minute (CFM) of compressed air is required for each nozzle to achieve a 100 psi nozzle pressure. Similarly, the labor estimates dictate the required number of pressure washers, spray pumps, spray guns, lines, and hoses required to complete the project. The estimator also needs to consider quality control equipment necessary to complete the work (e.g., wet- and dry-film thickness gages, surface profile measurement equipment, holiday testing equipment, ambient condition measurement equipment, etc.).

The equipment used can affect worker productivity substantially. Nearly all workers would agree that they are at their most productive when they feel safe and can properly see the surfaces they are cleaning and painting. Preplanning of the contractor and estimator determines the needs for access to the work area (e.g., lifts, scaffolding, swing-low stages, picks, etc.) and the required fall and respiratory protection. Proper levels of illumination benefit production, and explosion-proof lightingwhether standalone, blast helmet, or nozzle mounted-does not add significant costs to the project. In some instances, minimum illumination levels for the work area are specified by the contract documents. Both abrasive blast cleaning and spray paint application produce dust and diminish worker visibility. For many jobs, especially in confined or enclosed work areas, ventilation fans, air horns, or dust collection systems control dust and provide better visibility. Many painting projects involve disturbance of existing coatings that contain lead or other toxic metals in the paint. For these projects ventilation and dust collection may be required, depending on the specified surface preparation. The ventilation and dust collection system provides many benefits, including:

- Better visibility for workers
- Engineering controls required by the Occupational Safety and Health Administration (OSHA) before relying solely on respiratory protection
- Negative pressure inside the work area enclosure or containment so that surface preparation waste and paint debris cannot escape the enclosure
- Air for the dilution of flashing solvents to provide oxygen for workers, limit explosion hazards, and as required for working in permit-required confined spaces

Safety and ventilation systems for painting projects need to be designed by qualified personnel either within the organization of the painting company or subcontracted by the painting company. The design of such systems (fan sizes, dust collection equipment sizes, ductwork sizes, inlet air opening sizes, etc.) is beyond the scope of this article, but the costs associated with the design and necessary equipment must be included in the job cost estimate. In some painting projects, there is a need to provide heating and/or dehumidification systems. Heating systems used for painting projects must be indirect-fired or electric so that combustion contaminants do not affect surface cleanliness or create potential safety hazards. The advantages of heating and/or dehumidification systems are that they:

- Can extend the painting season in colder climates to eliminate winter shutdowns and the associated additional mobilization and demobilization costs
- Can control ambient conditions (temperature and relative humidity) required for painting to eliminate delays caused by adverse weather
- Are sometimes required to control ambient conditions in situations where the conditions for painting could otherwise never be obtained (e.g., underground tunnels, underground penstocks, some dam or marine projects)

Again, the size of heating and ventilation equipment depends on many variables, and a discussion of determining heating and/or dehumidification requirements is not included in this article. Once a determination is made that the equipment is desired or required, the estimator should add these costs to the estimates for the timeframe that the equipment will be used.

Once all of the equipment requirements are obtained, the cost (purchase, rental, or depreciation) for each piece of equipment should be added to the estimate, along with the operating costs (gasoline, diesel fuel, additional compressed air, electric power, or electric generators).

Remembering Forgotten Costs

Leaving items out of an estimate obviously is problematic and could potentially ruin an otherwise successful project. The estimate needs to provide for all direct and indirect costs. The examination of the scope of the work and project specifications performed in the beginning stages of the estimating process should reduce the number of omissions. Other cost items that are not part of the specification requirements may be neglected. Examples of often forgotten cost items include:

- Costs associated with managing subcontractors
- Costs associated with pre-job engineering or
- safety submittalsCosts associated with performance, war-
- ranty, or surety bonds
 Costs associated with various insurance and
- permits
- Freight costs for materials and equipment
- Costs for potential liquidated damages if the project falls behind schedule

No matter how diligent the estimator is, most projects have some degree of uncertainty. Therefore, some level of contingency should be added to the estimate. The amount, in fixed dollars or a percentage of the total project cost, depends on the understanding of the scope, the level of experience of the company with the work they are bidding, and successful completion of similar jobs. The author typically adds 3 to 15% contingency to the total project cost.

