Correlation of Laboratory to Natural Weathering

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The basic stresses in weathering are known and quantified. The time a material is stressed and the temperature during UV and water stresses are the primary variables in natural weathering. Reproducing them exactly in the laboratory can provide acceleration by eliminating idle time. Further acceleration is possible by maximizing UV, water and temperature stresses within natural limits. The tests reported here indicate that the most important factor in accelerated laboratory weathering is the proper balancing of these stresses.

Introduction

Until recently, the weight of the evidence on accelerated weathering suggested that it is not a reality. Thousands of attempts to reproduce natural weathering achieved only limited success at best. Our inability to explain why weathering could not be reliably duplicated in the laboratory had led many competent scientists to regard the entire concept as a myth, an unattainable goal.

In the past seven years, our company and other companies have been trying to erase some of the mythology surrounding accelerated weathering with a new tool, the fluorescent UV-condensation apparatus shown in Figure 1. In this apparatus, materials are alternately exposed to ultraviolet light alone and condensation alone in a repetitive cycle. The UV source is an array of fluorescent lamps with almost all of the lamp emission in the UV range. Condensation is produced by the mechanism of the Cleveland Condensation Tester - exposing the test surface to a heated, saturated mixture of air and water vapor, while cooling the reverse side with ambient room air.

The exposure conditions in fluorescent UV condensation apparatus may be varied by selection of the fluorescent UV lamp, the timing of UV and condensation exposures, the temperature of the UV exposure, and the temperature of the condensation exposure. The ability to vary all of these weathering stresses is unique to the apparatus, and either not available or not convenient in prior weathering apparatus or in natural weather exposures.

Our research has been directed to determining the limits for accelerating UV, water, and temperature stresses and learning how various conditions of test correlated with specific Florida exposure conditions on high gloss automotive coatings. Suggested limits and methods of operating the apparatus have recently been standardized and published in ASTM G-53-77, "Recommended Practice for Operating Light and Water Exposure Apparatus (Fluorescent UV-Condensation Type) for Exposure of Non-Metallic Materials."

The data generated by repeated tests on the same materials was analyzed and compared with Florida exposure results by graphic and statistical methods. Spearman rank correlation was found to be a convenient method of determining which of several test conditions produced the best correlation to outdoor exposure.

Florida exposures, in different years, or even at different sites in the same year, seldom result in the same absolute values. The average gloss of identical series after a year's exposure can vary a great deal. However, Florida exposure consistently produces good relative values. The objective of Florida exposure is to determine the relative merits of materials. The assumption is made that rankings established in a severe environment will prevail in more moderate weathering conditions.

Spearman rank correlation applies the same relative merit standard to accelerated weathering techniques. We are not asking "How many hours equal a year in Florida?"- we are asking whether the relative performance of a number of materials in the laboratory correlates with relative performance in the field.

Using the relative merit concept as our measure, we conclude that accelerated weathering is a reality, today. Nevertheless, the controversy over accelerated weathering has endured for over 65 years. Many solutions have been claimed as successes and then found wanting. The credibility of any claim to the ability to accelerate weathering is therefore suspect.

The purpose of this paper is to attempt to bridge this credibility gap by:

(1) Examining the natural weathering stresses induced by UV, water, and temperature and theorizing on the validity of the assumption that exposures in severe environments correlate with performance in less aggressive weathering conditions.

(2) Reporting what has been learned by reproducing and varying UV, water, and temperature stresses in the laboratory to illustrate the feasibility of accelerated weathering.

(3) Proposing methods for evaluating how any technique of accelerated weathering correlates with accelerated outdoor exposure or actual service conditions.

Figure 1 - Fluorescent ultraviolet-condensation apparatus

Degradation Stresses in Natural Weathering

The scope of this report is limited by defining weathering as that degradation which occurs when a material is exposed to the universal stresses of ultraviolet energy in sunlight, water as rain or dew, and temperature. It is recognized that there are other stresses from salt water, biological and air pollution. These are local weathering stresses that occur in some environments or on certain areas of a structure or vehicle.

The response to localized stresses tends to follow predictable patterns. The need to predict the resistance of materials to such local stresses has been met by single property testing in salt spray, SO_2 and mold chambers.

Our problems with predicting weatherability have always focused on reproducing the combined effects of UV, water, and temperature stresses. The response to these universal stresses can take many forms. Low gloss paints can chalk at a relatively steady rate until the paint erodes away. Weathering can induce a stable, adherent protective coating like the oxide on aluminum. In other instances, materials are not adversely affected by weathering until certain threshold levels of stress are attained. UV and temperature stresses frequently act in this manner. Alkyd enamels are acceptable coatings for automobile wheels because UV and temperature stresses on wheels are at very low levels.

Interactions between UV, water, and temperature stresses are the rule, not the exception. Temperature can alter the rate of photochemical or oxidation reactions, and photochemical attack can alter the rate of oxidation during wetness. Even though our approach to weathering has been limited by definition, it is still a complex multiple variable problem. Before we combine these stresses in the laboratory, we should understand how the individual stresses act in natural weathering.

Ultraviolet Stress in Sunlight

The European weathering literature and the medical profession divide the solar UV spectrum into three ranges. UV-A is the energy in wavelengths between 400nm and 315nm. UV-B is the 315nm - 290nm range. UV-C includes the solar radiation below 290nm, which never reaches the earth's surface. This classification is very convenient and useful.

