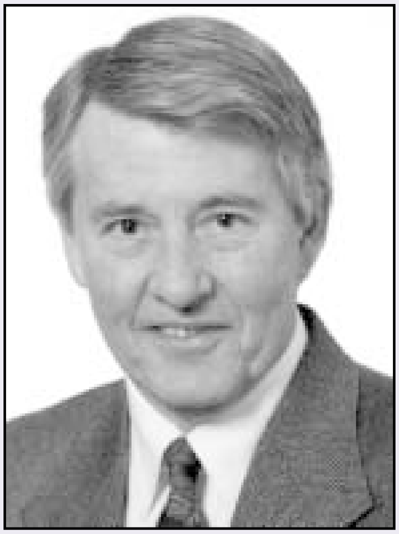
John L. Gerlock

Dr. Gerlock is well known for his innovative studies on the development of a means to anticipate the long-term weathering performance of modern automotive paint systems. He initiated research on the migration and longevity of stabilizing additives such as ultraviolet light absorbers (UVAs), and was the first to determine that UVAs were consumed during coating weathering, leading to a loss of protection. His research is based on the premise that it should be possible to relate the chemical composition changes that occur in automotive paint systems during outdoor exposure to their long-term weathering performance and thereby greatly augment the information afforded by traditional weathering performance metrics. Therefore, he developed a method to measure the rate of formation of free radicals during the earliest stages of paint weathering under natural exposure conditions.

Dr. Gerlock is currently working towards developing what he calls a "trustworthy accelerated weathering test." FTIR measurements have been carried out on isolated clearcoats exposed in Florida, Arizona, and a wide variety of accelerated weathering tests in order to compare degradation chemistries. Results indicate that distorted weathering chemistry can contribute to false accelerated weathering test results and go on to indicate that mismatch between artificial light spectral power distribution and sunlight is an important consideration. Currently, an attempt is being made to verify this contention and encourage the development of light sources whose spectral power distribution matches sunlight's more closely in the UV region.



Born in Atlanta, GA, Dr. Gerlock obtained a B.S. in Chemistry from the University of Georgia and a Ph.D. in Physical Organic Chemistry from the same university under a DEA Fellowship with Prof. E.G. Janzen. He used ESR spectroscopy to study the formation of hydroxy substituted nitroxyl radicals when nitro aromatics are photolyzed in hydrogen atom donor solvents. Following graduate school, Dr. Gerlock pursued Post Doctoral research with Prof. G.A. Russell at Iowa State University where he studied ion pair formation in semidione anion radicals. He joined Ford's Research Laboratory in 1974 in the Fuels and Lubricants Department to study the phase separation behavior of alcohol, gasoline, and water blends as part of an alternate fuels project. Later, he developed the means to recycle polyurethane foam with Dr. Jacob Braslaw of the Polymer Science Department.

In 1982, a casual lunchtime conversation proved to be interesting when it revealed that modern automotive paint systems commonly use nitroxyl radical precursors, hindered amine light stabilizer (HALS) antioxidants, to improve long-term weathering performance. The conversation led to a series of exploratory experiments on the behavior of 2,2,6,6-tetramethylpiperidinly-N-Oxyl free radicals in automotive clearcoats whose results prompted a move to the Laboratory's Polymer Science Department and opened the door to more than 20 years of sustained research on the chemistry of automotive paint weathering with a wide variety of very creative researchers.

Traditional methods for the evaluation of paint weatherability—accelerated exposure and long-term natural exposure—have well-documented deficiencies in reliability and timeliness. Dr. Gerlock's work has been of direct and important benefit to Ford Motor Company and its suppliers. Based on his research, chemistry-based weatherability tests are now used industry-wide to evaluate paint weatherability. These tests were first described in a series of Ford Laboratory Test Methods, and have led to changes in standard accelerated exposure conditions (SAE-1960) providing better correlation with outdoor exposures and more accurate predictions of long-term performance in service.

Dr. Gerlock's influence is evident throughout the automotive and coatings industries. He has provided extensive training to supplier engineers in the use and interpretation of chemically-based durability testing for automotive paint systems. He has also directly influenced the design coating resin systems and the formulation of automotive enamels by documenting the effects of resin structural changes on coating performance and the effects of stabilizer and UV absorber permanence on long-term coating weathering performance.

Dr. Gerlock's work has resulted in a new, fundamental understanding of paint weathering and stabilization. It has led to the development and use of chemically-based paint weathering tests at Ford and at all major paint suppliers to the industry. Dr. Gerlock is the recipient of four Henry Ford Technical Achievement Awards, two Henry Ford Technology Awards, and the Thomas Midgley Award for his research on paint weathering. He has published 43 papers on various aspects of the topic and presented research results at 73 invited lectures around the world.

* *The 2002 Mattiello Memorial Lecture* *

Testing Accelerated Weathering Tests for Appropriate Weathering Chemistry: Ozone Filtered Xenon Arc

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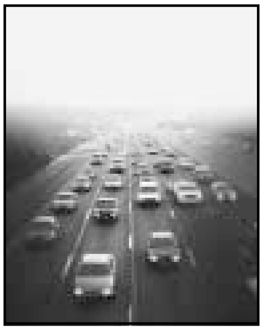

FTIR spectroscopy has been used to follow the weathering chemistry of a HALS and UVA free polyester/urethane and a HALS and UVA free acrylic/melamine clearcoat cured on silicon wafers and subjected to exposure in Florida, Arizona, and in a number of accelerated weathering tests. All accelerated tests except EMMAQUA-NTW, ozone filtered xenon arc, and 3M Proprietary exposures distort the polyester/urethane's weathering chemistry relative to its Florida and Arizona exposure weathering chemistry. Distorted weathering chemistry was attributed primarily to spectral power distribution mismatch between artificial radiation and sunlight. Experiments were initiated with an ozone filtered xenon arc radiation source whose spectral power distribution matches sunlight with great fidelity in the 290-400 nm region.

INTRODUCTION

Traditional monocoat automotive paint systems consist of a crosslinked binder with pigments that impart color and screen underlying primer and electrocoat layers from ultraviolet (UV) radiation. When the surface of the top layer in monocoat paint systems degrades during weather exposure, pigment particles are exposed that can scatter light. Thus, gloss, color change, and hardness measurements can provide direct insight into a coating's long-term weathering performance. In clearcoat/basecoat automotive paint systems, a clear layer of crosslinked binder with a UV screening additive overlays the pigmented layer, basecoat, that imparts color. When the surface of the clear layer degrades during weather exposure, pigment particles are not exposed. This is the primary reason why clearcoat/basecoat paint systems can look glossy much longer without waxing or polishing than monocoat paint systems. Therefore, clearcoat/basecoat systems have displaced monocoat paint systems in virtually all modern automobiles.

The difference in the gloss behavior of monocoat and clearcoat/basecoat paint systems also appears to be the primary reason for the large number of paint system failures observed when clearcoat/basecoat paint systems were first introduced in the mid-1980s. The weathering performance of clearcoat/basecoat paint systems was assessed on the basis of gloss loss and color change measurements and these metrics proved to be inadequate to correctly assess the weathering performance of such paint systems. Clearcoat/basecoat paint systems are entirely capable of failing suddenly and catastrophically by clearcoat cracking and/or peeling with little or no gloss loss indication that failure is imminent.

