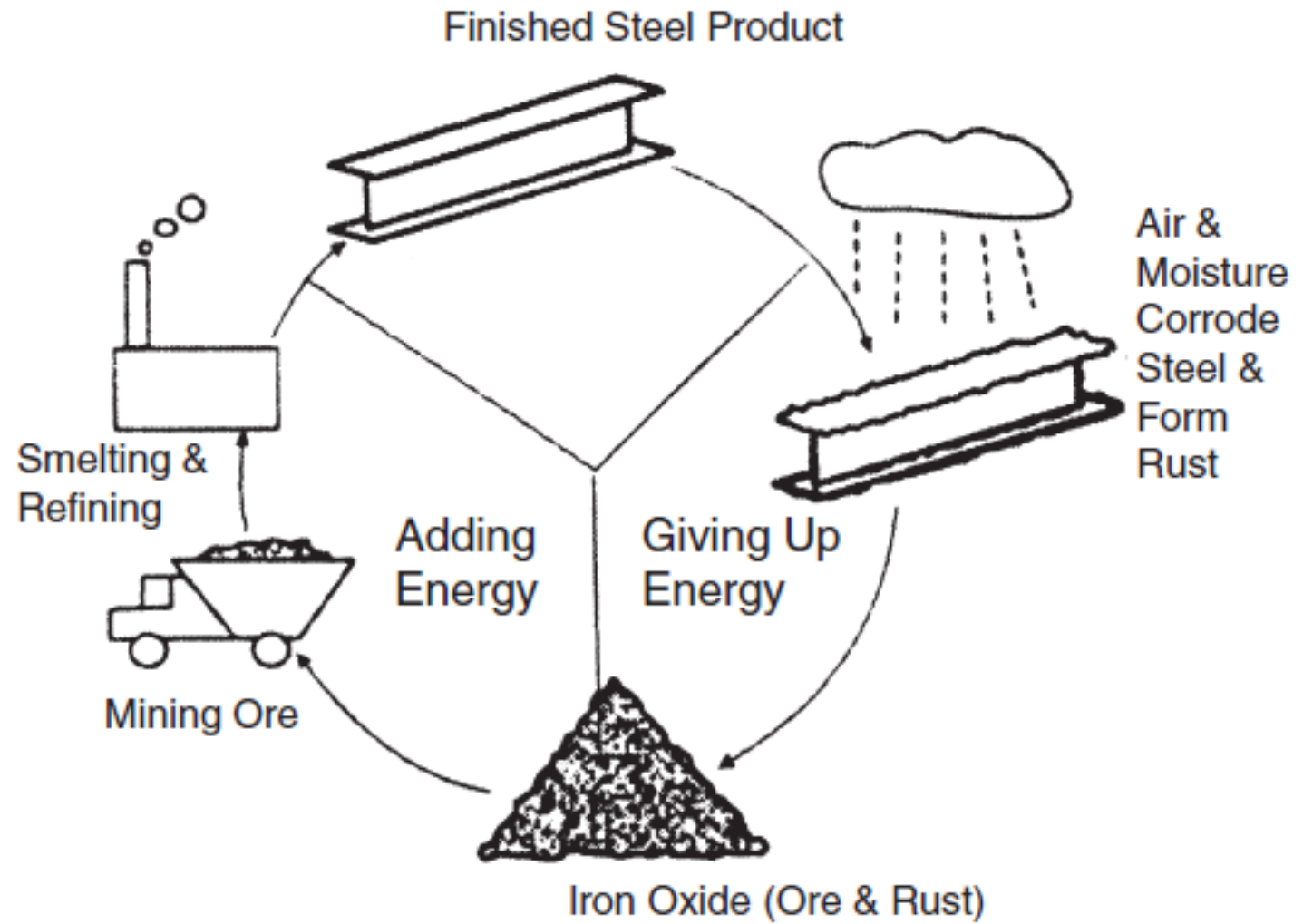# Unit 3
Corrosion And Its Prevention

Corrosion

Fig. 1 The corrosion cycle of steel

Corrosion

Corrosion of metals is defined as the spontaneous destruction of metals in the course of their chemical, electrochemical or biochemical interactions with the environment.

Thus, it is exactly the reverse of extraction of metals from ores.

Rusting of iron: A layer of reddish scale and powder of oxide (Fe_3O_4) is formed on the surface of iron metal.

Reference Jain and Jain, 16th edition Page 329

Significance of corrosion

Significance of corrosion

1. Efficiency of the machine becomes low and beyond a limit it leads to shutdown.

2. Replacement of corroded equipment.

3. Lot of waste (toxic and non-toxic) is produced.

4. Health (eg., from pollution due to a corrosion product or due to the escaping chemical from a corroded equipment).

5. Preventive coatings are required.

Reference Jain and Jain, 16th edition Page 329

Classification
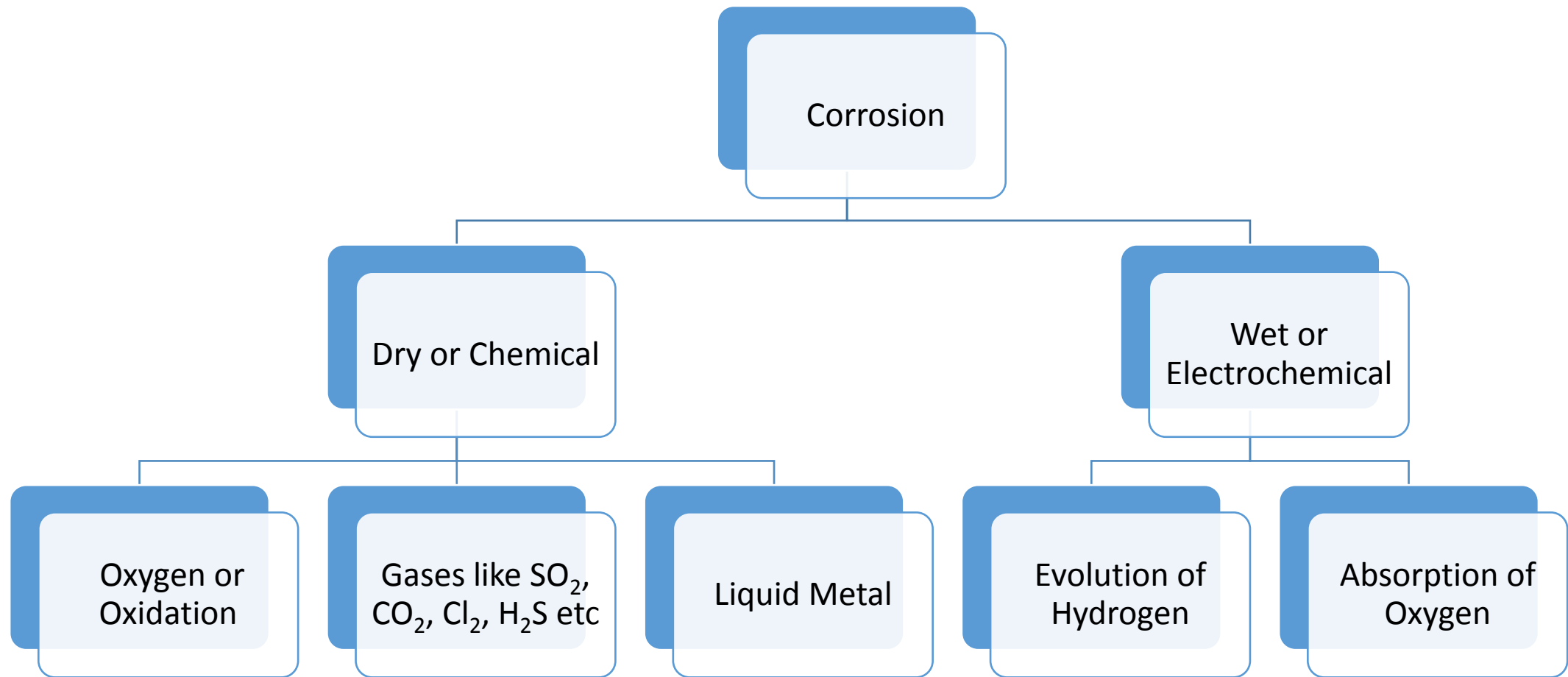
Dry or Chemical Corrosion

The chemical corrosion is due to the direct chemical attack of metal surfaces by the atmospheric gases such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen or anhydrous inorganic liquid, etc.

Types of Chemical Corrosion:

Oxidation Corrosion   **Corrosion by other Gases**   **Liquid Metal Corrosion**
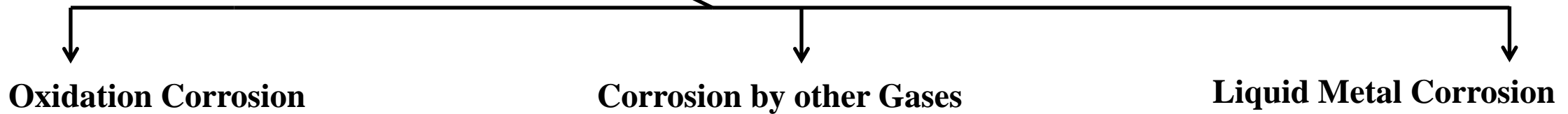
Example:

- Silver materials undergo chemical corrosion by Atmospheric H_2S gas.
- Iron metal undergo chemical corrosion by HCl gas.

1. Dry or chemical corrosion

1.1 Oxidation Corrosion

Direct attack of oxygen at low or high temperature on metal surfaces usually in the absence of moisture.

Alkali metals (Li, Na, K etc.,) and alkaline earth metals (Mg, Ca, Sn, etc.,) are rapidly oxidized at low temperature.