The 400nm upper limit for UV-A is the generally accepted boundary between visible light and ultraviolet light. The 315 nm boundary between the UV-A and UV-B ranges defines the point at which ultraviolet energy begins to cause adverse effects and pigmentation changes in the human skin. Erythema, what we call sunburn, begins to occur

at wavelengths below 315 nm and reaches a peak at 297 nm. The UV-C boundary of 290 nm is a sharp cutoff of solar radiation at the earth's surface caused by ozone absorption (Figure 2).

The quantum theory explains the different effects of UV-A, UV-B, and UV-C. Light energy is transmitted in discrete units called photons. The energy in photons is inversely proportional to wavelength. The sun emits radiation in wavelengths well below 242 nm. The energy of photons in wavelengths below 242 nm is high enough to dissociate oxygen and create ozone. Ozone, in turn, is a highly effective UV absorber, absorbing all solar radiation below 290 nm so that energy in such wavelengths never reaches the earth's surface at sea level. Ozone partially absorbs UV-B so that the amount of UV-B in sunlight varies with solar altitude.
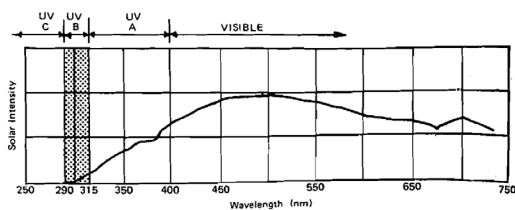

Figure 2 - Division and classification of solar ultra-violet spectrum

Photons in the UV-B 290 - 315 nm range are large enough to be completely absorbed by the atmosphere at solar altitudes below 14º. At a solar altitude of 19º, the sunlight cutoff is 310 nm and, at 40" altitude, sunlight cuts off at 303nm. At solar altitudes between 60º and 90°, the maximum amounts of UV-B reach the earth's surface and the sunlight cutoff is approximately 295 nm.

UV-A is always present in sunlight. Even at an 1 1" solar altitude, sunlight extends down to 320 nm. The photons in UV-A are smaller and they are only partially absorbed by passing through the atmosphere. A practical and convenient method of separating UV-A from UV-B is by filtering sunlight with window glass. Ordinary glass starts to absorb strongly at 350 nm and excludes wavelengths below 310 nm. It would be nearly impossible to sunburn human skin protected by window glass in any reasonable length of time.

Scott[1] has shown what occurs when the UV-B is excluded from sunlight by wintertime atmospheric filtering. However, the observed reduction in degradation could be partially attributed to reduced temperature stress. A more precise confirmation that UV-B is responsible for most photochemical changes can be obtained from paired direct and under glass exposures in the Arizona summer when the maximum UV-B intensities are present.

Both exposures would be at essentially the same temperature.

The difference between UV-A and UV-B effects can also be examined in the fluorescent UV-condensation apparatus by substituting fluorescent black lamps for the fluorescent sun lamps. We have conducted many experiments of this kind with black lamps on one side of the apparatus, sun lamps on the other. Black lamps have some emission in the UV-B range at 301 nm and 313 nm mercury lines.

Essentially the same type and order of failure occurs on both exposures. However, it normally takes 2 to 4 times as long to produce degradation with black lamps. As an example, a paired exposure reduced the 20" gloss of an alkyd enamel from 87 to 7 in 500 hr using the sun lamp. The black lamp exposure required 1096 hr to reduce the gloss level to 11. Since water stresses and temperature stresses were present during this test, they also contributed to degradation.

Quantum effect, the increase in energy level of light with decreasing wavelength, is repeatedly demonstrated by the behavior of UV light in the atmosphere on human skin and on polymers. Most of the light emission from the sun, 99% of the emission, simply does not have the energy to break bonds and cause photochemical degradation. The UV-B 290 - 315 nm band contains only 0.1% of the total energy in sunlight. In winter, UV-B is only 0.05%of the total; in summer, it is about 0.2% of the total.

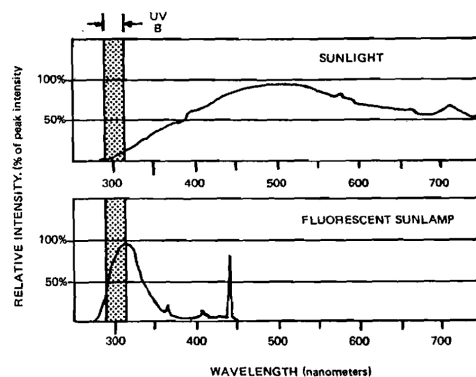**Figure 3 - UV intensity between sunlight and fluorescent sunlamp**

The ozone cutoff in sunlight and quantum effect make it possible to reproduce the effects of sunlight with relatively low cost, low energy demand 40 watt UV sources. The fluorescent sun lamp, with peak emission at 3 13 nm and a low cutoff at 280nm, is an excellent source of UV-B with some emission in the UV-A (Figure 3). Although the

cutoff of 280 nm is 10 nm below the sunlight cutoff, no unusual UV effects have yet been observed in seven years of testing.

