and center point of the rectangular patch of color.

Results and Discussion

Weathering Test Results

Data from the Atlas Weather-Ometer was correlated to one and two year data from the Brady outdoor weathering racks in Milwaukee. The results are summarized in Tables 1 and 2. The uncertainties, taken as two standard deviations, in the number of hours in the Weather-Ometer corresponding to a year outdoors are significantly higher for the SAE J1960 test cycle than for ASTM G26. The reasons for this will be addressed in the Results and Discussion section. The uncertainty is also relatively small for the only large data set, Ink Jet Vinyl, that was tested under SAE conditions.

The acceleration factor varies with the material tested, as is expected for an accelerated weathering test. The largest is approximately twice the smallest, so none of the numbers are unambiguously anomalous.

Table 1. SAE J1960 Weathering Results

Material	N	WOM hr = to 1 yr in MILW	Acceleration Factor
Ink Jet Vinyl	19	762 ± 236	11.5 ± 2.7
Aluminum	7	681 ± 344	12.9 ± 4.3
Polystyrene	7	1539 ± 1557	5.7 ± 2.9
Polystyrene with PET Overlaminate	7	894 ± 330	9.8 ± 2.7
Polyester with PVF Overlaminate	4	1665 ± 553	5.3 ± 1.4
Colored Vinyl	5	861 ± 475	10.2 ± 3.6

Table 2. ASTM G26 Weathering Results

Material	N	WOM hr = to 1 yr in MILW	Acceleration Factor
Aluminum	7	840 ± 330	10.4 ± 2.9
Polystyrene	7	1274 ± 552	6.9 ± 4.8
Polystyrene with PET Overlaminate	7	845 ± 58	10.4 ± 0.7
B-689 Polyester Pipe Marker	4	1329 ± 1262	6.6 ± 3.2
B-946 Vinyl	5	684 ± 175	12.8 ± 2.6

Failure Criteria

The effectiveness of an experimental weathering test is dependent upon the failure criteria chosen. One may choose to monitor changes in color, gloss, or mechanical properties. These categories may also be broken down further. For example, color change may be designated as color fade measured with an optical densitometer, color difference measured with a colorimeter, or yellowing as quantified by a yellowness index.

In this experiment two failure criteria were employed. Color fade was measured with a Gretag Macbeth Densitometer. The percent reduction in reflected optical density of one or two of the process color primaries was tracked as the samples weathered. Color difference, ΔE, was also measured with the Hunter Ultrascan Colorimeter. It may be defined in *L,a,b* color space as:

$$\Delta E = \left[(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2\right]^{1/2} \qquad (1)$$

where ΔE = color difference, ΔL = difference in lightness index, Δa = difference in a value (green/red axis), and Δb = difference in b value (blue/yellow axis).

In general, better results were obtained when optical densities were measured. This was particularly true for yellow and black samples. In both cases, only one value in *L,a,b* color space changes significantly as the specimen ages. For yellow, this is the b value. For black, only the lightness, L, changes unless there is a significant yellowing problem. Consequently, for specimens that appear visually to have the same degree of change, the yellow and black materials tend to have smaller ΔE values than other colors. Colorimeter results for black samples often show little correspondence to visual observations. Samples with a mid-gray appearance often still have relatively low L (lightness) values, and if there is no yellowing, both the a and b values will still be negligible.

Another problem with using color difference as the failure criterion is that a significant fraction of samples show a color change (ΔE) of 3 – 6 within the first day of exposure and then do not change again for hundreds or thousands of hours. Often, the failure criterion is exceeded on the first day for a sample that actually is quite resistant to sunlight and water. This can skew the results considerably. Essentially, this means that experiments must be long enough in time scale that the color change for all samples is several times the size of these initial step-changes.

The large Ink Jet Vinyl data set was used to examine any variations in the acceleration factor and correlation for different ink colors (Table 3). No differences were observed between cyan, magenta, and yellow, but the acceleration factor was a little lower for black. For that ink set, there appears to be little influence of color on weathering.

