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Photofading of Colored Materials

Atlas Material Testing Technology

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Photofading of Colored Materials

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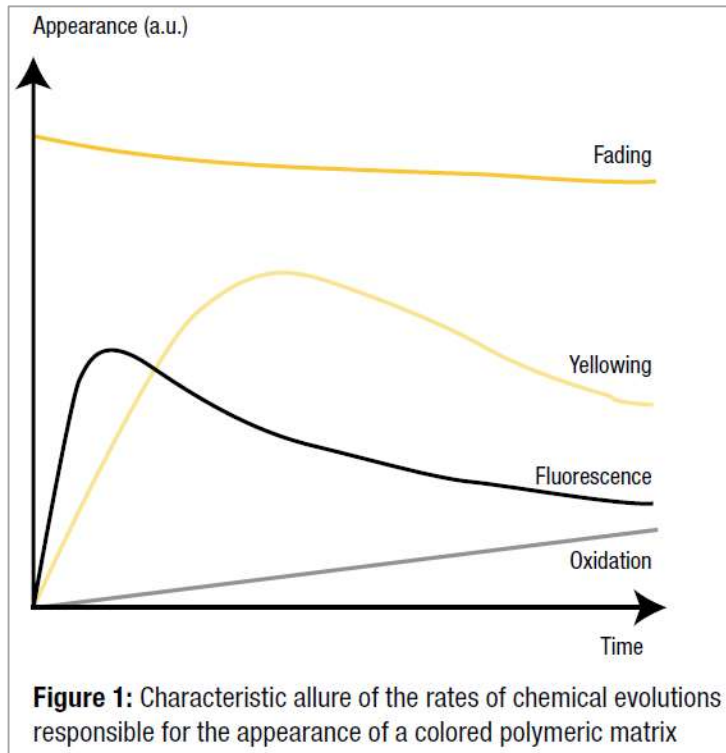
1. ABSTRACT

A colored polymeric object is a complex chemical system consisting of a macromolecular matrix (including processing agents), fillers, stabilizers, and colorants (pigments or dyes[1].

Environmental or artificially applied stresses (UV light, heat, oxygen, and moisture), induce chemical processes that cannot be accounted for by visual or colorimetric assessments only. The chemical evolution of the matrix with all its additives and the evolution of the colored products that are formed or transformed must be analyzed at the molecular level, as two or more of the four following processes can occur simultaneously[2]:

a) The photooxidation of the matrix produces chain scissions and reticulation reactions, which can alter the mechanical properties and cause appearance changes, such as gloss loss and whitening, as surface micro-cracks develop.[3] Meanwhile, inert degradation photoproducts accumulate linearly, measurable by spectroscopic techniques.

b) The formation of chemical groups able to absorb visible light leads to the discoloration of the polymeric system—from yellowing or browning to darkening, depending on the wavelength range of absorption.[4] These colored products, generally unsaturated molecules, are not photostable and do not accumulate linearly. Relatively early in the lifetime of a polymeric product, photobleaching reactions (decomposition of colored products into colorless products) compete with photo-discoloration processes. Colored photoproducts are therefore not a relevant criterion to represent the long-term evolution of a polymeric system and cannot be correlated with the evolution of the mechanical properties.

c) The formation of fluorescent products absorbed in the UV range and emitting visible light (frequent in aromatic matrices) changes the appearance in the presence of UV light. However, fluorescent photoproducts do not accumulate in the system, as they are easily photo-oxidized in non-fluorescent species and cannot account for the long-term degradation in a polymeric system.

d) The photofading of organic pigments and dyes (discussed in the next section) influences the appearance of the system. Inorganic pigments are generally photostable, rarely exhibiting a photocatalytic activity able to induce the photooxidation of the matrix with the consequences described in a). In very stable matrices. i.e., matrices undergoing no chemical evolution during the evolution of the colorants—the change in colorant concentration (different from the change of a colorimetric value) can be used as a criterion of degradation to convert accelerated lifetime into service lifetime.

While the evolution described in process a) mostly affects the mechanical properties, all four processes affect the overall appearance of a polymeric system and obey distinct kinetic laws represented in Figure 1. Moreover, unless coincidently, the relative rates of these processes are different in service-use and in laboratory testing.

