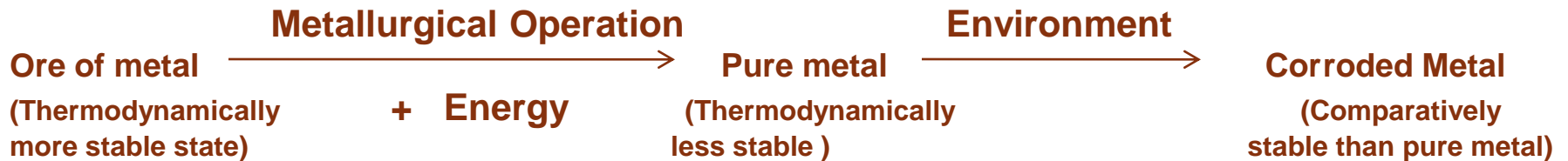# Fundamentals of corrosion and corrosion control

Corrosion: Corrosion may be defined as spontaneous destruction of material due to chemical, electrochemical or biochemical interaction of material with the environment in which it is exposed. The most common example of corrosion is rusting of iron.

Cause of Corrosion:

Ore of metal
(Thermodynamically more stable state)

Metallurgical Operation
→
+ Energy

Pure metal
(Thermodynamically less stable)

Environment
→

Corroded Metal
(Comparatively stable than pure metal)

The economic impact of corrosion

The economic impact of corrosion is incredibly large and significantly affects economy of government and industry. Some consequences are economic, and cause the following:

➢ Replacement of corroded equipment
➢ Preventive maintenance, example, painting, coating etc.
➢ Shutdown of equipment due to corrosion failure
➢ Contamination of a product
➢ Loss of efficiency
➢ Damage of equipment adjacent to that in which failure occurs

- Social consequences

➢ Safety (sudden failure can cause fire, explosion, release of toxic products)

➢ Health (pollution due to escaping products from corroded equipment)

➢ Appearance (as corroded material is unpleasing to the eye)

According to the National Association of Corrosion Engineers (NACE) India Section, the annual loss cost due to corrosion in India was reported as 4 % of GNP (Gross National Product), which is estimated to be around Rs. 375 billion per year

The major industries affected by corrosion:

- Oil and gas exploration and production industry

- Petroleum refining industry
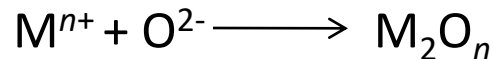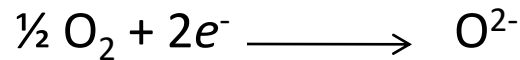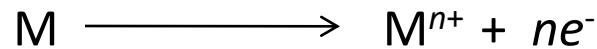
- Chemical industry
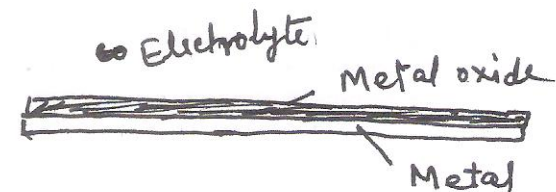
Types of Corrosion

- **Chemical corrosion or dry corrosion**

Oxidation corrosion

At low temperatures, alkali and alkaline earth metals are oxidized and at high temperatures, except Ag, Au and Pt, all other metals get oxidized.

$$M \longrightarrow M^{n+} + ne^-$$
$$\frac{1}{2} O_2 + 2e^- \longrightarrow O^{2-}$$
$$M^{n+} + O^{2-} \longrightarrow M_2O_n$$

➢ Stable (eg. Cu, Al)
➢ Unstable (eg. Ag, Au and Pt)
➢ Volatile (eg. Mo)
➢ Porous (eg. Na, K etc.)

