Coating Deterioration

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PAINTS AND COATINGS of all types are widely used to provide color and pleasing aesthetics, and to prevent deterioration of the underlying substrate when exposed to various environments. Besides protection and beauty, however, coatings provide light reflectivity, camouflage surfaces, reflect and absorb heat, and provide a variety of other functions.

However, in order to provide these functions, the protective coating must remain intact and adherent on the surface to which it has been applied. The vast majority of all protective coatings perform admirably until an old age, at which time natural deterioration and degradation occur. However, a coating can fail prematurely, preventing its aforementioned functions from being realized.

The major reasons for the occurrence of corrosion usually are poor or deficient surface preparation, or insufficient coating thickness. There are, of course, many other reasons why coatings deteriorate and corrosion occurs:

- A paint or coating is incorrectly formulated or manufactured by the coating supplier.
- An unsuitable coating is specified for a given environment.
- Environmental conditions are different than that understood by the specifier.
- There is improper, or deficient, mixing of the coating at the time of application.
- There are adverse ambient conditions when the coating system is applied.
- The drying and/or curing of the coating after application is impaired.
- There is chemical, physical, and/or mechanical damage to the coating system during exposure.

These causes of failure are relevant only when a premature coating failure occurs. As mentioned, however, premature coating failure is extremely rare: of the hundreds of millions of gallons of paint manufactured and applied each year in the United States alone, it is estimated that only a small fraction—less than one one-hundredth of one percent—of these coatings ever fail prematurely. Instead, most protective coatings are successfully specified and applied to a properly prepared surface to the appropriate thickness. These coatings perform as intended, but over time deteriorate and lose their protective or aesthetic function as a result of old age, combined with exposure to aggressive environments.

In this article, coating failures due to specification errors, poor surface preparation or application, deficient film thickness, or another abnormality during application are not discussed, even though, to a greater or lesser extent, all of them affect deterioration and resulting substrate corrosion during the normal service life of any coating.

Rather, the deteriorating effects of exposure environments and their interaction with the paint or coating are discussed. This discussion provides an introduction to the mechanism of premature corrosion of a metallic substrate when that substrate has been properly coated with a suitably resistant coating system in a given environment.

This article discusses some of the environmental influences on a protective coating film that can result in deterioration:

- **Energy**: solar, heat
- **Permeation**: moisture, solvent, chemical, and gas
- **Stress**: drying and curing-internal stress; vibration-external stress; impact and abrasion
- **Biological influences**: microbiological, mildew, and marine fouling

These generalized categories of environmental influences unfortunately do not act singly, but in combination, sometimes with unpredictable catastrophic results.

**Variability within a Properly Applied Coating Layer**

Coating materials—even when thoroughly mixed, applied, dried, and cured properly—have, from a molecular point of view, great variability in their compositional makeup.

The articles “Elemental Chemistry Introduction” and “Composition of a Paint Coating” in this Volume describe coating resins, the way atoms form molecules, and how the molecules react with other molecules to form a coating. Various ingredients such as pigments, fillers, co-reactants, and surfactants are included in the formulation to enhance application and performance properties. These diverse ingredients, along with the ways molecules react with each other and with the substituent ingredients, provide the variability in the molecular structure of a coating.

When a molecule crosslinks with another molecule, the reactive sites of each of the reacting molecules must align and come within very close proximity to each other (generally within 3 to 5 angstroms (Å = 1 × 10⁻¹⁰ m) for the chemical crosslinking reaction to occur (Ref 1).

For example, in an epoxy resin that is cross-linked with a polyamide copolymer, the molecular sizes of each co-reactant material are relatively large, and the reactive functional groups are interspersed along the ends or mid-chain of the molecule. Stoichiometric (complete theoretical crosslinking) reactions are rare, and quite often the reacting groups do not come into sufficient proximity to react. This is because the coating resin is dispersed in a solvent that evaporates, reducing mobility of the molecules of the reactants. Additionally, low reactant temperatures reduce molecular mobility. The presence of pigments and other ingredients also separate the reacting molecular chains. Because there are billions of reactive sites, and because formulators add excesses of reactive moieties as appropriate to ensure suitable reactions do occur at room temperature (or whatever the design reactive temperature is), suitable crosslinking generally occurs. However, there can be tens of millions of unreacted moieties remaining in the crosslinked coating resin. Also, resin molecular reactivity often initiates at discrete localized areas and progresses from these areas in a manner similar to the formation of frost on a window. The intersection of one reaction area with another results in an interstitial boundary with different properties than that of the reacted area. Similarly, the resin reactions around pigment particles and other paint constituents also have a different crosslinking density than that of the pure resin reaction.

Solvents in solvent-borne coatings, and water in latex or waterborne coatings, evaporate after application, leaving micro pores, microcracks, or capillaries within the coating. If evaporation is impeded, due to low temperature or other reasons, the solvent or water can accumulate
Environmental Effects Resulting in Coating Deterioration

Characterizing an environment is a daunting, almost impossible task. The environment at one end of a bridge can be different than that at another end, and both may be different than that of a center span that is suspended over water or high in the air. Similarly, an exterior environment at the top of building can be different than that near the bottom of the building relative to sunlight, wind intensity and direction, and even temperature. Ships hauling cargos have different environments, not only within the cargo tanks, but above and below the waterline.

The International Standards Organization has attempted to define principle environments for coatings (Ref 3). The environmental categories and descriptions are presented in Table 1. In addition, the standard discusses metal loss/year for each category and time of wetness; special conditions such as corrosion inside buildings, corrosion in box girders, and various stresses such as chemical, mechanical, condensation, temperature, and stress combinations.

The Society for Protective Coatings (SSPC) has also defined environmental zones for coating systems (Ref 4):

- **OA:** Dry interiors where structural steel is embedded in concrete, encased in masonry, or protected by membrane or noncorrosive contact type of fireproofing.
- **OB:** Interiors, normally dry (or temporary protection). Very mild (oil-base paints do not last six years or more).
- **OC:** Exteriors, normally dry (includes most areas where oil-based paints last six years or more).
- **OD:** Frequently wet with freshwater. Involves condensation, splash, spray, or frequent immersion. (Oil-based paints now last five years or less.)
- **OE:** Frequently wet by saltwater. Involves condensation, spray, or frequent immersion. (Oil-based paints now last three years or less.)

Environmental categories and examples of typical environments:

<table>
<thead>
<tr>
<th>Corrosivity category</th>
<th>Exterior environment</th>
<th>Interior environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1 very low</td>
<td>Heated buildings with clean atmospheres, e.g., offices, shops, schools, hotels.</td>
<td>Unheated buildings where condensation may occur, e.g., depts, sports halls.</td>
</tr>
<tr>
<td>C2 low</td>
<td>Atmospheres with low levels of pollution. Mostly rural areas</td>
<td>Production rooms with high humidity and some air pollution, e.g., food processing plants, laundries, breweries, dairies.</td>
</tr>
<tr>
<td>C3 medium</td>
<td>Urban and industrial atmospheres, moderate sulfur dioxide pollution. Coastal areas with low salinity</td>
<td>Chemical plants, swimming pools, coastal ship- and boating areas.</td>
</tr>
<tr>
<td>C4 high</td>
<td>Industrial areas and coastal areas with moderate salinity</td>
<td>Buildings or areas with almost permanent condensation and with high pollution</td>
</tr>
<tr>
<td>C5- very high</td>
<td>Industrial areas with high humidity and aggressive high atmosphere</td>
<td></td>
</tr>
</tbody>
</table>

Categories for water and soil:

- Im 1: Fresh water
- Im 2: Sea or brackish water
- Im 3: Soil

For the most part, these environmental descriptions are somewhat similar to the extent that they progress from a relatively mild, noncorrosive environment to a relatively aggressive environment. The more benign mild environments are generally warmer, dryer, and less polluted. The more severe environments generally have more moisture, or are in immersion, and have salts or chemical constituents. Moisture, salts, and chemicals are primary influences in the corrosion process on steel and most metals and other materials. These influences, and the degrading influences of other environmental effects can loosely be categorized as energy related (solar, heat/cold, and nuclear radiation); permeation related (moisture, solvents, etc.).
chelicals, and gases); mechanically related (internal crosslinking and curing stresses, external vibration and flexibility stresses, and impact abrasion); and biological (microbiological and macrobiological—mildew and fungus).

