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Corrosion protection by nanostructured coatings

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11.1 Introduction

This chapter focuses on coatings for corrosion protection. This is the most simple and cost effective method against metallic corrosion. Coatings can be applied to any surface, even by unexperienced people, and are often combined with other corrosion preventive methods. This chapter is divided into three parts. The first corresponds to Section 11.2 and provides a brief overview of the metallic corrosion process and methods for corrosion control. This part helps understanding the modes of action of the different types of coatings and puts them in perspective with the other methods of corrosion protection. The second part of the chapter describes the most representative types of coatings and surface films used today for protecting metal surfaces against corrosion. It corresponds to the Sections 11.3—11.7. The last part (Section 11.8) reports the state-of-the-art about new, environmentally friendly, nanostructured coatings for corrosion protection, with self-healing and "smart" properties. Reflecting the current body of knowledge and the maturity of the field, books, and handbooks were the preferred sources of information for the first two parts, while research papers published in the last years are the prime source of information for the third part.

11.2 Overview of the metallic corrosion process

Metals are omnipresent in modern civilization [1]. This is a consequence of their availability in the crust of the Earth and their exceptional properties, like strength, toughness, ductility, castability, machinability, recyclability, and electrical and thermal conductivities, to name just a few [2]. The major problem with metals and their alloys is the proneness to corrosion, that is, the spontaneous electrochemical reaction of a metal or alloy with the surrounding medium, resulting in changes in the metal, the medium, or the function of the technical system [3]. To understand why metals corrode it is important to realize that the majority exist in nature in the oxidized form. Metallurgy takes energy to turn the oxidized form (minerals and

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ores) into the reduced form (metallic state). Once produced, these metals are in contact with the same atmosphere that maintained them in the oxidized form for ages. They tend to return to the original state (oxidized) and the tendency is directly proportional to the energy spent in reducing them. The process responsible for this natural return to the native state is corrosion and can be considered the opposite of metallurgy—Fig. 11–1A. The oxidizing power of the Earth's atmosphere is not strong enough for noble metals and that is why their native state is the reduced (metal) form.

11.2.1 Corrosion reactions

Corrosion of a metal is thus a spontaneous process by which it returns to the original oxidized state. It is an electrochemical process, with an anodic reaction, the metal oxidation,

$$M(s) \rightarrow M^{n+}(\mathrm{aq}) + ne^- \tag{11.1}$$

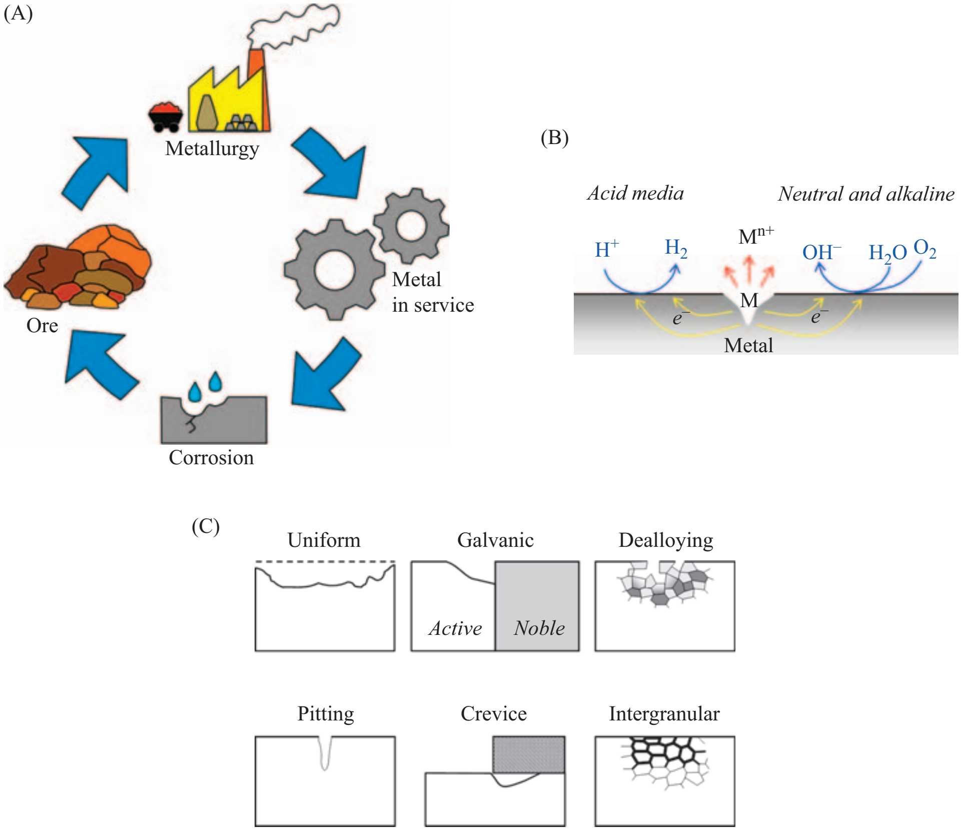

FIGURE 11–1 (A) Corrosion cycle, (B) Corrosion cell and (C) Types of corrosion.

and the simultaneous reduction of chemical species in the environment capable of accepting the electrons generated in reaction (1). The most common reactants are H_2O and O_2, which are present anywhere in the Earth's surface. The primary reduction reaction in neutral or alkaline media is

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq) \tag{11.2}$$

whereas the principal reduction in acidic media is

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \tag{11.3}$$

These reactions take place at the same rate but in separated places. Fig. 11–1B shows a schematics of a corrosion cell, with the reactions (1) to (3), the flux of electrons in the metal phase, and the flow of ions closing the electric circuit in the environment side. The corrosion rate is often controlled by the reduction reaction because of the scarcity of reactant (the concentration of oxygen dissolved in water is just 8 ppm [4]). The corrosion reactions sequence continues with the formation of solid products, as for example,

$$M^{n+}(aq) + nOH^-(aq) \rightarrow M(OH)_n(s) \tag{11.4}$$

The initial corrosion products change to more stable forms with time.

11.2.2 Types of corrosion

Metallic corrosion can appear in different forms, which depend on the type of metal or alloy, and on the environment. Fig. 11–1C illustrates some of the most common types of corrosion. In uniform or general corrosion, common for steel in atmospheric conditions or in acid, the anodic and cathodic reactions take place in many small anodic and cathodic areas, which change place with time, thus leading to homogeneous metal dissolution. Galvanic corrosion appears when a metal is in contact with other metals (or other conducting materials) immersed in the same conducting environment. It accelerates the corrosion of the metal with higher tendency to corrode and lowers or suppresses the corrosion of the other metal(s). Localized forms of corrosion like pitting, crevice, and intergranular corrosion occur typically on passive metals, that is, metals that are spontaneously covered by a thin layer of oxide that isolates the metal from the environment and prevents its corrosion. The local disruption of this protective layer leads to localized corrosion. The knowledge about corrosion types is important to select the most suitable methods for protection including the best types of coatings to be applied.

11.2.3 Costs of corrosion

The importance of metallic corrosion is huge with costs equivalent to 2%–4.5% of gross domestic product being encountered in different surveys [5,6]. The costs associated with corrosion include the expenses with protective measures, costs of equipment replacement and lost production, and investments with insurance and in research and development [6]. Given the great economic impact of metallic corrosion, an enormous effort has been undertaken to understand this phenomenon to control it.