At high temperature, almost all metals (except Ag, Au and Pt) are oxidized.
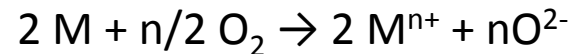
Mechanism

1.1 Oxidation Corrosion

1) Oxidation takes place at the surface of the metal forming metal ions M^{2+}

$$2M \rightarrow 2M^{n+} + 2ne^-$$

2) Oxygen is converted to oxide ion (O^{2-}) due to the transfer of electrons from metal.

$$n/2\ O_2 + 2n\ e^- \rightarrow n\ O^{2-}\ \text{(oxide ion)}$$

3) The overall reaction is of oxide ion reacts with the metal ions to form metal oxide film.

$$2\ M + n/2\ O_2 \rightarrow 2\ M^{n+} + nO^{2-}$$

The Nature of the Oxide formed plays an important part in oxidation corrosion process.

$$\text{Metal} + \text{Oxygen} \rightarrow \text{Metal oxide (corrosion product)}$$
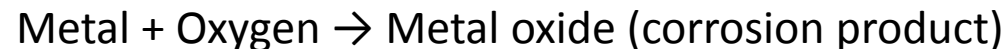
A thin layer of oxide is formed on the metal surface and the nature of this film decides the further action.
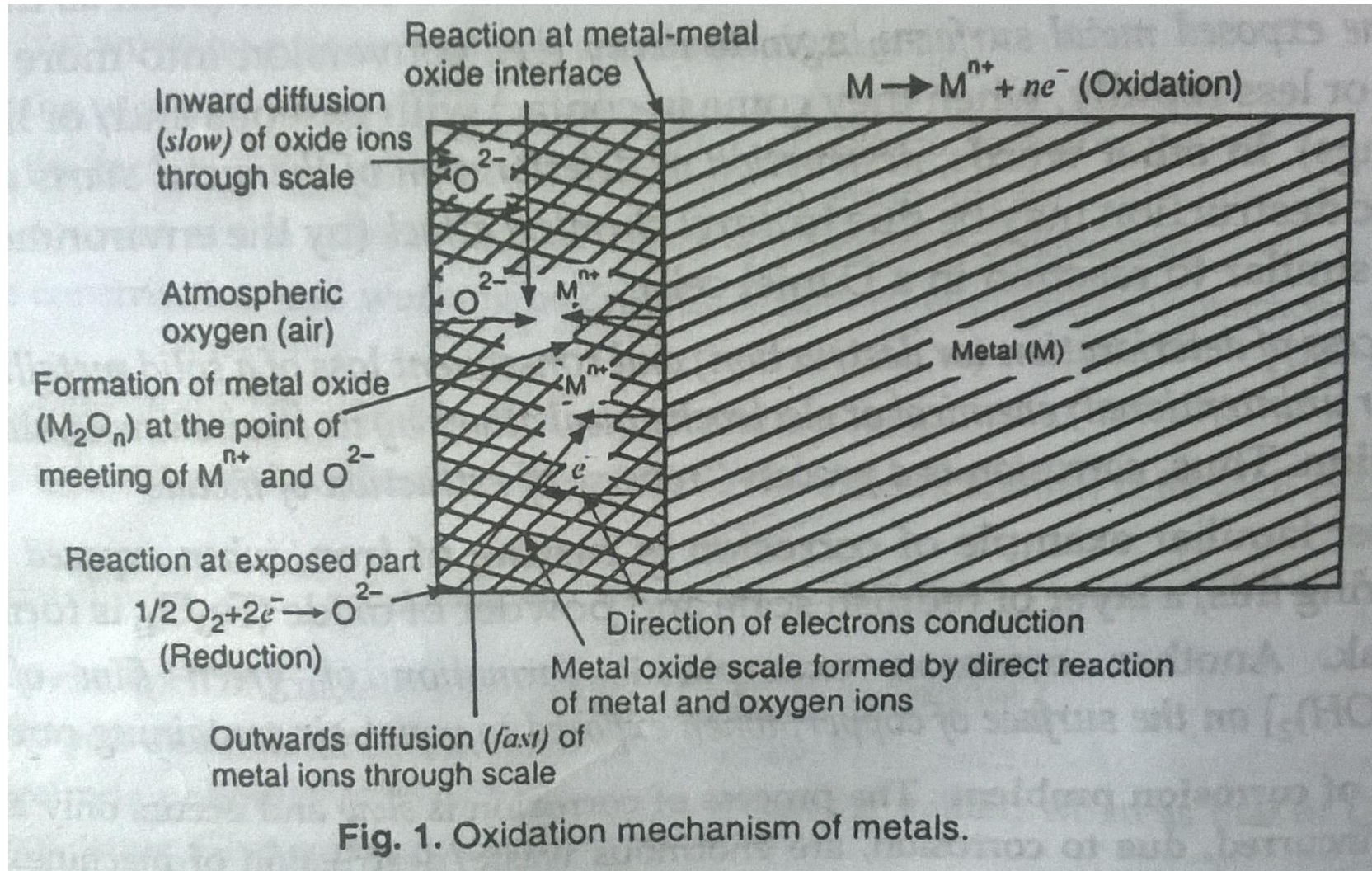
Mechanism

1.1 Oxidation Corrosion

➢ Oxidation occurs first at the metal surface, resulting a formation of metal oxide scale (barriers).

➢ For oxidation to continue:

    1. Metal must diffuse outwards through scale to the surface or

    2. Oxygen must diffuse inward through the scale to the underlying metal.

➢ Due to higher mobility of metal ions, outward diffusion is much more rapid

Mechanism

1.1 Oxidation Corrosion

Reaction at metal-metal oxide interface

$M \longrightarrow M^{n+} + ne^-$ (Oxidation)

Inward diffusion (*slow*) of oxide ions through scale

O^{2-}

Atmospheric oxygen (air)

O^{2-} M^{n+}

Formation of metal oxide (M_2O_n) at the point of meeting of M^{n+} and O^{2-}

M^{n+}

e

Metal (M)

Reaction at exposed part

$1/2\ O_2 + 2e^- \longrightarrow O^{2-}$ (Reduction)

Direction of electrons conduction

Metal oxide scale formed by direct reaction of metal and oxygen ions

Outwards diffusion (*fast*) of metal ions through scale

Fig. 1. Oxidation mechanism of metals.

Types of Oxide Films

1. **Stable**

   - Fine grained in structure and tightly get adhered to parent metal surface.

   - Impervious in nature or behaves as protecting coating.

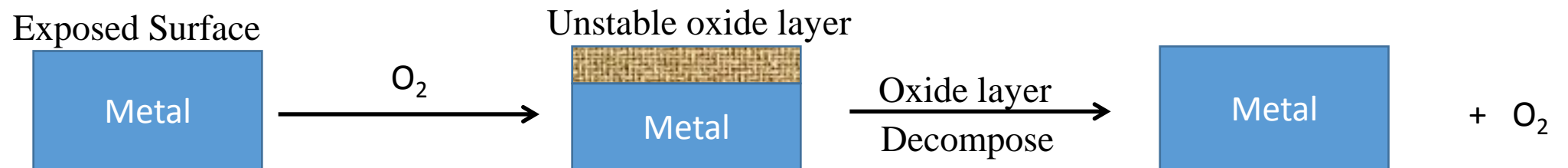   example: Oxide film on Al, Sn, Pb, Cu, Pt and so on.
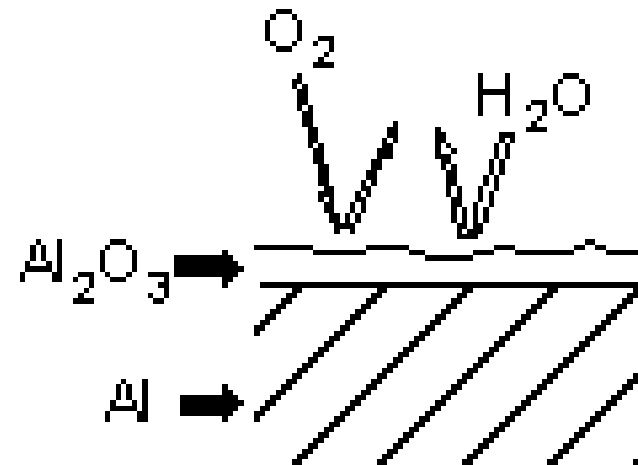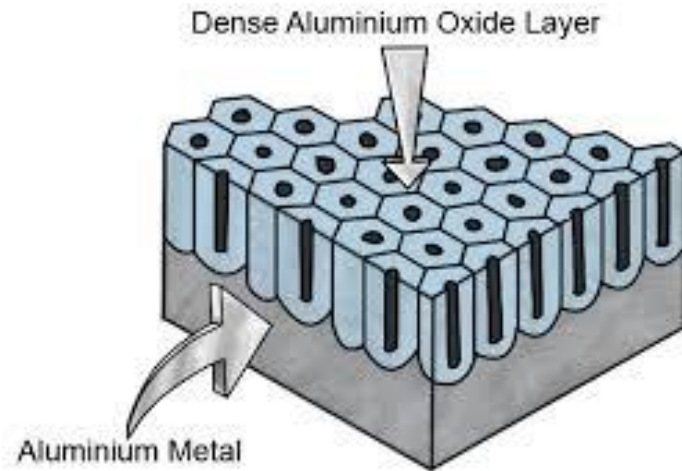
Types of Oxide Films

2. Unstable

- Oxide layer formed, decomposes back into metal and oxygen.

- Corrosion is not possible.

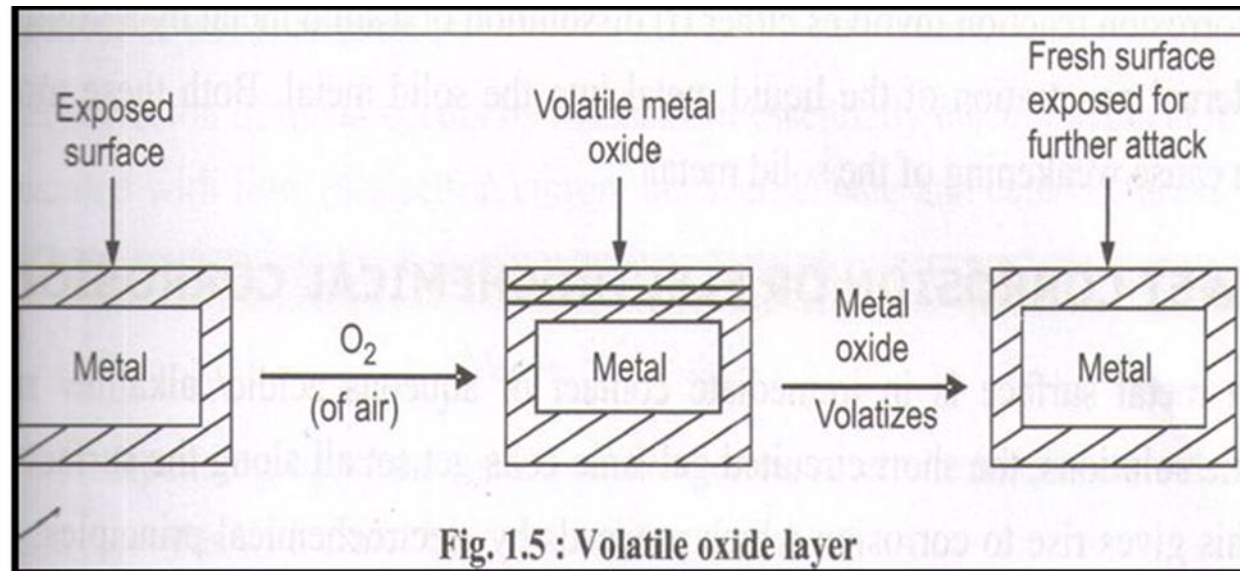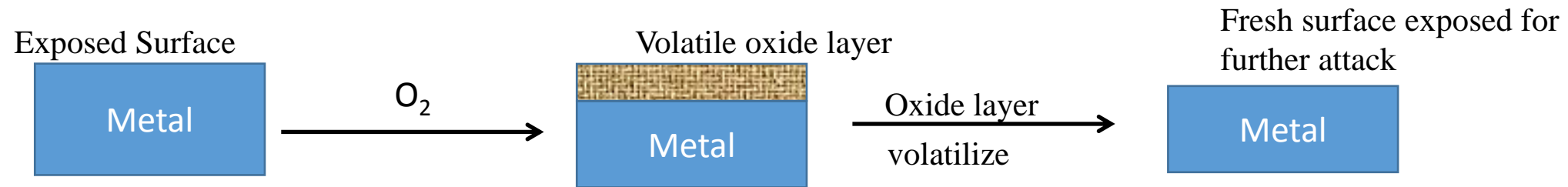 example: metals such as Ag, Au, Pt...