Since the mid-1980s a concerted effort has been made to develop nontraditional weathering performance metrics that will correctly assess the weathering performance of clearcoat/basecoat paint systems. For example, measuring the rate at which the concentration of clearcoat ultraviolet light absorber (UVA) additive decreases during weather exposure reveals how long the clearcoat can screen underlying basecoat from UV radiation.[1] Photooxidation of the clearcoat/basecoat interface can lead to failure by clearcoat peeling. Measuring the concentration profile of hindered amine light stabilizer (HALS) additives within the clearcoat and basecoat reveals how long and where HALS will inhibit oxidation.[2] Failure to inhibit clearcoat surface oxidation can lead to failure by clearcoat cracking. Several techniques have been developed to map the progress of photooxidation and hydrolysis across all layers in clearcoat/basecoat/primer/electrocoat paint systems.[3-8] Intense photooxidation and/or hydrolysis at any location within such paint systems is cause for concern.

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And finally, techniques have been developed to assess the mechanical repercussions of weathering chemistry.[9] Unfortunately, several years of outdoor exposure can be required to produce useful test panels for these tests.

The alternative to chemical analysis measurements is to wait many years to actually observe cracking and/or peeling failure during outdoor exposure. While this practice may be a reasonable approach when developing new coating chemistries, it is not a reasonable approach when trying to evaluate the impact of seemingly minor formulation changes on the weathering performance of existing paint systems. In practice, coating formulations continuously evolve such that three- to five-year old outdoor exposure test panels are rarely available for every formulation change. Clearly it would be very advantageous to be able to quickly weather test panels in the laboratory for chemical analysis. The problem is, how to quickly weather test panels and ensure that they accurately represent outdoor exposure test panels?

Early attempts to assess the usefulness of accelerated weathering tests for automotive clearcoat/basecoat paint systems relied on traditional appearance-based weathering performance metrics: gloss loss, color fade, or time to crack, for example.[10-13] In general, poor correlations were found. Bauer et al. used photoacoustic FTIR spectroscopy (PAS-FTIR) to follow the weathering chemistry of a polyester/urethane clearcoat in a complete paint system when it was subjected to Corex D filtered carbon arc, QUV UVB-313, borosilicate/borosilicate filtered xenon arc, equitorial mount with mirrors for acceleration (EMMA), and Florida exposure.[14] Corex D filtered carbon arc, QUV UVB-313, and borosilicate/borosilicate filtered xenon arc exposures produced rapid cracking. Cracking did not occur during EMMA or Florida exposure. PAS-FTIR spectra indicated that EMMA exposure was the only accelerated exposure that reproduced the clearcoat's Florida exposure weathering chemistry. False cracking results were attributed to inappropriate weathering chemistry. However, the authors did not conclude that EMMA exposure could necessarily correctly reveal the clearcoat's actual weathering performance. McEwen et al. compared the gloss behavior and weathering chemistry, as measured by attenuated total reflectance FTIR spectroscopy (ATR-FTIR), of several acrylic/melamine coatings subjected to Florida, Venezuela, EMMA, QUV UVB-313, and quartz/borosilicate filtered xenon arc exposure and found poor correlation for tests that appeared to distort weathering chemistry relative to outdoor exposure, namely, QUV UVB-313 and quartz/borosilicate filtered xenon arc exposure.[15] Wernståhl reached a similar conclusion when comparing measurements of weathering chemistry (ATR-FTIR) with gloss loss behavior for an acrylic/urethane subjected to Florida and borosilicate/borosilicate filtered xenon arc exposure with and without simulated acid rain.[16] Correlation was observed when ATR-FTIR spectra indicated a close match between accelerated and outdoor exposure weathering chemistry although a detailed analysis of the degree of match was not given. And finally, a number of review articles have addressed the correlation between accelerated and outdoor exposure results and the majority conclude that accelerated tests do not appropriately and consistently duplicate outdoor weathering behavior for all coating chemistries.[17-21] Some accelerated tests duplicate failure modes for specific coating chemistries, but not others. No consistency was found.

Taken together, reports like those cited above firmly establish a threshold requirement for accelerated weathering tests to begin to provide useful results, namely, accelerated and outdoor exposure weathering chemistry must match for every coating layer. In theory accelerated tests would be required to reproduce: (a) the outdoor HALS and UVA effectiveness and longevity, (b) the outdoor migration behavior of HALS, UVA, and low molecular weight debris between coating layers, and (c) the outdoor progress of photooxidation and hydrolysis across all coating layers. Mechanical stresses would have to be correctly proportioned to outdoor exposure weathering chemistry in order to reproduce outdoor exposure failure modes. While matching all of these criteria to produce an actual "what you see is what you will see in service test" is a formidable task, means are presently available to eliminate from consideration those accelerated tests that do not correctly reproduce outdoor weathering chemistry.

The present work uses transmission FTIR spectroscopy to follow the weathering chemistry of two clearcoats exposed in Florida and Arizona and in a number of accelerated weathering tests. An experiment is also conducted to begin to assess how closely artificial radiation must match sunlight in order to drive appropriate weathering chemistry.

EXPERIMENTAL

Sample Description

Two clearcoats, Y and R, have been studied. Clearcoat Y is as close as possible to the isophthalate extended polyester/urethane studied by Bauer et al.[14,22] Clearcoat R is a typical high solids acrylic/melamine.[7,23] Fully stabilized versions of both clearcoats in complete paint systems are known to perform well during Florida, Arizona, and in-service exposure. Clearcoat R is used as body paint and Clearcoat Y is used to paint flexible plastic components. HALS and UVA additive free versions of both clearcoats were studied to reduce the time required to observe chemical composition changes.

FTIR Sample Preparation

Clearcoat resin was smeared on 13 mm × 2 mm silicon wafers (Wilmad Glass 100N9-SP1) with a small glass rod. The thickness of the noncured resin was adjusted to produce cured samples whose strongest peak absorbance was in the 1-1.5 range. Samples were cured at 130°C for 20 min. The silicon wafer substrates were notched to allow them to be reproducibly positioned in the FTIR spectrometer using a sample holder with a corresponding pin as previously described.[7]

Sample Exposure Conditions

(A) *Florida*—Exposure was carried out in Miami, FL, according to Ford Specification BI-160-01. Specimens were mounted on nonbacked racks at a tilt angle of 5° from horizontal facing south. Specimen rinses were performed monthly at the end of morning dew formation in accordance with Ford Specification BI-160-01, Section A6.

(B) *Arizona*—Exposure was carried out in Three Rivers, AZ, according to ASTM G 7-89. Specimens were mounted on nonbacked racks at a tilt angle of 34° from horizontal facing south. Specimen rinses were performed monthly at the end of morning dew formation in accordance with Ford Specification BI-160-01, Section A6.

(C) *EMMAQUA-NTW*—Exposure was carried out in Three Rivers, AZ, according to ASTM G 90-94, Procedure B, standard spray cycle 3, which provides a water spray for a three-minute duration at a frequency of four per hour between 7:00 pm and 5:00 am. The specimens were mounted nonbacked in an aluminum frame and rotated at periodic intervals to ensure uniform exposure.

(D1) *Borosilicate/Borosilicate Filtered Xenon Arc*—Exposure was carried out at Ford Central Laboratory in an Atlas Ci35 Weather-Ometer® according to SAE J1960 JUN89 with reduced irradiance, 0.45 W/m^2*nm irradiance at 340 nm, and borosilicate inner and outer filters.

(D2) *Borosilicate/Borosilicate Filtered Xenon Arc*—Exposure was carried out at 3M's Weathering Resource Center in an Atlas Ci65/XW Weather-Ometer® according to SAE J1960 JUN89 with 0.55 W/m^2*nm irradiance at 340 nm.

(D3) Borosilicate/Borosilicate Filtered Xenon Arc—Exposure was carried out at GE Global Research in an Atlas 3-Sun Weather-Ometer® retrofitted to be identical to a Ci35a Weather-Ometer® with black panel temp. = 63°C, dry bulb temp. = 37°C, relative humidity = 50%, and 0.75 W/m^2*nm continuous irradiance at 340 nm.