Table 3. Effects of Color on Ink Jet Vinyl Weathering

Color	WOM hr = to 1 yr in MILW
Cyan	681 ± 205
Magenta	677 ± 284
Yellow	675 ± 136
Black	871 ± 150
Overall Average	715 ± 200

ASTM G26 vs. SAE J1960

Both ASTM G26[3] and SAE J1960[4] have their strengths as testing cycles that may make them particularly suited for testing certain types of materials (see the Materials and Methods section for complete descriptions of the testing cycles). The Borosilicate inner / Borosilicate outer filter combination used in ASTM G26 provides a better match to the spectral power distribution of sunlight, with less radiation in the 280 – 300 nm range. However, it also runs at a constant temperature with the xenon arc lamp on continuously. SAE J1960, on the other hand, includes a dark cycle with water spray at lower temperature to simulate the condensation that occurs when the temperature drops to the dew point at night. When the light comes back on and the temperature is increased, SAE J1960 test specimens experience simultaneous heating and drying. Materials that are sensitive to expansion and contraction, especially porous samples, may show early failures due to cracking in SAE tests that are not reproduced in ASTM tests. For automotive coatings, this is often deemed to be critical. Early in the development of the Ink Jet Vinyl topcoat the SAE test method was found to be a better predictor of outdoor performance, because the main failure mode was cracking and chalking of a somewhat brittle, silica-filled, porous, polyamide topcoat.

For the materials that were tested under each cycle (ink jet graphics were only tested under SAE J1960), better correlation with Milwaukee outdoor weathering was obtained with the ASTM G26 method. This may be seen to some extent in Table 4, but is even more evident in the overall data sets shown in Table 5. The standard deviation in Table 5 is approximately three times as large for current Brady products when tested by the SAE J1960 standard as opposed to ASTM G26. Other than Ink Jet Vinyl, all of the products investigated in this series of experiments comprise exclusively non-porous substrates, inks, and overlaminates. Thus, the effects of expansions, contractions, and water absorption are not strong, so the main factor determining the degree of correlation with outdoor weathering is expected to be the match between the spectral power distributions of the light sources.

Table 4. Correlation Coefficients Between Atlas Ci5000 Weather-Ometer and Milwaukee Outdoor Weathering

Sample Set	Test Cycle	Metric	N	r^2
All	ASTM G26	Density	76	0.68
All	ASTM G26	ΔE	39	0.67
w/o Ink Jet	SAE J1960	Density	60	0.64
w/o Ink Jet	SAE J1960	ΔE	36	0.27
All	SAE J1960	Density	207	0.70
Ink Jet Vinyl	SAE J1960	Density	147	0.75

Table 5. Overall Weathering Correlations

Sample Set	Test Cycle	Metric	HR/YR in Milwaukee
Overall	ASTM G26	Density	928 ± 564
Overall	ASTM G26	ΔE	1031 ± 862
Current Products	ASTM G26	Density	801 ± 284
Overall	SAE J1960	Density	864 ± 964
Overall	SAE J1960	ΔE	802 ± 1108
Current Products	SAE J1960	Density	807 ± 746

One unexpected result, however, was that the acceleration factors to the two methods were very similar. Because there is more radiation present in the damaging 280 – 300 nm range, SAE J1960 tests typically are more damaging and show a higher acceleration factor than ASTM G26 tests. For example, in a study of color and gloss changes in acrylic automotive coatings, Bauer[5] obtained acceleration factors of 8 – 20 and 6 – 9 for Xenon Quartz/Boro (SAE J1960) and Xenon Boro/Boro (ASTM G26), respectively. Bauer also found that acrylic coatings could be tested by either method, but outdoor weathering of polyester coatings only correlated with accelerated tests using the Borosilicate/Borosilicate filter combination.

It is the belief of the author that a combination of the two testing cycles may correlate even more closely to outdoor weathering. If the four-part SAE J1960 method were run with Borosilicate inner and outer filters, the resulting test would have a better match to the spectral power distribution of sunlight along with the expansion and contraction cycles that destroy many porous or brittle samples as well. Options that could further improve the match to the spectrum of sunlight, such as using ozone as a filter[1], are somewhat impractical at this time.

Discussion of Overall Correlations

To begin this discussion, a few caveats should be offered.

Correlations for an individual material are the most accurate. The accuracy will be even better if the data is for only a single color. With most Brady products, multiple layers of dissimilar materials also need to be considered. As can be seen in the preceding sections, weathering correlations vary strongly with the types and combinations of materials.

However, often in materials research and development we would like to predict the lifetime of a construction for which no previous test results exist. In order to provide a "rule of thumb" for this type of prediction, the data sets for different materials were combined (Table 5). The overall correlations show that a year of outdoor weathering in Milwaukee corresponds to approximately 800 ± 400 hr in the Atlas Ci5000 Xenon Arc Weather-Ometer. The average for each product tested lies within this range. Of course, the standard deviations for some materials are quite large. Most correlation coefficients are in the 0.6 – 0.8 range.

