Christian Byrne[1,2,], Oriana D'Alessandro[1,2]*

[1]Department of Chemistry, Faculty of Exact Sciences, National University of La Plata, La Plata, Argentina [2]CIDEPINT (CICPBA-CONICET-UNLP), La Plata, Argentina

Review paper
ISSN 0351-9465, E-ISSN 2466-2585
https://doi.org/10.62638/ZasMat1649

Zastita Materijala 67 ()
(2026)

Anticorrosive paints: A comprehensive review of fundamentals, formulation, degradation, and evaluation

ABSTRACT

This comprehensive review provides a vital reference for researchers and professionals by consolidating current knowledge on the fundamentals, components, formulation, manufacturing, and advanced evaluation techniques of anticorrosive paints, which are essential for combating the substantial global economic costs of metallic corrosion. It details the physicochemical composition of paints, covering binders, the shift to sustainable water-based solvents, and various pigments, with a special emphasis on the evolution from toxic chromates to modern, eco-friendly alternatives like phosphates. The review examines critical formulation aspects, such as Pigment Volume Concentration, and explains the crucial role of proper surface preparation for adhesion. Furthermore, it analyzes key under-coating corrosion mechanisms like blistering and anodic undermining, and explores diverse evaluation methods, highlighting Electrochemical Impedance Spectroscopy as a non-destructive tool for assessing coating degradation. Ultimately, this work underscores the multidisciplinary nature of anticorrosive paint design and the continuous need for research toward more efficient and sustainable formulations.

Keywords: *Anticorrosive paints, Corrosion, Pigments, PVC, Surface preparation, Electrochemical evaluation.*

1. INTRODUCTION

Corrosion is a pervasive and spontaneous phenomenon, representing the natural degradation of metallic materials back to their more stable, oxidized forms. This destructive process exacts an enormous economic toll, with global studies estimating corrosion-related costs at 3.0-3.5% of the Gross Domestic Product—a staggering U$S 1.8-2.5 trillion annually [1,2]. These figures encompass not only direct losses from repairs and replacements but also indirect costs like reduced efficiency and the investment in control measures. While thermodynamics dictates that corrosion is an inevitable process, its kinetics can be effectively controlled. Anticorrosive paints are a primary defense against this degradation. These specialized coatings are fundamentally designed to shield metallic surfaces, protecting the structural integrity, safety, and aesthetics of assets across industries like marine, infrastructure, and automotive. By acting as a crucial barrier, anticorrosive paints significantly extend material lifespan and reduce costly maintenance, making them indispensable in managing this widespread and economically impactful phenomenon.

2. COMPONENTS OF AN ANTICORROSIVE PAINT

From a physicochemical perspective, paint is a dispersed system. It consists of a dispersion of a finely divided solid or mixture of solids (pigments) in a fluid medium known as the vehicle, which includes binders and solvents [3]. Binders are the film-forming agents, while solvents regulate viscosity and enable paint application. Pigments, on the other hand, impart specific properties to the paint, such as opacity, hardness, resistance to ultraviolet radiation and chemical agents, and, crucially, anticorrosive capabilities. Additionally, paints contain small proportions of other constituents called additives, which provide specific functionalities to the paint in its liquid state or as a dry film [3]. Fig. 1 illustrates the basic components of an anticorrosive paint.

Correspondence: Christian Byrne
E-mail: c.byrne@cidepint.ing.unlp.edu.ar
Paper received: 12. 12. 2025.
Paper corrected: 08. 05. 2026.
Paper accepted: 09. 06. 2026.

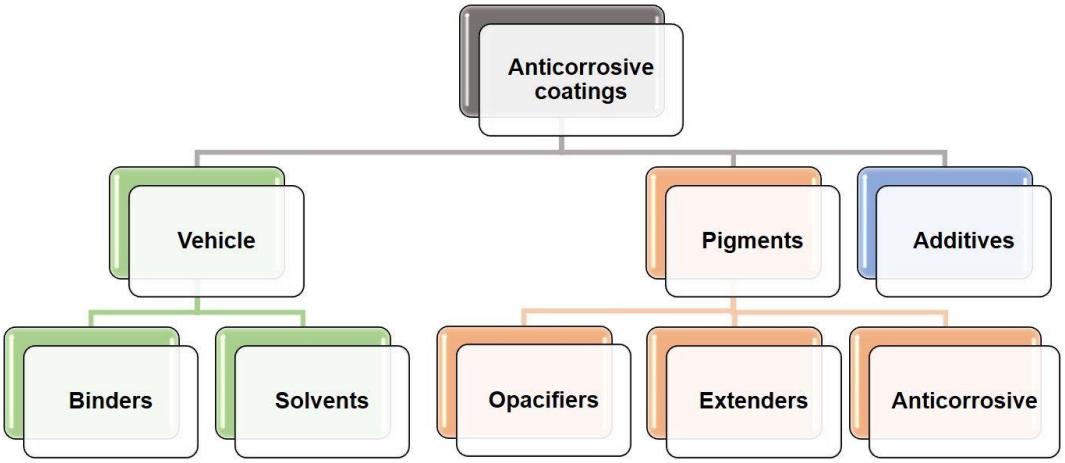

Figure 1. Schematic Representation of Anticorrosive Paint Components

2.1. Binders

The most important component of a paint formulation is the binder. The binder acts as the film-forming substance, responsible for the liquid-to-solid transformation that occurs when paint is applied as a thin layer [3]. Binders form the coating's matrix, the continuous polymeric phase in which all other components can be incorporated [3,4]. They are responsible for controlling the diffusion of water, oxygen, and electrolytes to the metal, maintaining pigments in intimate union within the dry film, and facilitating adhesion of the film to the substrate and between different paint layers [3]. Generally, binders determine the application method, drying and hardening behavior, adhesion to the substrate, mechanical properties, chemical resistance, and weather resistance [5,6].

Binders used in anticorrosive paints are almost exclusively synthetic organic polymers [7], commonly referred to as resins [8]. The resins most frequently employed in anticorrosive paint formulations include epoxies, polyurethanes, alkyds, vinyls, phenolics, and acrylics [9].

The formation of a solid, continuous, and adherent film from a freshly applied liquid coating can occur through either a physical or a chemical process [4-6].

In the physical process, known as physical curing or drying [4,5], the conversion from liquid material to a solid film occurs simply by the evaporation of solvents [2,4,5]. This primarily takes place in paints with high molecular weight polymeric binders, such as vinyl resins (polyvinyl chloride, polyvinyl chloride acetate, etc.) and some acrylic resins (polymethyl methacrylates) [1-3,5]. Films formed exclusively by this method are characterized by their ability to redissolve upon contact with solvents similar to those used in their original formulation [3].

The chemical process, termed chemical curing [4], involves low molecular weight monomeric binders that must react in situ to produce a crosslinked polymeric matrix [1,2,5], which is no longer soluble in the original solvent [3]. Chemical curing can be oxidative or reactive [4,6]. In oxidative curing, atmospheric oxygen reacts with the binder's low molecular weight monomers, thus inducing polymerization [2-6]. This reaction is often catalyzed by cobalt or manganese salts [3]. This type of curing occurs, for example, with alkyd resins. In reactive curing, a three-dimensional polymer network is formed by combining relatively low molecular weight components through polymerization, polycondensation, or polyaddition reactions [5,6]. If this curing occurs even at ambient temperature, the binder components must be kept separate and mixed only shortly before application, thus constituting two-component systems.5 Consequently, these paints are generally formulated in two packs: one containing the paint vehicle with dispersed pigments (base) and the other containing the curing agent for copolymerization (converter). Examples of such binders include epoxy and polyurethane resins [1,2,4,5].

In practice, solid film formation rarely occurs through a single process. With solvent-based paints, the physical process of solvent evaporation (drying) always precedes chemical curing [5,6]. Depending on the binder system's composition, physical and chemical processes can occur simultaneously, and various chemical curing mechanisms may proceed concurrently or consecutively [5].

2.2. Solvents

Solvents are primarily used to facilitate the manufacturing and application of paints [4]. Generally, solvent mixtures are employed, which

typically contain a resin solvent along with diluents that, in addition to thinning the product, help reduce manufacturing costs and ease application [10].

The most common solvents used in paint formulations, such as aliphatic hydrocarbons, aromatics, alcohols, ketones, esters, ethers, and glycols, belong to the group known as volatile organic compounds (VOCs) [3]. The most widely used aliphatic solvent is mineral spirits, a mixture of petroleum distillates primarily used with alkyd resins. The most common aromatic solvents are xylene and toluene, which are cost-effective and suitable for use with resins like epoxies.Various regulations aimed at reducing VOC emissions have compelled the coatings industry to explore different strategies, including the use of water as a solvent [2,10]. This necessitates innovation in paint manufacturing technology, as water, due to its polar characteristics, solubilizes few resins. Despite this, water-based resins are already available on the market, enjoying good acceptance and performance. Resins for water-based paints are primarily composed of polymeric particles dispersed in water and stabilized by emulsifying and thickening agents.

2.3. Pigments

Pigments are composed of finely divided particles. They are insoluble in the vehicle and are used to impart specific properties to the paint, such as color, opacity, corrosion inhibition, and resistance to ultraviolet (UV) radiation. Pigments vary in size, shape, wettability, composition, chemical reactivity, UV radiation absorption, and refractive index, among other characteristics. Pigments with a high refractive index impart opacity (opacifiers or hiding pigments) to the film, while those with a low refractive index (similar to that of the resin) produce transparent films. Pigments can be classified in several ways, such as by origin (natural and artificial), by nature (mineral and organic), and by function (opacifying or hiding, extenders, and anticorrosive).

2.3.1. Opacifiers or Hiding Pigments

These pigments possess a higher refractive index than the resins used, causing light entering the pigmented film to be refracted multiple times before reaching the substrate. The ultimate effect is that the substrate becomes invisible. Examples within this group include iron oxide, carbon black, and titanium dioxide.

Iron oxide pigments are extremely important due to their excellent hiding power, weather resistance, insolubility in water and organic solvents, alkali resistance, and toxicological inertness [5,10]. They constitute the most widely used group of colored inorganic pigments in the paint industry. The color range includes red (α-Fe_2O_3, hematite), black (Fe_3O_4, magnetite), yellow (α-FeOOH, goethite), and orange (γ-FeOOH, lepidocrocite) [5].

