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REVIEW PAPER

Anticorrosive coatings: a review

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Abstract The main objective of this review is to describe some of the important topics related to the use of marine and protective coatings for anticorrosive purposes. In this context, ‘‘protective’’ refers to coatings for containers, offshore constructions, wind turbines, storage tanks, bridges, rail cars, and petrochemical plants while ‘‘marine’’ refers to coatings for ballast tanks, cargo holds and cargo tanks, decks, and engine rooms on ships. The review aims at providing a thorough picture of state-of-the-art in anticorrosive coatings systems. International and national legislation aiming at reducing the emission of volatile organic compounds (VOCs) have caused significant changes in the anticorrosive coating industry. The requirement for new VOC-compliant coating technologies means that coating manufacturers can no longer rely on the extensive track record of their time-served products to convince consumers of their suitability for use. An important aspect in the development of new VOC-compliant, high-performance anticorrosive coating systems is a thorough knowledge of the components in anticorrosive coatings, their interactions, their advantages and limitations, as well as a detailed knowledge on the failure modes of anticorrosive coatings. This review, which mainly deals with European experience and practice, includes a description of the different environments an anticorrosive coating system may encounter during service. In addition, examples of test methods and standards for determination of the performance and durability of anticorrosive coatings have been included. The different types of anticorrosive coatings are presented, and the most widely applied generic types of binders and pigments in anticorrosive coatings are listed and described. Furthermore, the protective mechanisms of barrier, sacrificial, and inhibitive coatings are outlined. In the past decades, several alternatives to organic solvent-borne coatings have reached the commercial market. This review also presents some of these technologies and discusses some of their advantages and limitations. Finally, some of the mechanisms leading to degradation and failure of organic coating systems are described, and the reported types of adhesion loss are discussed.

Keywords Anticorrosive coatings, Corrosion, Accelerated testing, Degradation, Pigments and binders

Introduction

The annual costs related to corrosion and corrosion prevention has been estimated to constitute a significant part of the gross national product in the Western world.[1] Although the value of such numbers is always debatable, corrosion issues are clearly of great importance in modern societies. In addition to the economic costs and technological delays, corrosion can lead to structural failures that have dramatic consequences for humans and the surrounding environment.[2,3] Reports on the corrosion failures of bridges, buildings, aircrafts, automobiles, and gas pipelines are not unusual.

Throughout the last decades, both organic and inorganic coatings have been widely applied for the protection of metals against corrosion. In many areas of coatings technology, the fight against corrosion has made significant progress in recent years. For example,

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Fig. 1: Corrosion of steel on offshore structure due to premature failure of coating. Courtesy of Hempel A/S

development of new "corrosion resistant" alloys permits operation of critical processing equipment in highly corrosive environments over an ever wider range of conditions.[4] However, despite significant improvements in coating technologies, problems continue in the long-term protection of metal from aggressive environments. Although the oil and pipeline industry has developed reliable cathodic protection methods and monitoring systems that permit safe operation in difficult environments, these industries also experience coating failures.[5] One of the main reasons for the limited number of high performance anticorrosive coating systems is the complexity of the coating-substrate system and the number of factors affecting the performance and service life of anticorrosive coatings. Besides the composition of the coating, which consists of binders, pigments, solvents, extenders, and additives,[6] the performance and durability of anticorrosive coatings depends on several different parameters, such as type of substrate, pretreatment of substrate, curing, coating thickness, adhesion between the coating and substrate, as well as several external environmental parameters.[7–11] To perform its duty effectively, an anticorrosive coating must possess intrinsic durability, adhesion to the substrate, adequate flexibility, and toughness to withstand impacts and cracking as well as maintain its appearance when subjected to stress, swell, mechanical abuse, or weathering.

The coatings industry is a mature industry that has been undergoing a continual change in technology throughout the last few decades. International and national legislation aimed at reducing the use of volatile organic compounds has led to significant changes in the formulation of anticorrosive coatings, which traditionally have contained a relatively large amount of organic solvents. The present trend of aiming to reduce emissions of VOCs will urge the coatings industry to develop products with high-solid contents, powder coatings, or waterborne coatings with low amounts of organic solvents. Although high-solid, inorganic, waterborne, and powder coatings are becoming more frequently applied, it may be difficult to substitute solvent-borne organic coatings completely in harsh environments.

An important aspect in the development of high performance coating systems for anticorrosive purposes in the marine and protective sector is a thorough knowledge and understanding of the interactions between the components in coatings.[12] Furthermore, understanding of the fundamental physical and chemical mechanisms responsible for the failure of anticorrosive coatings during service may provide a basis for the design of novel new coatings. An example of premature coating failure on an offshore structure, leading to corrosion, is given in Fig. 1.

In contrast to previous reviews[13–15] that concern single (or a few) topics, the overall intention of this paper is to combine the main topics related to anticorrosive coatings technology. The review, which is mostly based on European experience and practice, includes a description of the different types of environments anticorrosive coatings may encounter during service, an introduction to the different types of anticorrosive coatings presently available, the main components in anticorrosive coatings, novel anticorrosive coating ideas, and a summary of some of the most important degradation mechanisms.

The corrosive environment

Anticorrosive coatings are exposed to various environments ranging from constant immersion in water and burial in soil, to atmospheric pollution in industrial areas and ultraviolet radiation. The specific requirements for anticorrosive coating systems are naturally highly dependent on the environment and elements that the coating may experience during service, and the time of exposure. The versatility of the environments in which anticorrosive coatings are applied to protect metal against corrosion may be exemplified by the fact that coatings in industrial areas may be exposed to chemicals and rain, whereas coatings buried in soil may be exposed to bacteria and humidity.

Classification of environments

The versatility and different corrosivities of the environments that anticorrosive coatings may encounter during service necessitate some sort of classification of the different types of environments. ISO 12944 "Coatings and varnishes—Corrosion protection of steel structures by protective coating systems"[16] divides the environment into three types of exposure: immersion, atmospheric, and splash zone. The different types of exposure may be subclassified as illustrated in Fig. 2.

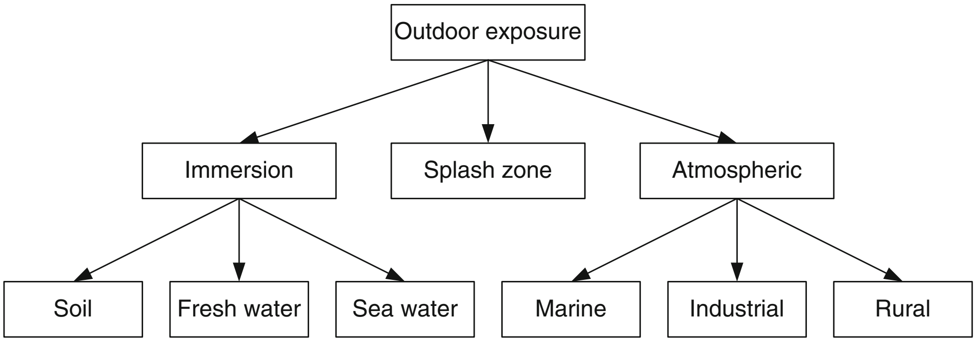


Fig. 2: Classification of environments encountered by anticorrosive coatings

Atmospheric exposure

Coatings applied in atmospheric environments are subjected to locally alternating conditions with respect to ultraviolet radiation, heat, and moisture, as well as salt and gas concentrations. The corrosivity of the atmosphere can vary significantly depending on climate, level of pollution, and distance to the sea. The atmospheric environment may be classified according to six corrosivity categories ranging from very low (C1) to very high corrosivity (C5-I and C5-M), as illustrated in Table 1.[17] Such categorizations will naturally be subject to debate because it is often difficult to specify corrosivity categories for one particular location (for example, roads may be heavily salted during the winter in rural areas where the location can, in principle, be categorized as both C3 and C5). However, they do provide a useful frame of reference for typical conditions encountered by coatings during service.

The corrosivity of rural environments is low compared to the corrosivity of industrial and marine atmospheres, which are categorized by a high or very high corrosivity. Industrial environments are characterized by a high content of solid particles in the atmosphere, particularly soot, sand, and sulphate salts. The combination of rain and a high content of sulphur dioxide in the atmosphere will result in acid rain and consequently expose the coating to an acidic environment.[18] In comparison to industrial atmospheres, marine atmospheres are characterized by having a very high content of chloride ions, which are very aggressive towards metals and may cause pitting corrosion.[19] Hence, marine and industrial environments with very heavy environmental impacts may provide very dissimilar conditions to anticorrosive systems. Therefore, they must be considered separately.

Splash zone

Structures situated near the waterline of the sea, such as parts of offshore plants and foundations of wind turbines, are located in a so-called "splash zone." Splash zones are extremely aggressive environments because they combine an oxygen-rich atmosphere with continuous splashing of electrolytes from the sea.[20] Hence, the corrosion process is not inhibited by a lack of oxygen or electrolyte solution. The degradation of coatings situated in the splash zone is likely to be accelerated further by exposure to ultraviolet radiation and the mechanical stress induced by continuous exposure to alternating periods of moisture and dryness.[21,22]

Immersion

In the case of structures immersed in water or buried in soil, the aggressiveness of the environment is very specific because the combination of temperature, salinity, pH, and the content of dissolved gasses, especially oxygen, determine the overall corrosivity

Table 1: Corrosivity categories and corresponding environmental impact factors

Corrosivity category	Environmental impact	Environmental examples
C1	Very low	Indoor in dry rooms (relative humidity <60%)
C2	Low	Indoor in non-heated and ventilated rooms
C3	Medium	Indoor with high humidity and pollution (production areas). Rural environments far from industrial areas
C4	Heavy	Urban or industrial areas
C5-I	Very heavy industry	Industrial areas with high relative humidity
C5-M	Very heavy marine	Coastal and offshore areas

After reference 16

of the environment. Thus, it is difficult to indicate a specific corrosivity category of the environments. The following corrosivity categories may be applied for immersion in fresh water, sea water, and burial in soil, respectively: Im1, Im2, and Im3. The aggressiveness of soil on buried structures and coatings is mainly determined by the type of soil, humidity, bacteria, salt, and oxygen content, as well as pH. In comparison, the aggressiveness of a fresh water environment is mainly determined by the type and content of dissolved salts and oxygen. As opposed to fresh water, sea water has a high content of dissolved salts, especially sodium chloride,[23] that are very aggressive towards metals and anticorrosive coatings. Structures immersed in water or buried in soil may also be affected by sand, gravel or stones. Structures immersed in water are also subjected to biofouling.[24]

Mechanism of wet corrosion

Corrosion may be defined as a physicochemical interaction between a metal and its environment that results in changes in the properties of the metal. Hence, corrosion may lead to significant impairment of the function of the metal, the environment, or the technical system of which these elements form a part. Accordingly, corrosion damage is defined as a corrosion effect that causes impairment of the function of the metal, the environment, or the technical system.

Corrosion is the result of an electrochemical reaction that requires an electrolyte solution and a metallic conductor between two separate areas with different potentials i.e., an anode and a cathode. The formation of ferrous oxides (rust) is a well-known consequence of the corrosion process when iron and steel corrode, but many other metals are also subject to corrosion. The green-colored patina on copper and the white rust on zinc are other examples of corrosion products.

The standard electrode potential may be used as a measure of the thermodynamic vulnerability of metals towards corrosion. This knowledge has been applied in the construction of the galvanic series in sea water (Table 2), which lists metals and alloys according to the potential they exhibit in sea water.

On a steel surface, some areas are anodic while other areas are cathodic.[25] At the cathode, oxygen is reduced on a catalytically active surface of oxidized metal, mainly to hydroxyl ions as given in reaction (1), but other reaction products such as peroxides, superoxides, and radicals may also be formed.[26–28] At the anode, several corrosion reactions take place,[29] and the net result is the production of ferrous ions and electrons given in reaction (2).

$$2H_2O(l) + O_2(aq) + 4e^- \rightarrow 4OH^-(aq) \qquad (1)$$

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \qquad (2)$$

Table 2: Galvanic series in seawater

- Anodic (active)
  - Magnesium
  - Zinc
  - Aluminum
  - Mild steel
  - Cast iron
- Stainless steel 18/8 (active)
  - Copper
- Stainless steel 18/8 (passive)
  - Graphite
  - Gold
  - Platinum
- Cathodic (noble)

Modified after reference 25

Note: "Passive" refers to a chromium-rich oxide film that forms naturally on the surface of steel. If the film is destroyed the surface is said to be "active"

The first step in the oxidation of iron hydroxide into ferrous oxides is the formation of green hydrated magnetite: $FeO \cdot Fe_2O_3 \cdot H_2O$.[25]

$$6Fe(OH)_2(aq) + O_2(aq) \rightarrow 4H_2O(l) + 2FeO \cdot Fe_2O_3 \cdot H_2O(s) \qquad (3)$$

However, hydrated magnetite is unstable and will decompose into black magnetite: $FeO \cdot Fe_2O_3$.

$$FeO \cdot Fe_2O_3 \cdot H_2O(s) \rightarrow FeO \cdot Fe_2O_3(s) + H_2O(l) \qquad (4)$$

In the presence of oxygen, black magnetite will subsequently oxidize into stable red-brown hydrated hematite ($Fe_2O_3 \cdot H_2O$), frequently referred to as rust.[25]

$$2FeO \cdot Fe_2O_3(s) + \frac{1}{2}O_2(aq) + 3H_2O(l) \rightarrow 3Fe_2O_3 \cdot H_2O(s) \qquad (5)$$

Hence, the overall reaction is

$$6Fe(s) + 4{}^1\!/_2O_2(aq) + 3H_2O(l) \rightarrow 3Fe_2O_3 \cdot H_2O(s) \qquad (6)$$

Thermodynamics of corrosion

The driving force in the corrosion of metals, illustrated in Fig. 3 for steel, is the potential difference between the anodic and cathodic sites. The overall potential difference between the anode and cathode is associated with a potential determined by the tendency of the involved half cells to occur spontaneously i.e., the standard potential of a half-cell reaction.

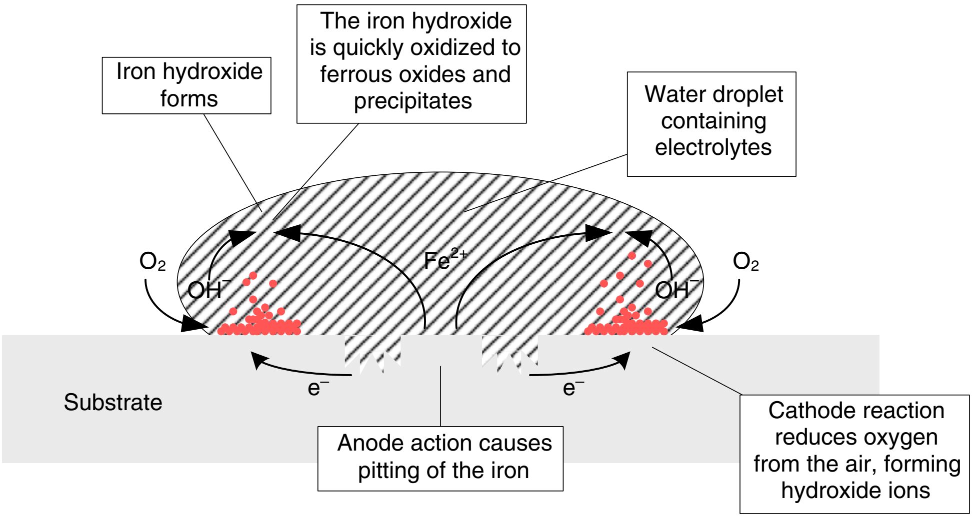


Fig. 3: Illustration of the corrosion process of steel in the presence of water, oxygen, and electrolytes. Pitting refers to a form of extremely localized corrosion that leads to the creation of small holes in the metal[25]

Table 3: Standard potentials against standard hydrogen electrode (SHE) of selected half-cell reactions[179]

Reaction	E^0 (V SHE)
$Al^{3+} + 3e^- \rightarrow Al(s)$	−1.662
$2H_2O(l) + 2e^- \rightarrow 2H(g) + 2OH^-(aq)$	−0.8277
$Zn^{2+} + 2e^- \rightarrow Zn(s)$	−0.7618
$Fe^{2+} + 2e^- \rightarrow Fe(s)$	−0.447
$Fe^{3+} + 3e^- \rightarrow Fe(s)$	−0.037
$Cu^{2+} + 2e^- \rightarrow Cu(s)$	+0.3419
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (pH 7)	+0.401

Note: Standard potential (E^0) is measured under standard conditions: 25°C, a 1 M concentration for each ion participating in the reaction, a partial pressure of 1 atm for each gas that is part of the reaction, and metals in their pure state

The overall electrical equilibrium potential of the galvanic cell is determined by the difference in standard potentials between the anodic and cathodic half-cell reactions: E^0_{Ox} and E^0_{Red}, respectively.[25]

$$E^0_{\mathrm{Cell}} = E^0_{\mathrm{Ox}} + E^0_{\mathrm{Red}} \tag{7}$$

The standard potentials of selected half-cell reactions relevant for corrosion processes are given in Table 3.

The overall potential of an electrochemical reaction is related to the standard potential of the reaction by the Nernst equation

$$E = E^0 + \frac{RT}{nF} \ln\left(\frac{a_{\mathrm{Red}}}{a_{\mathrm{Ox}}}\right) \tag{8}$$

where n is the number of electrons involved in the reaction, F is Faradays number, R is the gas constant, and T is the temperature. a_{Red} and a_{Ox} are the chemical activities for the reduced and oxidized species, respectively.

