

UNIT 6: Corrosion and its Prevention (17 M)

Q.7] a) 7

OR

b) 5

c) 5

Q.8] a) 7

b) 5

c) 5

Ref book: Engineering chemistry by Shashi Chawla.

Corrosion Science by Kodgire and Kodgire

(IM) Corrosion: It is the destruction of metal by the environment making chemical | electrochemical reaction at the surface of the metal.

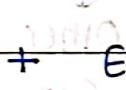
Causes of corrosion: Oxidation & Reduction.

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Metallurgy vs. corrosion.



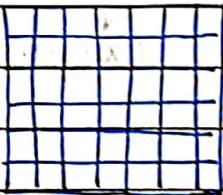
Metallic
compound



+ Energy

Metallurgy
(Reduction)

Corrosion
(Oxidation)



Pure metal

(Low energy state)

(Higher energy state)

Aluminum

Aluminum has no oxidation number & aluminum is said

to be both an oxidized & reduced species & said

as being polarized

Iron (Fe) is a metal (IDM) & is to be said to have

either an oxidized or reduced species & said

that this is due to oxidation & reduction

- Consequences or effects of corrosion.
 - 1) Life of machine decreases
 - 2) Failure of machines
 - 3) Efficiency of machines reduces
 - 4) Plants shut down
 - 5) Possibility of accidents and hazards.

Corrosion

Dry corrosion / Atmospheric corrosion | Direct chemical corrosion
 It occurs due to chemical reaction between metal and atmospheric gases such as O_2 , H_2 , Cl_2 , NH_3 , CO_2 , etc.

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Dry corrosion (Due to)

Oxygen

Hydrogen

Other gases

(CO_2 , Cl_2 , NH_3 , H_2S , etc.)

• Due to oxidation corrosion

It occurs due to direct action of O_2 on metal surface at low or high temperature in absence of moisture.

Mechanism:

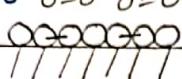
Step 1: Adsorption of oxygen molecule on metal surface.

Step 2: Dissociation of oxygen molecule into atoms, i.e. chemisorption

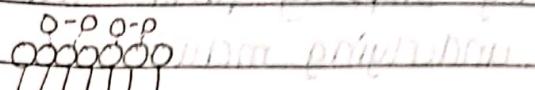
Step 3: Loss of e^- by metal (oxidation of metal) and gain of e^- by oxygen (reduction of oxygen)

Step 4: Formation of metal oxide layer.

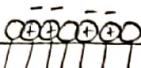
Diagram: $O=O \rightarrow O-O$ $\rightarrow O-O-O-O$



Step 1



Step 2

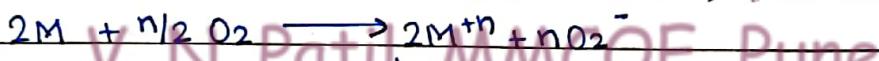
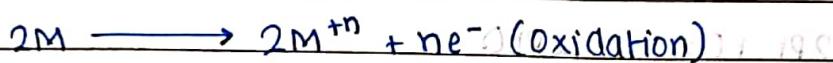


Step 3



Step 4

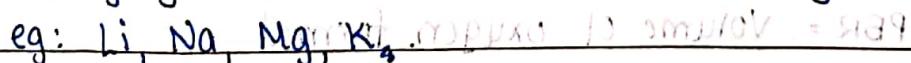
Reaction:



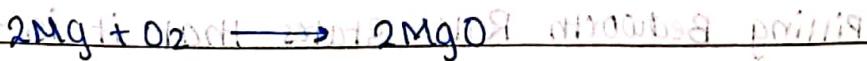
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Nature of oxide film.

- [1] Porous oxide film i.e. non-protective in nature. If the oxide film is porous then atmospheric oxygen penetrates through it and continues the corrosion of underlying metal until it is completely destroyed.



Reaction:



- [2] Non-porous oxide film i.e. protective in nature. It is stable, non-porous oxide film. It acts as a barrier.

by stopping further attack of metal thereby protecting underlying metal.

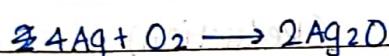
eg: Zn, Cu, Sn, etc.

Reaction:



- 3] Unstable oxide film decomposes back into the metal and oxygen thereby making net corrosion zero.

eg: Au, Ag, Pt



- 4] Volatile oxide film evaporates or vapourises as soon as it is formed thereby exposing underlying metal for further attack of oxygen

eg: Mo

Reaction:



It shows that volume of oxygen consumed is equal to twice the volume of metal consumed.

It is due to presence of volatile oxide film.

Pilling Bedworth Rule (PBR) against consumption of oxygen by metal.

PBR = $\frac{\text{Volume of oxygen formed}}{\text{Volume of metal consumed}}$

It gives the idea about nature of oxide film formed.

It is porous or nonporous in nature.

Pilling Bedworth Rule states that it is the volume of oxygen formed to volume of metal consumed.

It gives the idea about nature of oxide film formed.

If $P_{BR} < 1$, porous oxide film is formed

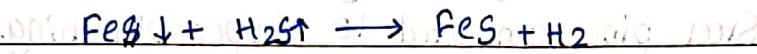
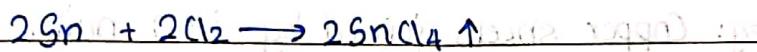
eg: Na, Li, K, Mg.