11.2.4 Methods of corrosion prevention and control

Many strategies are available to prevent and control metallic corrosion. Some can be implemented during the project stage but the majority is applied in service. The most important are summarized in Table 11–1. All the strategies fall within one of three groups: (1) act over the metal, (2) act over the environment, or (3) separate the metal from the environment. Acting over the metal can be done during the product design by choosing more corrosion resistant alloys or nonmetallic materials. In service, the action over the metal is done by changing its electric potential. A potential shift in the positive direction might promote the formation of a passive film protecting the metal from corrosion (anodic protection). A shift in the negative direction turns the metal into a cathode (cathodic protection) and the potential can be placed at values where the metal oxidation is thermodynamically impossible. It is then said to be immune to corrosion. Acting over the environment includes controlling room temperature and humidity, purging dissolved oxygen from aqueous solutions, removal of aggressive species like chloride or sulfate ions from the contacting liquid, and the use of corrosion inhibitors. The separation between metal and environment is achieved by applying surface coatings. The coating prevents the electrochemical reactions between the two. Even when pores and defects are present, the coating is still a barrier for the ionic path between anodes and cathodes, representing a high resistance in the electric circuit of the corrosion cell.

This short overview of metallic corrosion introduces basic concepts to help understand the action of surface coatings that are presented in the rest of the chapter. More information can be found in corrosion textbooks [7–9] or handbooks [10–12].

Table 11–1 Strategies for corrosion prevention and control.

In project	– Selection of materials – Design of structure – Selecting a less exposed place for the structure	
In service	Control of potential (electrical protection)	– Anodic protection – Cathodic protection
	Control of environment	– Humidity – Temperature – Removal of O_2 (and other oxidants) – Removal of aggressive species (e.g., Cl^-) – Control of fluid motion – Corrosion inhibitors
	Coatings	– Metallic – Inorganic (CCC, phosphating, anodizing) – Organic (paints)

11.3 Coatings and surface films for preventing metallic corrosion

A coating represents a barrier separating substrate and environment, thus preventing the interaction between the two. Coatings are applied to virtually all surfaces for two main reasons: protection and decoration. The field of surface coatings is vast, covering systems of very different nature. The functions can also be very different: apart from protection (not only corrosion) and decoration (color and gloss), coatings are applied to provide hardness and wear resistance, illumination, sanitation, and electrical resistance, to name just the most common. The coatings applied for corrosion control are usually classified as metallic, inorganic, and organic (paints). The types of coatings and the technologies described in the next pages (Sections 11.4–11.6) are well established, being applied worldwide for many years, with a long history of development, optimization, and industrial implementation.

11.4 Metallic coatings

Thin layers of selected metals are applied over other metals and alloys primarily for corrosion protection but also for aesthetics and the modification of surface properties, like color, gloss, hardness, wear resistance, weldability, and electrical conductivity.

11.4.1 Metals and functions

Metals frequently applied as thin films over other metals are zinc, cadmium, nickel, chromium, aluminum, tin, copper, and precious metals (gold, silver, platinum, and others) [13,14]. The most common metallic coating in tonnage is zinc and zinc alloys, mainly used for the corrosion protection of steel. Zinc can be deposited by hot-dip galvanizing (immersion in molten bath), electrodeposition and metallization (metal spraying). Other relevant zinc coatings are Galvalume (55% Zn, 43.5% Al, and 1.5% Si), Galfan (95% Zn and 5% Al), and Galvanneal [15]. In some environments *cadmium* can protect steel more efficiently than zinc, it is easier to weld than zinc and offer a lower contact resistance. However, it is more expensive and cadmium and its vapors are toxic. *Aluminum* is used for protection of steel and aluminum alloys of medium and high strength. It is also used for decoration of metallic and nonmetallic surfaces. *Tin* is used to coat steel cans to store foods, beverages, oil, paints, and chemicals. *Copper* is applied over steel or zinc substrates prior to the deposition of nickel or chromium, with the objective of reducing the costs of surface preparation and to improve adhesion. It is also used as a decorative finish for articles made of steel of zinc alloys, and to promote the electrical contact of nonmetallic materials in appliances and impressed circuits. *Nickel* was one of the first metals to be deposited. It is commonly applied on steel or zinc for corrosion protection, wear resistance and decoration. In this last case, the nickel layer is coated by a thin film of chromium (5–40 μm of Ni and final coat of 0.5 μm Cr). Ni is also applied by electroless (chemical deposition) on nonmetals, like polymer materials to provide a shiny metal appearance. *Chromium* is used for both aesthetical and protection purposes. Protective coats must be thick because they are porous and tend to crack. Since these layers are nobler than steel, the corrosion of the substrate exposed in pores and defects is high due to the large cathodic area provided by the chromium layer. *Precious metals* (Au, Pt, Ag, Pa, Ro, Ru, and Os) are applied for decoration. They are also used in electrical and electronic devices for low contact resistance and withstand local high temperatures. Gold and platinum are employed to coat equipment for the chemical industry when there are no other means to prevent corrosion of the substrate and contamination of reagents or products.

11.4.2 Forms of application

There are many forms of applying metallic coatings. For corrosion protection the most important ones are electrolytic deposition (electrodeposition), immersion in molten bath (dip coating), diffusion deposition, and metal spraying.

11.4.2.1 Electrodeposition

The coating process takes place in an electrochemical cell comprising an electrolytic solution with ions of the metal to be coated and, immersed there, the object to coat (working as cathode) and one or more anodes made of inert material or of the metal to be deposited. Electrical current from an external power source provides the electrons necessary for the reduction of the cations in solution to form the metallic coating. Additives are commonly added to the electrolytic solution with the objective of improving the quality of the coating or to aid the manufacturing process: brighteners, pH buffers, complexing agents, inert salts to increase solution conductivity, defoamers, and other surfactants are among the most common additives [16–18].

11.4.2.2 Hot dipped coatings

Hot dip galvanizing of steel corresponds to the largest amount of metal deposited every year worldwide. The parts to be coated are immersed in the liquid bath of molten metal or alloy and the coat is formed by inter-diffusion of one metal on the other. The coating thickness can range from 20 μm to several hundreds of micrometers. A cross-section reveals a stratified structure with layers of variable composition (Fig. 11–2A). The internal layer contains a significant amount of the metal from the substrate while the outer layer is exclusively constituted by the metal in the bath [19,20].

11.4.2.3 Diffusion coatings

The parts to be protected are placed inside chambers at high temperature together with the metal to be deposited in the form of powder or gas. The temperature is usually between 350°C and 500°C but can be up to 1500°C, depending on the metal to coat. The metal in the environment diffuses into the piece and modifies its surface, creating a layer with a new composition and properties, without changing the original dimensions. These coatings cannot be detached from the metal base because there is no separation between the two. Because of this, sometimes this process is also called *surface alloying*. This layer provides a diffusion barrier against corrosive environments. Deposition of chromium (chromizing), aluminum (aluminizing), and zinc (sherardizing) are used in different grades of steel. Other metals that are commonly subjected to these treatments are nickel, cobalt, and titanium. Similar process exists with nonmetallic elements like carbon (carburizing) and nitrogen (nitriding), with the intention of hardening the base material. Silicon (siliconizing) is used in refractory metals [21–24].