The UV stress obtained with the fluorescent sun lamp emitting UV-B is comparable to noon midsummer sunlight on a clear day. The intensity at low wavelengths near 300 nm in the fluorescent UV-condensation apparatus is above the intensities found in natural sunlight. However, the feasibility of increasing intensities in this manner has been demonstrated for many years in the EMMA apparatus where natural sunlight is intensified many times with reflectors.

Increasing UV stresses by employing UV-C radiation is not acceptable for evaluating materials of different chemical composition. The "Dew Cycle"* procedure was a step forward in accelerated weathering because it employed alternating UV and condensation exposure in place of simultaneous exposures with water sprays. However, the virtues of these advances were negated by use of UV-C radiation never found in sunlight on the earth's surface. Removing the filters from a xenon arc subjects the test specimen to UV-C radiation at wavelengths down to 190 nm where light can dissociate oxygen.

Photochemical reactions occur instantaneously with application of the energy and are directly proportional to time. While the natural exposure is limited to about six hours of UV-B daily by the earth's rotation, there are no constraints on the duration of the UV exposure in the laboratory.

The myth that reproducing the effects of sunlight requires laboratory duplication of the entire spectral energy distribution of sunlight deserves a prompt and decent burial. There is no harm in reproducing UV-A and visible light because these wavelengths are harmless to today's exterior materials, but it is a waste of energy. There are only two conditions to observe in reproducing the effects of sunlight-UV-B wavelengths and good simulation of the atmospheric ozone cutoff.

Water Forces in the Natural Environment

The chemical quality of rain or dew is fairly consistent all over the earth in rural areas. Both rain and dew are condensed from a mixture of water vapor and air and typically saturated with dissolved oxygen. Water in equilibrium with atmospheric carbon dioxide has a pH of about 5.6 and rainfall is usually acidic. In the Eastern U.S., the average pH of rain during 1972-73 was less than 4.3 and pH values as low as 2.1 have been observed in some locations. The increased acidity is attributed to sulfuric and nitric acids in the atmosphere.[3]

You might think that dew is innocuous but there is no reason to suspect that dew is any less acidic than rain. The tendency of air pollutants to remain near the ground may possibly make dew more acidic than rain. In any event, rain or dew condensed from an air-water vapor mixture are electrolytes bearing dissolved oxygen.

The duration and frequency of natural water cycles are extremely variable. Materials exposed outdoors are commonly wet with dew for 14 or 15 hr per day. Rain can be present for only 15 min in a summer shower or continue for two or three days. Clouds can prevent a material from radiating heat to the cold night sky and thus maintain the material above the dewpoint. Winds can maintain a material at the ambient dry bulb temperature and also inhibit condensation.

Identical materials exposed at the same site will vary in duration and frequency of wetness. Insulate a surface so that it can lose heat to the sky without gaining heat from radiation from the ground and it will be wet longer than an uninsulated surface. Dew forms first on the insulated rear deck and hood of a car.

Such extreme variation in natural wetness time and frequency obviously presents problems in duplication with laboratory cycles that are fixed in time and temperature. Our approach to this problem has been one of trial and error. Water cycles of 4 to 20 hr in length at temperatures ranging from 40°C to 60°C have been evaluated.

The chemical properties of rain or dew can be easily and accurately duplicated in the laboratory by employing the principles and apparatus of the Cleveland Condensation Test developed by the Cleveland Society for Coatings Technology in 1963.[4,5] This apparatus is now in use all over the world to test the water resistance of paints, plastics, metals, wood, rust-inhibiting oils, and other materials.

The Cleveland Society made a very significant contribution to weathering science in designing and evaluating the Cleveland Condensation Tester. This apparatus demonstrated how natural water could be simply and reliably reproduced in the laboratory at low cost. Further, the use of some 700 Cleveland Condensation Testers has provided limits for accelerating the effects of water with temperature.

Natural rain or dew usually occurs in a temperature range of 0°C to 20°C. The Cleveland apparatus is a vented still using ambient room air as the cooling influence. The lowest practical condensation temperature is 40°C. Experience with continuous condensation indicates that condensate temperatures of 40°C may be used with almost any material. At 50"C, it is necessary to limit the time of exposure for some materials. At 60°C abnormal effects can occur. Abnormal whitening of acrylic lacquers at 60°C was observed on Cleveland Condensation tests several years ago.

There are other indicators to establish when water cycles are too long or too hot. Spotting is rare in the fluorescent UV-condensation apparatus because of the purity of the condensate. When spotting occurs, it may be attributed to the extraction of solubles from the coating or the substrate. White paints appear to fail more rapidly in hot and long water cycles.

Using these indicators, we have established that good correlation to natural weathering can be obtained using a wide range of water cycles. Long, cool cycles such as 20 hr at 40°C and short, hot cycles such as 4 hr at 50°C can be used. Abnormal effects on many materials may be caused at 60°C condensation temperature. At 50°C, some coatings can withstand 8 or even 16 hr exposure without abnormal effect. Nevertheless, when testing unknowns, the time and temperature of the condensation exposure must be limited.

Elevated laboratory condensation temperatures accelerate water effects without abnormal results, provided that we do not go too high in temperature for too long a time. It appears that reciprocity exists between time of wetness and temperature of wetness. It is postulated that the higher laboratory temperatures increase the rate of permeation and the rate of oxidation reactions so that 4 hr at 50' C simulates 14 hr at 20" C.