If $P_{BR} > 1$, non porous oxide film is formed

eg: Al, Cr, Sn.

Dry corrosion due to other gases:

Occurs due to presence of Cl_2 , NH_3 , H_2S , CO_2 , etc. in the atmosphere.



Due to Hydrogen gas:

Hydrogen cracking i.e. hydrogen attack.

Hydrogen embrittlement. On (CO) infiltration

WET CORROSION / ELECTROCHEMICAL CORROSION / IMMERSIVE IMMERSSED CORROSION

It occurs due to aqueous conducting medium such as fog, dew, moisture, humidity with formation of anodic and cathodic areas

Types/ Conditions for wet corrosion:

Galvanic cell, presence of Concentration cell

corrosion, on metal due to corrosion

Galvanic cell corrosion: When two dissimilar metals come in contact with each other in aqueous condition, a galvanic cell is formed, then the metal which is

Mg

Al

Zn

Fe

Sn

Cu

Ni

Cr

Ag

Au

Pt

placed higher in the galvanic series acts as anode undergoes oxidations i.e. loss of e⁻ and gets corroded whereas the other metal undergoes reduction and is protected.

Subtypes of Galvanic cell corrosion

- ① Two dissimilar metals in contact with each other
- ② stressed and unstressed part on same metal
- ③ Impurities in metal

e.g.: Copper sheets joined by iron nails.

Steel pipe connected to copper plumbing.

Concentration Cell Corrosion

The concentration cell is formed due to variations in oxygen concentration (O₂) on a metal which undergoes corrosion.

The part of the metal which is exposed less to oxygen acts as anode, undergoes oxidation i.e. loss of electron and gets corroded whereas, the part of metal which is exposed more to oxygen acts as cathode, undergoes reduction i.e. gain of electron and gets protected.

Subtypes.

- 1) Partial immersion of metal in water, i.e. ships
- 2) Partial burial in ground, e.g. Poles
- 3) Partly ruptured oxide film on metal surface.

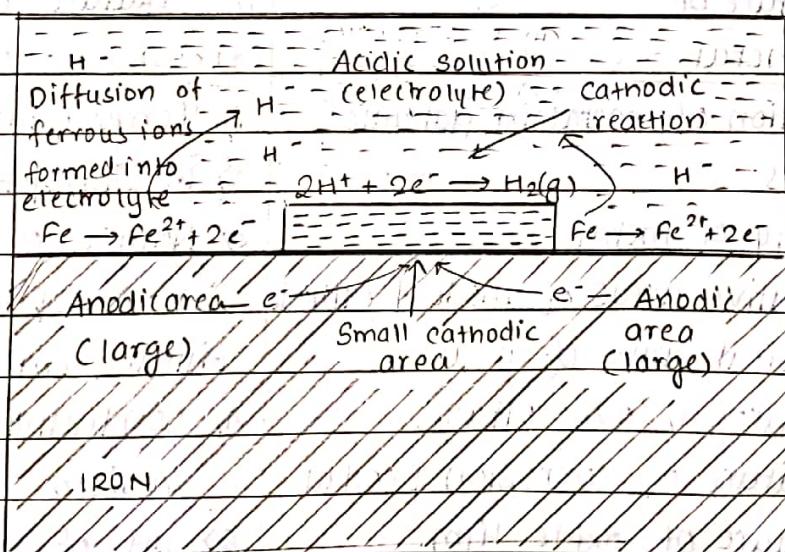
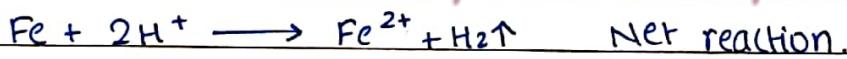
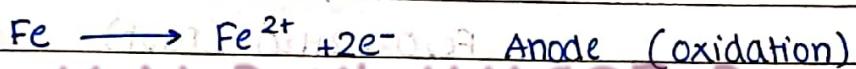
- * MECHANISM OF WET CORROSION.
- > Hydrogen evolution | (Oxygen absorption)
- liberation ($H_2 \uparrow$) | (O₂ \downarrow)

Hydrogen evolution | liberation mechanism.
(In acidic medium)

It occurs in acidic environment like industrial waste, non-oxidising acids, etc.

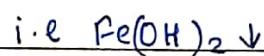
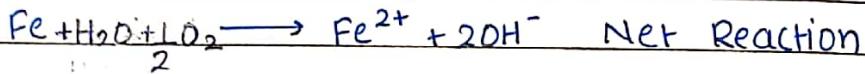
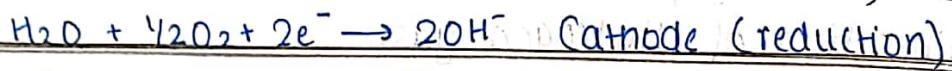
If corroding medium is acidic, then H⁺ ions from the medium capture electrons from cathode there is a liberation of Hydrogen gas.

Reactions:



2) Oxygen absorption mechanism: It occurs in neutral or slightly alkaline medium containing dissolved oxygen. If the corroding medium is neutral or slightly alkaline containing some dissolved oxygen, then the reaction of oxygen absorption takes place on cathode.