11.4.2.4 Metal spraying

Metal spraying, or thermal spraying, consists in projecting the metal in fusion at high speed in direction of the substrate where it coalesces and forms a layer. The projection can be made in many ways, the most usual being air or vacuum plasma spraying, high velocity oxy–fuel (HVOF) spraying, flame spraying, and wire arc spraying. A great advantage of this process is that it is possible to apply thick coats (up to millimeters) in large structures, like bridges and girders, on site. The main disadvantages are the significant porosity of the film and the imperfect bonding in some areas due to the existence of surface oxide films during application [25,26].

11.4.2.5 Displacement deposition

In this process the metallic part is immersed in a solution with ions of the metal to be deposited (which must be nobler than the part to be coated). A spontaneous reaction occurs, with the

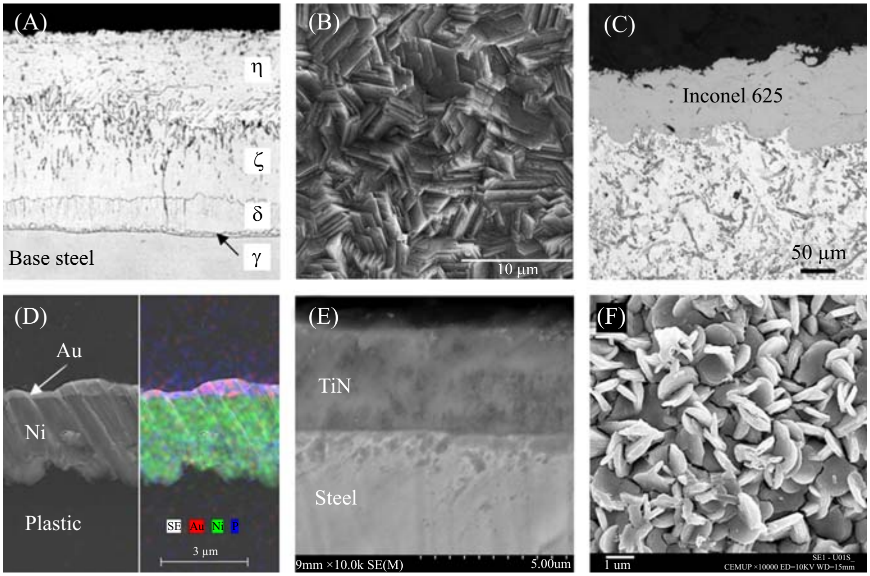

FIGURE 11–2 A selection of inorganic and metallic coatings. (A) cross-section of hot dip galvanized steel depicting the eta, zeta delta, and gamma layers, (B) top view of electrogalvanized steel, (C) cross-section of Inconel 625 applied on an aluminum alloy by HVOF, (D) SEM picture and EDS map of layers of nickel and gold deposited on a plastic substrate, (E) TiN layer on steel applied by PVD, and (F) zinc phosphate layer applied on galvanized steel. *EDS*, Energy dispersive X-ray spectroscopy; *HVOF*, high velocity oxy–fuel; *PVD*, physical vapor deposition; *SEM*, scanning electron microscope.

oxidation of the base metal, whose electrons are used in the reduction of metal ions from solution originating the metallic film. The deposit is uniform and covers even difficultly accessible areas.

11.4.2.6 Electroless deposition

This form of depositing a metal is also called *chemical reduction* or *auto-catalytic metal deposition*. It is performed without an external electrical current, hence the name. The metallic ions in solution are reduced at the substrate by oxidation of specific species, like formaldehyde, sodium hypophosphite, or hydrazine. Films of Ni, Co, Pd, Pt, Cu, Au, and Ag have been produced by this way. The source of ions are usually chloride or sulfate salts of the metal to deposit. The main advantages of this method are the simple installation (no power source, electrodes, or electrical cables), the capability of coating nonconducting substrates, like plastics, and the uniform and nonporous films obtained in complex geometries. The disadvantages are the higher cost, the necessity to activate the reaction, the slower deposition rate, and the difficulty in obtaining thick coats. Often, it is applied as a first layer in contact with the substrate before a thicker layer is applied by electrolytic deposition [27].

11.4.2.7 Chemical vapor deposition

In this process the substrate is introduced in a chamber where volatile chemical precursors react on its surface producing the desired film. The following are examples of reactions for depositing carbon (diamond), titanium, nickel, silicon, and tungsten [22,28]:

$$\mathrm{CH_4(g)} \rightarrow \mathrm{C(s)} + \mathrm{2H_2(g)} \tag{11.5}$$

$$\mathrm{TiI_4(g)} \rightarrow \mathrm{Ti}(s) + \mathrm{2I_2(g)} \tag{11.6}$$

$$\mathrm{Ni(CO)_4(g)} \rightarrow \mathrm{Ni(s)} + \mathrm{4CO}(g) \tag{11.7}$$

$$\mathrm{SiH_4(g)} \rightarrow \mathrm{Si(s)} + \mathrm{2H_2(g)} \tag{11.8}$$

$$\mathrm{WF_6(g)} + \mathrm{3H_2(g)} \rightarrow W(s) + \mathrm{6HF}(g) \tag{11.9}$$

11.4.2.8 Physical vapor deposition

In physical vapor deposition, the material to be deposited changes its physical state from a condensed phase at the source (or target), to the vapor phase and then back to the condensed phase (the thin film) deposited on the substrate. The most common processes are vacuum deposition, sputter deposition, and arc vapor deposition [22,29].

11.4.3 Corrosion protection by metallic coatings

Metallic coatings protect the metal substrate from corrosion by two mechanisms:

11.4.3.1 Barrier (or shield) effect

The metallic film represents a barrier between the environment and the substrate, isolating it. If the layer is uniform and defect free, it will corrode first. Since the metals selected for coatings are corrosion resistant their degradation is very small and the service life of the whole system is significantly extend.

11.4.3.2 Cathodic protection

A few coatings offer additional protection by corroding in place of the base metal when it becomes exposed at defects, pores, or cut edges. This is the principle of cathodic protection and occurs when the coating is less noble than the underlying metal. The coating corrodes and brings the base metal to a potential where it acts as a cathode (hence the name) and is immune to corrosion. In these cases (e.g., zinc layer on steel) the coating has more tendency to corrode than the substrate but corrodes at a slower rate. In addition, the corrosion products of the coating can seal the defects and pores restoring the separation from the environment. When the coating is nobler than the base metal (chromium layer on steel), cathodic protection does not occur and in fact it is the substrate that corrodes, usually at a rate accelerated by the high cathodic to anodic area ratio.

11.4.4 Degradation of metallic coatings

Metallic coatings do not degrade easily. Corrosion is usually incipient due to the choice of corrosion resistant metals as coating material. However, defects, pores, and cuts can expose the underlying metal and accelerate the degradation of the whole system. Early degradation can also occur by coating spalling due to bad bonding, chemical attack, wear, and when the service temperature is higher than the melting temperature of coat or substrate.