Unfortunately, these categories are not all inclusive, and most importantly, are not mutually exclusive. In any environment, most if not all of the environmental influences are present to varying degrees, along with perhaps other influences not mentioned here. It is the synergistic effect of the combinations of these and other environmental influences that degrade the coating, or for that matter any material, resulting in loss of suitability for its intended purpose. Each of these environmental categories is discussed subsequently.

**Energy Related Degradation**

Energy acting on a coating (or material) can degrade a material by breaking or interfering with the chemical bonds holding the resin (or a molecule) together and to a substrate. The influence of energy in virtually every case makes an organic molecule more susceptible to degradation by other environmental influences (i.e., permeation, mechanical, and biological). The primary energy influences are solar radiation, heat (and cold), and to a much lesser extent, nuclear radiation.

**Solar Energy.** The sun was formed 4.5 billion years ago and is composed of 91.2% H and 7.8% He gas. The remaining 1% is comprised of oxygen, carbon, silicon, iron, magnesium, neon, sulfur, and calcium. Each element is important because its presence contributes to the solar spectrum as it is received on earth. The sun emits energy created by the thermonuclear fusion of hydrogen into helium. Four hydrogen nuclei have more mass than one helium nucleus and as each helium atom is formed, the excess mass is converted into energy that powers the sun. The core of the sun contains more helium (65%) than hydrogen. Hydrogen has been brought to this lower level because of its conversion in the thermonuclear reaction. It is estimated that the remaining hydrogen should last another 4 billion years at its rate of consumption. Variations in the activity of the sun affect the wavelength of emitted radiation. Changes in ultraviolet light (UV) radiation are more pronounced than those of other ranges of radiation. The distribution of emitted energy is such that 9% is in the UV region, 45% is in the visible range, and the remaining 46% is in the infrared range (Ref 5). However, the emitted energy by the sun is not necessarily of the same wavelength or intensity as that absorbed by the earth. The atmosphere of the earth and variability within that atmosphere and, in particular, ozone absorption and scattering of solar radiation by clouds, moisture, and other small molecules, all change the incidence of radiation on the surface of the earth. Figure 2 depicts the solar spectrum as emitted and as absorbed on the surface of the earth (Ref 5).

Electromagnetic radiation with the shortest wavelengths has the greatest energy. However, the shorter wavelengths are more readily absorbed and have less penetrating effects than longer wavelengths (Ref 6), as can be seen in Fig. 3. Radio waves can be transmitted over long distances compared with shorter wavelength television and radar, which allow transmission generally along a line of sight. Very short radiation types such as cosmic rays, and α and β nuclear radiation, although high energy, cannot penetrate even the thickness of a sheet of paper. X-ray and γ radiation are not found in solar radiation but are man-made by bombardment of certain elements with electrons, or concentration of certain naturally radioactive elements (such as uranium). These high-energy shortwave radiations are powerful enough to ionize gases, readily cleave chemical bonds, and induce potentially deadly chemical changes in human and animal tissues.

Ultraviolet light falls within the wavelength from 10 to 400 nm (1 nm is one-billionth of a meter). This naturally occurring energy from the sun has a shorter wavelength than visible light (400 to 780 nm) and accordingly is more energetic. Ultraviolet light has sufficient energy to disrupt and break covalent bonds of organic molecules. The UV light range is from approximately 10 to 400 nm and is divided into three subcategories: UV A, 320 to 400 nm; UV B, 280 to 320 nm; UV C, 10 to 280 nm. The detrimental effects of UV radiation to paints was believed, approximately ten years ago, to start at 295 nm and extend to approximately 400 nm. Recently, however, experience has shown that there is sufficient radiation and penetration of UV light as low as 280 nm to cause deterioration of paint. Ultraviolet radiations below this wavelength are not considered detrimental, because they are generally absorbed by moisture and other small molecules in the atmosphere and therefore are of little consequence. Moreover, they have little ability to penetrate into the surface of an organic material.

The frequencies of radiation that are most harmful to polymeric systems are those from the blue part of the visible light spectrum and the near-UV light spectrum. The longer wavelength lengths are not energetic enough to harm molecules, and most of the other potentially harmful high-frequency rays are screened out by the atmosphere of the earth.

The breaking of molecular bonds and the formation of free radicals by UV energy results in a shortening of the molecular chain group of an atom and, accordingly, a reduction in its molecular weight.

Glass allows visible light to pass through it without any absorption but is opaque to the shorter wavelengths of UV light and reduces the transmission of UV light of longer wavelengths. Accordingly, materials exposed behind glass retain their color and last longer than those exposed in an exterior solar environment. However, fading and embrittlement of plastics and other materials upon long-term interior exposure still occurs in indoor environments exposed to sunlight. Even though window glass filters out most UV light, the energy that transmits through the glass is still sufficient to degrade and fade most materials, including coatings over time. It is generally accepted that radiation in the visible

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Fig. 2 Solar spectrum as emitted and after absorption and scattering. 1. sun spectrum before entering stratosphere (extraterrestrial radiation), 2. spectrum modified by ozone absorption (stratosphere and troposphere), 3. spectrum after Rayleigh scattering (by small molecules), 4. spectrum modified by aerosol (clouds) scattering and absorption (excluding influence of water). 5. spectrum after moisture related scattering and absorption. a.u. = arbitrary units; a ratio of solar irradiation intensity to a reference measurement. Source: Ref 5

Fig. 3 Electromagnetic spectrum of radiation types. Source: Ref 6
range and higher is nontoxic to most paints, organic materials, and plant or animal tissues.

Radiant solar energy in the form of light photons excites certain electrons in the molecules of a resin. Depending on the wavelength and frequency of the radiation, only certain electrons are affected, while other electrons remain unaffected. Excess electron energy as a result of UV photon excitation is dissipated by fluorescence, phosphorescence, and most importantly, a cascading down of the electronic energy into vibrational and rotational energy of a molecular electrical bond. If sufficient energy is absorbed by the bond, it may break. Molecular groups with double bonds such as carbon to carbon (C=C), carbon to nitrogen (C–N), and carbon to oxygen (C=O) absorb UV energy, and their electrons are lifted into higher-energy levels. When these electrons decay to lower-energy states, energy is released in the form of vibrations that can cause a bond to break and create free radicals. Free radicals results when a chemical bond is broken. A covalent bond can break in either of two ways: the atoms previously joined by the bond share the electrons (homolytic dissociation), or the more electronegative of the atoms retains the electrons (heterolytic dissociation) (Ref 6). These two types of dissociations are:

Homolytic dissociation: \[ A + B \rightarrow A^+ + B^- \]

Heterolytic dissociation: \[ A + B \rightarrow A^- + B^+ \]

Heterolytic dissociation produces ions. An ion is an electrically charged atom or molecule. A negatively charged atom has more electrons than protons and a positively charged atom has more protons than electrons. Such electrically charged atoms or molecules are polar and can dissociate from one another when placed in water solution. The high dielectric constant or insulting property of pure water enables the polar molecules to separate and exist separately in solution. Water itself is very weakly dissociated and forms hydrogen and hydroxide ions.

\[ (H_2O) \rightarrow HO^- + H^+ \]

Homolytic dissociation likely occurs if the two fragments are equally electronegative. This produces neutral atoms or groups, each with an unsatisfied valency or unpaired valency electron. Such groups are known as free radicals. Most free radicals are highly reactive and recombine either with each other or other free radicals to form chemical bonds.