2. ASSESSING THE CONTRIBUTION OF COLORANTS TO THE APPEARANCE CHANGE OF POLYMERIC MATERIALS

Figure 1: Characteristic allure of the rates of chemical evolutions responsible for the appearance of a colored polymeric matrix

The perceived color of an object is determined by the spectral distribution of either the reflected or the emitted visible light.[5] The addition of a pigment or dye will change that distribution by producing additional absorption of visible radiation and, in the case of fluorescent dyes, by emitting in the visible range. However, colorants, especially organic ones, exhibit a broad range of long-term lightfastness and it is not clearly established which wavelength ranges are mostly responsible for the degradation of organic colorants, as shown in several examples from the literature.[6,7,8,9,10,11] There is no universal degradation mechanism for all organic colorants. Any formulation consisting of a polymer matrix and colorants behaves specifically and such behavior should only be assessed through a scientific approach.

To determine how the fading of pigments or dyes contributes to the appearance change of a polymeric object aged in real or artificial conditions, it is essential that the matrix be sufficiently stabilized in order to:

- Preserve the normal environment of dyes and pigments in usage conditions, particularly to maintain the permeability to oxygen of the system to its normal value;

- Avoid any whitening, yellowing, or formation of fluorescent products due to the matrix oxidation;

- Prevent the attack of organic dyes and pigments by free radicals originating from the matrix (the unsaturated structure of organic colorants may be very reactive to free radicals);

- Avoid a reaction with photoactive inorganic pigments;

- Avoid any change in the protonation state of organic colorants through the acidic groups formed during the matrix oxidation that would fade the colorants.

2.1 Behavior of Mineral Pigments

Before focusing on organics colorants, as they are more easily degraded, here are some generalities on the different types of inorganic/mineral pigments. They can be classified relative to their crystalline structure:

- Pigments with highly organized crystalline structures and electronic bands: The probability of transitions between electronic bands is high, and such pigments are highly absorbing. Very often, those transitions occur in the UV range (e.g., TiO_2, ZnO), while some occur in the visible range (e.g., CdS, $CdSe$, Ce_2S_3).

- Pigments whose color property is associated to cations and anions in disorganized solids: Optical transitions are less likely in the visible and UV ranges, and the pigments are weakly absorbing, requiring their use in high concentration to obtain sufficient coloring properties.

- Carbon black absorbs any wavelength in the whole UV range, making it a universal UV absorber as well as the pigment of choice to obtain dark colors and black shades.

The long-term behavior of a polymeric matrix will be influenced by the type of pigment used in the formulation.

2.2 Weakly Absorbing Pigments

These pigments (e.g., iron oxide Fe_2O_3) are mostly neutral or even stabilizing. Other iron oxides have a pro-oxidant effect on thermo-oxidation, and since photooxidation is actually a photothermal oxidation process, UV radiation can activate this pro-degrading effect. Colored salts or oxides with a basic character—for instance, a basic iron oxide— may be transformed into photo-active carboxylates through reaction with the acidic species formed during the matrix oxidation.[12] These carboxylates will be a new source of radicals able to further oxidize the matrix (Figure 2). Thus, an iron oxide will exhibit a wide range of stabilizing properties depending on its origin and purity.

2.3 Highly Absorbing Pigments

Pigments with organized crystalline structure are relatively rare (TiO_2 anatase and rutile, ZnO, CdS, CdSe, Ce2S3). They are qualified as photo-active since they will profoundly affect the behavior of polymeric matrices they are added to.[13] Their influence can be evaluated by considering all their properties:

- Dispersibility;
- Internal filter property toward the matrix and oxidation products at x<400 nm;
- Photocatalytic activity toward the matrix and oxidation products;
- Photocatalytic activity toward non-absorbing stabilizers;
- Photoprotection of absorbing stabilizers;
- Photoprotection of yellowing products

