

Material Testing Product and Technology News

> Volume 40 Issue 87

# SunSpots

# The SEPAP 12/24 and the Mechanistic Approach of Polymer Photoaging in Weathering

By Professor Jacques Lemaire, General Manager of the Centre National d'Evaluation de Photoprotection from 1986 to 2007

## Introduction

The SEPAP<sup>1</sup> 12/24 unit was developed in the 1970s by photochemists from the University of Clermont-Ferrand (France) as an analytical tool to examine the chemical evolution at the molecular level and understand the aging mechanisms of polymers exposed outdoors. The unit was designed to replicate in accelerated controlled laboratory conditions the chemical evolutions responsible for the gradual loss in properties of polymers during their lifetime.

## **Principles of the Mechanistic Approach**

The SEPAP 12/24 was first tested on various classes of polymeric matrices containing a limited number of additives with known photochemical functions. This simplified approach was necessary initially, as the chemical evolution of a polymeric material submitted to light, heat,  $O_{2}$ , and  $H_{2}O$  is complex:

- » As the useful properties of polymers are primarily achieved in the solid state, the analysis of chemical evolution should be carried out in solid state, especially in examining the stability of intermediate products.
- » Chemical evolution should only be considered to a very small extent. When the evolution of degradation products exceeds 0.5 to 1% of the unreacted material, the loss of physical properties is nearly complete. Unless the ultimate properties of a polymeric material is being examined for the sake of environmental protection, it is pointless to study reactions in the fragments any further.
- » Chemical evolution includes many photochemically and thermally activated mechanisms that vary in importance, so it is necessary to identify the transformations that actually lead to physical degradation. The most important route usually involves a photooxidative or thermooxidative mechanism, giving rise to products in concentrations high enough to be detected with vibrational spectrophotometries, such as FT-IR spectroscopy.



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Science meets history at Mayan pyramid Art by Vlad Dumitrascu © National Geographic Page 14

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2010 25th EU PVSEC

Valencia, Spain September 6–10

Indiapack 2010 Mumbai, India September 30–October 3

Solar Power International Show Los Angeles, CA, USA October 12–14 K-Show 2010 Düsseldorf, Germany October 27–November 3

**Eurocoat** Genoa, Italy November 9–11

Vietnam Hanoi Textile & Garment Industry Expo Hanoi, Vietnam November 10–12 Visit our booth at these shows and learn about the latest weathering developments and how Atlas<sup>®</sup> can help advance your testing program.

For the latest on Atlas shows and presentations, visit www.atlas-mts.com.



**25th EU PVSEC** Valencia, Spain September 6–10

"Accelerated Weathering Testing to Predict the Environmental Durability of Organic PV Systems"

Speaker: Olivier Haillant, Ph.D., Senior Consultant

Atlas' education and training solutions will help you and your staff master the skills and knowledge needed to develop long-lived products in shortened development cycles. Our programs are designed for all levels to ensure that everyone on your team understands the fundamentals of weathering and how to operate our instruments. For the latest schedules and locations, visit www.atlas-mts.com,

or e-mail info@atlas-mts.com.

Weather-Ometer® Workshop	September 28	Chicago, Illinois, USA	Presented in English
Fundamentals of Weathering I	September 29	Chicago, Illinois, USA	Presented in English
	December 1	Leipzig, Germany	Presented in German
Fundamentals of Weathering II	September 30	Chicago, Illinois, USA	Presented in English
	December 1	Leipzig, Germany	Presented in German
Online Webinars	July 29 @ 9:00 am	Durability\Reliability Acros	is the PV Development Chain (US\$95/70 Euros)
	August 10 @ 9:00 am	Understanding the Relatio	n of Reliability, Durability, and Weatherability (Free)
	September 2 @ 9:00 am	Correlation Between Natu	ral and Artificial Weathering (US\$95/70 Euros)
	All times listed in -06:00 GMT.		







# Mumbai Textile Conference Set for January 2011

A tlas is joining with DyStar and ASTM International to host a oneday textile conference in Mumbai, India. The tentative date of the conference is January 21, 2011.

The impact of light- and weatherfastness on technical and high-performance textiles is a topic that is quickly growing in importance in India.

The three leading organizations are teaming up to create awareness and improve understanding in these specialized fields. The conference will provide a unique opportunity to learn about various aspects of light- and weatherfastness as well as exchange information.

Please contact Bruno Bentjerodt, bbentjerodt@atlas-mts.com, for more information. The Atlas website will be updated with information about this important conference as it becomes available.

## Preliminary Agenda Topics

- A. Textile Industry (retailer, sport garments, home textiles)
- B. Textile Institutes/Service Laboratories/Colourfastness Committees
- C. Instrument Manufacturers
- D. Dyestuff Companies and Chemical Industry
- E. Standards
- F. Student Papers
- G. Panel Session

## Mechanistic Approach vs. Simulation Approach

Subsequently, the SEPAP 12/24 unit has been used to investigate the long-term durability of thousands of polymer formulations at the Centre National d'Evaluation de Photoprotection (CNEP), a subsidiary of the Blaise Pascal University in France. The mechanistic approach, which explains how to use the chemical evolution of polymeric materials in artificial accelerated photoaging tests to predict the evolution of their useful properties, was recently approved by the ISO Committee ISO/TC 61-SC6N as an international standard.<sup>2</sup>

This approach is markedly different from the conventional empirical approach of artificially applying environmental stresses to simulate weathering, developed in the 1950s by the primary users of polymeric materials, e.g. machine tool designers and mechanical engineers.

Back then, when failures in use conditions were observed, particularly in outdoor conditions, machine tool engineers were urged to develop laboratory testing that could reproduce, on a shorter time scale, the phenomena causing the degradation of the polymeric systems. Those systems were handled as macroscopic units, easy to characterize based on physical (mostly mechanical) properties. The polymeric substrate was treated as a "black box" onto which any physical and chemical environmental stresses that could be possibly reproduced (light, heat, mechanical strains, O<sub>2</sub>, moisture, O<sub>3</sub>, and atmospheric pollutants) were artificially applied. Laboratory weathering instruments were designed to qualitatively and quantitatively simulate environmental stresses as close as possible to their natural maximum levels. That stress simulation approach is still widely used in control, development, and research on polymer durability.