Carbon black consists of carbon particles exhibiting an intermediate crystallography between graphite and amorphous carbon. These particles are nearly spherical and very small, with an average diameter ranging from 0.005 to 0.5 μm. They are manufactured through a variety of partial combustion and/or cracking processes of petroleum derivatives or natural gas [3,8]. Carbon black pigments offer several advantages compared to other inorganic and organic black pigments, including high opacity and tinting strength, color stability, thermal stability, and resistance to solvents, acids, and alkalis [11].

The white pigment par excellence utilized by the paint industry is titanium dioxide (TiO_2) [8,10]. Of the three known crystalline phases or forms, only rutile and anatase are synthetically produced and commercially used [12]. Thanks to its high refractive index (rutile n = 2.73, anatase n = 2.55), titanium dioxide's light scattering capability surpasses that of other white pigments, imparting excellent hiding power [3,5,8]. Furthermore, TiO_2 has moderate oil absorption, is easy to disperse, and exhibits low toxicity [10,13]. Rutile is much more widely used than anatase as it provides greater opacity and is more resistant to chalking upon outdoor exposure [14].

2.3.2. Extender Pigments

These pigments are economical and were originally used in the paint industry to increase volume and reduce the cost of the final product, which is why they are also referred to as fillers [3,5,6,10]. They are used to impart certain characteristics to the film such as hardness, adhesion, gloss, and durability. They also play a significant role in stabilizing rheological and mechanical properties [8]. They possess a refractive index similar to that of resins, thus contributing little to hiding power [5,8,14]. Based on their chemical nature, they are classified as carbonates, sulfates, and silicates.

Calcium carbonate can be used in its variants of calcite, chalk, or precipitated/synthetic calcium carbonate. Its disadvantage is alkalinity, which reduces the paint's acid resistance.

Among a large number of sulfates, only barytes (barium sulfate) is used as an extender in the paint industry. Barytes is resistant to water, acids, bases, corrosive gases, heat, and light, and is extremely insoluble in water, making it highly useful for paints requiring chemical resistance. Additionally, it imparts hardness to the film, making it an excellent

pigment for protective coatings [8,10]. Moreover, it has very low oil absorption and can be used in significant quantities without affecting paint viscosity [12]. However, its high density necessitates careful control of the paint's rheological properties to prevent sedimentation [10].

Three main silicate-derived extenders are distinguished: talc, kaolin, and mica [12]. These lamellar structured minerals are particularly suitable for corrosion protection systems as they provide better surface coverage compared to particles of other shapes [5,15]. Talc is chemically a natural magnesium silicate. It wets and disperses easily, and its presence in small quantities imparts anti-settling properties to paints. Mica is a natural mineral chemically consisting of potassium aluminum silicate. Due to its particular structure with a high aspect ratio, it is very effective in reducing film permeability, as the plate-shaped particles accumulate to form pigment layers within the dry film, forcing water and oxygen to follow a longer path through the binder to reach the metal [5-8].

2.3.3. Anticorrosive Pigments

As their name suggests, these materials are used to provide active protection against metallic corrosion. According to various authors, they can be subdivided into galvanic pigments and inhibitor pigments [4,6,10,12]. Galvanic pigments act as sacrificial anodes. These are small metallic particles of a metal less noble than the substrate, typically using zinc-based or zinc alloy primers for steel protection [4,10,12].

Inhibitor pigments are partially water-soluble and function by slowly releasing reactive species within the film, near the metal surface [10]. These species reduce the corrosion rate of the metallic substrate by interacting with it. As a result, reaction products are formed, into which the inhibitor can become incorporated. Inhibitor pigments must meet several conditions, although it is challenging to find one that fulfills all necessary requirements [15]:

- They must have low solubility to avoid rapid leaching from the paint film by permeating water. Conversely, solubility must be sufficient to supply the inhibitory species that directly interact with the base metal or repair defects in the protective film. Generally, organic inhibitors are more soluble and tend to leach from coatings much faster than inorganic inhibitors. Furthermore, both the polymeric binder matrix and the barrier properties of extender pigments also influence the inhibitor release rate. Inhibitor release from a wash primer is minimized by the barrier properties of the upper layers of the paint scheme.
- They must react with the metallic surface to yield a product that is as insoluble as possible over a wide range of pH and temperature.
- They must form a film at the metal/paint interface that does not diminish adhesion between the paint and the metal, and whose composition and structure do not change over time.
- They must be capable of decreasing the rate of the two most important cathodic reactions, oxygen reduction and proton reduction, although the latter is less likely beneath a coating.
- They must be effective over a wide pH range, as local pH conditions at the metal/paint interface can reach extreme values due to the very small volume of water present. It is desirable for the inhibitor to prevent the corrosion reaction before a highly concentrated solution forms, whose osmotic pressure could lead to further water incorporation.

Over the years, the paint industry has developed, commercialized, and utilized a considerable number of inhibitor pigments [10].

Chromate-based pigments contain hexavalent chromium. Despite being less popular today due to their harmful effects on the environment and health [7,12], these pigments are still used in anticorrosive paints and wash primers for aerospace, automotive, and military applications. Their use persists because the chromate ion is considered one of the most effective passivating agents known, providing outstanding protection against corrosion on metal surfaces [7]. The most common chromate-based inhibitor pigments are zinc tetroxychromate, zinc potassium chromate, and strontium chromate [7,12]. The first of these is the traditional anticorrosive pigment used in two-component polyvinyl butyral resin-based wash primers [7]. Current data indicate that Cr(VI) exposure causes respiratory tract cancer [10]. The mechanism by which the disease develops is believed to involve the reduction of Cr(VI) to Cr(III) and the generation of reactive intermediates. While Cr(VI) is the species preferentially entering cells, Cr(III) is the metabolically active agent capable of binding to nucleic acids, which can induce mutagenesis [16].

Other widely used inhibitor pigments include lead compounds, especially red lead or minium, Pb_3O_4 [7,10]. Lead compounds are highly toxic and affect almost all living organisms, with children and fetuses being particularly susceptible to lead poisoning. Lead poisoning primarily occurs orally from contaminated food or water, paint chips, and ceramics that children might ingest, lead compounds from industrial emissions, etc. The

most significant toxic effects are observed in the nervous system, gastrointestinal system, reproductive system, and renal function [17].

International regulations for human health and environmental protection, such as the IRAM 1221/18 standard and European Parliament Regulation 1907/2006, have restricted the use of chromates and lead compounds. This has compelled paint manufacturers to develop, evaluate, and adopt less toxic alternatives. Among these alternatives is the extensive group of phosphates, which can be classified into zinc phosphates and zinc-free phosphates [7].

Zinc phosphates are widely used with a variety of binders. These pigments can also be grouped into three generations, roughly following their chronological development [7]. The first generation consists of zinc phosphate itself, $Zn_3(PO_4)_2 \cdot 4H_2O$, which has the limitation of being very sparingly soluble in water [7]. In the second generation, modifications were made to increase solubility or introduce other functional groups that could also act as inhibitors [7]. An example of a second-generation phosphate is the commercial pigment Nubirox 106, an organophilized zinc phosphate and molybdate. Organophilization involves applying an organic surface treatment to the particles (using an organic titanate), which improves the continuity between the inorganic pigment and the surrounding organic binder [18]. Furthermore, the molybdate contributed by this pigment is a passivating inhibitor that acts synergistically with the phosphate [18]. The third generation of zinc phosphates includes polyphosphates (e.g., hydrated zinc aluminum polyphosphate) and silicate polyphosphates (e.g., hydrated zinc, calcium, aluminum, and strontium silicate polyphosphate) [19]. Among zinc-free phosphates, aluminum triphosphate dihydrate ($AlH_2P_3O_{10} \cdot 2H_2O$) and various polyphosphates or silicate polyphosphates can be mentioned [7,20]. Although phosphates do not exhibit the chronic toxicity associated with chromates and lead compounds, they have also been questioned because the anion can cause eutrophication in freshwater bodies, leading to excessive algal growth [21].

Other types of inhibitor pigments tested in anticorrosive coatings include molybdates [22,23], tungstates [24], borosilicates [25], and lanthanide-containing ion exchangers [26,27].

The use of organic inhibitor pigments in coatings has been explored, often in combination with inorganic inhibitors. These pigments encompass both synthetic varieties, such as benzoates and mercaptoazoles [28,29], and natural substances like tannins and plant extracts [30-33]. These organic compounds typically possess heteroatoms (like nitrogen, oxygen, or sulfur) or conjugated π systems within their molecular structure. These specific features provide electron-rich sites or delocalized electron clouds, which enable the compounds to adsorb onto or form coordination bonds with metallic surfaces, thereby facilitating their inhibitory action against corrosion [34].

2.3.4. Additives

Additives are generally defined as low-molecular-weight chemicals incorporated into the paint formulation in small quantities (between 0.05% and 2% by weight of the total formulation) to control the paint's properties both in the liquid state and after it has dried or chemically cured [3,5,7,10,12]. Each additive has a specific function. The wide spectrum of products includes [3,5,7,10,12]:

- *Surfactants and emulsifiers*: Alter surface tension, facilitating resin compatibility with water.
- *Wetting agents*: Surfactants that promote the wettability of solid surfaces.
- *Dispersing agents*: Surfactants that stabilize the system by keeping particles permanently separated.
- *Rheological agents*: Increase viscosity or provide thixotropy.
- *Adhesion promoters*: Improve adhesion between the polymer film and the substrate.
- *UV absorbers and stabilizers*: Protect coatings from ultraviolet light.
- *Driers*: Catalysts that accelerate the oxidative curing process.
- *Defoamers*: Surfactants that reduce surface tension and prevent or hinder foam formation.
- *Plasticizers*: Increase film flexibility.
- *Anti-settling agents*: Surfactants added to prevent sedimentation of high-density pigments.
- *Biocides*: Prevent the growth of fungi and other microorganisms.
- *Antifouling agents*: Prevent the accumulation of organisms on submerged surfaces.
- *Flash rusting inhibitors*: Completely soluble additives that prevent the rapid formation of superficial iron oxide stains in the case of water-based paints applied directly to freshly sandblasted steel.
- *Anti-skinning agents*: Prevent the formation of an insoluble layer on the surface.