Among these properties, the photocatalytic activity toward the matrix and the stabilizers or other colorants are particularly important. These photocatalytic properties can be drastically reduced through surface treatments. CdS and CdSe are exceptions since their photoactivity is so weak that they seem to act as photostabilizers.
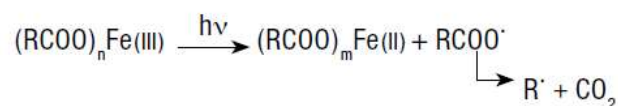
$$(RCOO)_n Fe(III) \xrightarrow{h\nu} (RCOO)_m Fe(II) + RCOO^{\cdot}$$
$$\longrightarrow R^{\cdot} + CO_2$$

Figure 2: Photoreactivity of iron (III) carboxylates

2.4 Carbon Blacks

These pigments are a specific case. They degrade UV and visible energy into harmless heat through vibrational relaxation (a non-radiative photophysical process). However, when the concentration is too low or the dispersion not sufficient in a matrix with low heat conductivity, hotspots may occur and lead to localized thermal oxidation,

affecting appearance (white spots). Therefore, carbon black must always be used in sufficient concentration to produce the thermal coalescence of particles that will dissipate the produced heat in a larger zone and out of the matrix and "thermostat" the system. Since carbon black does not provide sufficient photo-stabilization, the addition of an antioxidant is recommended (redox and conventional). Conventional antioxidants, which absorb in the UV range, are photochemically protected by the pigment.

3. PHOTOCHEMICAL BEHAVIOR OF ORGANIC PIGMENTS AND DYES

Due to the vast range of reactions that organic colorants can undergo, very few general statements can be made regarding the photochemical behavior of these compounds and their influence on the aging of polymeric matrices. The only long-term stabilizing property that can be anticipated for an organic colorant is that of a UV absorber that improves the matrix photoprotection.

The color of organic dyes and pigments is the result of an electronic transition from the ground state quoted as S_0 to the first excited state S_1 through the absorption of radiation in the visible range. Although the relaxation of the S_1 excited state of organic molecules may occur through several possible photophysical and photochemical processes, in the case of colorants it often evolves to the ground state S_0 through harmless heat release.[14]

Exposure to more energetic radiation, typically in the UV range, may activate the second electronic excited state S_2. In the condensed phase, a molecule excited in the S_2 state generally undergoes a quantitative internal conversion to the S_1 state via a radiationless process.[15] Thus, when a colorant absorbs strongly between 300 and 360 nm and when the probability of the internal conversion $S_2 \to S_1$ is higher than 0.999, it will protect the host matrix by competitive absorption of the UV radiation.

When the probability of the internal conversion $S_2 \to S_1$ is lower than 0.999, the colorant may undergo primary photochemical processes from S_2 that can either be independent of the chemical evolution of the host matrix or interact with it.[16] Both scenarios are reviewed below. Figure 3 summarizes the processes originating from the primary excitation of the colorant.

Note: Colorants that degrade under visible light exposure (typically poorly weatherable colorants) may undergo some of the processes described hereafter for S_2 from the S_1 state or from the lower energy state T_1.

3.1 First Case: The Evolution of the Matrix Does Not Interfere

The colorant may then evolve according to two pathways:

a) Non-oxidative (independent of surrounding oxygen concentration)
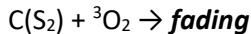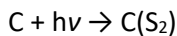
The result is the **photodissociation** or the **photoisomerization** of the colorant, yielding colorless products or a product with a different color
$C(S_0) + h\nu \to C(S_2) \to$ ***fading or discoloration***
where $C(S_0)$ and $C(S_2)$ refer respectively to the ground state and the second singlet excited state of the colorant C.
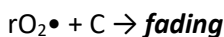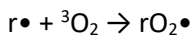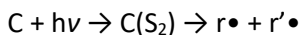
b) Oxidative

» Direct reaction

$C + h\nu \rightarrow C(S_2)$

$C(S_2) + {}^3O_2 \rightarrow$ ***fading***

where ${}^3O_2$ denotes molecular oxygen in the ground state.

Note: Fluorescent colorants typically undergo photooxidation from their first singlet excited state.[17]

» Indirect reaction (e.g., radicalar dissociation of the excited colorant and oxidation of the colorant in the ground state)

$C + h\nu \rightarrow C(S_2) \rightarrow r\bullet + r'\bullet$

$r\bullet + {}^3O_2 \rightarrow rO_2\bullet$

$rO_2\bullet + C \rightarrow$ ***fading***

Note: The addition of such a colorant to a photostable matrix may induce the photooxidation of the matrix through the attack by $rO_2\bullet$ radicals. This process can be prevented by adding antioxidants to the formulation.