The mechanistic approach has several advantages over the simulation approach:

- » Chemical evolution accounts for most of the physical damage occurring upon aging (e.g., changes in mechanical and appearance properties).
- >> Unlike changes in physical properties, for which there is no acceptable definition of acceleration factors, chemical evolutions can be accelerated with an appropriately defined acceleration factor. This factor expresses the relative rate of chemical evolution leading to lo



Spectral variations of LDPE film exposed in the SEPAP 12/24 during 0 hrs (A1), 152 hrs (A2), 502 hrs (A3), 595 hrs (A4), 1201 hrs (A5), 1600 hrs (A6), 1800 hrs (A7), 2002 hrs (A8), and 2192 hrs (A9) – A, B, C, D correspond to 1713, 1640, 1622, 1530 cm<sup>-1</sup> (B1, C1, D1 at initial time – B2, C2, D2 after 2192 hours of exposure).



#### Figure 2

Spectral variations of LDPE film weathered in the center of France during 0 hrs (A1), 264 days (A2), 355 days (A3), 605 days (A4), 1016 days (A5), 1322 days (A6), 1624 days (A7), and 2008 days (A8) – A, B, C, D correspond to 1713, 1640, 1622, 1530 cm<sup>-1</sup> (B1, C1, D1 at initial time – B2, C2, D2 after 2192 hours of exposure).

expresses the relative rate of chemical evolution leading to loss of the property of interest obtained in accelerated conditions to that in natural or end-use conditions<sup>3</sup>. On this basis, the lifetime of materials in end-use conditions can be predicted for a given climate.

» The relevant character of an accelerated photoaging experiment followed through the chemical evolution of the polymeric blend can be assessed through the invariance of the evolution mechanisms between different aging conditions.

<sup>2</sup> Draft International Standard ISO/DIS 10640 Plastics – Method of assessing accelerated photoageing by FTIR and UV/visible spectrometry

<sup>3</sup> For time reasons, the chemical aging rate in natural or end-use conditions is only determined over a limited exposure period, typically 6 months in temperate locations.

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» Understanding the mechanisms of chemical evolution enables one to develop rational photostabilization strategies.

## Follow-Up of Chemical Evolution and Service Life Prediction in SEPAP 12/24 Experiments

The characteristics of the SEPAP 12/24 are based on fundamental concepts of macromolecular photochemistry:

- » The unit has a parallelepiped exposure chamber equipped with four medium-pressure mercury arcs in borosilicate envelopes. The test specimens are homogeneously exposed on a rotating support in the center of the chamber.
- » The incident light contains quasi-monochromatic radiation at 296, 313, 365, 405, 436, 547, and 579 nm. The borosilicate envelope filters out radiation emitted at wavelengths shorter than 290 nm. Therefore, this source is not intended to simulate daylight but to activate the same photochemical processes as daylight<sup>4</sup>.
- » The temperature of the exposed surface of a reference film is controlled and maintained





#### Figure 3

Comparison of exposure durations to observe 50% decrease of elongation at break of agriculture films exposed in the Weather-Ometer (according to ISO 4892-2) and in the SEPAP 12/24. constant between 50 and 80°C. The reference film is chosen to have the same surface properties—that is, the same color and processing as the exposed specimens. Since any chemical evolution consists of intricate photoexcitation and thermoactivation processes, it is important to simultaneously control the intensity and spectral distribution of the light and the temperature of the specimens' exposed surface. Furthermore, as the evolution rate increases linearly with light intensity and according to an exponential law with temperature, it is more essential to control the temperature of the exposed surface than the light intensity.

>> Liquid water, or humidity, is an aggravating mechanical and chemical stress in polymer weathering. The most typical effect of water, beyond matrix swelling, erosion, and stabilizers extraction, is chemical. In the SEPAP 12/24, no external water is brought to the exposed specimen, enabling a precise control of temperature over the exposure. Nevertheless, the water formed through the decomposition of primary hydroperoxides can react locally through a cage effect with hydrolysable intermediate photooxidation products (like imides in PA, acylurethanes in PU, acid chlorides in PVC, and anhydrides). To amplify the effects of water, post-exposure immersions in neutral water at 60°C can be carried out according to predefined cycles.

The chemical evolution of any polymer matrix exposed to light, heat,  $O_2$ , and  $H_2O$  in the SEPAP 12/24 involves complex intricate photochemical and thermal processes. For a useful description of photoaging mechanisms, it is therefore essential to identify the main chemical sequence accounting for either mechanical damage or appearance change (which are quite different).

When changes in mechanical properties are predicted, vibrational spectrophotometry should be used, including FTIR, micro-FTIR, Raman-FTIR, micro-Raman-FTIR, FTIR with photoacoustic detection (PAS-FTIR), and ATR-FTIR, optionally complemented with chemical derivatizations. That analysis, for example, along

<sup>4</sup> In condensed phases (i.e., solid, liquid, and dense gaseous media), the reactivity of an electronic excited state following the absorption of light is independent from the spectral distribution of the incident light. Radiation emitted at different wavelengths will activate various vibrational levels in the excited state which are nearly instantly deactivated to the lowest vibrational level. This effect has been experimentally checked, for instance, through using bisphenol A-PC as a dual actinometer.

with additional chemical analysis techniques, allows identification of the main intermediate oxidation products (mainly hydroperoxides, ketonic groups, and alcoholic groups), the main conversion route of these intermediate products, and the major final products that accumulate in the matrix (e.g., acidic, ester, and lactonic groups).