3. FORMULATION OF ANTICORROSIVE PAINTS

In paint technology, the trend is to perform formulations by volume rather than by weight, as the latter approach is ineffective for studying formulation variables [8,15].

In anticorrosive formulations, the pigment volume concentration (PVC) has a significant effect on their properties. The PVC of a paint is the proportion of the pigment volume (Vp) relative to the total volume of the dry paint film, which is the sum of the pigment volume and the resin volume (Vr) [3,10,12]:

$$PVC = \frac{Vp}{Vp+Vr} \quad (1)$$

Fig. 2 illustrates how various properties of an anticorrosive paint change as a function of PVC [15]. It can be observed that an increase in PVC leads to a decrease in blistering tendency when the film is in contact with the corrosive environment, as well as a decrease in gloss. Furthermore, an increase in PVC entails an increase in the permeability of the dry film, which is associated with an increased degree of corrosion of the underlying metallic substrate. The curves for blistering, gloss, permeability, and substrate corrosion change their slope at a more or less defined point, known as the critical pigment volume concentration (CPVC). This concentration is termed critical because above and/or below it, the film's properties change drastically [1,3,8,10]. At the CPVC, a suitable balance among the involved properties is achieved. Up to this specific critical PVC value, increasing the pigment content does not drastically affect the substrate's anticorrosive protection. However, once this value is exceeded, the film's permeability to corrosive agents increases, reducing its protective capacity. Therefore, knowing this critical value is of utmost importance for correctly formulating an anticorrosive paint.

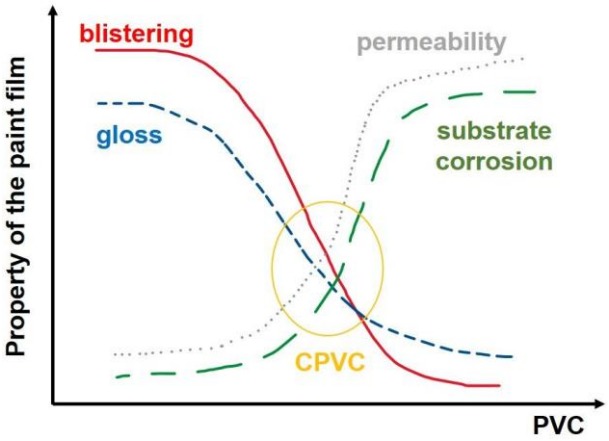

Figure 2. Properties of the paint film as a function of PVC

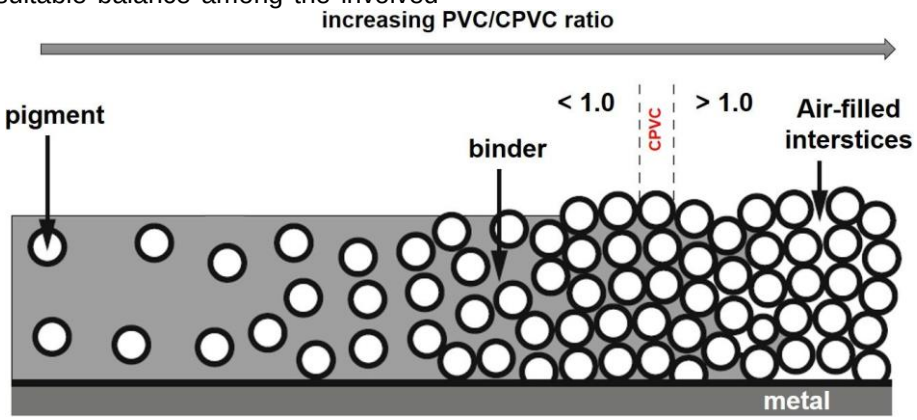

Figure 3. Schematic representation of a paint for different PVC/CPVC values

The PVC/CPVC ratio, also called reduced PVC [3,15], is the mathematical representation of the spatial structure of the dry film concerning pigment distribution and packing. As shown in Fig. 3, when PVC is less than CPVC, the pigment is completely coated with resin, and there is an excess of resin separating the pigment particles [8]. The film is glossy and impermeable. When the PVC/CPVC ratio equals 1 (i.e., PVC = CPVC), there is a sufficient amount of binder to coat the particles and fill all interstitial spaces [3]. Thus, CPVC is the condition where there is enough resin to satisfy the sorption demanded by the pigment (Vp) and to fill the interstices between individual pigment particles in a compact packing (Vb) [3,8]:

$$CPVC = \frac{Vp}{Vp+Vr+Vb} \quad (2)$$

If, however, PVC/CPVC is greater than 1 (i.e., PVC > CPVC), there is insufficient resin to fill all interstitial spaces. Under these conditions, the film becomes porous, with poor physical properties and reduced cohesion [3,8,15].

The coating's barrier properties are ideally maximized at the CPVC, but in practice, it is known that voids sometimes appear in real coating systems below CPVC. These air-filled voids form in local areas of the coating where the local PVC exceeds the CPVC, due to the non-uniform distribution of pigment and polymer throughout the

coating film [15]. These results help interpret the empirical observation that most anticorrosive coating formulations generally have an optimal PVC/CPVC ratio between 0.7 and 0.9 [15,27,35,36].

The CPVC value can be obtained experimentally by determining the corresponding oil absorption and the density of the pigment mixture [10]. Methods involving measuring paint or film properties, such as drying tension, reflectance, gloss, density, and adhesion, in a series of paints with different PVCs, can also be used to detect abrupt changes that indicate the CPVC [10].

4. PAINT MANUFACTURING

The fundamental aspects of the paint manufacturing process are the preparation of the vehicle and the dispersion of the solids (pigments) within this vehicle until the appropriate fineness is achieved. Dispersion is the process by which solid pigments are integrated into a liquid medium, composed of resin and solvent, to achieve a final product where the pigment is uniformly distributed. This process is one of the most important factors in paint preparation and comprises three stages [3,8,14]:

- *Wetting of particles*: This process involves displacing air and replacing it with the vehicle. The wetting of solid surfaces is facilitated by the use of surfactants known as wetting agents, which can be ionic or non-ionic.
- *Milling (Grinding)*: This is the mechanical breakdown process of agglomerated solids. Through milling, the size of pigment agglomerates is reduced to obtain an optimal particle size.
- *Dispersion Stabilization*: This final stage ensures a product capable of maintaining stability over prolonged periods without significant modifications or alterations in particle size and size distribution. A wetting agent, typically a short-chain surfactant molecule, can rarely prevent the re-agglomeration of primary particles after the dispersion process. Therefore, to prevent particle re-agglomeration, it is necessary to use a dispersing agent, which is a surfactant capable of forming a repulsive barrier (electrostatic and/or steric) around the particles.

A high degree of dispersion increases the durability and gloss of the paint film. It also enhances the hiding power (opacity) of white pigments and improves the tinting strength of colors. Furthermore, it improves particle flotation and reduces the tendency for sedimentation and film sagging.

Dispersion can be carried out in ball mills or high-speed disk dispersers.

A ball mill is a cylindrical container, horizontally mounted and partially filled with balls [3,8]. Generally, the balls are ceramic, and the mill's lining is porcelain. The paint components are added to the mill, which then rotates at a speed that causes the balls to lift on one side and then cascade down the other, imparting intense shear to the pigment aggregates. Balls of different sizes are used: smaller ones provide a maximum number of impacts and a maximum dispersion area, while larger ones provide greater interstitial space, allowing for the preparation of a larger quantity of paint. The optimal paint load is that which occupies the interstitial spaces. A smaller volume of paint would lead to the balls colliding with each other, causing unnecessary wear and inefficient dispersing action. Conversely, an excessively large load means that the excess will not be dispersed until randomly incorporated into the active portion, thus retarding the process [3].

Paint preparation can also be carried out using high-speed disk dispersers [3,8]. The dispersing system consists of a rotating drive head with a variable speed system, a hydraulic cylinder for vertical movement, and a shaft with a disk that rotates at high speed at its bottom. The disks have tabs around their perimeter, bent at an acute angle from the plane of the disk. The speed at which the disk rotates creates an area of turbulence with intense laminar product flow at the edge of the tabs [3]. This generates significant friction, producing shear and impact, which prevents the formation of agglomerates during the addition of solid components. At the junction of the disk and the shaft, the movement creates a vortex in the product, which is the main zone for the dispersion of solid elements. To achieve good dispersion, the container where the paint is prepared must be perfectly cylindrical, with a diameter 2-4 times the diameter of the disk [3,37]. Additionally, the recommended distance between the disk and the bottom of the container should not exceed the disk's radius [3].

5. SURFACE PREPARATION

Surface preparation exerts a decisive influence on the performance of the protective scheme. It is well-established that adequate preparation of the surface to be painted is essential to achieve effective and durable protection from the coating system. Surface preparation involves removing impurities that can interfere between the substrate and the first paint layer—such as oxides, greases, oils, dust particles, salts, and remnants of previous paint—using both physical and chemical methods

[5,38]. Additionally, some of these surface treatments impart roughness to the metal and increase the free surface area upon which the paint will be deposited, thereby also improving mechanical adhesion. Various surface preparation methods exist, and the selection of the appropriate one depends on the impurities present, the working environment, the type of paint to be applied, the initial condition of the base metal surface, and the size and shape of the structure. Some of these methods include:

(i) Solvent cleaning or detergent cleaning: Organic solvents, such as isopropanol, ketones, and aromatic or aliphatic hydrocarbons, are effective for removing oily dirt [2,5,38]. Manual cleaning, spraying, or immersion methods can be employed. Solvents and cloths become contaminated with this dirt and therefore must be changed frequently to avoid leaving oily residues on the surface [38]. Aqueous detergent solutions are also used to remove oily dirt. They are applied to metals by immersion or spray. After cleaning, surfaces are rinsed with clean water to remove the detergent [38].

(ii) Mineral acid cleaning (pickling): This involves immersing the metal in hot, strong inorganic acids to remove oxides formed on the surface during high-temperature manufacturing or corrosive attack. It is good practice to add suitable corrosion inhibitors to reduce metal loss during treatment, as well as hydrogen embrittlement [1,2]. Although phosphoric acid pickling is a relatively slow process, it offers the advantage of generating a thin metal phosphate conversion layer, which provides temporary corrosion protection and acts as a good base for subsequent coating [5,10]. After pickling, surfaces are rinsed with neutralizing solutions and finally subjected to a drying process [1].

