Advances in Anti-Corrosion Polymeric and Paint Coatings on Metals: Preparation, Adhesion, Characterization and Application

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1. Introduction and Scope

Metals currently remain the main structural material used by various industries for many centuries. However, with all their advantages, metals have a significant drawback—they are destroyed under the influence of the environment, i.e., corroded.

In parallel with the development of methods for manufacturing a wide range of products from structural metals, mankind has developed ways to reduce corrosion losses. The fight against corrosion is the oldest scientific and technical problem, the relevance of which was written by such famous scientists as Pliny the Elder in 77AD [1], Robert Boyle in 1675 [2], W.H. Wollastone in 1801 [3,4], Sir Humphry Davy in 1824 [5], Davy’s student M. Faraday also in 1824 [6], W.R. Witney in 1903 [7], etc.

Metallic corrosion has now become subject of many textbooks and scholarly compendia [8–12], and a number of introductory treatments dealing with corrosion and corrosion protection are also available [13–16]. In this context, the term “corrosion” refers to the chemical degradation of a metal by its environment. The reactions are mostly often heterogeneous redox reactions and occur at the metal-environment interface. The anodic reaction is typically the oxidation of the metal; the cathodic reaction is reduction of a non-metal, typically oxygen. If the product of the metal oxidation forms a tight and adherent film, the corrosion process may be self-limiting. If the products of the corrosion reaction are soluble in the corrosive medium, or are permeable to it, then metallic corrosion can proceed. Corrosion is often represented in terms of a simple electrochemical model. The anodic and cathodic half reactions of the corrosion cell may occur at adjacent or widely separated sites on the metal surface; the electrical circuit is completed by electronic conduction within the corroding metal and ionic conduction within the aqueous electrolyte. In natural corrosion, it is common for the sites of the anodic and cathodic corrosion reactions to become more or less widely separated. In such cases, the anodic sites tend to become acidic and the cathodic sites tend to become basic. These changes in pH can be large, and can have serious implications for the performance of polymeric materials.

The corrosion of iron is one of the most widespread and technologically important examples of metallic corrosion. In the presence of water and oxygen, the corrosion of iron proceeds to form a complicated mixture of hydrated iron oxides and related species; a complete description is beyond the scope of the present discussion, and the interested reader is referred to the previously cited general references on corrosion as well as to the well-known descriptions of electrochemical equilibria in aqueous solution given by Pourbaix [8,9] (so-called Pourbaix diagrams). Iron is a base metal, subject to corrosion in aqueous solutions. In the presence of oxidizing species, iron surfaces can be passivated by the formation of an oxide layer; if the oxide layer formed is imperfect, rapid corrosion may occur. In simplest form, the reaction of iron to form iron oxide can be written as:

\[ 4 \text{Fe} + 2 \text{H}_2\text{O} + 3 \text{O}_2 \rightarrow 2 \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \]
The first step in the corrosion process is the dissolution of iron to form ferrous ion:

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-
\]

In general, the pH decreases at sites of anodic dissolution due to hydrolysis reactions such as:

\[
\text{Fe}^{2+} + \text{H}_2\text{O} \rightarrow \text{FeOH}^+ + \text{H}^+
\]

The cathodic reactions commonly observed are the evolution of hydrogen and the reduction of oxygen; hydrogen evolution is kinetically favored under acidic conditions, while oxygen reduction is kinetically favored under neutral and basic conditions.

\[
\begin{align*}
\text{H}_3\text{O}^+ + e^- & \rightarrow \frac{1}{2} \text{H}_2 + \text{H}_2\text{O} \quad \text{(acid solutions)} \\
\text{H}_2\text{O} + e^- & \rightarrow \frac{1}{2} \text{H}_2 + \text{OH}^- \quad \text{(neutral/basic solutions)} \\
\frac{1}{2} \text{O}_2 + \text{H}_3\text{O}^+ + 2 e^- & \rightarrow 3 \text{H}_2\text{O} \quad \text{(acid solutions)} \\
\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2 e^- & \rightarrow 2 \text{OH}^- \quad \text{(neutral/basic solutions)}
\end{align*}
\]

The pH at cathodic sites tends to increase due to the production of hydroxide ion and/or consumption of hydrogen ion.

The annual costs of developed countries to combat corrosion amount to huge sums, estimated in the billions of dollars annually [11,16–18]. Corrosion can cause direct and indirect costs which can reach up to 6% of the gross domestic product of a developing country [19].

On the other hand, it is believed [20] that the use of advanced anti-corrosion technologies and approaches (e.g., advanced insulating coatings) will save of corrosion costs by approximately 20–25%.

Organic and paint coatings are the most common and oldest method of anti-corrosion protection of metals. So, organic coatings are the major protective measure accounting for up to 90% of expenditure on corrosion protection [19]. The global anticorrosion coating market was estimated to be $24.84 billion in 2017, having a cost growth rate over 5 years of approximately 5%/year [21].

Mankind has used paints and varnishes since ancient times. The earliest evidence of well-preserved prehistoric paintings, dating from the 16th millennium B.C. can be found in caves in Southern France (Font-de-Gaume, Niaux, Lascaux), Spain (Altamira), and South Africa. The colors used were pure oil paints prepared from animal fat mixed with mineral pigments such as ocher, manganese ore (manganese dioxide), iron oxide, and chalk. The oldest rock paintings from North Africa (Sahara, Tassili n’Ajjer) date from between the 5th and the 7th millennium B.C. Many examples of paintings from Babylon, Egypt, Greece, and Italy dating from the 1st and 2nd millennium B.C. are also known [22].

