

The Degradation of Coatings by Ultraviolet Light and Electromagnetic Radiation

Anatomy of Paint, Clive H. Hare, Editor, *Materials Technology Section*

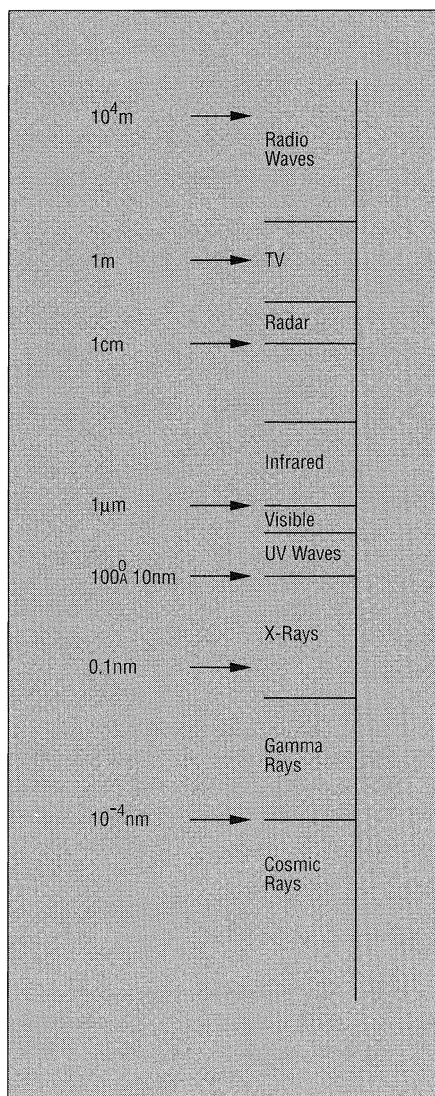
On earth, our major source of radiant energy is the sun. It supplies warmth (heat or infrared radiation), light radiation (both visible light and ultraviolet light), and a wide range of energy of other types (e.g., X-rays, gamma rays, and cosmic rays). These energy forms, as well as radio, television, and radar waves, are closely related manifestations of the same phenomenon, electromagnetic radiation. The energy forms differ only in their wavelength (the distance from peak to peak of the wave pattern), which may range from kilometers (thousands of meters) to less than a nanometer (one billionth of a meter).

The apparent diversity of these energy forms results primarily from the differences in the manner in which they are perceived. The human eye, for example, has the unique capacity to absorb radiant energy in the visible light range but will not serve adequately as a receptor outside of this rather limited range (380 nm-780 nm). Radio receivers may recognize energy in the 0.1-meter to 20-meter range but will not receive radiation in the visible range. This month, we will examine the effect of electromagnetic radiation on coatings.

The diverse forms of electromagnetic radiation may be classified in terms of their wavelength, λ (lambda), or their frequency, ν (nu), as shown in Fig. 1. The term "frequency" is a measure of the number of waves per second and is related to wavelength by the formula shown in Fig. 2, where c is the speed of light.

The Effects of Electromagnetic Radiation on Exposed Materials

Molecules of all types are excited by and selectively absorb radiant energy (energy from radiation) at specific wavelengths across the electromagnetic spectrum. Glass, which allows visible light to pass through it without absorption, is not as transparent to ultraviolet light and is virtually opaque to ultraviolet light of the shorter wavelengths. This is one reason why coat-



ing films last far longer indoors than outside. Most organic polymers are excited by and absorb radiant energy at a variety of specific wavelengths in the infrared section of the electromagnetic spectrum. This property is used to advantage in infrared spectroscopic analysis of the molecular structure of organic paint films.

As wavelengths get shorter, the energy of the radiation increases to the point at which it is energetic enough to cleave the bonds of chemical substances and produce profound changes in any material onto which the radiation falls. High energy X-rays, gamma rays, and cosmic rays are such powerful radiations that they can ionize gases and induce profound and potentially deadly chemical changes in animal tissue. While visible light is not as energetic and poses little health threat to humans, it will induce certain chemical reactions, such as the irradiation of silver salts in the photographic process.