Reaction:



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factors affecting rate of corrosion

Nature of metal

- 1) Position of metal in galvanic series
- 2) Purity of metal
- 3) Relative areas of anode & cathode
- 4) Physical state of metal
- 5) Hydrogen overvoltage.
- 6) Nature of corrosion product
- 7) Nature of oxide film.

Nature of Environment

- 1) Temperature
- 2) Moisture| Humidity.
- 3) Nature of ions present in atmosphere like chloride, silicate, nitrate, etc.
- 4) Conductivity of surrounding medium
- 5) pH of the environment

a) Nature of metal

i) Position of metal in galvanic series.

When two dissimilar metals are in contact with each other, higher placed metal in the galvanic series undergoes corrosion whereas the other metal is protected.
More the gap between the metals, higher will be the rate of corrosion.

2) Purity of metal.

More the purity of metal, lesser will be rate of corrosion.

3) Relative areas of anode and cathode.

If ratio of cathodic area to anodic area is greater, higher will be the rate of corrosion.

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4) Physical state of metal.

Smaller the grain size of the metal, higher will be its corrosion.

5) Hydrogen overvoltage.

Higher the Hydrogen overvoltage, lesser will be rate of corrosion.

6) Nature of corrosion product

Higher the solubility of corrosion product, higher will be rate of corrosion

7) Nature of oxide film.

Volatile oxide film - High rate of corrosion

Non porous (protective oxide film) - Low corrosion.

Porous (Non-protective oxide film) - Moderate rate of corrosion.

B) Nature of environment.

i) Temperature.

Higher the temperature, high will be rate of corrosion.

ii) Moisture/Humidity.

Higher the humidity, high will be rate of corrosion.

iii) Nature of ions:

Presence of anions like silicates, chlorides, nitrates increase rate of corrosion.

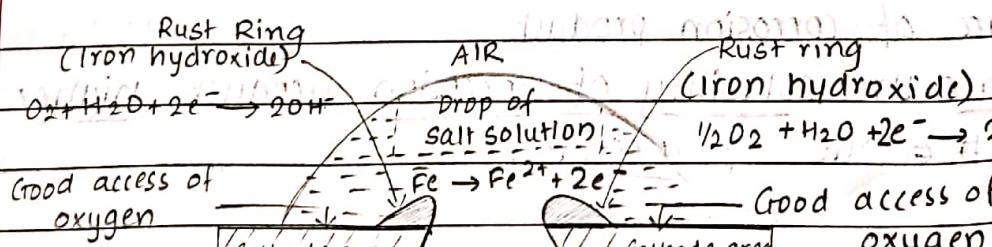
iv) Conductivity of surrounding medium.

Higher the conductivity of medium, higher will be rate of corrosion.

e.g. **V.N. Patil, MMCOE, Pune** which because of conductive nature of clayey soil, the more will be rate of corrosion.

v) pH of environment.

Acidic environment is more corrosive than neutral/alkaline medium.



(cathode area (protected))

(cathode area (protected))

(Anode)

(poor access of oxygen, attacked.)

Nature of metal

	Rate ↑	Rate of corrosion
1) Position in galvanic series	↑	↓
2) Purity	↑ (more impurities)	↓ (less impurities)
3) Relative areas (anodic, cathodic, intermediate)	↑ (anodic)	↑ (cathodic)
4) Physical state	↑ (solid)	↓ (liquid)
5) Hydrogen overvoltage	↑	↓
6) Nature of corrosion product	↑	↑
7) Nature of oxide film.	↑ (adhesive, porous)	↑ (liberal, non-porous)
	↑	↑ (volatile)

Nature of environment

- 1) Temperature
- 2) Moisture
- 3) Nature of ions
- 4) Conductivity
- 5) pH of environment

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Corrosion prevention / control methods

Cathodic Protection → Anodic Protection → Metallic Coating

- SACP
- ICCP

- Anodic
- Cathodic

- Electroplating
- Hot dipping
- Galvanising
- Tinning

- Metal cladding

- Cementation

Anodic Protection

- 1 Q] What is anodic protection?
- 2 Q] Describe the process of anodic protection (Diagram, explanation, application)
- 3 Q] What is passivity?

Principle: The metal to be protected is made more anodic.

Passivity: It is the phenomena in which metal or alloy exhibits higher corrosion resistance than expected from its position in electrochemical series by forming protective non-porous oxide film on its metal surface.

Passivity is shown by metals such as Al, Ni, Cr, Ti, etc.

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Method: The metal to be protected from corrosion is made more anodic by applying external direct current in the same direction as that of corrosion current using reference electrode and auxiliary electrode. Thus, a thin layer of non-porous oxide film is formed which protects surface of the metal from further corrosion.

Advantages:

- 1) Complex metallic structures can be protected.
- 2) Low operation cost.
- 3) Applicable to highly corrosive media like concentrated acids.

Limitations:

- 1) High installation costs.
- 2) High current is required at initial stage.
- 3) Applicable to only those metals which shows active-passive behaviour (Non-porous oxide film)

Applications:

- ▷ Pipes carrying corrosive liquids, industrial water waste coolers, chemical reactors such as storage of HCl, H₂SO₄, HNO₃, etc

Diagram:

Potentiostat



Metal tank to be protected (Anode)

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Electrode

Potential

-0.5

0

0.2

0.5

0.7

0.9

Passive

Active

Corrosion rate

Cathodic Protection.