(D4) *Borosilicate/Borosilicate Filtered Xenon Arc*—Exposure was carried out at GE Global Research in an Atlas Ci35 Weather-Ometer with black panel temp. = 75°C, dry bulb temp. = 40°C, relative humidity = 50%, 160 min light, 5 min dry/dark, 15 min dark/water spray, and 0.77 W/m^2*nm irradiance at 340 nm.

(D5) *SUPRAX Filtered Xenon Arc*—Exposure was carried out at Ford Research Laboratory in a Heraeus DSET Laboratories, Inc. Xenotest® 1200 Series machine at 80 W/m^2 integrated over 300-400 nm range. The irradiance corresponds to 0.55 W/m^2*nm irradiance at 340 nm and the exposure cycle corresponds to SAE J1960 JUN89.

(E) *QUV UVA-340*—Exposure was carried out at Ford Research Laboratory in a QUV accelerated weathering tester equipped with UVA-340 bulbs. The machine was operated in the "light only" mode at 25°C dew point, and 40°C black panel temperature.

(F1) *CIRA/Soda Lime Filtered Xenon Arc*—Exposure was carried out at Ford Central Laboratory in an Atlas Ci35 Weather-Ometer according to SAE J1960 JUN89 with 0.45 W/m^2*nm irradiance at 340 nm.

(F2) *CIRA/Soda Lime Filtered Xenon Arc*—Exposure was carried out at GE Global Research in an Atlas Ci4000 Weather-Ometer® with black panel temp. = 55°C, relative humidity = 30%, and 0.75W/m^2*nm continuous irradiance at 340 nm with no water spray.

(G1) *"Quartz/Borosilicate" Filtered Xenon Arc*—Exposure was carried out at Q-Panel Lab Products in a Q-Sun Xenon Arc Tester under exposure conditions that approximate SAE J1960 JUN89. Q-Sun employs a single filter designed to simulate quartz/borosilicate filtered xenon arc radiation in a Weather-Ometer.

(G2) *Quartz/Borosilicate Filtered Xenon Arc*—Exposure was carried out at Ford Central Laboratory in an Atlas Ci35 Weather-Ometer according to SAE J1960 JUN89 with 0.55 W/m^2*nm irradiance at 340 nm.

(H) *SEPAP 12.24*—Exposure was carried out at the Centre National d'Evaluation de Photoprotection in an SEPAP 12/24 exposure chamber. The SEPAP 12.24 uses four mercury vapor arc lamps with a borosilicate envelope to emit intense light in the wavelength range between 290 and 450 nm. Samples were mounted on a rotating carousel. Temperatures were controlled at 60°C. No external water was in contact with the samples.

(I1) *Filter 1*—Exposure was carried out at Atlas Materials Testing Technology LLC in a Suntest CPS—Xenon Table-top Weathering Device.

(I2) *Filter 2*—Exposure was carried out at Atlas Materials Testing Technology LLC in a Suntest CPS—Xenon Table-top Weathering Device.

(J) *Daylight Filter Filtered Xenon Arc*—Samples were exposed at Q-Panel Lab Products in a Q-Sun Xe-3-HS, according to SAE J1960 JUN89.

(K1) *Ozone Filtered Xenon Arc*—Exposure was carried out in a Ci5000 Atlas Weather-Ometer® with black panel temp. = 75°C, dew point = 25°C and 23 hr light at 1.2 W/m^2*nm irradiance at 340 nm followed by 1 hr dark.

(K2) *Ozone Filtered Xenon Arc*—Exposure was carried out in a Ci5000 Atlas Weather-Ometer at a black panel temp. = 75°C, dew point = 25°C, and 23 hr light at 1.2 W/m^2*nm irradiance at 340 nm, 1 hr dark with 20 min front panel water spray during the dark cycle.

(L) *3M Proprietary*—Exposure was carried out at 3M's Weathering Resource Center. Exposure details are not available.

FTIR Spectroscopy

FTIR spectra were recorded with a Mattson Galaxy Series Model 5020 spectrometer equipped with ATI Mattson Instruments First software version 1.70.

Light Measurements

Scanning spectroradiometer SPD measurements were made on a model OL 754 portable high accuracy UV-visible spectroradiometer (Optronic Laboratories Inc.) equipped with optOLab™ general operating software, a six-inch model OL IS-670 integrating sphere, and a model OL 730-7Q quartz fiber optic probe. A model OL 752-10 tungsten plug-in standard was used for calibration. Diode array detection spectroradiometer SPD measurements were made with an Oriel InstaSpec II model 77112 system equipped with silicon oil filled optical cable.

“Sunlight” SPD

Atlas Weathering Services Group and 3M’s Weathering Resource Center generously supplied high noon, midsummer SPD data measured at the Miami and Three Rivers locations. All measurements were averaged to produce the “sunlight” SPD used in the present work.

Ozone Filtered Xenon Arc System

A 46 × 46 cm cylindrical quartz cell (Walcom Quartz) with a 46 × 7.5 cm inner tube was used to contain ozone. The cell’s inner tube fits over the burner in the Ci5000 Weather-Ometer. Light passes through the 15.5 cm space between the inner tube wall and the outer wall of the cell before striking samples. Ozone is pumped into the cell at the bottom through a 24/40 male standard taper joint fitted with a 5 mm I.D. tube and exits through a 24/40 female standard taper port at the top. The 5 mm I.D. tube is aimed to blow entering ozone along the outside wall of the cylinder to produce vortex circulation within the cell. Air is blown into the space between the burner and the quartz cell to remove heat.

In operation, an MB-158 metal bellows inline pump (Senior Flexonics Inc.) circulates high purity oxygen through a GLS-3 ozone generator (PCI Wedeco) to the quartz cell in the Weather-Ometer chamber and back to the ozone generator through 3/8 in. diameter stainless steel tubing. An inline ~15l Teflon bag (Plastic Films Enterprises) acts as a ballast to compensate for changes in gas volume with changes in Weather-Ometer chamber temperature. Ozone generator power is controlled with a PID circuit that follows an HC-500 ozone monitor (PCI Wedeco) mounted in the return line from the quartz cell to the generator when the Weather-Ometer burner is on. The concentration of ozone in the gas stream returning from the cell to the ozone generator is ~3.2% when the burner irradiance is set at 1.2 W/m^2*nm at 340 nm. When the Weather-Ometer burner is off, the ozone generator power is turned off. It is necessary to constantly add oxygen, ~50 cc/min, to the system to keep the ozone generator efficiency high. Excess ozone/oxygen mixture escapes the system through a silicon oil bubbler equipped with an ozone decomposition catalyst. Pressure within the system is maintained at ~30 mm Hg above atmospheric at the quartz cell inlet and ~10 mm Hg above atmospheric at the quartz cell outlet by adjusting the level of silicon oil in the bubbler.

In practice, the burner is turned on and ozone generator power is manually adjusted until scanning spectroradiometer measurements using a six-inch integrating sphere located in a corner of the Weather-Ometer chamber outside the specimen rack indicates a match between ozone filtered xenon arc light SPD and sunlight SPD over the 250-400 nm region. Next, the ozone generator power is switched to automatic control and a diode array spectroradiometer is used to record SPD using an optical cable mounted on the Weather-Ometer power control post inside the specimen rack. The diode array detection SPD is stored and used to compare with current SPD. Small, weekly adjustments to ozone concentration were adequate to maintain an SPD constant at < ±0.5 nm for months.