Temperature Stress in Natural Weathering

Surface temperature is the most variable factor in weather. An automobile driven at 55 mph on a highway will attain' a surface temperature near ambient. The same car, locked and parked in direct sunlight, can reach a surface temperature 30°C above ambient. At night, with no wind and a clear sky, the surface temperature can drop 8°C below ambient.

Color is also a contributing factor in service temperature. White paints typically attain maximum temperatures 10°C to 15°C lower than black paints. This condition is difficult to reproduce in the laboratory.

When hot arc sources are used in laboratory chambers, radiation heats the chamber along with the test specimens. This requires the introduction of cooling air which cools the panels as well as the chamber. In the fluorescent UV-condensation apparatus, the 320 watts output from the UV sources is not enough to raise the panel temperature to more than 55°C or 60°C. Heated air is introduced to the chamber to raise the panel temperature during UV exposure. The temperature of a black panel will be only a few degrees higher than a white panel. From a practical standpoint, it is very difficult to match outdoor temperature differences between dark and light materials in the laboratory. Whenever air is introduced for heating or cooling, temperature differences between colors are reduced. This is a limitation to accelerated weathering with which we will have to live.

Over the years, service temperature stresses for materials have gradually increased as structures are insulated or enclosed. The current energy crisis will create more demand for temperature resistance in materials as we add insulation. Materials scientists have gradually increased the temperatures of outdoor exposures to meet the demand. Automotive paints have moved from 45°S open rack exposure to 5°S open rack and then to 5°S Black Box insulated exposures. Plastics are commonly exposed on plywood backing, which is an excellent insulation. Some manufacturers expose coated metal panels on plywood.

The most important piece of information needed for designing accelerated test methods is the maximum service temperature in direct sunlight. Service temperature during nighttime wetness is similar for all colors and predictable from weather records. UV stresses are also predictable but temperature in sunlight must be measured in

service. Uninsulated materials can be expected to attain temperatures around 50°C to 60°C while temperatures of 70°C to 80°C are common on dark, insulated horizontal surfaces.

Testing different colors at the same temperature in the laboratory does not appear to be a serious problem at this time. White paints are tested at higher relative temperatures causing more degradation, but our work indicates that the relative rankings of various colors are essentially unchanged. However, it is desirable to conduct laboratory evaluation of paint systems in several colors ranging from light to dark.

Combining UV, Water, and Temperature Forces

A persistent myth in weathering literature is the theory that the combination of sunlight and dew in the early morning causes unexplained synergistic effects that we have been unable to duplicate in the laboratory. This is an intriguing theory but it is not consistent with real weathering. Sunlight drys off materials before the sun elevation reaches a point where UV-B is transmitted through the atmosphere.

Nevertheless, simultaneous UV and water exposures have been commonly used in weathering apparatus in the past. In simultaneous exposures, heat from the UV source makes it difficult to keep the test specimen wet. Control of wetness temperature is also a problem. Natural weathering occurs in separate UV and water exposures that are at different temperatures. Such alternate exposures can and should be used in accelerated weathering.

The conditions necessary for reproducing natural weathering stresses in the laboratory are summarized in Table 1.

Any combination of UV, water, and temperature that satisfies these conditions can correlate reasonably well with natural weathering. Over the past seven years in our search for "the answer," we have recommended time cycles of 8 UV-4 CON, 4 UV-4 CON, 6 UV-6 CON, and 16 UV-8 CON. All of these cycles, at various temperatures, are being used in fluorescent UV condensation apparatus today to meet specific needs.

For several years, the basic thrust of our experimental work was to find the one set of conditions that could be called "accelerated weathering." We have concluded that "the answer" does not exist. Conditions of accelerated weathering must be matched to the specific requirements of outdoor

	UV Conditions	Water Conditions
Quality	UV-B emission with minimal emission below 290 nm.	Condensed from vapor phase, pH approximately 4.0 to 6.0 saturated with O_2.
Exposure Duration	No theoretical maximum or minimum. Practical minimum of 3 to 4 hr.	Time and temperature interact. 4 to 20 hr are practical limits.
Temperature	55°C to 80°C as required to duplicate service temperature.	60°C sometimes causes abnormal effects. 50°C for 8 hr can cause problems. 40°C is safe but slower.

Table 1 - Conditions for Reproducing Natural Weathering Stresses in the Laboratory

exposure or service conditions. Outdoor weather test facilities expose materials at 45°S, 5°S, vertical South or North in both insulated and open racks to correlate with specific service environments. We should not be surprised to learn that laboratory weathering conditions must also be varied to meet the need.

Methods of Correlation

We have made correlation studies between various accelerated test conditions and Florida exposure. The studies involved 27 automotive coatings in 9 proprietary paint systems. Each system has three identical colors-green, blue, and white. Five systems are used in insulated applications and usually tested in Florida on insulated 5°S racks. The other four are intended for use at lower service temperatures and are normally evaluated by 5°S open rack exposure. For the purposes of correlation, all 27 were exposed on both types of racks. Substrates were steel and flexible plastics.

