1 Introduction

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1.1 Why corrosion-protective coatings

Man has used metal since about 6,500 B.C. Dating back to this time long past, copper items were found in the neolithic settlement of Çatal Höyük (Catalhoyuk) in Anatolia, where their appearance coincided with the obvious decline in the use of stone tools \(^1\), \(^2\). While copper and its alloys served for decoration, everyday objects, cutlery, tools and weapons of their era, widespread use of metal only started with the establishing of iron making in the second half of the second millennium B.C. \(^3\).

Iron has dominated history, culture, engineering sciences and industrial manufacture grace to its properties, combining availability and convenient refining, versatile workability by casting, forging, rolling and machining, and, last but not least, structural strength and ductility. From Damascus steel scimitar blades to Stephenson's Rocket, from the common passenger car to the Sears Tower Building, from a washing machine to luxury cruise ships – the applications of iron and steel are innumerable.

However, since the discovery of iron and the invention of its relative, steel, man has also been confronted with the degeneration and decay of this so very useful material by corrosion. The corrosion of iron and steel is a very fast process that destroys valuable goods every day and causes a lot of economic damage. The prevention of corrosion therefore is of paramount importance.

Organic coatings offer a very attractive road to the corrosion protection of metals. Their purposes and applications span from the temporary protection of surfaces during storage, transport and onward processing, over the role as protective primers that may provide a number of additional features like surface structuring, biostatic finish, conductor properties, (dry) lubrication etc., cosmetic coatings for colour, haptic and gloss design of surfaces, and finally surface finishes that provide anti-graffiti, anti-fingerprint, or wear resistant properties. Organic coatings provide a unique combination of aesthetic appearance and protection against corrosive decay for man's most important construction material – metal.

A lot of literature has been issued on corrosion prevention, and a lot of scientific and engineering effort as well as public and institutional funding are spent to understand corrosion and deterioration phenomena and to find ways for their prevention. The protective coating of metals primarily intended to retard the start of corrosion damage has often been discussed. In particular, the organic coating of metals has been described in basic reference works by representatives of the paint industry, in papers by the scientific community, in guides to surface engineering, and in monographs dealing with single aspects of use. All authors had their specialist perspectives on metal and metal finishing, for example in steel making, on passivation and surface treatment, on the vast number of uses and their respective anticorrosive measures, and the expertise to formulate and apply coatings. However, it has proven difficult to obtain the big picture that would demonstrate the interdependence and the interplay of all parties.

The intention and the purpose of the present book is to provide a synopsis on all aspects of corrosion protection coatings for metal, from the substrate quality and its chemical proper-
ties, the importance of proper cleaning and surface preparation by conversion treatment, the role of paint ingredients, in particular novel resins and anticorrosive pigments, surface engineering techniques, and the ongoing research for novel trends that will lead the way into the future of corrosion-protective coatings.

Five authors, each of them with a good record in the industrial and scientific community, have joined in this work.

1.2 Literature


2 Corrosion protection coatings

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2.1 Principles of function

2.1.1 Electrochemistry of corrosion inhibition

Corrosion is an electrochemical process that destroys the surface of metals by dissolution reactions and formation of corrosion products. On a coated metal surface corrosion takes place at the interface between substrate and coating. Consequently, a coating must provide sufficient protection to retard an onset and propagation of corrosion reactions. Strategies for corrosion prevention therefore involve a number of possible measures that either improve electrochemical stability of metal surface or restrict access of corrosive media to surface and along metal/coating interface. Common preventive strategies are summarised below, that have been discussed elsewhere [1,2].