Thermodynamically speaking, the linkage between the change in Gibbs free energy (ΔG) of an electrochemical reaction and the electrochemical equilibrium potential (E^0_{Cell}) means that the corrosion of metal is associated with a change in the Gibbs free energy, as illustrated in equation (9)

$$\Delta G = -n \cdot F \cdot E^0_{\mathrm{Cell}} \tag{9}$$

where n is the number of electrons exchanged in the reaction and F is Faradays constant.

A specific example of the application of standard potentials in relation to thermodynamic studies of the corrosion of iron may be given by considering the formation of ferrous hydroxide from solid iron, given in reaction (10).

$$2Fe(s) + O_2(aq) + 2H_2O(l) \rightarrow 2Fe(OH)_2(aq) \tag{10}$$

The electrochemical equilibrium potential for this reaction is given by the half-cell standard potential for oxidation of iron to ferrous iron and the half-cell standard potential for reduction of oxygen to hydroxyl ions, as given in equation (11).

$$E^0_{\mathrm{Cell}} = 0.447\,\mathrm{V} + 0.401\,\mathrm{V} = 0.848\,\mathrm{V} \tag{11}$$

Since the standard potential for the overall reaction is positive (see equation (12)), the reaction is thermodynamically favored ($\Delta G < 0$), and the reaction will take place if the reaction rates are sufficiently fast.

$$\begin{aligned} \Delta G &= -2 \times 96485\,\mathrm{coulomb/mol} \times 0.848\,\mathrm{V} \\ &= -163.6\,\mathrm{kJ/mol} \end{aligned} \tag{12}$$

However, thermodynamic studies do not consider the kinetics of an electrochemical reaction. This means that metals may be thermodynamically unstable for a given set of environmental conditions but degrade slowly due to reaction kinetics. The difference between thermodynamics and kinetics may also be illustrated by calculating the Gibbs free energy for the reaction between water and aluminum, as illustrated in reaction (13).

$$Al(s) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 1\tfrac{1}{2}H_2(g) \qquad (13)$$

The Gibbs free energy for this reaction is –241.5 kJ/mol, which means that the reaction is thermodynamically favored. However, at neutral pH aluminum will corrode very slowly because a tough layer of aluminum oxides protects the metal against corrosion.

Thermodynamic studies of corrosion are typically performed with Pourbaix diagrams, which show the stable phases for a given set of conditions of pH and potential, *E*. The stable phases in a Pourbaix diagram are separated by solid lines, whereas the dashed lines enclose the practical region of stability of water to oxidation or reduction (see Fig. 4). Hence, water is unstable and is decomposed directly into hydrogen below Line B. In the intermediate region between Lines A and B, water is stable and dissolved oxygen and hydrogen are respectively reduced and oxidized to water. At potentials above Line A, water is unstable and is oxidized into oxygen. Thus, outside the dashed region it is not the metal that decomposes, but the water. The Pourbaix diagrams do not consider reaction kinetics. Hence, thermodynamically unstable intermediate phases formed at prior stages may still be present due to slow decomposition, although not shown in the region of interest in the Pourbaix diagram.

In the Pourbaix diagram for the $Fe–H_2O–Cl^-$ system, it is shown that solid iron is thermodynamically stable at potentials less than −0.4 V SHE at pH values of −2 to around 5. Hence, iron is stable against corrosion (immune) from a thermodynamic point of view in this region. The principle of making steel immune to corrosion is utilized when metals are protected by cathodic protection. Cathodic protection can be obtained by an impressed current cathodic protection (ICCP) of steel, where the negative pole of an external direct current source is coupled to the metal, while the positive pole is coupled to an auxiliary anode. In this way, electrons from the external current source are used instead of those that would have been liberated from iron by the corrosion process.[25] Sacrificial anodes (usually Zn, Mg, or Al) can also be used to provide cathodic protection of metals. The different systems and their potential applications have been thoroughly discussed.[23,30]

The rate of corrosion is influenced by several factors. In general, the rate of corrosion increases when temperature increases. Furthermore, the temperature and pressure of the medium govern the solubility of the corrosive species in the fluid, such as oxygen, carbon dioxide, chlorides, and hydroxides. For coatings immersed in nonstagnant water, another important factor is the water velocity. When the water velocity is extremely high, the impact of the water tends to remove the protective layer of metal oxide,

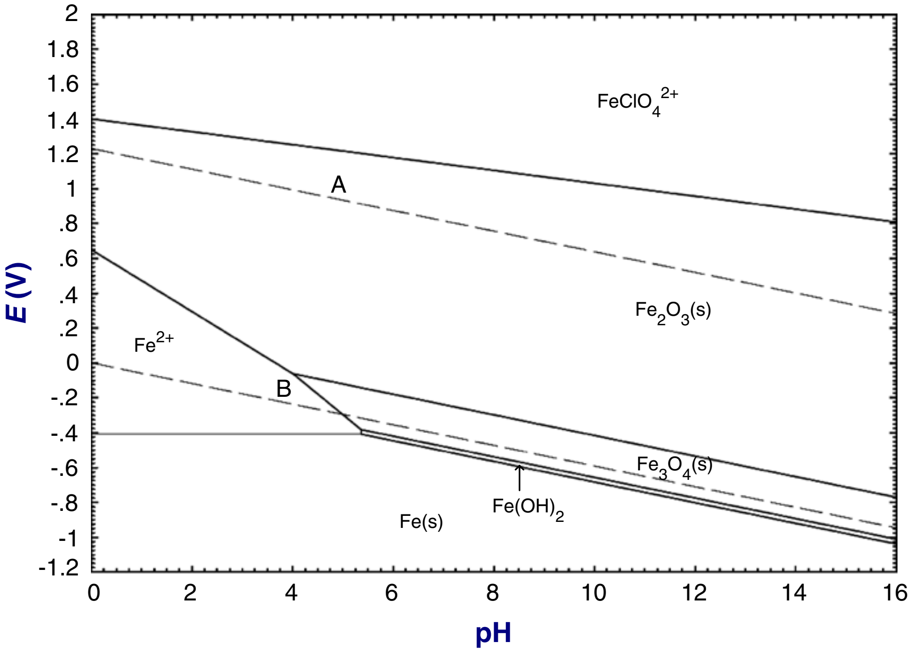


Fig. 4: Pourbaix diagram of the $Fe–H_2O–Cl^-$ system at 25°C. *E* on the *y*-axis refers to the overall potential given in equation (7). Dashed lines indicate the theoretical region of stability for water. The diagram was generated using FactSage 5.2

any salt deposits, and some of the metal under it, thus exposing more metal to corrosion.[18]

To predict the vulnerability of metals, thermodynamics, reaction kinetics, and experimental conditions may need to be considered. Thermodynamics can, in many cases, be calculated a priori, whereas kinetics can only be measured experimentally. A detailed characterization and description of some of the most common types of metal corrosion may be found in some of the numerous textbooks dealing with corrosion.[25,31]

Anticorrosive coatings

An anticorrosive coating system usually consists of multiple layers of different coatings with different properties and purposes. Depending on the required properties of the coating system, the individual coats can be metallic, inorganic, or organic. A typical anticorrosive system for highly corrosive marine environments usually consists of a primer, one or several intermediate coats, and a topcoat.[31] The function of the primer is to protect the substrate from corrosion and ensure good adhesion to the substrate. For this reason, metallic zinc or inhibitive pigments are often formulated into coatings applied as primers for structures situated in the splash zone or in an atmospheric environment. The function of the intermediate coat is generally to build up the thickness of the coating system and impede transport of aggressive species to the substrate surface. The intermediate coat must also ensure good adhesion between the primer and the topcoat. The topcoat is exposed to the external environment and must provide the surface with the required color and gloss. In addition to adequate resistance to alternating weathering conditions and impacts from objects, the topcoat should also have a high resistance to ultraviolet radiation. The environmental degradation caused by moisture, temperature, and ultraviolet radiation will reduce the lifetime of the coating.[32,33]

The overall performance and durability of a coating system is very difficult to assess because it is affected by several internal and external factors. The complexity of the coating system and some of the variables that affect the performance and durability of an anticorrosive coating system are illustrated in Fig. 5. Many of the factors, such as chemical, mechanical, and physical properties, as well as the chemical characteristics of the coating, can be manipulated by the formulators by their choice of binder system, pigmentation, solvents, and additives. However, it is also clear that several of the depicted factors, such as environmental properties, are outside the influence of the coating formulator. Consequently, any guarantee on anticorrosive performance and durability of a coating system must subsequently be based on ‘‘full-scale'' (natural) exposure in combination with controlled accelerated laboratory tests with a specific coating and substrate.

In addition to the physical and chemical properties of the coating and the substrate surface, a coating system applied to a metal surface may contain inhomogeneities such as air bubbles, cracks, microvoids, contaminants, trapped solvents, nonbonded and weak areas, pigment-resins, and coating-substrate interfacial layers.[12] Each of these factors will influence the transport of aggressive species through the coating and along the coating-substrate interface (extending from a defect or damage in the coating) and subsequently affect the degradation process. The importance

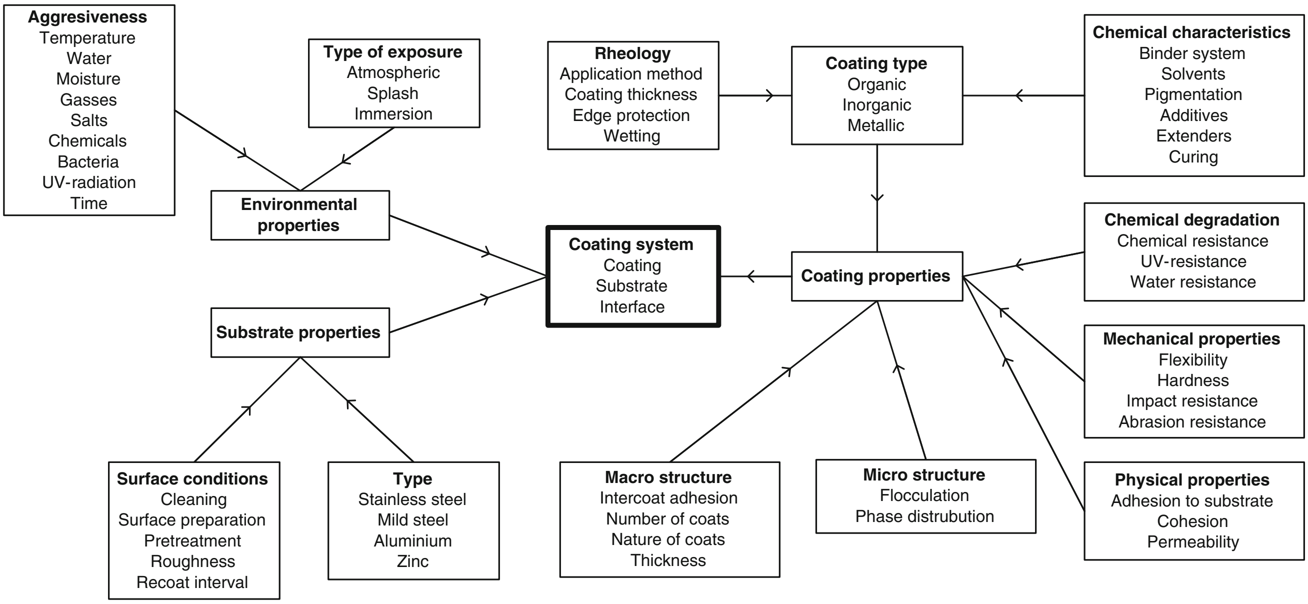


Fig. 5: Factors affecting the durability of an anticorrosive coating system. Modified from reference 12

of avoiding defects in a coating is evident because nondefective anticorrosive coatings that primarily protect the substrate by obstructing the passage of water, oxygen, and cations may have lifetimes up to 20 years. In comparison, the lifetime of coatings containing a physical damage will be much less. Consequently, the permeability of anticorrosive coatings to aggressive species is of great importance in the ability of a coating system to protect metals against corrosion. In a recent review focusing on the permeability of water and oxygen, several structural attributes of polymers in relation to the permeability of organic coatings to oxygen and water have been addressed.[34]

The existence of internal stress in the coating, which develops due to an inability of the coating to shrink, may add further to the complexity of the coating system. Internal stress in coatings can significantly affect the durability of anticorrosive coatings by resulting in loss of adhesion, cracking, or cohesive failure.[35] Some of the most important types of physical and aesthetic defects are described in coating textbooks on technology.[31] Some textbooks also discuss[25] the causes of the failure, and possible ways to avoid failures in anticorrosive coatings.

Protective mechanisms

Anticorrosive coatings are generally classified in accordance with the mechanisms by which they protect a metal against corrosion. Figure 6 illustrates the three basic protective mechanisms of anticorrosive coatings: barrier protection, passivation of the substrate surface (inhibitive effect), and sacrificial protection (galvanic effect).

Barrier protection is obtained by impeding the transport of aggressive species into the surface of the substrate by application of a coating system with low permeability for liquids, gases, and ions. Passivation of the substrate surface can be obtained by a chemical conversion layer, or by addition of inhibitive pigments to the coating. Metallic, organic, and inorganic coatings have all been widely applied for protection of metals against corrosion by means of sacrificial protection i.e., protection is obtained by sacrificial corrosion of an electrochemically more active metal, which is in electrical contact with the substrate.[31] Although metallic anticorrosive coatings have been subjected to extensive research, they are considered to be outside the scope of this paper. Further information on metallic coatings may be found in some of the reviews on metallic coatings.[36,37]

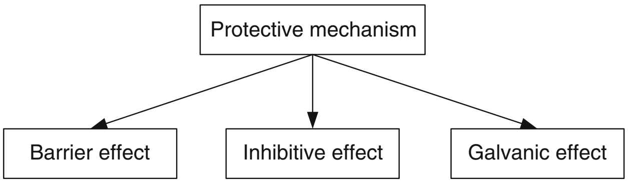


Fig. 6: Protective mechanisms of anticorrosive coatings

Barrier coatings

Barrier coatings may be used as primer, intermediate, or topcoat, and are often applied on immersed structures.[38] Barrier coatings are typified by an inert pigmentation, typically titanium dioxide, micaceous iron oxide, or glass flakes, at lower pigment volume concentrations, but lamellar aluminum is also often applied. The lower pigment volume concentration results in dense and cohesive coatings with significantly lower permeability towards aggressive species than any of the other two types of coatings.[39]

The degree of protection offered by a barrier coating system is highly dependent on the thickness of the coating system as well as the generic type and nature of the binder system. The delamination of both defect-free and artificially damaged barrier coatings has been reported to be significantly reduced when the thickness of the coating is increased[40,41] because coatings behave as semipermeable membranes.[42] In general, the anticorrosive performance of barrier systems increases when the same film thickness is built up from multiple successive thin coats rather than a single coat, but labor costs and potential revenue loss due to downtime push towards fewer and thicker coats.[43]

The original assumption was that barrier coatings inhibit corrosion by acting as a barrier to water and oxygen from the environment.[44] However, studies indicate that the mechanism of barrier protection relies on the ionic impermeability of the coatings.[45–47] The ionic impermeability of barrier coatings ensures that moisture at the coating-substrate interface has a very high electrical resistance. Thus, the conductivity of the electrolyte solution at the substrate is so low that the transfer of corrosion current between the anode and cathode is minimized.[38]

Cathodic protection may be used as a supplement to barrier coatings with immersed and buried systems to ensure satisfactory protection of the substrate in the case of damage to the coating system. The main principle of cathodic protection is to impress an external current to the material, which forces the electrode potential into the immune region.

The external current can be produced in two different ways:

- By means of a less noble material in the form of sacrificial anodes, which are connected by metallic conductors to the metallic structure.
- By means of an external current source, usually a rectifier. A reference electrode may be used to control the current from the rectifier.

The majority of offshore structures are protected with sacrificial anodes. On submerged parts of the structures, this may even be the only protective system.[18] For bare steel on offshore structures in seawater, the sacrificial anodes are commonly made of special aluminum alloys because these give the highest current output and the lowest costs. Zinc anodes are usually applied on coated or buried pipelines offshore, where the risk for passivation of aluminum anodes is higher due to a lower current density. For some other applications in high resistivity environments, such as steel structures in soil, and in hot water tanks for fresh water, magnesium anodes are used to a larger extent because magnesium anodes have a higher driving voltage than aluminum and zinc anodes.

The largest benefits of impressed current compared with sacrificial anodes are lower anode weight and lower drag forces from the sea. Theoretically, it should be economically beneficial to apply impressed current compared to sacrificial anodes, but practical experience with the breakdown of the impressed cathodic current protection system has led to fewer applications of impressed current systems.[18,48] The combination of cathodic protection and coatings constitutes another challenge because coatings are subject to alkalis produced by the reduction of oxygen to hydroxyl ions. This means that coatings that are subject to saponification are not suitable choices in combination with cathodic protection. For further study of arrangements and requirements, the reader is referred to the literature.[30,49,50] Arguments for and against the different systems under various conditions are listed in reference 23.