If the free radicals are so reactive, why don’t they recombine? If they are in a fairly rigid structure, it is likely that they will combine. If after separation the free radicals are held in a relatively confined area and maintain close proximity to each other, recombination is likely. If the molecular structure is crystalline and has relatively tight rigid chains in close proximity, or if it is in the cyclical aromatic ring or a very tightly and closely crosslinked molecular structure, it will be difficult for the

free radical ends of the molecule to separate sufficiently after the break in the bond occurs. Accordingly, the free radicals will remain in close proximity and will likely recombine. However, if the molecular chains are somewhat flexible, and the temperature is sufficiently high that there is vibrational and rotational movement of molecules of the polymer, the free radicals on opposite ends of the broken bond can become so separated that they will not recombine. A radical might pick up a hydrogen atom from an adjacent chain upon the breaking of that bond and therefore transfer the radical to another portion of the chain. If the free radicals are on a flexible molecule that is moving around quite rapidly, then there is a high probability that the radical will pick off a hydrogen atom of its own chain five or seven carbon atoms back along the chain. Then there will be a transfer of the radical to a position away from the chain and a termination of activity at the chain end. The newly formed free radical might pick up another hydrogen atom somewhere else, or react with a monomer, or react elsewhere to continue growth. Free radical reactions result in chain scission (breaking of the molecular chain); depolymerization (reducing a polymeric chain to its monomer units); branching (a short growth at a free radical site); self cyclization (forming a circular molecule by joining with another portion of a backbone of a molecule); and the formation of double bonds.

All of these free radical reactions, when they occur billions of times in a molecule exposed to ultraviolet light, shorten the molecular chains, reduce their flexibility, and increase permeability of the molecule and resin, thus degrading it. Certain resins, such as an epoxy, and particularly an amine crosslinked epoxy, are very susceptible to UV degradation. Exposure to even relatively low amounts of sunlight is sufficient, in many cases, to cause a chalking deterioration of the surface of the resin or paint. This chalking is composed of pigment particles and broken segments of the colorless molecular resin that refract light to give a white appearance. However, certain other resins, notably the acrylic and polyurethane, are mostly transparent to UV light and allow UV energy to pass through them with no molecular absorption. Accordingly, there is little deterioration to these resins when exposed to UV light.

Heat Energy. The addition of heat to a material increases the vibrations of atoms, and when uniformly applied, all atomic vibrations are uniform throughout the molecule. This is in contrast with radiation. For instance, both UV and nuclear radiation affect only certain electrons in the atoms of the molecule. Other electrons on other atoms remain unaffected.

If the heat applied is of sufficient intensity, the molecular vibrations increase to such a degree that a bond can break. When that happens, free radicals are formed and they react as previously described. Again, the end result is:

- A decrease of molecular weight of the chains comprising the resin of the coating
- A reduction of the tensile strength, modulus of elasticity, and toughness
- Potential introduction or formation of reactive polar groups that can cause changes in compatibility and electrical and optical behavior of the polymer
- Introduction of light absorbing groups that can cause discoloration and internal cyclization of the chains, resulting in hardening and a decrease in toughness

Free radical initiation can also include additional crosslinking between hitherto independent macromolecules, which, in excess, may reduce impact strength and create brittleness. Energy in the form of UV light can pass through some resins with little or no effect or be absorbed in other molecular combinations without breaking bonds. In the latter case, vibrational and rotational movement between atoms is increased and the energy is dissipated as heat, which is generally harmless to the molecular structure. However, where absorbed heat energy is high enough, bonds can break and free radicals can form. In a rigid, dense, closely packed, immovable, solid resin or structure, the free radicals may recombine with little effect on the molecule. However, in most cases, particularly in paints and most plastics, the structure is not rigid enough to allow immediate recombination of free radicals, and a variety of unanticipated secondary and tertiary reactions often occur, resulting in a shortening of the molecular weight of the resin molecule and other detrimental side effects, all resulting in deterioration and loss of properties.

Permeation Effects

Permeation of a coating by materials in a service environment is a major factor in the deterioration of the coating. Coatings are specifically formulated and tested to resist certain environments in immersion or in the atmosphere. Pigments and resins must be carefully chosen for their resistances to a given set of environmental conditions, and they must also be compatible. Even with utmost care, coating systems are still vulnerable to permeation and the ultimate destruction of protective capability. The following permeating species and mechanisms are discussed subsequently: moisture, solvents, chemicals, gases, and ions.

Moisture Permeation. The water molecule, \[ H_2O \], is a very small molecule consisting of one oxygen and two hydrogen atoms. Both the weight and size of this molecule is small relative to virtually all other molecules commonly encountered in an environment. Water in liquid form comprises oceans, lakes, and rivers, condensed from the atmosphere as dew, and falls as precipitation in the form of rain or snow. Water in vapor form is always in the air to some degree, as humidity. Any material used in exterior environments, including coatings, must be resistant to the effects of water.

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Water, in addition to being small in molecular size, also is polar, because oxygen has a high electronegative attraction to other polar molecules, including itself. Accordingly, water can readily penetrate into microscopic pores, holidays, cracks, and defects inherent in almost any coating system. Water vapor, carried by air, can move in and out of porous materials with ease, as long as there is a driving force causing its movement.

What are driving forces causing water movement? Simply placing the material in water immersion provides sufficient pressure from the pressure head (depth) of the water, even though the immersion is relatively shallow to provide a driving force for water movement into a material. Water molecules, because of their relatively small size, can pack quite tightly, and accordingly, a mass of water (measured as specific gravity, pound per gallon, or unit mass) is quite dense compared to many liquids and all gases. In immersion, there is sufficient water head pressure to cause water molecules to migrate into cracks, crevices, pinholes, and microscopic fissures inherent in any coating system. Water, in permeating a coating, fills any “free” space left by solvents and other materials that have migrated from the coating during application and curing. Additionally, due to slight polarity of the water molecule, water can be drawn into the coating if there are any polar solvents, polar groups, or polar materials retained or comprising the dry film. Thus, the presence of ester groups, ether linkages, carboxyl groups, and other polar groups within a coating resin can draw water into the paint. An electric charge applied across the coating film, such as with cathodic protection or resulting from a corrosion cell, can induce or accelerate the permeation of water into a coating. This phenomenon is called electroosmosis. Additionally, corrosion inhibiting pigments (chromates, borates, molybdates), due to their water solubility, may draw water through the coating film in an osmotic process. These pigments require water to partially dissolve the oxygenated metal inhibitor that then can wet and passivate the underlying steel or aluminum metal substrate.

Finally, rust deposits, dirt, salts, and other contaminants remaining on a surface can both prevent bonding of the paint and establish osmotic driving forces further promoting water permeation. At areas where paint adhesion is relatively poor, crosslinking is less dense, or there are agglomerations of pigments not completely wet out by the organic binder, water can collect and “pool,” causing a swelling of the film and additional water penetration. Water-soluble salts, including sodium chloride, calcium chloride, and other chlorides (found in marine environments and in deicing salts), and sulfates (from acid rains) are notorious for causing osmotic blistering of coatings in immersion service and/or accelerated rates of corrosion in atmospheric service if they are allowed to remain on a substrate before painting or between coats of paint.