Exposed Surface   Unstable oxide layer

Metal $\xrightarrow{\text{O}_2}$ Metal $\xrightarrow[\text{Decompose}]{\text{Oxide layer}}$ Metal $+ \text{O}_2$

Types of Oxide Films

3. Volatile

- Oxide layer volatilizes as soon as formed.

- Rapid and continuous corrosion, causing excessive damage.

  example: Molybdenum Oxide

Exposed Surface

Volatile oxide layer

Fresh surface exposed for further attack

Metal

O_2

Metal

Oxide layer volatilize

Metal
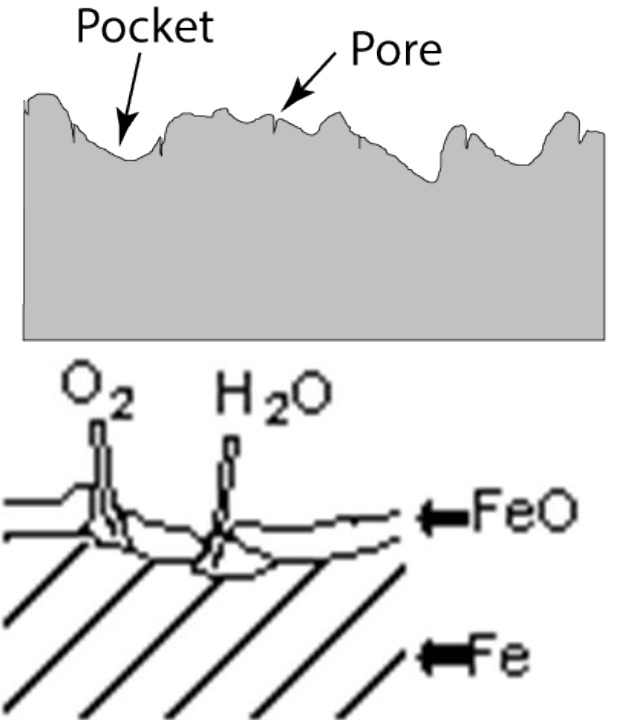

Fig. 1.5 : Volatile oxide layer

Types of Oxide Films

4. Porous

- Oxide layer has pores or cracks.

- the atmospheric oxygen have access to the underlying surface of metal

- Entire metal is completely converted into its oxide..
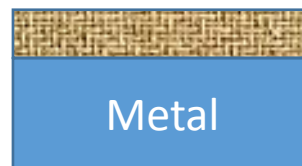
example: Iron Oxide

Bare Cast Iron

Pocket   Pore

O_2 H_2O

←FeO

←Fe

Exposed Surface
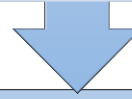
| Metal |

O_2 →

porous oxide layer

| Metal |

Further attack through pores/crack continue

Types of oxide films
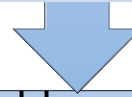
If the oxide film is

Stable layer

Fine grained, tightly adhering. Hence, Impervious and Protective. Example: Oxide films on Al, Sn, Pb, Cu, Pt etc.

Unstable oxide layer

Metallic state more stable than metal oxide. Hence unstable oxide layer formed decompose back into metal and oxygen. Example: Noble metals a Ag, Au, Pt, etc.

Volatile oxide layer
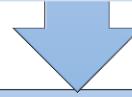
Volatilizes immediately. Hence, fresh metal surface available for attack, causing continuous corrosion. Example: MoO_3

Porous layer
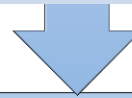
Layer having pores or cracks. Hence, atmospheric oxygen has access to the underlying metal surface and corrosion continues unobstructed.

Pilling Bedworth Rule

An oxide layer is protective if

- Volume of Oxide > Volume of Metal

An oxide layer is non-protective if

- Volume of Oxide < Volume of Metal

Example

- Oxides of Aluminium are protective.
- Oxides of alkali and alkaline earth metals are non protective.

Reference Jain and Jain, 16th edition Page 331

1.2 Corrosion by other gases

Hydrogen Embrittlement:

Loss in ductility of a material in the presence of hydrogen.

Mechanism:

A metal is exposed to hydrogen environment. Iron liberates atomic hydrogen with hydrogen sulphide in the following way.

$$Fe + H_2S \rightarrow FeS + 2H$$
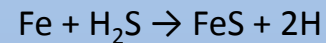
Hydrogen diffuses into the metal matrix in this atomic form and gets collected in the voids present inside the metal. Further, diffusion of atomic hydrogen makes them combine with each other and forms hydrogen gas.

$$H + H \rightarrow H_2\uparrow$$
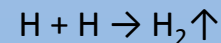
Collection of these gases in the voids develops very high pressure, causing cracking or blistering of metal.

Reference Jain and Jain, 16th edition Page 331

1.3 Liquid metal Corrosion

Liquid metal corrosion

Is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy.

Such corrosion occur in devices used for nuclear power.

The corrosion reaction involves either:

Dissolution of a solid metal by a liquid metal

Internal penetration of the liquid metal into the solid metal.

Both these modes of corrosion cause weakening of the solid metal.

Reference Jain and Jain, 16th edition Page 332

2. Wet or electrochemical corrosion

Electrochemical corrosion involves:

- The formation of anodic and cathodic areas or parts in contact with each other.
- Presence of a conducting medium.
- Corrosion of anodic areas only.
- Formation of corrosion product somewhere between anodic and cathodic areas. This involves flow of electron-current between the anodic and cathodic areas.

Reference Jain and Jain, 16th edition Page 332

Mechanism of electrochemical Corrosion

It involves following steps;

1. **Anodic Reactions:**
   Oxidation reactions
   Dissolution of metal
   Liberation of free electrons

$$M_{(s)} \longrightarrow M^{n+}_{(aq)} + ne^-$$
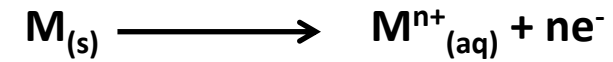
2. **Cathodic Reactions:**
   It takes electrons in two ways;

a. **Evolution of hydrogen**
b. **Absorption of oxygen**

2. Mechanism of Wet or electrochemical corrosion
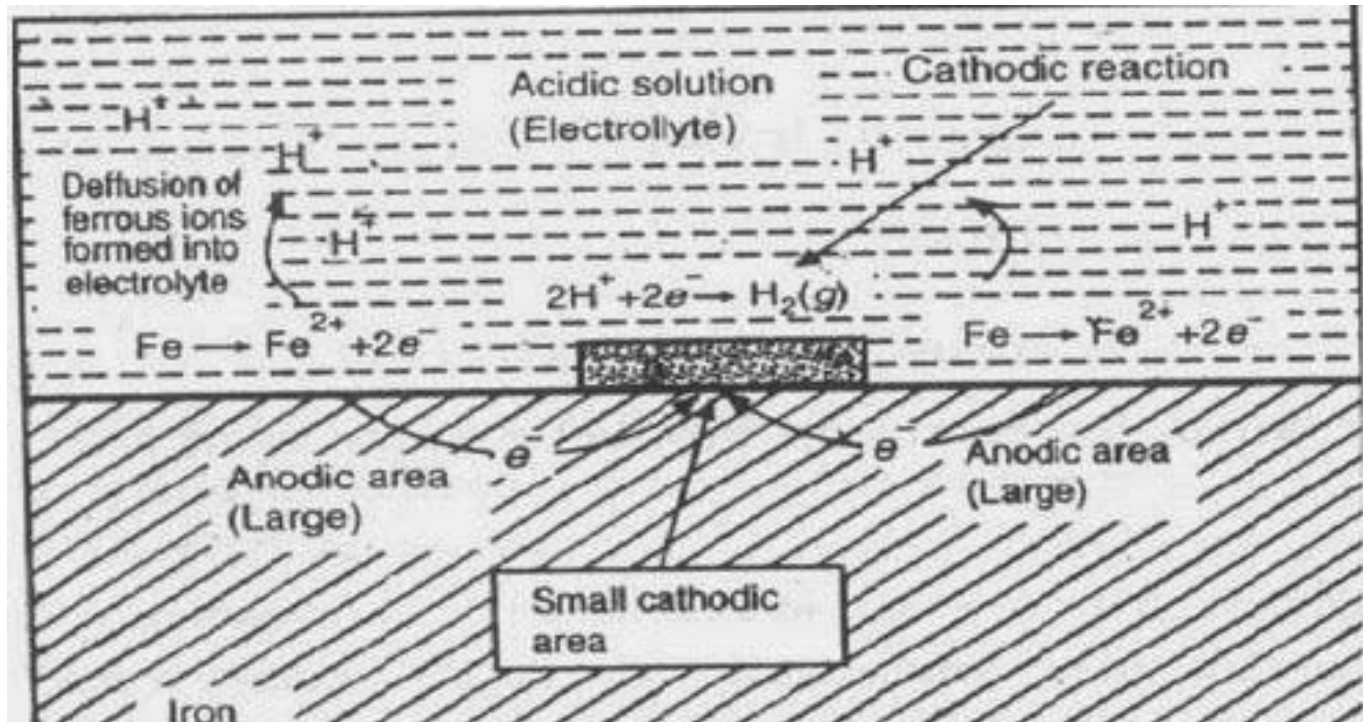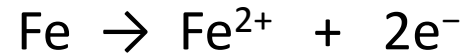
2.1 Evolution of hydrogen

➢ It occurs in acidic environments.