- i) What is principle of cathodic protection?
 Explain its types.
- Principle (1 mark)
- [types - 1) SSCP, method, application, diagram - (2-2.5 M)
 2) ICCP, diagram, method, application - (2-2.5 M)]

Principle:

The metal to be protected is forcefully made to behave as cathode, by two ways (types) -

- i) SACP [Sacrificial Anode Cathodic Protection]
- ii) ICCP [Impressed Current Cathodic Protection]

SACP [Sacrificial Anode Cathodic Protection] Galvanic Protection

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In this method, the metal to be protected is connected to more active (^{i.e.} anodic) metal, i.e. the metal placed higher in the galvanic series than that the metal to be protected. The more active metal works as anode, i.e. sacrificial anode which is placed in backfill, which is coke, breeze, gypsum, etc. For eg: Mg, Al, Zn acts as sacrificial anode.

Advantages:

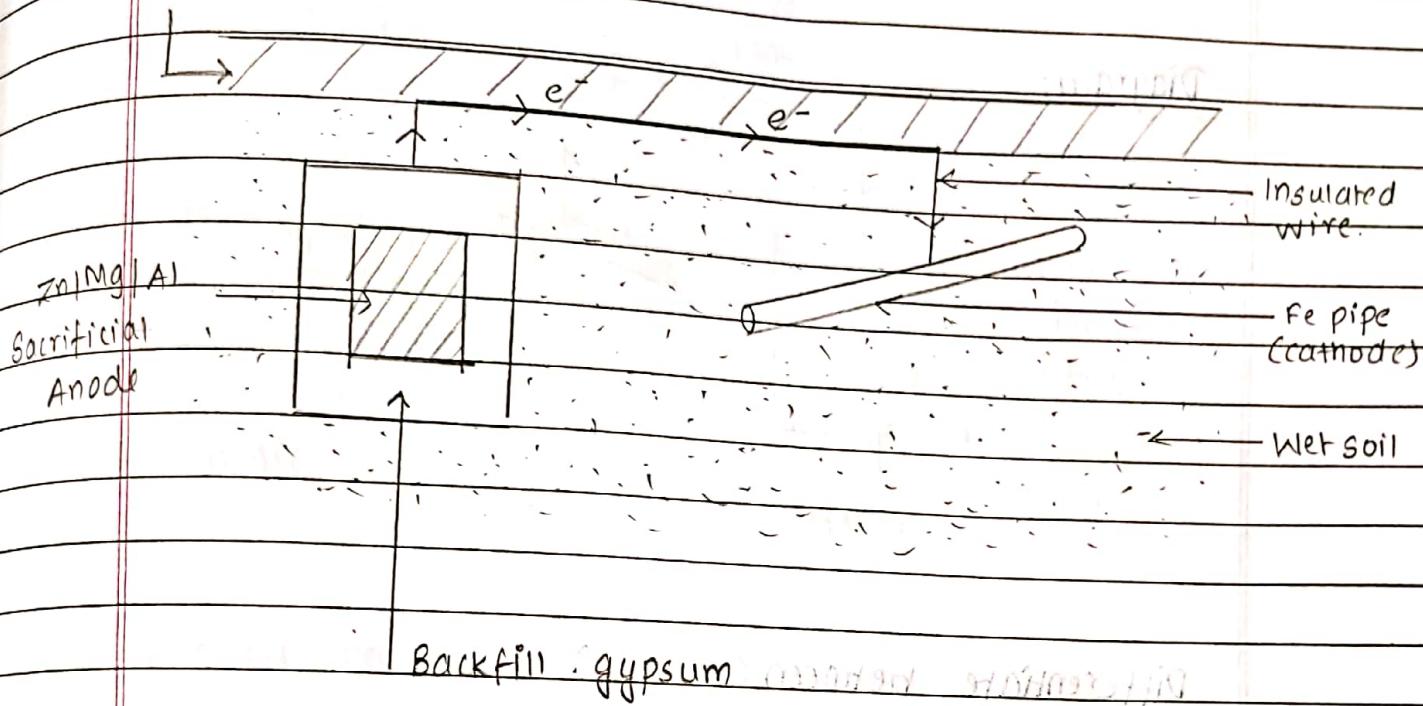
- 1) Easy to install
- 2) No external power required
- 3) Minimum maintenance required.

Limitations:

- 1) Installation can be expensive if it is installed after construction.
- 2) It can be ineffective in high resistivity environment.

Applications:

Underground cables, buried pipelines, ship hulls



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ICCP (Impressed current cathodic protection)

In this method, an impressed current is applied in the opposite direction to the metal to nullify the corrosion current thereby protecting the metal. Here DC source is used connected with an insoluble anode like graphite, stainless steel buried in soil and to the metal to be protected.

The anode is kept in backfill containing gypsum, coke to increase electrical contact with surrounding soil.