Not all binders are suitable for the design of barrier coatings. Polymers bearing many hydrophilic groups, e.g., alkyds, do not generally produce barrier systems better than polymers containing hydrolyzable stable bonds, e.g., epoxies and urethanes.[51,52] On the other hand, the existence of polar groups generally improves the adhesion to the metal substrates because polar groups are thought to bind to the metal oxide surface by means of secondary bonds or hydrogen bonds.[52] Furthermore, the environments in which barrier coatings are applied further restrict the choice of binder. Well-formulated barrier coatings are efficient in maintaining corrosion control under demanding conditions including combinations with inhibitive primers, immersion in both fresh and salt water, burial in soils, and service in highly corrosive chemical environments.[38]

A key element for high-performance barrier coatings is a high crosslink density.[53,54] A series of papers have addressed ionic conduction through coatings,[53,55–57] and it has been shown that there is a direct relationship between the presence of low crosslinked density areas in the film and the occurrence of underfilm corrosion.[58]

Sacrificial coatings

Sacrificial coatings rely on the principle of galvanic corrosion for the protection of metals against corrosion. This means that the substrate is protected by a metal or alloy that is electrochemically more active than the material to be protected. In this respect, coatings formulated with metallic zinc powder have been extensively employed for corrosion protection of steel structures for several decades.[59] Unlike barrier coatings, sacrificial coatings are only applied as primers because they are only effective if the coating is in direct contact with the substrate due to the requirement of electrical contact between the substrate and the sacrificial metal. Furthermore, sacrificial coatings should only be applied with great care on structures submerged in water due to the subsequent permeation of water, which may cause the sacrificial metal to corrode.[60]

In zinc-rich primers, zinc is used to produce an anodically active coating.[60] Zinc will behave as an anode and sacrifice itself to protect the metal, which becomes a cathode. The resistance towards corrosion is dependent on the transfer of galvanic current by the zinc primer, but as long as the conductivity in the system is preserved, and as long as there is sufficient zinc to act as anode, the metal will be galvanically protected. The electrochemical activity in a damaged zinc coating system results in the formation of zinc corrosion products, which tend to seal the pores between the zinc particles to a point at which the system becomes electrically nonconductive, as illustrated in Fig. 7. Subsequent protection is attributable to the barrier effect by corrosion products.[61,62]

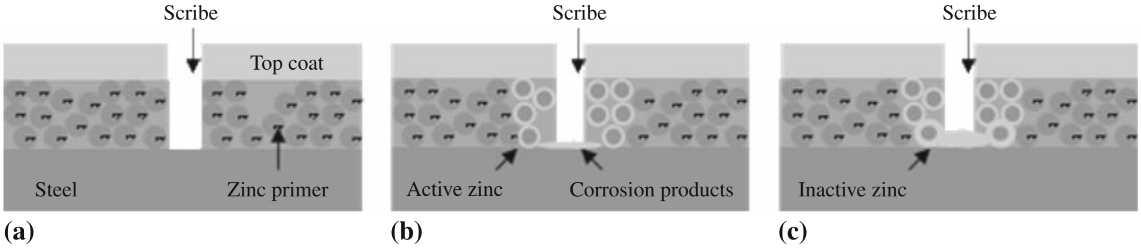


Fig. 7: Stylistic sketch of the working mechanisms of a zinc-rich coating system. (Step a) Damage is introduced down to the steel surface. (Step b) Zinc around the score is still active while zinc-iron corrosion products are being built up. (Step c) The zinc is not galvanically active any longer but the coating provides barrier and inhibitive protection

The performance of sacrificial coatings is based on transfer of the galvanic current. This means there must be metallic contact between the individual particles of the sacrificial metal. Hence, sacrificial coatings usually are very highly pigmented, typically just below the critical pigment volume concentration. Indeed, the highest electrical conductivity is typically reached at a concentration of zinc particles in the range of 92–95 wt% of the dry film.[63,64] Since such a coating only contains 5–8 wt% of binders and very low amounts of other components for securing the mechanical properties, the adhesive and cohesive strength, as well as its resistance to impacts, is significantly reduced.

Inhibitive coatings

Inhibitive coatings are primarily applied as primers because they are solely effective if dissolved constituents can react with the metal.[31] These coatings are mainly applied to substrates subject to environments with a risk of atmospheric corrosion, in particular industrial environments, and are generally not recommended for immersion in water or burial in soil.

The anticorrosive mechanism of inhibitive coatings relies on passivation of the substrate and build-up of a protective layer consisting of insoluble metallic complexes, which impede transport of aggressive species by acting as a barrier. The inhibitive pigments are inorganic salts, which are slightly water soluble. In Europe, phosphates are the most used cations.[65,66] On a worldwide basis, however, chromates,[67–69] molybdates,[67,68,70] nitrates,[67,68] borates,[71] and silicates[72] are also frequently used as cations in the inorganic salts. When the coating is permeated by moisture, the constituents of the pigments are partly dissolved and carried to the substrate surface. At the surface of the substrate, the dissolved ions react with the substrate and form a reaction product that passivates the surface of substrate.[73] This means that inhibitive pigments must be high enough to ensure sufficient leaching from the coating. However, if the solubility of the inhibiting pigments is too high, blistering can occur.[74]

An ideal inhibitive coating should form a barrier against water and detrimental ions and simultaneously release a sufficient quantity of inhibitor on demand. These two requirements are antagonistic in principle. Therefore, a balance between the barrier properties and the effectiveness of the inhibitor has to be reached. The efficiency of inhibitive pigments is very dependent on the barrier properties of a coating. If the permeability of the coating system is low, the observed effect of the barrier pigments will be predominant. However, the effect of the inhibitive pigments will be more apparent in coatings with a certain degree of permeability because the solubility of the pigments and the mass transfer within the coating will be important in this case.[75]

Inorganic coatings

Inorganic coatings are made of natural compounds from the earth strata, such as quartz, minerals, and inorganic mineral colorants. Among the most widely applied inorganic coatings are zinc silicates. Zinc silicates are unusual coatings and are one of the few coatings that are pigmented above the critical pigment volume concentration.[76] This means that not all of the solid pigment particles are covered with polymer, and all of the gaps between particles are not filled with polymer i.e., the coatings are designed to be porous. The high pigmentation of zinc silicates provides excellent protection against corrosion if the coating is applied as specified. However, the high level of pigmentation means that zinc silicates have a high risk of mud cracking. Mud cracking occurs as a result of internal stress that develops during curing if zinc silicates are applied too thick. Hence, the application of zinc silicate or zinc epoxies as primers in anticorrosive coating systems is subject to debate[77,78]

Another type of inorganic coatings is based on the sol–gel technique, which relies on dispersions of inorganic metal salts with solid particles. The sol–gel process technique of creating ZnO, SiO_2, and SiO_2–TiO_2 coatings for protection against metal corrosion has been extensively studied.[79–83] The microcrystalline structure of inorganic coatings results in excellent aesthetic appearance, high abrasion resistance, and the lower absorption of UV-radiation with no significant loss of gloss or change of color. The inorganic particles in the sol–gel coatings generally provide an excellent barrier against aggressive species.[84] However, it is difficult to apply sol–gel coatings in the thickness required for obtaining excellent anticorrosive properties without a risk of cracking. Furthermore, sol–gel coatings are brittle and use a high processing temperature not applied to large-scale structures.[85]

In recent years, the desire to combine the properties of organic polymeric materials and inorganic ceramics has resulted in extensive research in hybrid organic-inorganic coatings for corrosion protection.[86] The development of hybrid inorganic-organic materials using the sol–gel method allows incorporation of organic polymeric materials into an inorganic network. In addition to increasing the compatibility with most organic coating systems, the presence of polymeric materials increases the mechanical flexibility and toughness of the coating.[87] The presence of inorganic materials may enhance the adhesion in comparison to a pure organic coating because certain inorganic components are capable of reacting with the metal surfaces.[88] The incorporation of polymeric materials is also believed to reduce the porosity of the coating by sealing open pores between the inorganic particles, which subsequently improves barrier properties. The most widely applied hybrid inorganic-organic material is modified organosilanes (polysiloxanes), which are prepared by hydrolysis and condensation of organically modified silicates with traditional alkoxide precursors.[89] The solution-based nature of the hybrid sol–gel coatings allows for the incorporation of water-soluble alkoxides. In present anticorrosive coating research, great attention is paid to the use of inorganic-organic hybrid sol–gel coatings modified with inorganic particles or extenders for replacement of pretreatments such as phosphatizing.[90]

Summary of applications

A brief summary of the most important advantages and disadvantages for barrier, sacrificial, and inhibitive coatings, as well as suggested areas of application, are given in Table 4.

Accelerated testing of anticorrosive coatings

Modern high-performance anticorrosive coating systems are so durable that they may show little signs of deterioration for several years after exposure to natural weathering. As a consequence, accelerated weathering methods have become an important tool in the development of anticorrosive coatings. The purpose of accelerated testing is twofold. Coating suppliers use accelerated weathering methods to screen and develop novel high-performance coatings, whereas potential customers may use the accelerated methods to compare the performance of different anticorrosive coatings (e.g., prequalification tests). The accelerated laboratory weathering methods seek to intensify the effects from the environments so the coating breakdown occurs more rapidly than in naturally occurring environments. Thus, it is essential that the utilized accelerated methods reflect the type of environment encountered by the coating during service. However, many of these accelerated exposure tests will not, within their exposure time, visually show the negative effects on intact coated surfaces. Therefore, the behavior of coatings around artificially made damages is given significant consideration in the design of novel high-performance anticorrosive coatings.

Accelerated weathering methods

An important aspect in relation to the accelerated testing of coating performance is the correlation with natural outdoor exposure. Traditional accelerated testing, such as simple salt spray chambers where aerosols of seawater are continuously sprayed on coatings containing an artificial damage, have been largely discredited due to poor correlation with natural exposure.[91] Cyclic corrosion tests have been reported to correlate better with natural outdoor exposure than traditional salt spray.[22] In cyclic corrosion tests, coatings are exposed to alternating conditions in terms of electrolytes and weathering e.g., moisture, dryness, ultraviolet radiation, and temperature gradients. As a result, current attention is primarily paid to cyclic corrosion testing. Several organizations have published standards containing guidelines for the testing of anticorrosive coatings in an attempt to obtain a globally recognized standard. In Europe, ISO 12944 has found widespread acceptance as the most important standard for the testing of anticorrosive properties. Typical prequalification standards only evaluate coating properties to a limited extent e.g., general corrosion protection, underfilm corrosion, or delamination from artificially induced damage, water resistance, and (in some cases) UV resistance. Only a few properties related to the later performance of anticorrosive coatings are tested in such a limited approach. Hence, care must be taken not only to sort various coating systems according to the amount of underfilm corrosion or disbondment from an artificially made scribe. The selection of coating systems must also be based on principles of generic types of primers and topcoats, the minimum number of coats, and the minimum coating thickness.[92]

It should be noted that the correlation between accelerated test methods and natural outdoor exposure concerns a progression of corrosion or disbondment from mechanical damage, which cannot necessarily be translated into lifetime predictions of intact coatings. In Norway, the introduction of prequalification tests as technical selection criteria has, despite its original intent, resulted in lower lifetime and higher maintenance costs of the coating systems.[93]

A schematic overview of some of the most important test methods for determination of the anticorrosive performance of coatings is given in Table 5 for corrosivity categories starting from C2, and durability ranges from low to high. Several other test methods that do not measure the anticorrosive performance may also be considered relevant for anticorrosive coatings. The methods specified by NACE TM 0104, 0204, 0304, and 0404 include similar procedures as ISO 12944 for the testing of anticorrosive properties, although the standards are not identical. However, the NACE standards also address the appropriateness of usage by evaluating flexibility, edge retention, and thermal cycling, etc.

Despite the continuous review of procedures for accelerated weathering methods, many problems continue to persist. The continuous high temperature (35°C) and salt concentration (5 wt%) of the salt fog do not fit any common conditions for usage. An important aspect in relation to application of elevated temperatures is to ensure that the temperature during accelerated weathering does not exceed the glass transition temperature (T_g) of the coating, because this will result in false failures.[94] The curing of the coating may also be affected by elevated temperatures because homopolymerization of polymer chains is more likely to occur at elevated temperatures.

Table 4: Summary of application areas, advantages and disadvantages for barriers, and sacrificial and inhibitive coatings

Coating type	Application areas	Advantages	Disadvantages
Barrier	Immersed Marine and industrial atmospheres	Low permeability towards liquids, gases and ions In general good strength and abrasion resistance as well as good resistance towards UV-radiation May be applied along with impressed cathodic current protection or sacrificial anodes May be applied as primer, intermediate or topcoat	Risk of solvent retention Aluminum pigment will dissolve in acidic environments and cause evolution of hydrogen Risk of galvanic corrosion of aluminum pigmented coatings applied on zinc rich primer in environments with high relative humidity In splash zones and atmospheric environments, damaged coatings offer insufficient protection against corrosion Risk of providing rapid transport of aggressive species to the metal in case of wrong orientation of lamellar pigments
Organic sacrificial	Marine and industrial atmospheres Splash zones	Excellent protection against corrosion due to cathodic protection of metal substrate	High material costs Low adhesion and cohesion due to high content of metal Zinc rich coatings are generally not recommended for immersion or application along with ICCP
Inorganic sacrificial	Marine and industrial atmospheres Splash zones	Zinc silicates are resistant to heat and immersion in water with mild solutions of chemicals	Zinc silicates have low compatibility with subsequent coats and require specific conditions for curing Requirement of electrical contact between metal particles for proper protection
Inhibitive	Industrial atmospheres	Formation of a water insoluble passivation layer which persists or remains insoluble in most environments Lower costs than zinc pigmented coatings	Not applicable for immersed structures Coatings must be semi-permeable to water for effective inhibition of substrate Risk of increasing the rate of corrosion by addition of insufficient amounts of anodic inhibitor

Note: ICCP stands for impressed current cathodic protection

Table 5: **Example of test methods and exposure times (in h) for determination of the performance of protective coatings**

Corrosivity category (ISO 12944-2)	Durability range (ISO 12944-1)	Neutral saltspray test (ISO 9227) (h)	Water immersion test (ISO 2812-2) (h)	Water condensation test (ISO 6270-1) (h)	Chemical resistance test (ISO 2812-1) (h)	Cyclic corrosion test (ISO 11997) (h)	Cyclic corrosion test (ISO 20340) (h)	Cathodic protection test (ISO 15711) (h)	Cathodic disbonding test (ASTM G 8, 42, 96) (h)
C2	Low	–	–	–	–	–	–	–	–
	Medium	–	–	48	–	–	–	–	–
	High	–	–	48	–	–	–	–	–
C3	Low	120	–	120	–	–	–	–	–
	Medium	240	–	48	–	–	–	–	–
	High	480	–	120	–	1680	–	–	–
C4	Low	240	–	240	–	–	–	–	–
	Medium	480	–	120	–	–	–	–	–
	High	720	–	240	–	2016	–	–	–
C5-I	Low	720	–	480	168	–	–	–	–
	Medium	1440	–	240	168	–	–	–	–
	High	2160	–	480	168	2688	–	–	–
C5-M	Low	720	–	720	–	–	–	–	–
	Medium	1440	–	240	–	–	–	–	–
	High	–	–	–	–	–	4200	4368[a]	–
Im1	Medium	–	2000	720	–	–	–	–	–
	High	–	3000	1440	–	–	–	4368	–
Im2	Medium	1440	2000	–	–	–	–	–	–
	High	2160	3000	–	–	–	–	4368	–
Im3	Medium	1440	2000	–	–	–	–	–	–
	High	2160	3000	–	–	–	–	–	4368

Modified after reference 16

Notes: Cyclic corrosion test may include exposure to saltspray, UV, water condensation, and dry out. Durability refers to the expected timeframe prior to the first maintenance painting would normally need to be carried out: low: 2 years to 5 years; medium: 5 years to 15 years; high: more than 15 years

[a] Should be used if the coating is applied in the splash zone

Electrochemical methods

In view of the electrochemical nature of corrosion processes, it is not surprising that measurements of electrical properties of the metal-solution interface are so extensively used across the whole spectrum of corrosion science and engineering, from fundamental studies to monitoring and control in service. Over the last few decades, electrochemical methods have found widespread use for characterization of anticorrosive coatings, and are commonly employed to assess the performance and durability of anticorrosive coatings in the laboratory. The advantage of electrochemical methods is their ability to obtain information regarding the degradation of both coating and substrate before the degradation can be visually observed.

Traditional electrochemical testing of anticorrosive coatings relies on coating resistance as a measure of performance.[46,53,57,58] Correspondingly, coatings that are able to maintain a high electrical resistance for several weeks of immersion have traditionally been regarded as excellent coatings for immersion. The occurrence of pin-holes, craters, low coating thickness, and other defects, which allow oxygen, water, and existing free ions to penetrate the polymer, form the basis for the ability of electrochemical methods to monitor the degradation of anticorrosive coatings. This so-called ionic attack alters the insulating structure of the polymer, which results in the modifications in the electrochemical characteristics of the overall coating-metal system. This change may then be monitored by a variety of suitable electrochemical methods.

Among the most widely applied electrochemical methods for characterization of anticorrosive coatings is electrical impedance spectroscopy (EIS), which is a nondestructive method that has been applied by several authors to study the degradation of organic coatings.[94–100] The usefulness of EIS lies in its ability to distinguish the individual contributions of components under investigation. When the behavior of a coating on a metal immersed in an electrolyte solution is of interest, a value of resistance and capacitance for the coating can be determined through modeling of the electrochemical data. The modeling procedure uses electrical circuits built from components such as resistors and capacitors to represent the electrochemical behavior of the coating and the metal substrate. Consequently, changes in the values for the individual components indicate the behavior and performance of a coating system.