Pilling Bedworth rule

specific volume ratio $\quad=\quad\dfrac{\text{volume of metal oxide}}{\text{volume of metal}}$

Electrochemical Corrosion or Wet corrosion

Wet corrosion or electrochemical corrosion occurs in presence of moisture or an electrolyte. When metal comes in contact with the electrolyte, electrochemical cell is generated at the surface of the metal. Thus anodic and cathodic sites are generated at the metal surface. At the anodic site, metal ions form and electrons are generated (oxidation occurs). At the cathodic site anions are formed and electrons generated from anodic site are consumed (reduction occurs). Due to flow of electrons from anode to the cathode, a current is generated which is known as corrosion current. Corrosion current is proportional to the rate of corrosion. Since cations (metal ions) are formed at the anode and anions are formed at the cathode, therefore, both cations and anions combine to form corrosion product at the metal surface. Since dissolution of metal occurs at the anode, therefore corrosion occurs at anodic site. For example in case of rusting of iron Fe^{2+} ions are formed at anode and OH^- is formed at cathode. The corrosion product iron hydroxide is formed at the surface of iron.   .

Anode
e⁻
corrosion current
Cathode
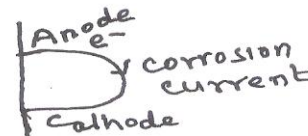
- **Electrochemical Corrosion or Wet corrosion**

Electrochemical Theory of corrosion

$$\boxed{\textit{Rate of oxidation = Rate of reduction}}$$

In the absence of O_2

In acidic medium; Anodic reaction

$$M \longrightarrow M^{n+} + ne^-$$

Cathodic reaction

$$2H^+ + 2e^- \longrightarrow H_2$$

In neutral or basic medium; Anodic reaction

$$M \longrightarrow M^{n+} + ne^-$$

Cathodic reaction

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$
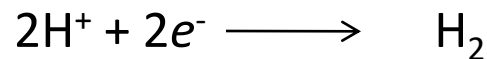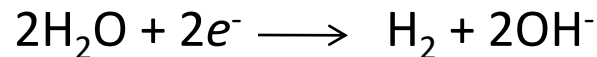
In the presence of dissolved oxygen

In acidic medium Anodic reaction
$$M \longrightarrow M^{n+} + ne^-$$
Cathodic reaction
$$4H^+ + O_2 + 4e^- \longrightarrow 2H_2O$$
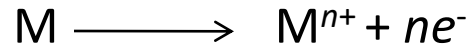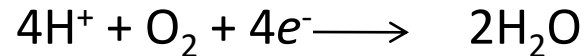
In neutral or basic medium; Anodic reaction
$$M \longrightarrow M^{n+} + ne^-$$
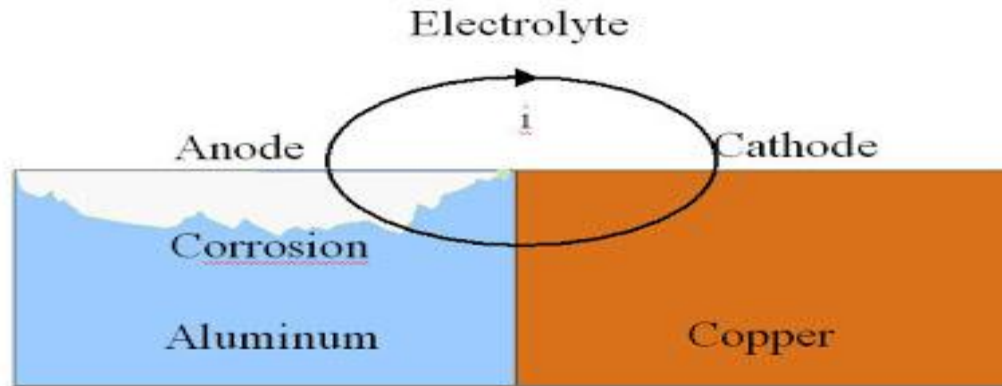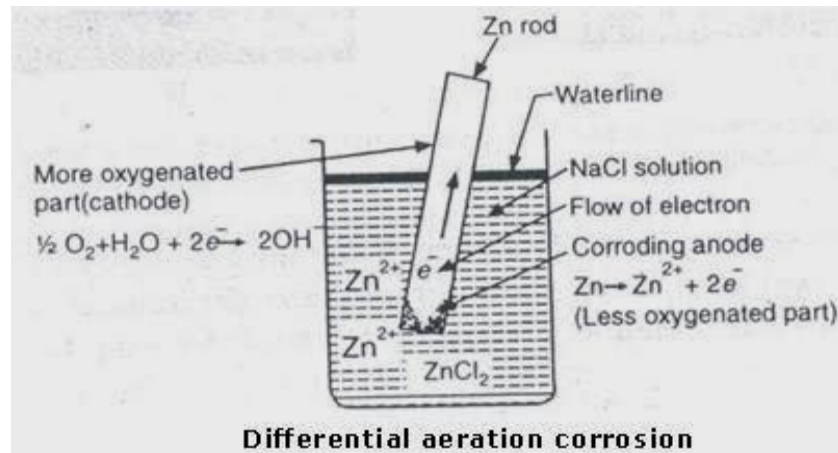Cathodic reaction
$$2H_2O + O_2 + 4e^- \longrightarrow 4OH^-$$
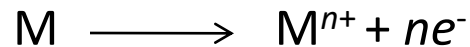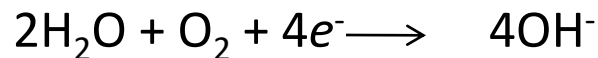
Forms of Corrosion