Ultraviolet light, however, has sufficient energy to disrupt and break the co-valent bonds of organic molecules. This property may be employed to advantage in certain radiation-curing methodologies (the radiant energy is

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■ Fig. 1
The electromagnetic spectrum of radiation types

$$\nu = \frac{\lambda}{c}$$

frequency of wave cycles/second = $\frac{\lambda}{c}$ wavelength (nanometers to kilometers) / speed of light (3×10^8 meters/second)

■ Fig. 2
The relationship between frequency and wavelength

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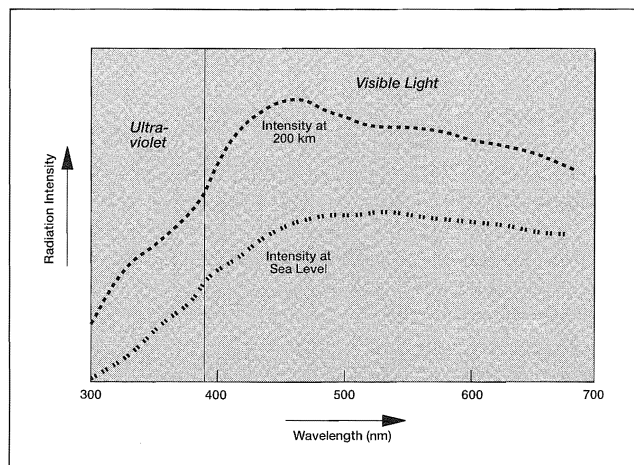
used to activate photochemically reactive initiators, which then set off polymerization reactions). Ultraviolet light, along with oxygen and water, is one of the 3 primary agencies that induce slow degradation (aging) of many organic polymers. These organic polymers include those that bind paint film and those that make up the tissue of the human body.

The effects of ultraviolet light increase directly with the intensity of the radiation and inversely with the wavelength of the radiation. As may be noted in Fig. 3, our atmosphere acts like a huge filter and absorbs the larger part of the more powerful shorter wavelength radiations, including shortwave ultraviolet light, before they reach ground level. Radiation of wavelengths below 300 nm is almost completely absorbed by the atmosphere, and only a relatively small amount of long wave ultraviolet light remains (between 300 nm and 380 nm). But the harmful effects of even this small amount of radiation on the molecular structure of paint films are now well recognized.

The Mechanism of Coating Degradation by Ultraviolet Light

To adequately address the problem of ultraviolet light degradation, we must understand the photodegradation mechanism. We will first consider its effect on unpigmented films. Photochemical degradation proceeds in stepwise fashion as noted in Fig. 4. The first phase is known as photolysis, where the polymer absorbs ultraviolet radiation, and, as it does, becomes excited and is raised to a higher energy state than normal. This excess energy must be eliminated.

One way this elimination is accomplished is by the cleavage of the primary bonded structure of the polymer to form highly reactive free radicals. The ease with which such co-valent bonds are cleaved depends upon the strength of the bond (for example, — C — C — bonds have greater bond strength than — C = C — bonds). Polymers made up entirely of the stronger bonds have more resistance to ultraviolet-induced breakdown at any given wavelength. However, these polymers become more



■ Fig. 3
The effect of the atmosphere on the intensity of solar radiation at sea level in the ultraviolet and visible light bands

vulnerable as the wavelength of the radiation gets lower.

After the onset of photolysis, the second phase in the photochemical degradation of polymers, autoxidation, may then proceed via reaction of the free radicals with oxygen to form peroxy radicals.

The peroxy radical may then react with the polymeric backbone by abstracting (removing) a hydrogen atom to form a hydroperoxide and another free radical. Because the hydroperoxide is extremely vulnerable to photolysis, it will readily fragment to provide more free radicals. These free radicals will then attack other sites on the polymeric backbone.