Chromatography and mass spectrometry are generally used to characterize the low molecular weight compounds that escape from the matrix. However, the extent of the chemical evolution is better determined from the accumulation in the matrix of a critical product that, when properly chosen, provides a measurement of the main degradation route of the matrix. The critical product should be chemically and photochemically inert in the matrix, should not migrate out of the matrix, and should accumulate linearly with time until the functional property is completely lost.

The lifetime of the polymeric material in artificial conditions can be determined from the relationship established between the variation of a physical property (e.g., mechanical, permeability) and the associated change in critical product concentration under accelerated conditions. This result is converted into an estimate of the lifetime in natural or end-use conditions by applying the predetermined acceleration factor. The next sections will present practical examples of lifetime determination.

When appearance or visual changes are predicted, lifetime determination is more complex since several chemical routes might be involved, varying in relative importance depending on the chemical nature of the matrix and additives. For instance, classes of aromatic polymers (PC, TPU) are prone to yellowing that may result from two very different mechanisms with different kinetic laws, which cannot be differentiated through visual or colorimetric assessment. UV-visible absorption spectrophotometry and microspectrofluorimetry could be used to characterize the nature and concentration of the products that produce the variation in appearance.

## **Practical Examples of Application of the Mechanistic Approach**

#### Agricultural and Horticultural LDPE Films

The most important chemical route accounting for the mechanical detriment of LDPE greenhouse films involves the formation of chain end carboxylic acids on the normal methylenic groups and on the vinylidene defects of LDPE. The carboxylic acid groups were absorbing at 1715 cm<sup>-1</sup>. The vinyl groups formed on the intermediate ketonic groups through Norrish type II process and absorbing at 1640 and 909 cm-1 contribute to cross-linking (see Macromolecules, 1984, 17, 332).

Twenty-one specimens of LDPE greenhouse films ( $200 \,\mu$ m thick), with various stabilizers (UV-absorbers, phenolic antioxidants, and redox antioxidants like HALS), were exposed in the SEPAP 12/24 and weathered over 7 years in Clermont-Ferrand where the climatic conditions are temperate. (The average annual total solar radiations for a 45° surface oriented south is 4.87 Gj/m<sup>2</sup>.)

The chemical modifications were followed using FTIR spectrophotometry in the transmission mode. The equivalence of oxidation mechanisms observed in the SEPAP 12/24 and in natural conditions was shown considering FTIR spectra presented in Figures 1 and 2.

The "acceleration factor" determined for the LDPE matrix showed that 300 hours of exposure in the SEPAP 12/24 were approximately equivalent to one year in the center of France.

Moreover, it has been established that a 50% decrease of the percent of elongation break was observed when the oxidation extent corresponded to an absorbance increase at 1715 cm<sup>-1</sup> of x/1000 (where x was the thickness of the film, in microns).

According to the Task Force CEN/TC 249/WG7, the final draft pr EN 13206 and, more precisely, the section "Resistance to artificial ageing of covering thermoplastic films," mentioned that the "artificial weathering is described in ISO 4892-2. It consists of xenon arc sources with a double filter borosilicate for simulating the direct sunlight. Other test methods or test conditions may be used to check the film classification, only when it can be shown that there is a correlation with the test and the method ISO 4892-2. This may be useful when the ISO method test needs times which are too long for testing." SEPAP 12/24, from previous page

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An experiment was carried out in the Centre National d'Evaluation de Photoprotection with two objectives:

• To confirm that the experimental results obtained with the SEPAP 12/24 unit are consistent with the experimental results obtained on the same set of agricultural films with the Weather-Ometer<sup>®</sup>

• To point out the advantages of the accelerated technique based on the SEPAP 12/24 unit

Fourteen films (3 coverings "4 seasons," 3 coverings "3 seasons," 3 coverings "2 seasons," 1 covering "1 season," 1 black silage, 2 black and 1 transparent mulchings) were studied and exposed simultaneously in the Ci4000 (according to ISO 4892-2) and in SEPAP 12/24. The chemical evolutions were followed using FTIR spectrophotometry in the transmission mode, and



#### Figure 4a

Percent loss of butadienic units in various formulations E1, E2, E3, E4, E5 of ABS specimens exposed to environmental weathering in the center of France.



#### Figure 4b

Percent loss of butadienic units in various formulations E1, E2, E3, E4, E5 of ABS specimens exposed in the SEPAP 12/24 in dry conditions. the variations of mechanical properties were determined after exposure durations according to French standard NFT 510.34. The variations of the percentage of elongation at break were determined as functions of the matrix oxidation extent.

In Figure 3, the lifetimes of the 14 films determined as corresponding to the 50% mechanical loss figures shows the consistency between the data collected in both aging units and the acceleration observed in the SEPAP 12/24 compared to the Ci4000 Weather-Ometer. No ranking was possible for the 4-season films after 7000 hours of exposure in the Weather-Ometer, whereas a ranking was obtained after less than 2500 hours in the SEPAP 12/24).

The SEPAP 12/24 can be used also for testing mulching and silage films or for irrigation devices (see list of standards on page 9).

## Stabilized TiO,-Pigmented PVC Systems

The rather complex photooxidation mechanism of PVC and  $\text{TiO}_2$ -pigmented PVC has been described in full detail (see, for example, Polym. Deg. Stab. 1987, 18, 135 – 1988, 16, 147 – 1989, 25, 293 – 1991, 33, 17 – 1991, 33, 77 – 1991, 34, 135 ; Chemtech. 1996, 10, 42).

The main photooxidation products were observed using FTIR spectrophotometry, absorbing at 1785 cm-1 (acid chlorides), 1745 cm-1 ( $\alpha\alpha$ '-dichlorinated ketones), 1718 cm-1 ( $\beta$ -chloro-carboxylic acids). The acid groups formed could be used as a "critical photoproduct"; its accumulation in the matrix could be correlated with microcracking, whitening, chalking, and loss of physical properties.