Advantages:

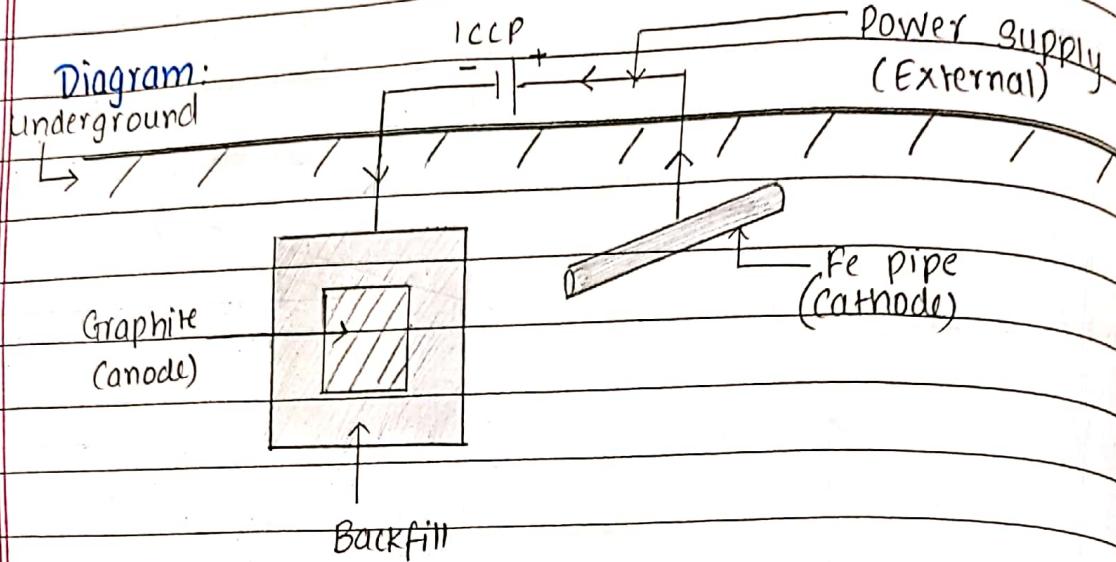
- 1) Effective in high resistivity environment
- 2) Effective in poorly coated structures
- 3) Applicable for long term for large structures.

Limitations

- 1) Requires external power supply
- 2) High investment cost.

Applications

Open water cooler box, condensers



Differentiate between

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Cathodic Protection

Anodic Protection

Principle

The metal to be protected is forcefully made to behave as cathode.

The metal to be protected is forcefully made to behave as anode.

Application

Underground cables, buried pipings, ship hulls, open water cooler box, condensers

Initial cost

High

Low

Operation cost

High

Low

Applicable for:

All metals

Metals which shows active-passive behaviour, that is non-porous oxide film.

Metallic Coatings.

- Q) What are metallic coatings?
 2) Define the types of metallic coatings.
 Which one is preferred? Why?

Ans: When one metal is coated on another metal, it is called as metallic coating.

2 types.

- 1) Anodic coating | Sacrificial coating
 2) Cathodic | Noble coating

Anodic coating

If the coating metal is placed higher in the galvanic series than the base metal, it is called as anodic coating. For example: Zn, Al, Mg, on Steel (Fe).

Anodic coatings are always preferred because:

- 1) If pores break occur on anodic coating, then galvanic cell is formed between coating metal anode and exposed part of base metal.

As the coating metal is anode, it undergoes corrosion, thereby protecting the base metal. Hence it is known as sacrificial coating.

Therefore anodic coatings are more preferred.

Cathodic | Noble coating

If the coating metal is placed lower in the galvanic series than the base metal, it is called as cathodic coating. e.g: Sn coated on Fe, Au coated on Steel (Fe), Au on Ag.

Cathodic coatings are less preferred because:

- If the coating is broken, a galvanic cell is formed between coating metal and exposed part of base metal, but as the coating metal is cathodic in nature to the base metal, exposed part of base metal acts as anode, undergoes corrosion, thereby damaging it.

Therefore cathodic coatings are less preferred.

Differentiate between

Anodic / Sacrificial coating

Definition: If coating metal is placed higher in galvanic series than the base metal, it is called anodic / sacrificial coating.

More preferred

It protects underlying base metal by sacrificing itself

If coating is ruptured, broken, base metal remains safe as long as coating metal is present on base metal.

eg: Zn coated on Fe

Cathodic / Noble coating

If coating metal is placed lower in galvanic series than the base metal, it is called cathodic / noble coating.

Less preferred

It protects underlying base metal upto certain period only.

If coating is ruptured, broken base metal undergoes faster corrosion to produce pits, cracks etc. on the base metal.

eg: Sn coated on Fe.

Surface preparation before metallic coating

Step 1: Removal of grease and other impurities.

Step 2: Removal of oxide film, rust, etc.

Step 3: Etching of surface for better adhesion of coat.

Removal of grease and other impurities

i) Solvent cleaning: using CCl_4 , toluene, xylene, acetone, naphtha, etc. Followed by hot water cleaning.

ii) Alkali cleaning: Using trisodium phosphate, soap, caustic soda, dilute acid.

Removal of oxide film, rust, etc.

iii) Mechanical cleaning - Using chisels, scrappers, brushes, grinding wheels, etc.

iv) Flame cleaning - Using hot flame

v) Sand blasting - For removing oxides scales to get roughed surface (slightly)

Etching of surface for better adhesion of coat.