A simple equivalent electrical circuit model for organic-coated metals in solution is illustrated in Fig. 8. R_s refers to the electrolyte resistance, C_c indicates the coating capacitance, R_c refers to the coating or pore resistance, and element Z_f represents the electrochemical process at the metal interface. For a dry coating (before immersion), R_c and Z_f tend to be negligible, and the total impedance (Z_T) is simplified as $Z_T = R_sC_c$. Prolonged immersion leads to a declining of R_c as a result of water penetration through the coating. Thus, the equivalent electrical circuit becomes $Z_T = R_s(C_cR_c)$. After water and oxygen molecules arrive at the metal surface, the electrochemical element Z_f becomes significant, and the complete model can be regarded as shown in Fig. 8. Detailed equivalent electrical circuit models for the different stages in the degradation of organic coatings are well established within the topic.[101]

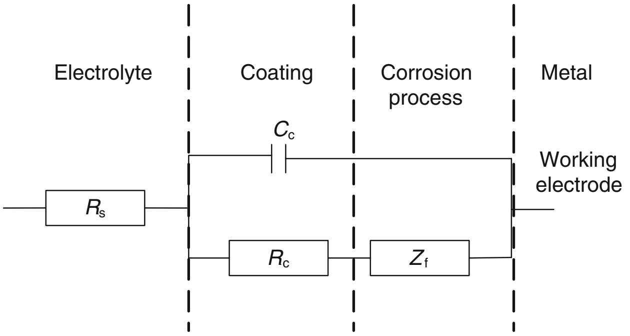


Fig. 8: General equivalent electrical circuit for coated metal (simple single coat illustration). Modified after reference 101

The combination of EIS and equivalent circuits provide a possibility of modeling the physical behavior of coatings as they degrade, which may help to provide physical models for the failure of protective coating systems. Due to difficulties in producing identical coating samples and large variances between replicates, EIS is mostly applied in a qualitative or semiqualitative manner.[102] EIS has been extensively applied for investigation of corrosion processes, water transport, and sorption of organic coatings.[101,103–105] In recent years, however, EIS has also been applied in studies of ionic transport through coatings.[105,106] Despite the wide application of EIS for characterization of anticorrosive coatings, a model relating EIS measurements directly to lifetime prediction has not been successfully implemented. Some researchers,[94,102] however, have attempted to interpret the data from measurements in the low-frequency region and relate it to lifetime predictions. Guidelines for application of EIS in relation to anticorrosive coatings may be found in standards for EIS-coated specimens.[107]

The electrochemical noise analysis method was one of the first electrochemical methods applied to anticorrosive coatings.[108,109] In this method, the natural voltage and current fluctuations generated in corrosion cells are recorded and used to obtain information on coating behavior. These voltages and currents are small and variable with time, so a large number of measurements have to be made to get a statistically significant result. The advantages of this method are that electrochemical noise measurements (ENM) are relatively low-cost and that no external source of current or voltage is needed.[110] Hence, interference with the system is minimal and monitoring can be continuous. The most useful parameter to obtain is the noise resistance derived as the standard deviation of the voltage noise divided by the standard deviation of the current noise.[111] The noise resistance measurements have been found to correlate with both the DC resistance measurements for coated specimens, and the polarization resistance measurements for bare metal.[112] Comparative studies between impedance spectroscopy and noise analysis show similar results.[113,114] By measuring the potential noise, it has been shown that the amplitude spectra of the low-frequency electrochemical potential noise correlate with the performance of an anticorrosive coating.[115] In addition to evaluating organic coatings, ENM can be used to distinguish between various types of corrosion.[116] However, the application of ENM for corrosion studies remains a controversial subject because there are no established test methods or consensus on a theoretical framework for interpreting data.[117]

Another widely applied technique for studies of performance and durability of anticorrosive coatings is the scanning Kelvin probe, which is a noninvasive, no-contact vibrating capacitor technique. The scanning Kelvin probe measures the voltage between a vibrating microelectrode and a sample with a high resolution. The scanning Kelvin probe has been frequently applied in the study of coating-metal interfaces.[118–121] The ability of the scanning Kelvin probe to measure the interfacial potential between a defect and a random location at the coating-steel interface has allowed the rate of cathodic delamination to be the measured nondestructively.[122–124] Recently, the scanning Kelvin probe has been applied in the study of interfacial diffusion between a coating and a steel surface. The studies show that the diffusion of hydrated ions along the coating-metal interface was several orders of magnitude larger than the diffusion of ions in the bulk coating.[125]

Mathematical modeling of coating behavior

Coating formulators experience an increasing number of raw materials, complexity of formulations, intolerance of raw material variability, and performance expectations.[126] At the same time, the formulators are urged to reduce raw material costs and development time. This means that there is insufficient time for initial screening and selection of the best candidates. Consequently, there is a risk of not finding the best coating due to inadequate or insufficient testing. A part of the solution for the coating industry may be fundamental mathematical models of coating behavior, as encouraged in the literature.[126,127]

Fundamental mathematical models quantifying the most important physical and chemical mechanisms responsible for the degradation of anticorrosive coatings may be a powerful tool in the analysis and development of anticorrosive coatings. It has been demonstrated that mathematical models combined with accelerated testing can be applied to obtain a reliable estimation of the lifetime of antifouling coatings in given coating composition and seawater conditions.[128] The developed model has been applied to discuss the effect of seawater parameters and coating formulation parameters on coating behavior,[129] as well as the effect of pH, sailing speed, temperature, and salinity on the polishing and leaching rates of coatings.[130] Subsequent modification of the model has enabled simulation-based exploration and screening of seawater soluble pigments for their potential use in self-polishing antifouling coatings,[131] and application to other types of modern self-polishing binders.[132] Such models may also prove useful in the design and development of anticorrosive coatings.

A mathematical model capable of estimating the lifespan of anticorrosive coatings under a given set of exposure conditions may be applied to ensure proper correlation between accelerated laboratory exposure tests and natural atmospheric exposure tests. This may provide important information leading to optimization of the anticorrosive performance, and help to identify properties new efficient and environmentally friendly high-performance anticorrosive coatings should possess. Such models are not currently available for anticorrosive coatings.

Adhesion

Adhesion is an interfacial phenomenon that may occur when two surfaces approach each other to form an interface by the action of physical and chemical forces. Proper adhesion of anticorrosive coatings to the substrate is essential for the anticorrosive properties of a coating system. Inadequate adhesion will promote failure of the coating and expose the bare metal to the aggressive environment, causing corrosion. Theories of interfacial chemistry, such as the wetting theory,[133–137] starting with Young's equation[138] and acid-base interactions,[139,140] are frequently applied in the study of adhesion. In the specific case of an organic coating applied to a metallic substrate, two types of adhesion are frequently referred to in the literature[141]:

- Mechanical adhesion (or large surface areas with many points of interaction), where the coating penetrates the surface pits and forms mechanical anchoring into the substrate. This type of adhesion is mostly found on primed or porous metallic surfaces.
- Chemical adhesion, where the chemical bonds at the interface may be divided into three groups—primary bonds, which consist of covalent or ionic bonds with energies ranging from 40 to 400 kJ/mol; secondary bonds, which include dispersion forces, dipole interactions, and van der Walls forces with typical energies between 4 and 8 kJ/mol; and finally hydrogen bonds having bond energies from 8 to 35 kJ/mol.[141]

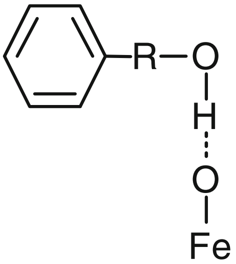


Fig. 9: Adhesion of epoxy to the ferrous oxide layer on steel by hydrogen bonds

It is generally believed that most organic coatings adhere to metals via hydrogen bonds or secondary bonds as illustrated in Fig. 9.[52] Most metallic surfaces are covered with a thin oxide layer.[142] Therefore, hydrogen bonds develop when an organic coating and a metallic surface are brought closely together and subsequently binders with polar groups display excellent adhesion characteristics. Although the bond strength of epoxy resins on steel is strongly dependent on the hydroxyl group content,[143] this type of adhesion may not be general in the case of binders such as epoxy resins and zinc silicates. This is partly because the suggested adhesion mechanism cannot satisfactorily explain why bond strengths vary from metal to metal, and why epoxy resins have superior adhesion compared to other organic polymers having an equal amount of hydroxyl groups. The generally accepted model for the adhesion of organic coatings on steel has been challenged by one research group,[144–147] who found that the epoxy compounds were dissociated between the phenoxy oxygen and the aliphatic carbon. The surface interactions were believed to be via the phenoxy and hydroxyl oxygen atoms, as illustrated in Fig. 10. They also suggested that the previously observed dependence of adhesion strength on the content of hydroxyl groups is because the epoxy resin was inevitably oriented on the surface of water in such a way that the hydrophilic part of the molecule pointed down to the interface while the hydrophobic part turned away from the interface.

Regardless of the adhesion mechanisms of organic coatings on metals, much stronger adhesion can be obtained if the coating reacts with the metal as in the case of pretreatments based on chromatizing and phosphating.[10,11] The deposition of a conversion layer on the metal surface may passivate the surface and enhance the adhesion for subsequent applications of a coating, or work as a barrier to aggressive species.[31]

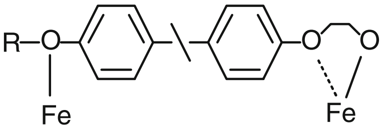


Fig. 10: Adhesion of epoxy to steel by interfacial bonds. Modified after reference 147

In the case of metal surfaces, contaminants such as oxides, dust, grease, oil, salts, and old coatings influence the adhesion of coatings significantly. When such debris is painted, the mechanical and chemical adhesion of the coating to the substrate is reduced, and the risk of coating failure is increased. The majority of the water-soluble contaminants must be removed by thorough rinsing with water and detergent. Subsequently, abrasive blasting is often applied for surface preparation to remove residues of rust, mill scale, and old coatings from the surface of the substrate before painting. Another consequence of surface preparation is an increase in the surface area of the substrate where adhesion can occur.[148] The need to remove water-soluble contaminants is evident because these may dissolve when moisture penetrates the coating and cause blistering, delamination, and accelerated underfilm corrosion.[9] The effect of different types of cleaning and pretreatment of metallic substrates, as well as application procedures, has been thoroughly described elsewhere.[31,149–152]

The adhesion between an organic coating and a metal substrate or pigments may also be improved by means of coupling agents that create stronger interfacial interaction (covalent bonds) between the coating and the media. These coupling agents are often referred to as adhesion promoters, and their role in improving adhesion of organic coatings to metal substrates has been extensively reviewed.[153] Adhesion promoters usually consist of molecules with short organic chains having different chemical composition on either end of the chains. On one end is an organofunctional group that is particularly compatible with the given adhesive material. At the other end of the chain is an inorganic functionality that is especially compatible with the substrate. Therefore, the adhesion promoter acts as a chemical bridge between the adhesive and the substrate. For enhanced adhesion between polymeric and inorganic materials, modified silanes are the most common commercial adhesion promoter.[154] They can be formulated into the coating or applied directly to the substrate. When incorporated into the coating, adhesion promoters are believed to migrate to the interface regions and attach themselves to the substrate or pigments before extensive curing has taken place. Adhesive promoting molecules are known to orient themselves perpendicular to the surface to which they are attached. Thus, a rough surface can break up the first ordered layer, preventing formation of a second layer. On the other hand, thin but continuous films appear to provide stronger and more durable adhesive bonds.[155]

Main components in anticorrosive coatings

The correct combination of components and process steps can lead to an anticorrosive coating system, which offers long-lasting protection against the elements while preserving an aesthetic appearance. Coatings can be formulated from a wide variety of chemicals and materials or a combination of different chemicals. Each component in the formulation serves a specific function. The five main groups of components in coatings are pigments, binders, extenders, additives, and solvents. Additives are auxiliary products that are added in small amounts to improve certain coating properties of the coating or solve technical problems such as formation of foam during manufacturing and application.[51] Specific examples of additives may be thickeners for improving pigment antisettling properties and surfactants for enhancement of the wetting of pigments. Nonpigment additives include stabilizers for absorption of ultraviolet light or heat, curing additives to speed up the crosslinking reactions, cosolvents to decrease viscosity and plasticizers to improve film formation. Extenders are normally naturally occurring minerals from processed deposits such as magnesium silicates or limestone that are added to coatings to reduce costs. Extenders do not generally improve the anticorrosive performance of coatings, but certain extenders are reported to improve the specific properties of the coating.[6,156]

Solvents

Traditionally, solvents have constituted a major part of organic coatings. Solvents are added to coatings to dissolve or disperse the other constituents of the formulation (such as viscous polymeric binder material and pigments). Furthermore, the solvents reduce the viscosity of the liquid coatings, thereby enabling application of the coating by spraying or dipping. In organic solvent-borne coatings, a combination of several solvents is generally applied to balance the evaporation rate and dissolution of the viscous polymeric binder.[51] Despite the temporary presence in the coating, the solvent plays a major role in how well the coating will perform because insufficient solvents may cause partial wetting of the substrate leading to nonprotected areas. Most of the time, a combination of solvents is used because formulators are seeking to dissolve the binder and have good compatibility with the other components while maintaining good film formation properties.

A wide range of organic liquids, such as aromatic and aliphatic hydrocarbons, glycol esters, and alcohols have been applied in organic coatings. However, these solvents are a major source of environmental concern because they are capable of volatilizing at normal temperatures and pressures. Exposure to solvent vapors is dangerous for a number of reasons. Long-term exposure to solvent vapors generally affects the central nervous system and may result in a number of human health risks. Solvent vapors may also pose fire or explosion hazards, necessitating careful storage and handling procedures.

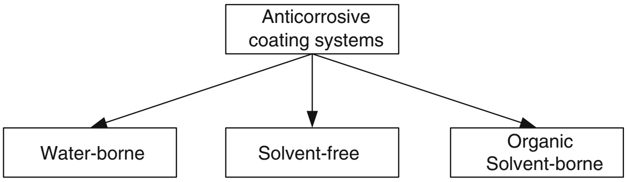


Fig. 11: Classification of anticorrosive coating systems according to solvent content

The problems related to organic solvents have resulted in legislation aiming at reducing VOC emissions. In Europe, the European Solvent Emission Directive and the Solvent Emissions Directive have already pushed the industry towards "good manufacturing processes" and improved application efficiency. The proposed tightening to the directives and the implementation of REACH will urge the coating industry towards development of new VOC-compliant products with high solids content and low amounts of organic solvents. This has resulted in great attention to environmentally friendly water-borne or powder coatings.

The correct choice of solvent technology for anticorrosive coatings depends on the required properties in relation to the conditions of the environment, method of application, curing, pigmentation, and nature of the substrate. Increased demands for environmentally friendly coating systems require the substitution of hazardous coatings with environmentally friendly compounds. Among the alternatives are water-borne coatings and solvent-free coatings, as illustrated in Fig. 11.

Water-borne coatings

The solubility of polymers traditionally applied in anticorrosive coatings, such as epoxy, urethane, alkyd, and acrylic, is significantly higher in most organic solvents than the corresponding solubility in water. The reduced solubility of the polymer molecules in water means that dissolution of the binder constitutes a challenge for coating formulators. The largest group of water-borne coatings is aqueous dispersion coatings. The first type of water-borne dispersion coatings was single component anticorrosive coatings based on styrene–butadiene and vinyl acrylic polymers. In the following stage, chemically curing water-borne two-component epoxy anticorrosive coatings, largely dependent on the synthesis of new binders, were developed.[157]

Water-borne coatings contain different additives than organic solvent-based coatings, and an appropriate choice among various alternatives of these additives brings a challenge to both manufacturers and researchers. Several groups have reported the influence of pigment morphology, surface treatment of inorganic pigments, corrosion inhibiting additives, extenders, dispersing agents, and the nature of the binder material on the performance of water-borne coatings.[158,159]

Alkyd, acrylic latex, epoxy, polyurethane, and other resins may be used in the formulation of water-borne coatings. For general finishing applications, alkyd coatings are commonly used. Acrylics also are frequently selected for finishing applications. Water-soluble epoxy esters and alkyds dominate the anticorrosive segment. Water-borne coatings are widely used as architectural coatings for the maintenance of homes, public buildings, offices, and factories, but many solvent-borne, industrial, high-performance coatings are difficult to replace.[160] Although defect-free water-borne coatings are capable of protecting metal substrates against corrosion in marine atmospheres of very high corrosivity categories if a zinc rich primer is applied, the water-borne coating technology faces several challenges.