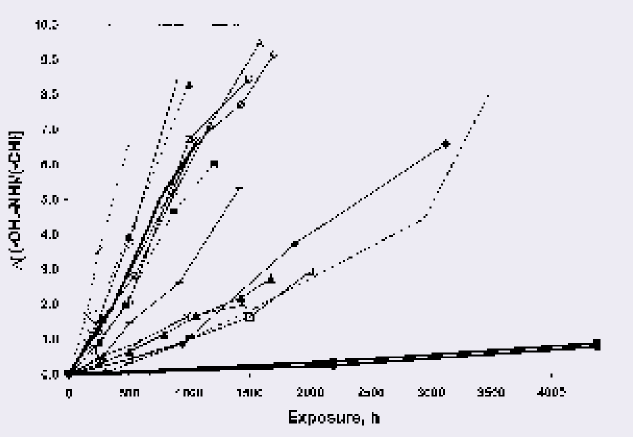

Figure 1—Photooxidation/hydrolysis rate as measured by Δ((–OH, –NH)/–CH) ratio for Clearcoat Y subjected to: (a) Florida (━◆━) exposure; (b) Arizona (━■━) exposure; (c) EMMAQUA-NTW (—◆—) exposure; (d) CIRA/soda lime F1 (—✕—) and F2 (—▲—) filtered xenon arc exposure; (e) Borosilicate/borosilicate D1 (—▬—), D2 (—⊖—), D3 (—◇—), D4, (—△—), and, D5 SUPRAX (· · ■ · ·), D5 filtered xenon arc exposure; (f) Quartz/borosilicate G1 (· · ▲ · ·) and “quartz/borosilicate” filtered xenon arc G2 (—┼—); (g) Daylight Filter (—□—) filtered xenon arc exposure; (h) SEPAP 12/24 (- - ✕ - -); and (i) 3M Proprietary exposure (- - ○ - -), QUV UVA-340 “light only” (▬ ▬), and Ozone filtered xenon arc (━━━) K1.

RESULTS AND DISCUSSION

The object of an accelerated weathering test for automotive paint systems is to learn well in advance of actual outdoor exposure results which paint systems will perform well in service. Unfortunately, the time advantage afforded by such tests is often offset by the possibility of both false positive and false negative results that can be directly attributed to inappropriate weathering chemistry. The present work surveys a number of accelerated tests to determine which are most likely to distort the weathering chemistry of coatings relative to their outdoor exposure weathering chemistry. It then goes on to provide evidence that spectral power distribution (SPD) mismatch between the radiation sources used in accelerated tests and sunlight plays a key role in weathering chemistry distortion.

Two clearcoats were studied in the present work. Clearcoat Y is as close as possible to the polyester/urethane clearcoat previously studied by Bauer et al.[14] Clearcoat R is a typical acrylic/melamine also examined in previous work.[25] The actual weathering performance of both clearcoats in complete paint systems is well known. Both exhibit superior long-term weathering performance. Paint systems incorporating each of the clearcoats resist cracking and peeling after extended Florida, Arizona, and in-service exposure. The two clearcoats do however perform quite differently in accelerated weathering tests.

Clearcoat R resists cracking when subjected to quartz/borosilicate and borosilicate/borosilicate filtered xenon arc exposure, QUV UVB-313, EMMA, and EMMAQUA-NTW exposures. Clearcoat Y rapidly cracks when subjected to quartz/borosilicate and borosilicate/borosilicate filtered xenon arc, and QUV UVB-313 exposure, but does not crack when subjected to EMMA or EMMAQUA-NTW exposures. The difference in behavior can be attributed to the weathering performance information used to guide the development of the two coatings. Clearcoat R was developed primarily in response to weathering information afforded by harsh exposure accelerated tests. Accordingly, it is safe to assume that the formulation components that caused Clearcoat R to perform poorly in such tests have been minimized. In contrast, Clearcoat Y was developed primarily in response to weathering information afforded by outdoor exposure tests. Here it is safe to assume that the formulation components that caused Clearcoat Y to perform poorly during outdoor exposure have been minimized, but this does not mean that formulation components that could cause Clearcoat Y to perform poorly in harsh exposure tests have been minimized. While both coating development strategies produced coatings with superior weathering performance, both have drawbacks in practice. Less costly components that perform well during outdoor exposure may have been needlessly eliminated from Clearcoat R. In addition, additives chosen based on harsh accelerated tests may not be effective during outdoor exposure. Previous work has, in fact, shown that harsh exposure conditions can distort additive effectiveness.[24] Early versions of Clearcoat R were formulated with a HALS that was effective in harsh exposure tests but later discovered to be ineffective during outdoor exposure. On the other hand, since Clearcoat Y was formulated primarily with components that are effective in outdoor exposure, it is difficult to use harsh accelerated tests to test future formulation changes. This precludes rapid testing for basic formulation changes to Clearcoat Y. The difficulty in both cases lies in the tests, not in the materials. A truly useful accelerated weathering test would reveal that both coatings would exhibit superior long-term weathering performance during outdoor exposure. From the point of view of the present work, Clearcoat Y is much better suited to test accelerated tests for chemical distortion than Clearcoat R. In theory, an accelerated test that does not distort Clearcoat Y's weathering chemistry would be less likely to distort the weathering chemistry of an unknown coating and therefore would be more likely to produce useful results.

The rate at which Clearcoat Y undergoes photooxidative/hydrolytic degradation during exposure in Florida and Arizona and in a number of accelerated weathering tests is illustrated in *Figure* 1. Here, the progress of photooxidation/hydrolysis has been assessed by measuring the accumulation of photooxidation/hydrolysis products as measured by (–OH,–NH)/–CH FTIR spectrum peak ratios.[25] As can be seen, all accelerated tests accelerate photooxidation/hydrolysis chemistry relative to outdoor exposure. The acceleration is dramatic, >50, for SEPAP 12.24 and quartz/borosilicate filtered xenon arc exposures. However, when the FTIR spectra recorded for these tests as a function of exposure are compared with one another, there are indications that not all tests drive the same weathering chemistry. SEPAP exposure is typically adjusted to fit the structure of the polymer being weathered.[26,27] No adjustment has been made here. In theory, excessive excitation of phthalate could be avoided by filtering the incident light with a thicker borosilicate filter without extending exposure duration excessively.

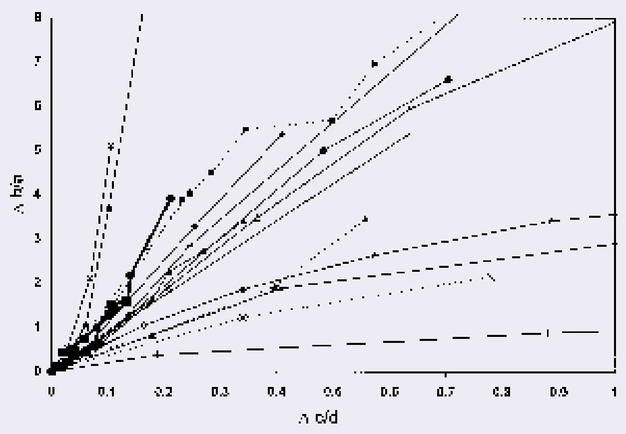

Figure 2—Plot of Δ(b/a) peak ratio versus Δ(c/d) peak ratio (peak labels Figure 3a) for Clearcoat Y subjected to: (a) Florida (—●—) exposure; (b) Arizona (—■—) exposure; (c) EMMAQUA-NTW (—◆—) exposure; (d) CIRA/sodalime F1 (—✕—) and F2 (—▲—) filtered xenon arc exposure; (e) Borosilicate/borosilicate D1 (—▬—), D2 (—□—), D3 (—◇—), D4 (—△—) and D5 SUPRAX (· · ▲ · ·) filtered xenon arc exposure; (f) Quartz/borosilicate G1 (—+—) and "quartz/borosilicate" G2 (—✳—) filtered xenon arc exposure; (g) SEPAP12/24 (- - ✕ - -) exposure; (h) QUV UVA-340 "light only" (—●—) exposure; (i) daylight filter filtered xenon arc (—■—) exposure; (j) 3M Proprietary (- - ● - -); and (k) Ozone filtered xenon arc K1 (· · ■ · ·) exposure.