Photolysis of other atoms in the coating is also possible, again producing excited, high energy moieties and then free radicals. At a higher energy level, free radicals may react with oxygen, water, or other atoms not associated with the binder. All of these reactions produce more, equally dangerous free radicals, which may subsequently set off reactions that may eventually result in attack and cleavage of the binder molecules.

The increase in production of the highly reactive free radicals within the film can result in the occurrence of many complex intrapolymeric reactions. These reactions may include chain scission (splitting), depolymerization, and even the volatilization (evaporation) of smaller polymeric fragments. Conversely, interchain cross linking, leading to excessive

cross link density and embrittlement, is possible.

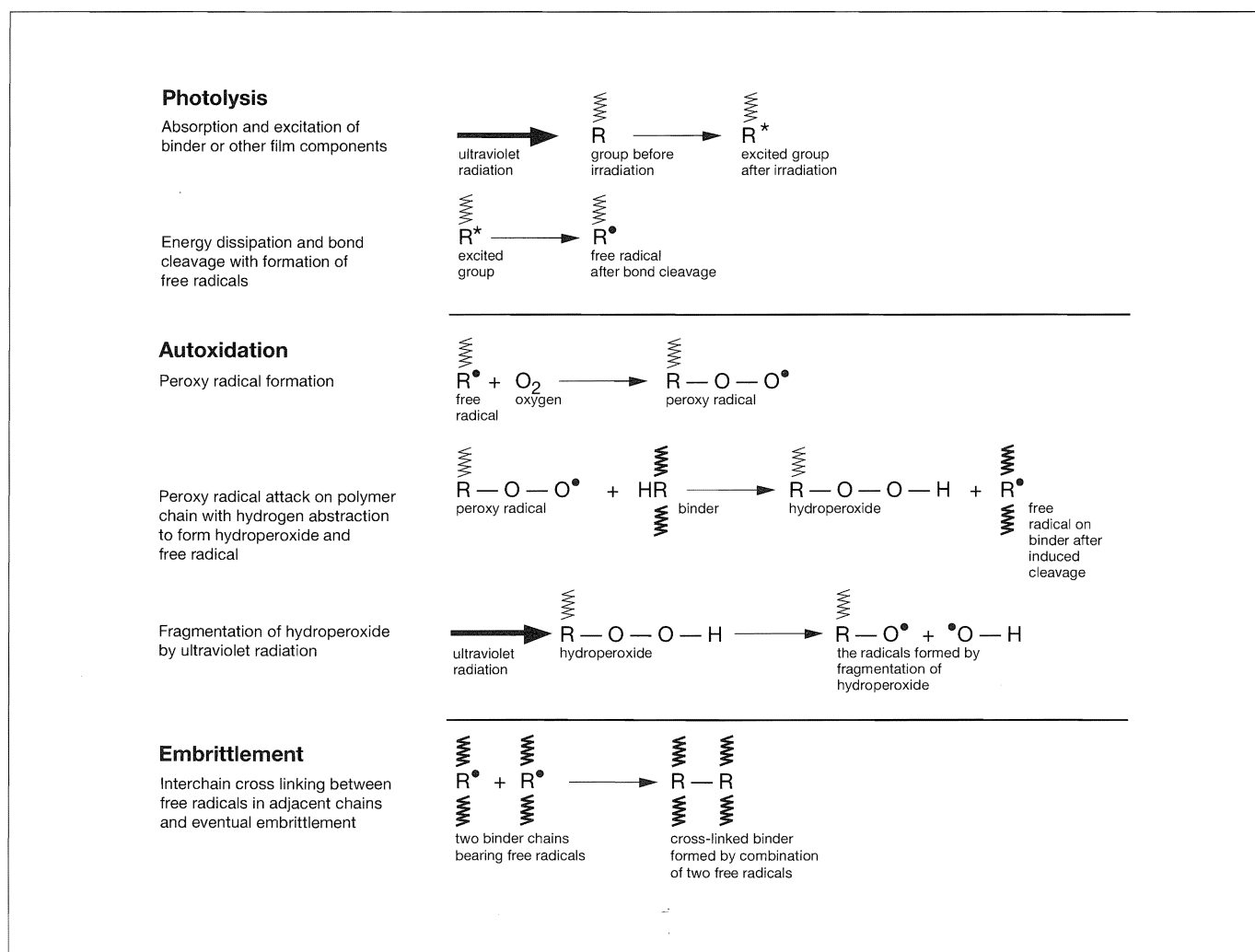
While the exact nature of the changes will depend upon the polymer structure, the net effect is a marked change (deterioration) in physical, chemical, and performance properties. In some reactions, such as the dehydrochlorination of chlorinated species, the reaction products (in this case HCl) may produce corrosion of the substrate that the film was originally intended to protect.