Exposure in SEPAP 12/24 was carried out using either thin film (10–100 µm) or thick plaques. Since the permeability of atmospheric oxygen is fairly low in PVC, control by oxygen diffusion should be avoided in thick systems, and the oxidation extent should be determined in the most superficial layers (using FTIR spectrophotometry in the photoacoustic mode or micro-FTIR spectrophotometry). Photooxidation should proceed

with any discoloration due to oxygen starvation. In  $\text{TiO}_2$ -pigmented PVC, the light penetration was limited, avoiding any oxygen starvation effect, and the usual photocatalytic activity of non-passivated  $\text{TiO}_2$  was not observed in PVC unlike in most halogenated matrices.  $\text{TiO}_2$  acting as an inner filter absorbing incident photons up to 400 nm was an excellent photostabilizer of the PVC matrix, affording photoprotection of the chromophoric polymeric defects, which initiated PVC photooxidation. It should be noted that the follow-up of PVC photooxidation through colorimetry is mainly misleading. The aspect changes and the oxidative mechanical detriment involve different primary photochemical processes.

For example, two formulations of stabilized  $TiO_2$ pigmented PVC, whose lifetimes in Europe were around 10 years, were exposed in the SEPAP 12/24 either as 70 µm thick films or 120 µm thick films, and as 3 mm thick plaques during 300 hours. The increase of the absorbance at 1718 cm<sup>-1</sup> was, respectively, 0.33 and 0.53 for an optical path of 60 µm (or 0.26 for an optical path of 70 µm). After 10 years of weathering in Europe, the increase of absorbance in the most superficial layers at 1718 cm<sup>-1</sup> was 0.16 for an optical path of 60 µm.

Based on the formation of the  $\beta$ -chloro-carboxylic acid groups, the correlation between hours of artificial exposure and years of weathering was 500–1000 hours/10±3 years according to formulation. This is an extreme case of accelerated artificial photoaging as the excitation of the controlling chemical defects should involve 3 or 4 consecutive photon absorptions to initiate the oxidation mechanism.

In the same series of experiments, oxidation profiles within the thick specimen, weathered or artificially aged, were shown to be very similar, the penetration of light being around 200  $\mu$ m.

#### ABS-Based Systems

ABS is a polymeric material with poor resistance to photodegradation as the polybutadiene units are very photooxidable and the SAN units are very sensitive to appearance changes (yellowing by absorption and by emission; see Polymer Degradation and Stability 1997, 55, 147).

An evaluation of the photochemical degradation of black ABS blends was carried out for comparison between the following different conditions of exposure:

- » Exposure in SEPAP 12/24 ( $\lambda$ ≥ 290 nm temperature of the exposed surface 60°C)
- » In dry conditions without any contact with water
- » With periodic 1-hour immersion in demineralized water of an external bath regulated at 60°C after every 50 hours of exposure
- Accelerated artificial conditions of a device equipped with a xenon lamp according to ISO 4892-2 – xenon arc lamp: 0.55 W/(m<sup>2</sup>•nm) at 340 nm – black panel temperature: 70°C – temperature of chamber air: 50°C – RH 50% - exposure period: 18 min water spray, 102 min dry)
- » Outdoor natural aging in Clermont-Ferrand (France) where the climate can be considered as temperate; facing south at a 45° angle with open back

The chemical degradation was checked by FTIR with photoacoustic detection that allows for analysis of the changes of superficial layers (<  $10 \mu m$ ) of the exposed plates.

The IR spectral changes of ABS blends are similar under outdoor exposure and under the different conditions of artificial exposure previously described. The evolution of ABS is mainly observed by plotting vs. the exposure times:

- » The decrease of the absorbance at 987 cm<sup>-1</sup> assigned to the 1-4 trans microstructure of butadiene units (see Figures 4a, 4b, 4c, and 4d)
- » The increase of the absorbance at 1732 cm<sup>-1</sup> assigned to the accumulation of photooxidation groups (see Figures 5a, 5b, 5c, and 5d)



Figure 4c

Percent loss of butadienic units in various formulations E1, E2, E3, E4, E5 of ABS specimens exposed in the SEPAP 12/24 with periodic immersions in neutral water.



Figure 4d

Percent loss of butadienic units in various formulations E1, E2, E3, E4, E5 of ABS specimens exposed in a xenon instrument (18 mn spray – 102 mn dry)

#### SEPAP 12/24, from previous page

When the required oxidation level was reached, water can lead to a bleaching of the surface by leaching and extraction of ultimate carbonylated oxidation products. The discoloration can therefore be checked by colorimetric measurements. Bleaching is a consequence of oxidation, so water was not necessary for ranking the ABS specimens in terms of photostability when oxidation, notably oxidation of butadiene segments, was analytically followed by appropriate means as FTIR spectrophotometry.

As shown in the following table, an acceptable correlation between mercury lamps photoaging in dry and wet conditions, xenon-arc lamps, according to ISO 4892-2, and natural outdoor weathering (in the center of France) was achieved by comparing the time to reach the beginning of significant bleaching (defined as an arbitrary 70% degradation of butadiene).

Photoaging shown in Figures 5a and 5b	Specimens E2 and E3	Specimens E1, E4, and E5	
	Time to reach 70% degradation of butadiene	Time to reach 30% degradation of butadiene	
Artificial accelerated aging using mercury vapor lamps	160 hours	100 to 140 hours	
Artificial accelerated aging using xenon-arc lamp	210 hours	300 to 350 hours	
Natural outdoor weathering in center of France during summer	60 days	90 days	

There was good correlation between the two artificial accelerated weathering tests and natural outdoor weathering.

Specimens E2 and E3 presented similar behavior and degraded approximately three times faster than specimens E1, E4, and E5.