The FTIR spectra recorded for the tests illustrated in *Figure* 1 were compared with one another by plotting the ratios of sets of peaks versus one another as a function of exposure. Ideally, peaks that are linked to physical performance and change with exposure should be selected for comparison. This treatment is advantageous because it eliminates time from consideration to allow accelerated and outdoor exposure results to be plotted on the same scale. In theory, the curve obtained when two sets of peak ratios are plotted against one another reveals how the amount of chemical composition change represented by each set of peaks changes over time. When accelerated tests yield the same peak ratio curves, the indication is that the FTIR spectra change in the same fashion during exposure and therefore the tests drive the same gross chemical composition changes and vice versa.

The results of this FTIR spectrum comparison technique are shown in *Figure* 2 for Clearcoat Y subjected to a number of accelerated tests, Florida, and Arizona exposure. The change in the ratio of peak c to isophthalate peak d has been plotted versus the change in the ratio of peak b to urethane crosslink peak a as per the labels shown in *Figure* 3a. The curves clearly indicate that Clearcoat Y

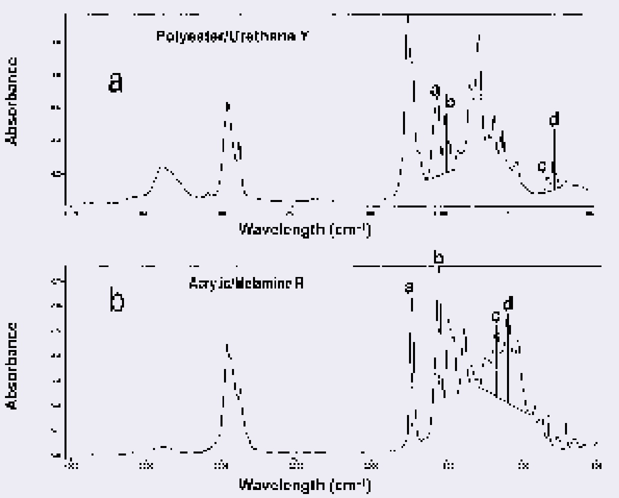

Figure 3—FTIR peak labels for: (a) Clearcoat Y and (b) Clearcoat R.

undergoes different weathering chemistry in different accelerated tests. A similar plot is shown in *Figure* 4 for Clearcoat R subjected to several accelerated tests, Florida, and Arizona exposure. Peak labels are shown in *Figure* 3b. Here, the curves suggest that Clearcoat R undergoes similar weathering chemistry regardless of exposure conditions. The difference in the weathering chemistry behavior of the two clearcoats in accelerated tests appears to be in agreement with the manner in which they were developed. Namely, Clearcoat R is much less sensitive to harsh exposure conditions than Clearcoat Y.

Returning to *Figure* 2, the curves suggest that Clearcoat Y undergoes similar weathering chemistry during Florida and Arizona exposure but few accelerated tests reproduce the Florida/Arizona weathering chemistry curves. It is difficult to accurately estimate the experimental error associated with these experiments to rigorously determine which tests do or do not reproduce Florida/Arizona weathering chemistry. The results shown in *Figures* 2 and 4 were obtained over a five-year period using several allegedly identical samples of each clearcoat. Test specimens were exposed in a number of laboratories and repeatedly returned to Ford Research by mail for analysis. Repeated experiments on Clearcoat Y in the same laboratory are reproducible to within <±10% although slope differences as large as 20% are occasionally observed for seemingly identical samples exposed side by side in the same machine. The error in peak height measurements is small at the onset of exposure in all cases, but increases as peaks decrease in intensity and become more difficult to measure. If the experimental error in these experiments is taken to be as large as ±30%, the curves obtained for Clearcoat Y subjected to CIRA/soda lime F1, daylight filter, and quartz/borosilicate G1 and G2 filtered xenon arc exposures, SEPAP, and QUV UVA-340 "light only" exposures are still significantly different from the curves obtained for Florida and Arizona exposure. Thus, if the ability of an accelerated weathering test to reproduce Clearcoat Y's Florida/Arizona weathering chemistry is taken as a threshold requirement for an accelerated weathering test to produce useful results, these tests are not expected to reveal Clearcoat Y's weathering performance correctly. Therefore, the ability of these tests to accelerate weathering is of questionable value for unknown coating chemistries. It is not as clear that the curves shown for the other accelerated tests examined in this work indicate a real difference in weathering chemistry relative to Florida/Arizona exposure. It can be noted that complete paint systems rapidly crack when subjected to borosilicate/borosilicate filtered xenon arc exposure according to SAE J1960 JUN89. And it can also be noted that the curves shown for EMMAQUA-NTW, 3M Proprietary exposure, and ozone filtered xenon arc exposure (to be discussed later) do match the Florida/Arizona curves very well.

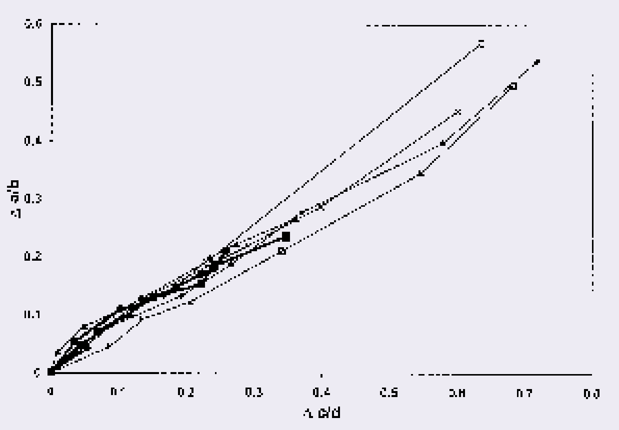

Figure 4—Plot of Δ(a/b) peak ratio versus Δ(c/d) peak ratio (peak labels Figure 3b) for Clearcoat R subjected to: (a) Florida (—◆—) exposure; (b) Arizona (—■—) exposure; (c) EMMAQUA-NTW (—▲—) exposure; (d) CIRA/soda lime F1 (—◆—) filtered xenon arc exposure; (e) Borosilicate/borosilicate D1 (—□—) filtered xenon arc exposure; (f) Quartz/borosilicate G1 (—○—) filtered xenon arc exposure; (g) D5 SUPRAX (—×—) exposure; and (h) QUV UVA-340 "light only" (—△—) exposure.

While the curves shown in *Figure* 2 indicate that Clearcoat Y undergoes different weathering chemistry in different accelerated tests, they provide no information as to why this is the case. If this aspect of the tests could be understood, it could provide valuable insight into how to design an accelerated test that would be suitable for all coating chemistries.