(iii) Alkali cleaning: Alkaline aqueous solutions containing phosphates, carbonates, borates, and hydroxides are also employed to remove oily dirt, similar to the action of detergents. Following this cleaning step, the surfaces are thoroughly washed with clean water [38].

(iv) Mechanical cleaning methods: This includes scraping, wire brushing, and sanding [38].

(v) Abrasive blasting: Abrasive cleaning is performed only after oily dirt has been removed. Sandblasting or blasting with particles or grits of aluminum oxide, steel, cast iron, silicon carbide, glass, or polymeric materials (shot/grit blasting) can be used [1,2,7,38]. The abrasive material impacts the surface, removing contamination and increasing roughness, which creates a profile of peaks and valleys that serves for mechanical anchoring of the coating [2,10]. Sanded or abrasive-blasted surfaces are often covered with dust and must therefore be cleaned by wiping, solvent washing, or blowing air over them [5,7]. Likewise, it is crucial to apply the coating as soon as possible to prevent oxidation of the metallic surface, which becomes highly reactive after sanding or blasting [1,10].

(vi) High-speed water jetting: This method removes oxides, salts, paint residues, and other impurities but does not increase surface roughness [2,7,38].

6. APPLICATION OF PAINTS

Organic coatings can be applied to surfaces using various methods. The choice of method primarily depends on [4]:

- The purpose of the application: protection or decoration.
- The type of coating, its thickness, and the number of layers.
- The size and geometry of the object to be coated.
- The application location: in a conditioned room, a confined space, or outdoors.

6.1. Application

Brushes commonly feature a large number of bristles that retain paint in the spaces between them [8]. The selection of the appropriate brush (quality and size) should correspond to the dimensions of the surface to be painted and the desired finish. Key qualities of a brush include bristle quality (origin: animal, vegetable, or synthetic), length, quantity, mechanical properties, tip nature, and how they are attached to the handle [12]. It is also important for the fibers to have good flexibility so that the brush easily regains its shape.

Brush application is essential for painting small and hard-to-reach areas, such as edges, angular parts, and welds. Furthermore, this technique is considered to allow better penetration of paints into the pores and irregularities of the surface [4,38]. However, when applying paint with a brush on a relatively smooth surface, brush marks are common [8]. Therefore, it is desirable to formulate the coating so that these marks flow out and disappear, achieving adequate leveling of the paint before the film dries [8]. If persistent, brush marks not only affect the decorative appearance of the paint but can also become centers for corrosion deterioration, cracking, or blistering.

A proper brush application process can be divided into two stages. In the first, an appropriate amount of paint is deposited onto the substrate surface, relative to the brush size and area to be painted, and then rapidly spread to obtain as uniform a film as possible. In the second stage, a pass perpendicular to the previous one is made to minimize brush marks and improve the final finish

characteristics. Nevertheless, one of the main disadvantages of this method is that the resulting paint films often exhibit non-uniform thickness across the surface [5,38].

6.2. Roller Application

Roller application is faster than brush application, making it ideal for painting large, smooth surfaces [4]. Careful selection of roller material and fiber length are essential factors for work speed and achieving a good finish. Rollers used in domestic and construction work are loaded with paint using trays with integrated drainers, typically angled at 40-45°. The tool is immersed in the tray, and through successive passes on the drainer, a uniform distribution of the material is achieved. This method allows for a continuous, well-leveled film of appropriate thickness. For anticorrosive primers or base coats applied directly to sandblasted or shot-blasted surfaces, it is advisable to apply the first coat with a brush to ensure the product penetrates all irregularities, then apply subsequent layers with a roller [38]. Conversely, on very smooth surfaces such as pickled steel, galvanized sheet, or aluminum, the first coat can also be applied with a roller.

6.3. Spray Painting (Pulverization or Spraying)

For large surfaces, spray application is recommended due to its high application speed [4,8,12]. This method is ideal for fast-drying paints, avoiding the drawbacks associated with using brushes or rollers. It can be performed with a compressed air spray gun (air spraying), which uses relatively low pressures and requires prior paint dilution, or with airless spraying systems, which operate at high pressures and are designed for applying specific products [3,5,8,12,38]. With compressed air spray guns, film thicknesses of approximately 10-15 µm per coat are achieved, which are lower than the 20-25 µm obtained with a brush [39]. In contrast, airless equipment can achieve thicknesses of 80-120 µm per coat for conventional paints, and even greater for high-solids formulations [3].

7. CORROSION OF PAINTED METALLIC SURFACES

An organic anticorrosive coating protects a metallic substrate in two ways [1,4,38,40]. Firstly, the coating serves as a physical barrier to separate the metallic substrate from the environment. Once the barrier effect is lost and water and corrosive agents reach the metallic surface, the coating can offer protection through active corrosion inhibition, thanks to the anticorrosive pigments incorporated into its polymeric matrix.

Organic coatings are not perfect barriers; rather, they possess certain permeability and can be penetrated by water, oxygen, and ions like chloride [4,7,38,40]. When this occurs, corrosion can take place underneath the organic coating, at the interface between the coating and the metal. The corrosion of a substrate beneath an organic coating is an electrochemical process that follows the same principle as an uncoated substrate, although the reactions are confined to the narrow region beneath the coating [38,40]. The small volumes of liquid present during the initial stages of corrosion can lead to extreme values of both pH and ionic concentrations [40].

The local electrolyte that accumulates beneath the organic coating not only leads to metal dissolution but also weakens the adhesion of the organic coating to the substrate. Therefore, if corrosion occurs under the coating, a loss of adhesion will also result. Conversely, if the coating does not have good adhesion to the metallic substrate, localized areas with electrolyte accumulation will appear, promoting the corrosion process [40]. Thus, the processes of corrosion and adhesion loss are directly related and jointly contribute to the failure of the protective system [40].

7.1. Permeability of Organic Coatings to Water, Oxygen, and Ions

The penetration of water into an organic coating can occur through three mechanisms [4,38,40]:

(a) Diffusion: Water diffuses into the coating due to a concentration gradient, originated by immersion in an aqueous solution or exposure to a humid atmosphere.

(b) Osmosis: Water penetrates the film by osmosis, due to an ionic concentration gradient that exists between the film (which may contain ionic impurities) and the environment.

(c) Capillary action: Water enters the film via capillary action, through voids, pores, or cracks in the organic coating.

The permeability of organic coatings to oxygen is generally much lower than for water. For some types of coatings, the rate-determining step in corrosion beneath the film is the slow permeation of O_2, while in other cases, oxygen diffusion through the coating is large enough to allow unlimited corrosion [4,15,38,40].

Permeability to Cl^- ions is even lower than for O_2 [15,40]. The role of chloride ions in corrosion that occurs beneath a film is twofold: they provide the necessary electrolytic conductivity for localized corrosion cells to operate and accelerate the anodic reaction once it has initiated [40].

7.2. Corrosion Processes Underneath a Defective Coating

The sequence of events in the microenvironment under the coating that leads to the breakdown of an organic coating is as follows [7,9,15,38,40]:

(i) Initial Migration: Firstly, water, oxygen, and ions migrate through the coating, generating an aqueous phase at the interface between the coating and the substrate.

(ii) Localized Initiation: Corrosion is initiated locally due to various causes, such as defects in the coating (dust, dirt, oil or grease, lack of coverage, lack of adhesion), mechanical rupture of the coating (abrasion or impact), or chemical rupture (generation of osmotic pressure at sites containing soluble salts, exposure to acids or solvents).

(iii) Anodic Dissolution: The metallic substrate dissolves in the anodic region of the local cell. The metal ion undergoes acidic hydrolysis, causing the anodic site to become locally acidic. Subsequently, chloride ions migrate towards this acidic medium (Fig. 4).

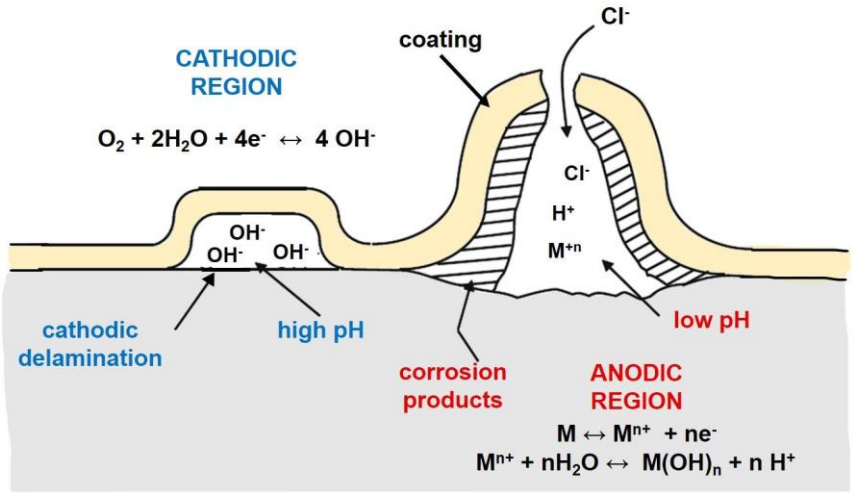

Figure 4. Corrosion processes underneath a defective coating

(iv) Cathodic Delamination: A localized cathodic site is generated at a different location. The operation of the cathodic half-cell is fueled by O_2 and H_2O molecules that have previously permeated the organic coating. Due to the production of OH^- ions, the cathodic site becomes locally alkaline. As osmotic forces drive water through the coating towards the alkaline solution, the coating deforms upwards. This causes the detachment and removal of the organic coating from the metal surface, a process known as cathodic delamination (Fig. 4). Suggested mechanisms for coating detachment include base-catalyzed hydrolysis of interfacial bonds, base-catalyzed polymer degradation, dissolution of the amphoteric metal oxide film at the metal-coating interface, and attack on the polymer by reactive intermediates of oxygen reduction.

(v) As the coating system continues to deteriorate, the protective separation between adjacent anodic and cathodic areas breaks down. This allows for increased galvanic action, which accelerates the corrosion process and ultimately leads to the failure of the organic coating.