Done by pickling method.

Pickling method - acid/alkali wash to metal to be coated.

Methods for applying metallic coating.

1) Metal cladding

2) Cementation

3) Electroplating

4) Hot dipping

Galvanizing

Tinning

Metal Cladding (3M)

Short Note on metal cladding.

Definition: It is the process by which coating metal is bonded firmly and permanently to the base metal on one or both sides.

Coating metal is called as cladding metal.

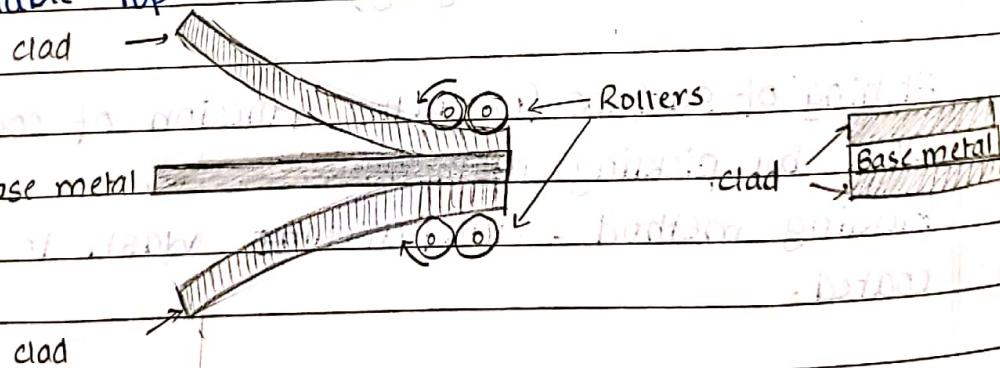
e.g.: Ni, Cu, Ag, Sn, Cr, Al and their alloys.

Base metal (e.g.: Al, Cu, Ni and their alloys) process.

Base metal is sandwiched between the sheets of cladding metal. Then it is passed through rollers and bonded under the action of heat and pressure.

Applications:

- Al clad sheets in aircraft industries.
- Ni and Ni alloy cladded steel in soap, petroleum, rubber industries.
- Cu clad steel in electrical industries.
- Steel table top



(3M) Cementation

Explain corrosion protection method: Cementation.
It is the process of formation of strong layer of an alloy of coating metal and base metal on the surface of base metal by heating the base metal in a revolving drum containing a powder of coating metal.

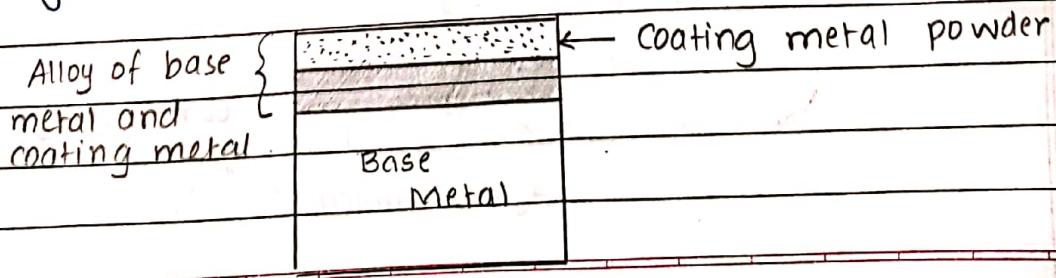
Method:

- Base metal is packed in drum containing a powder of coating metal and heated, drum is revolved.
- The powdered coating metal diffuses into the surface of base metal.
- It results in formation of an alloy of coating metal and base metal on the surface of base metal.

Types of V.N.Puri, MMCOE, Pune

	LITTON LA	Colorizing	Chromizing LA
→	Zn dust	→ Al powder	→ Cr powder
→	2-3 hours	→ 4-6 hours	→ 3-4 hours
→	350-370°C	→ 840-930°C	→ 1300-1400°C
use →	Screws, nuts, bolts, washers, etc.	use → Furnace parts, valves, condensers, etc	use → gas turbine blades.

Diagram:



Electroplating:

- Q] What is electroplating? (1M)
- Q] Explain its method (1M)
- Q] Give reactions involved for anode and cathode (2M)
- Q] Give its applications. (1M)

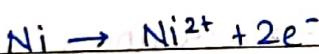
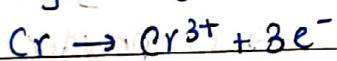
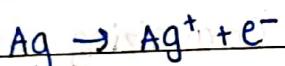
It is the process in which coating metal is deposited on the base metal on the basis of electrolytic principle.

The base metal is usually made cathode of electrolytic cell and anode is made of coating metal. Coating metal is deposited on the base metal by passing D.C. through electrolyte solution containing soluble salt of coating metal.