Conducting a Coating Condition Assessment

As mentioned in the previous section "Calculating Labor Quantities and Rates," the existing condition of the surface being prepared or painted is one of the variables that can affect production rates. A coating condition assessment is sometimes performed as part of the estimating process to determine whether the coating can be painted over, or if it is in such poor condition-having poor adhesion, too many coats already, and/or is brittle with little integrity-that it must be removed prior to the application of a new coating system. The coating condition assessment is often performed as part of planned future work, and the estimating portion of the assessment is to develop budgets for the work long before it is put out for bid. The purpose of the coating condition assessment is to determine the condition of the existing coatings on the structure(s) or equipment in the project being estimated, in order to develop a future maintenance painting strategy or to define the scope of work if the scope is not defined in a contract.

A coating condition assessment generally includes:

- *Field Examination/Visit.* This typically involves a detailed visual assessment of all areas of the project to determine the type, extent, and location of coating breakdown and corrosion on the structure(s) or equipment; measurements of coating dry film thickness, number of coats, adhesion, substrate condition, and relative humidity; paint sample removal; and photography of areas important to the visual assessment.
- *Laboratory Investigation*. This typically consists of determining the existing coating type and determining if the coatings contain any toxic metals or materials.

The end product of the assessment is a report that typically contains the following:

- Summary of findings with photographs
- Information on the background of the project
- Results of the field inspection and testing
 - Results of a laboratory analysis of field samples
 - Discussion section, which includes:
 - a. General discussion of maintenance painting strategies
 - b. Determination of the available painting strategies for the structure(s)
 - c. Recommendations for the specific project

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Fig. 4 Chalking of existing coatings. Courtesy of KTA-Tator, Inc.

• Table summarizing cost opinions for the recommended work

Figures 4 through 9 are photographs that were included in an actual coating condition assessment report, showing problems found in the detailed visual inspection that was performed during the field visit.

Putting It All Together and Determining the Selling Price

Once all of the costs are known, the estimator could simply sum the costs, apply the overhead rate percentage of the company, and add the desired level of profit. This step in the estimating process, however, cannot be taken lightly. The amount of profit could vary depending on how much the company wants this particular job, how many other bidders are expected, and the success of the company in bidding similar projects. Once the level of profit is determined, the final bid price can be calculated. The presentation of the bid pricing may be defined by the project specifications, and the proposal must be presented accordingly. Some jobs are bid as a lump sum for all work. Other projects may require separate pricing for labor and materials. Some jobs even may be bid by unit prices (e.g., price per square foot, price per tank, price per length of pipeline, etc.). The price produced from the developed cost estimating method then should be adjusted to fit the required bid format.

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Fig. 5 Chipping and corrosion on girder bottom flange at expansion joint. Courtesy of KTA-Tator, Inc.



Fig. 6 Area of chipping and peeling paint and corrosion. Courtesy of KTA-Tator, Inc.



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Fig. 7 Pitting depth measured on a KTA-Tator, Inc.

ge ramp. Courtesy of KTA-Tator, Inc.



Fig. 9 Abrasive blast cleaned substrate. Note under-film corrosion. Courtesy of KTA-Tator, Inc.

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Coating Deterioration

Kenneth B. Tator, KTA-Tator, Inc.

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 insufficient, 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.

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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 ($\mathring{A} = 1 \times 10^{-10}$ m) for the chemical crosslinking reaction to occur (Ref 1).

For example, in an epoxy resin that is crosslinked 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 midchain 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 micropores, microcracks, or capillaries within the coating. If evaporation is impeded, due to low temperature or other reasons, the solvent or water can accumulate

and cause a void within the coating cross section. The inner or outer surface of the void can provide a means of moisture penetration into the dried film. Similarly, pigment agglomerations, which are pigment particles in contact with each other, can impede resin wetting, leaving a microvoid or discontinuity in the crosslinked coating. All of these result in the apparent presence of inhomogeneities and phase separations in a crosslinked coating film. Even if the film is thermoplastic, and not crosslinked, such inhomogeneities and phase separations still are present, and for the same reasons.

The presence of low-molecular-weight regions in coating films has been demonstrated by electron and light microscopy studies. Films made of epoxy, phenolic, and phthalate resins were observed to consist of micelles or granules of high-density segments separated by narrow boundary regions of low-molecular-weight material. At the film-substrate interface, the lowmolecular-weight material exists as a thin continuous film or as channels between micelles, thereby providing pathways for easy entry of water to the interface (Ref 2).

Accordingly, there is great variability in the crosslinking density of a coating, even if it is formulated, mixed, applied, and cured properly. Figure 1 illustrates some of this variability.