➢ It cause displacement of hydrogen ions from the acidic solution by metal ions

➢ Metals above hydrogen in electrochemical series: dissolve in acidic solution

2. Mechanism of Wet or electrochemical corrosion

2.1 Evolution of hydrogen

Example: Corrosion of Fe in HCl: when a metal like Fe is placed in acidic environment. The anodic reaction is dissolution of iron as ferrous ions with the liberation of electrons

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

These electrons flow through the metal, from the anode to cathode, where H^+ ions are eliminated as hydrogen gas

$$2H^+ + 2e^- \rightarrow H_2\uparrow$$

The overall reaction is $\qquad$ $Fe + 2H^+ \rightarrow Fe^{2+} + H_2\uparrow$
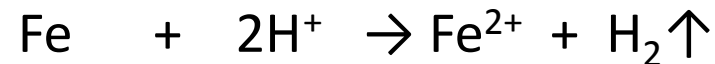
This type of corrosion causes displacement of hydrogen from the acidic solution by metal ions. Consequently all metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen.

2. Mechanism of Wet or electrochemical corrosion

2.2 Absorption of Oxygen

Rusting of iron in neutral aqueous solution (NaCl soln.)

Anodic Area:

$$Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2e^{-} \qquad \textbf{Oxidation}$$

Cathodic Area:

$$1/2 O_2 + H_2O + 2e^{-} \longrightarrow 2OH^{-} \qquad \textbf{Reduction}$$
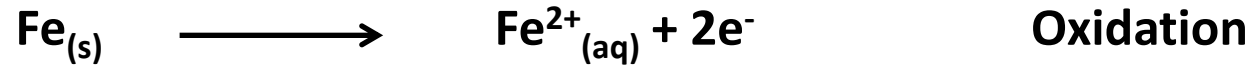
Fe^{2+} (at anode) and OH^{-} (at cathode) diffuse and when they meet, ferrous hydroxide is precipitated.

$$Fe^{2+} + 2OH^{-} \longrightarrow Fe(OH)_2 \qquad \downarrow$$
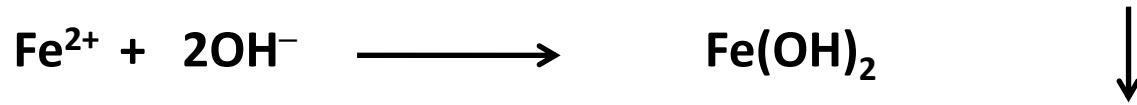
(i) If enough oxygen is present;

$$Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3$$
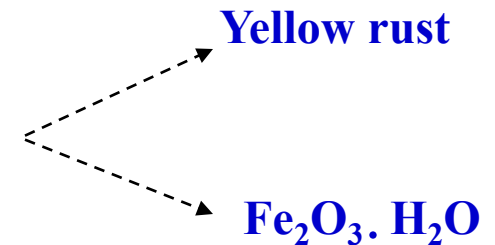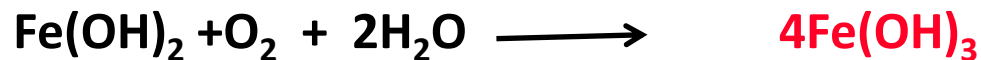
(ii) If oxygen supply is limited;

Corrosion product: Black anhydrous **Fe_3O_4** (Magnetite)

Yellow rust

$Fe_2O_3 . H_2O$

2. Mechanism of Wet or electrochemical corrosion

2.2 Absorption of Oxygen

Air

O_2 – Oxygen

Water

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

$O_2 + 4e^- + H_2O \rightarrow 4OH^-$

Cathode Area

Rust

$2Fe_{metal} \rightarrow 2Fe^{2+} + 4e^-$

Anode Area

Metal
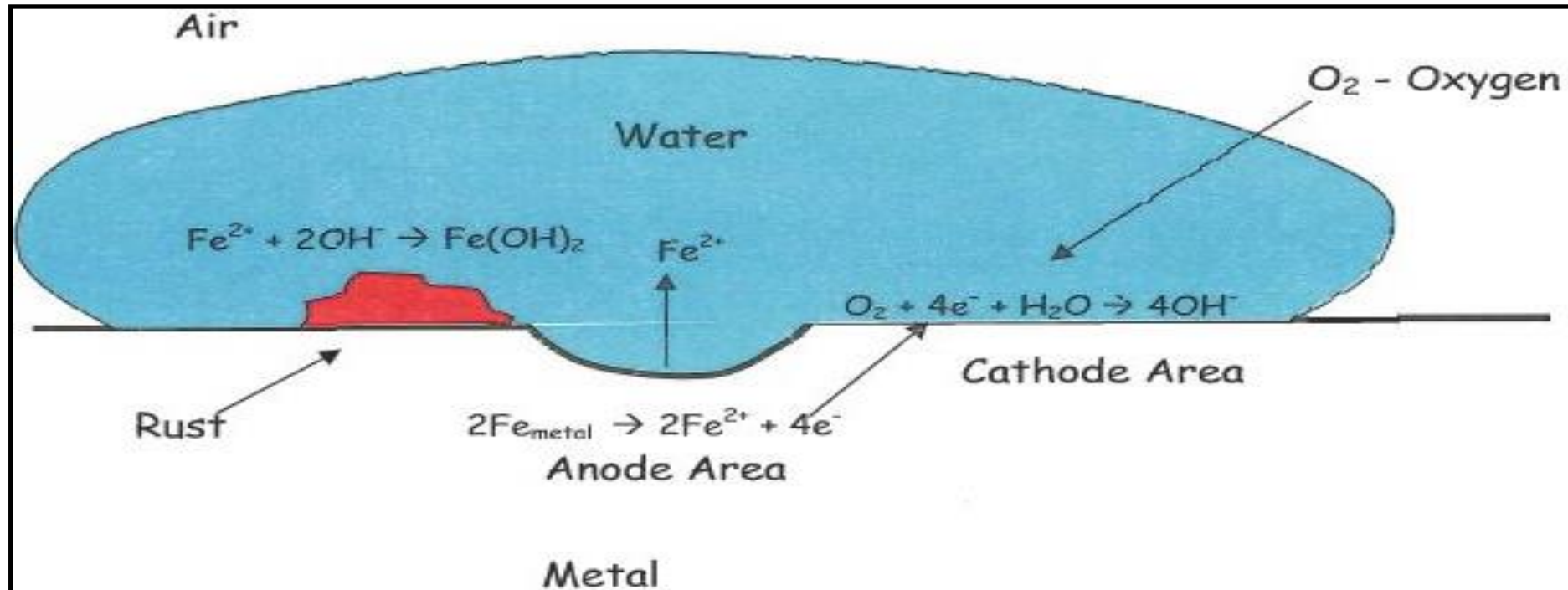
Questions

1. Corrosion occurs at anode, but why does the rust is deposited at cathode?
2. What could be effect of oxygen on rate of corrosion reaction?

Difference between Dry and Wet Corrosion

Dry corrosion

- Corrosion occurs in the absence of moisture.
- It involves direct attack of chemicals on the metal surface.
- The process is slow.
- Corrosion products are produced at the site of corrosion.
- The process of corrosion is uniform.

Wet corrosion

- Corrosion occurs in presence of conducting medium.
- It involves formation of electrochemical cells.
- It is a rapid process.
- Corrosion occurs at anode but rust is deposited at cathode.
- It depends on the size of the anodic part of metal.

17

Factors influencing corrosion rate

1. **Nature of the metal**

1.1 Position in the galvanic series: when two metals are in electrical contact in presence of an electrolyte, the more active metal suffers corrosion.

1.2 Relative areas of the anodic and cathodic parts: corrosion is more rapid and severe if the anodic area is small because the current density at a smaller anodic area is much greater.

1.3 Purity of the metal: Impurities in a metal generally causes heterogeneity and form tiny electrochemical cells and the anodic parts gets corroded.

1.4 Physical state of the metal: smaller the grain size more is corrosion

1.5 Passive character of the metal: Metals like Al, Cr, Mg, Ni and Co can form protective surface of their oxides. Therefore exhibit much less resistance than expected .

Reference Jain and Jain, 16th edition Page 342

Factors influencing corrosion rate

2. Nature of the corroding environment

2.1 Temperature: the reaction and diffusion rate increases with the increase in temperature,

thereby corrosion rate is enhanced.

2.2 Presence of impurities in atmosphere: Corrosive gases like CO_2, H_2S, SO_2 and fumes of HCl ,

H_2SO_4 increases the acidity of the liquid adjacent to metal surfaces.

2.3 Presence of suspended particles: If the suspended particles are chemically active like NaCl

and $(NH_4)_2SO_4$, they absorb moisture and act as strong electrolyte which increases corrosion.

2.4 Influence of pH: generally acidic media is more corrosive than alkaline or neutral media.

Electrode potential

Electrode potential of a metal is the measure of the tendency of the metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of unit molar concentration at 25 °C. Consequently, the tendency of an electrode to lose electrons is a direct measure of its tendency to get oxidized ; and this tendency is called oxidation potential. Similarly, the tendency of an electrode to gain electrons is a direct measure of its tendency to get reduced ; and this tendency is know as reduction potential.
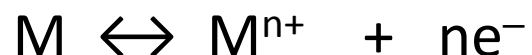
$$M \leftrightarrow M^{n+} + ne^-$$

Reference Jain and Jain, 16th edition Page 279
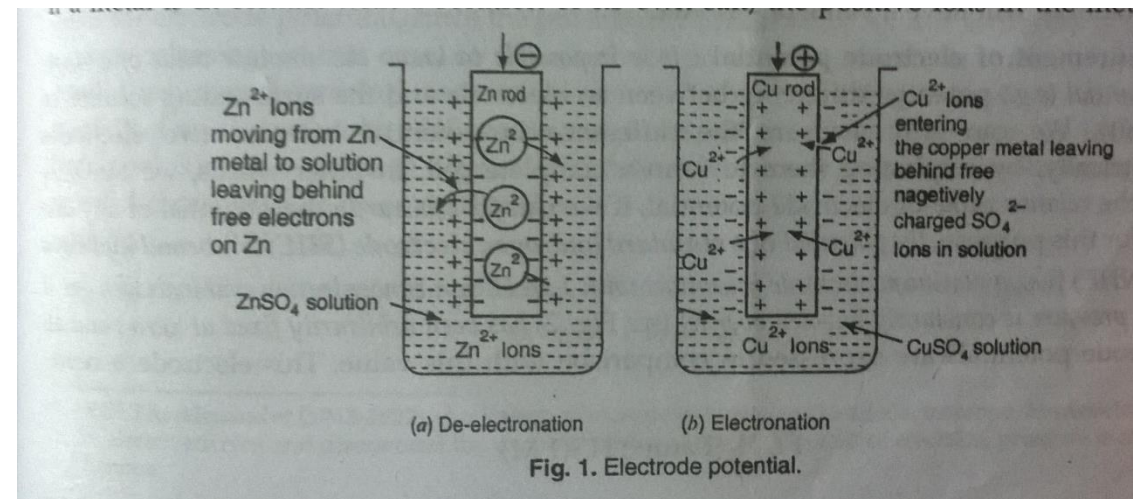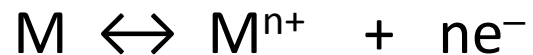
Electrode potential

Electrode potential of a metal is the measure of the tendency of the metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of unit molar concentration at 25 °C.

