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# **METAL PRETREATMENT**

## **FOR CORROSION CONTROL**

**N D BANIK**

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# METAL PRETREATMENT FOR CORROSION CONTROL

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**METAL  
PRETREATMENT**  
FOR CORROSION  
CONTROL

**Dedicated to  
All Those Engaged in  
Metal Pretreatment**

# Preface

Metal pretreatment is a subject not widely known. Though part of engineering courses, it is studied cursorily. It receives scant attention even in the paint shop of engineering firms, due to poor knowledge of the management and operators regarding the subject.

During my long association with the subjects of corrosion and metal pretreatment I had an opportunity to visit various Indian engineering industries, manufacturing different products, from ships to tiny wrist watches. Everywhere metal pretreatment is done with proprietary chemicals, whose suppliers furnish details containing only the operational parameters. Everywhere I went, I found that people engaged in the job were keen to know the fundamentals of metals pretreatments, and this inspired me to write the book.

Control of corrosion is the main aim of metal pretreatment. With rapid industrialization, the use of metals has risen phenomenally, bringing in its wake the colossal problem of corrosion, involving losses valued at billions of dollars.

This book is primarily on metal pretreatment, but a preliminary discussion on corrosion has been incorporated at the beginning to acquaint the readers with the subject. Salient properties of steel and other metals and also of their alloys have been given for the convenience of the fabricators of industrial equipment.

Surface preparation of metals is a must for any subsequent protective finish. The common industrial processes involved in this have been elaborately discussed. Similarly, all aspects of phosphate coatings including their types, applications, and chemistry of formation have been dealt with exhaustively. A different oxalate coating for stainless steel and other coatings for steel have

## **viii Preface**

also been covered. Pretreatments of the principal non-ferrous metals and their alloys have been discussed in a separate chapter, while another chapter is devoted to miscellaneous subjects, such as water in the pretreatment shop, effluent treatment, and waste disposal. An appendix containing useful information is given at the end of the book.

In writing the book I consulted many journals, periodicals and books, and these have been mentioned at the end of each chapter. I acknowledge my gratitude to their authors and publishers.

I am thankful to Tata McGraw-Hill Publishing Company, for their guidance and encouragement in preparation of the text.

Science and technology are ever-widening subjects, and I have made every endeavour to update the book with the latest information. Any suggestions in this regard will be welcome.

I shall consider my efforts amply rewarded if the book proves useful to those for whom it is primarily intended.

**N D Banik**

# Contents

<b>Preface</b>	<b>vii</b>
<b>1. Corrosion: Nature and Typology</b>	<b>1</b>
1.1 Corrosion	1
<i>References</i>	14
<b>2. Protection from Corrosion</b>	<b>15</b>
2.1 Control and prevention of corrosion	15
<i>References</i>	48
<b>3. Pretreatment of Ferrous Metals</b>	<b>50</b>
3.1 Surface preparation	50
<i>References</i>	74
<b>4. Phosphate Coatings</b>	<b>75</b>
4.1 Classification of phosphate coatings	76
4.2 Pre-paint phosphate coatings	77
4.3 Phosphate coating for unpainted corrosion resistance	89
<i>References</i>	95
<b>5. Cold Drawing of Steel</b>	<b>96</b>
5.1 Cold mechanical deformations	96
5.2 Borax in wire drawing	110
5.3 Cold deformation of stainless steel	115



## **x Contents**

- 5.4 Cold deformation of titanium and zirconium 117
- 5.5 Rinsing, passivation, and sealing 118
- 5.6 Testing of phosphate coatings 122
- 5.7 Chemistry of phosphating and factors influencing coat formation 123
- 5.8 Coating steel with copper and copper-tin alloy 128
- 5.9 Chemical blackening 129

*References* 132

## **6. Pretreatment for Non-Ferrous Metals 134**

- 6.1 Aluminium 134
- 6.2 Zinc and galvanised iron 152
- 6.3 Magnesium 157
- 6.4 Copper and its alloys 159
- 6.5 Tinning on copper and brass articles 159

*References* 161

## **7. Water in the Pretreatment Shop 162**

- 7.1 Control of quality 163
- 7.2 Economy in water use 164
- 7.3 Effluent treatment and waste disposal 166

*References* 170

## **Appendix 171**

## **Index 177**

# Corrosion: Nature and Typology

## 1.1 CORROSION

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Corrosion is nature's way of destructive disintegration of metals. Ever since man started using metals, he has been facing the problem of corrosion. During the last few centuries there has been rapid industrialisation throughout the world, and corrosion too has grown proportional to it. Today it has reached such gigantic dimensions that it can rightly be called "the greatest killer" of metals.