11.5 Inorganic coatings

Inorganic coatings for corrosion protection include phosphate and oxide (anodized) layers for finishing and base for paint, ceramic thermal barrier coatings (TBCs) for high temperature applications, vitreous enamels for decoration and protection, and chromate conversion coatings for metal finishing or pretreatment for paint. These coatings provide a barrier to the environment and the corrosion resistance can be enhanced by impregnating the film with inhibitive compounds. Inorganic coatings are inert and their degradation usually occurs by mechanical damage or by contact with extreme acid—base conditions.

11.5.1 Phosphate coatings

The deposition of thin phosphate layers is very common on steel, aluminum, zinc, and cadmium. Phosphating is used mainly as pretreatment before painting. It can be combined with oil or wax for temporary corrosion protection. Other applications are lubrication in metal sheet forming, wear resistance in gears and bearings, electric insulation, and decoration. Alone, phosphate layers are not effective against corrosion but very good results are achieved when combined with painting. This layer promotes very good adhesion and also provides high resistance to ionic flow beneath the paint. Industrially the process is performed with the metal sheet or workpiece immersed in tanks, or sprayed, following a sequence of steps that include degreasing, washing, phosphating, rinsing, and drying. The process can take from minutes for thin coats to about 1 h in the case of thick manganese phosphate coatings. Chemically the process consists in a bath of diluted phosphoric acid with soluble iron, zinc, or manganese phosphates, alone or mixed, where the metal is immersed. The phosphoric acid attacks the metal producing a primary (soluble) phosphate and liberating hydrogen. The soluble zinc, iron, or manganese phosphates in the bath react with the cations of the base metal following a series of reactions until tertiary phosphates are produced which precipitate and adhere to the surface forming a phosphate layer [30].

Modern processes use accelerators like nitrite, nitrate, nickel ions, and hydrogen peroxide to reduce the reaction time, to work at lower temperatures and to obtain smaller phosphate grains. With such conditions, thin smooth phosphate layers can be produced in 1–5 min and temperatures from 40°C to 70°C. After phosphating the surface must be rinsed with water to remove any trace of salts that could lead to paint blistering. The resistance to corrosion improves if the final rinse solution contains corrosion inhibitors. Depending on the thickness, the films can be amorphous or crystalline. Manganese phosphates are mainly hurealite, $(Mn, Fe)_5H_2(PO_4)_4.4H_2O$. Iron phosphates have the structure of hurealite but with iron only, $(Fe_5H_2(PO_4)_4.4H_2O$. The most common form of zinc phosphate is hopeite, $Zn_3(PO_4)_2.4H_2O$.

11.5.2 Anodizing

The anodic oxidation or anodizing of metals consists in producing an oxide layer on the metallic surface through an electrolytic treatment in adequate solution, where the part to be coated is the anode. Many metals can form films by this process, such as aluminum, magnesium, titanium, tantalum, vanadium, and zirconium, but only aluminum, and magnesium in a lower extent, are anodized in an industrial scale for corrosion protection. Anodized layers on magnesium need complex solutions containing phosphates, fluoride, and chromates and are not fully protective. For this they need to be covered by a paint film. Aluminum, on the contrary, needs relatively simple solutions to produce thick, hard, compact, well adherent, and protective films. The most common anodizing processes use sulfuric or chromic acids, this one now abandoned due to health and environmental concerns. Oxalic, boric, phosphoric, and tartaric acids are also used, usually in a mixture of some of them. Applied voltage, current density, temperature, and time are important parameters to produce films that can range from 2 to 5 μm in chromic acid, and up to 100 μm in hard coatings produced in sulfuric acid. The films have a two-layer structure, one very thin at the bottom, the barrier layer, and another, called porous layer that constitutes most of the thickness of the film. The anodizing process ends with a sealing step, in which the alumina of the porous layer is hydrated, filling the open volume of the pores, thus making it more compact and impermeable. If the objective is to apply paints or adhesives on the top of the anodized layer, the sealing step is skipped because pores help the adhesion of the organic layer [31,32].

11.5.3 Black oxide

Black oxide is a conversion coating applied to ferrous substrates to provide a black surface, reduce light reflection, and decrease friction between sliding and bearing surfaces. The process is also called bluing due to the blue–black appearance of the finish. It is commonly used by gun manufacturers and owners to improve the cosmetic appearance, protect against corrosion, resisting superficial scratching, and reduce glare to the eyes of the shooter. The coating is thin (~ 1 μm) and porous. Corrosion resistance can be improved by applying oil or wax but it is still limited even under mild corrosive conditions.

11.5.4 Thermal barrier coatings

TBCs are used in exhaust systems and gas turbines in aircraft and industrial engines, where temperature can reach 1650°C. A TBC is typically constituted by three layers: a ceramic layer on the top (usually 250–1000 μm thick yttria stabilized zirconia) with very low thermal conductivity for thermal insulation of the hot components, a layer to bond the ceramic layer to the metallic substrate (75–150 μm thick NiCrAlY or NiCoCrAlY), and a thin thermally grown oxide layer necessary for the adhesion between the ceramic layer and the intermediate bond layer. The TBC is applied by several forms including HVOF, vapor deposition, and air plasma spray [33,34].

11.5.5 Vitreous (porcelain) enamels

A vitreous enamel consists of fused powdered glass applied on a metal substrate (steel, cast iron, stainless steels, and various aluminum alloys) between 750°C and 850°C. The color is obtained by the addition of various minerals, most of them are metal oxides. It is used in external and internal walls of kitchen appliances, ovens, cooking pots, sinks, bathtubs, chemical reactors, and tanks. Architectural elements, advertising panels and traffic signs are also made of enameled steel. Vitreous enamel can also be applied to gold, silver, and copper alloys for jewelry and decoration. It is hard, smooth, easy to clean, chemically resistant, scratch resistant, heat resistant, and the color does not fade even under ultraviolet (UV) light. The main problem is the tendency to crack and shatter [35].

11.5.6 Diffusion coatings

Diffusion coatings have already been presented as a way of applying metallic coatings. Similar process exists for nonmetallic elements like carbon (carburizing) and nitrogen (nitriding). These are heat treating processes in which carbon or nitrogen (sometimes the two, in so-called nitrocarburizing) diffuse into the metal to increase the surface hardness of the material. These processes are commonly used on steels, and sometimes on titanium, aluminum, and molybdenum. Typical applications include gears, valve parts, extruder screws and extrusion dies, die-casting tools, injectors, plastic-mold tools, and many other. The source of carbon is usually carbon dioxide or methane, in gas or plasma form. For nitrogen, the source can be NH_3 (gas nitriding), a cyanide salt (bath nitriding), or pure nitrogen (plasma nitriding). Apart from carbon and nitrogen, boron is also used (boriding or boronizing) and silicon is used in refractory metals [22,23].

11.5.7 Chromate conversion coatings

Chromate conversion coatings have been applied to steel, zinc, copper, silver, and aluminum alloys mainly for corrosion resistance and as base prior to painting, but also for metal coloring and chemical polishing [36]. Chromate films are thin and provide satisfactory protection only to metals already resistant to corrosion, like cadmium, copper, silver, and some aluminum alloys. For more active metals such as zinc, steels, and many aluminum alloys, the protection is less effective and the films are better used as pretreatments for painting. The process, called chromating, is usually obtained by immersing the metals in chromic acid solutions, where hexavalent chromium, Cr(VI), is reduced to trivalent chromium, Cr(III), together with the oxidation of the metal substrate, resulting in a thin oxide/hydroxide film of base metal ions, many times incorporating Cr(III). The hexavalent form may appear in the film according to some authors [37], while others defend that Cr(VI) is only adsorbed at the surface of the film [38]. In any case, when Cr(VI) stays in the film it may be later reduced to Cr(III) thus playing a sort of self-healing role.