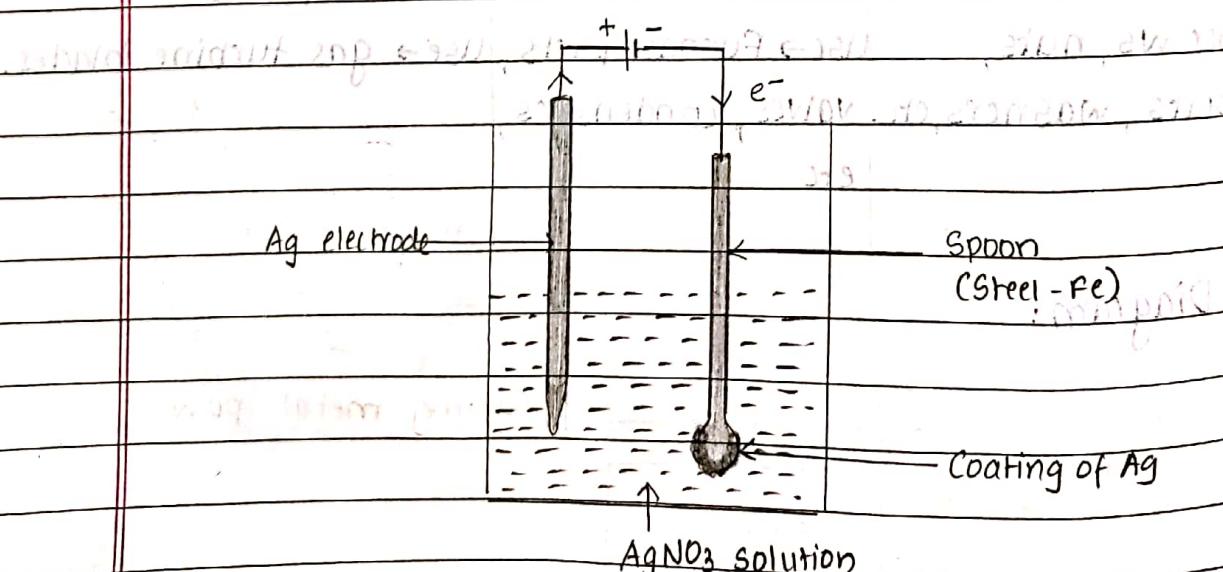
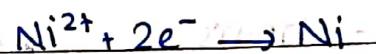
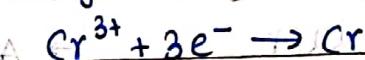
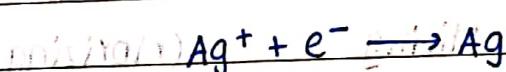
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Reactions:

At anode



At cathode



Process:

- i) The base metal to be plated is cleaned to remove impurities, oil, grease, etc.
- ii) Power supply is connected. The base metal is connected to -ve terminal of power supply, i.e. made cathode. Coating metal is made anode.
- iii) Cathode and Anode are dipped in electrolyte solution of coating metal.
- iv) pH and current density is adjusted.
- v) As electrolysis proceeds, metal ions reduces and gets deposited at cathode.

Applications:

- 1) Corrosion protection
- 2) Decoration purpose (Better appearance)
- 3) Automobile, aircraft, radio industries
- 4) Copper plating for PCB (Printed Circuit Boards)
- 5) To increase strength of non-metallic material.

Hot dipping

Q) What is meant by hot dipping? Explain its types with help of block diagram.

Definition:

It is the process of producing a coating of low melting metals such as Zn (419°C) and Sn (232°C), Pb, Al, etc on steel (iron), Cu, brass, etc. which have comparatively higher MP.

Two types : @ Galvanizing
② Tinning.

Galvanizing : (Anodic Coating)

It is process of coating of Zn on a base metal (steel) by hot dipping method.

Process: 1) The base metal, steel article is cleaned with dil. H_2SO_4 (pickling), washed well with water and dried.

2) Then it is dipped in bath of molten Zn ($425-450^{\circ}\text{C}$) followed by covering it with flux, NH_4Cl for better adhesion.

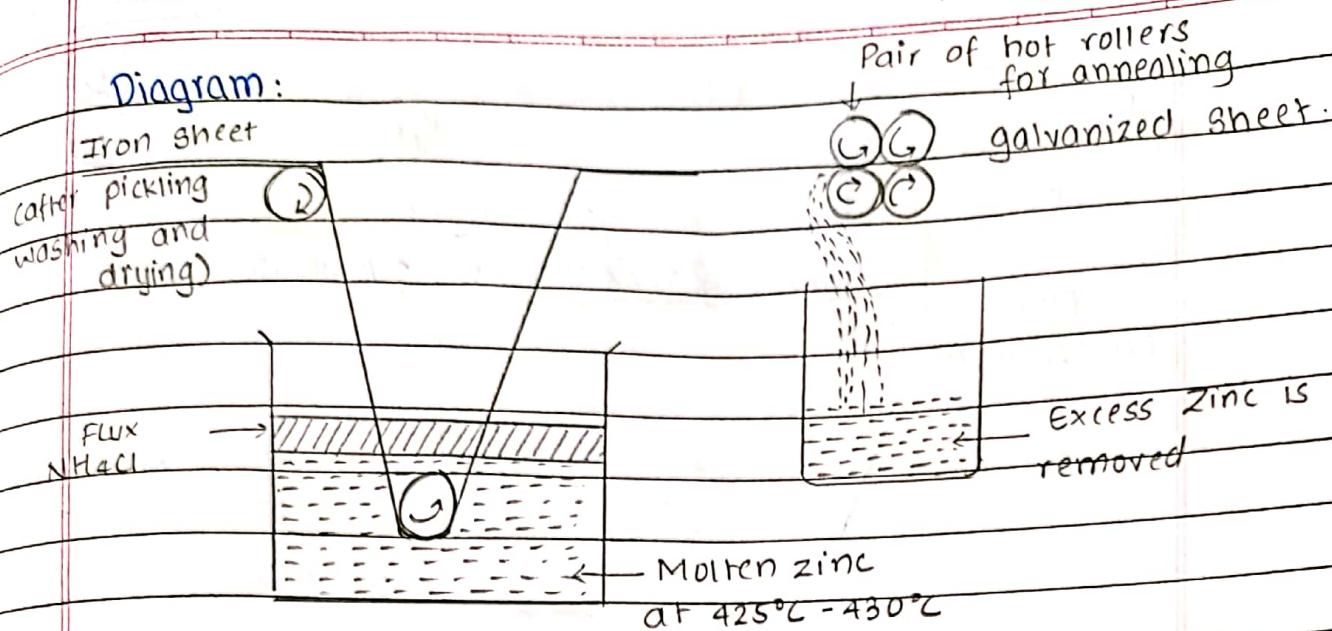
3) It is passed through hot rollers to remove excess Zn and also to produce thin uniform coating.