The UV spectra shown in *Figure* 5 for Clearcoats R and Y suggest that the spectral power distribution (SPD) of the radiation sources used to drive weathering in accelerated tests could play an important role in determining weathering chemistry. As shown in *Figure* 5, neither clearcoat absorbs sunlight strongly. However, Clearcoat Y contains an isophthalate component that causes it to absorb more UV radiation than Clearcoat R at wavelengths just shorter than those contained in natural sunlight. This behavior suggests that Clearcoat Y could be more sensitive than Clearcoat R to the shorter than natural wavelength UV present in some radiation sources, and therefore, undergo chemical composition changes that do not occur during outdoor exposure. It does not necessarily imply that aromatic esters should be avoided in coatings intended for

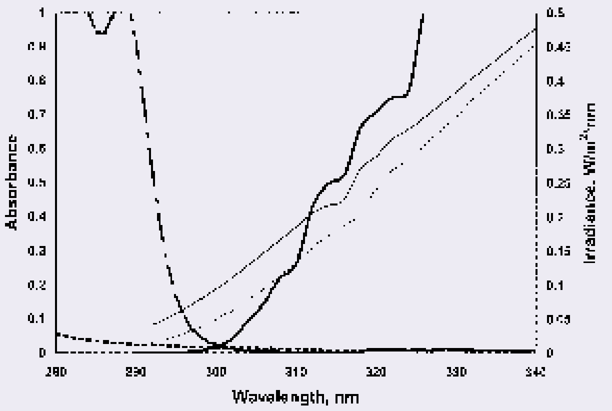

Figure 5—UV absorbance spectra of Clearcoats Y (▬ ▬) and R (▪ ▪ ▪) with sunlight (▬▬▬), and quartz/borosilicate (———), and borosilicate/borosilicate (- - - - - -) filtered xenon arc SPD overlays.

outdoor use. Very weather resistant metal roof coatings are routinely formulated with a high aromatic diacid content.[28]

One way to examine the impact of radiation SPD on Clearcoat Y's weathering chemistry is to follow the behavior of its isophthalate component as a function of exposure. This can be done by plotting the ratio of isophthalate peak d to –CH peak versus urethane crosslink scission as measured by the ratio of urethane crosslink peak a to –CH peak. Peak labels are shown in *Figure* 3a. Division by –CH absorbance is necessary to compensate peak intensities for decrease due to film erosion. Previous work has shown that –CH absorbance is directly proportional to film thickness for clearcoats weathered on silicon wafers.[29] The results of this IR spectrum analysis procedure are shown in *Figure* 6 for Clearcoat Y. Isophthalate content increases slightly for samples subjected to Florida, Arizona, EMMAQUA-NTW exposure, 3M Proprietary exposure, and CIRA/soda lime F1 and F2, and Daylight Filter filtered xenon arc exposure up to ~70% urethane crosslink scission. The crosslink peak becomes too weak to measure accurately after 70-80% crosslink scission although the isophthalate peak is easily measured. Measurements on a fully stabilized version of Clearcoat Y, HALS and UVA, indicate that more than nine years of Florida exposure would be required to drive urethane crosslink scission to 70% loss. Thus, isophthalate behavior beyond 70-80% urethane crosslink scission is not important in the present work. Isophthalate content remains relatively constant and/or decreases slightly during borosilicate/borosilicate D1, D2, D3, and D4 filtered xenon arc exposures and QUV UVA-340 "light only" exposure up to 60-70% urethane crosslink loss. And finally, isophthalate content decreases rapidly from the onset of exposure for SEPAP and quartz/borosilicate G1 and G2 filtered xenon arc exposures. When isophthalate behavior is related to the radiation sources used to drive weathering chemistry, there appears to be a link between isophthalate loss and the presence of shorter than natural wavelength UV radiation (*Figures* 7 and 8). Isophthalate loss is greatest for quartz/borosilicate filtered xenon arc xenon and SEPAP radiation (*Figure* 7), slower for borosilicate/borosilicate filtered xenon arc exposure, and does not occur during Florida, Arizona, EMMA-NTW, F1 and F2 CIRA/soda lime and Daylight Filter filtered xenon arc and QUV UVA-340 exposure (*Figure* 8). Thus, the indication is that SPD plays a key role in determining Clearcoat Y's weathering chemistry. The link is tenuous however because so many exposure variables are different in the accelerated tests examined. For example, daylight filter and CIRA/soda lime filtered xenon SPDs are very similar (*Figure* 8), and exposure to these radiation sources does drive similar isophthalate loss chemistry but it does not drive the same overall weathering chemistry (*Figure* 2). A simpler, more controlled experiment is required to convincingly demonstrate a link between radiation SPD and Clearcoat Y's weathering chemistry.

Towards this goal, Clearcoat Y was exposed in side-by-side Suntest CPS—Xenon Table-top Weathering devices equipped with slightly different filters to examine the impact of radiation SPD on its weathering chemistry. The two devices were operated as close as possible to the same temperature, humidity, and irradiance conditions using "light only" exposure. The SPD curves for the two filters, filter 1 and filter 2, are shown in *Figure* 9 along with SPD curves for sunlight and borosilicate/borosilicate filtered xenon arc for comparison. All curves are normalized to sunlight irradiance at 388 nm. The curves for filters 1 and 2 are identical above 340 nm. Both indicate a deficiency in UV from 295-388 nm relative to sunlight when normalized at 388 nm. Neither filter provides shorter than natural UV. As shown in *Figures* 10 and 11, respectively, the seemingly small difference in the radiation supplied by

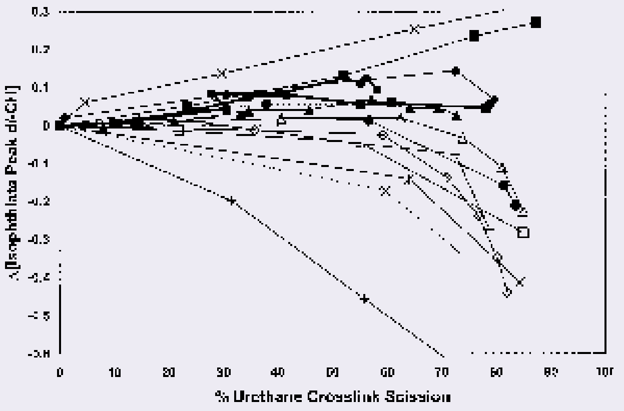

Figure 6—Δ(Isophthalate peak d/ –CH) versus urethane crosslink scission (Δ(a/ –CH)) for Clearcoat Y (peak labels Figure 3a) subjected to: (a) Florida exposure (—■—); (b) Arizona exposure (—◆—); (c) EMMAQUA-NTW exposure (—◆—); (d) CIRA/soda lime F1 (—×—) and F2 (—▲—) filtered xenon arc exposure; (e) Daylight Filter (—■—) filtered xenon arc exposure; (f) Borosilicate/borosilicate D1 (—▬—) D2 (—□—) D3 (—◇—), and D4 (—△—) filtered xenon arc exposure; (g) QUV UVA-340 "light only" exposure (—●—); (h) 3M Proprietary exposure (- - ● - -); (i) Quartz/borosilicate G1 (—✳—) and "quartz/borosilicate" G2 (—+—) filtered xenon arc exposure; and (j) SEPAP 12/24 exposure (- - × - -).

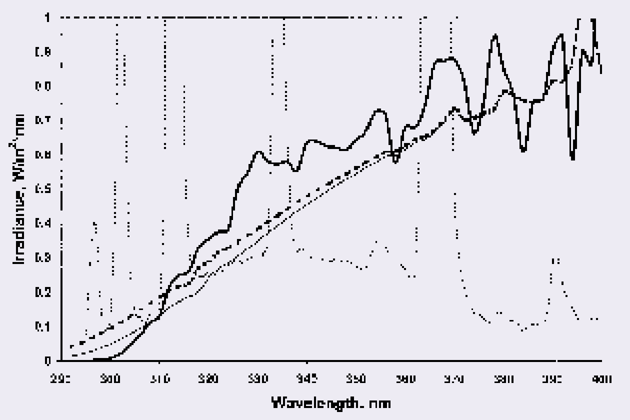

Figure 7—Spectral power distributions for: (a) SEPAP (- - - - - -); (b) Quartz/borosilicate (▬ ▬ ▬) and borosilicate/borosilicate (———) filtered xenon arc; and (d) Sunlight (▬▬▬).

the two filters produces an easily measured difference in isophthalate behavior and overall weathering chemistry. The results observed for filter 1 are similar to those observed for borosilicate/borosilicate filtered xenon arc exposure while the results observed for filter 2 approximate Florida/Arizona exposure behavior. These experiments unambiguously demonstrate that radiation SPD plays a pivotal role in determining Clearcoat Y's weathering chemistry, and the finding has substantial bearing on how to approach the development of an accelerated weathering test that would be appropriate for all coating chemistries.