11.5.8 Mechanisms of protection and degradation of inorganic coatings

These coatings provide a barrier to the environment, sometimes having an extra protection by incorporating corrosion inhibitors. Often, optimal performance is attained only when a paint film is applied on the top. Inorganic coatings are inert and their degradation usually occurs by mechanical damage, bad adhesion, or under extreme acid—base conditions, where they tend to be dissolved.

11.6 Organic coatings

Organic coatings, or paints, are pigmented liquid (sometimes solid) compositions applied in thin layer that are transformed after a certain time into a solid, colored, and opaque film. Varnishes are similar but do not contain pigments. Organic coatings are often the simplest and cheaper form of corrosion control. They are applied with a variety of objectives, being decoration and protection the most common, but also for illumination, visibility, and sanitation. This is a wide scientific and technological field with many aspects to consider [39—44].

11.6.1 Classifications

An organic coating is a composite material in the form of thin film applied to any surface, with mineral particles dispersed in a polymer matrix. During production, storage and application, it is a colloidal dispersion of solid micro-particles (pigments), and also an emulsion of some liquid constituents in a liquid matrix. The dry film thickness range from just a few to about 100 μm but in some applications it can reach the millimeter scale. Before the formation of a dry film on a surface, a paint can appear as solvent-based or water-borne liquid paint, high-solids, powder coating, electrophoretic, or radiation curing coating. Depending on the function and on the order in the application scheme, a paint can be wash-primer, primer, shop-primer, midcoat, topcoat, enamel, lignin, or varnish.

An uncountable number of compositions and combination of paint layers in different application schemes are possible due to the great variety of substrates, environments, and applications. Fig. 11—3 shows a few examples.

11.6.2 Components of a paint

The components of a paint can be divided into five groups: binder (resin and other film forming agents), pigments, extenders (fillers), solvents, and additives—Table 11—2. Sometimes pigments and extenders are considered together. The *binder* or film forming agent (nowadays mainly synthetic resins) is the principal component of a paint, which, after drying, ensures the adhesion to the substrate, is the matrix that holds together all other constituents and is responsible for all main characteristics of a paint: continuity, chemical, wear and weather resistances, elasticity, hardness, and impermeability. The film forming agent is so important that paints are classified according to it. *Pigments* are mineral particles added to the paint to give color and opacity (hiding power). They differ from dyes (most of them of organic nature) because these have no or weak hiding power. Pigments can also increase the resistance to weather, heat, chemical agents, and sunlight (UV radiation). Other pigments are incorporated to provide fire retardancy. *Anticorrosive pigments* are added for promoting the corrosion resistance of the metal substrate. Usually only the primer is formulated with them because it is the layer directly in contact with the metal. Red lead (Pb_3O_4) was used for decades to protect steel structures with great success until being prohibited. Chromates (zinc yellow or zinc basic chromate, strontium chromate, and lead silicochromate) were also successfully used for protecting steel, zinc, and aluminum alloys, but they have also been banned, recently. Anticorrosive pigments in use today are zinc phosphate and modifications, orthophosphates and polyphosphates of calcium, strontium, aluminum, and magnesium.

Extenders are mineral particles with weak opacity and no coloring ability. They are incorporated in the paint partially replacing the more expensive pigments thus reducing the price of the formulation. Nonetheless, they are able to improve paint characteristics, such as wear, chemical and fire resistance, thermal and acoustic isolation, adhesion, and nonslip properties, depending of the type of extender. They also contribute to rheological

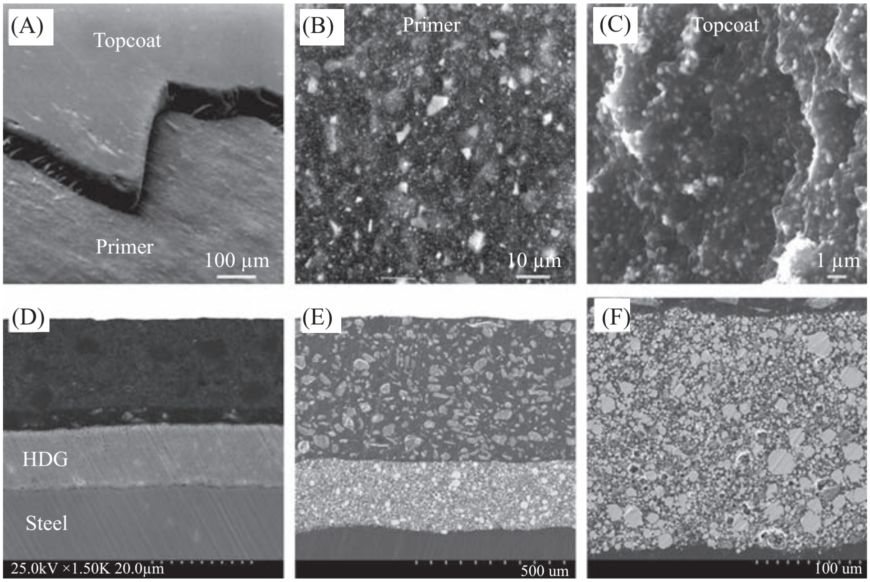

FIGURE 11–3 Examples of organic coatings: (A) water-borne white glossy alkyd topcoat applied over water-borne styrene–acrylate anticorrosive primer, (B) detail of the primer with small pigments and larger fillers, (C) detail of the topcoat with only small TiO_2 particles well dispersed in the binder, (D) galvanised steel with a primer and a PVC–plastisol topcoat, (E) ZRP and a thick topcoat used in ship hulls and immersed structures, and (F) detail of the ZRP with the zinc powder particles in electrical contact for efficient cathodic protection. *PVC*, Polyvinyl chloride; *ZRP*, zinc-rich primer. *HDG*, hot dip galvanized steel.

properties, in particular the anti-sedimentation of dispersed solid particles. *Solvents* are employed to dissolve the binder. *Thinners* are related compounds but only partially miscible with the binder, being used to facilitate the paint application and to clean the material. The variety of chemical compounds used as solvents and thinners are presented in Table 11–2.

Additives are compounds added in small quantities with the objective of facilitating the production, correct defects, or promote specific properties. Important examples are:

Wetting and *dispersing* agents help the pigment dispersion in the liquid phase and its stabilization to avoid flocculation, color flotation, phase separation, and sedimentation. *Defoamers*, as the name implies, are used to avoid foam during manufacturing and later, during the paint application. *Thickeners* and *rheology modifiers* are used to optimize rheological properties, in particular viscosity, which is of paramount important in liquid paints, during storage, application, and formation of a uniform and levelled film without sagging. *Dryers* catalyze the reaction of oils with atmospheric oxygen decreasing the drying time of oil containing paints from days to just a few hours. *Biocides* (bactericides, algaecides, and fungicides) are necessary in water-borne paints to decrease the proliferation of bacteria, fungi, and algae, in the storage bucket and in the architectural walls where they are applied.