Corrosion prevention strategies

- Conversion coatings
- Cathodic protection
  - Galvanising
  - Zinc dust primers
- Sealing of pores
  - Multi-layer coatings
- Barrier effect
- Dielectric properties of a coating
- Reduced moisture and gas uptake
- Interception of corrosive agents
  - Active anions
  - Ion exchange pigments
- Improvement of substrate adhesion
  - Adhesive primers
  - Silane/siloxane coatings
- Increase of alkalinity
  - Cement coatings

The metallic state is defined as a feature of solid matter, where atoms are located, densely packed, at the sites of a crystal lattice, and one or more of their electrons (bonding electrons) released to be freely distributed across the entire macroscopic crystal [3]. Therefore, in principle all metals are prone to corrosion due to free availability of their electrons at the outer surfaces of the metal crystal.

One driving force for corrosion is the ease of electrons to be released, or in other terms, of the metal to be oxidised. This depends on the kind of metal, and is usually characterised by the metal’s electrochemical potential. The chemical reactions that take place during atmospheric corrosion can be resolved into a pair of red-ox reactions, shown in Equations 2.1 and 2.2.
Equation 2.1  \[
\text{Zn} \rightarrow \text{Zn}^{2+} + 2 \text{e}^- \quad \text{Anodic reaction}
\]

Equation 2.2  \[
\frac{1}{2} \text{O}_2 + \text{H}_2 \text{O} + 2 \text{e}^- \rightarrow 2 \text{(OH)}^- \quad \text{Cathodic reaction}
\]

The metal serves as the anode, i.e. the source of free electrons which are released upon the dissolution of metal atoms. These are oxidised to metal cations (e.g. \(\text{Zn}^{2+}\)) in the first reaction, and the corresponding equivalent amount of electrons (\(\text{e}^-\)) is made available for the second reaction. In case of atmospheric corrosion, these electrons pass through the interface into the surrounding solution, where they are consumed for the reduction of oxygen. Figure 2.1 shows a schematic view of this situation \[4, 5\].

This description, in fact, leads directly to the major strategic principle of any anticorrosive coating: If either of the reaction branches is slowed down effectively, the onset and development of corrosion can be largely retarded. Corrosion inhibition (passivation) hence can be achieved by the formation of a physical barrier that either insulates electrically, i.e. prevents the transition of electrons from the metal to surrounding electrolyte, or mechanically, i.e. blocks the direct access of electrolyte or atmospheric oxygen to the metal surface.

### 2.1.2 Metal oxide formation

A passivation or conversion coating, therefore, usually involves formation of a dense coating of metal oxide, in order to display this barrier effect. The metal oxide, most often incorporating dissolved ions of the substrate metal itself, precipitates on the substrate surface and forms a physical barrier. This barrier can only be penetrated by oxygen or ions through diffusion, thereby slowing down the access of these materials to the base metal.

An effect of metal oxide coatings is sometimes also described in terms of a band model. Many oxides of transition and higher main group metals have semiconductor properties. For example, zinc oxide (\(\text{ZnO}\)) displays characteristics of an n-semiconductor, which means that electrons in the valence band of the oxide can be promoted to the conducting band by relatively low energy input. The energy gap (i.e. the distance of energy levels between the valence and conducting bands) is a characteristic feature for each substance. The band gap of magnesium oxide, \(\text{MgO}\), for example, is much wider, which makes the compound an insulator. Oxides of alloys, like the species \(\text{MgZn}_2\), display energy gap values between those observed for oxides of the pure elements. Additionally, defects in the oxide coating result in a reduction of the energy gap. A better resistance of an oxide coating against corrosion is obtained with the widening of the energy gap. Though \(\text{MgZn}_2\) is the prevailing component in the new \(\text{Zn-Mg}\) galvanising coatings, the situation in technical \(\text{Zn-Mg}\) coatings is complicated by the additional presence of aluminium. The effect of the various corrosion products in this model is also not entirely understood \[8\].
One approach for a rationalisation of this effect is the respective stability of corrosion products (oxides and hydroxides) in alkaline conditions, as occur under the regime of oxygen reduction. MgO and Mg(OH)$_2$ are insoluble in alkalis, and therefore form stable barrier layers. Consequently, zero-corrosion current densities are observed for lower (more negative) electrode potentials and higher alkalinities, the more Mg is present in the overall metallic coating composition (cf. Figure 2.2) [7]. In coherence, micrographic and photo electron spectroscopic (XPS) studies have shown mainly Zn corrosion products in defective areas with high dissolution, while areas with a low corrosion aspect were found to be covered by an MgO/Mg(OH)$_2$ film.