While rusting of iron is familiar to every one, it is not generally recognised that metal corrosion entails colossal economic, social and personal losses.

The financial implications of corrosion damages are so staggering that no nation can afford to overlook the need for corrosion control measures. Corrosion losses to the economy have been estimated at about \$ 15 billion in U.S.A., £ 1500 million in U.K. and Rs 600 crores in India per year.

Corrosion is a silent wrecker, operating at all times, at all levels and in all establishments. It poses perennial problems to industries big and small; petrochemicals and fertilisers; power houses and nuclear establishments; dyestuffs and pharmaceuticals; to mention only a few. The deadly effects of

## **2 Metal Pretreatment**

corrosion on structural stability and on product purity have even been highlighted in fiction.

India is far behind the western countries in corrosion-consciousness. We have hardly any corrosion engineers even in very big industrial units, and the subject of corrosion is rarely included in the syllabi of our universities.

Corrosion problems must, therefore, be effectively tackled. Fortunately, today there has been a national and international awareness to contain this menace by sharing one's knowledge and expertise with others.

### **1.1.1 Nature of Corrosion**

Corrosion reactions are broadly classified into two groups, based on the nature of the corroding agent: (1) Dry oxidation, and (2) Wet corrosion. Atmospheric corrosion occupies an intermediate position.

#### ***Dry oxidation***

When mild steel is exposed to dry air at ordinary temperature, it oxidises forming a very thin, transparent and barely discernible film of iron oxide. The oxidation nearly stops within an hour, as the thin oxide film is hardly permeable to oxygen to cause further reaction with the metal underneath. Thus dry air does not have a corroding effect on the metal except at elevated temperatures when the films formed become thick and visible. The 'Ashoka pillar' in Delhi has withstood corrosion for centuries only because of the mildness of the Delhi atmosphere and not because of the superiority of the metal itself.

Dry oxidation is a serious problem only at high temperatures or under conditions where the oxide film is constantly being scrapped away exposing fresh metal to attack. While the oxide layer on aluminium is sufficiently uniform to hinder the attack of many salt solutions, the oxide layer on ordinary carbon steels is non-uniform and has little or no protective capacity when exposed to humid atmospheres or

salt solutions or industrial waters. Corrosion occurs at those parts of the metal at which the film is either cracked or absent for some reason.

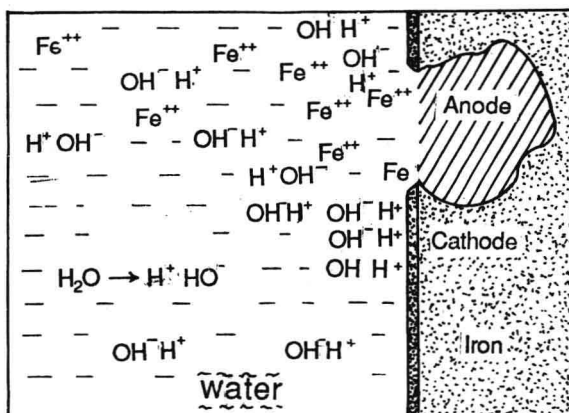
### ***Wet corrosion***

If mild steel is kept moist, it rusts rapidly. The presence of acid is not necessary as was supposed at one time. Rusting is rapid when air is dissolved in water. Wet corrosion involves the flow of electricity between certain areas of a metal surface, known as anodes and cathodes, through a solution called electrolyte capable of conducting electric current. The current results in corrosion of the anode areas.

An electrolyte is usually a liquid that contains ions. Ions are positively or negatively charged atoms or groups of atoms in solution. In equilibrium the negative and positive charges are in chemical balance.