Table 11–2 Paint components.

Component	Examples	
Resins (and other film forming agents)	Epoxy, polyurethane, polyester, vinyl, acrylic, alkyd, polyvinyl chloride, ethyl silicate, silicone, melamine–formaldehyde, urea–formaldehyde, phenol–formaldehyde, chlorinated rubber, cellulose esters, shellac, Tung oil, and linseed oil.	
Pigments	Titanium dioxide, zinc oxide, zinc sulfide, iron oxide (red, brown, black, and yellow), carbon black, chromium oxides, white lead oxide, lead chromate, cadmium sulfide, organic pigments (azo and diazo pigments, phtalocyanines, dyphenylmethane, antraquinones, etc.)	
Extenders	Talc, mica, barite, dolomite, calcite, kaolin, silica, diatomaceous silica, and anhydrous calcium sulfate.	
Solvents	Alcohols (methyl, ethyl, isopropyl, and isobutyl), esters (ethyl and butyl acetate), ketones, (acetone, methylethylketone, isobuthylketone, and cyclohexanone), glycol ethers, aliphatic, and aromatic hydrocarbons.	
Aditives	*Wetting and dispersing agents*	Polycarboxylic acid salts, esters and polyesters, polyacrylates, phosphoric acid ester, polyalkoxylates, polyamines, polyamines, fatty acids, and siloxanes.
	Defoamers	Hydrocarbons, oils, siloxanes, and micronized hydrofobic silica.
	Thickeners	Cellulose derivatives (hydroxyethylcellulose), polysaccharides, polyurethanes, polyacrylates, pyrogenic silica, and lamellar clays (laponite and bentonites).
	Dryers	Naftenates and octoanoates of cobalt, manganese, zirconium, lead, calcium, and strontium.
	Anti-skins	Metylcetoxime.
	Biocides	CMIT, MIT, formaldehyde, bronopol, zinc pyrithione.
	Flash-rust inhibitors	Sodium and ammonium benzoate, sodium nitrite.

CMIT, Methylchloroisothiazolinone; *MIT*, methylisothiazolinone.

In maritime paints they are used to control biofouling in ship hulls and in underwater structures. *Corrosion inhibitors* are different from anticorrosive pigments. They are added to water-based coatings to avoid corrosion in the can and flash-rust of the metallic substrates while the coating is still wet.

11.6.3 Corrosion protection by organic coatings

Organic coatings provide corrosion protection by two main mechanisms: barrier effect and active action through anticorrosive pigments. The barrier effect is the most obvious role of a protective coating. By isolating the substrate from the environment it hinders the contact of the metal with water and oxygen. However, paints are not defect free and contact always exists. Under these circumstances the resistance to the flow of ions between anodes and cathodes become the most important factor in retarding corrosion [44]. Anticorrosive primers usually contain anticorrosive pigments which are in its majority sparingly soluble corrosion inhibitors. One exception is zinc powder which protects iron and steel by cathodic protection.

11.6.4 Degradation of organic coatings

Organic coatings degrade like any other polymeric material [43,45]. UV light breaks chemical bonds in the polymeric binder and depending on the pH and temperature, hydrolysis and oxidation reactions can occur. Physical degradation includes abrasion, cracking by mechanical impacts, and crazing at low or high temperatures [44]. When the paint is applied to a metal substrate corrosion occurs in pores and defects. The most common forms of degradation in painted metals are blistering, cathodic delamination, and filiform corrosion. *Blisters* are formed when the coating loses adhesion to the substrate, accumulating water, and facilitating the progress of corrosion [46]. *Cathodic delamination* is the detachment of the paint from the metal substrate in cathodic areas. The oxygen reduction leads to local high pH which attacks the polymer and the bonding of the paint to the substrate. *Filiform corrosion* appears in the form of small filaments, in paints applied to salt-contaminated steel or aluminum alloys exposed to humid environment [46].

11.7 Environment and health concerns

The coatings and surface treatment industries have been facing tremendous challenges in the last years for substituting well-established technologies due to environmental and health concerns.

11.7.1 Volatile organic compounds

Until recently, the paint market was dominated by solvent-based systems, most of them easy to produce and to apply. However, these paints possessed about 60%–70% in mass of organic volatile content that was released to the atmosphere. This amount was even higher counting with the thinner used for paint application and for cleaning the material. The volatile organic compounds (VOCs) react in the atmosphere with sunlight to produce tropospheric ozone and smog, which have been associated to respiratory, allergic, and immune effects. The paint industry was a major anthropogenic source of VOC, together with motor vehicle exhaust and industrial emissions. Government regulations limited the amount of VOC in paints and the industry responded with water-borne systems, high-solids, powder coatings, electrophoretic, and radiation curing coatings.

11.7.2 Lead pigments

White lead, $2PbCO_3 \cdot Pb(OH)_2$, red lead (Pb_3O_4), and chrome yellow ($PbCrO_4$) were among the most used pigments in paints. However, since the end of the 19th century that lead is known as a highly poisonous metal when inhaled or swallowed. It is a neurotoxin, mimics calcium, and can lead to damage of the brain, kidneys, and ultimately, death.

11.7.3 Chromates

A significant part of the corrosion protection has been played by chromates, either in the form of pigments in protective paints, as soluble inhibitors in recirculating systems or in conversion coatings. In spite of its unmatched properties, chromates are associated to health and environment issues. The investigation about the toxicity and carcinogenicity of chromate ions have been made through: (1) epidemiologic analysis of workers in sectors manipulating these compounds, (2) in vivo studies reproducing in animals the same tumors found in humans, (3) in vitro experiments with single cells and unicellular organisms to observe the effect on cellular reproduction and genetic activity [47–51]. Results showed the hexavalent form to be carcinogenic, mutagenic, and teratogenic, but were inconclusive regarding Cr(III) and Cr(0). The risk of chromium compounds to human health and other living organisms, forced the prohibition.

11.7.4 Biocides and antifouling agents

Mercury and arsenic compounds, and organotins, were very effective antifouling agents that have been prohibited due to adverse environmental and health risks. The alternatives in use today include metallic copper, cuprous oxide, cuprous thiocyanate, copper pyrithione, chlorothalonil, methylchloroisothiazolinone, methylisothiazolinone, dichloro–octyl isothiazolin, thiram, zinc oxide, zinc pyrithione, and thiocyanomethylthio–benzothiazole. None has the performance of the previous products.

11.8 New systems

The legislation emanated to meet environment and health concerns has forced the industry to look for alternative systems. Due to the legal restrictions, many products market today have worst performance compared to past counterparts. This is the price for having a safer and greener planet. Yet, intense research and development is underway to find better systems. The most representative are now briefly described.

11.8.1 Thin films and pretreatments

11.8.1.1 Sol–gel

Sol–gel coatings based on inorganic zirconia, silica, and ceria were among the first attempts to use sol–gel coatings as corrosion protective layers against corrosion in different metals [52–58]. These coatings have good adhesion to the metallic substrate by forming covalent bonds at the metal/coating interface. However, inorganic sol–gel coatings are prone to crack, thereby limiting the protective effect. Contrasting with inorganic sol–gel, hybrid sol–gel films combine the properties of polymeric materials (low density, elasticity, and compatibility with organic coatings) with those of ceramic-like materials (increased scratch resistance, durability, and adhesion). These systems can be prepared as thick and crack-free coatings [59]. Furthermore, the wide variety of precursors that can be used, namely organo-modified silanes, allows the development of systems with varied chemical reactivity, tailored compatibility, and wetting properties [60].