Most disadvantages of water-borne coatings are related to the use of water as a solvent. Although the alkaline nature of some curing agents such as amine counteracts flash rust, an effective inhibitor such as sodium nitrate must normally be formulated into water-borne coatings to prevent flash rust on weld seams.[158] Other disadvantages of water-borne coatings are their inability to endure freeze/thaw cycles and the influence of relative humidity on the evaporation rate of water. Besides expensive raw materials, the drying and formation of a solid coating of latex particles constitutes another problem. The evaporation of water from water-borne coatings is relatively fast, which means that edge marks may be produced when a freshly applied paint is lapped on previously painted areas. Another drawback of water-borne coatings is that there may be insufficient time to make corrections to the freshly applied wet coating without leaving brush marks (too short "open time").[160] Water-borne coatings must contain biocides to prevent the formation of bacteria and fungi. Furthermore, some types of water-borne coatings have problems with development of foam.[161] The technical challenges in the formulation of environmentally friendly coating systems have been thoroughly discussed elsewhere.[162]

Solvent-free coatings

The most widely applied type of solvent-free coating is powder coatings. Powder coatings have found widespread usage in the coating of automobile and machine parts. Similar to other polymeric materials, powder coatings are classified as either thermoplastic or thermoset. Thermoplastic resins typically melt and flow at elevated temperatures while maintaining their chemical integrity. On the other hand, thermoset resins provide similar melting and flow properties while changing their chemical properties upon curing. Among the thermoset powders available for coatings are acrylics, polyesters, polyester-epoxies, acrylic-epoxies, and polyurethanes.[163] Commercially available thermoplastic powders include, among others, fluoropolymers, vinyl- and acrylic-based polymers, as well as polyethylene, polypropylene, and polyamides.[13] Recent developments within the powder coatings industry include segments within hybrid sol–gel coatings technology.[89]

The advantages associated with powder coatings include durable finishes, high application efficiency, easy clean-up and recycling. Powder coatings represent a technology solution that is environmentally friendly because it contains essentially 100% solids. The disadvantages of this technology include high capital costs for ovens and specially designed spray equipment, high-bake temperatures (only a limited number of binders are solid at ambient temperature) that make powder coatings of large, complex objects difficult, limited color changeability, and an inability to modify a coating composition or film thickness during application. Another application problem is that, in the case of contamination causing significant defects such as craters, the line must be stopped, all of the contaminated powder must be removed, and the system must be cleaned thoroughly before a new powder can be added.

Binders in anticorrosive coatings

A common feature among the different types of anticorrosive coating technologies is the basic structure and reactivity associated with the binders or resins used in the formulation of coatings. The binder must ensure a number of properties, of which some of the most important ones are adhesion to the metal, cohesion within the coating, high mechanical strength, and low permeability. These properties are gradually formed as individual molecules of the binder crosslink during the curing stage. Consequently, the development of both aesthetic appearance and anticorrosive performance, exhibited by a dry coating, relies on the chemical composition and curing of the binder. The importance of the binder in anticorrosive coating systems is reflected by the fact that coatings are often named according to the generic type of binder.[51] In this section, an attempt to describe the structure and reactivity associated with some of the most common types of resins used in the formulation of anticorrosive coatings will be made.

Mechanism of film formation

The film formation (i.e., the transition from a liquid product to a solid coating) can occur in three ways: either by evaporation of solvent, by a chemical reaction, or by a combination of both.[51] Physically drying coatings rely on evaporation of solvents from the liquid coating for the transformation into a solid coating, whereas chemically cured coatings are formed by a chemical reaction between a resin reactant and a

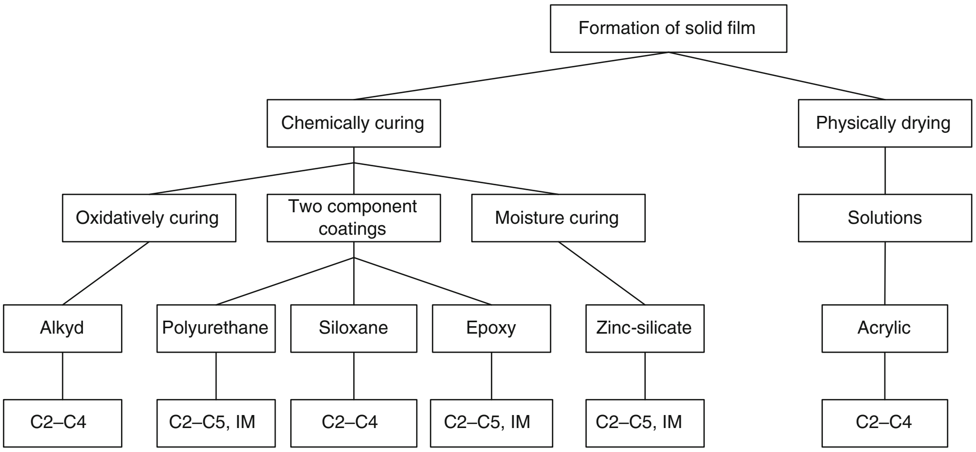


Fig. 12: Classification of binders according to curing mechanisms and suggested areas of application ranging from low to very heavy impact (C2–C5), and immersion in soil, freshwater, or seawater (IM) according to reference 16. Environmental examples of corrosivity categories are given in Table 1

crosslinker (also termed a curing agent). Chemically curing and physically drying coatings may be further divided into subgroups according to the type of chemical reaction or agent used to liquefy the coating, as illustrated in Fig. 12. It should be noticed that only binders curing at ambient temperature have been included because only this type of binders is relevant for heavy-duty coatings intended for large-scale structures. Furthermore, hybrid binders (e.g., acrylic modified epoxy resins and epoxy esters) have not been included in the figure.

The chemically curing binders for anticorrosive coatings curing at ambient temperature may be divided into three subgroups depending on the type of chemical process that forms the basis for the formation of a solid coating. Oxidatively curing coatings absorb and react with oxygen from the air in the presence of a catalyst. Similarly, moisture-curing coatings, such as zinc silicates, react with moisture from the air during the curing process. Two component systems rely on a reaction between a binder and a curing agent (often in the presence of catalysts such as various types of solvents) that must be supplied in separate containers by the coating manufacturer.

Physically drying coatings may be divided into two subgroups depending on the nature of the agent used to liquefy the binder. Conventional physically drying coatings contain large amounts of organic solvents that are capable of dissolving the individual polymer molecules. Aqueous dispersion coatings that contain large undissolved molecules dispersed in water are generally not applied as anticorrosive coatings due to insufficient performance, and are hence considered outside the scope of this review (not shown in Fig. 12). The mechanism of film formation for aqueous dispersion coatings is generally considered to be divided into three phases: evaporation of water, followed by coalescence and deformation of polymer particles, and finally development of cohesive strength by gradual coalescence of adjacent polymer particles.[164] Contrary to physically drying water-borne coatings, physically drying solvent-borne coatings do not imply changes in the composition of the binder. Consequently, physically drying solid organic coatings tend to be partly reversible (i.e., an underlying coat may redissolve a little when topcoated), which may improve adhesion between subsequent applied coats.

Epoxy technology

Epoxy resins (coating jargon for polyepoxide) have found widespread usage in the coating industry due to excellent adhesion to metals and high resistance to heat, water, and chemicals.[165] The high chemical stability of cured epoxy has been ascribed to the presence of stable carbon–carbon and ether bonds in the backbone of the epoxy molecule.[52] The use of epoxy coatings is limited to maintenance work, as well as primer and intermediate coatings due to yellowing and chalking of epoxy coatings upon exposure to ultraviolet radiation. There are special epoxy formulations with enhanced resistance to yellowing and UV damage. Such coatings, however, do not give good corrosion protection. In many cases, epoxy coatings are used as a primer, or intermediate coat, upon which a polyurethane topcoat with low color change and high gloss retention is applied.[13]

SOLVENT-BORNE: Traditional solvent-borne epoxy coatings have been used in aggressive environments for several decades. This means that the technology has been thoroughly reviewed,[13,166,167] and that the track record of commercial solvent-borne epoxy coatings is extensive.

Epoxy resins are synthesised by a condensation reaction between diphenyl propane derivatives and epichlorohydrin. The most widely applied derivative of diphenyl propane for preparation of solvent-borne epoxy resins is bisphenol A (reaction product of phenols and acetone), but bisphenol F (reaction product of phenols and formaldehyde) and other modified epoxy resins such as epoxy ester and epoxy functional silanes have also been developed to accommodate the need for special applications.[167] For very aggressive environments, coatings based on epoxy novolacs are often preferred due to their high chemical resistance. The high chemical resistance of novolacs originate from a high number of epoxy groups per molecule compared to bisphenol A or bisphenol F epoxy resins. This results in a tightly crosslinked structure of the solid coating, which gives a stronger and superior coating.

A wide range of properties can be achieved by blending of epoxy resins with different molecular weights in varying proportions, because many general characteristics of the epoxy resin are highly dependent on the molecular weight, as shown in Fig. 13. Unreacted low molecular-weight epoxy resins have more functional groups per unit resin weight compared to unreacted high molecular weight epoxy resins. This means that coatings made from low molecular-weight epoxy resins can have greater crosslink density than coatings made from high molecular-weight epoxy resins. The reduced crosslink density of coatings made from high molecular-weight epoxy resins results in coatings with low hardness, increased flexibility, and high fracture toughness (impact resistance).[168] Other properties, which are lowered when the crosslink density is reduced, include solvent and chemical resistance of the cured coating.[169,170] A higher degree of crosslinking indicates that less free volume and segmental mobility is available in the coating. Hence, it is difficult for molecules to penetrate the coating.[171] Unreacted high molecular-weight epoxy resins have higher hydroxyl functionality than unreacted low molecular-weight epoxy resins, which results in improved substrate wetting and adhesion on metals.[52]

	Molecular weight of unreacted resin
	Low → High
Crosslink density	Decreases →
Hardness	Decreases →
Flexibility	Increases →
Impact resistance	Increases →
Solvent resistance	Decreases →
Substrate wetting	Increases →
Adhesion	Increases →
Viscosity	Increases →

Fig. 13: General characteristics versus molecular weight of epoxy resin. Modified after reference 167

The curing of epoxy resins, illustrated in Fig. 14, is based upon the opening of the epoxide ring by an active hydrogen atom present in the amine curing agent.

Traditionally, cyclo aliphatic amines have been widely used as curing agents for epoxy resins because they provide a high degree of corrosion resistance, but they are slowly disappearing from the commercial market.[167] Polyamines and amides are among the replacements, and are often used in combination to control film formation and obtain superior coatings. The reaction between a polyamide and an epoxy resin is typically slower and more controllable than the reaction between an amine and an epoxy resin.[13] From a performance point of view, the coating formed by a reaction with polyamides is more flexible than those cured by amines. However, amides only have moderate acid, solvent, and corrosion resistance, and are (like amines) subject to chalking.[167] The toxicity associated with amine curing agents has forced many manufacturers to supply coatings in a form where an initial amine-epoxy adduct already exists. In these coating formulations, additional epoxy resin is required to complete the reaction. However, adducts may also be used to improve the performance of a coating, because polyamine adducts are reported to limit reactivity and increase resistance to ultraviolet light and color change while maintaining the basic properties of aliphatic amine-cured epoxy.[167]

Water-borne: Water-borne epoxy coatings have evolved into two fundamentally different technologies. Early developments centered around the application of liquid epoxy resin, primarily diglycidyl ether of bisphenol A, and a water-soluble amine curing agent that serves a dual function as it also acts as an emulsifier for the epoxy. The curing of liquid epoxy is typically performed with modified polyamidoamines or polyamides, which are rendered water soluble by salting with a volatile organic acid such as acetic acid.[172]

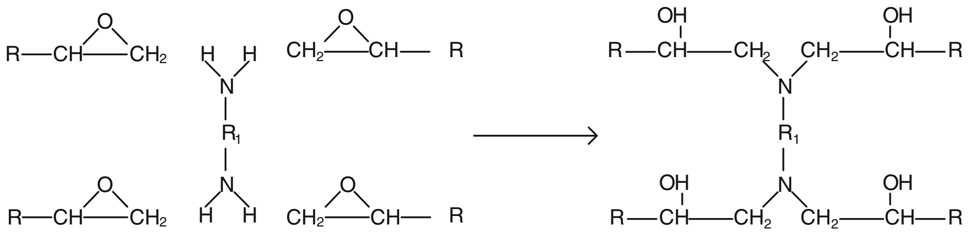


Fig. 14: Simplified curing mechanism of epoxy resin with diamine

The second type of water-borne epoxy technology has centered on solid epoxy predispersed in water and cosolvents. In this type of coating, water is added during mixing of the curing agent and resin. Hence, curing occurs as the curing agent migrates from the aqueous phase into dispersed epoxy particles. The principal weakness of the predispersed epoxy is the risk of formation of heterogeneous films with epoxy and amine or amide-rich domains due to incomplete coalescence.

Traditionally, most water-borne epoxies have had insufficient resistance to corrosion compared to solvent-borne epoxy coatings. However, cationic electrodeposited epoxy primers, which are used on automobiles, provide good protection against corrosion because of excellent adhesion under wet conditions.[173,174] Recent developments within water-borne technology (e.g., polyfunctional resins and curing agents) has enabled coatings suppliers to formulate water-borne coatings that are capable of protecting metal substrates against corrosion in marine atmospheres of very high corrosivity categories if a zinc rich primer is applied.[175] The combination of metallic zinc pigments and water-borne coatings constitute another challenge for coating formulators, because metallic zinc is not stable in water. In dilute acidic solutions, zinc will react with hydroxonium ions and produce hydrogen, which may react explosively with oxygen. Hence, zinc-pigmented water-borne epoxy coatings are normally supplied as three component coatings.

Although modern water-borne coatings are able to overcome most of the earlier drawbacks, major differences between water-borne and solvent-borne coatings remain.[172] Table 6 shows some typical advantages and disadvantages of water-borne epoxy coatings compared to solvent-borne epoxy systems.

Acrylic technology

Acrylic polymers and copolymers are widely used for the formulation of protective coatings, due to their good adhesion and film forming properties and photostability. Acrylic binders have high industrial interest and relevance due to their physical and chemical properties: nonwetability, chemical inertness, and environmental stability.[176] The key attribute of acrylic coatings is their resistance to hydrolysis and ultraviolet radiation during extended weathering. However, this is not true for acrylic-melamine automotive clearcoats exposed to weathering that includes acid rain. These coatings suffer hydrolysis and can be severely etched. They have been replaced by modified acrylics such as epoxy-acid acrylics, silane-modified acrylics, and carbamates. Acrylic latex coatings exhibit superior performance with respect to resistance to hydrolysis and ultraviolet radiation compared to their solvent-borne analogs. However, acrylic coatings are generally not applied for constant immersion in water or soil due to their limited resistance in this application.[31]

SOLVENT-BORNE COATINGS: Solvent-borne acrylic coating technology has traditionally held a strong position in the protective segment. The primary advantage of solvent-borne technology compared to water-borne technology is improved adhesion, quick drying, and high durability.

Acrylic resins are prepared through the polymerization of acrylic and methacrylic acids, or their corresponding esters. Thermoplastic resins form hardened coatings simply through solvent evaporation. The curing of thermoset resins is typically performed using isocyanates or amino resins as crosslinking agents. In principle, the curing of thermoset acrylic coatings is identical for both solvent- and water-borne acrylic coatings. The curing may be accelerated by the incorporation of a catalyst, such as organometallic compounds and tertiary amines, into the formulation at a concentration level of 0.1–1.0 w/w%.[13]

Modified acrylic resins can be used in the design of coatings with superior performance compared to pure acrylic coatings. It has been reported that epoxy coatings modified with methacrylate showed improved chemical and corrosion resistance without compromising the hardness and impact resistance.[177]

WATER-BORNE COATINGS: Industrial water-borne acrylic-based coatings have gained importance due to

Table 6: Typical advantages and disadvantages of water-borne epoxy coatings compared to solvent-borne epoxy systems

Advantages	Disadvantages
Low content of organic solvents: no air pollution, no fire and health hazards	Short pot life compared to organic solvent-borne coatings
Excellent interlayer adhesion	Limited gloss stability
Excellent adhesion on difficult substrates (e.g. wet concrete)	Risk of flash rust on unprotected steel surfaces
Ease of cleaning application equipment	Lower chemical resistance
Water may plasticize coatings: increase flexibility during service	Slow evaporation of water at high RH

Modified after reference 163

Note: *RH* relative humidity

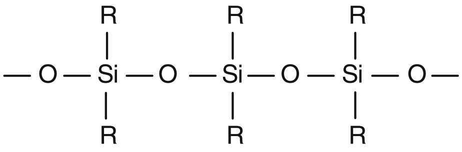
the desire to reduce VOC emissions. Compared to solvent-borne acrylic coatings, the water-borne acrylic coatings offer better VOC compliance, but may suffer from adhesion limitations and high cost.[13] There are also waterborne electrodeposited acrylic coatings. These coatings do not have the corrosion resistance of the electrodeposited epoxy primers, but they are adequate single layer coatings for a variety of applications including some for outdoor use.

Blends of acrylic based copolymers and latexes with increased corrosion resistance and durability at thinner thicknesses have been developed to improve upon the deficiencies of pure latex coatings, which offer insufficient protection against corrosion. Acrylic coatings have also formed the basis for the development of radiation-curable coatings, which in the future may provide environmentally friendly anticorrosive coatings.[178]

Siloxane technology

Polysiloxanes are polymers with a silicon–oxygen (Si–O) backbone and are made from monomeric building blocks, as the typical structure of a polysiloxane backbone in Fig. 15 illustrates.