Once water enters the paint film, the small water molecules have the ability to penetrate between and within molecular chains comprising the organic resin, and the interstices between the resin and pigment, if the pigment is not completely wetted by the resin. As the water molecule penetrates, it separates loose bonds holding the resin particles together, such as polar bonds, and becomes attracted to and swells the molecule at sites of covalent bonds that are polar. This swelling forces the bonds even further apart, diminishing their tightness and close packing. The volume of the coating expands due to the increased presence of the water intrusion. Some films increase 20 to 50% or more in volume when in contact with water (Ref 8). The swelling caused by the coating film can separate polar bonds and other weak forces holding the molecule together and to the substrate such that polar attractions, so necessary to coating film adhesion/cohesion, no longer occur. Additionally, the oxygen of the water molecule can be attracted to and replace what otherwise would have been a polar attraction between two long-chain resin molecules. When this happens, the charge between the resin molecules is terminated, and attraction to water molecules by each chain end occurs instead. The dried coating film, when wetted and saturated with water, becomes plasticized and swollen. Wet adhesion of most coatings is considerably less than dry adhesion. When the film dries out, often dry adhesion reestablishes, but usually not to the same extent as was before moisture saturation.

This phenomena of swelling by moisture penetration into a coating film occurs with virtually all coating materials except those that are extremely tightly crosslinked with a high crosslink density (such as some phenolic epoxies or phenolic coatings formulated for water resistance) or some highly crystalline coating materials (such as the fluoropolymers). These materials are relatively impervious to water permeation, penetration, and swelling due to their dense molecular crosslinking or the tight polar bonding between molecular chains.

The effect of heating (either using hot water or a hot or warm environment) increases molecular movement, enabling more rapid water penetration. Conversely, cooling, particularly below the glass transition temperature (T_g), reduces molecular movement and retards water permeation.

Solvent Permeation. Solvents are not usually found in most environments, and the presence of a solvent in a paint film occurs primarily as a result of solvent addition to the resin when manufacturing the paint. Solvents are added in order to reduce the viscosity of a resin, thinning it for application purposes. Upon drying and curing, the solvent must volatilize from the coating into the atmosphere in a timely manner. If sufficient solvent volatilization does not occur, and solvent is retained in the film, the coating can remain soft and plasticized, because the relatively large solvent molecules separate resin molecules from adjacent resin molecules. Bonding that could otherwise occur cannot be done because the bonding moieties are not close enough for attraction to occur. Moreover, many solvents are somewhat polar, particularly the oxygenated solvents (including the ketones, esters, and alcohols). These solvents are generally used to dissolve polar or somewhat polar resins and to provide hydrogen bonding to other polar groups of the resin, or to keep or slow the solvents from completely evaporating from the resin. Hydrogen bonding is the attraction of the oxygen atom in a molecule to nearby hydrogen atoms in other molecules. Retained polar solvents may draw water into the resin. This is a particular problem with slowly evaporating alcoholic solvents such as the glycol ethers. Coatings used in immersion service, particularly for the interior of deionized water or freshwater storage tanks, often blister due to retained solvents. This is a problem on the tank bottoms because the tank bottom is cooled by the earth (acting as a heat sink), while the tank sidewalls are warmed by the sun and air convection. The warmer temperatures assist in volatilization of solvents, while the cooler temperatures of the tank bottom result in a slower evaporation of retained solvents in the paint film. The entrapped solvents can draw water into the coating at the bottom of the tank, causing osmotic blistering. This can be a problem not only on tank bottoms, but anywhere a heat sink might occur, such as exterior steel supports, cradles, or bracing. Baking, or heating of tank interior coatings, is often done both to ensure solvent evaporation from the paint film and to elevate the temperature above the T_g to attain a higher crosslinking density of the chemically reacted coating resin.

Chemical Permeation. Coatings are widely used to protect against chemical attack on a variety of different substrates and in a variety of different chemical environments. The widespread use of coatings for such protection attests not only to the diversity of coating formulations, but also to the inherent capability of resin and pigment technologies.

In the simplest sense, chemical attack can be categorized as that by acids and bases. Chemical attack does not occur at neutrality (pH of 7). However, water, salts, and solvents, all of neutral pH, can dramatically affect and degrade a coating. This type of “neutral” degradation is described elsewhere in this article.

Acids and bases, and the strength of the acid or base, are a simple function of the degree of dissociation of the chemical into hydrogen ions, H⁺ (acids), or hydroxyl ions, OH⁻ (alkalis or bases). Acidic or alkaline strength is measured on the logarithmic pH scale, a scale with each number being ten times greater than the preceding number. A pH of 3 is ten times more acidic than a pH of 4, for example. A pH of 7 is exactly neutral, while 1 is strongly acidic and 13 is strongly basic or alkaline.

For all practical purposes, the medium in which the acid or alkaline dissociation occurs is water. Even very small amounts of water are
sufficient to dissolve and disassociate most chemical compounds into their acidic or basic constituents. At the molecular level, where such disassociation occurs and the acid or base comes in contact with a coating material, chemical attack can take place.

However, many chemicals are hydroscopic: they attract and react with water. Examples are most sulfur chemicals, including sulfuric acid, sulfamic acid, and sodium sulfide; sodium and potassium hydroxides; sodium carbonate; zinc chloride; most salts, such as sodium, potassium, and zinc chlorides; and many solvents, in particular the alcohols and glycols.

**Acid Attack.** Acids consist of inorganic mineral acids such as hydrochloric, sulfuric, and nitric acids, which disassociate completely in water. Organic acids such as carboxylic acids, including formic acid and butyric acid, do not completely disassociate and as a consequence are considered weaker acids. However, even these acids can aggressively attack most coating systems.

Acid gases such as sulfur dioxide (SO₂), sulfur trioxide (SO₃), hydrogen sulfide (H₂S), and nitrogen oxide (NOₓ) react with moisture in the air in the form of precipitation or condensation to form sulfuric and nitric acids. Even carbon dioxide (CO₂) as a normal constituent of the atmosphere reacts with moisture to form a weak carbonic acid (H₂CO₃).

Chemical attack by condensation on a coating is more aggressive than that deposited by precipitation such as acid rain, because moisture condensing on a surface containing acidic constituents usually evaporates as the substrate warms during the day. As the moisture evaporates, the acids within the condensation droplet concentrate and more aggressively attack the substrate on which the condensation resides. Acid rain, on the other hand, is diluted by successive rainfall, and the chemical contaminant can be diluted or even washed from the surface.

The chemicals thus deposited, however, attack and cleave chemical bonds that are susceptible to deterioration. Chemical groups specifically vulnerable to acidic attack and cleavage are ether, urea, and urethane linkages, where cleavage occurs by a reaction of the hydrogen ion (the susceptible portion of the linkage).

**Alkaline Attack.** Similarly, strong alkalies such as sodium, potassium, and calcium hydroxides attack susceptible chemical groups in coatings. Perhaps the most widespread type of alkaline attack is saponification, the alkaline attack of the ester linkage of drying oils used in most oil-base coatings and alkyds. The attack can occur when oil-containing coatings or alkyls are applied over concrete, which contains alkali salts, which, when combined with water, form caustic alkalis. In a similar fashion, application of oil-based alkyls over zinc-rich coatings can also result in saponification because zinc reacts with moisture to form alkaline zinc hydroxides. The hydroxyls (OH⁻) cleave (break) the ester linkage in the drying oil to form an organic acid and alcohol. The bond breaking reduces molecular flexibility and embrittles the film; this ultimately leads to resin deterioration and the formation of a sticky soft coating under damp conditions, or a brittle powdery coating when dried. All coating resins containing ester groups are susceptible to such attack. However, some of those resins, such as the polyesters and vinyl esters, are much more highly crosslinked and formulated with epoxy resins and other materials to sterically hinder the ester group, protecting it from alkali attack. Saponification (reaction with an alkali) and hydrolysis (reaction with water) are similar, but the saponification reaction is much faster and more debilitating. An illustration of alkaline and hydrolytic (water) saponification is shown in Fig. 4.