Problems with certain types of materials are to be expected in weathering tests. For some materials the spectral power distribution of the artificial light source, the thermal energy, and the water applied in a test do not result in a simple acceleration of the weathering chemistry that exists for outdoor exposure. Instead, other degradation pathways are activated, and the test results are anomalous. For example, Gerlock[1] used FTIR spectroscopy to follow the weathering chemistry of polyester/urethane and acrylic/melamine automotive clear coats. The acrylic/melamine clear coats were found to be much less sensitive to exposure conditions than the polyester/urethane clear coats. Changes in the weathering chemistry of the polyester/urethane coatings resulted in poor correlation of xenon arc weathering with South Florida and Arizona weathering. The effectiveness of light stabilizers added to the coating formulations was also found to be distorted due to thermal migration of the stabilizers.[1]

Another factor that may have affected the acceleration factors that were determined is the two-year time scale of our experiments. For all materials, the acceleration factor was lower for two-year than for one-year outdoor data. For example, for Ink Jet Vinyl, one year of outdoor weathering was equivalent to 983 hr of SAE J1960 Weather-Ometer testing, but after a second year of testing this equivalent had dropped to only 715 hr. Indeed, this figure may drop even further in a longer test (which corresponds to a higher acceleration factor). It is expected that it may eventually approach a stable, long-term value.

When these experiments commenced, the author was expecting to find that about 400 - 600 hr in the WOM was equivalent to a year outdoors in Milwaukee. However, the overall average for this experiment is approximately 800 ± 400 hr in the WOM / year outdoors, which corresponds to an acceleration factor of 11.0 ± 3.7. It is difficult to compare this to the literature, because nearly all of the published studies cite data for the Atlas South Florida Test Service or for DSET in Arizona. In a comprehensive study of the accelerated weathering of polyester gel coats, Crump[2] found an acceleration factor of 8.4 relative to South Florida weathering for ASTM G26 xenon arc weathering. Model predictions and experimental values of Bauer[5] for acceleration factors in South Florida and Arizona weathering range from 4.5 to 15.0 (Borosilicate/Borosilicate filters) depending upon the type of material. Bauer has estimated that one year in Florida or Arizona is approximately equal to two years at Ford Motor Company in Dearborn, Michigan.[6] In order to make a fair comparison, data collected at the South Florida Test Service is needed.

Conclusions and Recommendations

The Atlas Xenon Arc Weather-Ometer is an effective accelerated weather-testing device. When used with Borosilicate inner and outer filters, as is recommended for the ASTM G26 method, the xenon arc lamp provides the best available fit to the spectral power distribution of sunlight of all available artificial light sources. This is the "gold standard" of accelerated weather testing chambers that employ artificial light sources (as opposed to solar reflectors and concentrators). The Quartz inner / Borosilicate outer filter combination used for the SAE J1960 exposes samples to more light in the 280 – 295 nm range that is screened out by the earth's ozone layer. The strength of the SAE test method is that it includes a dark cycle with water spray at lower temperature to simulate nightly condensation and the subsequent drying concurrent with temperature increase during the morning. Because of the expansion and contraction due to the thermal cycling and drying provided by this method, it often works well for materials that are brittle, porous, or hygroscopic. A hybrid test method in which the Borosilicate inner and outer filters of ASTM G26 are combined with the four-part SAE J1960 cycle is predicted to be superior to either standard test method.

Correlations for color changes are better when reflected optical densities are measured on a densitometer than when color differences are tracked with a colorimeter. This is especially true for very minute changes, or for black or yellow samples. For white materials, yellowness indices should be measured with a colorimeter.

A more comprehensive future study is recommended. The duration of the study should be long enough that the acceleration factor for each material becomes essentially constant. It is surmised that five years may be sufficient. In order to be able to compare results with literature values, it is imperative that some samples be tested at the South Florida Test Service weathering site run by Atlas Material Testing Technology.

References

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Biography

Bruce M. Klemann is a Senior Materials Scientist at Brady Corporation. He received a B.S. in chemical engineering and a Ph.D. in Materials Science from the University of Wisconsin – Madison. Since 1994 he has been with Brady Corporation. His research interests include digital printing media, ink jet printing inks, novel imaging and marking processes, thermal stability of coatings, accelerated weather testing, rheology of thin films and viscous liquids, materials for flat panel displays, and security imaging. He is a member of IS&T, MRS, and SPE.