As a result of structural and chemical inhomogeneities existing in metals and environments metal surfaces develop anodic and cathodic sites. The term 'anode' is used to describe that portion of the metal surface that is corroded and dissolved as ion and from which current leaves the metal to enter the solution (electrolyte). Such transfer of ions is, therefore, termed the anodic oxidation. The term 'cathode' is used to describe the metal surface at which the current leaves the solution and returns to the metal. As a result, the cathodic reaction is one of reduction and the metal is not affected. The electrons that are generated by the formation of metal ions at the anodes pass through the metal to the cathode areas also immersed in the electrolyte. Here they restore the electrical balance of the system by reacting with and neutralising positive ions in the electrolyte. Figure 1.1 illustrates the wet corrosion of iron in water. It shows an atom detaching itself from the anode as ferrous ion with two positive charges, and entering into water leaving behind two electrons. These electrons travel through the metal to the cathode to neutralise two hydrogen ions into hydrogen atom.

During the actual corrosion of metal, as in the presence of



**Fig. 1.1** Corrosion of iron in water

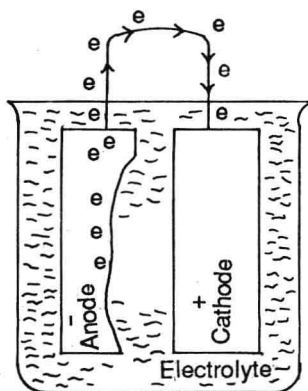
acid, the anodic and cathodic sites interchange causing uniform dissolution of the metal.

### ***Electrochemical series and galvanic series of metals***

When a metal is placed in a solution containing 'normal' concentration of its ions, the metal ions either tend to enter the solution, or the ions from the solution tend to enter the metal lattice. Before immersion, both the metal and solution are electrically neutral. As the number of metallic ions in solution is altered after immersion, a difference in potential is established between the metal and the solution. This is known as 'normal potential' of the metal. When this value is taken as zero for hydrogen, the corresponding value for a noble metal like silver is +0.8 V, for copper +0.35 V, for iron - 0.44 V, for zinc - 0.77 V and for aluminium -1.34 V. The arrangement of the metals in the order of their normal potentials constitutes the "electrochemical series". The negative sign attached to aluminium, zinc, iron, etc. denotes that these metals readily pass into solution either in water or acid giving ions with a positive charge (cations) and thereby themselves becoming negatively charged. These are, therefore known as electronegative metals. The positive sign in

the case of silver, copper, etc. means that the positive metal ions (cations) pass from the solution on to the metal more readily charging it positively. These are, therefore, called electropositive metals.

The electrical contact of metals having different electrode potentials, such as copper and zinc, results in setting up a current, one of them (zinc) going into solution being known as the 'anode' and the other (copper) with no corrosion known as the 'cathode'. When corrosion occurs through dissimilar metals being coupled together and immersed in an electrolyte, the process is known as galvanic action. This is illustrated in Fig. 1.2.



**Fig. 1.2** Galvanic action—movement of electrons from anode to cathode and consequent corrosion at the anode

While the electrochemical series is of considerable value to electrochemists, it is of less use in corrosion problems where the solutions (electrolytes) are quite different. In studying galvanic action another table is used which is based on experience and laboratory experiments with combinations of metals in a great variety of environments.

Table 1.1 shows metals and alloys in sea water moving at high velocity. It is known as the "Galvanic series of metals and alloys in sea water". In any couple, the metal near the top of the series will be the anode and will suffer corrosion whilst

## 6 Metal Pretreatment

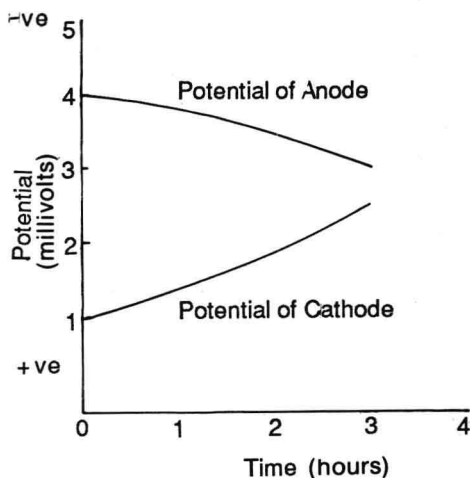
the one nearer the bottom will be the cathode and will receive some galvanic protection.