Figure 5 illustrates the vulnerability of various organic linkages to hydrolysis (reaction with water) and saponification (reaction with alkali) (Ref 9).

Acids and alkalies not only cleave covalent bonds of organic resins but can also attack acid or alkaline susceptible pigments in the paint. Where there are pinholes and permeability through the coating, chemical species can penetrate, concentrate, and aggressively attack both the pigment and binder. Pigment agglomerations not completely wetted out by the resin of the coating are susceptible to this, particularly if there are pinholes and voids in the coating. However, ionic permeation is much slower than moisture permeation, and unless the pigment is exposed on the surface (by chalking or surface resin deterioration) or the chemical environment has access through pinholes, voids, or other discontinuities in the paint film, chemical attack to pigments is not usually a major problem.

Table 2 shows sensitivity of some of the more common pigment types to chemical attack (Ref 9).

**Oxygen and Other Gas Permeation.** Oxygen permeation at the cathode in a metallic corrosion cell is usually the rate determining factor in the corrosion reaction. The common anodic and cathodic reactions of metallic corrosion are:

Anodic reaction: \[ M \rightarrow M^{n+} + ne^- \]

where \( M \) = metal, \( n \) = number (of valency electrons), and \( e^- \) = electrons.

Cathodic reactions:

- In near-neutral and alkaline environments
  \[ \frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \]
- In acidic environments
  \[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \] (in the presence of oxygen)
  \[ 2H^+ + 2e^- \rightarrow H_2(gas) \] (in highly acidic solution and/or absence of oxygen)

Thus, permeation of molecular oxygen is necessary for metallic corrosion in near-neutral, alkaline, and mildly acidic environments, and in many instances it determines the rate of corrosion. Corrosion is an expansive process, and undercutting corrosion beneath a well applied coating produces undermining and undercutting.
Table 2 Chemical sensitivity of selected organic and inorganic pigment families

<table>
<thead>
<tr>
<th>Pigment type</th>
<th>Examples</th>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Titanium dioxide | ...    | Excellent    
| Zinc oxide    | ...    | Moderate to good |
| Antimony oxide | ...    | Poor        
| Red iron oxide | Syn. red ox., Spanish, Indian, or Persian Gulf red | Excellent |
| Cadmium red   | ...    | Excellent    
| Molybdate orange | ...  | Poor to fair  
| Lead          | Minium, mineral orange | Poor |
| Yellow iron oxide | Ferrite yellow, sienna, ochre,umber | Poor to fair |
| Chrome yellow | ...    | Poor        
| Zinc yellow   | Zinc potassium chromate | Fair |
| Cadmium yellow | ...    | Excellent    
| Nickel titanate yellow | ...  | Excellent    
| Bismuth vanadate yellow | ... | Excellent |
| Zinc ferrite  | ...    | Excellent    
| Chrome green  | Brunswick green | Excellent |
| Chromium green oxide | ...  | Poor        
| Iron blue     | Prussian blue, Midori blue, Chinese blue, mineral blue | Excellent |
| Ultramarine blue | ...    | Very good    
| Carbon black  | ...    | Excellent    
| Black iron oxide | ...  | Excellent    
| Micaceous iron oxide | ...  | Excellent    
| Zinc dust     | ...    | Poor        
| Aluminum oxide | ...    | Poor        
| Stainless steel flake | ...  | Very good to Excellent |

<table>
<thead>
<tr>
<th>Organic</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Metalized azo reds</td>
<td>Lithols, permanents, rubines</td>
<td>Poor</td>
</tr>
<tr>
<td>Nonmetalized azo reds</td>
<td>Toluidines, paras, naphthols</td>
<td>Poor</td>
</tr>
<tr>
<td>Azo-based benzimidazolone reds</td>
<td>...</td>
<td>Poor</td>
</tr>
<tr>
<td>Quinacridones</td>
<td>...</td>
<td>Excellent</td>
</tr>
<tr>
<td>Vat reds</td>
<td>Dibromanthrone, anthraquinone, brominated pyranthrene, perylenes</td>
<td>Excellent</td>
</tr>
<tr>
<td>Azo-based orange</td>
<td>Dinitroaniline, pyrazolone, tolyl</td>
<td>Good</td>
</tr>
<tr>
<td>Azo-based benzimidazolone oranges</td>
<td>...</td>
<td>Good</td>
</tr>
<tr>
<td>Metalized azo orange</td>
<td>Clarion red</td>
<td>Poor</td>
</tr>
<tr>
<td>Munsyrykide yellows</td>
<td>Hansa yellows</td>
<td>Moderate</td>
</tr>
<tr>
<td>Diarylyle yellows</td>
<td>Benzidine yellows</td>
<td>Excellent</td>
</tr>
<tr>
<td>Azo-based benzimidazolone yelows</td>
<td>...</td>
<td>Excellent</td>
</tr>
<tr>
<td>Heterocyclic yellows</td>
<td>Isoindoline, quinophthalone, azomethine, tetrachloroisodolone, triazinyl</td>
<td>Excellent</td>
</tr>
<tr>
<td>Phthalocyanine greens</td>
<td>...</td>
<td>Excellent</td>
</tr>
<tr>
<td>Phthalocyanine blues</td>
<td>...</td>
<td>Excellent</td>
</tr>
<tr>
<td>Carbazole violets</td>
<td>...</td>
<td>Very good</td>
</tr>
</tbody>
</table>

Source: Ref 9

In most cases, heat or radiation deterioration does not act alone but acts in conjunction with oxygen. Oxygen is a very reactive molecule, and if a free radical forms in its presence, then the oxygen can combine immediately with it to form a different radical. This radical can then abstract a hydrogen atom and form a hydroperoxide. A hydroperoxide is unstable and decomposes into two radicals. From the initial two radicals, a total of six possible radicals can form. This explains the danger in chain scission in the presence of oxygen leading to a chain reaction (Ref 10).

The oxygen free radicals thus formed can further react with molecules in a coating or organic material in the same manner as described previously, causing chain scission, depolymerization, and fragmentation of the molecule, reducing its flexibility and resistance to permeation.

Permeation of Water, Oxygen, and Ions through Weak Areas of Crosslink Density in the Coating. Water is in virtually every environment around the world to some degree. Water in freshwater lakes, saltwater oceans, and in ponding rainwater results in a water immersion environment for materials exposed to these environments, and in relatively rapid water permeation through a coating.

In non-immersion atmospheric environments, water is present as humidity, condensation, and precipitation. In these environments, moisture permeation into a coating is much slower, dependent principally on the duration of time the coating is wet. There is little penetration driving force if water is present only as a gas, such as humidity, but if it is present as condensation or precipitation (rain, dew, fog droplets, and melted sleet or snow), the water can penetrate the coating system. Furthermore, in atmospheric environments, oxygen is present, and the water has absorbed or entrained oxygen. Oxygen, as a gas in the atmosphere, has little or no driving force to penetrate a coating film, but it is almost omnipresent, at least at the initiation of corrosion. Accordingly, the penetration by water of a coating in an immersion or semi-immersion environment is the principle cause of corrosion of the underlying substrate.