» Photooxygenation (production of excited oxygen by transfer of energy)[18]

$C + h\nu \rightarrow C(S_2)$

$C(S_2) \rightarrow C(T_2) \rightarrow C(T_1)$

$C(T_1) + {}^3O_2 \rightarrow C + {}^1O_2 \rightarrow$ ***fading***
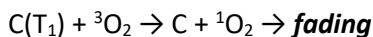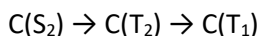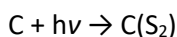
where $C(T_2)$, $C(T1)$, and ${}^1O_2$ refer, respectively, to the second and first triplet state, and oxygen in its excited singlet state.

Note: To check whether ${}^1O_2$ is produced, DABCO (1,4-diazabicyclo[2.2.2] octane) is usually added.

3.2   Second Case: The Evolution of the Matrix Interferes

When the long-term behavior of the system is controlled by the evolution of the matrix, both the colorant and the matrix may present a reactivity that influences each other through
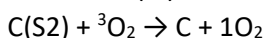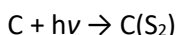
c)   Photosensitization of the matrix

» by energy transfer from the excited state of the colorant to the matrix MH (very rare)

$C + h\nu \rightarrow C(S_2)$

$C(S_2) + MH \rightarrow C + MH^*$

$MH^* + {}^3O_2 \rightarrow$ ***photooxidation of the matrix***
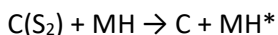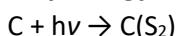
where MH^* refers to an excited state of the matrix

» indirectly, by energy transfer to atmospheric oxygen and production of singlet oxygen

$C + h\nu \rightarrow C(S_2)$

$C(S2) + {}^3O_2 \rightarrow C + 1O_2$

$MH + {}^1O_2 \rightarrow$ ***photooxidation of highly unsaturated matrices***

» through photoreduction of the excited state by the matrix or any additive bearing labile hydrogen atoms.[19] Atmospheric oxygen can regenerate the colorant in its ground state while the matrix undergoes photooxidation

$C + h\nu \rightarrow C(S_2)$
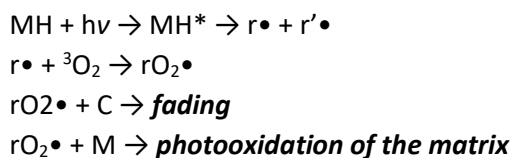
$C(S_2) + MH \rightarrow CH\bullet + M\bullet$

$M\bullet + {}^3O_2 \rightarrow$ *photooxidation of the matrix*

$CH\bullet + {}^3O_2 \rightarrow C + HO_2\bullet$
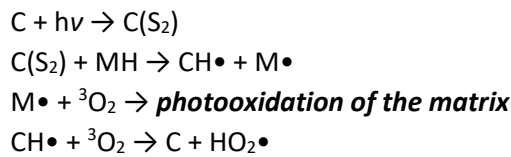
Although all three processes have a stabilizing effect on the colorant, they occur relatively infrequently.