Commercial coatings invariably contain a wide assortment of chromaphores that can absorb radiation to initiate free radical oxidation. Chromaphores might include the coating matrix itself, as appears to be the case for Clearcoat Y, unwitting polymer synthesis products and low molecular weight debris, pigments, additives, a host of trace impurities, and, of course, the photolysis products of all of the above when the coating is exposed to sunlight. The photolysis of trace chromaphores appears to be the primary reason why all acrylic/melamine clearcoats do not exhibit the same photooxidation resistance.[30] It can be noted that Clearcoat R does not absorb sunlight strongly (*Figure* 5), and yet it does photooxidize during outdoor exposure.

If the threshold criterion for an accelerated weathering test to produce useful results is set at reproducing Florida/Arizona weathering chemistry, and it is recognized that the weathering chemistry of coating families need not be generic, then it holds that the first step toward minimizing the possibility false and/or misleading results in accelerated weathering tests would be to use a radiation source whose SPD matches sunlight as closely as possible in the UV region. Pickett et al. have reached a similar conclusion.[31] This line of reasoning makes it difficult to see the value of unraveling the interplay between exposure variables for radiation sources that contain shorter than natural wavelength UV radiation[23] capable of driving weathering chemistry that cannot be driven by sunlight. And, the value of pursuing such work for radiation sources that only approximate sunlight poorly in the UV region does not increase dramatically. Clearly, the process of unraveling the interplay between exposure variables would be greatly simplified if experiments could be performed with a radiation source whose SPD matched sunlight's SPD exactly in the critical UV region. This would eliminate radiation SPD as an exposure variable to focus entirely on photochemistry that can be driven by sunlight. Unfortunately, to the best of our knowledge, no such radiation source exists other than reflected sunlight. As shown in *Figure* 8, xenon arc filters that can reproduce the sunlight cutoff in the 295-300 nm region invariably absorb too much UV at longer wavelengths because their absorbance is too broad. UVA-340 fluorescent radiation approximates the sunlight cutoff, but it is very deficient in UV above 350 nm (*Figure* 8).

One way to produce radiation whose SPD matches sunlight in the UV region is to use ozone to filter xenon arc radiation in the same fashion that stratospheric ozone filters solar radiation to produce sunlight. Ozone is by definition the ideal filter in this regard. It should be possible to obtain an excellent SPD match because the slopes

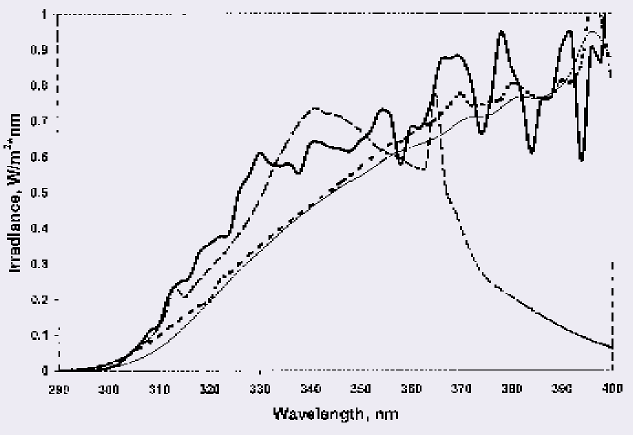

Figure 8—Spectral power distribution for: (a) CIRA/soda lime (- - - - - -) and Daylight Filter (———) filtered xenon arc; and (b) UVA-340 fluorescent light (- - —), and sunlight (▬▬▬).

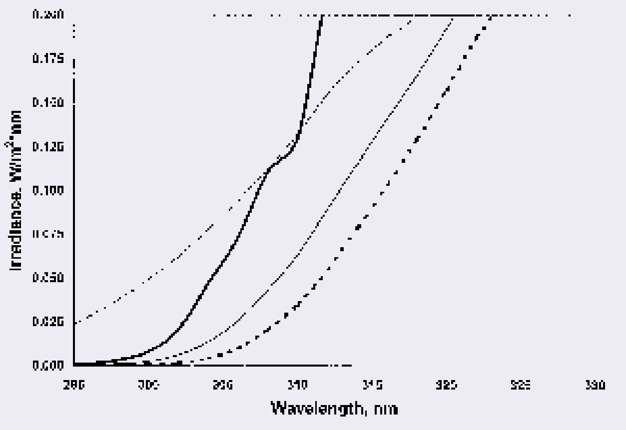

Figure 9—Spectral power distribution for: Filter 1 (———), Filter 2 (▬ ▬ ▬), and borosilicate/borosilicate (- - —) filtered xenon arc, and sunlight (▬▬▬).

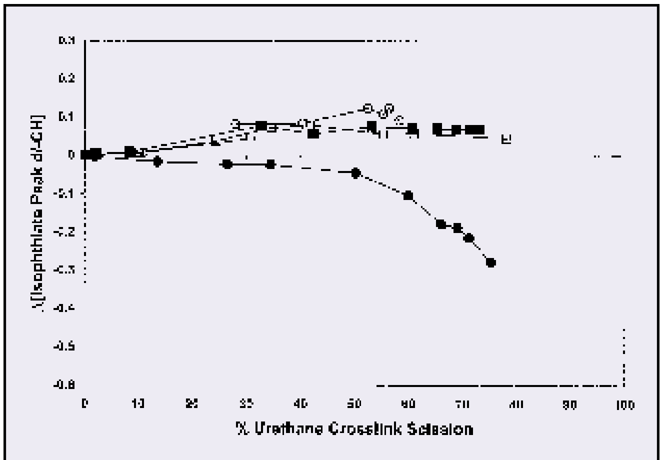

Figure 10—Δ(Isophthalate peak d/ –CH) versus urethane crosslink scission (Δ(a/ –CH)) for Clearcoat Y (peak labels Figure 3a) subjected to: (a) Filter 1 (—●—) and Filter 2 (—■—) filtered xenon arc, Florida (—□—), and Arizona (—⊖—) exposure.

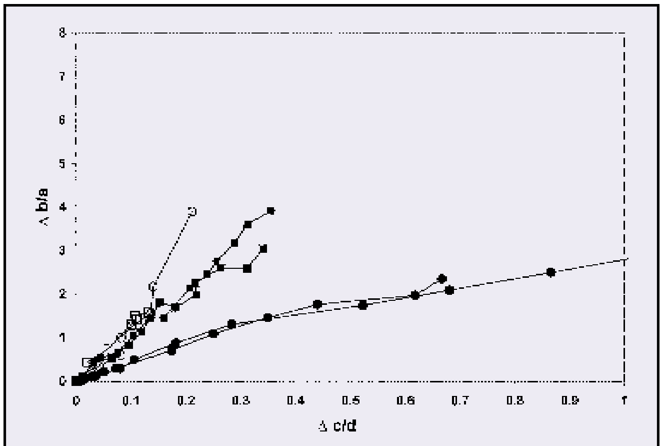

Figure 11—Plot of Δ(b/a) peak ratio versus Δ(c/d) peak ratio (peak labels Figure 3a) for Clearcoat Y subjected to: (a) Filter 1 (—●—) and Filter 2 (—■—) filtered xenon arc exposure; (b) Florida (━⊖━); and (c) Arizona (━□━) exposure.

of solar and xenon arc irradiance curves are very similar in the 290-400 nm region.