Moreover, the painting was used not only for decorative, but also for protective purposes. The first painted objects come from China [21]. Furniture and utensils were covered with a layer of paint in an artistic design. The oldest tradition work dates from around 200 B.C. The lacquer used was the milky juice from the bark of the lacquer tree (Rhus vernicifera). This was colored black or red with minerals, and later also with gold dust or gold leaf.

Pliny the Elder in 77 AD referred [1] to the rust preventing properties of a mixture of “ceruse” (a white lead carbonate), gypsum and tar (paint) as useful method for protecting iron against rust [6].

However, methods of protecting metal from corrosion with polymeric or paint coatings in addition to undeniable advantages, they also have some disadvantages. For example, in the case of a defect in the coating (which may be formed during transportation or installa-
tion of the structure or during operation of the coated structure), intensive dissolution of
the metal through the defect in the coating is possible, often leading to through perforation
of the metal wall.

In addition, near the defect, after a short time, delamination of the coating from the
metal, the penetration of aggressive components of the medium between the metal and the
coating, and under film corrosion of the metal often occurs.

Moreover, sometimes there is a delamination of the coating without a visible defect
in it.

This delamination can provoke the metal corrosion because water and oxygen can
diffuse through the coating to the metal surface.

Sometimes it is even believed that such a dangerous type of corrosion destruction of
metal underground structures as stress corrosion cracking occurs under a peeled (defect-
free) coating.

Therefore, it is very important that the coating not only has good adhesion to the metal,
but also retains it for a long period of operation, being exposed to the environment (mainly
water and aqueous electrolytes) and operating conditions (such as, for example, the cathode
potential in the electrochemical protection of underground and underwater structures.

Another important aspect of the use of organic and paint coatings is the pre-treatment
(before coating deposition) of the metal surface. Such pre-treatment is carried out to im-
prove the adhesion and anti-corrosion characteristics of the coating. For many years, metal
surface pre-treatment has been carried out using chromate-based treatment compounds,
as a result of which a conversion coating is formed on the surface, which is responsible
for increasing adhesion and inhibiting metal corrosion. However, in recent decades it has
come clear that hexavalent chromium compounds do not meet modern environmental
safety requirements, being toxic and even carcinogenic. Therefore, developed countries
introduced a ban on their use, thereby initiating increased interest of researchers in scientific
and technical work aimed at replacing the chromate pretreatment of metal [23].

Thus, it is obvious that research aimed at the development of new or improvement
of already used organic coatings can be of great importance, both for fundamental (since
the mechanism of the anticorrosive action of polymer and paint coatings will be detailed
as a result), and for industry science (due to the developed as a result of improved anti-
corrosion coatings).

The content of the Special Issue of Metals «Advances in Anti-Corrosion Polymeric
and Paint Coatings on Metals: Preparation, Adhesion, Characterization and Application»
will reflect the most advanced development trends (which are briefly presented above) in
those areas of physical chemistry that are associated with surface phenomena, the science
of corrosion, electrochemistry, adhesive phenomena, etc.

2. Contributions

The Special Issue of Metals with title “Advances in Anti-Corrosion Polymeric and
Paint Coatings on Metals: Preparation, Adhesion, Characterization and Application” is
scheduled to release this year.

Research articles presented in the Special Issue will cover a wide range of studies
related to the use of polymer and paint coatings for metal corrosion control.

It will be discussed in detail environmently friendly methods of metal surface prepa-
ration (chromate-free surface pretreatment methods), which provide high adhesion of the
coating, inhibition of underfilm corrosion and can replace toxic chromate pretreatment.

Compositions with different chemical structure for surface pretreatment will be pre-
sented, as a result of which surface nanolayers will be formed, simultaneously combining
the properties of a coating adhesion promoter and a metal corrosion inhibitor.

Particular attention will be paid to the problem of improving the adhesion of coatings
to metal and its preservation under the environment and operating conditions action.

An important issue regarding the mechanism of action of coatings is the relationship
between coating adhesion and metal corrosion.
So, modern views on the mechanism of the anti-corrosion action of polymer and paint coatings will be considered and discussed in the Special Issue of Metals “Advances in Anti-Corrosion Polymeric and Paint Coatings on Metals: Preparation, Adhesion, Characterization and Application”.

3. Conclusions and Outlook

A variety of topics will be compiled in Special Issue of Metals ‘Advances in Anti-Corrosion Polymeric and Paint Coatings on Metals: Preparation, Adhesion, Characterization and Application’, covering large-scale ideas about the mechanism of the anticorrosive action of polymer and paint coatings and many related issues dealing with corrosion control by using coatings, such as surface preparation before coating deposition, adhesive aspects of using polymer coatings, etc.

As a guest editor, I want to express my gratitude to the authors who have already submitted their articles to the special issue, for their contributions, to the reviewers and editors, for their work with these articles.

I also want to thank in advance those researchers who will be ready to submit their papers in the coming months.

I additionally wish to give sincere thanks to all reviewers and editors of Metals for their valuable and continuous help in Special Issue preparation and their inexhaustible engagement ensures high-quality publication during the preparation. In particular, sincere thanks to the editor Zach Ma for his great help and his huge personal contribution to the preparation of this Special Issue.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The author declares no conflict of interest.

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