## *Evaluation of the Environmental Fate of Oxobiodegradable Polyolefinic Film Submitted to Daylight*

In an oxobiodegradable polyolefinic film, the correct on-purpose antagonism between the phenolic antioxidant and the two pro-oxidant species—the photoinducer (Fe III stearate) and the thermoinducer (Co II or Mn II stearate or other)—could only be observed in the SEPAP 12/24. It is essential to control the temperature of the exposed surface to correctly assess the photoconversion of the phenolic antioxidant into inert compounds, the accelerating



#### Figure 5a

Accumulation of photooxidation carbonylated products throughout exposure time in ABS specimens of various formulations E1, E2, E3, E4, E5 of ABS specimens exposed to environmental weathering in the center of France.



#### Figure 5b

Accumulation of photooxidation carbonylated products throughout exposure time in ABS specimens of various formulations E1, E2, E3, E4, E5 of ABS specimens exposed in the SEPAP 12/24 in dry conditions.

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#### Figure 5d

Figure 5c Accumulation of photooxidation carbonylated products throughout exposure time in ABS specimens of various formulations E1, E2, E3, E4, E5 of ABS specimens exposed in the SEPAP 12-24 with periodic immersions in neutral water.

Accumulation of photooxidation carbonylated products throughout exposure time in ABS specimens of various formulations E1, E2, E3, E4, E5 of ABS specimens exposed in a xenon instrument (18 mn spray – 102 mn dry).

influence of the photoinducer on the photothermal oxidation of the matrix, and the accelerating influence of the thermoinducer on the thermooxidation of the matrix, whose surface is maintained at 60°C.

The correct evaluation of the photooxidability in the SEPAP 12/24 and the thermooxidability in an aerated oven of oxobiodegradable polymers is a pre-requisite for the control of the acquired biodegradability, which can be assessed using the protocol designed at the University of Clermont-Ferrand and published in scientific journals—for example, Polym. Deg. Stab. 2006, 91, 1495; 2010, 95, 1011.

The field of oxobiodegradable polymer is presently expanding to non-polyolefinic polymers.

#### Industrial Acceptance of the SEPAP 12/24

As shown in the following list of standards and UV-resistance controls based on SEPAP 12/24, the use of SEPAP 12/24 is largely accepted by standards committees and by industrial companies in fields where long-term quality control is more stringent (e.g., automotive, sport equipment, plasticulture equipment, electrical, building, industrial packaging).

#### **STANDARDS**

NF T 54-190	February 1992	Greenhouse films
NF T 54-194	December 1995	Silage films
NF C 32-062-1	January 1995	Communication cables with halogens
NF EN -132-06	2002	Greenhouse films (extension to Europe)
NF EN -132-07	2002	Silage films (extension to Europe)
NF T 51-195-5	2005	T2 – Method of exposure to laboratory light sources T3 – Medium pressure mercury lamps
prEN 50289-4.17	September 2007	Draft test method for resistance of cables to UV (extension to Europe of NFC 32062-1 and 32062-2 [CENELEC])
ISO/TC 61-SC 6N	September 2008	Plastics: Methodology for assessing accelerated photoaging approved by Task Force WG2, Sept. 24, 2008, technical report possibly extended to ISO standard

#### **UV – RESISTANCE CONTROLS**

France TELECOM	Technical specification CNET/n°6750 FORMATION	Cables
FREYSSINET		
International	Requirement H H2000 SP A 001	Strand Internal Technical Specification for span bridges (Pont de Normandie, Viaduc de Millau, Stade de France)
SOLLAC		
ARCELORMITTAL		
SIGMAKALON, PPG	Test method	Coil coating
PSA (Hutchinson)	Test method D27-5435	Painted coatings for rubber items
RENAULT	Test method D27-3064	Accelerated photoaging test for exterior car systems
ATOFINA - HUNTSMAN	ACT-1 and ACT-2	PVC pinking
GROSFILLEX	Test method	External furniture – stadium seats
INNOVAC	Test method	Indoor electrical equipment
PSA	Test method	Jacksonville test for car coatings
PHILIPS LIGHTING	Test method	Outdoor lighting equipment
Association NEOSAC		
Sainte-Sigolène (43) France	Test protocol	Oxodegradable PE: control of abiotic degradation and biodegradability
SCOTTS	Test method	Printed packaging for compost
AIXAM.CIV-LIGIER	Test method	Thermoformed multilayer plaque for cars without licenses
OWENS CORNING (OCV Chambéry International)	Test method	UV – resistance of TWINTEX
ARKEMA	Test method	UV – resistance of PEBAX
DESJOYAUX Piscines	Test method	UV – resistance of swimming pool equipment
MDB TEXINOV	Test method	UV – resistance of agricultural nets
AKZO NOBEL Nippon Paint	Test method	UV – resistance of protective films in coil coating







2nd Place



Brd Place

## Atlas® Sweeps 2009 CEEES Photo Competition

A tlas is honored to have received 1st, 2nd, and 3rd place in the Confederation of European Environmental Engineering Societies (CEEES) photography competition. CEEES is a forum for international cooperation and information exchange around the resistance and integrity of products and systems against environmental influences. The competition is held through their national affiliates of the GUS (Gesellschaft für Umweltsimulation) in Germany.

CEEES awarded first place to the Atlas photograph titled "Ci5000 interior" that shows the rotating three-tier specimen rack of an Atlas Weather-Ometer<sup>®</sup> with samples ready for accelerated laboratory weathering testing. The judges considered the winning photograph to be "colorful and interesting." Second prize was given to the photograph "EMMAQUA (Equatorial Mount with Mirrors for Acceleration, with Water [aqua])" and was judged to be "intriguing and technically practical." Atlas' "Fisheye Static Florida" was said to be "impressive in scale and unusual." The image, which shows exposure racks at Atlas Testing Services' Florida test site for direct outdoor weathering, received third place honors.

All photographs submitted for review were judged on content by a group of CEEES members from different countries as well as on technical quality by Professor Mervyn L. de Calcina-Goff \* and Professor Raymond P. Clark\*\*.