Native oxide coatings of this kind develop on zinc (Zn), aluminium (Al), magnesium (Mg), or chromium (Cr), sometimes also incorporating carbonate ions from atmospheric carbon dioxide (cf. Chapter 3.3.3.1).

Most oxides and hydroxides are instable when contacted with chloride containing electrolytes. Chloride can replace oxygen in the crystal lattice, so that mixed oxy/hydroxy chlorides are formed that are known as intermediates in the dissolution process which often leads to local (pitting) corrosion. Hydrotalcite pigments are reported to act as chloride scavengers by virtue of their ion-exchange properties [8]. Calcium compounds are also known to intercept residual chloride in coatings for polyalkylene packaging foils [9]. A similar effect can be expected from calcium compounds in organic coatings for metals.

### 2.1.3 Cathodic protection

The native oxide layer of ferrous materials is too porous to withstand further corrosive attack. Iron (Fe) and steel are often saved from corrosion by a coating with less noble metals, e.g. with a Zn layer in galvanising. Further to its less penetrable native oxide barrier, Zn corrodes preferentially on cut edges or scratches, serving as a "sacrificial anode", thus keeping the base metal from destruction. This behaviour is driven by the different electrochemical potentials. While the potential of Fe is $E_{\text{pot}} = -0.44$ V, (cf. Chapter 7.3.2.1, Table 7.2), that of Zn is lower, i.e. $E_{\text{pot}} = -0.76$ V. Protection is even active at some distance from the border of the Zn layer, and may be attributed to a local increase in electron density in front of the Zn border (cf. Chapter 7.3.4.1). This long-range effect is usually called cathodic protection.

Cathodic protection can also be made a function of the primer. Zinc pigmented primers have been used as anti-corrosion barrier for various artisan and industrial coating applications, in particular in heavy machinery, architecture and industrial construction, bridge engineering, water engineering, shipbuilding, etc. For these purposes, primer coats are used with gauges of 50 µm and more [10–13]. The usefulness of zinc-rich primers is often attributed to the cathodic protection provided by zinc particles to otherwise unprotected steel surfaces. Zinc dust primers have also been reported as protective coatings under powder coatings.
As the authors did not observe any influence of the zinc content in various primer formulations, they conclude that the major contributions to the improved performance are made by the mechanical barrier effect and the adhesion promotion that is brought about by the extra primer layer \cite{14}.

The principle of cathodic protection has also been used in corrosion protection primers (CPP) that are applied on sheet for car manufacture \cite{15,16}. By their use, improved corrosion protection is achieved particularly in critical areas of a car body, like seams, box sections or flanges, where a pretreatment is geometrically difficult to apply and may therefore be faulty, or the cathodic electro-dip primer is only insufficiently deposited due to shielding effects.

### 2.1.4 Passivation and conversion coating

Native oxide layers may serve well as efficient anticorrosive barriers for bare bulk metal, but from the perspective of technical surfaces, it is often desired to create a more uniform, controlled passivation layer, to better preserve the surface aspect and features. To this end, it is necessary to remove the native oxide film (cf. Chapter 3.3.3.1), and replace it by a similar film under controlled conditions, with improved features, for instance, uniform thickness, lower porosity, better transparency, or higher electrical resistance.