➢*Galvanic Corrosion*

➢*Concentration cell corrosion*

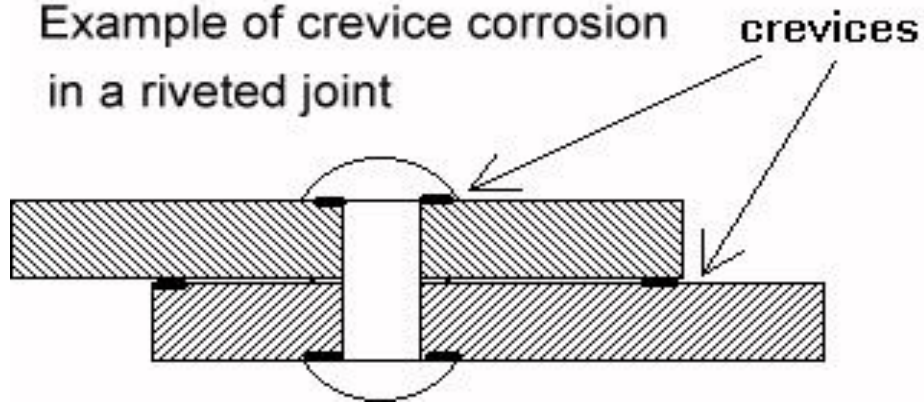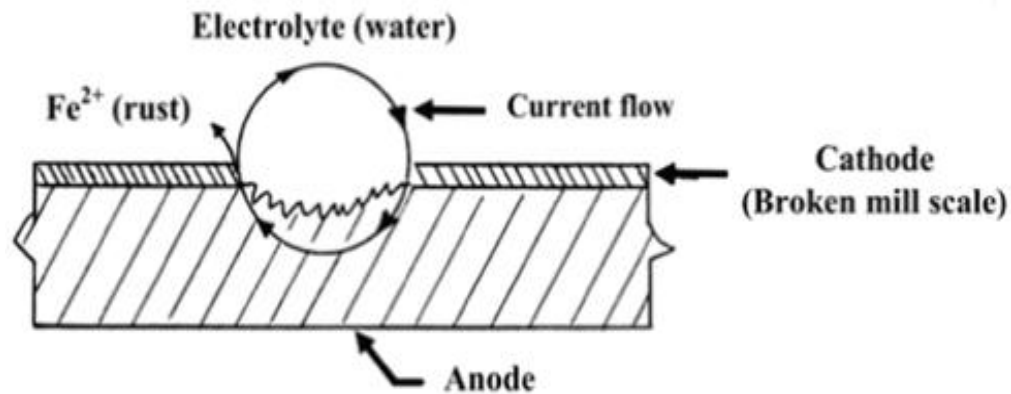Differential aeration corrosion

➢ Crevice Corrosion

Example of crevice corrosion
in a riveted joint

crevices

➢ Pitting Corrosion

Electrolyte (water)

Fe^{2+} (rust)

Current flow

Cathode
(Broken mill scale)

Anode

➤ *Water-line Corrosion*

poor oxygenated anodic part is corroded

$Fe \rightarrow Fe^{2+} + 2e^-$

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

Highly oxygenated cathodic part (protected)