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

(a) De-electronation   (b) Electronation

Fig. 1. Electrode potential.

Measurement of electrode potential

- Standard hydrogen electrode (SHE) potential is arbitrarily assumed as zero Volts

- All potentials are measured as the potentials difference w.r.to SHE

- According to modern conventions, if on coupling of an electrode with SHE reductions occur at the given electrode, the electrode potential is given a positive sign

$Cu^{2+} + 2e^- \rightarrow$ Cu reduction reaction when coupled with SHE,

electrode potential (reduction) is +0.34V.

- If oxidation occurs at the given electrode, the electrode potential (reduction) is given a negative sign

eg   **Zn $\rightarrow$ Zn^{2+} oxidation reaction when coupled with SHE,**

electrode potential (reduction) is -0.76V.

Measurement of electrode potential

- If oxidation occurs at the given electrode, the electrode potential (reduction) is given a negative sign

   eg   **Zn → Zn²⁺ oxidation reaction when coupled with SHE, electrode potential (reduction) is -0.76V.**

Thus, in order to measure the electrode potential (say of Zn electrode dipping in 1M ZnSO₄), couple this electrode with SHE through a salt bridge [see Fig. 3]. The voltmeter reading directly

Voltmeter

Electron flow e⁻   Anode   Cathode   e⁻

H₂ at 1 atm

Salt bridge

Zinc plate

1 M H⁺ solution

1 M ZnSO₄ solution

Pt foil

Fig. 3. Measurement of electrode potential of zinc electrode (Zn²⁺/Zn). Here Zn electrode acts as *anode* w.r.t. SHE, so electrode potential of Zn is given a negative sign (*viz.,* – 0.76 volt).

Reference Jain and Jain, 16ᵗʰ edition Page 280

Electrochemical series

When elements are arranged
In increasing order of their
electrode potential, a series
called Electrochemical series
is obtained.

Table 1. *Standard electrode potentials (reduction) at 25°C.*

Metal ion		Potential in volts	
$Li^+ + e^- \rightarrow Li$	(BASE)	−3.05	(ANODE)
$K^+ + e^- \rightarrow K$		−2.93	
$Ca^{2+} + 2e^- \rightarrow Ca$		−2.90	
$Na^+ + e^- \rightarrow Na$		−2.71	
$Mg^{2+} + 2e^- \rightarrow Mg$		−2.37	
$Al^{3+} + 3e^- \rightarrow Al$		−1.66	
$Zn^{2+} + 2e^- \rightarrow Zn$		−0.76	
$Cr^{3+} + 3e^- \rightarrow Cr$		−0.74	
$Fe^{2+} + 2e^- \rightarrow Fe$		−0.44	
$Ni^{2+} + 2e^- \rightarrow Ni$		−0.23	
$Sn^{2+} + 2e^- \rightarrow Sn$		−0.14	
$Pb^2 + 2e^- \rightarrow Pb$		−0.13	
$F^{3+} + 3e^- \rightarrow Fe$		−0.04	
$H^+ + e^- \rightarrow 1/2H$		0.00	(Reference)
$Cu^{2+} + 2e^- \rightarrow Cu$		+0.34	
$Ag^+ + e^- \rightarrow Ag$		+0.80	
$Pt^{4+} + 4e^- \rightarrow Pt$		+0.86	
$Au^+ + e^- \rightarrow Au$		+1.69	
$1/2F_2 + e^- \rightarrow F^-$	(NOBLE)	+2.87	(CATHODIC)

Reference Jain and Jain, 16th edition Page 283

Galvanic series

- **The galvanic series (or electropotential series) determines the nobility of metals and semi-metals**

- When two metals are submerged in an electrolyte, while also electrically connected by some external conductor, the less noble (base) will experience galvanic corrosion.

- The rate of corrosion is determined by the electrolyte and the difference in nobility.

- The difference can be measured as a difference in voltage potential: the less noble metal is the one with a lower (that is, more negative) electrode potential than the nobler one, and will function as the anode (electron or anion attractor) within the electrolyte device functioning as described above (a galvanic cell). Galvanic reaction is the principle upon which batteries are based.

Galvanic series

- **The galvanic series (or electropotential series) determines the nobility of metals and semi-metals**

Table 1. *Galvanic series.*

Active (or *anodic*)		
	1.	Mg
	2.	Mg alloys
	3.	Zn
	4.	Al
	5.	Cd
	6.	Al alloys
	7.	Mild steel
	8.	Cast iron
	9.	High Ni cast iron
	10.	Pb-Sn solder
	11.	Pb
	12.	Sn
	13.	Iconel
	14.	Ni - Mo - Fe alloys
	15.	Brasses
	16.	Monel (7 = Ni, 30 = Cu, rest = Fe)
	17.	Silver solder
	18.	Cu
	19.	Ni
	20.	Cr stainless steel
	21.	18 – 8 stainless steel
	22.	18 – 8 Mo stainless steel
	23.	Ag
	24.	Ti
	25.	Graphite
Noble (or *cathodic*)	26.	Au
	27.	Pt

Reference Jain and Jain, 16th edition Page 341

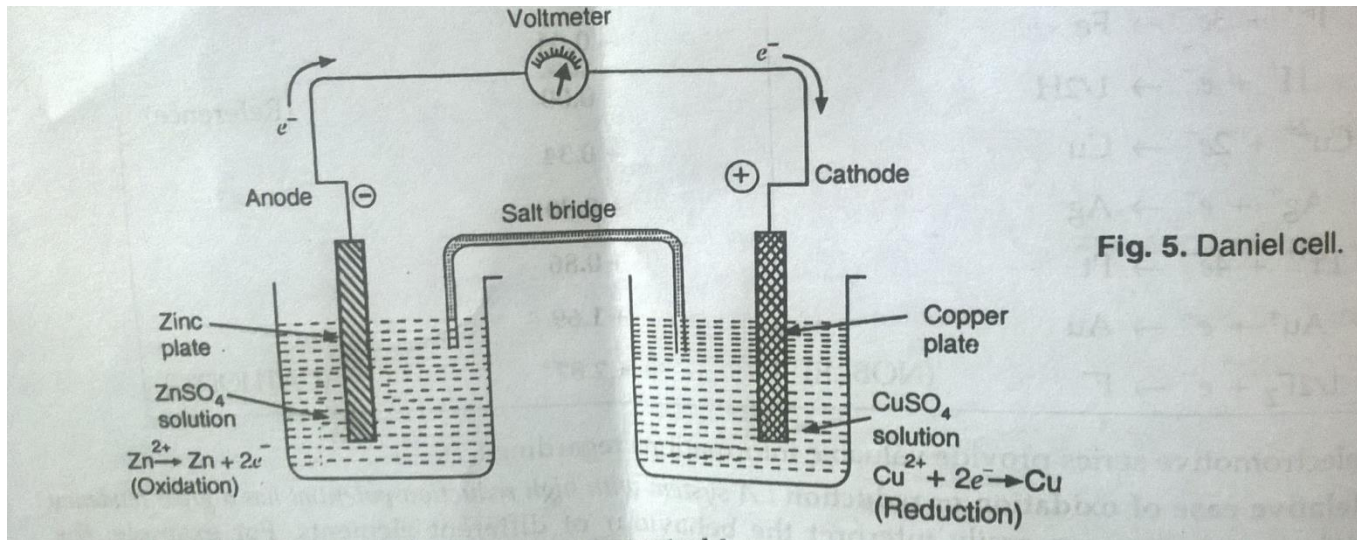## Electrochemical series   versus   Galvanic series

- Electrode potentials are measured by dipping pure metals in their salt solutions of 1M concentration without any oxide film on them.

- Series comprise of metal and non-metals

- The position of a given metal in electrochemical series is fixed.

- It predicts the relative displacement tendencies.

- This series was developed by studying corrosion of metals and alloys in unpolluted sea water, without their oxide films.

- Series comprises of metals and alloys.

- The position of given metal when present in the form of alloys, is different from that of pure metal.

- It predicts relative corrosion tendencies.

Reference Jain and Jain, 16th edition Page 342

Electrochemical cell

An electrochemical cell (galvanic or voltaic)is a device in which a redox reaction is utilized to get electrical energy. The electrode where oxidation occurs is called anode; while the electrode where reduction occurs is called the cathode.

Fig. 5. Daniel cell.

$$E = E^0_{cell} + \frac{0.0592}{n}\log\frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$Zn|Zn^{2+}||Cu^{2+}|Cu$$

Nernst's equation

$$M^{n+} + ne^- \rightarrow M$$
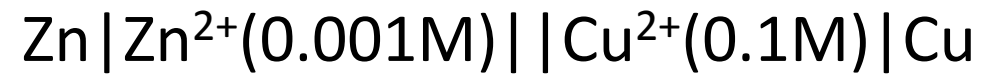
$$E = E^o + \frac{RT}{nF} \ln \frac{[M^{n+}]}{[M]}$$

$$E = E^o + \frac{RT}{nF} \ln[M^{n+}]$$

Since [M]=1

$$E = E^o + \frac{0.0592}{n} \log[M^{n+}]$$

Numerical1

Calculate the emf of a Daniel cell at 25 °C, when the concentration of $ZnSO_4$ and $CuSO_4$ are 0.001M and 0.1M respectively. The standard potential of the cell is 1.1V.

$$Zn|Zn^{2+}(0.001M)||Cu^{2+}(0.1M)|Cu$$

$$E = E^0{}_{cell} + \frac{0.0592}{n}\log\frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$E = 1.1 + \frac{0.0592}{2}\log\frac{0.1}{0.001}$$

E = 1.1592V

Numerical2

Calculate the emf of a concentration cell at 25 °C consisting of two Zn electrodes immersed
In solution of Zn^{2+} ions of 0.1M and 0.01M concentrations.

$$E = E^o{}_{cell} + \frac{0.0592}{n} \log \frac{[C_2]}{[C_1]}$$

$$E = 0 + \frac{0.0592}{2} \log \frac{[0.1]}{[0.01]}$$

$$E = 0.0296V$$

Numerical 3. What is concentration of Ni^{2+} in the cell at 25 ^{0}C , if the emf is 0.601V?