4) Then it is cooled to room temperature.

Uses: GI (Galvanised iron) sheets, wires, pipes, buckets, bolts, screws, etc.

Limitation: GI utensils cannot be used for storing food as there is formation of poisonous products by action of food on Zn.

Diagram:



Tinning (Cathodic Coating)

Definition: It is process of coating of Sn on base metal (steel) by hot dipping method.

Process: 1) The base metal, steel article is cleaned with dil. H_2SO_4 (pickling), washed well with water and dried.

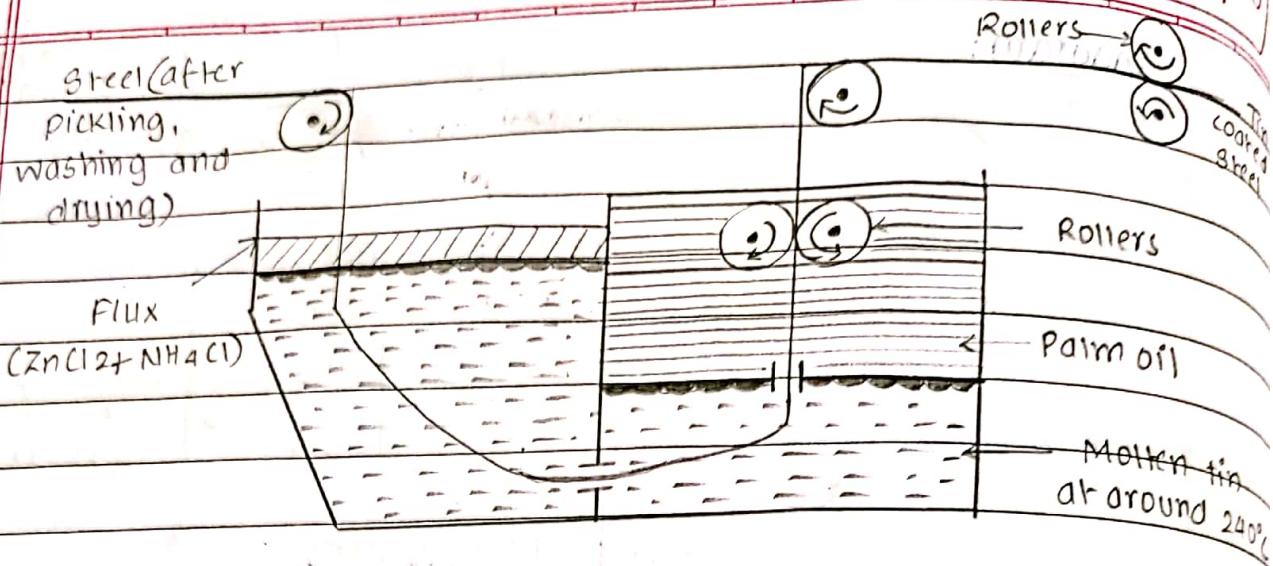
2) Then it is dipped in molten tin (240°C) followed by covering it with flux of ZnCl_2 with NH_4Cl , then through palm oil for better adhesion.

3) It is passed through rollers to remove excess Sn and also to produce thin, uniform coating.

4) Then it is cooled to room temperature.

Uses: Tinned containers for storing food, ghee, oil, pickles, medicines, etc.

It has high corrosion resistance and does not form poisonous products with food.



Distinguish between :

Galvanizing

1) Zn coating on iron

2) Temp. of coating is about

450°C

3) Anodic cathodic Coating

4) In galvanized article,

even if coating is

ruptured, still the Zn

continues to protect the metal

underlying base metal

5) Applicable for G.I., wires,

sheets, pipes, etc.

6) Cheaper

Coking

Tinning

1) Tin coating on iron

2) Temp. of coating is about

250°C

3) Cathodic Coating

4) In tin coated article, if

coating is ruptured, it causes

rapid corrosion of base

continues to protect the metal

underlying base metal

5) Applicable for food containing

medicines, etc.

6) Costlier