Virtually all organic coating materials are permeable to water to some degree. Thick, highly crosslinked coatings are much more impermeable to water penetration than coatings with a lesser crosslinked density. However, even with relatively thick, highly crosslinked coatings, as described previously, there are areas of variability resulting in lesser crosslink density. It is coatings in these areas that water penetrates.

Numerous studies conclude that coating films contain microscopic regions that absorb large amounts of water and have low ion resistivity. That water does not disperse into the film uniformly, but in a dense layer along boundaries in the polymer structure, followed by penetration of the structure itself. Further, corrosion spots on the substrate have been found to be directly related to these regions (Ref 11, 12).
Initially, the water can penetrate the coating only partially to random depths at numerous sites. In atmospheric environments where there is no drying by the sun, or increasing daily temperatures, the penetrating water may diffuse out and evaporate. However, the water penetration even in these areas can swell the coating and dissolve any water-soluble constituents. Thus, subsequent water penetration may be even easier at these same sites and penetrate further, and penetration can potentially initiate at other new adjacent sites. One study estimated the apparent area of the pores increased from an initial 0.6 to 6700 μm² per cm² of coatings after 100 days of exposure to 0.6 mol/L sodium chloride solution (Ref 13).

With sufficient time, and duration of wetness, water permeation through the coating cross-section down to the underlying substrate ultimately occurs.

**Oxygen and Ionic Permeation along with Water into the Coating.** Water precipitation (most often as rain or melted snow and ice) is not a pure liquid. Even pure distilled water reacts with carbon dioxide in the air to form a weak carbonic acid (H₂CO₃), giving it a pH of approximately 5.6. Air pollutants can contribute further to ionic contaminants in rainwater. Acid rain consists of sulfur and nitrogen compounds—principally in the form of sulfur dioxide and nitrogen dioxide—that hydrolyze with water to form sulfuric acid (H₂SO₄) and nitric acid (HNO₃). These rainfall pollutants principally result from electrical power generation and the burning of fossil fuels, gasoline combustion in motor vehicles, and industrial smokestack output. Natural sources consist of volcanic emissions contributing sulfur dioxide, biological decay contributing dimethyl sulfide, and lightning contributing nitric oxide.

Rainwater dissolves particulate materials in the atmosphere when droplets of water form on atmospheric particles. Additionally, rainwater dissolves atmospheric gases including pollutants and oxygen. Oxygen is ubiquitous, is dissolved in water, and permeates with water into a coating.

In coastal areas rainwater has a salt content essentially like that of seawater, but much more dilute. Generally within a mile or so of the seashore, and often much further depending on wind velocity and direction, wind-borne salt spray deposits upon and contaminates most surfaces and structures, and concentrates due to the evaporation of water.

Predictably, the composition of rainwater varies geographically because atmospheric contaminants also vary from place to place. Besides the previously mentioned inorganic contaminants, organic contaminants also have been found in rainwater (Ref 14).

The outcome of all of this is that water precipitation is not pure H₂O, because there are many other materials dissolved in or combined with the water droplet, including oxygen. Water, as precipitation, when in contact with a coating for any considerable amount of time, permeates the coating through weak areas of crosslink density, micropores and cracks, voids, and pathways, ultimately to the underlying substrate. That permeating water carries with it oxygen and other materials, depending on the atmospheric environment.

Of particular interest for corrosion purposes is the prevalence of ionic contaminants—acids and salts, notably anions, chlorides, sulfates, and nitrates, and their cations—that dissociate in the permeating water, which increases its conductivity, and the rapidity of corrosion when these ions access a metallic substrate through the coating. However, ionic permeation through a coating film is so extremely low that under-film corrosion may not be caused by ionic permeation, but by surface contamination prior to coating. Also, the observation that cathodic blisters are highly alkaline provides strong evidence that paint films also are impermeable to hydroxyl ions (Ref 15).

Under the influence of electric fields (such as cathodic protection), functional groups associated with pores can become ionized and exchange ions with an exterior electrolyte solution. This, combined with the plasticizing effect of water on some polymers, can, in certain coatings, result in infiltrated pores, which may increase ionic penetration to the substrate. Increasing temperature also has a profound effect by increasing the rates of moisture permeation and ionic exchange through a coating film (Ref 16).

However, it is the general consensus of virtually every research document on the subject that ionic permeation through a paint film is far slower, if it occurs at all, than permeation by moisture and oxygen. Moreover, moisture (H₂O), as a result of a smaller molecular size, permeates much more rapidly than oxygen (O₂).

**Steel Substrate Reactions Due to Permeating Water.** After water permeates through a coating, it ultimately comes into contact with the underlying substrate and can react with that substrate. The substrate reaction, if any, with the permeating water depends on the nature of the substrate (wood, concrete, masonry, galvanized metal, plastic, aluminum, titanium, stainless steel, or other metal, etc.). Furthermore, the constituents within the permeating water strongly influence any reactions that might occur with the underlying substrate. Accordingly, the discussion of such substrate reactions with permeating water is beyond the scope of this article. However, because coatings are widely applied to structural steel for corrosion protection, the reactions of permeating water with a steel substrate are discussed.

The reactions that occur on a steel substrate (or, for that matter, on any other substrate) essentially are similar to those that occur at a scratch, mechanical damage, or other large-scale visible defect in a coating layer. The major difference is that the corrosion reactions that occur with these large-scale defects occur much more rapidly due to the ready access to moisture, oxygen, and conductive ion contamination to the substrate. At these large-scale defects, permeation through a coating film is not necessary, because the coating film has been damaged and the metal substrate is exposed. Corrosion is defined as the deterioration of a material due to exposure to an environment. In every case with a metallic substrate, when corrosion occurs, it is an electrochemical reaction with the formation of an anode and a cathode. The anode forms at areas where there is more energy in the steel, for example at scratches, impacts, and damaged areas; at areas of higher temperature; at grain boundaries within the steel alloy; and for many other reasons. The cathodic areas form adjacent to the anodic areas.

For steel, those reactions are detailed previously and summarized herein:

\[
\text{Fe(iron/steel)} \rightarrow \text{Fe}^{++} + 2e^{-} \\
(\text{The iron in the steel dissolves in the moisture solution into positively charged ferrous ions, liberating two negatively charged electrons.})
\]

The corrosion continues as a depolarizer removes (reduces) the electrons from the solution at the cathode. Accordingly, in a neutral or near-neutral pH environment, the cathodic reaction with the most common reduction depolarizer, oxygen, is:

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^{-} \rightarrow 4\text{OH}^{-} \\
(\text{Oxygen in the water/air and the water itself reacts with the liberated electrons from the iron to form hydroxyl ions.})
\]

The hydroxyl ions formed at the cathode react with sodium, potassium, and other positively charged cations to form an alkaline solution, commonly NaOH, a strong alkali. This alkali has a very high pH (often around 11 to 13), and the alkalinity disbands the coating at the cathodic metal interface. Three possible mechanisms have advocated for the cathodic delamination of a coating: dissolution of an oxide layer on the substrate surface, alkaline hydrolysis of the coating polymer, and interfacial failure due to the high alkalinity at the cathode. It is likely that some or all of these occur in combination, simultaneously or in stages. However, irrespective of mechanism, high alkalinity at the cathode is responsible for cathodic disbonding. Additionally, the accumulation of hydroxyl groups (OH⁻) attracts more water due to hydrogen bonding, resulting in cathodic blistering at corrosion sites in immersion or even in severe atmospheric exposures. If cathodic protection is used, either in the form of an impressed current or sacrificial anodes, disbondment and blistering at the cathode may be substantially increased. Figure 6 depicts cathodic blistering around a scribe on a test panel.