- \* Professor Mervyn L. de Calcina-Goff, CEnv ASIS FSEE FRPS FBP. Accredited Senior Imaging Scientist, Honorary Member and Fenton Medalist of The Royal Photographic Society and previously Trustee and Past Chairman of The Imaging Science Qualification Board.
- \*\* Professor Raymond P. Clark, OBE CEng ASIS, Hon.FSEE, Hon FRPS Honorary Fellow, Fellow & Accredited Senior Imaging Scientist of The Royal Photographic Society and Past President.

# Atlas Adds Coastal/Marine Option to Atlas 25<sup>PLUS</sup>

**R**esponding to customer feedback on evaluating the effects of salt corrosion on photovoltaic modules used in seaside installations and marine applications, Atlas has added a coastal/marine test option to the Atlas 25<sup>PLUS</sup> PV Module Durability Testing Program. This new option may be added to either the standard "Global Composite" or "Tropical/ Sub-Tropical" climate tracks of the test program.

The coastal/marine option adds a PV module to the standard test program and extends the total test time from 12 to 13 months. The additional module is exposed at the Atlas sub-tropical, South Florida test site where standardized synthetic seawater is applied via spray five days a week to the front and back of a near-horizontal module. Furthermore, the laboratory-accelerated aged module in the standard  $25^{\rm PLUS}$  program undergoes an additional final month of salt fog and condensing humidity chamber exposure. These added stresses provide data on the effects of saltwater exposure on both new and severely weather-aged modules for data comparison to the non-saltwater exposed performance.

Atlas will introduce the following new test enhancements to the Atlas 25<sup>PLUS</sup> program in 2010:

- Accelerated dust/dirt pickup and retention
- Mold and mildew growth
- Other secondary environmental stress factors such as urban/industrial soot and pollution

Atlas can custom design or modify outdoor or laboratory based tests to meet your specific objectives and requirements.

For more information, please contact your local sales representative or visit **www.solardurability.com**.

# Atlas Testing Services' U.S. Operations Reaccredited

A tlas Testing Services' U.S. outdoor test sites and accelerated laboratory were recently reaccredited by the American Association for Laboratory Accreditation (A2LA) to the requirements of ISO/IEC 17025:2005.

New to the Atlas 2010 mechanical scope are the additions of solar (PV and thermal) testing at our DSET facility in Phoenix, AZ and corrosion testing at our accelerated lab in Chicago, IL. Atlas is now accredited to perform the following solar standards: IEC 61215, IEC 61646, IEC 62108, ASHRAE 93, UL 1703, ISO 9806, SRCC Standard 100, and IEC 60904-9. For corrosion testing, Atlas has added the following methods: ASTM B117, D5894, G85, FLTM BI 103-01, GM 4298P, 9540P, GMW 14872, ISO 6270, ISO 9227, and SAE J2334.

Atlas is the world leader in weathering testing services. Our SFTS (Miami) and DSET (Phoenix) outdoor test sites are known for their world class testing capabilities. Our Center of Excellence at the Atlas Headquarters in Chicago offers the most advanced accelerated laboratory testing available, using xenon, carbon-arc, fluorescent, metal halide, and corrosion instruments.

Atlas also operates outdoor weathering sites in France, India, and The Netherlands, and accelerated labs in Germany, the UK, and France. In addition, Atlas maintains a worldwide exposure network with over 20 laboratories in various climates around the world.

For accelerated lab/corrosion quotes, please contact Carmen Zimmer at +1-773-289-5543 or email czimmer@atlas-mts.com. For all other quotes, please contact John Wonders at +1-623-201-1029 or jwonders@atlas-mts.com.



Atlas' DSET facility in Phoenix, AZ











# **Two-Variable Experiments: Squares**

By Henry K. Hardcastle, Atlas R&D

Weathering experiments become more sophisticated when designs utilize more than one input variable. Often, these experiments are called "Square" designs. Two-variable experiments involve different research questions than those of simpler designs, including interactions between input variables, for example:

- Which affects color change more, UV irradiance level or condensation level?
- Do exposure irradiance and film thickness interact, or are the effects on one independent of the other in the weathering performance?
- If higher process temperatures cause unacceptable yellowing after four years in Florida and higher thermal stabilizer levels cause unacceptable yellowing after four years in Florida, will both higher process temperatures and higher stabilizer levels produce unacceptable yellowing after two years, four years, as an additive effect, as a multiplicative effect, or at all?
- How much acceleration is achieved by increasing the irradiance in a Xenon arc Weather-Ometer from 0.35 W/m<sup>2</sup> at 340 nm to 0.60 W/m<sup>2</sup>? How much acceleration is achieved by increasing Black Panel Temperature from 75°C to 85°C? How much by increasing irradiance while increasing Black Panel Temperature?

One of the most popular applications of these Square designs involves identifying a low and high setting for each independent variable. Four trials are then conducted according to the following array:

- Trial 1 Both variables at low setting
- Trial 2 Variable "A" at low setting Variable "B" at high setting
- Trial 3 Variable "A" at high setting Variable "B" at low setting
- Trial 4 Both variables at high setting

Multiple identical samples or trial replicates are often included for each trial to characterize the background variance within each trial. Output from each trial may be graphed on the same coordinate system for easy comparison. These graphs are read differently than traditional Cartesian coordinate systems. Often, intermediate input variable settings between the high and low settings are added to this design as additional trials and reveal intermediate topography.

These designs are also referred to as "Full Factorial" designs and are said to be orthogonal or balanced: two trials with "A" set low, two trials with "A" set high, two trials with "B" set low, and two trials with "B" set high. The orthogonal characteristics of these designs result in greater experimental efficiency, power, and sophistication than the traditional weathering experiments common in the industry today.

As an example, we were interested in determining if angle of exposure or daytime spray had a greater effect on color change of a Red Automotive Coating after 12 months' exposure in Arizona. We also wanted to see if there was an obvious interaction between these variables. We selected the low and high setting for the angle variable as  $45^{\circ}$  and  $5^{\circ}$ , respectively. We selected the low and high setting for the spray variable as either no spray or with spray. After 12 months' exposure in Arizona, the data shown at left were obtained.