The use of corrosion inhibitors to provide active corrosion protection has been investigated in sol–gel-coated substrates. The simplest approach corresponds to the direct addition of inhibitors which do not react with the sol–gel matrix and are released by diffusion when water penetrates the sol–gel matrix [61]. Instead, the inhibitor can react with sol–gel matrix being chemically bonded or interact with organic functional groups or the inorganic network. The number of works and the type of corrosion inhibitors used, ranging from inorganic to organic species is too broad to be referred in detail in this work. Among the most studied inorganic corrosion inhibitors in sol–gel coatings one can find cerium (III) salts [62–64], vanadates, and molybdates [60,62]. With respect to organic corrosion inhibitors compounds derived from azoles have been the focus of different works [65,66].

11.8.1.2 Conversion films based on rare earth ions

Other type of conversion coatings relies on the ability of rare earth elements to inhibit corrosion in aluminum alloys [67–70]. For that effect, rare earth compounds have been introduced into protective layers as conversion coatings [70,71]. The inhibition mechanism is attributed to the reaction of rare earth ions with the OH^- ions generated at the cathodic sites, which produces a precipitated oxide/hydroxide layer, covering the cathodic area and stopping its activity.

11.8.1.3 Conversion films of layered double hydroxides

Layered double hydroxides (LDHs) are anion-exchangers, consisting of positively charged layers of mixed metal hydroxides between which anions and water molecules are intercalated [72]. These materials are capable of ionic exchange. LDHs are therefore capable of releasing of anionic corrosion inhibitors (e.g., vanadates, molibdates, nitrite) and entrap aggressive species (chloride, sulfate). The direct growth of LDH pretreatment layers on the surface of different substrates has been a topic of intensive research in recent years [73–76], following the early works of Buchheit and colleagues [75,76]. In spite of the attempts to impart active corrosion protection, the controlled release of inhibitors had not been proved until the works of Tedim et al. [77–79]. The strategy followed in these studies was to intercalate vanadates as corrosion inhibitors which are then released by anion-exchange. XRD analysis of the substrates showed patterns similar to LDH powders and corrosion protection of the substrate was found to occur for long immersion times, even in the presence of defects [78]. Recently, a strategy consisting of the growth of LDH nanoplatelets containing corrosion inhibitors in TSA anodized layers has been reported [80]. In this manner, LDH platelets can load and release corrosion inhibitors by ion-exchange. An identical strategy was carried out in films formed by plasma electrolytic oxidation (PEO) in an attempt of reducing the intrinsic porosity of these layers [81,82].

11.8.1.4 Plasma electrolytic oxidation

PEO, also known as electrolytic plasma oxidation, spark anodizing or micro-arc oxidation, is an anodizing process in which much higher potentials (>200 V) are used, usually in AC regimen, to exceed the dielectric breakdown potential of the growing oxide film, which produces spark discharges and gas evolution. The discharges create localized plasma reactions, with local high temperature, and pressure that modify the oxide layer. Usually the layers are well adherent, thick, hard, and porous. Direct applications can be wear resistance, electrical insulation, and heat shielding. It has been applied mainly with aluminum, magnesium, and titanium [83–85].

11.8.1.5 Atomic layer deposition

With this deposition method perfectly uniform coatings can be deposit around particles, in porous materials, and inside deep channels [86,87]. The method is based on the sequential reaction of the surface with two chemical precursors, one at a time. The process starts with the introduction of the material to be coated in a chamber which is purged with inert gas. Then a precursor is introduced in the chamber and the molecules react with the surface creating a (sub)monolayer. The reaction is self-limiting because no further reaction takes place once the (sub)monolayer is formed. The chamber is purged with inert gas and the second precursor is introduced, which reacts with the sub(monolayer) creating the first monolayer of the film to be deposited. The surface film can grow in a controlled way by repeating these steps until the desired thickness. The film thickness can be between 1 and 500 nm and the control of film growth as fine as 0.1nm per monolayer.

11.8.2 Smart coatings

Smart coating is the designation given to functional coatings with ability to respond to changes (so-called triggers) in the environment. Other designations for these systems include stimuli–responsive or feedback active coatings. Since the field of smart coatings is too broad, this section focuses on coatings with ability to provide active corrosion protection by controlled release of corrosion inhibitors (e.g., pH, presence of aggressive species, electrochemical potential, and mechanical action) [88–95].

11.8.2.1 Additives in organic coatings for controlled release

The direct addition of soluble corrosion inhibitors to coating formulations can be challenging: detrimental interaction between them and the other coating components, spontaneous leaching of the active species thereby causing lower protective performance, reducing the service life of structures and having also environmental issues associated with inefficient release of species with some degree of toxicity into the environment. To overcome these limitations, several research groups and leading industries have been focusing on the immobilization of corrosion inhibitors within hosting structures with ability to store and release in a controlled way these active species, ideally only when specific conditions associated with coating degradation and/or corrosion onset are verified [96]. These hosting structures are generally referred to as micro/nanocontainers. Depending on their structure, composition and properties, different species can be immobilized and later released by desorption, pH change, ion-exchange or mechanical damage. Several works in the literature describe oxide nanoparticles as host structure to immobilize corrosion inhibitors. One example is the use of ZrO_2 nanoparticles modified with Ce^{3+}, subsequently added to sol–gel films [97]. The dependence of permeability of polyelectrolytes on pH can also be used to impart a pH-triggered release of corrosion inhibitors. In the early works of Shchukin and Zheludkevich, different types of carriers were designed following this approach, including silica nanoparticles [98] and halloysite nanotubes [99] coated with polyelectrolyte shells. Another way of immobilizing and releasing corrosion inhibitors relies upon the use of ion exchangers. Several works describe the use of cation exchangers such as bentonites loaded with Ca^{2+} or Ce^{3+} to render corrosion protection [100,101]. Another class of ion exchangers widely studied are LDHs. The advantage of an anion exchanger when compared to a cation homologue is that the former responds to the presence of aggressive species such as chlorides, while the latter are responsive to less harmful species in what corrosion concerns (e.g., Na^{+}). In this way, LDHs play a double action: liberation of corrosion inhibitors and capture of aggressive species. There are several works in the literature describing the benefits of using LDHs as nanocontainers for different corrosion inhibitors [102–104]. Another important trigger from a corrosion standpoint is the mechanical degradation of coatings during service life due to scratches, stone-shipping, and other abrasive related processes which can induce defects on coatings. To circumvent the effect of these processes, the use of polymeric microcapsules enclosing different healing agents and releasing them upon mechanical rupture has been proposed [105] (Fig. 11–4).

11.8.2.2 Polymer reservoirs

In this section, we describe some systems with controlled release ability, intrinsically associated to the polymeric matrix, namely conducting polymers and biopolymers.