Mitigation Techniques

Use of Non-Absorptive (Ultraviolet Transparent) Binders

Fortunately, formulation can do much to mitigate these destructive effects. Vehicles can be selected from those families of aliphatic polymers that do not absorb ultraviolet light but are transparent to the radiation (acrylic, vinyl acetate, aliphatic urethanes, etc.) and therefore are not affected by exposure. Vehicle binders made up of aromatic moieties, such as bisphenol A epoxies and phenolics, are far more absorptive and therefore subject to ultraviolet light attack.

It must be emphasized that if the polymer does not absorb the radiation, it cannot be affected by it. It may, however, be sensitive to attack by free radicals derived from the absorption and excitation of other materials in the film (e.g., additives). Ultraviolet radiation will attack ultraviolet light-sensitive layers beneath transparent top-



■ Fig. 4
Photolysis, autoxidation, and embrittlement of paint film

coats. In the use of such ultraviolet light-transparent vehicles, care must also be taken to ensure that light-sensitive undercoats and substrates are properly protected.

Selective Absorption

This may be done by properly modifying the light-stable topcoats with pigments or other ultraviolet absorbers or reflectors or by properly pigmenting the undercoats. Certain pigments also absorb ultraviolet light that may be available to attack ultraviolet light-sensitive coating vehicles. Some pigments may themselves change radiant energy into destructive energy forms (chemical energy), and these materials must be used carefully. If properly selected, however, pigments can effectively dissipate the destructive ra-

diant energy in less harmful ways (as heat, for example), instead of changing it into chemical energy. The selective absorption of ultraviolet light by pigments protects the vehicle binder and increases the durability of the coating film. Materials such as zinc oxide, zinc sulfide, red iron oxide, carbon black, and rutile titanium dioxide are all effective ultraviolet light absorbers and provide good protection to sensitive polymers. As may be noted in Fig. 5, zinc oxide is a particularly valuable pigment in this regard. It absorbs virtually all ultraviolet light radiation at dangerous wavelengths below 360 nm and offers its binder outstanding protection.

Not all pigments are equally efficient ultraviolet light absorbers. Extenders such as magnesium silicate and

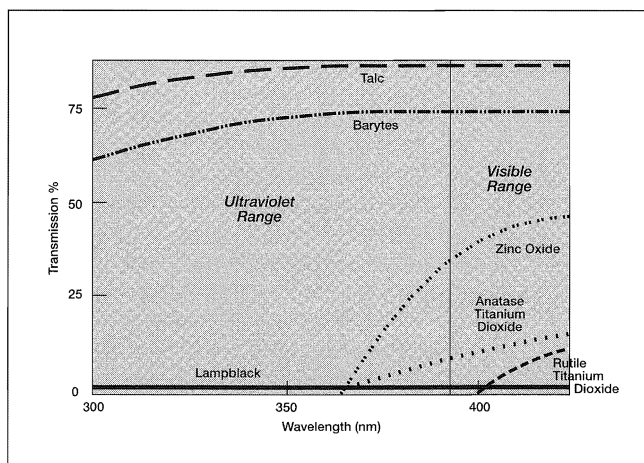
barytes are relatively transparent to ultraviolet light and offer little protection. Others, such as anatase titanium dioxide, may actually make matters worse through a mechanism known as photocatalytic degradation.