Relative to the properly pigmented, dried, and cured portions of the cross section of a coating layer, the areas of the deficiencies mentioned are quite small, both in area and in crosssectional dimension. Thus, multiple layers of a coating system is not likely to provide an overlap of deficient areas, and a porosity or area of moisture penetration in one layer almost certainly will not coincide with that in another layer, even though the weak areas for moisture penetration remain. A three-coat system usually is better than a two-coat system, and both are better than a one-coat system, even if that layer is relatively thick.

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 that than 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 Standard 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):

- 0: Dry interiors where structural steel is embedded in concrete, encased in masonry, or protected by membrane or noncorrosive contact type of fireproofing
- *IA:* Interior, normally dry (or temporary protection). Very mild (oil-base paints do not last six years or more)
- *1B*: Exteriors, normally dry (includes most areas where oil-based paints last six years or more)
- 2*A*: Frequently wet with freshwater. Involves condensation, splash, spray, or frequent immersion. (Oil-based paints now last five years or less.)
- 2B: Frequently wet by saltwater. Involves condensation, spray, or frequent immersion. (Oil-based paints now last three years or less.)
- 2C: Freshwater immersion
- 2D: Saltwater immersion
- *3A:* Chemical atmospheric exposure, acidic (pH 2.0 to 5.0)

- *3B*: Chemical atmospheric exposure, neutral (pH 5.0 to 10.0)
- *3C*: Chemical atmospheric exposure, alkaline (pH 10.0. to 12.0)
- 3D: Chemical atmospheric exposure, presence of mild solvents, intermittent contact with aliphatic hydrocarbons and their derivatives (mineral spirits, lower alcohols, glycols, etc.)
- *3E:* Chemical atmospheric exposure, severe. Including oxidizing chemicals, strong solvents, extreme pHs, or combinations of these with high temperatures

For the most part, these environmental descriptions are somewhat similar to the extent that they progress from a relatively mild, non-corrosive 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,



Fig. 1 Crosslinking density of a coating varies greatly, resulting in very different degrees of moisture penetration: (A) No moisture penetration/high crosslink density. (B) Penetration through or over void. (C) Penetration through a pigment agglomeration. (D) Penetration through a microcrack or capillary. (E) Penetration through area of low crosslink density

Table 1 Atmosphere corrosivity categories and examples of typical environments

Corrosivity category	Exterior environment	Interior environment
C1 very low		Heated buildings with clean atmospheres, e.g., offices, shops, schools, hotels
C2 low	Atmospheres with low levels of pollution. Mostly rural areas	Unheated buildings where condensation may occur, e.g., depots, sports halls
C3 medium	Urban and industrial atmospheres, moderate sulfur dioxide pollution. Coastal areas with low salinity	Production rooms with high humidity and some air pollution, e.g., food processing plants, laundries, breweries, dairies
C4 high	Industrial areas and coastal areas with moderate salinity	Chemical plants, swimming pools, coastal ship- and boatyards
C5-I very high (industrial)	Industrial areas with high humidity and aggressive atmosphere	Buildings or areas with almost permanent condensation and with high pollution
Categories fo	r water and soil	
Im 1	Fresh water	River installations, hydroelectric plants
Im 2	Sea or brackish water	Harbor areas with structures such as sluice gates, locks, jetties; offshore structures
Im 3	Soil	Buried tanks, steel piles, steel pipes

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chemicals, 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



Fig. 2 Solar spectrum as emitted and after absorption and scattering. 1. sun spectrum before entering stratosphere (extraterrestial radiation), 2. spectrum modified by ozone absorption (in 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

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 wave 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



Fig. 3 Electromagnetic spectrum of radiation types. Source: Ref 6

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.

$$(H_2O)$$
 HOH $H^+ + OH^-$

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 cyclicization (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 chalk 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, condenses 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 electroendosmosis. 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, dirts, 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 substantially less than dry adhesion. When the film dries out, often dry adhesion reestablishes, but usually not to the same extent as is 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_{σ} 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 disassociation 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 disassociation occurs is water. Even very small amounts of water are

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 (NO_X) 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 alkalis 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 alkyds are applied over concrete, which contains alkali salts, which, when combined with water, form caustic alkalis. In a similar fashion, application of oil-based alkyds 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 alkalis 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:
$$M \rightarrow M^+ + ne^-$$

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

Cathodic reactions:

· In near-neutral and alkaline environments

$$^{1}/_{2}O_{2} + H_{2}O + 2e^{-} \rightarrow 2OH^{-}$$

• In acidic environments

 $O_2 + 4H^- + 8e^- \rightarrow 4OH^-$ (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