In comparison with traditional organic binders, polysiloxane coatings exhibit superior gloss and color retention, but suffer from poor mechanical properties. The improved durability compared to organic carbon based systems may be partly explained by comparing the chemical properties of the siloxane and typical organic binders. The silicon–oxygen bond strength of 443 kJ/mol polysiloxane binders is greater than the typical bond strength of 360 kJ/mol for the carbon–carbon bond of organic binders.[179] In addition, the siloxane coatings are already in an oxidized state, which prevents further oxidation. Typically, organometals or compounds, which react with the side groups of the polysiloxane, are used to catalyze the curing of polysiloxane coatings. Siloxane can be chemically reacted with epoxy, acrylic or other organic compounds to form hybrid siloxane coatings, which have found widespread usage for industrial application. The epoxy modified siloxane generally exhibits improved gloss and color retention. Some authors describe how the anticorrosive performance of diglycidyl ether of bisphenol A has been improved by modification with hydroxyl-terminated polydimethyl siloxane.[180]



$$-O-\underset{R}{\overset{R}{\mathrm{Si}}}-O-\underset{R}{\overset{R}{\mathrm{Si}}}-O-\underset{R}{\overset{R}{\mathrm{Si}}}-O-$$

Fig. 15: Structure of polysiloxane backbone

Zinc silicates: Zinc silicates are inorganic zinc coatings that have the ability to provide cathodic protection. The curing of zinc silicate involves moisture from the atmosphere and is initiated by a reaction between polysilicic acid and metallic zinc, in which the major part of the metallic zinc, which has not reacted, is surrounded by an insoluble matrix of zinc silicate.[181] The curing process is also believed to involve some reaction with the metallic zinc and the steel surface. The curing of moisture-curing zinc silicate binders requires a sufficient content of moisture in the atmosphere, typically a minimum relative humidity of 50–60%.[182] If this humidity is not present during the curing process, there is a danger of silica precipitating out and optimum film strength never being obtained. Figure 16 shows an idealized porous zinc silicate coating, where zinc has been joined by a silicate binder.

Although ethanol is formed in the polymerization process, ethyl silicate has traditionally been widely applied as a binder in zinc silicate systems. This is because solvent-borne ethyl silicate binders have generally been found to be more effective than water-borne alkali metal zinc silicates.[183]

Alkyd technology

Alkyd-based coatings are characterized by good adhesion, flexibility, resistance, and durability. The choice of resin for a particular usage depends on a number of factors including performance, characteristics, processing requirements, application properties, and economic requirements.

Alkyd coatings are often used as primers, along with an inhibitive pigment in corrosive environments where the influence from water on the surface is not too extensive.[16] Alkyd coatings, however, should be applied with care in corrosive environments because they are subject to saponification,[184] which is the process in which ester linkages in the alkyd resin are attacked by alkaline materials to form an alcohol and the salt of a carboxylic acid. Saponification is known to be a common problem when alkyd primers are selected for application over galvanized surfaces, in zinc-rich primers, and is also observed on steel, especially when

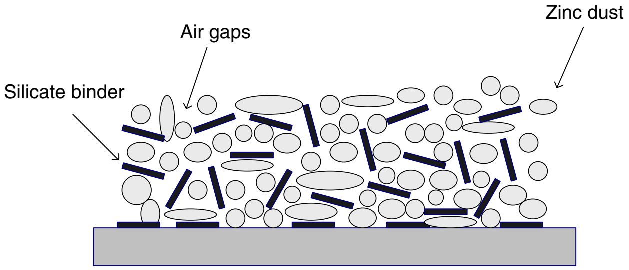


Fig. 16: Idealized porous zinc silicate coating showing zinc dust joined by a silicate binder

impressed cathodic projection or sacrificial anodes is applied in conjunction with alkyd coatings.[31]

SOLVENT-BORNE COATINGS: Synthetic alkyd resins represent the resin group that has traditionally found the most widespread utilization in solvent-borne coatings. Alkyd resins are fatty acid-containing polyester resins obtained through a reaction between oils or fatty acids, polyols, and a dibasic acid or anhydride, such as phthalic anhydride, isophthalic acid, or maleic anhydride.[13] The addition of fatty acids or oils can be varied to produce alkyds with specific properties. An overview of some of the most important fatty acids used in coatings is listed in reference 185.

The curing of the oil chains in alkyd coating is the result of an oxidative reaction, which involves oxygen from the air and catalysts (e.g., organic complexes of transition metal ions). In this process, oxygen attacks the diallylic methylene hydrogen present in the hydrocarbon chain, resulting in a series of additional reactions.[186]

Alkyd resins have been modified by the incorporation of urethane, polyamide, silicone, or vinyl resin constituents during the manufacturing process to obtain alkyd-based resins exhibiting improved chemical and physical properties. Although alkyd resins also have been modified to increase the compatibility with a water medium for use in water-borne coatings, they are not applied in water-borne anticorrosive coatings.[13]

WATER-BORNE COATINGS: The majority of water-borne anticorrosive alkyd coatings are water-reducible coatings, which are based on alkyd resins that have been modified to make them more compatible with the water medium. This modification is typically accomplished by malinization of the fatty acid prior to its reaction with the dibasic acid and polyol, or by using hydroxyl rich prepolymers as the starting material from which the resin is made. When used in water-reducible coatings, the drying properties of the coating have been found to be improved either by including acidic resins or multifunctional acrylates in the formulation, or by modifying the alkyd resin with methyl methacrylate.[13] No reports on the use of alkyd emulsion for anticorrosive purposes have been found.

Polyurethane technology

Compared to the epoxy coatings technology, the advantage of polyurethane coatings is their excellent resistance to weathering. This type of coating exhibits low loss of gloss and color change when exposed to ultraviolet radiation.[187] This means that polyurethane coatings are often applied as topcoats in environments where the coating system is exposed to sunlight. However, polyurethane coatings are also commercially available as primers and intermediate coatings. Another advantage of these coatings is the "self-healing" (scratch resistant) ability due to hydrogen bonds between the urethane linkages, which may reform after "breakage."

The major drawbacks of most polyurethane coatings are poor resistance towards mechanical strains and deformation and/or degradation at high temperatures.[188] Polyurethane coatings can be both single-component (moisture cured) and two-component. Only the two-component coatings will be considered here.

SOLVENT-BORNE COATINGS: Although several types of polyurethane coatings are commercially available, the majority of solvent-borne polyurethane coatings are formed by the reaction of an isocyanate, with compounds containing an active hydrogen atom (e.g., hydroxyl or amine group).[13] The formation of polyurethane is illustrated in Fig. 17, which shows the reaction between an isocyanate and a diol.[189]

The presence of crosslinks in a polyurethane coating provides enhanced tensile strength, abrasion and mar resistance as well as acid, alkali, and the solvent resistance, which thermoplastic polyurethane coatings are lacking. Such performance criteria are essential for most industrial coatings.[188] Crosslinked polyurethanes have shown great potential in the coatings sector due to their high glass transition temperature, ability to form high quality films, good solvent resistance and ease of synthesis and processing.

Aliphatic polyurethanes based on aliphatic isocyanates and mostly polyester and/or acrylic polyols are more expensive than aromatic polyurethanes, which are polyurethanes based on aromatic isocyanates and mostly polyether polyols. However, the aliphatic polyurethanes provide the best UV resistance and color stability among industrial polyurethane coatings. Therefore, aliphatic polyurethane coatings are often used for exterior applications and any other places where color stability is important.[13]

WATER-BORNE COATINGS: Water-borne polyurethanes are typically two component coatings based on separate dispersions of polyols and isocyanates in water. Compared to two-component solvent-borne coatings, water-borne urethane coatings are deficient in chemical and corrosion resistance and not frequently

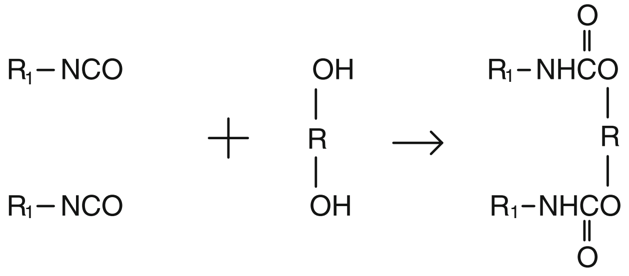


Fig. 17: Curing of isocyanate by diol

applied as anticorrosive coatings.[190] Proper dispersion of the constituents may also provide a challenge to coating formulators.

Other types of binders

Several other types of binders are applied by the coating industry for formulation of anticorrosive coatings. In this subsection, some of the less frequently applied binders are briefly presented.

Chlorinated rubber: Chlorinated rubber coatings are physically drying single-component coatings based on solutions of chlorinated rubber in organic solvents. This type of coating is widely used as an industrial coating and has also been used on ships and other marine structures both above and below the waterline due to a very good resistance to water. This type of coating, however, suffers from a poor solvent resistance and high VOC content.[31,51] The application of chlorinated rubber coatings is further restricted by the fact that they will decompose at high temperatures and release toxic compounds such as hydrogen chloride.[191]

Vinyl: Vinyl coatings are closely related to chlorinated rubber coatings and will also release hydrogen chloride at high temperatures. They are single-component coatings based on solutions of different copolymers and polyvinyl chloride in organic solvents. Vinyl coatings may be used in most industrial environments and are capable of withstanding exposure in quite aggressive areas (e.g., C2–C4).[31] They have a good resistance to inorganic acids and alkalis but suffer from poor resistance against strong solvents, a low content of solids, and a high content of VOC. For application under the waterline, vinyl is typically modified with tar.[31,51]

Epoxy ester: Epoxy esters are oxidatively curing single-component coatings where the binder has been produced by a reaction between an epoxy compound and an alkyd at a high temperature. Epoxy esters behave similar to alkyds and cure through reaction with oxygen in the air. This type of coating is relatively quick-drying, harder, and somewhat more chemically resistant than alkyds, but tends to chalk.[31]

Polyester: Polyester coatings are high-build, glass-flake reinforced coatings that are typically applied in thick layers, often 500–1000 μm thick.[31] This type of coating belongs to the group of chemically curing coatings, and catalysts such as cobalt octoate and certain amines may be added to accelerate curing. Polyester coatings are characterized by a very high abrasion resistance, and the use of polyester coatings in sea- or freshwater is not uncommon due to an excellent resistance to water. However, polyester coatings suffer from a short pot life (often less than 1 h at room temperature) and short recoating intervals.[51]

Cementitious: Cementitious coatings are two-component cement-based coatings where cement is mixed with water or a latex solution before use. These coatings are highly alkaline and passivate the steel surface because the hydration of cement produces strong alkalis such as calcium hydroxide.[192] This type of coating is typically used in connection with maintenance of reinforcing iron in concrete, but is otherwise little used on steel.[31]

Bituminous: Bituminous coatings are nonpigmented, physically drying single-component coatings that are made from the remains of fractional distillation of crude oil. The limited resistance to direct sunlight, discoloration when overcoated, mechanical weakness, and their black and brown colors result in a rather limited area of use. However, this type of coating is well-suited for structures immersed in water and are widely used in humid areas where the risk of mechanical impacts are small.[31]

Tar: Tar coatings are physically drying single-component coatings that are made from the remains of pyrolysis of organic matter (e.g., coal). This type of coating contains no corrosion-preventive pigments and protects the steel by means of a barrier effect. Tar coatings have a high water-resistance and are also resistant to dilute alkali and acid solutions. They have poor resistance to sunlight, however, and are considered to be carcinogenic.[31]

Coal tar epoxy: Coal tar epoxy is a two-component coating where epoxy has been modified with coal tar. The modification results in increased flexibility and water resistance and provides a less expensive coating. This type of coating contains no corrosion-preventive pigments and protects the steel by means of barrier effect. Coal tar epoxy coatings are widely used for immersed structures. Some of the weaknesses of coal tar epoxy coatings are sensitivity to sunlight and discoloration when overcoated. Furthermore, this type of coatings is considered to be carcinogenic. As a result, restrictions are already in place in many countries.[31]

Pigments in anticorrosive coatings

The ratio of pigment to binder is a vital measure by which several properties of coatings are determined.[193,194] An important issue in this respect is the pigment volume concentration (PVC), which indicates the proportion of pigment and extenders in the dry coating[195]

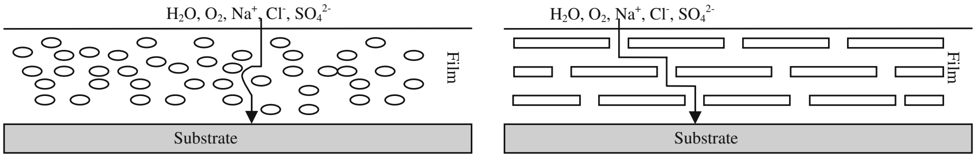


Fig. 18: Idealized sketch of the effect of barrier pigments. In coatings pigmented with spherical pigments, the aggressive species can migrate almost straight through the coating. When the coating is pigmented with lamellar pigments, the aggressive species are provided a tortuous path of diffusion

$$\mathrm{PVC} = \frac{V_\mathrm{p}}{V_\mathrm{p} + V_\mathrm{b}} \tag{14}$$

where V_p is the volume of pigments and extenders, and V_b is the volume of the binder system (polymeric compounds such as resin, cobinder, and plasticizer).

The critical pigment volume concentration (CPVC) was first clearly recognized and characterized in 1949.[196] CPVC is defined as the level of pigmentation where there is just sufficient polymer matrix to wet and fill the voids between the individual pigment and extender particles. CPVC is often determined by the amount of linseed oil a specific type of pigment can absorb (according to equation (15)) because this method is fast

$$\mathrm{CPVC} = \frac{1}{1 + \left(\frac{\mathrm{OA} \times \rho_\mathrm{p}}{\rho_\mathrm{Oil} \times 100}\right)} \tag{15}$$

where OA is the oil absorption value expressed in terms of mass of oil per 100 g pigment, ρ_p the pigment density, and ρ_Oil the density of the linseed oil.

Linseed oil, however, bears little resemblance to the polymers and oligomers used in modern coatings. Therefore, a CPVC value determined by absorbtion of linseed oil has questionable meaning because the equation rests on the assumption that oil absorption and CPVC are approximately independent of the binder. Various experimental methods[197,198] such as density measurements,[196,199] optical properties,[200,201] and measurement of transport properties,[202,203] may provide more accurate results. However, these techniques may be time consuming because they require examination of changes in coating properties over a range of pigment volume concentrations.

In the work of formulating coatings, it is convenient to introduce the reduced PVC, λ, which is defined as the ratio between PVC and CPVC. Hence, for λ-values less than unity, the dry coating may be pictured as a composite consisting of pigments randomly embedded in a continuously connected matrix of polymer. At λ-values above unity, there is not sufficient polymer matrix to cover the pigment surfaces, and small voids are formed. The presence of air in the voids caused by the insufficient amount of binder affects the properties of a coating drastically, especially with respect to mechanical, thermal, transport, and optical properties.[195,204–206]

Barrier pigments

Barrier protection is, to a certain extent, offered by any particle that is impermeable to aggressive species and incorporated into a coating.[207] However, some pigments are specially designed to impart barrier properties to an organic coating by impeding the transport of aggressive species to the surface of the substrate. Such pigments are typically lamellar pigments, which orientate themselves parallel to the substrate surface and protect the substrate by providing a tortuous path of diffusion to the substrate. In addition, lamellar pigments may have a reinforcing effect on the mechanical properties of the coating.[54]

The effect of barrier pigments on the permeability of pigmented coating is illustrated in Fig. 18. In coatings insufficiently pigmented with spherical pigments, the aggressive species may migrate almost straight through the coating, whereas coatings formulated with lamellar pigments impede the transport of aggressive species by providing a tortuous path of diffusion.

The most widely used lamellar pigment for anticorrosive barrier coatings is micaceous iron oxide (MIO), which essentially is a type of haematite (Fe_2O_3).[208–211] The influence of particle diameter, measured as an average of the corresponding spherical diameter of MIO on adhesion and corrosion resistance, was investigated by some authors[212] who compared the average diameters of 28, 32, 36, and 40 μm. They found that the lowest particle size led to the highest anticorrosive performance. The optimum anticorrosive performance of MIO-pigmented coatings is typically obtained for λ-values in the range of 0.67–0.82 dependent on the type of binder.[213] The demand for improved protection and limited resources has encouraged researchers to modify and synthesize MIO pigments that can be formulated into barrier coatings.[214,215]

Lamellar aluminum pigments are commercially available in leafing and nonleafing grades. Leafing aluminum pigments are surface-treated, typically with stearic acid, so they have a low surface tension. When the coating is applied, they orient themselves at the top of the coating because of the difference in surface tension between the coating and the surface treated aluminum. In the case of nonleafing aluminum pigments, which are stabilized by oleic acid, the pigments will remain evenly distributed throughout the film.[216] The majority of the aluminum used to formulate barrier coatings is the leafing grade, which is applied as a paste to facilitate the formulation of coating.

The application of leafing aluminum in anticorrosive barrier coatings may be questionable because aluminum pigments have an insignificant effect on the rate of cathodic disbondment if they are not applied directly on the steel in the first coat.[217,218] Aluminum is an amphoteric metal that will corrode at greater than 9.[219] This means that aluminum may act as a buffer and reduce cathodic delamination by reacting with the hydroxyl ions generated by the cathodic reaction.[220] The buffer theory is supported by electrochemical studies and microscopic investigation of aluminum pigmented coatings.[217,218]

Although not used in the same extent as aluminum and MIO pigments, glass flake pigments are also used in anticorrosive organic coatings. The large size of the glass particles (100–400 μm) only allows them to be used in very thick coatings. In spite of the reflective properties and the impermeability of glass flakes towards oxygen and moisture, glass flakes do not appear to improve the resistance towards cathodic delamination.[217] Inert or chemically resistant pigments such as titanium dioxide, and extenders such as silicates, are typically applied as barrier coatings in chemical environments involving acid or alkaline conditions, as encountered in many industries.