Anatase titanium dioxide has deformed ions in the crystal lattice of its surface. These ions are easily reduced to a lower oxide state by ultraviolet light of wavelengths below 405 nm. This reduction releases highly reactive nascent oxygen, which rapidly oxidizes the surrounding vehicle to form water-soluble breakdown products. While the reduction reaction at the pigment sur-

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■ Fig. 5
Absorptive properties
of different pigments
in the ultraviolet and
visible range
(stylized)

face is reversible by subsequent oxidation, the oxidation of the vehicle is not. The oxidation of the vehicle is manifested as a severe chalking. The degraded vehicle around the pigment is essentially washed away, and the unbound pigment is left as a loose, chalky layer on the surface. Photocatalytic attack on the vehicle is most intense near the surface of the pigments (unlike simple photochemical attack where the presence of the pigment lessens the effect). With anatase titanium dioxide, the interfacial integrity at the pigment/vehicle boundary is more readily damaged, and the chalking is more severe as the pigment becomes loosened. This extreme propensity to chalk typifies all anatase titanium dioxide pigments. While generally considered a disadvantage, the aggressive chalking tendency of the pigment has been used in certain self-cleaning house paints for exterior wood siding. Unlike photochemical degradation, photocatalytic degradation of anatase base coatings does not measurably increase as the wavelength of the radiation decreases.

Rutile titanium dioxide, unlike anatase titanium dioxide, has a more compact lattice structure with less deformation, and the oxygen is less readily abstracted. Further mitigation of chalking is also afforded by the surface treatment of the pigment with inorganic hydrates such as silica, alumina, and zirconia. These treatments, now used extensively, make rutile titanium dioxide an excellent ultraviolet light

screen for paint vehicles.

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irradiation through the coating film (i.e., the efficiency of the pigment dispersion) may have a profound effect on the ultraviolet light stability of the coatings. Dispersion may also produce variable effects depending upon the type of pigment used. Where the pigments are absorptive and protect the vehicle, their excessive agglomeration (resulting from poor dispersion) or excessive flocculation (resulting from poor dispersion stability) can result in lower ultraviolet light resistance of the film (compared to well dispersed systems). Some areas of the film are locally deprived of the pigment because of the presence of pigment-satiated (agglomerated and flocculated) areas of the film. Where such agglomeration and/or flocculation occur in a paint film formulated with a photocatalytically sensitive pigment like anatase titanium dioxide, potential sites of photocatalytic oxidation are localized and somewhat shielded, resulting in a reduced chalking compared to a similarly pigmented but better dispersed system.

Reflective Pigments

Selective absorption is not the only methodology by which pigments reduce ultraviolet light attack on coating films.

Highly reflective pigments, such as leafing aluminum, may be employed to reflect ultraviolet light from the coating film in the same way that a mirror reflects light. These pigments

will be discussed in a forthcoming segment of this series.

Luminescent Pigments

Luminescent pigments absorb radiant energy in the near ultraviolet and violet wavelengths and re-emit it as a longer wavelength to produce colors of a much higher chroma or intensity in the red, orange, yellow, and green wavelengths. This concept, which is used to produce flamboyant fluorescent colors, has not been employed to specifically protect the coating vehicle from attack.

Organic Additives

In clear coatings, as well as in some pigmented coatings requiring the highest levels of ultraviolet light resistance that selectively absorb ultraviolet light are used.

These ultraviolet light absorbers are chemically varied but include hydroxybenzophenone derivatives, hydroxy phenyl benzotriazoles, and substituted acrylonitriles. They are essentially similar to the sunscreen agents used in suntan lotions. Like pigments, they absorb short wave ultraviolet light and convert it to heat energy without being degraded themselves by the ultraviolet light.

More efficient are synergistic combinations of these materials and non-ultraviolet light-absorbing light stabilizers such as sterically hindered amines. The amines take up the free radicals that are generated by the degradation process. These combinations are often used in clear coatings applied over light-sensitive substrates, such as wood and high chroma organically pigmented coating films. These substrates might otherwise degrade beneath ultraviolet light-transparent clears such as acrylics and aliphatic urethanes. □