$H_2O \rightarrow H^+ + OH^-$

$4H^+ + O_2 + 4e^- \rightarrow 2H_2O$

Waterline corrosion
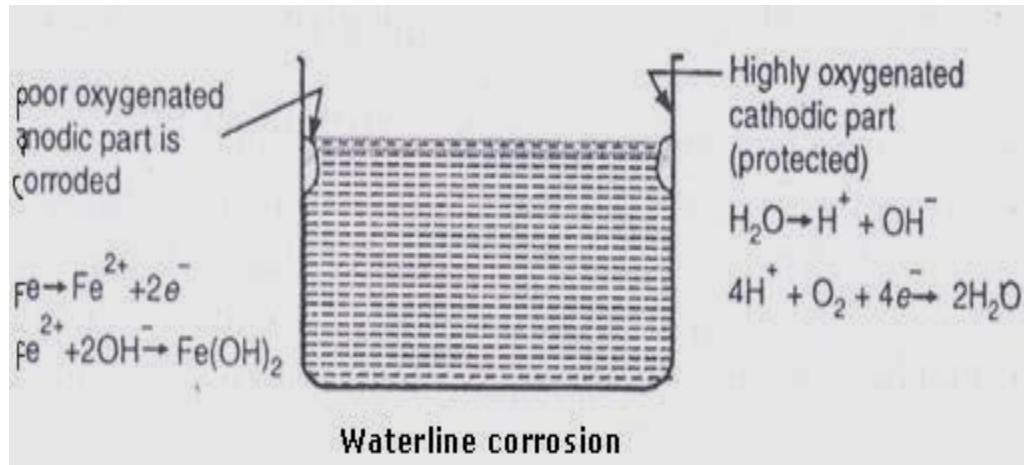
➤ *Underground or Soil Corrosion*

Earth Surface

Mg Sacrifcial anode

insulated Cu wire
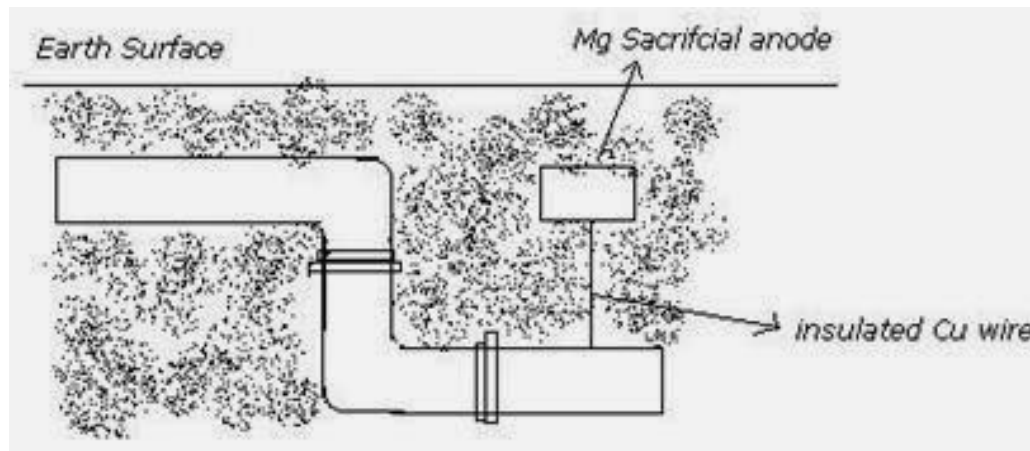
➢ *Intergranular Corrosion*
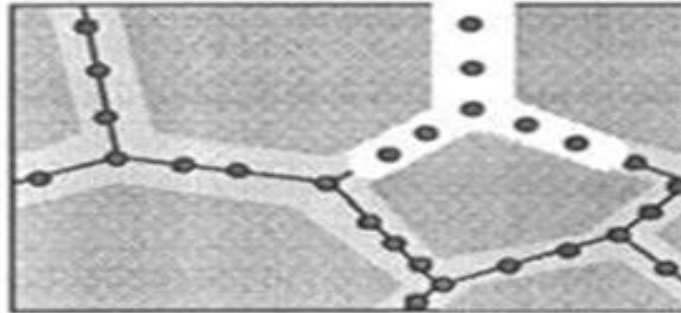
➢ *Stress Corrosion*

Stress corrosion cracking

Fe₂O₃, Fe₃O₄
(Corrosion products)