7.3. Blistering

Blistering is an early sign of coating-substrate system failure [7,38]. Various factors can cause blistering, with osmotic processes being the most significant. When water penetrates through the coating, it dissolves ionic material from the film or the substrate (soluble pigments, remnants from phosphating, salts present due to inadequate surface cleaning, etc.), leading to an increase in osmotic pressure [38]. This drives more water ingress, which accumulates at the contact surface between the coating and the metal in sufficient quantities to force the film upwards, forming a blister [4,7,9,38]. Depending on the materials and specific circumstances, blisters can grow due to a combination of osmotic pressure and electrochemical propagation mechanisms [4,38].

There are two types of blistering in anticorrosive paints: alkaline blistering and neutral blistering, which occur through different mechanisms [7,38]. Alkaline blistering occurs when corrosion takes place underneath a defective coating, with alkalinization and cathodic delamination occurring at a localized cathodic site. For neutral blistering, a differential aeration mechanism has been proposed

once water enters an intact coating: the center of the blister is relatively oxygen-poor and becomes anodic, while the edges, where oxygen can more easily reach the base metal, become cathodic. Thus, the blister propagates through a cathodic delamination process at its edges.

7.4. Anodic Undermining and Filiform Corrosion

Anodic undermining occurs when the primary adhesion loss process is an anodic dissolution reaction occurring beneath the coating [38,40]. Anodic undermining can initiate at coating defects, but in most cases, it is associated with a corrosion-sensitive site underneath the coating, such as a remnant particle from a surface preparation procedure (e.g., sand) or a site on the metal surface with potentially higher corrosion activity (e.g., sanding scratches). These sites become active once the corrosive medium has penetrated to the metal surface.

Filiform corrosion is a specific form of crevice corrosion and anodic undermining that occurs beneath organic coatings. It results in numerous narrow, interconnected filaments that spread across the metal surface [9,38,40]. This form of corrosion is particularly prevalent beneath organic coatings applied on aluminum [3,38]. The corrosion filaments consist of a mobile electrolyte-filled head (containing metal cations and aggressive anions at a low pH) and a tail of dry, porous corrosion products [3,15]. Once initiated, the filament travels in a relatively straight line for long distances. The filament propagates via a differential aeration cell where oxygen enters the filament through its tail and diffuses towards the head [3,9,15,38,40]. The filament head has a low O_2 level compared to the tail, making the head the primary anodic site [9,40]. Ions produced at the anodic head diffuse towards the tail and form insoluble hydroxides and/or oxyhydroxides [38,40].

The occurrence of cathodic delamination or anodic undermining in defective coatings depends on the relationship between the transport rates of oxygen through the coating and through the formed corrosion products. When the oxygen transport rate through the coating exceeds the transport rate through the corrosion products, the cathodic delamination mechanism develops [4]. Conversely, when the transport rate through the corrosion products is higher, anodic undermining occurs [4].

8. EVALUATION OF PAINTED METALLIC SURFACES

8.1. Weathering Tests

8.1.1. Natural Weathering or Simulated Service

In these tests, a series of painted metallic panels are exposed to real atmospheric conditions for prolonged periods. Because the rates of coating degradation and substrate corrosion are typically slow, several years of exposure are often required to obtain significant results [9]. The main weathering stress factors contributing to the degradation of organic coatings are UV radiation, humidity (rain, water vapor, condensation), elevated temperatures, and chemical damage (salts in coastal environments, atmospheric pollutants like sulfur oxides, acid rain, etc.) [9,41]. Factors influencing the atmospheric corrosion of metals constantly change depending on the climatic zone, latitude, wet or dry periods, rural or urban areas, and proximity to the sea. To classify corrosion behavior in different geographical areas, the following four types of environments are generally considered [1]:

(i) Rural environment: Basically unpolluted, far from industrial gas emissions and coastal areas.

(ii) Urban environment: Residential or commercial areas with light or moderate pollution, due for example to car traffic or light industrial activities.

(iii) Industrial environment: Characterized by significant pollution due to the presence of heavy industrial activities, primarily chemical and metallurgical.

(iv) Marine environment: Areas directly influenced by the sea, close to the coastline. These locations are characterized by high levels of salinity and chloride ions from sea spray, which act as a powerful electrolyte to significantly accelerate the corrosion of metals and the degradation of coatings.

This environmental classification helps to make a first approximation of the corrosivity of the medium, but what truly matters is the microenvironment to which the painted substrate is exposed. In this regard, ISO 9223 classifies atmospheric corrosivity by defining six categories of increasing environmental corrosivity—C1, C2, C3, C4, C5, and CX—based on determinations of time of wetness (the period during which atmospheric conditions are favorable for the formation of a surface moisture layer) and the deposition rates of SO_2 and chlorides [1,15,42,43].

The weathering resistance of coated metallic panels is generally tested by placing them on racks at a 45° angle to the horizontal, oriented towards the direction that ensures greater solar exposure [15,41].

8.1.2. Accelerated Artificial Weathering

The aging and degradation of a quality coating on a well-prepared substrate can take several years to manifest under real-world conditions. However, evaluating the suitability of a specific coating requires results within a much shorter period, which explains the need for accelerated

testing methods [4,7,41]. Accelerated laboratory tests are techniques that generally aim to reproduce, in a brief timeframe, the conditions a sample will endure throughout its service life. To accelerate result acquisition compared to field tests, the aggressiveness of the test conditions is increased by intensifying one or more stress factors [15].

The most commonly used tests of this type to evaluate the anticorrosive protection provided by a paint or coating system to a metallic substrate are exposure in the salt spray chamber and exposure in the humidity chamber.

The salt spray test (or salt fog test) primarily aims to reproduce conditions of exposure to a highly aggressive marine environment [2,15]. Paint films applied to metallic panels are subjected to a sodium chloride mist under conditions standardized by ASTM B117: temperature of 35 ± 1ºC, saline solution pH between 6.5 and 7.2, and a sodium chloride concentration of 5 ± 1% w/w.44 The mist does not directly impinge on the panels, which are placed at an angle of 10 to 30° from the vertical; instead, it first impacts a baffle. The condensate is recirculated, but what drains from the panels is removed from the bottom of the chamber. Despite the widespread consensus among experts that the salt spray test has limited value for predicting coating efficacy in service, it remains the most commonly used test for evaluating paints and substrates [7].

The humidity chamber consists of a thermally insulated cabinet in which painted substrates are exposed to an environment of 100% relative humidity at an operating temperature of 38-40ºC. The basic principles and operating procedures are specified in ASTM D2247 [45].

A challenge with accelerated tests is that a significant factor in a pigment's anticorrosive efficacy is its leaching rate from the film [8]. Furthermore, the high chloride content in the salt spray test prevents the formation of passive layers or results in passive layers with a composition entirely different from those obtained under field conditions [46]. Moreover, these tests typically study one stress factor at a time, whereas in service, multiple factors are combined. For these reasons, accelerated corrosion tests often have a limited correlation with actual field exposure [2,4,46].

8.2. Evaluation of Adhesion, Blistering, and Rusting

Both under natural exposure conditions and in salt spray or humidity chambers, the degree of adhesion, blistering, and rusting of painted metallic surfaces is evaluated as a function of exposure time.

8.2.1. Adhesion Tests

Adhesion measurements are performed to obtain information on the mechanical strength of the bonds between the coating and the substrate, and the deterioration of these bonds when coatings are subjected to environmental stresses [7]. Thus, two aspects of adhesion are important: the initial strength of the coating-substrate bond (initial adhesion) and what happens to this bond as the coating ages [7]. Several methods exist to measure the adhesion of a coating to a substrate, which can be grouped into direct pull-off methods and cross-cut method [7].

The basic principle of direct pull-off methods is to glue a metallic tensile device, called a dolly, to the painted substrate. A perpendicular force is then applied to the dolly until the paint detaches from the substrate or a failure occurs within the paint layers [4,7]. An example of a cross-cut method is Method B described by ASTM D3359 [47]. A cutting device is used to make deep cuts in the coating, extending down to the metal, thereby creating a grid pattern. The spacing of the cuts is usually determined by the coating's thickness. Subsequently, adhesive tape is applied over the grid and, after a certain time, is removed. The amount of paint detached serves as a measure of adhesion [41]. The highest rating, 5B, corresponds to no detachment. In 4B, small flakes of paint have detached at the intersections, with the detached area being less than 5%. In 3B, small flakes of coating have detached along the edges and at the intersections of the cuts, with the detached area being between 5% and 15%. In 2B, the paint has partially or completely detached at the edges and/or some squares of the grid have partially or completely detached, with a detached area of 15% to 35%. In the 1B rating, the detached area is 35-65%, and in the lowest rating, 0B, the detached paint area exceeds 65%.

8.2.2. Degree of Blistering

The degree of blistering refers to the appearance of blisters on the painted surface. ASTM D714 provides a scale for evaluating both the size and frequency of formed blisters [2,48]. For size, a numerical scale from 10 to 0 is used, where 10 corresponds to the absence of blisters, 8 to the smallest blisters visible to the eye, and ratings of 6, 4, and 2 correspond to progressively larger blisters. Regarding the frequency of blistering, this can be dense (D), medium dense (MD), medium (M), or few (F).

8.2.3. Degree of Rusting

The existence of rust spots can be attributed to the ineffective anticorrosive properties of the entire applied coating system. Rust formation can also

occur because the substrate has been exposed due to blistering, cracking, or mechanical damage (shocks, impacts). The first case manifests as isolated spots that, at a given moment, surface on the film, while in the second case, localized oxidation is observed in the damaged area. For steel, ASTM D610 provides a scale of values for different degrees of corrosion, as well as photographic patterns for comparison [49].

8.3. Electrochemical Tests

In addition to accelerated tests, electrochemical tests are also used to evaluate the degree of protection and/or degradation of a given organic coating on a metallic substrate. This is because the effectiveness of a paint depends, among other factors, on its electrical and chemical behavior in the corrosive environment to which it is exposed. Although these types of tests can be considered accelerated, given that the painted metal is in constant contact with an aggressive medium (electrolyte), they have the advantage of being more objective than the methods mentioned previously, where the rating could depend on the evaluator's subjectivity [50].