Chromate containing chemicals have been quite commonly used for the generation of passivating layers, due to the very high oxidative power of the chromate ion in acid systems. This results in a very fast superficial red-ox reaction (cf. Chapter 8.2.4, Equations 8.8 to 8.10), forming an insoluble, very dense mixed oxide layer of Cr\(^{3+}\) and the substrate metal, e.g. Zn. The cathodic branch of this reaction system is also described by Equation 2.3. Its standard potential is \(E_{\text{pot}} = 1.195\ \text{V} \) \cite{17}.

\begin{equation}
\text{Equation 2.3} \quad (\text{CrO}_4)^{2-} + 8\ \text{H}^+ + 3\ \text{e}^- \rightarrow \text{Cr}^{3+} + 4\ \text{H}_2\ \text{O}
\end{equation}

The long-lasting corrosion resistance provided by chromate passivation is also due to the so-called self-healing effect. This is usually attributed to residual chromate ions that are incorporated in the oxide layer. In case of mechanical damage of the passivation layer that penetrates through the underlying substrate metal these chromate ions are available for a quick passivation reaction at the newly exposed metallic location. Other “active anions” that may also serve as strong oxidants for metals, like the oxo-anions ferrate, (per)manganate, molybdate, tungstate, or vanadate, are considered as possible direct replacements for chromate \cite{18}. For example, Patent WO 0036182 \cite{19} describes a pretreatment for aluminium and its alloys, based on an alkaline ferrate (VI) solution and additional oxo-anions like molybdate. The patent is valid in several European states, but no commercial application is known yet.
2.2 Design of organic coating systems

2.2.1 Diffusion barrier features – humidity uptake and electrolyte permeation

While cross-linking of a coating renders a macroscopically intact and closed network with the required mechanical and chemical features, on a molecular scale, any polymer film will remain penetrable to some extent by gases and electrolytes, due to diffusion and migration. Increasing the film thickness is one possible measure to improve on this situation. For instance, in coil coating, primer coatings are normally used at 5 µm dry-film thickness. For high anticorrosive requirements, e.g. certain appliances and marine architectural applications, coil primer coats of up to 30 µm are common.

The uptake of water or moisture is considered an important feature of organic coatings, as it is linked with changes in the density and dielectric properties of the polymer film. Absorption and incorporation of water molecules will lead to physical swelling (volume expansion) and results in a softening of the coating surface. Moreover, as water is an electrolyte carrier, its presence is related with the ease of dissolved ions to penetrate through a coating, where they may accumulate and, finally, cause degradation of the polymer film and corrosion of the metal substrate [20].

Water uptake is influenced by chemical and physical properties of the coating, and therefore it is determined by the molecular design of the polymer. Typical coating resins like epoxies or polyurethanes display a modest water uptake in humid atmosphere. However, the rate of incorporation is strongly accelerated when approaching the dew point. In principle, polar (hydrophilic) polymers will allow better wetting and hence also a higher water absorption [21].

The elasticity of a coating, on the other hand, plays a role in the diffusion transport of molecules through the interstices of the polymer film, which can be interpreted as the relative mobility of polymer moieties [22]. While this property changes with temperature, usually showing a jolt from the rigid to the elastic regime at the glass transition temperature (T_g), it will also be affected when the film is plasticised by incorporation of water [23]. The design of the polymer therefore includes the task of reconciling disparate features like flexibility (formability) vs. curing temperature vs. diffusion barrier properties, or water miscibility vs. chemical resistance vs. adhesion vs. wetting.

Another strategy involves the use of nanoscale particles like titanium dioxide (TiO_2) preparations, or natural or synthetic mineral pigments like clays and hydrotalcites. The latter two contain agglomerates of nanosized crystalline platelets that can be separated from the agglomerate and distributed in the bulk coating. The idea is that these platelets can form an additional barrier to penetrating media, as they could extend the diffusion path for any corrosive ion or media through the coating, cf. Figure 2.3. The observation of the expected effect was reported for oxygen, carbon dioxide and water vapour [24].

![Figure 2.3: Schematic view of the extension of the diffusion path by a nano-platelet filled coating; according to Lewis](0)