Fe₂O₃, Fe₃O₄
(Corrosion products)

M^{2+}

M^{2+}

Tensile force ← → Tensile force

Advancing crack tip
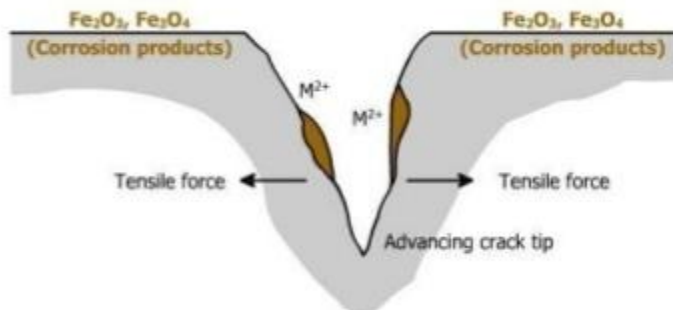
It can occur without an externally applied load or at loads significantly below yield stress

➢ *Microbiological Corrosion*

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Factors affecting corrosion

Nature of Metal

➢Purity of metal
➢Physical state of metal
➢Nature of the oxide

$$\text{Specific volume ratio} = \frac{\text{Volume of metal oxide}}{\text{Volume of metal}}$$

➢Position in the Galvanic series
➢Relative areas of the Anode and Cathode

$$\text{Rate of corrosion} \ \propto \ \frac{\text{Cathodic area}}{\text{Anodic area}}$$

➢Solubility of corrosion products
➢Volatility of corrosion products

Nature of Environment

➤ Temperature

➤ Humidity

➤ Effect of pH

➤ Conductance of environment

➤ Formation of oxygen concentration cell

➤ Presence of impurities in atmosphere

Methods of corrosion control

➢Modification of the corrosive environments.

➢Modification of materials by further alloying or de-alloying

➢Modification in Design

➢Cathodic Protection (Sacrificial anode method and Impressed current method

➢Use of protective coatings (Metallic and nonmetallic coating)

➢Use of corrosion inhibitors.

Modification of the corrosive environments.

Corrosion Prevention

1. Modification of environment

The metal is protected from corrosion by removal of corrosion stimulants from the environment. For example

(a) Corrosion caused by dissolved oxygen can be reduced by deaeration or by addition of reducing Substances like hydrazine (N_2H_4) or Na_2SO_3 etc.

(b) Corrosion caused by acid is reduced by neutralization by addition of lime.

(c) Corrosion caused by moisture is reduced by ~~determi~~ dehumidification using ~~get~~ silica gel.

# Modification of materials

② Modification of Material (Metal)

(a) Alloying :- Alloying the metal by addition of corrosion resistant Component. Example. Addition of Cr in steel to make stainless steel

(b) Refining :- It is done by lowering the Content of S and P in steel and C in stainless steel.

(c) Annealing :- Heat treatment of metal to remove the residual stress.

Modification in Design

③ <u>Modification in design</u> :— Some extent of corrosion can be reduced by minor modification in design of the object to be protected from corrosion. Example —

wrong structure

right structure

wrong way

right way
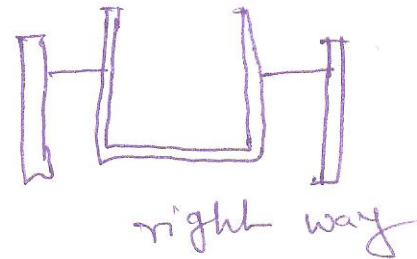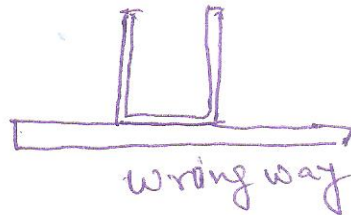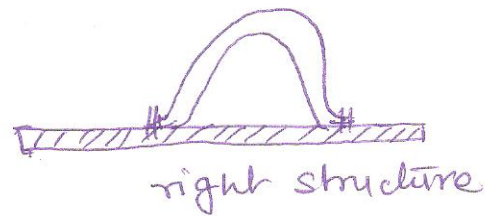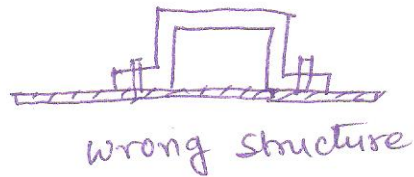
Cathodic Protection

④ **Cathodic Protection**

During the cathodic protection, the object to be protected from corrosion is converted to cathode. It is done by two methods

(a) **Sacrificial anode method** :- the object to be protected from corrosion is converted to cathode by attaching a more active metal with the object. which act as anode and ultimately corroding.