d) Co-photooxidation of the matrix M and the colorant

$MH + h\nu \rightarrow MH^* \rightarrow r\bullet + r'\bullet$

$r\bullet + {}^3O_2 \rightarrow rO_2\bullet$

$rO2\bullet + C \rightarrow$ *fading*

$rO_2\bullet + M \rightarrow$ *photooxidation of the matrix*

Co-photooxidation occurs frequently, where both the matrix and the colorant are simultaneously degraded. However, the photostabilization of the matrix automatically brings about the photostabilization of the colorant.
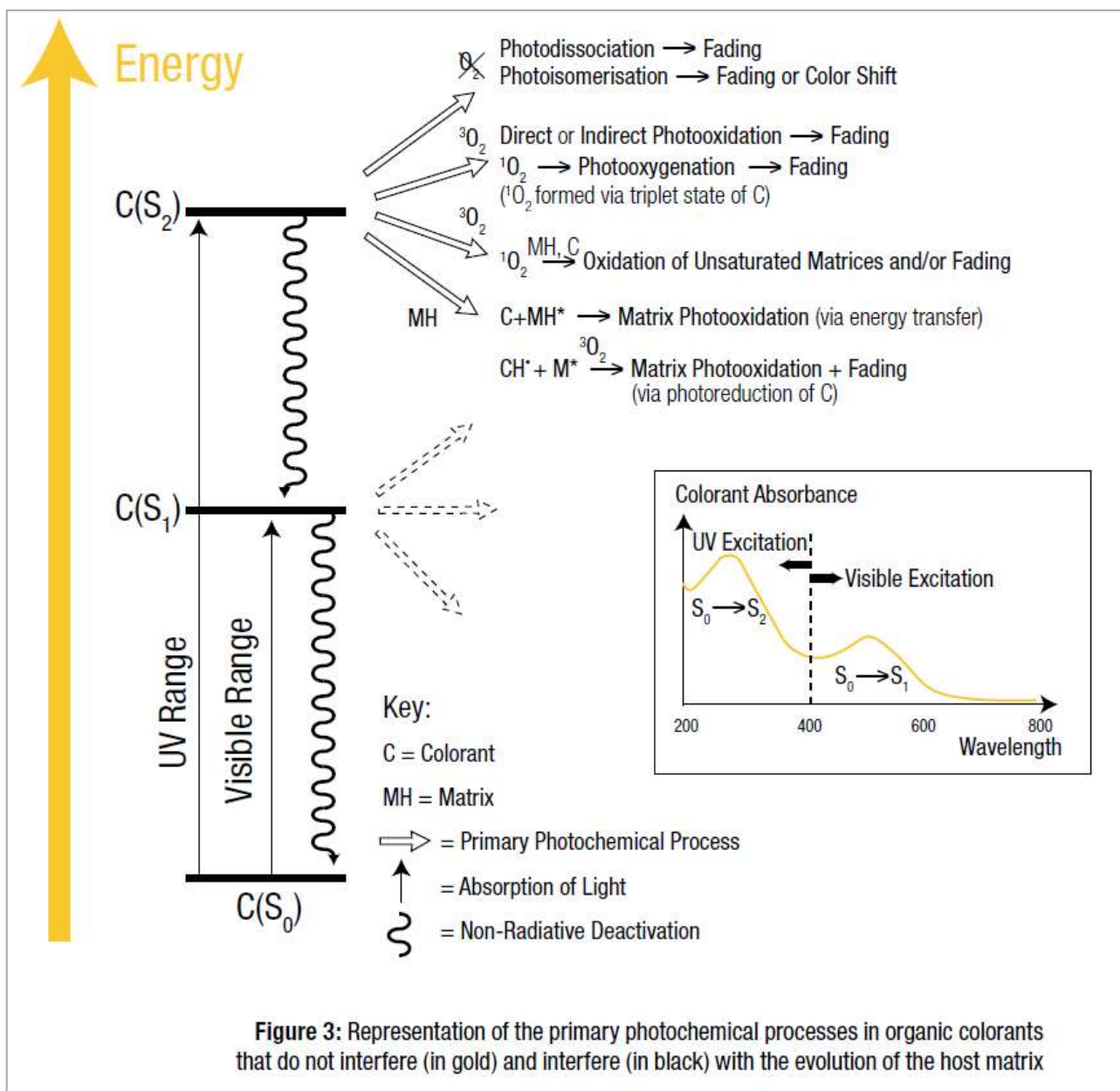
The study of the phototransformation of colorants in a polymeric medium is therefore greatly affected by the permeability of the matrix to oxygen. This should be kept in mind particularly when performing accelerated weathering tests where oxygen diffusion is not always representative of environmental conditions. Obviously, any such study is only possible if the radicals formed through the photooxidation of the matrix are neutralized beforehand to prevent any reaction with the non-excited pigments or dyes.