The sole property examined for correlation was 20" gloss, but color change and other effects were noted as they occurred. In the first analysis, percent loss of gloss was the value used in calculation. However, it was felt that customers respond more to final gloss than to percent loss. Therefore, all of the correlations relate 20° gloss after a period of time in Florida exposure to 20° gloss after a period of time in fluorescent UV condensation test.

The validity of using 20" gloss values as a measure of relative appearance was tested by submitting two completed tests in separate color sets to ranking by five individuals not associated with the testing. The rank correlation with gloss values was very good and visual discrimination differences of about 5 points in 20° gloss appears to be possible.

System and Color	Exposure X 12 Mo. Fla. Insulated Site A	Exposure Y 12 Mo. Fla. Insulated Site B	Exposure Z 12 Mo. Fla. Open Rack Site A
A Green	1	1	3
A White	2	2	1
B Green	3	3.5	6.5
C Green	4	6	10.5
B White	5	3.5	4.5
A Blue	6	9	10.5
B Blue	7.5	13	12
F Green	7.5	7.5	8
E White	9	5	6.5
D Green	10	11	4.5
C White	11	10	13
D White	12	7.5	9
G Green	13	17	16
D Blue	14.5	13	14.5
C Blue	14.5	13	14.5
E Green	16	16	17
E Blue	17	15	2
H Green	18	21	22
F White	19	18	18
J Green	20	25	19
H White	21	19.5	20
F Blue	22	19.5	21
G Blue	23	24	23
H Blue	24	22	24
G White	25.5	23	25
J White	25.5	26	26
J Blue	27	27	27

Table 2 - Ranking of 20° Gloss Values After Simultaneous Exposures

System and Color	Exposure X 12 Mo. Fla Insulated Site A	Exposure Y 12 Mo. Fla Insulated Site B	Exposure Z 12 Mo. Fla Open Rack Site A
A Green	63	71	63
A White	60	69	67
B Green	54	66	57
C Green	53	60	53
B White	51	66	58
A Blue	50	52	53
B Blue	48	48	51
F Green	48	54	55
E White	47	65	57
D Green	46	50	58
C White	45	51	49
D White	43	54	54
G Green	39	37	41
D Blue	37	48	46
C Blue	37	48	46
E Green	26	44	39
E Blue	22	46	64
H Green	19	18	17
F White	18	21	29
J Green	15	4	22
H White	14	19	20
F Blue	12	19	19
G Blue	10	10	11
H Blue	7	15	8
G White	4	11	7
J White	4	3	4
J Blue	2	2	3
Median	37	48	46
Mean	32.4	37.3	38.9

Table 3 - 20° Gloss Values After Simultaneous Exposures

Two common methods of correlation could be applied to the analysis, Pearson linear correlation and Spearman rank correlation. The Pearson method assumes that the property under consideration can be measured on an interval scale. Perfect correlation of 1.0 requires a linear relationship between two sets of data. It is questionable whether gloss values are true interval data and whether linear relationships exist between laboratory methods and outdoor exposures.

Spearman rank correlation is intended to handle nonparametric data such as visual rankings of appearance or chalking. Mitton[6] has shown how Spearman rank correlation can be applied to evaluating the correlation of accelerated weathering methods to Florida for the property of chalking. Perfect correlation under the Spearman method can be achieved without a linear relationship.

No matter how much gloss and color difference data is generated, a final decision is almost always made by comparing the tests visually. The Spearman procedure is thus similar to actual practice. The calculations are also simpler. The Spearman method was selected and all sets of gloss values converted to rankings as shown in Table 2.

How Consistent Are Outdoor Exposures?

The first question to be answered was the selection of an outdoor exposure or exposures as the standard for comparison. Our initial tests were compared to a single Florida exposure, but there were doubts that one exposure could be duplicated by subsequent exposures. A claim that accelerated test methods are unreliable can be answered with the counter-claim that Florida exposures are not the same from year to year.

Three simultaneous Florida exposures were subsequently conducted on the 27 coatings. Two were 5°S insulated exposures at different sites in the Miami area. At one site, a 5°S open rack exposure was also made. The 20° gloss values after one year of exposure are shown in Table 3.

Differences in rate of failure between exposures are immediately evident. Median gloss is perhaps a better expression of the rate difference but both median and mean indicate exposures Y and Z are the closest in rate. Our company did not participate in conducting or measuring the Florida exposure panels and, therefore, we can only speculate as to the reason for rate differences between the two insulated exposures. Examination of the original gloss values at both stations showed the initial readings were essentially identical.

In Table 2, rankings are made for each exposure series. Using gloss readings of 47, 46, 45, and 43 to rank coatings 10, 11, 12, and 13 in the X exposure immediately raises the question of whether such a procedure is splitting hairs. It is recognized that another operator or another gloss meter could rank these coatings differently. Such potential