**Table 1.1** Galvanic series of metals and alloys

1. Magnesium	24. Inconel
2. Magnesium alloys	25. 80 Ni 20 Cr (active)
3. Zinc	26. Brasses
4. Aluminium (work hardening)	27. Copper
5. Cadmium	28. Bronze
6. Duralumin	29. Nickel-silver
7. Carbon steel	30. Copper nickel
8. Copper steel	31. Monel
9. Cast iron	32. Nickel
10. 4-6% Cr steel	33. 80 Ni 20 Cr (passive)
11. 12-14% Cr steel	34. 12-14% Cr steel
12. 16-18% Cr steel	35. 16-18% Cr steel
13. 23-30% Cr steel	36. 7 Ni 17 Cr steel
14. 2% Ni 17% Cr steel	37. 8 Ni 18 Cr steel
15. 8% Ni 18% Cr steel	38. 14 Ni 23 Cr steel
16. 14% Ni 23% Cr steel	39. 23-30% Cr steel
17. 20% Ni 25% Cr steel	40. 20 Ni 25 Cr steel
18. 12% Ni 18% Cr Mo steel	41. 12 Ni 18 Cr 3 Mo steel
19. Lead-tin solder	(passive)
20. Lead	42. Silver
21. Tin	43. Graphite
22. Nickel	44. Gold
23. 60 Ni 15 Cr steel	45. Platinum

### **Polarization**

As the galvanic corrosion reaction proceeds there will generally be an accumulation of corrosion products, i.e., metal ions at the anode and hydrogen at the cathode. This results in polarization which causes the initial potential both at the anode and cathode to diminish. Figure 1.3 shows how the anode and cathode potentials alter and drift towards each other; that is, polarization causes the cathode to become negative and the anode less negative. In practice, cathodic polarization is usually of greater importance than anodic polarization in its effect on corrosion.



**Fig.1.3** Polarization of anode and cathode in time

### ***Factors influencing corrosion rate***

These factors may be associated either with the nature of the metal or alloy used as electrodes or the environment to which it is exposed.

The factors that depend on the nature of the metal or alloy include:

- (i) The electrode potential of the metal or its position in the galvanic series. Usually anodic metals corrode faster.
- (ii) The hydrogen overvoltage, i.e., the ease of hydrogen evolution at the cathode.
- (iii) The chemical inhomogeneities, e.g., inclusions, impurities, and different phases which promote the formation of anodic and cathodic sites.
- (iv) Physical inhomogeneities, i.e., regions of high residual stress in the metal. These tend to become anodic with respect to those regions which are free from stress. An iron nail is a typical example, the head and the tapered end are anodic because of stress caused by pressing while the middle unworked stem is cathodic.

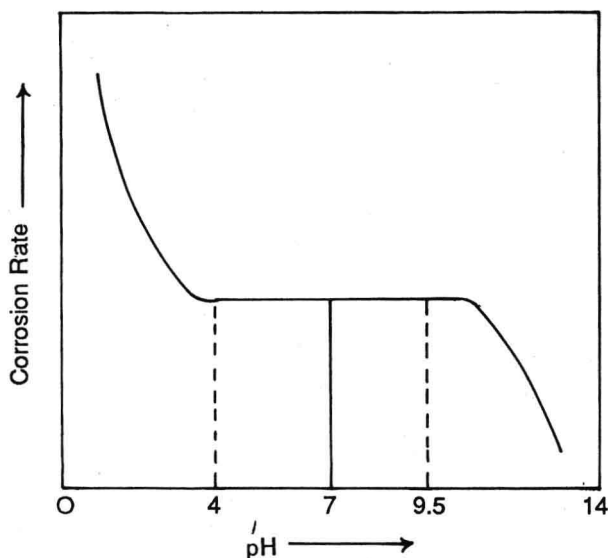


## 8 Metal Pretreatment

- (v) Passivity of the metal, i.e., formation of thin films of oxide of high protective value. Titanium, chromium, aluminium and stainless steel are good examples of passive metals.

The factors that are dependent on the nature of the environment include:

- (i) The hydrogen ion concentration or pH value of the solution. The solutions at pH 7 and above usually cause less corrosion than acid solutions (pH less than 7). Figure 1.4 shows the relation between the rate of corrosion and pH in the case of iron and mild steel. In the pH range 4-9.5, which is the neutral zone, the rate of corrosion is constant, and at pH exceeding 9.5 the rate of corrosion decreases.



**Fig. 1.4** Effect of pH on the corrosion rate of iron and mild steel

- (ii) The nature and concentration of other ions, and the degree of agitation. Excessive agitation is always detrimental because of abrasion and breakage of the protective film. Such an environment exists in the sea coasts.