Electrochemical studies of bare metals have revealed the complexity of processes occurring at the metal/corrosive medium interface. These include electrochemical reactions, chemical reactions, solvation, adsorption of reaction intermediates, and mass transport by migration, diffusion, and natural or forced convection. The presence of an organic coating on the metal introduces additional electrical and electrochemical properties, such as the dielectric behavior and ionic resistance of the film, as well as the barrier effect of the film on the diffusion of chemical species.

Among the various electrochemical tests that enable the study of organic coatings on metals, ionic resistance measurements, open circuit potential measurements, linear polarization resistance tests, and electrochemical impedance spectroscopy are prominent.

8.3.1. Ionic Resistance Measurements

Perhaps the most relevant corrosion protection mechanism of organic coatings is the creation of an extremely high electrical resistance path between anodic and cathodic areas, which reduces the current flow available for corrosion reactions. This resistance is associated with the film's barrier effect against ionic species, with a linear relationship found between ion diffusion and the reciprocal of the film's resistance [7,15]. This capacity of the protective film to retard the passage of the electrolyte has been termed electrolytic resistance or ionic resistance (Ri) [7]. Numerous researchers have conducted extensive work to establish a correlation between the ionic resistance of a coating and its ability to protect the substrate from corrosion [7]. In the case of steel, the classic work by Bacon, Smith, and Rugg established good corrosion protection for coatings that could maintain an ionic resistance of 10^8 Ω·cm^2 during the exposure period, fair protection for an ionic resistance between 10^6 and 10^8 Ω·cm^2, and poor protection for an Ri less than 10^6 Ω·cm^2 [7,15,51-53]. Knowing the coating thickness is crucial when measuring ionic resistance due to its significant impact on this parameter. For example, a doubling of thickness can lead to a change of many orders of magnitude in resistance [52].

8.3.2. Open Circuit Potential Measurements

The simplest of all electrochemical tests is the measurement of the open circuit potential (OCP) of the painted metal as a function of exposure time to the corrosive medium [50].

Potential measurements are useful as a comparative test, observing the evolution over time of the painted substrate's potential relative to a reference value, which is the potential of the bare metal. Movement towards more negative potentials, characteristic of bare metal, may indicate coating degradation and the development of active corrosion, while a shift towards more noble potentials can suggest the initiation of passive protective film formation [54,55]. Generally, the longer it takes for the painted substrate to reach the bare metal's potential value, or the more positive the coated metal's OCP remains, the better the protection system.

It is important to note, however, that open circuit potential is not an unequivocal indicator of corrosion, and noble potentials do not necessarily mean reduced corrosion rates [54,55]. For this reason, it is mandatory to relate OCP variation measurements over time with the results from other techniques that provide complementary information [50,55].

8.3.3. Linear Polarization Resistance Tests

In this popular direct current (DC) based electrochemical technique, a small potential perturbation (typically 10-20 or even 30 mV with respect to the open circuit potential) is applied to the metallic substrate, and the resulting current is measured. Polarization resistance (Rp) is defined as the slope of the potential-current plot in the vicinity of the corrosion potential, and it is a parameter inversely proportional to the metal's corrosion rate [50].

The polarization resistance method approaches what is considered a non-destructive test. This is because the applied potentials are generally limited to short durations of around a few tens of millivolts

and are periodically reversed, such that the movement of ions in the anodic direction is quickly balanced by the movement of ions in the opposite direction, resulting in a net effect close to zero [50].

Linear polarization tests are not capable of discriminating the contributions of each individual process at the metal/corrosive medium interface; instead, they detect the overall system response. Furthermore, it is important to highlight that there are limitations in using this technique in cases involving high ohmic resistance values, such as metals with organic coatings of average thickness [50,56]. This high resistance leads to a large ohmic potential drop, which reduces the driving force for electrochemical reactions at the coating-metal interface [9]. Often, the extent of this ohmic potential drop across the paint film is not characterized, making it difficult to interpret experimental data [9]. Thus, linear polarization tests are primarily applied for studying primer films, which have a small thickness and low resistance to ion flow. These tests are also justified for studying deteriorated coatings that have lost their barrier effect, which is generally associated with Ri values below the threshold of $10^6\ \Omega{\cdot}cm^2$ [53].

8.3.4. Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is a non-destructive alternating current (AC) technique that serves as a powerful tool for studying the protection and/or degradation of an organic coating applied to a metallic substrate [3,53,55,56]. The method is generally used qualitatively or semi-quantitatively due to the large variations among replicates and the difficulty in producing identical coating samples [57].

In EIS, the metallic substrate is polarized by applying an alternating potential, which, in turn, produces an alternating current response. For corrosion studies, the frequency range of the applied AC typically varies from mHz to several hundred kHz, with a perturbation within 10 mV relative to the open circuit potential [3]. When an electrochemical system is perturbed by an AC signal, the system relaxes to a new steady state. The time τ required for this relaxation is known as the time constant, and for a given electrochemical system, it is given by:

$$\tau = RC \qquad (3)$$

where τ is the time constant in seconds, R is the resistance in ohms, and C is the capacitance in farads [40]. Thus, when using an alternating current over a broad frequency range, it is possible to discriminate the various processes occurring in the painted metal/solution system based on their distinct time constants. In this way, EIS not only allows for predicting a model that physically represents the system at a given exposure or immersion time (achieved by constructing an equivalent electrical circuit) but also enables the estimation of the contribution of each individual process or component within the model [58].

Following the path of electrical current from the electrolyte to the metal (Fig. 5), the resistance of the electrolyte between the working and reference electrodes (Rs) must first be overcome. Then, the current must pass through the paint film, characterized by an ionic flow resistance (R1) and a dielectric capacitance (C1) [53]. Resistance R1 is also often referred to as pore resistance, and it is associated with the relative ease with which ionic species can penetrate the coating and reach the metal surface, following paths or pores resulting from imperfections, whether intrinsic or developed in service [40,53]. Its value depends on the size, mobility, and charge of the ions, as well as the number and dimensions of pores per unit area. The magnitude of R1 typically decreases with increasing exposure time due to the progressive deterioration of the film [3,40,53,59]. The value of C1 represents a measure of the coating's dielectric constant and usually increases over time due to the absorption of water and ions present in the electrolyte [4,40,53,59,60].

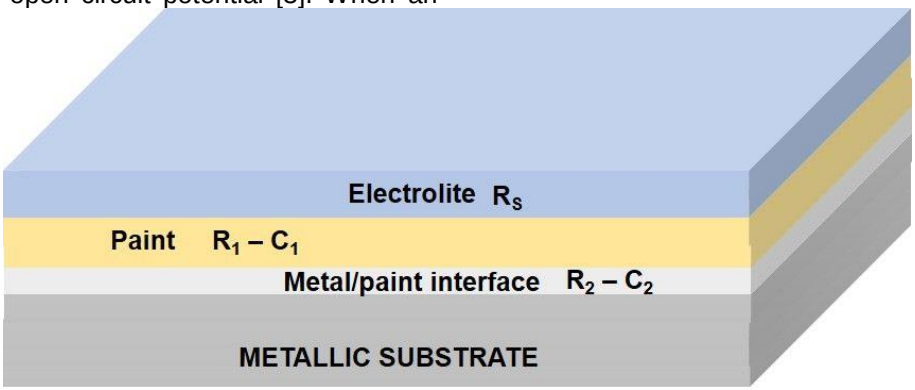

Figure 5. Schematic representation of a metal coated with paint and its respective interfaces

At the metal/paint interface (Fig. 5), the electrochemical corrosion reaction leads to the emergence of a second time constant [56]. Thus, in most cases, it is possible to observe that, in parallel with the electrochemical double-layer capacitance (C2) formed at the base of the organic film defects, the faradaic process induces a charge transfer resistance (or polarization resistance) (R2) due to its finite reaction rate [53,56]. A higher R2 value implies greater corrosion resistance and, therefore, slower development of corrosion processes beneath the coatings [56,60].

In the particular case of a painted metal in contact with an aggressive environment, the equivalent circuit that describes the system varies as a function of exposure time and the degree of deterioration of the protection system, following the sequence indicated in the schematic of Fig. 6 [56]. Initially, when the coating is intact, the system's behavior is defined as "purely capacitive" and can be described by a simplified Randles circuit in which the paint film resistance (R1) is very high [7,56]. With increasing exposure times to the corrosive medium, coating degradation leads to the formation and growth of micropores or pathways, causing the film's resistance to decrease [56]. Some authors have related the decrease in R1 to an increase in the delamination area beneath the coating [60]. As mentioned before, the aging kinetics of the coating are also generally characterized by an increase in C1, which can be related to an increase in the amount of absorbed water [53,60]. Finally, when corrosion processes develop on the coated metallic substrate, it is necessary to incorporate new elements into the equivalent circuits, such as elements C2 and R2 corresponding to the metal-paint interface. The circuit located to the right of Fig. 6 is the most commonly used model, sometimes referred to as the extended Randles circuit [7,40,59,60]. In some cases, it is necessary to incorporate more electrical elements into the equivalent circuit to explain experimental findings. For example, if an electrochemical system has a component under diffusional control, it is necessary to introduce an element called Warburg impedance (Zw) into the circuit [3,40,56,58,60]. The impedance spectra in these cases of deteriorated coatings can adopt different forms, depending on the limiting step of the corrosion process.

