

SunSpots®

Summer 2010

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 SEPAP¹ 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, O₂, and H₂O 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.



Science meets history
at Mayan pyramid

Art by Vlad Dumitrascu © National Geographic
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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.²

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, O₂, moisture, O₃, 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 loss of the property of interest obtained in accelerated conditions to that in natural or end-use conditions³. 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.

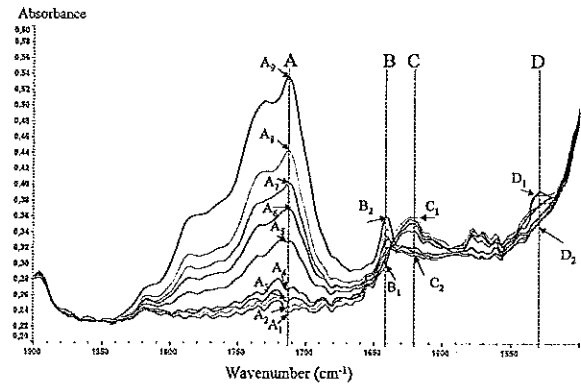


Figure 1
Spectral variations of LDPE film exposed in the SEPAP 12/24 during 0 hrs (A1), 152 hrs (A2), 502 hrs (A3), 595 hrs (A4), 1201 hrs (A5), 1600 hrs (A6), 1800 hrs (A7), 2002 hrs (A8), and 2192 hrs (A9) – A, B, C, D correspond to 1713, 1640, 1622, 1530 cm⁻¹ (B1, C1, D1 at initial time – B2, C2,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

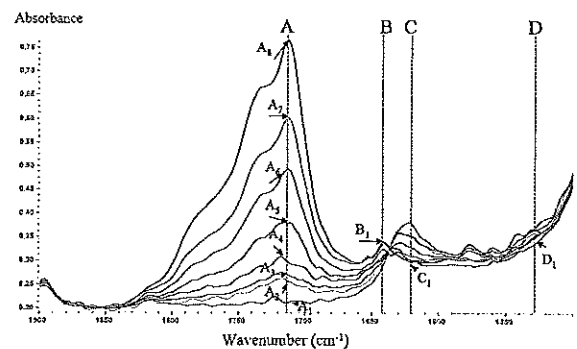


Figure 2
Spectral variations of LDPE film weathered in the center of France during 0 hrs (A1), 264 days (A2), 355 days (A3), 605 days (A4), 1016 days (A5), 1322 days (A6), 1624 days (A7), and 2008 days (A8) – A, B, C, D correspond to 1713, 1640, 1622, 1530 cm⁻¹ (B1, C1, D1 at initial time – B2, C2, D2 after 2192 hours of exposure).

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

³ 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.

Continued on next page

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^{-1} . 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 μm 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^2 .)

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^{-1} 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."

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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®

- 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 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 TiO₂-Pigmented PVC Systems

The rather complex photooxidation mechanism of PVC and TiO₂-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 (β -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 μ m) 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 TiO₂-pigmented PVC, the light penetration was limited, avoiding any oxygen starvation effect, and the usual photocatalytic activity of non-passivated TiO₂ was not observed in PVC unlike in most halogenated matrices. TiO₂ 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.

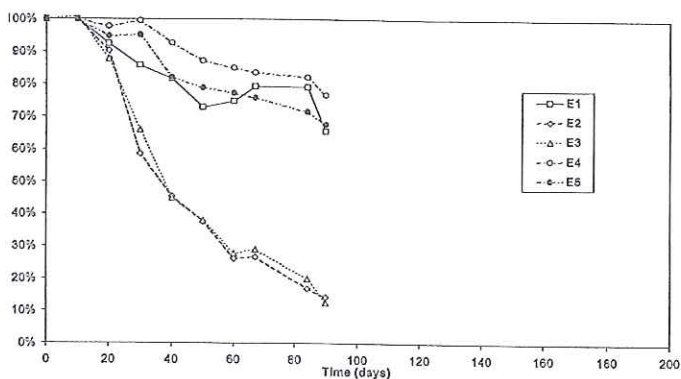


Figure 4a

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.

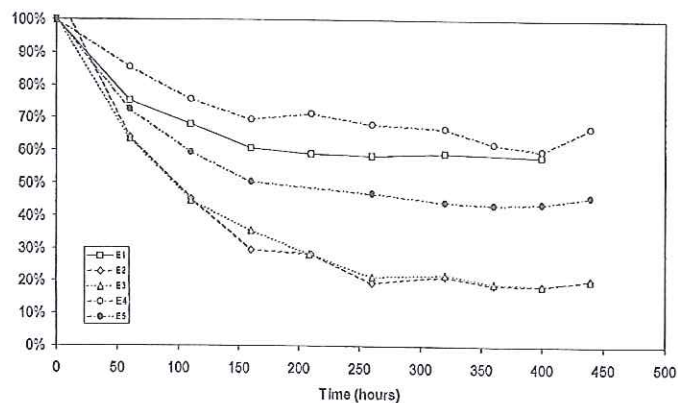


Figure 4b

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.

For example, two formulations of stabilized TiO₂-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⁻¹ 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⁻¹ was 0.16 for an optical path of 60 μm.

Based on the formation of the β-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 μm.