The positively charged ferrous ions migrate to the cathode, attracted by the negative hydroxide ions, and react with them, forming
an oxidized ferrous hydroxide brown colored rust product. These ferrous ions going into solution at the anode result in a metal loss that forms pits in the steel substrate. This is depicted in Fig. 7.

Subsequent oxidation and hydrolysis result in a decrease of the pH and the formation of a complex mixture of hydrated iron oxides (rust):

\[ xFe^{++} + yO_2 + zH_2O \rightarrow Fe_3O_4 \cdot xH_2O \]

Initially, a lesser oxidized rust product is formed: Fe_2O_3. With further oxidation, a fully oxidized rust product results: Fe_3O_4. These rust products are almost always formed with hydrated water (H_2O) attached.

In coastal and chemical areas where chloride ions are present, those negatively charged ions can enter into the corrosion reaction to help present charge neutrality. They react with excess ferrous ions to form hydrated ferrous chloride in a reversible reaction that can move in both directions, because ferrous chloride is water soluble:

\[ Fe^{++} + 2Cl^- + H_2O \rightarrow FeCl_2 \cdot H_2O \]

Thus, the products in the corrosion solution at the anodes beneath the rust layers at the bottom of a large-scale mechanically damaged area of a coating, and also at a corroded area where moisture has permeated through an otherwise intact coating, most likely are hydrated Fe_2O_3 and FeCl_2. Oxidized corrosion products are anion-selective (Ref 18), allowing the chloride ions to continuously permeate through the rust layers and reach the steel surface. A model for the degradation of steel in a neutral NaCl solution environment is presented in Fig. 8.

In summary, variability within a properly dried and cured coating film in the form of microscopic cracks, porosities, capillaries, pigment agglomerations, and areas of low cross-linking will, in time, enable penetrating moisture access to an underlying substrate. Virtually all organic coating materials are water permeable to some degree. On a metallic substrate this permeating moisture, along with dissolved oxygen, enables the formation of anodic and cathodic areas, resulting in corrosion of the substrate. The corrosion mechanism beneath a coating is essentially similar to that occurring at a scratch, mechanical damage, or any large-scale coating defect. The corrosion reactions differ depending on the metal substrate; those for steel are illustrated previously.

Soluble salts—such as those found in coastal environments (notably NaCl) or where deicing salts are used, in chemical environments, or where acid rain might deposit, carrying nitrogen and sulfur oxides (NO_x and SO_x)—can be present in pits or on a substrate prior to painting and can also permeate with water, increasing the water conductivity and thus the rate and severity of corrosion (Ref 20). In the prior examples, the chloride ion (Cl^-) has been used as the anionic species salt example, but the effect of nitrates, sulfates, and other anions is similar.

**Stress Influences**

Internal coating stresses build up during drying and curing and on aging. These internal stresses are considered by some to be a primary cause of premature coating failure. Additionally, external stresses to a coating system are applied by movement of the substrate and by
mechanical damage. The role of stresses in the deterioration of a coating system are the subject of this section.

Coating, Curing, and Drying Internal Stresses. When one chooses to protect an object from corrosion, to “spruce it up,” change its color, provide an antigraffiti or sanitary surface, or to provide for a myriad of other functions, that individual usually turns to paints or coatings. Why? Because paints and coatings can be formulated to provide all of these attributes and are applied in liquid form, allowing them to cover and coat all surfaces of the object in a relatively fast, convenient, and inexpensive means of application. The reason this can be done is that the coatings are spray applied in liquid form and convert by drying and/or curing to a solid coating. The fact that a paint can be applied in liquid form gives it the ability to wet, penetrate, seal, cover, and adhere to most substrates, even those with complex shapes. Moreover, application of the liquid by brush, roller, or spray is fast and inexpensive and relatively convenient. However, the conversion of a paint from liquid to solid provides some inherent stress to the coating and, in extreme conditions or if adhesion is not adequate, can cause failure of the coating.

If a coating is not 100% solids and contains a volatile material such as water or solvents, drying of the coating and its conversion from a liquid to a solid result in a volume decrease as the water or solvent evaporates into the atmosphere. Most coating materials initially gel within seconds to hours after application as most of the volatiles leave and the paint dries on the surface. The shrinkage that occurs with the loss of volatile materials provides some initial stress to the coating and to the adhesion of the coating. However, this stress is minimal, because the paint has not sufficiently solidified, is still deformable, and can internally dissipate these initial stresses. However, as the paint dries further, and particularly if chemical crosslinking occurs, further stresses are applied to the now dry coating. Sometimes low-molecular-weight plasticizers such as phthalates, phosphates, adipates, and chlorinated biphenyls can migrate to the surface of the paint and volatilize, or at least collect onto the surface. When this happens, the molecular volume of the resin decreases. This diminishment in volume applies a tensile stress to the cross section of the paint film, and in extreme cases can result in cracking, peeling, or loss of adhesion. In a similar fashion, progressive crosslinking—either by reaction with oxygen from the air (auto oxidation) or covalent bonding between reactive moieties of part A and part B components of a coating—provides a further hardening, increasing brittleness, and a tensile stress to the coating. In many coatings these latent crosslinking reactions occur slowly over time, often years, such that the coating slowly hardens and embritles with age. Where coating has been applied thickly, stresses are greater than areas where coating is applied thinly. Variation in thickness causes an uneven distribution of stress on the coating, further aggravating the potential for cracking or failures that have been applied to excessive thicknesses.

Highly crosslinked coatings, particularly 100% solid materials formulated with low-viscosity co-reactants, are particularly susceptible to internal crosslinking stresses. Polyessters, vinyl esters, and other thick-film highly crosslinked coatings must be properly formulated and pigmented to satisfactorily reduce these internal stresses. The low-molecular-weight epoxies, including bisphenol F and novolac epoxies, must also be properly plasticized and pigmented to dissipate internal curing stresses.

How does one measure the extent of internal stress/curing stress on a coating? Until recently, the best means of assessing such stresses was to apply the coating system to a test panel or a test patch in the area of intended service, wait for curing and drying to occur, and then evaluate the coating over time to see if stress cracking, peeling, disbonding, or other evidence of distress occurred. Recently, however, there have been some tests developed (but not yet standardized) whereby a coating material is applied to one side of a thin foil strip that is held in position at one end and allowed to deflect at the other. The amount of deflection at the free end is indicative of the internal shrinkage stress as the coating dries and cures.

External Stress—Vibration, Flexibility, Stress-Strain. External stresses on a coating are many and varied and usually affect an applied coating to a greater extent than internal stresses. When a person walks across a bridge while either a heavy truck or train is also crossing the bridge, the movement, flexing, and vibration of that bridge is readily evident. In a similar fashion, any time a municipality fills or empties a water storage tank, flexing and bowing of the sidewalks and tank bottom occur. Wind, snow loads, ponding water, and other forces can deflect a metal surface, stressing the coating applied to it. Cyclical stresses resulting from a vibration and flexing are most detrimental and can readily degrade both the metal substrate and any coating applied to that substrate.

Solar heating by day and cooling by night cause expansion and contraction of all materials. Stress resulting from such thermal expansions and contractions can be aggravated under winter conditions in cold weather climates where a coating becomes somewhat embrittled due to cold temperatures. Relatively rapid heating and cooling during daily temperature fluctuations is often more of a problem in the winter than in the summer. Some accelerated tests performed by laboratories have used a freeze-thaw cycle to provide additional stress on a coating to assess its potential for a service environment, even in a warm climate where no freezing is expected. This is because if the coating can survive the freeze-thaw cycling, it is quite likely that it will be able to resist any thermal cycling encountered in actual service. The external stresses resulting from vibration, flexibility, and cyclical stress-strain from thermal expansion and contraction are major deterrents to coating systems, particularly those that have high internal stresses or have been applied to excessive thicknesses.