Sacrificial pigments

In principle, all metals that are electrochemically more active than the substrate to be protected can be applied as sacrificial pigments in anticorrosive coatings. At present, however, metallic zinc particles are the most widely used among sacrificial pigments. The anticorrosive performance of sacrificial coatings is largely determined by the amount of metallic pigments. Both the size and shape of the pigments, however, also significantly affect the ability to protect the substrate against corrosion. Large spherical particles tend to offer lower anticorrosive protection than small spherical particles. The best anticorrosive performance of spherical zinc particles is reported to be obtained with an average diameter of 2 μm.[59,221] This phenomenon may be explained by the filling of free spaces between the zinc particles of smaller size. For larger-size particles, the filling of pores by means of zinc corrosion products is incomplete, and the presence of leakage increases the permeability of the coating.[221] The packing ability of spherical particles can be improved by applying a broader shape factor distribution as a function of equivalent spherical particle size.[222] The improved packing ability will reduce the porosity, and very often the permeability, while increasing the number of electrical points of contact for a zinc-rich coating. Thus, a larger galvanic current can be transferred away from the metallic surface.

The influence of the shape of pigment particles is caused by the greater surface area to volume ratio of nonspherical particles compared to spherical particles.[223] Coatings pigmented with lamellar zinc require less zinc to obtain similar degrees of corrosion protection as coatings pigmented with spherical zinc. This is because the large surface area of lamellar zinc yields better electrical conductivity.[59,224] Furthermore, coatings pigmented with lamellar zinc exhibit lower permeability than coatings pigmented with isometric zinc particles. Using a combination of lamellar and spherical zinc, some authors[225] have been able to significantly reduce the zinc content without compromising the anticorrosive properties. The effect was ascribed to the increased number of electrical contacts between the particles e.g., a larger galvanic current can be transferred.

The protective mechanism of metallic zinc involves precipitation of insoluble corrosion products. Insoluble $ZnFe_2O_4$ have been found near defect sites in zinc-rich epoxy coatings exposed to cyclic corrosion tests.[226] Furthermore, it has been reported that high corrosion-resistant coatings can be obtained by incorporating zinc-ferrite pigments in organic coatings.[227] The Pourbaix diagram in Fig. 19 illustrates how the presence of $ZnFe_2O_4$ is possible in a Fe–Zn–H_2O–Cl system at 25°C.

High raw materials costs urge coating manufacturers to reduce the amount of zinc in coatings. Partial replacement of metallic zinc particles with conductive pigments can be used to reduce corrosion underneath a coating.[228] For this purpose, carbon black has been extensively studied, with contradicting results.[229–232]

Among the metallic coatings used to protect steel against corrosion, those based on metallic zinc applied under different deposition conditions have been important, but requirements for longer service life have led to partial replacement of zinc with zinc alloys for corrosion protection in the automotive industry,[233] as well as on fasteners and bicycle parts.[234] The increased corrosion resistance of alloyed zinc under atmospheric conditions is well-documented[235–237] and the metallurgy of zinc-coated steel has been extensively reviewed.[195] The most widely used alloys for anticorrosive purposes are Zn–Ni,[237–239] Zn–Co,[237,240,241] Zn–Mn,[242,243] and Zn–Mo.[236,244] The protective mechanisms of these alloyed zinc compounds are not completely documented. For nickel alloyed zinc, the enhanced corrosion resistance is believed to be a result of the formation of a nickel rich alloy layer, which acts as a protective barrier.[245] In a Zn–Mn system, it has been suggested that the formation of hydroxo-salts of zinc and manganese is responsible for the enhanced resistance against corrosion.[242]

Inhibitive pigments

Inhibitive pigments may be classified according to their effect on the anodic and cathodic reactions. Cathodic inhibitors, such as inorganic salts of magnesium and manganese, suppress corrosion at the cathode by forming insoluble deposits with hydroxyl ions in neutral environments. These pigments increase the

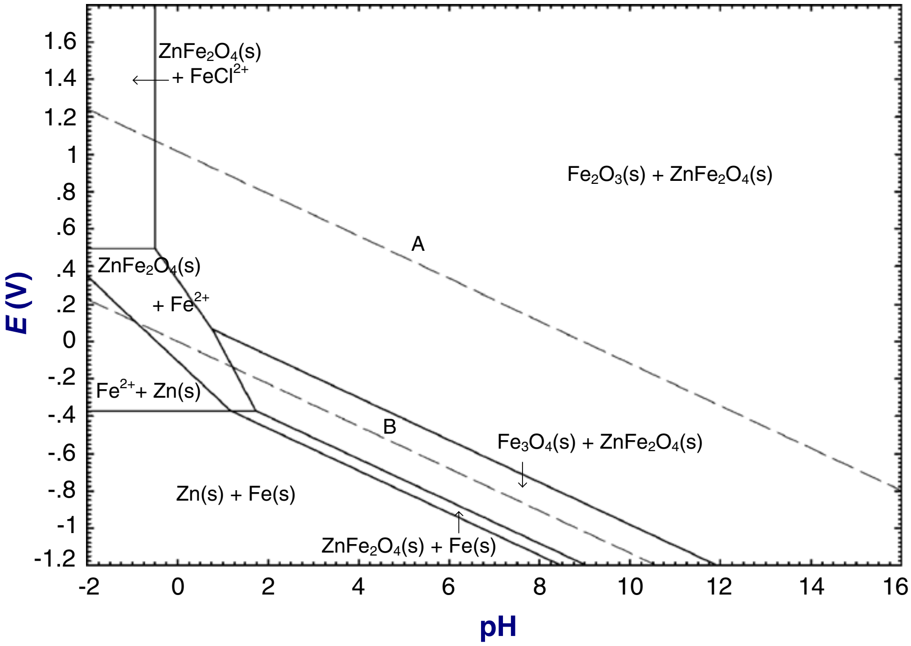


Fig. 19: Simplified Pourbaix diagram of the Fe–Zn–H_2O–Cl system at 25°C. Dashed lines A and B indicate theoretical region of stability of water. The diagram was generated using FactSage 5.2

Table 7: Inhibitive character and oxygen dependency of various inhibitors

Cation	O_2 dependency	Inhibitive character
CrO_4^{2-}	No	Anodic
PO_4^{3-}	Yes	Anodic
Mo_4^{2-}	Yes	Anodic
BO_2^{-}	Yes	Buffer
$\left(SiO_3^{2-}\right)_{n,n>1}$	Yes	Anodic
OH^-	–	Buffer
NO_2^-	No	Anodic

cathodic resistance against polarization, forming visible films on metallic surfaces. In acidic environments, inhibitors are believed to raise the concentration of positively charged hydrogen ions at the cathode, which will enhance the polarization process. Anodic inhibitors, such as inorganic salts of phosphate, borate, and silicate compounds, form a protective oxide film on the metal surface. Anodic inhibitors are absorbed onto the surface of the substrate and reduce the rate of corrosion by increasing the anodic polarization.[246] In the case of insufficient addition of anodic inhibitors, an undesirable anode to cathode area will be formed, which increases the rate of corrosion.[247] Insufficient amounts of cathodic inhibitors, as opposed to insufficient amounts of anodic inhibitors, still decrease the rate of corrosion as the active cathodic area is reduced. The inhibitive character and oxygen dependency of various cations are given in Table 7.

PHOSPHATES: At present, phosphates containing pigments are the most widely applied type of inhibitive pigments in the European coating industry.[248] Among the phosphates containing pigments, zinc phosphate has found the broadest range of application.[249,250] However, several other types of phosphates containing pigments such as magnesium phosphate are commercially available.

Zinc phosphates have been used with different generic types of binders[66,248,251] with contradictory results.[248,252,253] In general, zinc phosphate shows good performance in industrial environments because it is capable of passivating the substrate in acidic media.[254] The protection offered by zinc phosphate on steel relies on passivation of the metal surface, and the protective mechanism of zinc phosphate is thought to involve polarization of the cathodic areas due to precipitation of basic insoluble salts on the surface.[66,255] The formation and subsequent precipitation of insoluble iron phosphate presumably occurs according to reaction (16).[72]

$$\begin{aligned} Fe^{2+} + H_2PO_4^- &\rightarrow FeH_2PO_4^+ + 2H_2O \\ &\rightarrow FePO_4 \cdot 2H_2O + 2H^+ + e^- \end{aligned} \qquad (16)$$

The highest anticorrosive performance of zinc phosphate-pigmented coatings for application in industrial environments is generally reported to be achieved for reduced PVC-values around 0.7.[206,256]

Modification of zinc phosphate with molybdenum or organic corrosion inhibitors is also reported to improve the anticorrosive performance of inhibitive coatings in highly polluted industrial environments. In these environments, the molybdate ions behave like inhibitive pigments due to their preferred absorption on the steel surface. The active inhibitive species in this type of pigment is the molybdate anion, which is thought to repassivate the corrosion pits in steel. Polarization measurements have shown that the anodic protective film formed on steel suppresses the reduction of oxygen by blocking the active cathodic sites.[257] The main features of the generally accepted inhibition mechanism, in the context of corrosion of steel, is the formation of protective hydrated oxide films of modified compositions, as follows: in the presence of dissolved oxygen, $FeMoO_4$ forms in MoO_4^{2-} inhibited systems, which incorporated into the outer layers of hydrated Fe_2O_3 films developed over actively corroding anodic sites, enhance the stability of the Fe_2O_3 film.[72] At present, condensed phosphates containing various cations are reported to offer the highest degree of protection.[258,259]

Chromates: Throughout the years, various inorganic salts, such as lead compounds and chromate pigments, have been used in anticorrosive coatings.[260,261] However, these compounds are toxic and have carcinogenic effects. Therefore, there is a need to find ‘‘nontoxic’’ substitutes, which offer the same degree of protection. In Europe, legislation has restricted the use of hexavalent chromium,[262] and the use has therefore dropped rapidly.[263] In other parts of the world, the use of hexavalent chromium has not declined in similar ways. In the Far East, the use of chromium salts is actually increasing.

Inorganic salts of zinc or strontium chromate have long been the primary choice in coatings for many applications, such as aircraft parts fabricated from aluminum because of their ability to passivate metals.[264] Although not fully understood, the inhibitive action of chromate pigments is now well accepted to depend on leaching of chromate ions to the solution.[265] The passivation of aluminum alloys with chromium salts has been extensively studied.[266–270] It is the trivalent chromium that is usually found in the passive layer[266] because chromate ions in the solution are of the hexavalent form and will be reduced to the trivalent form to counterbalance the anodic oxidation of the metal substrate. However, no general agreement on the structure and composition of the passive films exists.

Some reports state that the protective layer consist of a layer of hydrated chromium(III) oxide over a layer of mixed aluminum oxide,[268,269,271] while others state that it consists of chromium(III) hydroxide.[272] Duplex layers, with an external more hydrated layer of $Cr(OH)_3$ and an internal less hydrated layer of CrOOH have also been reported.[273,274] Although hydrated chromium(III) hydroxide has been suggested as a preliminary step for the growth of less hydrated oxides such as chromium oxides,[273] it seems that the structure and composition of the protective layer depends on several factors, such as pH and potential.[273–275]

On iron, films of oxide spinels with Cr^{3+} and Fe^{3+} have been reported.[276–278] The Cr/Fe atomic ratio seems to depend on the pH, oxygen and chromate content of the solution. Other authors describe the film composition as a mixture of oxides and hydroxides of iron and chromium.[279–281] Hydroxylated layers[277] and adsorbed Cr(VI) have also been reported.[281,282] Studies of chromate passive layers on zinc are scarce but studies report about a passive film of chromium(III) with the absence of zinc.[265,283]

Spinel pigments: Another group of inhibitive pigments are spinel-type pigments based on mixed metal oxides.[284] Spinel-type pigments are substances of a crystalline character whose properties depend on the characteristics of the lattice. The first generation of spinel-type pigments consisted of a ferrite type of combination of two cations in the lattice structure ($ZnFe_2O_4$, $CaFe_2O_4$). The mechanism of corrosion protection of these pigments is based on the formation of zinc or calcium soaps obtained through a reaction with a suitable binder, thus simultaneously improving the mechanical strength of the binder and reducing its permeability towards aggressive species.[285] Recent studies indicate that the anticorrosive performance of spinel pigments is significantly enhanced in industrial atmospheres by the incorporation of three cations, i.e., pigments of the following type $Mg_{1-x}Zn_xFe_2O_4$, $Ca_{1-x}Zn_xFe_2O_4$.[286] In industrial atmospheres, the performance of coatings containing spinel pigments with three cations was superior to coatings containing Zn–Al phosphomolybdate, which has been reported to be more efficient than ordinary zinc phosphates.[287] Anticorrosive properties exposed to a cyclic corrosion test, however, were not enhanced but deteriorated. The prospect of the spinel-type pigment is the reduced toxicity compared with most pigments in presently applied inhibitive coatings, but further research must be conducted before spinel-type pigments can be widely applied in industrial coating formulations.

Degradation of organic coatings

The degradation of organic coating systems may be divided into cosmetic defects and those involving defects in the coating leading to corrosion. Evidently, the mechanisms involved in the degradation of organic coatings depend on the specific environments coating systems encounter during service. In atmospheric environments, a coating system may be subject to various kinds of cosmetic defects, such as loss of gloss, color change, and chalking. The majority of cosmetic defects are caused by decomposition of the binder by UV radiation, and the details are given by references 185, 288–291. Nevertheless, the most severe defects are those that concern failures in the coating or loss of adhesion.[31]

Although several factors are involved in the degradation of organic coatings, the mechanisms responsible for reduced adhesion between organic coatings and metallic substrates are of great importance for most coating failures because diminished adhesion must come prior to the onset of corrosion. This is because an electrolyte connection, which is a prerequisite for corrosion, cannot be established near or at the intact interface between coating and steel before the occurrence of diminished adhesion.[292]

Two typical types of failure of anticorrosive coatings are illustrated in Figs. 20 and 21. In atmospheric environments, zinc silicate coatings may peel as illustrated in Fig. 20 due to inadequate curing conditions. Thus, the protection against corrosion is largely compromised. Figure 21 shows corrosion in a ballast tank due to premature coating failure. This type of coating failure constitutes a large economical problem for most shipping companies.

Fig. 20: Peeling of coating due to inadequate curing conditions

Fig. 21: Corrosion in ballast tank due to insufficient protection

Weak wet adhesion

The first sign of degradation of organic coatings with no apparent defects that are exposed to a high relative humidity or constant immersion is often reduced adhesion between the organic coating and the substrate. The mechanism responsible for the reduced adhesion has been proposed to be a weak "wet adhesion," which refers to the adhesion of the coating to a metal surface in the presence of water.[292] The mechanism of weak wet adhesion is referred to as being physical–chemical, and is not limited to anticorrosive coatings. Upon exposure to high humidity or liquid water, the coating is eventually penetrated by water molecules. The water molecules may place themselves at the coating-substrate interface and thereby reduce or disrupt the attractive forces between coating and metal oxides because of their hydrogen bonding ability.[293] Few polymer-metal bonds are able to resist hydrolysis over a long period of time. When this happens, a weak wet adhesion is established and the coating allows the presence of an electrolyte solution at the interface, whereby corrosion can be initiated. Using FTIR-MIR techniques, quantitative information on the thickness of the water layer at the coating substrate interface has been provided.[294,295] It was found that multiple coats delay the accumulation of water at the interface, and that the thickness of the water layer at the interface increased with increasingly applied potential. Similar results have been obtained by other authors.[296] Further evidence for accumulation of water at the coating-substrate interface is provided by comparative studies of water uptake in attached and free films because the water uptake of attached coatings is higher than in the corresponding free films.[297] The possibility of water displacement of the coating (i.e., weak wet adhesion) is supported by the fact that typical values for secondary metal-adhesive interactions are in the range of about 25 kJ/mol or lower, while metal-water interactions have binding energies in the range of 40–65 kJ/mol.[298]

Filiform corrosion

An important degradation mechanism of organic-coated metals exposed to humid atmospheres is filiform corrosion. Although filiform corrosion is usually observed on organic-coated aluminum parts,[299–301] it has also been observed on magnesium and cold-rolled steel.[25] Filiform corrosion normally initiates at small, sometimes microscopic, scratches or defects in the coating. Filiform corrosion is usually only superficial and has the appearance of thin threadlike attacks progressing along the surface beneath the coating.[293] The filaments consist of an active corroding head followed by an inactive tail filled with porous corrosion products. Oxygen is consumed at the active corroding head, which will become deaerated.[302] This results in differential aeration because oxygen and water is supplied to the filament head by diffusion through the porous tail.[293,303] The only sure way to prevent filiform corrosion is to dehydrate the filament head by reducing the relative humidity below to around 60%. Improved low water vapor transmission, multiple coatings, and inhibitors will retard, but will not totally prevent filiform corrosion in environments where the humidity can not be controlled.

Degradation of immersed organic coatings

Among the most severe and common forms of visible failure in immersed organic coating systems are those of blistering and delamination (illustrated in Fig. 22). The difference between cathodic blistering and cathodic delamination is addressed by the events that occur after the hydroxyl ions have interacted with the metallic substrate. Blistering is the result of an osmotic pressure, which develops due to the high water solubility of the reaction products from the cathodic reaction. Delamination from damage is the result of bonds breaking at the coating-metal interface resulting from the alkalinity of the cathodic reaction products.[12]

The alkaline environment underneath a disbonded coating and in cathodic blisters is associated with the basic corrosion processes of steel in seawater. The presence of imperfections or defects in the coating will expose the steel to the surrounding environment. Therefore, a galvanic cell with anodic and cathodic regions is established.