System and Color	Exposure X 12 Mo. Fla. Insulated Site A Gloss	Rank	RD	RD²	Exposure Y 12 Mo. Fla. Insulated Site B Gloss	Rank	RD	RD²	Exposure Z 12 Mo. Fla. Open Rack Site A Gloss	Rank
A Green	63	1	0	0	71	1	2	4	63	3
A White	60	2	0	0	69	2	1	1	67	1
B Green	54	3	0.5	0.25	66	3.5	3	9	57	6.5
C Green	53	4	2	4	60	6	4.5	20.25	53	10.5
B White	51	5	1.5	2.25	66	3.5	1	2	58	4.5
A Blue	50	6	3	9	52	9	1.5	2.25	53	10.5
B Blue	48	7.5	5.5	30.25	48	13	1	1	51	12
F Green	48	7.5	0	0	54	7.5	0.5	0.25	55	8
E White	47	9	4	16	65	5	1.5	2.25	57	6.5
D Green	46	10	1	1	50	11	6.5	42.25	58	4.5
C White	45	11	1	1	51	10	3	9	49	13
D White	43	12	4.5	20.25	54	7.5	1.5	2.25	54	9
G Green	39	13	4	16	37	17	1	1	41	16
D Blue	37	14.5	1.5	2.25	48	13	1.5	2.25	46	14.5
C Blue	37	14.5	1.5	2.25	48	13	1.5	2.25	46	14.5
E Green	26	16	0	0	44	16	1	1	39	17
E Blue	22	17	2	4	46	15	13	169	64	2
H Green	19	18	3	9	18	21	1	1	17	22
F White	18	19	1	1	21	18	0	0	29	18
J Green	15	20	5	25	4	25	6	36	22	19
H White	14	21	1.5	2.25	19	19.5	0.5	0.25	20	20
F Blue	12	22	2.5	6.25	19	19.5	1.5	2.25	19	21
G Blue	10	23	1	1	10	24	1	1	11	23
H Blue	7	24	2	4	15	22	2	4	8	24
G White	4	25.5	2.5	6.25	11	23	2	4	7	25
J White	4	25.5	1.5	2.25	3	26	0	0	4	26
J Blue	2	27	0	0	2	27	0	0	3	27

rho X-Y = 0.95   rho Y-Z = 0.90

rho X-Z = 0.88

Table 4 - Spearman Rank Correlation for Ranked 20° Gloss Values

experimental error is compensated for in the correlation calculation. The classification of the data into broader groups will not influence the correlation coefficient to any great degree. In order to maintain the 1 to 27 rank difference between best and worst, ties were ranked as shown in Table 2.

The term "reversal" has often been used to describe variation in weathering tests. It can mean that the best coating in one test is the worst in another test, or only that slightly different results are obtained. Calculating rank differences, as in Table 4, is a quantitative way to express the magnitude of reversals. The impact of the rank difference on the final correlation is proportional to the square of the rank difference. Rank differences below 4 or 5 influence the resulting correlation coefficient very little in a series of 27. The difference between the open rack and insulated exposure is centered on the variation in performance of the system E Blue coating. In the last six months of the exposure, E Blue dropped from 53 to 22 in the insulated X exposure and dropped only from 68 to 64 on the open rack Z exposure.

The completion of the calculation shows better correlation between the two insulated exposures, X and Y. The Spearman rank correlation coefficient is calculated by the formula:

$$rho_s = 1 - \left[\frac{6 \Sigma (Rank\ Diff)^2}{n^3 - n} \right]$$

(n is the number of items ranked)

It was concluded that the reason why coatings and materials from all over the world are sent to Florida and Arizona for exposure is that the relative merits established by such exposures are quite consistent. Duplicate Florida exposures do contain "reversals" and differences in rate, but the overall rank correlation is quite good. In that context, all of the laboratory tests were correlated to exposure X with some confidence that it represented "reality."

The value of rho between separate Florida tests is a limit for the value of rho between laboratory and outdoor tests. One can hardly expect laboratory tests to correlate with Florida better than Florida correlates with itself. The correlation between Florida exposures X and Z (rho X-Z) was 0.88, while rho Y-Z was 0.90. Attaining the same level of correlation in a few weeks of laboratory testing could be considered real progress.

The rank correlation coefficient derived from this type of relative merit analysis is also relative. Values of 0.90 to 0.95 obviously indicate excellent correlation. At lower levels, the principal value of rho is in comparing two or more sets of data to another set. In Table 5, rank correlation comparisons of exposures X, Y, Z for the five best systems only are shown. This is a comparison of systems that are of the same general type used for the same purpose.

System System and Color	Exposure X 12 Mo. Fla. Insulated Site A				Exposure Y 12 Mo. Fla. Insulated Site B				Exposure Z 12 Mo. Fla. Open Rack Site A	
	Gloss	Rank	RD	RD²	Gloss	Rank	RD	RD²	Gloss	Rank
A Green	63	1	0	0	71	1	2	4	63	3
A White	60	2	0	0	69	2	1	1	67	1
B Green	54	3	0.5	0.25	66	3.5	3	9	57	6.5
C Green	53	4	2	4	60	6	3.5	12.25	53	9.5
B White	51	5	1.5	2.25	66	3.5	1	1	58	4.5
A Blue	50	6	2	4	52	8	1.5	2.25	53	9.5
B Blue	48	7	5	25	48	12	1	1	51	11
E White	47	8	3	9	65	5	1.5	2.25	57	6.5
D Green	46	9	1	1	50	10	5.5	30.25	58	4.5
C White	45	10	1	1	51	9	3	9	49	12
D White	43	11	4	16	54	7	1	1	54	8
D Blue	37	12.5	0.5	0.25	48	12	1.5	2.25	46	13.5
C Blue	37	12.5	0.5	0.25	48	12	1.5	2.25	46	13.5
E Green	26	14	1	1	44	15	0	0	39	15
E Blue	22	15	1	1	41	14	12	144	64	2