Impact and Abrasion. While coating, curing, and drying stresses, as well as vibration flexing and stress-strain (as discussed previously) are relatively slow transient influences, impact and abrasion to a coating, in contrast, is usually sudden, localized, and abrupt. Mechanical damage from dropped tools or stones, or other types of mechanical damage where the coating surface is impacted either directly or reversely (from the side the coating is on or from the opposite side), can cause the coating to crack and/or spall. Impact damage is greatest when a coating has high internal stress and is very brittle, or is at or below its glass transition temperature ($T_g$).

Abrasion occurs as a result of scraping, scuffing, or erosion due to contact with small moving particulate matter such as sand or slurry. As a general rule, harder more brittle coats are more susceptible to abrasion damage than rubbery softer coatings. However, specific resistances are dependent on the formulation of the coating, because many hard coatings have abrasion-resistant pigments—such as aluminum oxide, quartz, silica (sand), garnet, and other hard materials—embedded in them to resist abrasion and erosion wear. Rubbery elastomeric coatings have the ability to deform under abrasion, up to a critical point, after which they recover their original form. Energy absorbed during the abrasion and/or impact is absorbed by the elastomeric resin and dissipated as heat within the flexible molecular structure.

However, hard brittle coatings and coatings in cold temperatures, or below or close to their $T_g$, may not have the flexibility to resist abrasion or erosion wear. In these instances, the coating may tear on the surface or be scraped or ablated away, resulting in a thinning of the coating at the areas of abrasion/erosion.

At areas where abrasion erosion are expected, natural or synthetic rubbers should be used. Anti-abrasion paints should be added to the resin or it can be embedded into the top surface of the coating to make it more abrasion resistant. In some cases a softer more elastic thick film coating can also be used to resist scuffing and abrasion.

Biological Influences

Microorganisms (nonvisible to the unaided eye) are the earliest and most numerous life forms on earth. They are ubiquitous, occurring in virtually all natural environments, including those considered until recently to be inhospitable to life: undersea volcanic vents with high concentrations of sulfur, hot springs, extremely acidic and alkaline chemical environments, anaerobic (no oxygen) environments, and in locations devoid of sunlight. Degradation of coatings and other materials results from
Electrochemical and biological processes resulting from the presence of microbes.

Similarly, microorganisms (visible) such as mildew and marine flora and fauna can cause considerable damage to coatings and dramatically affect the properties and functions of coating systems, negating their purpose.

**Microbiologically Induced Corrosion.** Microbial adhesion, establishment, and growth into colonies are prerequisites for deterioration of organic materials. Much, but not all, microbial growth occurs in a biofilm—a gel consisting principally of polysaccharides that protects the microbe and enables it to form an environment that is conducive to its reproduction and colony growth (Ref 21). The process by which a material is decomposed or otherwise altered by a microbe colony results in degradation products of the polymer, which the microbe uses as a source of energy, notably, carbon and electrons. This can result in the depolymerization of the organic molecule, breaking it up into smaller units that can be assimilated by the organism.

**Mildew.** In warm moist environments, and particularly in the southeastern part of the United States and in tropical countries, the presence of molds and mildew on paint (and many other materials) are of concern. Molds and mildews are both forms of fungi whose spores are ubiquitous in the environment. The spores require moisture and heat in order to germinate and grow. Generally, humidity of 70% is necessary for mold and mildew growth, with temperatures between approximately 5 and 50 °C (40 and 120 °F). Slightly acidic pHs (in the range from 4.5 to 6.5) are preferable, although alkaline conditions above a pH of approximately 8.5 are not conducive to most fungal growth.

In order for fungal growth to occur, the spore must remain in contact with the surface and have a source of food. Accordingly, a rough textured surface that collects dirt and holds moisture provides a good surface for fungal growth. Food sources for the spore can be dust and dirt picked up from the atmosphere, windblown contamination on the painted surface, or from the paint itself. Oil-based coatings, alkyls, and polyamide-cured epoxies are susceptible to fungal attack due to the fatty acids in the oils or crosslinking copolymers. Phthalate plasticizers can also be a food source for fungi. Latex paint systems, particularly those containing oil or alkyl modifications for adhesion to chalky surfaces, are also very susceptible to mildew or mold growth. The fungal spores can either feed directly on the fatty acid constituents in the paint or secrete enzymes that break down portions of the paint binder into components which then can be used as food.

When a mold or mildew grows on the surface of a paint, the growth can collect dirt and dust from the atmosphere and hold moisture, perpetuating its growth. As the fungus feeds on the paint, the resinous binder is degraded by scission of ester linkages, oxidation of oil fatty acids, and accumulation of metabolic acidic products. Not only is the paint degraded, but it is also covered with an unsightly black growth. Fungicides can be added to paint to reduce or eliminate mildew and mold growth. Basic zinc oxide added to oil-base and latex paints in amounts of one to three pounds per gallon, perhaps in combination with some organic fungicides, can substantially reduce or eliminate fungal growth.

Molds and mildews can be killed by a dilute hypochlorite solution (bleach). Bleach kills the fungus, turning it white. If dirt is present, it will not be bleached and will remain a dark color. After the fungus is killed, it should be removed from the paint surface by scraping and/or scrubbing prior to painting. However, if heat, moisture, and a food source are still present after repainting, it is likely that spores will again reattach and grow. Mildews and molds are relatively easy to kill by bleaching, but their spores can often survive a bleach treatment and comeback growth if conditions are right.

**Marine fouling** consists of attachment of plant or animal life to an immersed structure. Virtually all underwater surfaces have some type of marine attachment, including ships, piers, pilings, and even whales, large fish, crabs, and other crustaceans. Animal fouling species are most commonly barnacles, muscles, or tubeworms. Fouling vegetation are algae, or seaweeds (Ectocarpus, Enteromorpha, or Laminaria). Both animal and plant fouling requires contact with the substrate for 24 hours or more in order to attach. Consequently, if water is fast moving (over approximately ten knots) or if the surface is smooth with no fissures or crevices, marine fouling is minimized or eliminated.

Marine foulants generally do not attack the paint and degrade it, but by virtue of their adhesion, roughen the surface to which they are attached, providing considerable friction to the smooth flow of water around the fouled object. If that object is a ship, even minimal marine fouling can reduce its speed and increase fuel consumption by 10% or more.

Antifouling coatings are used to kill or prevent attachment of marine organisms. Tributyl tin antifoulants have been used very successfully in the past, but because they are toxic to most marine life, have been banned from use on most U.S. flagships. Currently antifoulants based on copper oxides are most commonly used, but these too are toxic, and there is concern that ultimately they could also be prohibited. Nonstick fluorinated hydrocarbon resins and silicone-based binders are being used with only limited success at present. These materials function by providing a surface to which the marine fouling organism cannot attach tightly. When a ship is underway, the friction from flowing water is sufficient to wash growth from the nonstick antifoulant paint surface. Even when marine fouling does attach, it can be readily removed by scraping or hosing down with high-pressure water washing.

**Conclusion**

There are a variety of environmental stresses that combine to degrade coatings exposed in a service environment. Some of the individual major influences are discussed in this article. However, this discussion does not include the stress from combinations of influences, which always happens in nature. Accordingly, failure analysis of coatings is as much an art as a science, although science always underlies any attempt to explain what has happened when a coating system fails.

**REFERENCES**

4. Society for Protective Coatings


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