Ni(s)l Ni^{2+} (a=?) || Cu^{2+}(0.75M) l Cu(s)

Given $E^0_{Ni/Ni2+}$ = 0.25V, and $E_{Cu2+lCu}$ = 0.34V

$$E = E^0_{cell} + \frac{0.0591}{2}\log \frac{[Cu^{2+}]}{[Ni^{2+}]}$$

$$0.601 = 0.59 + \frac{0.0591}{2}\log \frac{0.75}{[Ni^{2+}]}$$

$$[Ni^{2+}] = \mathbf{0.3188M}$$

Do practice of numerical based on electrochemical cell

Corrosion control methods:

1.   Proper design: the design of the material should be such that "corrosion, even if it occurs, is uniform and does not result in intense and localized corrosion".
Important design principles are:

1.1   Avoid the contact of dissimilar metals in the presence of a corroding solution. If this principle is not followed, then corrosion is localized on the more active metal while the less active metal will remain protected.

1.2   When two dissimilar metals are to be in contact, the anodic material should have as large area as possible; whereas the area of the cathodic material should be small.

1.3   The two dissimilar metals should be in close proximity in the electrochemical series.

Electrochemical series

When elements are arranged
In increasing order of their
electrode potential, a series
called Electrochemical series
is obtained.

Table 1. *Standard electrode potentials (reduction) at 25°C.*

Metal ion		Potential in volts	
$Li^+ + e^- \rightarrow Li$	(BASE)	−3.05	(ANODE)
$K^+ + e^- \rightarrow K$		−2.93	
$Ca^{2+} + 2e^- \rightarrow Ca$		−2.90	
$Na^+ + e^- \rightarrow Na$		−2.71	
$Mg^{2+} + 2e^- \rightarrow Mg$		−2.37	
$Al^{3+} + 3e^- \rightarrow Al$		−1.66	
$Zn^{2+} + 2e^- \rightarrow Zn$		−0.76	
$Cr^{3+} + 3e^- \rightarrow Cr$		−0.74	
$Fe^{2+} + 2e^- \rightarrow Fe$		−0.44	
$Ni^{2+} + 2e^- \rightarrow Ni$		−0.23	
$Sn^{2+} + 2e^- \rightarrow Sn$		−0.14	
$Pb^2 + 2e^- \rightarrow Pb$		−0.13	
$F^{3+} + 3e^- \rightarrow Fe$		−0.04	
$H^+ + e^- \rightarrow 1/2H$		0.00	(Reference)
$Cu^{2+} + 2e^- \rightarrow Cu$		+0.34	
$Ag^+ + e^- \rightarrow Ag$		+0.80	
$Pt^{4+} + 4e^- \rightarrow Pt$		+0.86	
$Au^+ + e^- \rightarrow Au$		+1.69	
$1/2F_2 + e^- \rightarrow F^-$	(NOBLE)	+2.87	(CATHODIC)

Reference Jain and Jain, 16th edition Page 283

Corrosion control methods:

1. Proper design:

1.   Proper design:

1.4   Whenever the direct joining of dissimilar metals is unavoidable, an insulating fitting may be applied in-between them to avoid direct metal-metal contact.

1.5   the anodic metal should not be painted when in contact with a dissimilar metal because any break in coating would lead to rapid localized corrosion.

1.6   Prevent the occurrence of inhomogeneity both in the metal and in the corrosive environment

1.7   Formation of stagnant pools or damp areas should be avoided.

1.8   Design of the equipment must allow easy cleaning of the critical parts.

1.9   Uniform flow of a corrosion liquid is desirable.

Corrosion control methods:

2. Cathodic protection

2. **Cathodic protection:** the principle involved is to force the metal to be protected to behave like a cathode, thereby corrosion does not occur. There are two types of cathodic protections

2.1 Sacrificial anodic protection method: the metal (to be protected) is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal. The more active metal itself gets corroded slowly; while the parent structure (cathodic) is protected. The more active metal so employed is called sacrificial anode. Examples: Zn, Mg, and Al etc. Applications are water tanks, buried pipelines etc.

2.2 Impressed current cathodic protection: An impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode. This kind of protection is particularly useful for large structures in long term operations. Examples: Transmission line towers, buried oil and water pipes etc.

Methods of application of metal coatings

1. **Hot dipping:** is used for producing a coating of low-melting metal such as Zn (m.p=419 ^{o}C), Sn (m.p. =232 ^{o}C), Pb, Al etc on iron steel and copper, which have relatively higher melting points. The process consists of immersing the base metal in a bath of the molten coating metal, covered by a molten flux layer (usually zinc chloride). For good adhesion, the base metal surface must be very clean. Two most widely applied hot dipping methods are:
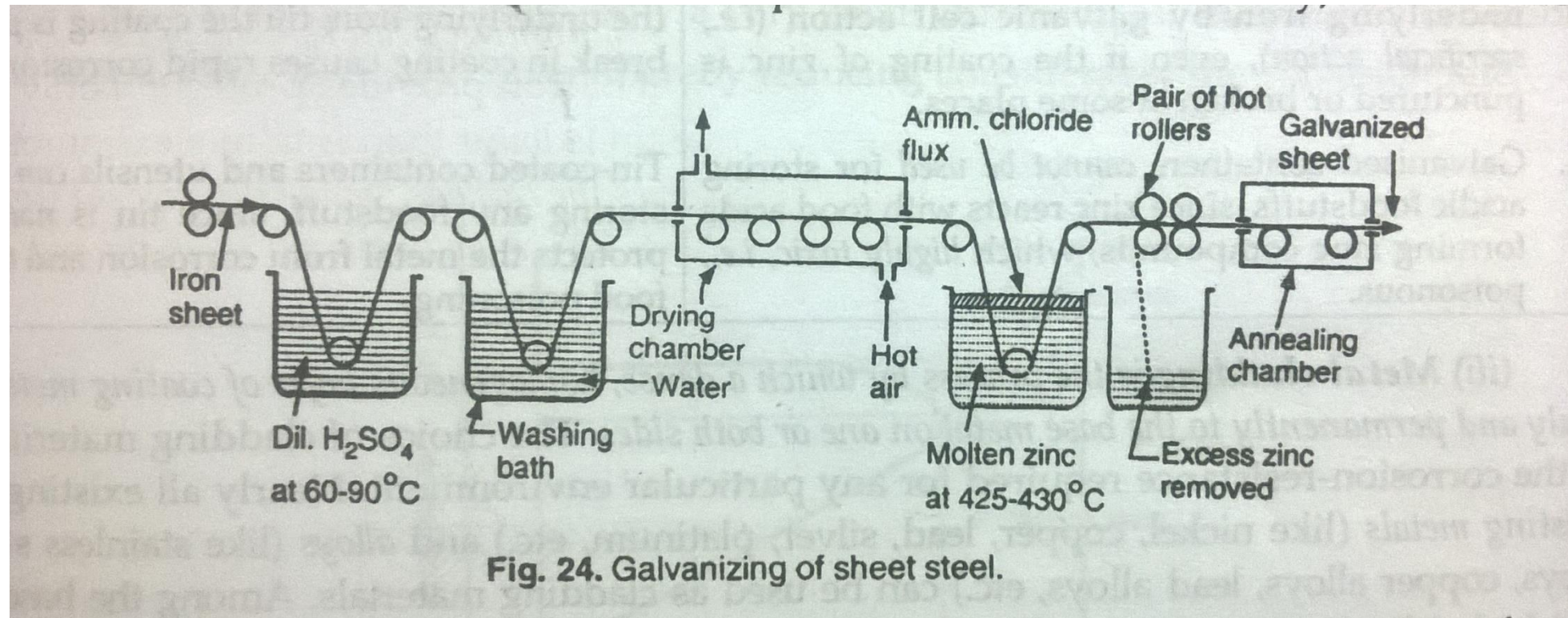
a) Galvaninizing

b) Tinning

Methods of application of metal coatings

1.a) Galvanizing: is the process of coating iron or steel sheets with a thin coat of zinc to prevent them from rusting. The process is carried out as follows: the iron or steel article is first cleaned by pickling with dilute H_2SO_4 solution for 15-20 minutes at 60-90 ^{o}C. This treatment also removes any scale, rust and impurities. It is then dipped in bath of molten Zinc, maintained at 425-430 ^{o}C. the surface of the bath is covered with a flux (ammonium chloride) to prevent oxide formation. It is then passed through a pair of hot rollers. Then it is annealed at a temperature of 650 ^{o}C and finally cooled slowly.

Reference Jain and Jain, 16th edition Page 351

Methods of application of metal coatings

1.a) Galvanizing:

Fig. 24. Galvanizing of sheet steel.