In the anodic region, solid steel is dissolved in accordance with reaction (1). The anodic reaction is balanced by the cathodic reaction, which is catalyzed by oxidized metals and does not occur to a significant degree in the absence of a solid metal.[220] Under most naturally occurring conditions, the cathodic reaction will involve the reduction of oxygen as illustrated in reaction (2).

Although the modes of degradation for intact and defect organic coatings exposed to a neutral electrolyte solution by principle are different, the processes involved in the degradation are similar.[304]

Cathodic delamination

If an anticorrosive coating containing a defect is exposed to the elements, which is often the case in practice, corrosion may initiate much more rapidly than for a defect-free coating. The main principles of cathodic delamination are generally understood.[220,305,306] The reason for the delamination is proposed to be so-called cathodic polarization,[54] either by direct action of the hydroxyl ions or by chemical reactions as previously described. The oxygen and water required to depolarize the adjacent cathodic area must be provided by permeation through the coating or along the coating-substrate interface. Subsequently, oxygen diffusing to the damaged areas may also be consumed by oxidation of Fe^{2+} to Fe^{3+}.

Great attention has been paid to the transport of water, oxygen, and cations through organic coatings to the metallic surface. It has been shown that typical organic coatings are sufficiently permeable by water and oxygen so that typical organic coatings cannot inhibit delamination by preventing water and oxygen from reaching the metal surface.[173,307,308] It has also been observed that the rate of oxygen diffusion is practically independent of the simultaneous water diffusion (i.e., swelling of the coating).[54]

Regardless of the rate-controlling mechanism, the transport of ions from the environment to the steel surface is through discrete low-resistance pathways in the coating. To balance the charge of the negatively charged hydroxyl ions (e.g., preserve local charge neutrality), positively charged ions must be transported from the bulk solution to the cathodic sites. The cations can reach the cathodic sites by penetrating the coating via diffusion along the coating-substrate interface.[309] The presence of alkali metal ions and hydroxyl ions results in an alkaline environment underneath the coating. Several authors have demonstrated that

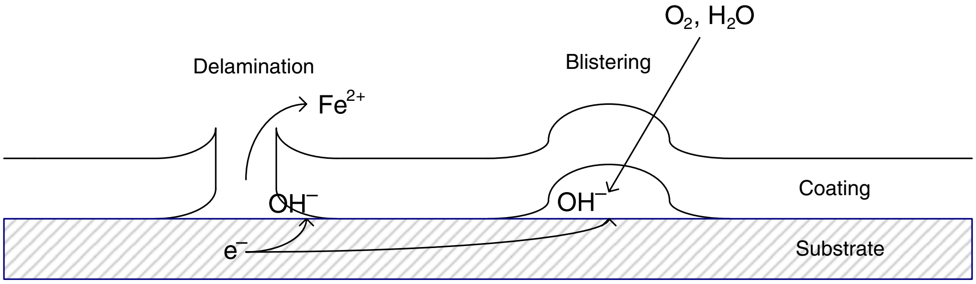


Fig. 22: Idealized sketch of delamination and blistering

the pH at the cathodic site may get as high as 12–14.[173,292,310,311] The diffusion of cations for charge neutralization of the cathodically produced hydroxyl ions is generally believed to be the rate-determining step.[101,220] If the cations are transported through the coating, they may be transported along the coating-steel interface upon entering it because the transport of ions along the coating-steel interface has been found to be much faster than that through the coating.[125]

The linear evolution of delaminated area with time, which is in agreement with a delamination process under Fickian diffusion control, identified by several researchers, suggests that delamination is controlled by diffusion of cations aligning the coating-steel interface.[305,312,313] The dependency of the rate of delamination on the hydrated size of the cations supports this hypothesis. However, referring to a negligible change in delamination rate of cation diffusion in a more stable silane-modified epoxy coating, it has been argued that interfacial transport alone can not determine the rate of cathodic delamination.[125]

It is generally accepted that an alkaline environment develops at the coating-metal interface due to the cathodic reaction. The alkaline environment underneath the coating in cathodic blisters and disbonded areas may very well be the cause of coating breakdown. However, the exact mechanism is in dispute.[311] The mechanisms of loss of adhesion caused by an alkaline environment can be divided into three groups according to the literature:

- reduction of the oxide layer
- chemical degradation of the polymer
- interfacial fracture

Reduction and dissolution of the thin ferrous oxide layer deposited on steel surfaces has been suggested as the predominant mode of delamination.[312,314] This mechanism of adhesion loss has been reported for epoxy and heat-cured acrylic and polybutadiene coatings on cathodically protected steel. This type of behavior is also predicted from the Pourbaix diagram for iron at pH 14 and at cathodic potentials less than 960 mV SHE.[219] Indeed, in situ x-ray photoelectron spectroscopy measurements have shown that in an alkaline media, a significant reduction of iron oxide is possible only at cathodic potentials less than 800 mV SHE.[315] It remains unknown whether the dissolution of iron oxide occurs following interfacial separation, or if the oxide layer is a precursor for the loss of adhesion.[220,316]

Saponification refers to chemical degradation of the polymer matrix caused by an elevated pH, and has been observed in the case of polybutadiene, polyethylene, and epoxy ester coatings on cathodic protected steel.[317,318] On polybutadiene coatings, degradation by means of saponification has been found to occur at a pH of 11.8 or above.[311] It is supposed that the locus of failure is in the polymer in the immediate vicinity of the surface. Thus, a thin layer of polymer remains on the steel surface.[319]

Interfacial fracture is the result of complete segregation of the polymeric film and the thin layer of iron oxide.[320] This type of failure has been reported following natural exposure and examination of the epoxy steel joints using XPS,[321] and polyethylene coatings on cathodic protected steel.[254] In addition, it has been proven that intermediate radicals such as HO_2^-, OH, and O_2^- form during oxygen reduction and may contribute significantly to the degradation of the organic layer.[315]

A principal sketch of the mechanisms responsible for cathodic delamination based on the literature is given in Fig. 23. A galvanic cell is established near a defect in the coating due to the presence of water, oxygen, end electrolytes. The hydroxyl ions generated by the cathodic reaction are balanced by transport of cations to the delamination front. This leads to a very alkaline environment, and although a high pH helps passivate the steel,[219] this results in disruption of the bonding between coating and metal oxides. Subsequently, cathodic protected steel will increase the rate of cathodic delamination because the applied current will increase the rate of the cathodic reaction. An added complexity is the presence of internal stress in coatings, originating from the initial curing process or from cycles of high and low temperatures and/or high and low humidity. The occurrence of cathodic delamination is not confined to neutral solution. Cathodic delamination will also occur in alkaline solutions,[322,323] although the delamination rate is significantly slower.[42,120]

Delamination of organic coatings from metal surfaces can occur in a number of different ways e.g., as pure cathodic delamination, as filiform corrosion, or a mixture of these. Delamination of organic coatings on phosphate or chromate-treated surfaces is a consequence of the dissolution of the conversion layer.[306] The delamination of an epoxy coating on chromate-treated steel has reportedly been caused by failure

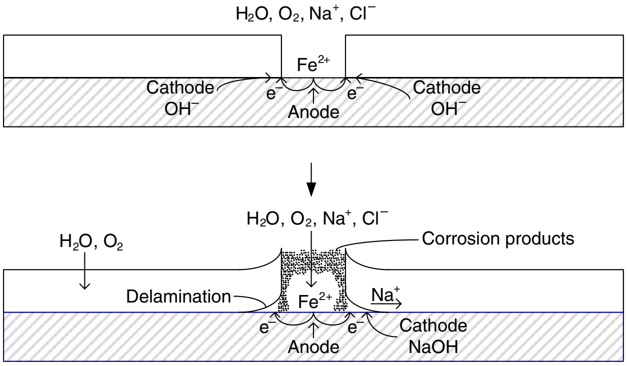


Fig. 23: Illustration of delamination process following coating damage. Adapted from reference 304

within the conversion coating itself.[316] The cathodic conditions underneath the epoxy coating resulted in the reduction of Cr^{6+} to Cr^{3+}. Similar results have been observed for phosphate conversion coatings.[324] Experimental data indicate that phosphate-containing pigments may reduce disbondment under cathodic conditions.[325] The results, however, show that the performance of phosphate-pigmented coatings under cathodic conditions also reflects the resistance of the binder towards alkali displacement at the coating-steel interface. Some authors[326] believe that the observed reduction of the delamination rate in the presence of phosphate pigments is caused by precipitation of a phosphate layer on the cathodic sites, which polarizes the cathodic reaction. Another aspect of the cathodic delamination of coatings is the possible oxidation and fragmentation of polymers at the delamination front. The degradation of the polymeric network may be caused by reactive intermediates such as H_2O_2 and HO_2, and OH radicals formed in the oxygen reduction reaction.[26–28] It has been argued that the effects of these intermediates can more be damaging for the coating system than the alkalization itself.[327]

Cathodic blistering

The formation of blisters or localized corrosion is usually the first visible sign of insufficient protection of organic coatings against corrosion. Blistering on coatings with no apparent defect has been discussed and attributed to several governing mechanisms: expansion due to swelling, gas inclusion, and osmotic processes.[328–330] Osmotic processes, however, are considered the most important mechanism for the development of blisters.[293] The general interpretation is that water-soluble contaminants at the substrate surface are responsible for osmotic blistering. This has resulted in several studies of the maximum allowable concentration of contaminants.[331] Despite wide variation in the suggested limits for the acceptable amount of water-soluble contaminants on the substrate prior to the application of coatings, attempts have been made to provide guidance levels.[332]

A conceptual model for the degradation of organic coatings with no apparent defect on steel in a neutral electrolyte[304] assumes that cathodic blistering occurs following the transport of ions through conductive pathways. The cations are believed to diffuse through the coating as a result of an attack by water in low molecular weight or low crosslinked regions, followed by the interconnection of these regions. Subsequently, cations migrate through the conductive pathways to the metal surface, where they migrate along the coating-metal interface from the defect to the cathodic sites to neutralize the hydroxyl ions generated by the cathodic reaction. The degradation of a coating with no apparent defects exposed to a neutral electrolyte can be summarized in the eight steps given below.

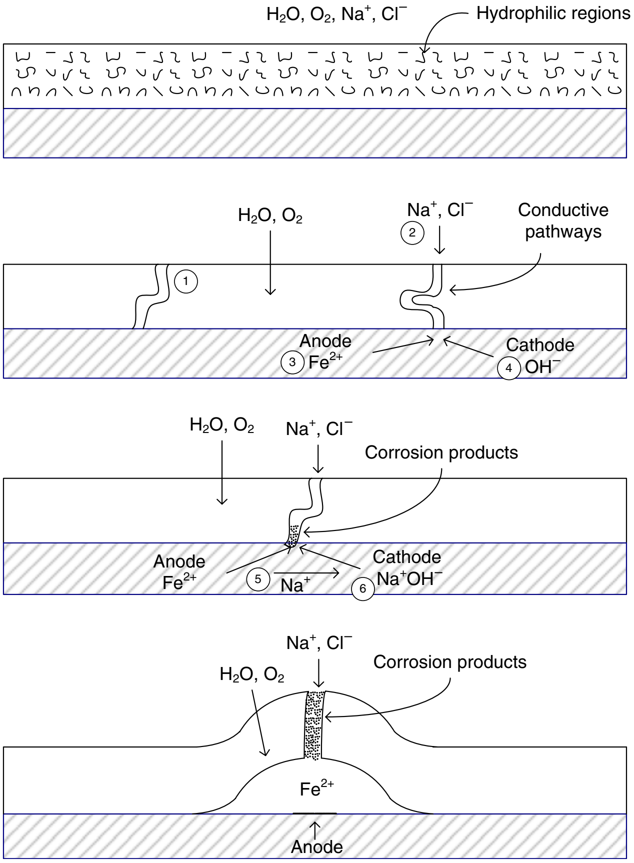


Fig. 24: Degradation of nondefect organic coatings on steel in a neutral electrolyte solution. Adapted from reference 304

The number of the steps corresponds to the numbers circled in Fig. 24.

(1) Conductive pathways develop due to attack of water in hydrophilic or low crosslink density regions.
(2) Ions migrate to the substrate surface through conductive pathways.
(3) Anodes develop at the base of the pathways.
(4) Cathodic area develops at the periphery of the pathways.
(5) Sodium ions migrate along the coating-substrate interface to the cathodic sites for charge neutralization.
(6) The alkalinity of the sodium hydroxide causes cathodic delamination.
(7) Water is driven through the coating to the cathodic sites due to hygroscopic material at the cathodic sites.
(8) Blisters enlarge and possibly coalesce.

The corresponding mathematical models for blistering resulting from corrosion processes based on diffusion of cations along the coating-substrate interface from defect to cathodic sites underneath the coating have been successfully used to model the concentration of sodium ions in an artificial blister.[12] Neither of the models, however, addresses the initialization of blistering. Thus, it remains unknown if cathodic blisters are formed randomly or are associated with certain weak sites at the coating-substrate interface, such as interfacial microvoids or defects in the surface structure of the substrate.[304]

Cathodic blisters, which are associated with the corrosion process, may develop adjacent to an exposed area or at damaged sites of the coating. The damaged site may be an inherent fault of the coating (i.e., pores and microvoids), or a hidden defect such as low crosslinked regions. The principal difference between neutral and cathodic blisters is that the liquid in neutral blisters is weakly acid to neutral, whereas the liquid in cathodic blisters is highly alkaline.

New technologies

Nanostructured materials are believed to extend the possibility of engineering ''smart coatings'' by utilizing environmental changes to induce a response in the coating or substrate that changes surface composition to improve the inhibition of corrosion. The ability of coatings to modify their physical characteristics is already applied within other segments of the coatings industry. During the last few decades, electroactive conducting polymers for corrosion control has been a topic of a large number of researchers. Their unique electrical conductivity may make them useful in a wide area of applications. Most studies have shown that these types of coatings can provide meaningful protection efficiency, especially for mild steel. However, their ability to protect metals from corrosion in very aggressive environments is limited. Polypyrrole[333,334] and polyaniline[335–337] have been the strongest candidates, and have certain advantages for this purpose. It has been reported that polyaniline-containing coatings with scratches and pinholes are able to protect steel in acidic and neutral environments by repassivation of exposed areas. However, the exact protective mechanism of conducting polymers in anticorrosive coatings is in dispute because electroactive polymer coatings have been reported to provide both anodic protection and a barrier effect to prevent attack by a corrosive environment on steel.[338] In addition to reviewing the relating electroactive polymers' ability to protect against corrosion, some reviews provide an overview of the general properties and processing of electroactive polymers.[339,340]

Electroactive polymers may be applied in the development of smart corrosion inhibiting coatings, which will generate or release an inhibitor only when demanded by the initiation of corrosion. Thus, coatings may be able to release corrosion inhibitors on demand when, for example, the coating is mechanically or chemically stressed, or when an electrical or mechanical control signal is applied to the coating. The concept of self-healing polymers is inspired by biological systems in which damage triggers an autonomic healing response. The self-healing is accomplished by incorporating microcapsules containing functional constituents (healing agent and catalyst) within a polymer matrix prior to production.[341] These microcapsules will be manufactured to release their content when mechanically ruptured, which will occur when the coating is damaged by impact or abrasion. Subsequently, the content of the microcapsules is transported to the damaged regions, where the healing agent contacts a catalyst incorporated in the polymer matrix, polymerization is initiated, and the damage is repaired.

Coatings relying on the electrical signal arising from the onset of corrosion to initiate self-healing may be the future of anticorrosive coatings. Presently, a European[342] and a U.S. patent[343] describe a galvanically stimulated release of an inhibitor. The United States describes inhibitor release as the result of cathodic-induced alkaline hydrolysis, whereas the European patent describes a release resulting from alkaline hydrolysis under cathodic polarization of microcapsules filled with inhibitors.[344] Self-healing technology is new, however, and although some initial results indicate a possible usage of the technology for protection against corrosion, several challenges persist. In a recent review of the present technology, the technical issues relative to the development of self-healing coatings is addressed.[345,346] It is clear, however, that several years of research are needed to mature the technology for commercial use.

Discussion

Meeting environmental regulations and reducing production costs remain a key challenge and a major driving force for new developments in anticorrosive coatings. The challenge to coating suppliers is to find a solution with a more environmentally friendly profile, without sacrificing the proven performance features of the traditional formulations. This challenge is more severe for the protective coatings sector than for less-demanding segments of the coatings market, which explains the lower penetration of new technologies such as water-borne coatings in the protective segment to date. The next generation of high-performance anticorrosive coatings faces many challenges, and the incomplete understanding of the physical and chemical mechanisms responsible for the failure of anticorrosive coatings during service needs to be clarified. Thorough understanding and quantification of the degradation mechanisms by mathematical models may provide a useful tool in the development of new interesting products and be applied to ensure correlation between accelerated exposure and natural exposure tests. In addition, further studies on the degradation mechanisms of coating systems and progress in the development of binders and pigments may result in anticorrosive coating systems capable of providing excellent protection against corrosion. Novel ideas such as self-healing coatings need time to mature, but may be a part of the solution. High anticorrosive performance, however, must be achieved without compromising other properties inherent in present systems. The next decade will help elucidate whether the goal will be achieved.

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