Anode ☐ Mg

Cathode | Steel

underground Pipe line
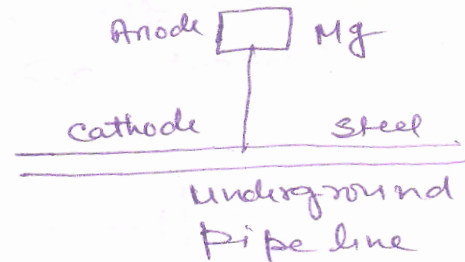
Impressed current method

(b) Impressed current method

To reduce corrosion by this method, a current is applied to the object in opposite direction to the corrosion current. It is generally done by attaching the object with a battery. The negative end of the battery is attached with the object and positive end with ~~gra~~ Pt. Thus the object work as cathode and remains safe. The applied current nullify the corrosion current and object is protected from corrosion.

Pt
Anode

object
Cathode
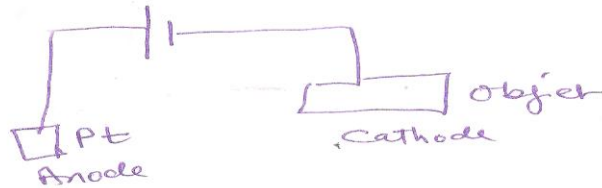
Use of protective coatings
(Metallic and nonmetallic coating)

⑤ By using coating — The function of coating is to prevent contact of metal with the environment. It is of two types-

(a) Metallic coating — Coating of one metal over the other. It is also of two type.

(i) Anodic coating — Coating metal work as anode with respect to the metal to be protected. The coating metal corrodes. Example. Galvanization coating of steel by Zinc.

(ii) Cathodic coating — Coating metal is cathodic with respect to metal to be protected. Example Coating of steel by Sn.

coating   environment   enviroment.
Zn   Sn   coating paint
steel   coating
                   steel

(b) Non metallic coating — Using paints and varnishes.
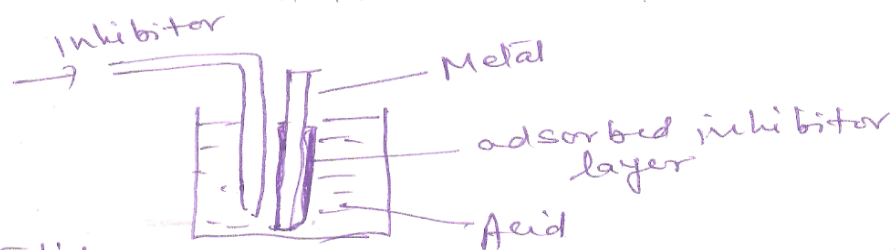
Use of **Corrosion inhibitors**

According to recent ISO definition, "an inhibitor is a chemical substance which decreases the corrosion rate when present in the corrosion system at a suitable concentration without significantly changing the concentration of any other corrosive agent"

Corrosion inhibitors

(6) <u>Using corrosion inhibitors :-</u>

Corrosion inhibitors are substances which when added to the environment in small amount, reduces the rate of corrosion of the metal. The inhibitor is adsorbed on the surface of the metal and prevent the contact of the metal with the environment and prevent the corrosion of the metal.

The inhibitor must contain large number of S, N and O atoms, which facilitate the adsorption process.

Types of corrosion inhibitors

Anodic inhibitor

Anodic inhibitors are those substances which reduce corrosion by adsorbing on the anodic sites.

Cathodic inhibitor

Cathodic inhibitors are those substances which reduce corrosion by adsorbing on the cathodic sites.

Ambiodiodic inhibitor

Those substances which affect both the cathodic and anodic reactions are called ambiodic inhibitors.

Properties of Corrosion inhibitors

- More number of active centres

- Larger size

- More number of delocalized π-electron

THANK YOU....