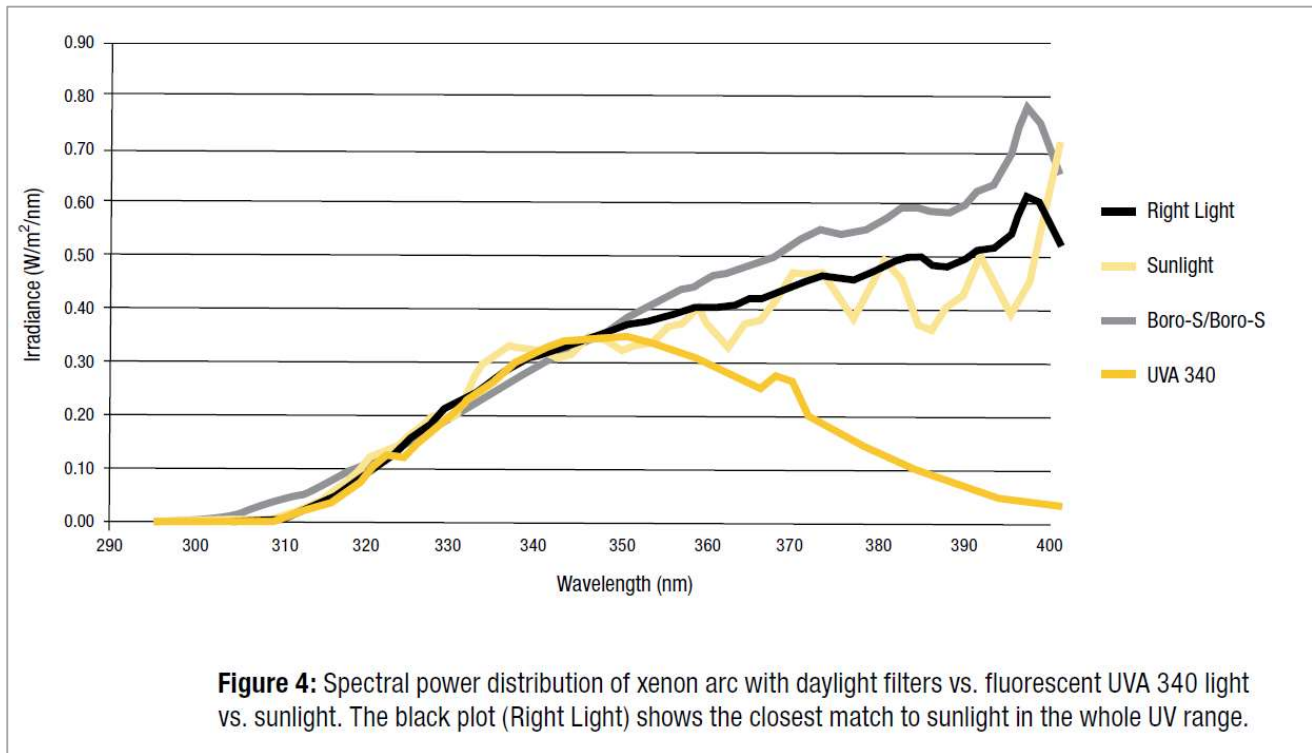# 4. RECOMMENDATIONS FOR ACCELERATED TESTING

Besides the generalities reported above on the photochemical evolution of colorants, each formulation of colored polymeric material presents a specific behavior. The data provided by colorant producers on the long-term durability of their products is only fragmentary since it is not possible to consider all possible end-use conditions. Nevertheless, this knowledge may help to improve the reliability of the accelerated testing of colored materials, with the following recommendations:

- Spectral distribution of the light source: It was shown that the long-term behavior of organic colorants is generally more influenced by the spectral distribution of the light source in the UV range than by that of the visible range. It is therefore important to monitor the spectral characteristics of the UV range of the light source used in laboratory tests. In particular, only wavelengths longer than 300 nm should be used to reproduce outdoor conditions and longer than 340 nm to reproduce indoor conditions. This broadly accepted principle was used in the development of Atlas' new Right Light™ filter, which incorporates a filtered xenon light that very closely matches the average SPD of solar radiation in the UV range (Figure 4).

  - The intensity of the source should be limited to 3 to 4 times the average irradiance level in end-use conditions to avoid the unnatural case of oxygen starvation in the inner layers of a material. This effect may become significant in coated materials.[20]

  - Uniformity of stresses: The rate of photooxidative processes is affected by the value of the temperature and the light intensity. Thus, control of the uniformity of the light intensity and the temperature at the surface of the exposed samples during an accelerated test is essential to ensure good repeatability and reproducibility.