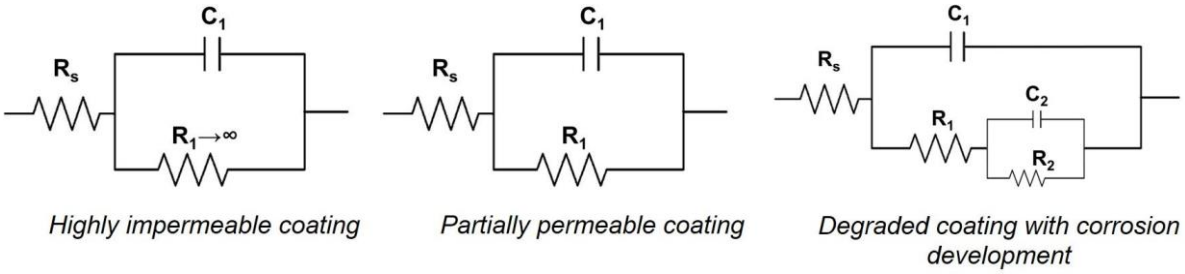

Figure 6. Equivalent electrical circuits interpreting the impedance response of a painted metal as a function of the system's deterioration degree

Some processes, such as the lateral penetration of the electrolyte at the metal/paint interface, the heterogeneity of the metallic surface beneath the paint due to topological or chemical composition causes or distribution of energy sites, or diffusion processes that might occur during coating degradation and metallic substrate corrosion, lead to distortions in the resistive/capacitive contributions of the impedance responses, causing a deviation from theoretical models [61]. These factors cause the impedance/frequency relationship to be nonlinear. For this reason, to obtain a better fit, a constant phase element (CPE) is used instead of capacitive components (Ci) [61]. The transfer function for a CPE is given by Equation 4 [53,61]:

$$Z = \frac{Y_0}{(j\omega)^n} \quad (4)$$

where Z denotes the impedance of the constant phase element, j the imaginary unit ($j^2=-1$), ω the angular frequency (in rad), and Y_0 is a frequency-independent parameter (in Ω^{-1}). Furthermore, n is the CPE exponent, a dimensionless parameter between 0 and 1, and is given by $n=\alpha/(\pi/2)$, where α is the phase angle (in rad). When n=1, the CPE is an ideal capacitor, and the parameter Y_0 represents its capacitance [62]. Otherwise, the CPE deviates from an ideal capacitor, and Y_0 no longer directly represents the capacitance. Thus, the deviation of the n value from unity is a quantitative way to measure the deviation from ideality in the coating's dielectric behavior [53]. If the exponent n is between 0.8 and 1, models exist to convert the CPE into its equivalent capacitor. Using the parameters Y_0 and n, these models calculate the corresponding equivalent capacitance, which facilitates the

visualization and physical interpretation of the results [62].

9. CONCLUSIONS

This comprehensive review has elucidated the multifaceted science and engineering underpinning the design, application, and performance of anticorrosive paint systems. We have underscored that effective and durable corrosion protection is not a singular achievement but rather the culmination of a synergistic interplay among carefully selected material components, precise formulation strategies, and diligent application methodologies.

The foundational role of binders in forming the protective film, controlling the diffusion of corrosive species, and ensuring strong adhesion to the substrate is undeniable. Concurrently, the industry's ongoing evolution in solvent use, driven by stricter environmental regulations, highlights a continuous push towards greener, more sustainable coating technologies without compromising performance. The in-depth discussion of pigments clearly demonstrates their diverse contributions, extending far beyond aesthetics to encompass critical functions like opacity, film reinforcement, and, most importantly, active corrosion inhibition. The shift away from historically effective but toxic chromate and lead-based inhibitors towards more benign alternatives, such as the various zinc phosphates and novel organic and inorganic compounds, signifies a critical advancement in both environmental responsibility and human safety within the coatings sector. The principle of CPVC emerges as a paramount formulation concept, emphasizing the precise balance required to achieve optimal barrier properties, minimize porosity, and maximize the protective lifespan of the coating.

Furthermore, the review has emphatically reinforced that even the most advanced paint formulation will ultimately fail without meticulous surface preparation. Proper cleaning, profiling, and treatment of the substrate are not merely preliminary steps but integral to establishing the robust adhesion necessary for long-term protection. The various application methods — from brushing small details to high-speed spraying of large surfaces — each demand specific paint rheologies and skilled execution to ensure uniform film thickness and optimal coverage.

Our detailed examination of corrosion mechanisms beneath coatings underscores that organic films, while formidable barriers, are never entirely impermeable. The ingress of water, oxygen, and ions inevitably leads to localized electrochemical reactions at the metal-coating interface, culminating in phenomena like cathodic delamination, blistering, and filiform corrosion. Understanding these complex degradation pathways is essential for designing more resilient coating systems.

Finally, the review has highlighted the indispensable role of robust evaluation methodologies in predicting and understanding coating performance. While natural weathering and accelerated tests offer valuable insights, electrochemical techniques, particularly EIS, stand out as powerful, non-destructive tools. EIS provides objective, quantitative data on a coating's barrier properties, water uptake, and the onset of corrosion processes. The ability to model these complex behaviors using equivalent electrical circuits, often incorporating CPE to account for deviations from ideal capacitive behavior in real coatings, offers a sophisticated means to interpret degradation mechanisms and predict long-term protective efficacy. These advanced diagnostic tools are crucial for the continuous improvement and innovation in anticorrosive coating technology.

In conclusion, the development of superior anticorrosive paints is an ongoing scientific and technological endeavor. Future advancements will undoubtedly focus on integrating novel, self-healing materials, smart sensing capabilities, and even more environmentally benign components, all while leveraging advanced characterization techniques to meet the ever-increasing demands for sustainable, high-performance corrosion protection in a diverse range of industries.

Acknowledgment

The authors gratefully acknowledge the sponsorship of the National Scientific and Technical Research Council (CONICET), the National University of La Plata (UNLP), and the Scientific Research Commission of the Province of Buenos Aires (CICPBA), whose funding facilitated the completion of this research.

10. REFERENCES

[1] P. Pedeferri (2018) Corrosion Science and Engineering, Springer International Publishing, Cham, Germany.

[2] P. R. Roberge (2008) Corrosion Engineering Principles and Practice, McGraw-Hill, New York, USA.

[3] S. X. Zheng (2020) Principles of Organic Coatings and Finishing, Cambridge Scholars Publishing, Newcastle upon Tyne, UK.

[4] P. Marcus (2012) Corrosion Mechanisms in Theory and Practice (3rd ed.), CRC Press, New York, USA.

[5] D. Stoye, W. Freitag (1998) Paints, Coatings and Solvents (2nd ed.), Wiley-VCH, New York, USA.

[6] P. A. Schweitzer (2009) Fundamentals of Corrosion: Mechanisms, Causes, and Preventative Methods (1st ed.), CRC Press, New York, USA.

[7] O. Knudsen, A. Forsgren (2017) Corrosion Control Through Organic Coatings(2nd ed.), CRC Press, Boca Raton, USA.

[8] Z. Wicks (2007) Organic Coatings, Science and Technology(3rd ed.), John Wiley & Sons, Inc., Hoboken, USA.

[9] R. G. Buchheit (2005) Corrosion Resistant Coatings and Paints, book Handbook of Environmental Degradation of Materials, Elsevier, New York, USA, pp 367-385.

[10] A. Marrion (2004) The Chemistry and Physics of Coatings (2nd ed.), The Royal Society of Chemistry, London, UK.

[11] G. Pfaff (2022) Carbon Black Pigments, Phys. Sci. Rev., 7 (2), 109-125. https://doi.org/10.1515/psr-2020-0152

[12] D. G. Weldon (2009) Failure Analysis of Paints and Coatings, John Wiley & Sons, Ltd., Chichester, UK.

[13] G. Pfaff (2022) The World of Inorganic Pigments, ChemTexts, 8 (3), 15. https://doi.org/10.1007/s40828-022-00166-1

[14] T. F. Tadros (2018) Formulation Science and Technology, Volume 4: Agrochemicals, Paints and Coatings and Food Colloids, De Gruyter, Berlin, Germany.

[15] R. A. Cottis (2010) Shreir's Corrosion (4th ed.), Elsevier, Amsterdam, Netherlands.

[16] T. L. DesMarias, M. Costa (2019) Mechanisms of Chromium-Induced Toxicity, Curr. Opin. Toxicol., 14, 1-7. https://doi.org/10.1016/j.cotox.2019.05.003

[17] A. L. Wani, A. Ara, J. A. Usmani (2015) Lead Toxicity: A Review, Interdiscip. Toxicol., 8 (2), 55-64. https://doi.org/10.1515/intox-2015-0009

[18] J. Molina, M. Puig, M. J. Gimeno, R. Izquierdo, J. J. Gracenea, J. J. Suay (2016) Influence of Zinc Molybdenum Phosphate Pigment on Coatings Performance Studied by Electrochemical Methods, Prog. Org. Coat., 97, 244-253. https://doi.org/10.1016/j.porgcoat.2016.04.029

[19] G. Blustein, M. C. Deyá, R. Romagnoli, B. D. Amo (2005) Three Generations of Inorganic Phosphates in Solvent and Water-Borne Paints: A Synergism Case, Appl. Surf. Sci., 252 (5), 1386-1397. https://doi.org/10.1016/j.apsusc.2005.02.096

[20] D. El-Hamid, G. Blustein, M. Deyá, B. Del Amo, R. Romagnoli (2011) The Anticorrosive Performance of Zinc-Free Non-Toxic Pigment for Paints, Mater. Chem. Phys., 127 (1–2), 353-357. https://doi.org/10.1016/j.matchemphys.2011.02.018

[21] L. Ngatia, R. Taylor (2019) Phosphorus Eutrophication and Mitigation Strategies, IntechOpen. https://doi.org/10.5772/intechopen.79173

[22] S. N. Roselli, G. Lendvay-Györik, G. Mészáros, C. Deyá, R. Romagnoli (2017) Anticorrosive Water Borne Paints Free from Zinc and with Reduced Phosphate Content, Prog. Org. Coat., 112, 27-36. https://doi.org/10.1016/j.porgcoat.2017.04.023

[23] C. E. Byrne, N. V. Quesada Cangahuala, O. D'Alessandro, C. Deyá (2024) Cerium and Aluminum Molybdates as Inhibitors of the Aluminum AA1050 Corrosion Process in Aqueous NaCl Solutions, Mater. Corros., 75 (1), 73-83. https://doi.org/10.1002/maco.202313940

[24] A. Kalendova, T. Hájková (2015) Synthesis and Investigation of the Properties of Tungstate-Based Anticorrosion Pigments in Coatings, Anti-Corros. Methods Mater., 62 (5), 307-321. https://doi.org/10.1108/ACMM-01-2014-1343

[25] H. Kukackova, A. Vraštilová, A. Kalendova (2013) Non-Toxic Anticorrosive Pigments Intended for Applications in High-Solids and Waterborne Paints, Phys. Procedia, 44, 238-246. https://doi.org/10.1016/j.phpro.2013.04.029

[26] S. Roselli, N. Bellotti, C. Deyá, M. Revuelta, B. Del Amo, R. Romagnoli(2014) Lanthanum-Exchanged Zeolite and Clay as Anticorrosive Pigments for Galvanized Steel, J. Rare Earths, 32 (4), 352-359. https://doi.org/10.1016/S1002-0721(14)60078-8