It is obvious from this graphical analysis that presence of spray had a greater effect on the 12 month Delta E values. There does not appear to be an obvious interaction between the angle and spray variable in this environment.



Effect of Water Spray and Angle on Delta E of Red and Coating Arizona, 12 Months



## Summer 2010

# Atlas Well-Positioned to Meet Harmonized General Motors Test Methods

A lthough the recent economic downturn has been especially challenging for the automotive industry, automotive companies and their suppliers have continued their technical efforts, striving to improve their products. Using more streamlined and efficient business models, car companies are maximizing their testing efforts, showing compliance in as many markets as possible. Thus, many companies are harmonizing their test methods globally, enabling suppliers to reduce their testing costs in order to supply materials to automotive OEMs with global divisions and subsidiaries.

For over 10 years, General Motors has been harmonizing its test methods for use by all of its divisions worldwide. The company is currently incorporating all GM North America, GM Europe, and other GM Global standards into one harmonized standard set, known as GM Worldwide (or GMW) standards and specifications. This is an ongoing process, but many of the standards used for accelerated weathering have already been incorporated into GMW standards.

At the same time, the primary standard historically used for xenon arc weathering of automotive interior materials, SAE J1885 (Accelerated Exposure of Automotive Interior Trim Components Using a Controlled Irradiance Water Cooled Xenon-Arc Apparatus) was being revised and replaced by its performance-based equivalent, SAE J2412 (Accelerated Exposure of Automotive Interior Trim Components Using a Controlled Irradiance Xenon-Arc Apparatus). Due to these

standards' limitations, most car companies were developing their own methods with the goal of providing more realistic test conditions in their accelerated weathering test methods. General Motors has been transitioning its material specifications from the SAE test methods. Visit http://www.atlas-mts.com/graph to see some of the more popular test methods being specified by GM for automotive interior applications.

Many Atlas instruments, with flexible options available, offer users the option to run several of these methods in the same test cabinet. For example, the Atlas Ci3000, Ci4000, and Ci5000 See page 14 to see some of the more popular test methods being specified by GM for automotive interior applications.

Weather-Ometers offer irradiance control options at 340 nm, 420 nm, and 300–400 nm, allowing users to run most of the methods listed above. These options, along with dual Black Panel and Black Standard Temperature monitoring and control, give users much flexibility. To date, only Atlas has shown full compliance to the new methods as recommended by SAE J2413 (Protocol to Verify Performance of New Xenon Arc Test Apparatus) for the Ci water-cooled product line.

With superior temperature and irradiance uniformity offered by rotating rack designs, the Atlas models listed above are the obvious choice to meet current General Motors test requirements. New improvements to the lamp water cooling system employed by the Atlas Ci Series drastically reduces tap water consumption in these new high irradiance tests. These changes coupled with improvements to the instrument control system, significantly reduce operating and maintenance costs.

As car companies such as General Motors streamline and harmonize their test methods, users are faced with the challenge of ensuring that their test instruments will meet the new as well as the legacy test methods. Atlas instruments, with their flexible irradiance control and black panel/standard control, and proven rotating rack design, give companies the comfort of knowing that their investment will keep them testing now and into the future, as their customers harmonize and revise test methods.





# **General Motors Test Methods**

Test Method		Atlas Model Approved	Reference Method	Atlas Filter Combination	Comments
GMW14162	A	Ci3000, Ci4000, Ci5000	ISO 105 B05 - 3)	Boro S / Soda Lime	Rotating Rack specified
	в	Ci3000, Ci4000, Ci5000 Alpha Beta	ISO 105 B06 - 3	Boro S / Soda Lime 10 WG or 4IR+3WG Xenochrome 320nm	Rotating Rack specified
	С	Alpha	ISO 105 806 - 1	10 WG or 4IR+3WG	
	D	Ci3000, Ci4000, Ci5000	SAE J1885/J2412	Quartz / Boro S	
GMW3414	A	Ci3000, Ci4000, Ci5000 Alpha Beta		Quartz /CIRA on Soda Lime + Lant 10 WG Xenochrome 320nm	Only Atlas instruments listed are specified in the standard.
	B	Ci3000, Ci4000, Ci5000 Alpha Beta		Quartz /CIRA on Soda Lime + Lant 10 WG Xenochrome 320nm	Only Atlas instruments listed are specified in the standard.
SAE J2412		Ci3000, Ci4000, Ci5000	SAE J1885	Quartz / Boro S	Instruments must meet SAE J2413 Acceptance Protocol
SAE J1885		Ci3000, Ci4000, Ci5000		Quartz / Boro S	Only Atlas Ci instruments specified, Standard withdrawn by SAE.
ISO 105 B06	1	Alpha		4IR + 3WG	Rotating Rack specified
	2	Alpha		4IR + 3WG	
	3	Ci3000, Ci4000, Ci5000 Alpha Beta		Boro S/ Soda Lime 10 WG or 4IR+3WG Xenochrome 320nm	Rotating Rack specified
	5	Ci3000, Ci4000, Ci5000	SAE J1885/J2412	Boro S / Soda Lime	Rotating Rack specified
	6	Alpha		Xenochrome 320	1



Image 1 Art by Vlad Dumitrascu © National Geographic





Image 3

# **Science Meets History in Guatemala**

tlas Weather Stations have become a staple in outdoor weathering durability sites And projects all over the world. However, this highly adaptable product can also be found in some non-traditional settings.

Case in point: Atlas recently installed a Dual Environmental Monitoring Station (built on the framework of the Weather Station) at San Bartolo, a pre-Columbian Mayan archeological site in Guatemala.

San Bartolo was brought into the spotlight by National Geographic in its March/ April 2002 issue. The article discussed the site as one of the most important archeological finds to date. Las Pinturas, a pyramid on the site discovered by archeologist Dr. William Saturno, holds the best-preserved complete Mayan murals in existence. Researchers believe the murals date to 100 A.D. In a recent piece by CNN, San Bartolo was cited as only a portion of what many now believe to be the center of the Mayan civilization with the largest known clustering of Mayan structures-the Mirador Basin.