Table 2 Chemical sensitivity of selected organic and inorganic pigment family	anic and inorganic digment families
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		Sensitivity	
Pigment type	Examples	Alkali	Acid
Inorganic			
Titanium dioxide		Excellent	Excellent
Zinc oxide		Moderate to good	Poor
Antimony oxide		Poor	Poor
Red iron oxide	Synthetic red oxide; Spanish, Indian, or Persian Gulf red	Excellent	Excellent
Cadmium red		Excellent	Poor
Molybdate orange		Poor to fair	Poor
Lead	Minium, mineral orange	Good	Poor
Yellow iron oxide	Ferrite yellow, sienna, ochre, umber	Excellent	Fair
Chrorme yellow		Poor to fair	Fair
Zinc yellow	Zinc potassium chromate	Fair	Poor
Cadmium yellow	•	Excellent	Poor
Nickel titanate yellow		Excellent	Excellent
Bismuth vanadate		Excellent	Fair
Zinc ferrite		Excellent	Good
Chrome green	Brunswick green	Poor	Poor
Chromium green oxide	· · · ·	Excellent	Excellent
Iron blue	Prussian blue, Midori blue, Chinese blue, mineral blue	Poor	Very good
Ultramarine blue		Very good	Poor
Carbon black		Excellent	Excellent
Black iron oxide		Excellent	Fair
Micaceous iron oxide		Excellent	Excellent
Zinc dust		Poor	Poor
Aluminum		Poor	Poor
Stainless steel flake		Excellent	Very good to Excellent
Organic			
Metallized azo reds	Lithols, permanents, rubines	Poor	Poor
Nonmetallized azo reds	Toluidines, paras, naphthols	Very good	Very good
Azo-based benzimidazolone reds		Very good	Very good
Quinacridones		Excellent	Excellent
Vat reds	Dibromanthrone, anthraquinone, brominated pyranthrone, perylenes	Excellent	Excellent
Azo-based oranges	Dinitroaniline, pyrazolone, tolyl	Good	Good
C C	Naphthol orange	Very good	Very good
Azo-based benzimidazolone oranges		Very good	Very good
Metallized azo oranges	Clarion red	Poor	Moderate
Monoarylide yellows	Hansa yellows	Very good	Very good
Diarylide yellows	Benzidine yellows	Very good	Very good
Azo-based benzimidazolone vellows		Excellent	Excellent
Heterocyclic yellows	Isoindoline, quinophthalone, azomethine, tetrachloroisoindolinone, triazinyl	Excellent	Excellent
Phthalocyanine greens	••••	Excellent	Excellent
Phthalocyanine blues		Excellent	Excellent
Carbazole violets		Very good	Very good
Source: Ref 9			

coating system often causes the coating to crack and spall from the substrate, exposing the underlying surface to the environment and further corrosion attack. A means of corrosion protection in the oil industry is to remove oxygen from well injection water, and in the nuclear, chemical processing, and other industries, to *inert* the vapor space in a tank or vessel by adding nitrogen, carbon dioxide, combustion gases, or other gases to displace oxygen, thereby reducing or eliminating metallic corrosion.

Oxygen species (nascent atomic elemental oxygen, O; molecular oxygen, O₂; ozone, O₃) are very influential in the degradation of organic materials by ultraviolet light and solar radiation. Molecular oxygen absorbs solar radiation in the range of 176 to 210 nm. Upon absorption of UV radiation, the molecular oxygen is transformed into singlet oxygen, which

dissociates, forming two oxygen atoms. The oxygen atoms recombine with molecular oxygen to form ozone. Ozone absorbs UV between 200 to 320 nm and absorbs in the visible range at 420 and 700 nm. In the UV range, stratospheric ozone dissipates energy as heat. This is beneficial, because less high-energy UV, which is detrimental to life on earth (sunburn for example), is absorbed. Ozone in the stratosphere does not influence the formation of ozone near the surface of the earth. On the earth's surface, ozone is produced by industrial combustion. Ozone is formed indirectly from nitrous oxide, which absorbs UV, forming molecular oxygen, which further reacts with more molecular oxygen to form ozone. Ozone is a strong oxidizer that reacts with most organic materials, including coatings, to form free radicals and ultimately photochemical embrittlement degradation.

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 defuse 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 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 μ m² 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 compoundsprincipally 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 H_2O , 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 inflated 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 largescale 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:

$$Fe(iron/steel) \rightarrow Fe^{++} + 2e^{-}$$

(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:

$$O_2 + 2 H_2O + 4e^- \rightarrow 4 OH^-$$

(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 disbonds 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