47 = median   52 = median   54 = median

rho X-Y = 0.88   rho Y-Z = 0.60

rho X-Z = 0.49

Table 5 - Spearman Rank Correlation for Ranked 20° Gloss Values of 15 Similar Coatings

rho = 0.62

rho = 0.89

rho = 0.84

System and Color	Exposure X 12 Mo. Fla. Insulated		Test #18 4 UV/50C 4 CON/50C 514 hrs.		Test #16 4 UV/70C 20 CON/40C 1000 hrs.		Test #7 6 UV/70C 18 CON/50C 332 hrs.	
	Gloss	Rank	Gloss	Rank	Gloss	Rank	Gloss	Rank
A Green	63	1	76	1.5	82	2.5	58	8 *
A White	60	2	69	4	73	4	50	13 *
B Green	54	3	76	1.5	90	1	87	1
C Green	53	4	48	9	68	6	54	10
B White	51	5	69	4	82	2.5	84	2
A Blue	50	6	44	11.5	47	12	32	18 *
B Blue	48	7.5	44	11.5	62	9	55	9
F Green	48	7.5	47	10	54	10	73	4
E White	47	9	61	6	68	6	67	5.5
D Green	46	10	37	14	48	11	31	19 *
C White	45	11	69	4	67	8	74	3 *
D White	43	12	36	15	42	14	37	15
G Green	39	13	32	18	46	13	34	16.5
D Blue	37	14.5	19	21	10	23 *	2	25.5 *
C Blue	37	14.5	40	13	35	15	52	12
E Green	26	16	58	7 *	68	6 *	67	5.5 *
E Blue	22	17	52	8 *	28	18	53	11
H Green	19	19	35	16	33	16	10	22.5
F White	18	19	30	19	29	17	45	14
J Green	15	20	5	25.5	14	21.5	65	7 *
H White	14	21	15	22	3	26	1	27
F Blue	12	22	8	24	7	24	17	21
G Blue	10	23	10	23	14	21.5	10	22.5
H Blue	7	24	21	20	25	19	19	20
G White	4	25.5	33	17 *	21	22	7	24
J White	4	25.5	1	27	2	27	2	25.5
J Blue	2	27	5	25.5	6	25	34	16.5 *
			37 = median		37 = median		42 = median		39 = median

* Indicates largest rank differences with Exposure X

Table 6 - Rank Correlation of Fluorescent UV-Condensation Exposures to Exposure X

It may be observed that limiting the comparison in this manner reduces the coefficient. Rho X-Y drops from 0.95 to 0.88, rho Y-Z from 0.90 to 0.60, and rho X-Z from 0.88 to 0.49. However, the conclusion is the same, exposures X and Y have the closest correlation. The coefficient is expected to be lower when materials of similar durability are compared, simply because it's harder to discriminate between similar materials.

Correlation of Fluorescent UV-Condensation Tests to Florida

Twenty-one separate tests of the 27 coatings were conducted over a two-year period. The program was exploratory with 14 of the tests outside of the limits now published in ASTM Recommended Practice G-53-77. A few tests were discontinued at 168 and 336 hr because of abnormal effects. Most tests had a length of 500 to 1000 hr, 3 to 6 weeks.

Twenty degree gloss values were taken on a weekly basis. The tests were concluded when the median gloss reached a level near the 37 median gloss of exposure X. However, some tests were concluded at 1000 hr without reaching that level of degradation.

Table 6 illustrates how the 27 coatings in 9 systems responded to different temperature and water stresses. The UV source was the same in tests #18, # 16, and #7. The largest rank differences in each test as compared to exposure X are designated by an asterisk.

Good correlation was obtained on test # 18 and test #16 but with different test conditions. Test #16 required twice as much time and did not reduce the gloss of the five best coatings as much as Florida.

Poor correlation was obtained in test #7 by using 18 hr of condensation at 50°C. The time of wetness in test #7 was less than in test #16 and 70°C UV temperature was the same in both tests. System A was reduced in rank along with system D. System E still had a higher ranking than Florida. System J, the least durable system, exhibited better rankings in the Green and Blue colors. The rho of 0.62 for X to test #7 is a fair appraisal of the poor correlation. Correlating systems A through E only to exposure X gave an rho of 0.26.

Repeated tests on these 27 coatings at various levels of UV, water, and temperature stresses has provided enough information to generalize on how the systems and colors responded.

(1) None of the nine systems were appreciably changed in ranking by reducing UV stress using black lamps.

(2) Two systems were changed in rank by water stresses beyond those encountered in service. Three systems were resistant to such water stresses.

(3) Three systems exhibited varying degrees of temperature sensitivity at temperatures within the range encountered in insulated service.

(4) Three systems, expected to show temperature sensitivity because they are used at moderate temperatures in service, did not do so. Accelerated tests at temperatures higher than might be expected in service did not influence rankings.

(5) The color relationship in Florida may generally be expressed as Green 2 White > Blue. The relationship in fluorescent UV-condensation tests, in most instances, was Green > White > Blue. The temperature difference between Green and White in accelerated testing was less than the difference in outdoor exposure.