The project involving the modified Atlas Weather Station provides data to aid in the preservation of the San Bartolo murals. The murals are located inside the Las Pinturas pyramid (Image 2). The station monitors both ambient environmental and climate data on the exterior and interior of the pyramid, as well as micro-environment and climate data on the wall paintings.

The station is designed to be solar powered—challenging considering the pyramid is under a dense tree canopy with minimal light and must be of research-grade instrumentation. Due to the location of the site and no chance of access from June to December, a remote system was also necessary to transmit all data recorded in real time.

In February, Atlas engineer Duncan Maciver-tool bag in tow-traveled a day and a half from Guatemala City to the site, nestled in the jungles of northeast Guatemala (Image 3). Over several days, complete with deluxe accommodations under the stars (Image 4), local cuisine, and cold showers, Duncan installed the station with the support of the onsite archeological team. The finishing touch was mounting the data transmitter on top of the 70-foot-high pyramid (Image 5).

Atlas' years of technical experience were key in designing and installing this customized environmental monitoring station in the most challenging conditions.

## **Bibliography:**

http://en.wikipedia.org/wiki/San Bartolo (Maya site) http://news.nationalgeographic.com/news/2002/03/0312 0314 mayamurals.html http://www.cnn.com/video/#/video/international/2009/10/14/wus.mirador.bk.a.cnn Figure 1: http://www.news.harvard.edu/gazette/2005/12.15/03-maya.html





Image 4

Image 5 15 **SunSpots** 

# New Filters Offer More Precision in Xenon-Arc Testing

Two new developments in Atlas' filter technology offer users a much better simulation of natural sunlight and significantly improve filter reliability. Atlas' Right Light filter provides a better spectral match to natural sunlight, and CIRA coated filters are now available as outer filters instead of inner filters.

In 2008, Atlas introduced Right Light, a specially formulated filter with unique transmittance properties to better replicate the short wavelength UV cut-on of natural sunlight. The new filter combinations, Right Light/Quartz and Right Light/ CIRA on Quartz, are recognized as the closest simulation to natural sunlight. The special formulation of Right Light also has inherent qualities that significantly reduce aging during exposure. Studies have proven that the filter lasts for at least 2000 hours, or the recommended use of the xenon lamp. Right Light meets the ASTM G155 and ISO 4892-2 requirements for daylight (with both the Quartz and CIRA on Quartz outer filters).

In support of our quality initiatives, Atlas changed its CIRA filters from inner filters to outer filters. We now offer three options for CIRA outer filters: CIRA on Soda Lime, CIRA on Type S, and CIRA on Quartz. With newer methods requiring higher irradiances and higher temperatures, as well as the introduction of the Right Light filter, it was important to relocate the CIRA coating to the outer filter. CIRA filter systems allow for weathering tests requiring a full spectrum match and cooler test temperatures.

Due to the recent changes, Atlas is revising its recommendations for the ideal filter combinations to meet the requirements of popular test methods. Shown at right are Atlas' recommended filter combinations for its water-cooled xenonarc testing devices that meet these standards.

None of these revisions invalidate previous filter recommendations. The filters currently being used to meet testing standards are still valid for testing. Newer technology allows Atlas to provide its users with filters that provide more precise spectral matches to natural sunlight, with increased filter reliability and durability.

For more information regarding these exciting new filters, please contact your local Atlas sales representative.

# Filter Settings for Ci Weather-Ometers

Standard	Inner Filter	Outer Filter	Lantern Ring
ISO 105 BO2 Normal	Quartz	CIRA on	Float Glass
		Soda Lime	
ISO 105 B02 Low Humidity	Quartz	CIRA on Soda Lime	Float Glass
ISO 105 B02 High Humidity	Quartz	CIRA on Soda Lime	Float Glass
ISO 105 B02 USA Conditions	Boro S	Soda Lime	-
ISO 105 B04	Right Light	Quartz	-
ISO 105 B06 Method 1 (BST 115°C)	HL	HL	-
ISO 105 B06 Method 3 (BST 100°C)	HL	HL	-
ISO 105 B06 Method 5 (BPT 89°C)	Quartz	Boro S	-
ISO 105 B10	Right Light	Quartz	-
AATCC 16 Method 3	Boro S	Soda Lime	-
AATCC 16 Method 4	Boro S	Soda Lime	-
AATCC 16 Method 5	Boro S	Soda Lime	-
AATCC 169	Right Light	Quartz	-
M & S	Quartz	CIRA on Soda Lime	-
ISO 4892-2 Method A	Right Light	Quartz	-
ISO 4892-2 Method B	Boro S	Soda Lime	-
ISO 11341 Method A	Right Light	Quartz	-
ISO 11341 Method B	Boro S	Soda Lime	-
ASTM G155 Cycle 1	Right Light	Quartz	-
ASTM G155 Cycle 2	Right Light	Quartz	-
ASTM G155 Cycle 3	Right Light	Quartz	-
ASTM G155 Cycle 4	Boro S	CIRA on Soda Lime	-
ASTM G155 Cycle 5	Boro S	Soda Lime	-
ASTM G155 Cycle 6	Boro S	Soda Lime	-
ASTM G155 Cycle 7	Quartz	Boro S	-
ASTM G155 Cycle 7a	Right Light	Quartz	-
ASTM G155 Cycle 8	Quartz	Boro S	-
ASTM G155 Cycle 9	Right Light	Quartz	-
ASTM G155 Cycle 10	-	-	-
ASTM G155 Cycle 11	Boro S	Soda Lime	-
ASTM G155 Cycle 12	Right Light	Quartz	-
Mil-STD 810G, Method 505.5, Proc. 2	Right Light	CIRA on Quartz	-



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