The equipment necessary to filter xenon arc radiation with ozone in a Ci5000 Weather-Ometer® is described in detail in the Experimental section. In essence, the Weather-Ometer's burner is surrounded by quartz chamber containing a mixture of oxygen and ozone. Xenon arc radiation passes through the ozone in the quartz chamber before striking samples. An ozone generator continuously replenishes the ozone in the quartz chamber and controls adjust the optical density (concentration) of ozone in the quartz chamber. The equipment allows xenon arc radiation to be filtered to match sunlight SPD with great fidelity at any geographic location. In theory, the concentration of ozone in the quartz chamber could be varied over time to reproduce seasonal or even sunrise to sunset variations if necessary although this equipment is not in place.

A typical ozone filtered xenon arc SPD is shown in *Figure* 12 along with an average of noon, midsummer sunlight SPDs for Florida and Arizona. As can be seen, the match to sunlight is rigorous up to 400 nm. The filter cannot reproduce the increase in sunlight irradiance that occurs in the 400 nm because this step (Fraunhofer Structure) is present in solar radiation but not present in xenon arc radiation.

A first ozone filtered xenon arc experiment was carried out with an ozone filtering set to reproduce an average of noon, summer sunlight SPDs measured for Florida and Arizona as previously described. This selection maximizes the intensity of short UV radiation but there is no fundamental reason why it is necessarily the best choice. Irradiance was set as high as possible, 1.2 W/m^{2}*nm at 340 nm (~2 suns), to achieve maximum test acceleration. This selection is based primarily on the observation that EMMA exposure provides high irradiance, >4 suns at 340 nm, and appears to reproduce Clearcoat Y's Florida and Arizona weathering chemistry. Researchers at NIST have designed an exposure system that can supply up to 200 suns irradiance[32] and researchers at NREL have performed experiments with reflected sunlight at >100 suns irradiance.[33] The degree to which high irradiance can actually be used to accelerate the weathering chemistry of complete paint systems as opposed to the isolated clearcoat samples studied here is, however, open to considerable question. It seems unlikely that the migration of UVA and HALS additives between coating layers in multilayer paint systems could be accelerated in proportion to very rapid photooxidation/hydrolysis without resorting to sample temperatures that could distort thermal oxidation chemistry. Absolute humidity was set at 21.5 g/m^{3} (25°C dew point). This is the highest value that could be achieved with existing equipment while holding the black panel temperature 75°C. The temperature of the silicon disk samples was ~55°C. Absolute humidity averages ~29 g/m^{3} during the summer in Miami and ~18 g/m^{3} during the summer in Arizona. Test panel temperatures can exceed >80°C during outdoor exposure at both locations. Light/dark cycle was arbitrarily set at 23 hr light and 1 hr dark to maximize photolysis time and allow a dark period for machine maintenance.

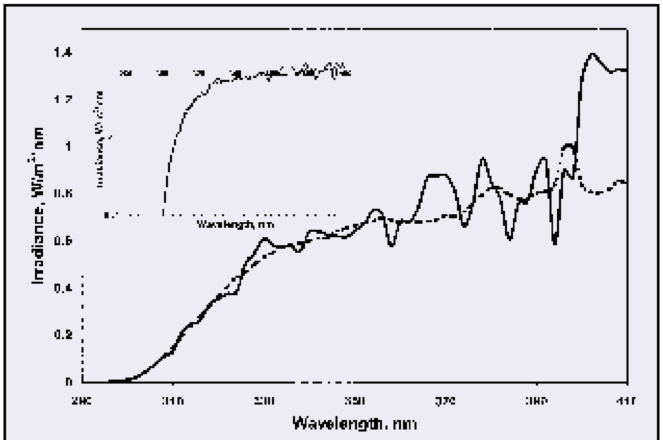

Figure 12—Spectral power distribution for ozone filtered xenon arc (- - - - - -) and sunlight (━━━━), with log irradiance versus wavelength insert.

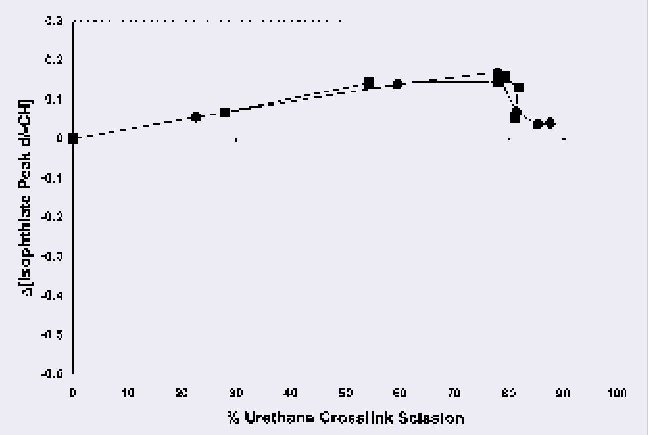

Figure 13—Δ(Isophthalate peak d/ –CH) versus urethane crosslink scission (Δ(a/ –CH)) for Clearcoat Y (peak labels Figure 3a) subjected to ozone filtered xenon arc exposure K1 (—●—) and K2 (—■—).

As shown in *Figure* 1, Clearcoat Y photooxidizes/hydrolyzes rapidly when subjected to ozone filtered xenon arc radiation under the conditions described above. The speed was unexpected and led to the collection of fewer than a desirable number of data points during the early stages of exposure. Nevertheless, results indicate that exposure reproduces Clearcoat Y's isophthalate loss, *Figure* 13, and overall Florida/Arizona exposure weathering chemistry, *Figure* 2. In a second experiment, 20 min of front surface water spray was added during the dark cycle to ensure that test specimens were thoroughly wet. As shown in *Figure* 13, the addition of front water spray does not affect isophthlate loss chemistry. However, when results for stabilized and nonstabilized samples are compared, it is obvious that additive effectiveness is distorted. The addition of HALS and UVA to Clearcoat Y suppress photooxidation/hydrolysis as measured by Δ[(–OH,–NH)/–CH] by ~40% but the suppression exceeds 80% during ozone filtered xenon arc exposure. Similar distortion is observed for EMMAQUA-NTW and 3M Proprietary exposures. Distorted additive effectiveness during accelerated exposure is of course unacceptable and the root cause of the distortion (specimen temperature?) will be investigated in future work. The distortion cannot be attributed to SPD mismatch with sunlight in the case of EMMAQUA-NTW or ozone filtered xenon arc exposure.

CONCLUSIONS

Transmission FTIR spectroscopy has been used to follow the weathering chemistry of a HALS and UVA free polyester/urethane clearcoat and a HALS and UVA free acrylic/melamine clearcoat as each was exposed in Florida, Arizona, and in a number of accelerated weathering tests. The weathering chemistry of the acrylic/melamine was found to be far less sensitive to exposure conditions than the polyester/urethane. This behavior is consistent with the strategy used to develop the two clearcoats. All accelerated weathering tests except EMMAQUA-NTW, 3M Proprietary exposure, and ozone filtered xenon arc exposure appear to distort the polyester/urethane's weathering chemistry relative to its outdoor exposure weathering chemistry. The distortion is attributed primarily to SPD mismatch between artificial radiation and sunlight.

Preliminary results are reported for an accelerated exposure system that employs ozone to filter xenon arc radiation. An irradiance SPD is obtained that rigorously matches sunlight in the 290-400 nm region and therefore eliminates SPD as an exposure variable. Exposure with this radiation source does not distort the polyester/urethane's gross weathering chemistry relative to Florida/Arizona exposure, however, additive effectiveness is distorted (specimen temperature?). Future work will employ this radiation source to help unravel the interplay between exposure variables to begin development of an accelerated weathering test that is suitable for all coating chemistries.

Taken together, the results of the present work strongly suggest that the usefulness of accelerated weathering tests could be improved considerably by seeking radiation sources whose SPD match sunlight in the critical UV region.

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