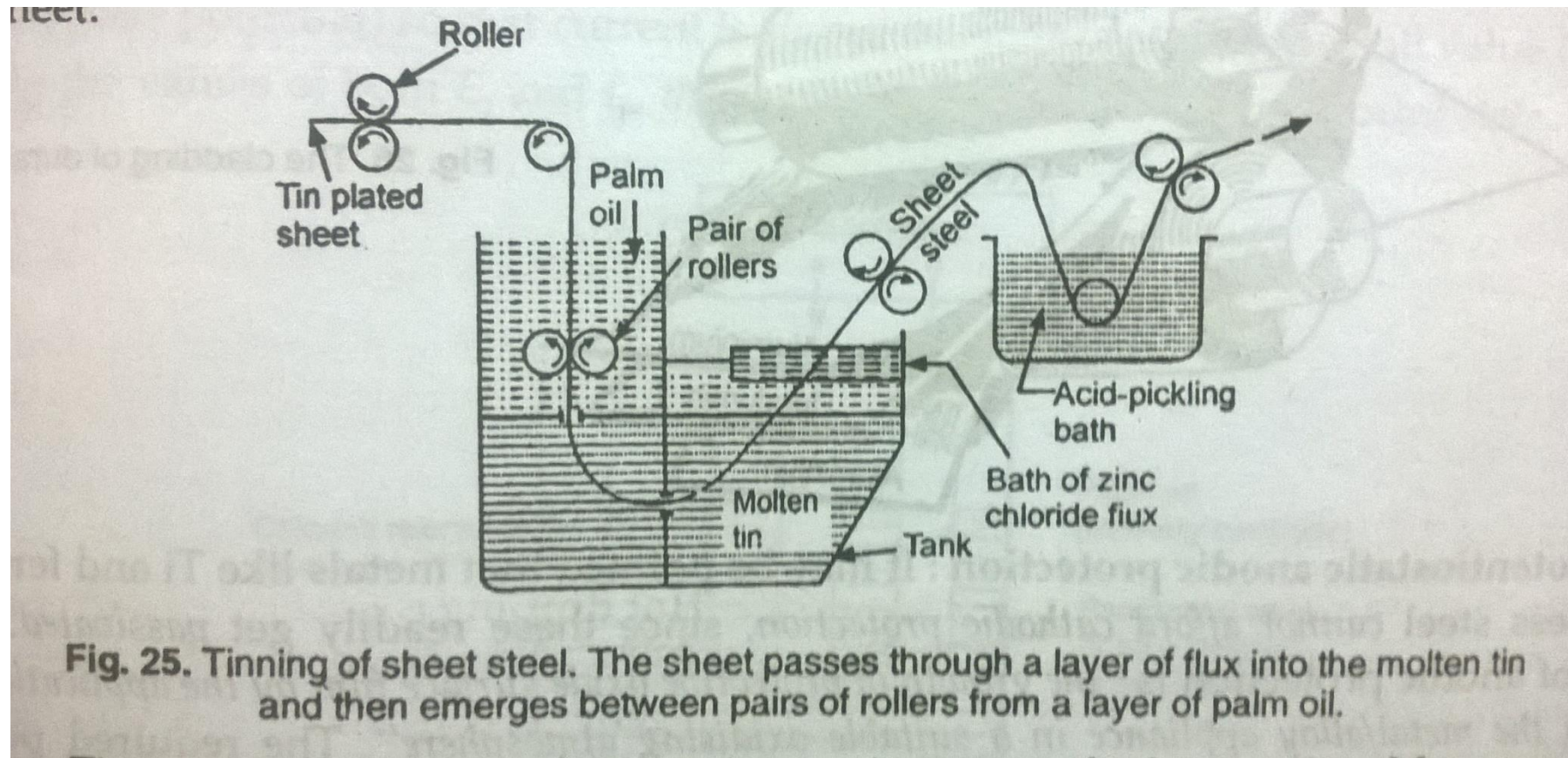Reference Jain and Jain, 16th edition Page 351

Methods of application of metal coatings

1.b) Tinning: is coating tin over the iron or steel articles. The process consists of first treating steel sheet in dilute sulphuric acid to remove any oxide film. After this, it is passed through a bath of Zinc chloride flux. The flux helps the molten metal to adhere to the metal sheet. Next the sheet is passed through a tank of molten tin and finally though a series of rollers from the underneath the surface of a layer of palm oil. The palm oil protects the hot tin coated surface against oxidation. The rollers removes any excess of tin and produce a thin film of uniform thickness on the steel sheet.

Reference Jain and Jain, 16th edition Page 351

Methods of application of metal coatings

1.b) Tinning:

Fig. 25. Tinning of sheet steel. The sheet passes through a layer of flux into the molten tin and then emerges between pairs of rollers from a layer of palm oil.

Reference Jain and Jain, 16th edition Page 351

Organic Coatings

Organic Coatings

➢ *Organic coatings are inert organic-barriers applied on metallic surfaces and other constructional materials for both corrosion protection and decoration. An organic coating is made up of two principal components: a vehicle and a pigment. Vehicle contains the film-forming ingredients that enable the coating to convert from a mobile liquid to a solid film. It also acts as a carrier and suspending agent for the pigment. Pigments are the colouring agents and, in addition, contribute a number of other important properties.*

➢ *Organic coatings are commonly divided based on the types and combinations of vehicle and pigment used in their formulation. They are **paints, enamels, varnishes, lacquers, dispersion coatings, emulsion coatings, and latex coatings.***

Organic Coatings

Features of a good organic coating materials

➢ *Its chemical inertness to environments*

➢ *Good surface adhesion behavior*

➢ Impermeable nature

➢ Ease of application

Paint

Paints: is mechanical dispersion mixture of one or more pigments in a vehicle. The vehicle is a liquid, consisting of non-volatile, film forming material, drying oil and highly volatile solvent. thinner. When a paint is applied to a metal surface, the thinner evaporates; while the drying oil slowly oxidizes forming a dry pigmented-film.

Paints

Requisite of a good paint:

1. It should be fluid enough to be spread easily over the protected surface.

2. It should possess high covering power.

3. It should form a quite tough, uniform, adherent and impervious film.

4. Its film should not get cracked on drying.

5. It should protect the painted surface from corrosion effects of environment.

6. The color of the film should be stable.

7. Its film should be glossy

8. Easily applicable with brush or spraying device

9. It should possess high adhesion capacity to the materials.

Constituent of paint

1. **Pigment:** is a solid substance which is an essential constituent of paint. Pigment is

    usually mixture of inorganic metal salts.

Colour	Chemical Formula
Red	Pb_3O_4, Fe_2O_3, HgS
Cobalt blue	$CoO.Al_2O_3$
Green	$2\ CuCO_3.Cu(OH)_2$
Yellow	$BaCrO_4$, As_2S_3
White	TiO_2

Constituent of paint

Functions of pigments are:

    a) to provide capacity to the paint

    b) provide strength to paint

    c) provide desired color to paint

    d) give aesthetical appeal to paint film

    e) reflecting harmful UV light

    f) provide resistance to paint film against abrasion/wear

    g) improve the impermeability of film to moisture

    h) increase weather resistance of the film.

Constituent of paint
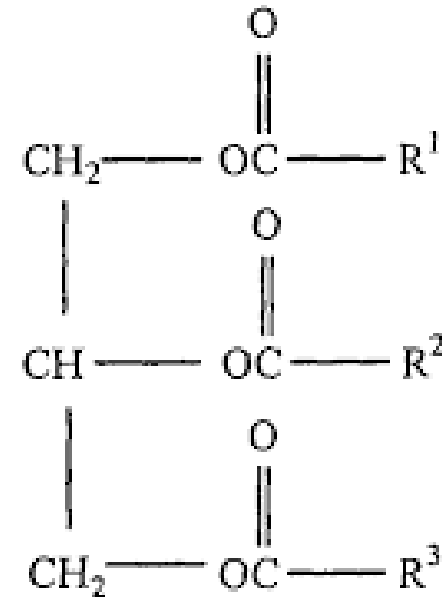
Characteristics of good pigment:

1. Opaque

2. Chemically inert

3. Non-toxic

4. Freely mixable with the film forming constituent, oil

5. Cheap

Constituent of paint

2. Vehicle or Drying oil: is a film forming constituent of the paint. These are glyceryls esters of high molecular weight fatty acids, generally present in animal and vegetable oils. The most Widely used drying oils are linseed oil, soyabeen oil and dehydrated castor oil.
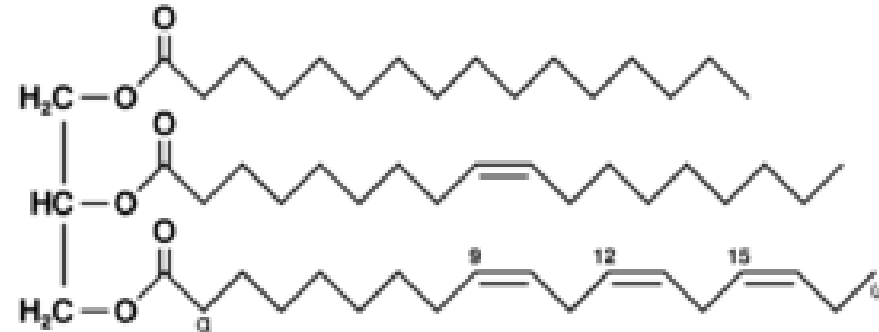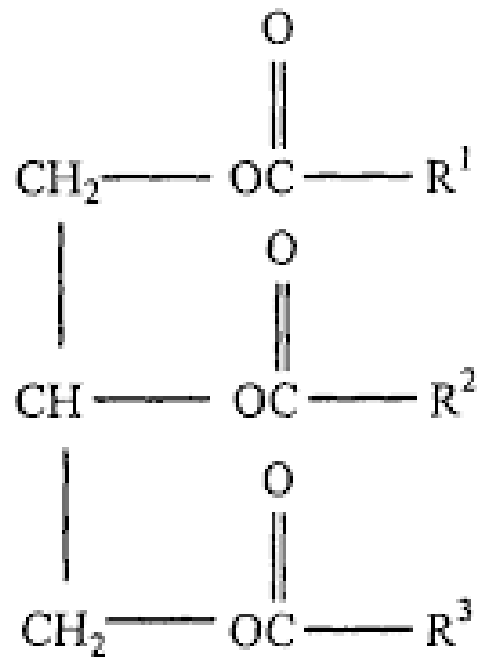
Functions of drying oils:

1. Main film-forming constituent

2. vehicle or medium

3. Toughness

4. Adhesion

5. Durability

6. Water proof

$$
\begin{array}{c}
\text{CH}_2 - \text{OC} - \text{R}^1 \\
\quad\quad\quad \| \\
\quad\quad\quad \text{O} \\
\text{CH} - \text{OC} - \text{R}^2 \\
\quad\quad\quad \| \\
\quad\quad\quad \text{O} \\
\text{CH}_2 - \text{OC} - \text{R}^3
\end{array}
$$

Constituent of paint

2. Vehicle or Drying oil:

palmitic acid,

oleic acid,

alpha-linolenic acid.