It may be concluded that the general limits for UV, water, and temperature stresses may be violated when testing specific systems. We are aware that they are being violated to reduce test time. However, it is more than evident that weathering stresses must be balanced to compare even slightly different systems.

By the time we reached tests #16 and #18 with correlation coefficients around 0.85, our confidence had reached corresponding levels. The principles learned with high gloss coatings were

applied to a test of low gloss white coatings on hardboard substrates. It was assumed that degradation would result in a few weeks but six weeks of test only produced a little chalking. Twelve weeks of test on fluorescent UV-condensation apparatus in another laboratory gave the same result. However, Cleveland Condensation tests using water alone produced the desired change in properties. Hard and fast rules for accelerating weathering cannot be drawn for all materials and coating substrates.

A test trend of nonlinearity with Florida exposure was observed, and every test was examined graphically for linearity. The best coatings held gloss longer in relation to Florida and weak coatings degraded much faster. The tests seemed to magnify the differences between coatings. A median gloss of 37 in 500 hr for the entire set would indicate an acceleration ratio of about 17: 1 when compared to exposure X. Estimating the ratio for each individual coating produced acceleration ratios of perhaps 8:1 for the most durable coatings and ratios of 25:1 for the least durable.

It can be speculated that nonlinearity also exists with respect to moderate and severe weathering environments. Maximizing the levels of stress by insulated exposures in Florida and in laboratory tests could be expected to degrade weaker coatings much faster than good coatings.

The magnification of differences by maximizing stresses can be both an advantage and a disadvantage. Obviously, such procedures sort out the weaklings very rapidly, frequently within a week. However, differences between similar coatings can be overvalued. Two almost identical systems in the study exhibited a fairly consistent rank difference of 1. It is doubted that such a difference would be revealed in service, and examination of other properties could alter relative merit.

This test program was initiated by observations of rank differences between Florida and fluorescent UV condensation tests on two of the systems. The test program has never ranked these two systems exactly the way they rank in Florida insulated exposure. However, the magnitude of the reversal was found to be one or two ranks in nine. With understanding of the reason for this difference, fluorescent UV-condensation tests on both systems are being used.

Spearman rank correlation has proved useful in handling the observed nonlinearity between accelerated testing and Florida exposure. The Spearman method valued a test procedure's ability to place coatings in the same order without demand-

ing a linear time relationship. As few as seven samples can be handled by the Spearman method but the significance of rho is proportional to the number of samples. From a practical viewpoint, ranking more than 30 coatings is cumbersome. However, 15 values can be handled easily and 27 was not an unreasonable number. If five systems are under evaluation, each should be prepared in four or five colors. Controls, coatings of known durability, should always be included if available.

Conclusion

Thousands of tests in aggressive environments, such as Florida and Arizona, demonstrate that natural weathering can be accelerated by various techniques. A consensus exists that such tests have useful correlations to weathering in more moderate environments. An analysis of natural weathering has indicated the reasons why such correlations between different environments can be obtained. Maximum UV, water, and temperature stresses are similar everywhere.

The time a material is stressed and the temperature during UV and water stresses are the primary variables in natural weathering. Hot, humid environments cause the most degradation. However, even duplicate exposures in one area can be expected to vary in rate. When annual, seasonal, and location rate differences are excluded by rank correlation procedures, natural accelerated weathering is shown to consistently and reliably predict the relative merits of materials.

Today's coatings and plastics are the products of a natural evolutionary process. The weaklings have disappeared from use. Thresholds of sensitivity to UV, water, and temperature have been raised. With today's materials, natural weathering is not a continuous process. It is a sporadic, intermittent process that occurs only when stresses reach certain levels. Much of the time on outdoor test racks is wasted because no deterioration is happening.

The basic stresses in weathering are known and quantified. Reproducing them exactly in the laboratory can provide acceleration by eliminating idle time. Further acceleration is possible by maximizing UV, water, and temperature stresses within natural limits.

Weathering research in past years has concentrated almost exclusively on a single weathering stress, the ultraviolet energy in sunlight. Water and temperature stresses were relegated to a secondary status. Little attention was given to balancing these stresses.

The work of the Cleveland Society for Coatings Technology gave a new dimension to weathering research. It is difficult to conceive of a simple apparatus in a wood frame as a breakthrough, but the Cleveland Condensation test showed how to reproduce the quality of natural water. More important, the test established limits for combining time and temperature to accelerate water effects. Our tests show how violating these limits can cause abnormal degradation.

It would be difficult to rank the relative importance of water, temperature, and UV. Some materials are degraded by UV alone, some are degraded by water alone, and most materials are weathered by the combined stresses.

The tests reported here indicate that the most important factor in accelerated laboratory weathering is the proper balancing of these stresses. The fluorescent UV-condensation apparatus has the capacity to vary the balance of weathering stresses.

We conclude that accelerated weathering is a reality. More precisely, accelerated weathering procedures can match the various realities of natural weather. There isn't one answer, there are answers. The best answer for a particular purpose can be determined by relative merit procedures such as Spearman rank correlation.

Many years of testing will pass before a final decision is rendered. It is hoped that the theories and practices proposed in this paper can serve as a framework for such tests.

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