Electrically conducting polymers based on π-conjugated systems have to possibility of conducting charge depending on the doping state, arising from the creation of charge carriers which move in the delocalized π-systems. Examples of these systems include

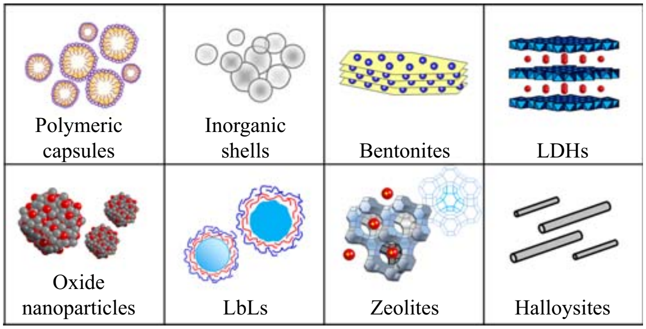

FIGURE 11–4 Examples of micro/nanoreservoirs.

polypyrrole and polythiophene. Conducting polymers present a set of unique properties not available to insulating coatings mentioned earlier which may be used in corrosion protection [106]. There are several works which propose different corrosion protection mechanisms for conducting polymers, namely barrier effect [107–109], displacement of interface [110], and ennobling effect [111]. Another mechanism that can be associated with conducting polymers is the controlled release of corrosion inhibitors as dopant ions used to compensate charge in oxidizing states. It means that when damages occur in the oxidized polymer the ingress of electrolyte will allow establishment of a galvanic couple between the oxidized polymer with the underlying metal causing a reduction of the former with release of the inhibiting dopant ions. Therefore this can lead to the self-healing of defects triggered by the electrochemical potential [112–114].

In another direction, the search for environmentally sustainable solutions capable of replacing more toxic and harmful materials have prompted scientists to look for the corrosion inhibiting properties of naturally occurring, benign polymers. Chitosan (CTS) is a biopolymer obtained from the deacetylation of chitin, the second most abundant polysaccharide after cellulose. CTS is low toxic, biodegradable, and biocompatible [115]. In a work by Kumar and Buchheit [116], vanadates were immobilized in CTS to be released upon local pH changes associated with the onset of corrosion in AA2024-T3. However, one of the challenges in using CTS in corrosion protection is its high degree of permeability to water. To circumvent this drawback Zheludkevich et al. used CTS as reservoir for Ce^{3+}, coated with a hybrid sol–gel layer [117]. While the CTS had the release ability, the sol–gel coating conferred the barrier effect that CTS lacks. The attempt to confer higher barrier properties to CTS was carried out in subsequent works functionalizing CTS within its matrix as well as at the interface, thereby acting on the wetting properties of the coated substrate [118,119]. Other groups tried to improve the corrosion properties of CTS coatings by cross-linking of CTS [120] and polymer blends [121] and nanocomposites [122].

11.8.2.3 Additives for biofouling control

The use of additives with controlled release ability can be extended to other functionalities. One of the major challenges associated with maritime transportation is biofouling. The growth of algae and barnacles in the hull surface can increase the roughness which may lead to increase in fuel consumption up to 40%. At the same time, the used biocides are still quite toxic and its continuous leaching to the aquatic environments limits on one hand a long-term performance of existing coatings whereas at the same time has some environmental issues associated. In this context, encapsulation of biocides can prevent spontaneous leaching and deliver the compounds with more appropriate leaching rates. Several works available in the literature report different strategies for encapsulation of biocides and their biological activity [123–125]. However, the environmental impact end ecotoxicity effects associated with new materials must be considered. Recently several works have shown the decrease in toxicity when commercial biocides and corrosion inhibitors are immobilized in certain nano-engineered materials, showing the benefits of carefully selecting and designing materials for controlled release technologies [126,127].

11.8.2.4 Early detection of corrosion

Another issue that controlled release technologies can help solving is the early detection of degradation in general and of corrosion in particular. For instance, current nondestructive inspection techniques used for structural health monitoring in the aeronautical industry are complex and expensive. Literature reports the use of microcapsules loaded with fluorescent additives [128] and mesoporous silica loaded with pH indicators [129,130] to detect corrosion processes in coated substrates. Nevertheless, there are still some challenges to be overcome, namely the correlation between signal and degree of degradation. In this sense, the combination of several spectroscopic and electrochemical techniques is relevant to assist on the adjustment of coating formulations, so that detection and variation in spectroscopic signals correspond to specific levels of degradation, enabling the users to act at earlier stages, and lowering the associated maintenance costs.

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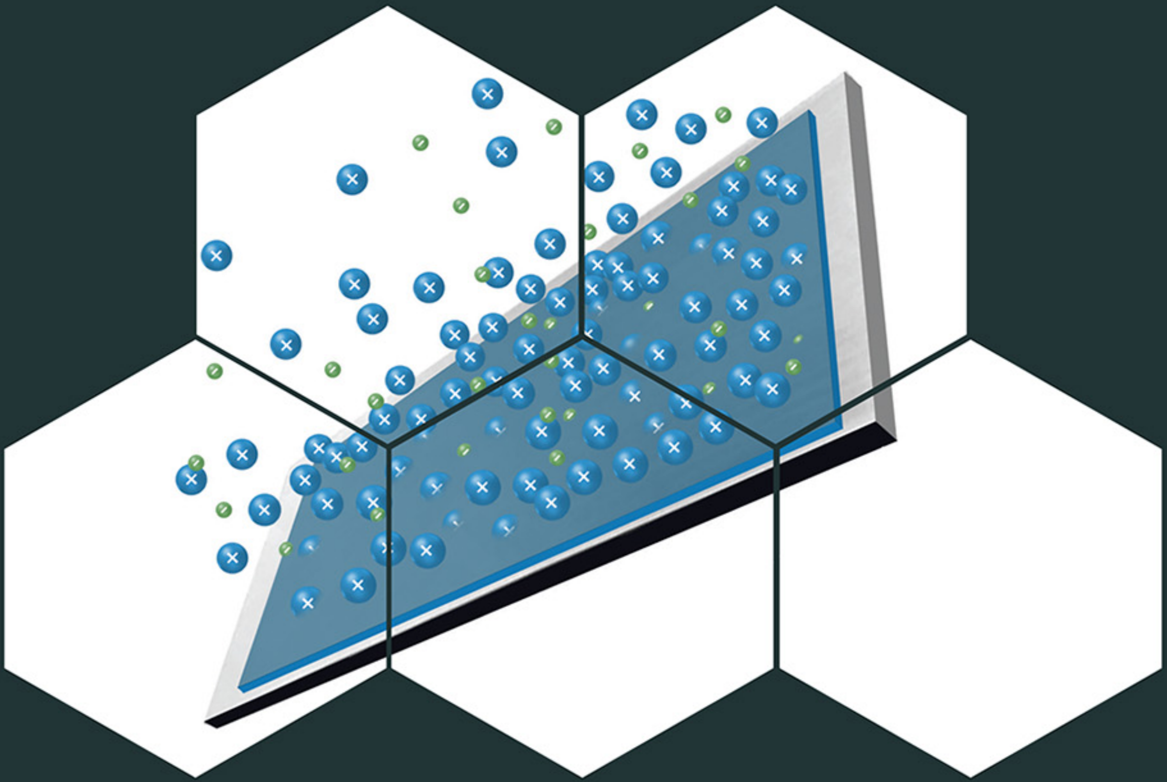

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Volume 1

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