[27] S. Roselli, C. Deyá, M. Revuelta, A. R. Di Sarli, R. Romagnoli (2018) Zeolites as Reservoirs for Ce(III) as Passivating Ions in Anticorrosion Paints, Corros. Rev., 36 (3), 305-322. https://doi.org/10.1515/corrrev-2017-0090

[28] G. Blustein, A. R. Di Sarli, J. A. Jaén, R. Romagnoli, B. Del Amo (2007) Study of Iron Benzoate as a Novel Steel Corrosion Inhibitor Pigment for Protective Paint Films, Corros. Sci., 49 (11), 4202-4231. https://doi.org/10.1016/j.corsci.2007.05.008

[29] M. Mahdavian, S. Ashhari (2010) Mercapto Functional Azole Compounds as Organic Corrosion Inhibitors in a Polyester-Melamine Coating, Prog. Org. Coat., 68 (4), 259-264. https://doi.org/10.1016/j.porgcoat.2010.04.002

[30] C. Byrne, O. D'Alessandro, G. J. Selmi, R. Romagnoli, C. Deyá (2019) Primers Based on Tara and Quebracho Tannins for Poorly Prepared Steel Surfaces, Prog. Org. Coat., 130, 244-250. https://doi.org/10.1016/j.porgcoat.2019.02.003

[31] C. Byrne, G. J. Selmi, O. D'Alessandro, C. Deyá (2020) Study of the Anticorrosive Properties of "Quebracho Colorado" Extract and Its Use in a Primer for Aluminum1050, Prog. Org. Coat., 148, 105827. https://doi.org/10.1016/j.porgcoat.2020.105827

[32] C. E. Byrne, O. D'Alessandro, C. Deyá (2022) Tara Tannins as a Green Sustainable Corrosion Inhibitor for Aluminum, J. Mater. Eng. Perform., 31 (4), 2918–2933. https://doi.org/10.1007/s11665-021-06437-1

[33] G. Ong, R. Kasi, R. Subramaniam (2021) A Review on Plant Extracts as Natural Additives in Coating Applications, Prog. Org. Coat., 151, 106091. https://doi.org/10.1016/j.porgcoat.2020.106091

[34] C. A. Barbu, I. Fierascu, A. Semenescu, C. M. Cotrut (2025) Critical Review Regarding the Application of Plant Extracts as Eco-Friendly Corrosion Inhibitors—A Sustainable Interdisciplinary Approach, Molecules, 30 (18), 3722. https://doi.org/10.3390/molecules30183722

[35] H. C. Hare, J. S. Kurnas (2000) Reduced PVC and the Design of Metal Primers, J. Coat. Technol., 72 (11), 21-27. https://doi.org/10.1007/BF02729973

[36] M. Rodríguez, J. J. Gracenea, J. Saura, J. Suay (2004) The Influence of the Critical Pigment Volume Concentration (CPVC) on the Properties of an Epoxy Coating Part II. Anticorrosion and Economic Properties, Prog. Org. Coat., 50 (1), 68-74. https://doi.org/10.1016/j.porgcoat.2003.10.014

[37] A. A. Tracton (2006) Coatings Technology Handbook(3rd ed.), CRC Press, Boca Raton, USA.

[38] P. Schweitzer (2006) Paint and Coatings: Applications and Corrosion Resistance, CRC Press, Boca Raton, USA.

[39] W. Lee, H. M. Cho (2023) Changes in Thickness and Gloss of Dry Films According to Spray Methods of Water-Soluble Metallic Base Coat, Int. J. Mech. Eng. Rob. Res., 12 (6), 396-400. https://doi.org/10.18178/ijmerr.12.6.396-400

[40] E. McCafferty (2010) Introduction to Corrosion Science, Springer, New York, USA.

[41] M. E. Nichols (2005) Paint Weathering Tests, book Handbook of Environmental Degradation of Materials, Elsevier, New York, USA, pp 597-619.

[42] International Organization for Standardization (2012) International Standard ISO 9223, Corrosion of metals and alloys - Corrosivity of atmospheres - Classification, determination and estimation, Geneva, Switzerland.

[43] C. I. Elsner, P. R. Seré, A. R. Di Sarli (2012) Atmospheric Corrosion of Painted Galvanized and 55 % Al-Zn Steel Sheets: Results of 12 Years of Exposure, Int. J. Corros., 2012, 1-16. https://doi.org/10.1155/2012/419640

[44] ASTM International (2019) ASTM Standard B117-19, Standard Practice for Operating Salt Spray (Fog) Apparatus, West Conshohocken, USA.

[45] ASTM International (2020) ASTM Standard D2247-15, Standard Practice for Testing Water Resistance of Coatings in 100 % Relative Humidity, West Conshohocken, USA.

[46] M. Dornbusch (2018) Corrosion Analysis (1st ed.), CRC Press, Boca Raton, USA.

[47] ASTM International (2023) ASTM Standard D3359-23, Standard Test Methods for Rating Adhesion by Tape Test, West Conshohocken, USA.

[48] ASTM International (2017) ASTM Standard D714-02, Standard Test Method for Evaluating Degree of Blistering of Paints, West Conshohocken, USA.

[49] ASTM International (2019) ASTM Standard D610-08, Standard Practice for Evaluating Degree of Rusting on Painted Steel Surfaces, West Conshohocken, USA.

[50] G. W. Walter (1986) A Critical Review of d.c. Electrochemical Tests for Painted Metals, Corros. Sci., 26 (1), 39-47. https://doi.org/10.1016/0010-938X(86)90121-6

[51] R. C. Bacon, J. J. Smith, F. M. Rugg (1948) Electrolytic Resistance in Evaluating Protective Merit of Coatings on Metals, Ind. Eng. Chem., 40 (1), 161-167. https://doi.org/10.1021/ie50457a041

[52] D. J. Mills, S. S. Jamali (2017) The Best Tests for Anti-Corrosive Paints. And Why: A Personal Viewpoint, Prog. Org. Coat., 102, 8-17. https://doi.org/10.1016/j.porgcoat.2016.04.045

[53] I. C. P. Margarit-Mattos (2020) EIS and Organic Coatings Performance: Revisiting Some Key Points, Electrochim. Acta, 354, 136725. https://doi.org/10.1016/j.electacta.2020.136725

[54] J. Wolstenholme (1973) Electrochemical Methods of Assessing the Corrosion of Painted Metals—a Review, Corros. Sci., 13 (7), 521-530. https://doi.org/10.1016/S0010-938X(73)80002-2

[55] A. Trentin, A. Pakseresht, A. Duran, Y. Castro, D. Galusek (2022) Electrochemical Characterization of Polymeric Coatings for Corrosion Protection: A Review of Advances and Perspectives, Polymers, 14 (12), 2306. https://doi.org/10.3390/polym14122306

[56] F. Meng, L. Liu (2019) Electrochemical Evaluation Technologies of Organic Coatings, IntechOpen. https://doi.org/10.5772/intechopen.79736

[57] B. R. Hinderliter, S. G. Croll, D. E. Tallman, Q. Su, G. P. Bierwagen (2006) Interpretation of EIS Data from Accelerated Exposure of Coated Metals Based on Modeling of Coating Physical Properties, Electrochim. Acta, 51 (21), 4505-4515. https://doi.org/10.1016/j.electacta.2005.12.047

[58] G. W. Walter (1986) A Review of Impedance Plot Methods Used for Corrosion Performance Analysis of Painted Metals, Corros. Sci., 26 (9), 681-703. https://doi.org/10.1016/0010-938X(86)90033-8

[59] F. Mansfeld (2006) Electrochemical Impedance Spectroscopy, book Analytical methods in corrosion science and technology, CRC Press, New York, USA, pp. 463-506.

[60] L. Yang (2020) Techniques for Corrosion Monitoring(2nd ed.), Elsevier, Amsterdam, Netherlands.

[61] S. M. Gateman, O. Gharbi, H. Gomes De Melo, K. Ngo, M. Turmine, V. Vivier (2022) On the Use of a Constant Phase Element (CPE) in Electrochemistry, Curr. Opin. Electrochem., 36, 101133. https://doi.org/10.1016/j.coelec.2022.101133

[62] B. Chang (2022) The Effective Capacitance of a Constant Phase Element with Resistors in Series and Parallel, J. Electrochem. Sci. Technol., 13 (4), 479-485. https://doi.org/10.2139/ssrn.4079679

IZVOD

ANTIKOROZIVNE BOJE: SVEOBHVATNI PREGLED OSNOVA, FORMULACIJE, DEGRADACIJE I EVALUACIJE

Ovaj sveobuhvatni pregled pruža vitalnu referencu za istraživače i stručnjake konsolidovanjem trenutnog znanja o osnovama, komponentama, formulaciji, proizvodnji i naprednim tehnikama procene antikorozivnih boja, koje su neophodne za borbu protiv značajnih globalnih ekonomskih troškova metalne korozije. Detaljno opisuje fizičko-hemijski sastav boja, veziva za pokrivanje, prelazak na održive rastvarače na bazi vode i različite pigmente, sa posebnim naglaskom na evoluciju od toksičnih hromata do modernih, ekološki prihvatljivih alternativa poput fosfata. Pregled ispituje kritične aspekte formulacije, kao što je koncentracija zapremine pigmenta, i objašnjava ključnu ulogu pravilne pripreme površine za adheziju. Štaviše, analizira ključne mehanizme korozije ispod premaza, poput stvaranja mehurića i anodnog podrivanja, i istražuje različite metode procene, ističući elektrohemijsku impedansnu spektroskopiju kao nedestruktivni alat za procenu degradacije premaza. U krajnjoj liniji, ovaj rad naglašava multidisciplinarnu prirodu dizajna antikorozivnih boja i kontinuiranu potrebu za istraživanjem ka efikasnijim i održivim formulacijama.

Ključne reči: *Antikorozivne boje, korozija, pigmenti, PVC, priprema površine, elektrohemijska procena.*

Pregledni rad
Rad primljen: 12.12.2025.
Rad korigovan: 08.06.2026.
Rad prihvaćen : 09.06.2026

Christian Byrne: https://orcid.org/0000-0003-0813-9157
Oriana D'Alessandro: https://orcid.org/0000-0001-7096-5527