- The impact of moisture on the degradation of the material needs to be examined and understood to determine the most relevant water cycle for a test.

- The change of chemical composition and color/appearance shall be assessed on parts of the finished product, so the effect of the processing operations can be accounted for.

Figure 3: Representation of the primary photochemical processes in organic colorants that do not interfere (in gold) and interfere (in black) with the evolution of the host matrix

5. CONCLUSION

Figure 4: Spectral power distribution of xenon arc with daylight filters vs. fluorescent UVA 340 light vs. sunlight. The black plot (Right Light) shows the closest match to sunlight in the whole UV range.

The behavior of a colored material can only be correctly understood through the simultaneous study of the chemical evolution of the matrix and the evolution of the coloring species, so it is possible to detect any premature failure of the colored system.

When the failure is triggered by the photoreactivity of the matrix, it is possible to develop a stabilization strategy (either by adding stabilizers to the formulation or using an external photoprotective layer such as a stabilized coating).

When the failure is initiated by the photoreactivity of the colorant, a more photostable colorant is recommended.

6. Notes & Literature References

1   Pigments are colorants of inorganic or organic nature that do not dissolve in the host medium, whereas dyes are organic colorants that are soluble in the host medium. See for instance: Harris, R.M., *Coloring Technology for Plastics,* New York: Plastics Design Library, 19992

2   Haillant, O., Sun Spots, 76, 2006, 1.

3   When micro-cracks develop on the surface, the ratio of diffused light to specular light reflected by the surface increases, resulting in a less glossy and whiter appearance**.**

4   For instance, substances absorbing light between 400 nm and 440 nm will appear yellowish.

5   Visible light is the portion of the electromagnetic spectrum ranging from ca. 400 nm to 720 nm.

6   Searle, N., Sun Spots, 38, 1987, 1.

7   Rosenberg, A. et al., Fogra Research Report No. 52.024, München, December 2002, p. 9.

8   Suhadolnik, J.C. et al., Proc. International Conference on Digital Printing Technologies, San Diego, California, September 29, 2002, 348.

9   Batchelor, S.N. et al., Dyes and Pigments, 59, 2003, 169.

10   Wilhelm, H., The Permanence and Care of Color Photographs: Traditional and Digital Color Prints, Color Negatives, Slides, and Motion Pictures, Preservation Publishing Company, Grinnell, Iowa, USA, 1993, p. 145.

11   Duxbury, D.F., Chem. Rev., 93, 1993, 381.

12   Zuo, Y., and Hoigné, J., Environ. Sci. Technol., 26, 1992, 1014.

13   Lemaire, J., Pure Appl. Chem., 54, 1982, 1667.

14   Photophysical processes are the photoexcitation and subsequent events that leave the initial molecule unchanged, such as fluorescence, phosphorescence, or internal conversion. Photochemical processes yield new chemical species through isomerization, addition, ionization, or dissociation.

15   Turro et al., J. Am. Chem. Soc., 1978, 125.

16   Lemaire et al., Caoutch. Plast., 793, 2001, 32.

17   The relatively long lifetime of the S1 state of fluorescent molecules (10^{-10} s, compared with the lifetime of S_1 states of non-fluorescent organic molecules 10^{-12}–10^{-9} s) enables a reaction with atmospheric oxygen and further degradation. This accounts for the generally poor lightfastness associated with fluorescent dyes.

18   Rabek, J.F., Polymer Photodegradation. Mechanisms and Experimental Methods, London: Chapman and Hall, 1995, p. 405.

19   Allen, N.S., and McKellar, J.F., Photochemistry of Dyed and Pigmented Polymers, London: Applied Science Publ., 1980, p. 247.

20   The use of a coating is recommended when the matrix undergoes discoloring rearrangement reactions that cannot be prevented by chemical stabilizers, such as in aromatic polymers. However, the use of a physical barrier may produce an unrealistic oxygen depletion at the matrix-coating interface in accelerated aging that would not occur during service life.

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