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 ($\lambda \geq 290$ 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/(m²·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 μm) 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⁻¹ 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⁻¹ assigned to the accumulation of photooxidation groups (see Figures 5a, 5b, 5c, and 5d)

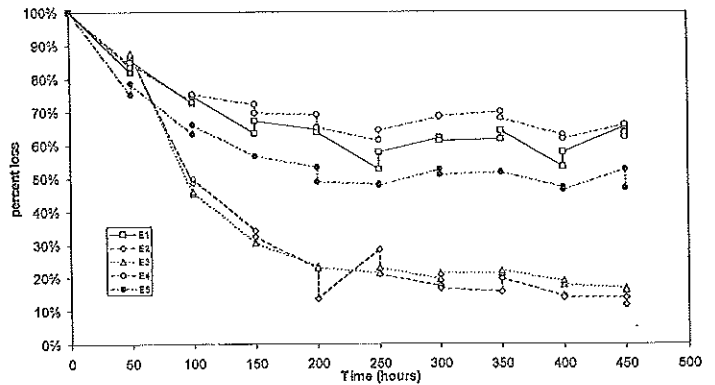


Figure 4c
Percent loss of butadienic units in various formulations E1, E2, E3, E4, E5 of ABS specimens exposed in the SEPAP 12/24 with periodic immersions in neutral water.

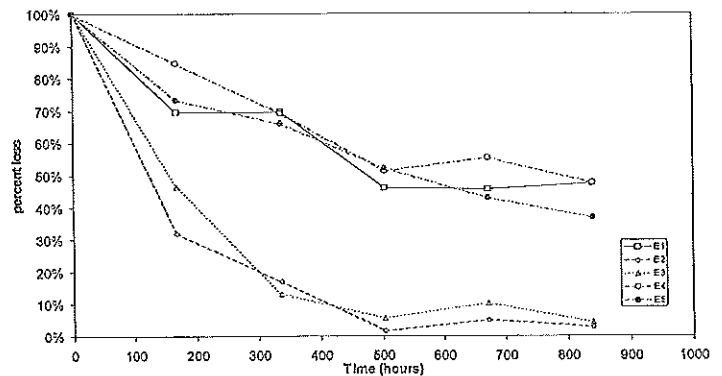


Figure 4d
Percent loss of butadienic units in various formulations E1, E2, E3, E4, E5 of ABS specimens exposed in a xenon instrument (18 mn spray - 102 mn dry)

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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

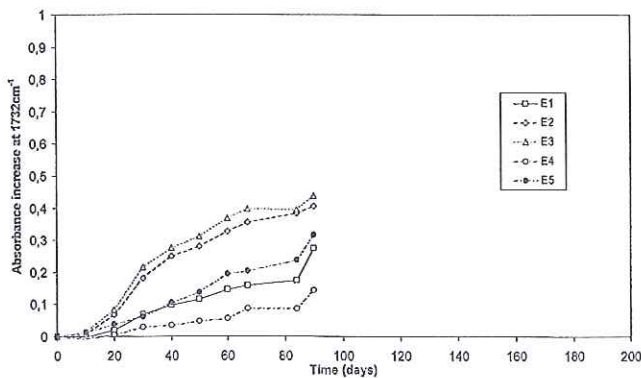


Figure 5a

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.

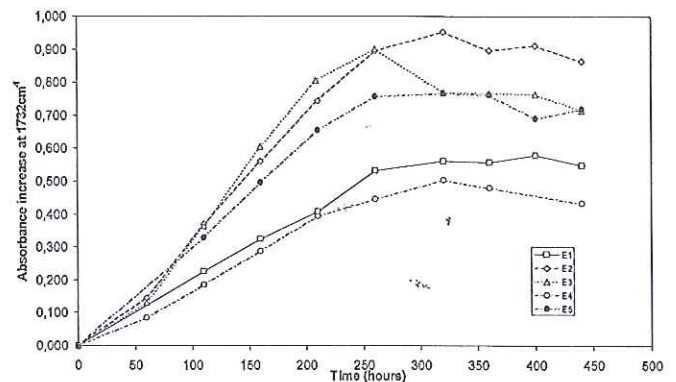


Figure 5b

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.

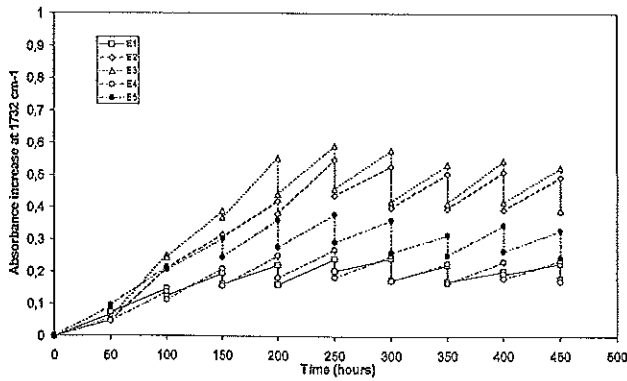


Figure 5c

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.

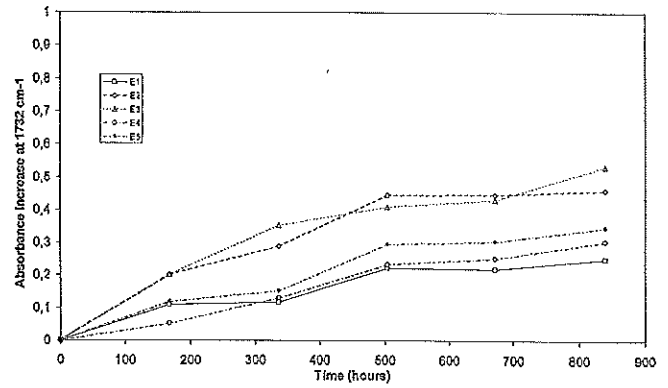


Figure 5d

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).

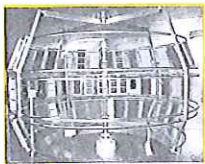
STANDARDS

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

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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



1st Place



2nd Place



3rd Place

Atlas® Sweeps 2009 CEEES Photo Competition

Atlas 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® 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**.

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