Constituent of paint

2. Vehicle or Drying oil:

Table 4. *Fatty acids present in oils and fats.*

| Name of acid	Formula	Position of unsaturation (if any)
Caproic	$C_5H_{11}COOH$	Saturated
Caprylic	$C_7H_{15}COOH$	Saturated
Capric	$C_9H_{19}COOH$	Saturated
Lauric	$C_{11}H_{23}COOH$	Saturated
Myristic	$C_{13}H_{27}COOH$	Saturated
Palmitic	$C_{15}H_{31}COOH$	Saturated
Stearic	$C_{17}H_{35}COOH$	Saturated
Arachidic	$C_{19}H_{39}COOH$	Saturated
Behenic	$C_{21}H_{43}COOH$	Saturated
Lignoceric	$C_{23}H_{47}COOH$	Saturated
Cerotic	$C_{25}H_{51}COOH$	Saturated
Oleic	$C_{17}H_{33}COOH$	Unsaturated 9th carbon atom
Linoleic	$C_{17}H_{31}COOH$	6th and 9th carbon atoms (*two* double bonds)
Linolenic	$C_{17}H_{29}COOH$	3rd, 6th and 7th carbon atoms (*three* double bonds)
Eleostearic	$C_{17}H_{29}COOH$	5th, 7th and 9th carbon atoms (*three* double bonds)

Constituent of paint

3. Thinners:

The function of thinners are

a) reduce the viscosity of the paint to suitable consistency

b) Dissolve vehicle and the additives in the vehicle

c) Suspend the pigments

d) Increase the penetration power of the vehicle

e) Increase the elasticity of the paint film

f) Help in drying of the paint film as they evaporate

Common thinners used are turpentine, mineral spirit,, benzene, dipentene, kerosene etc
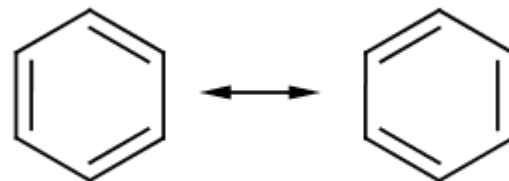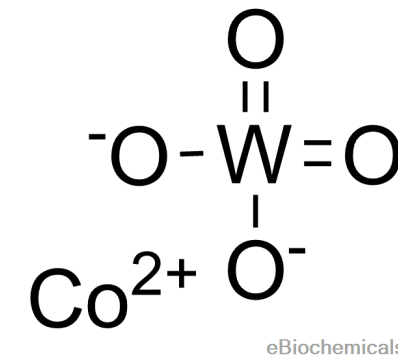
Constituent of paint

4. Driers: are oxygen carrier catalysts. They accelerate the drying of the oil film through oxidation

polymerization and condensation. Thus, their main function is to improve the drying quality

of the oil-film. The most effective driers are resinates, linoleates, tungstates, and naphthenates

of Co, Mn, Pb and Zn.

Cobalt substances are the most efficient of all and are surface driers

Lead substances are bottom driers

Manganese substances are bottom driers

Too much of the driers tends to produce hard and brittle films.

$$\overset{\displaystyle O}{\underset{\displaystyle Co^{2+}\ O^-}{{}^-O-W=O}}$$

eBiochemicals

Cobalt tungsate

Constituent of paint

5   Extenders or fillers: are low refractive indices materials, generally of white color, added to

5.1   Reduce the cost

5.2   Increases the durability of the paint

5.3   Provide negligible covering power to the paint   ground silica

5.4   Help to reduce the cracking of dry paint film

5.5   Act as carrier for the pigment color
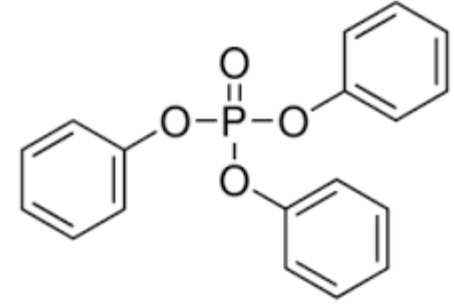

Important extenders used are baryted ($BaSO_4$), talc, asbestos, ground silica, gypsum etc.

Constituent of paint

6. Plasticizer: sometimes plasticizer are incorporated in the paint to

a)   To provide elasticity to the film

b)   To minimize its cracking

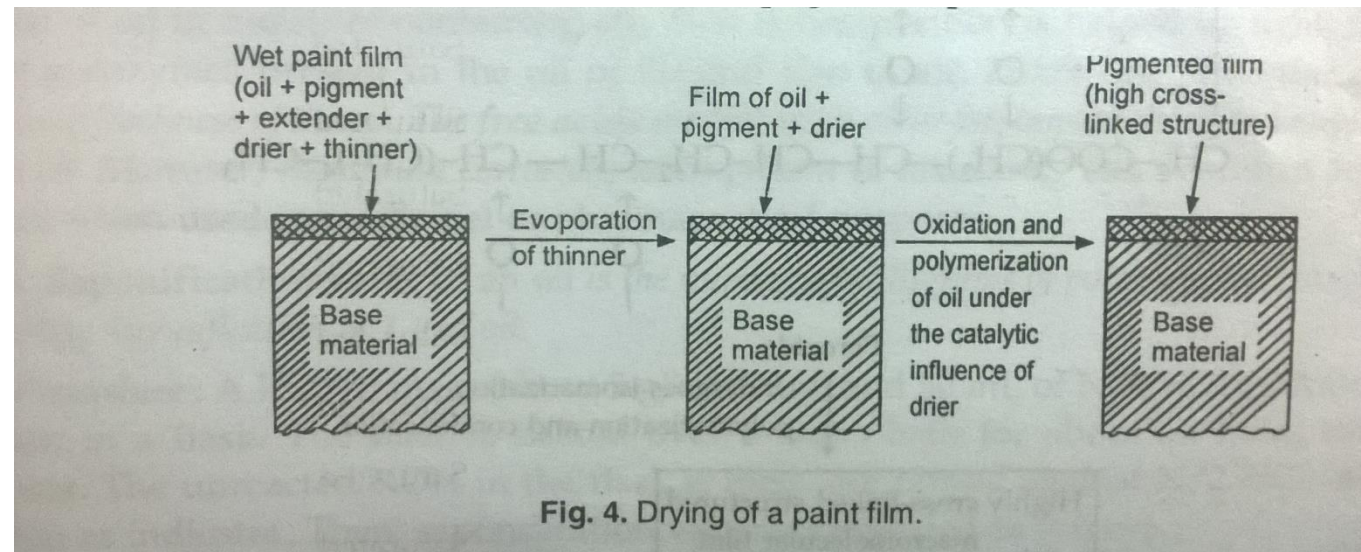Common plasticizer aretricresyl phosphate, triphenyl phosphate, tributyl phthalate and
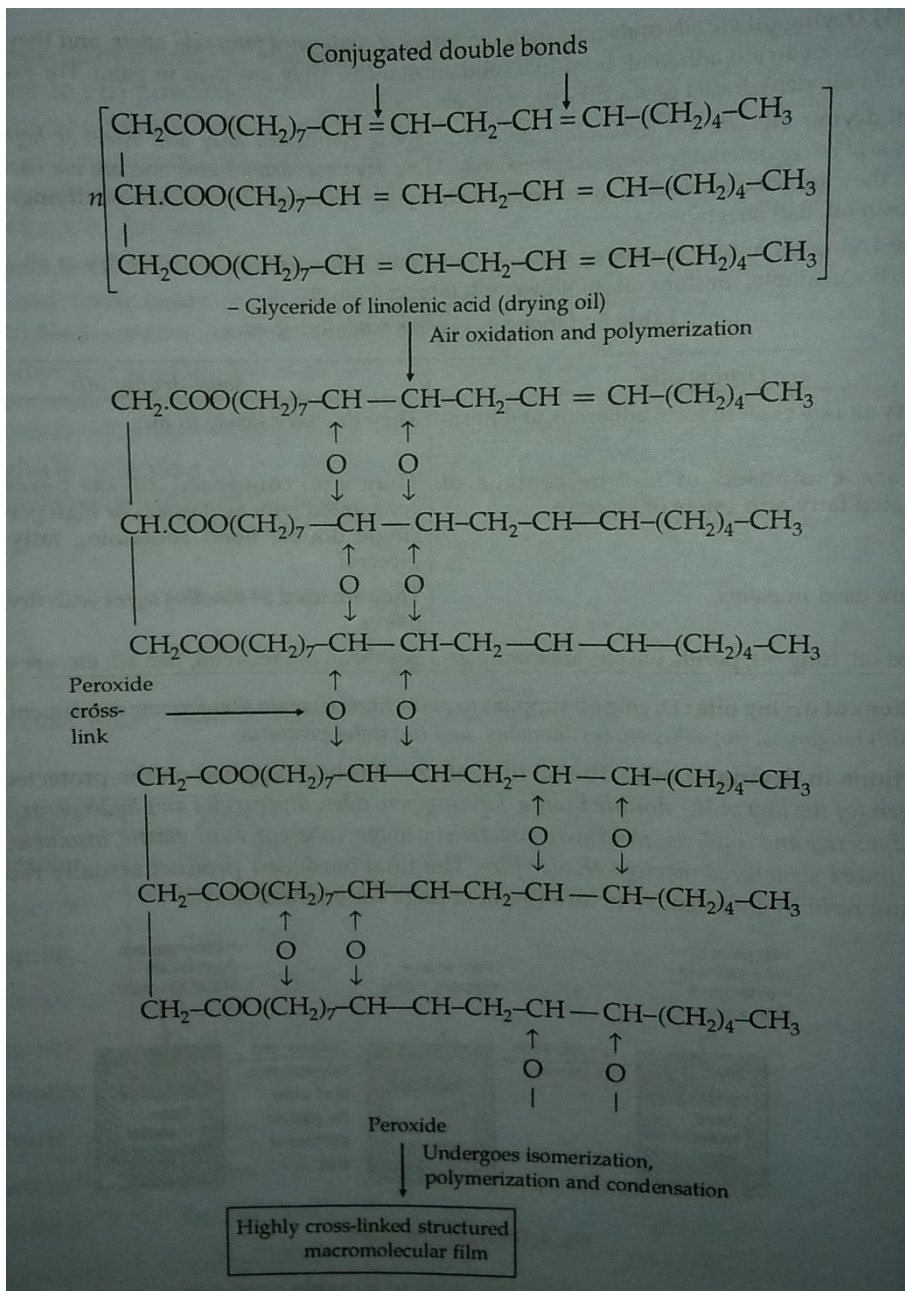
 dibutyl tartarate

7. Antiskinning agents: are sometimes added to some paints with the objects of preventing

   gelling and skinning of the paint film. Important antiskinning agents are polyhydroxy phenols.

Drying mechanism of oil

The oil film after it has been applied on the protected surface, absorb oxygen at the double bond, forming peroxides, diperoxides and hydroperoxides, which isomerise, polymerize and condense to form a characteristics tough, coherent, hard, elastic, insoluble, highly cross linked structured macromolecular film. The final hardened product actually resembles a thermosetting resin in chemical structure.

Fig. 4. Drying of a paint film.

Reference Jain and Jain, 16th edition Page 377

Drying mechanism of oil

Conjugated double bonds

$CH_2COO(CH_2)_7-CH=CH-CH_2-CH=CH-(CH_2)_4-CH_3$

n $CH.COO(CH_2)_7-CH=CH-CH_2-CH=CH-(CH_2)_4-CH_3$

$CH_2COO(CH_2)_7-CH=CH-CH_2-CH=CH-(CH_2)_4-CH_3$

– Glyceride of linolenic acid (drying oil)

Air oxidation and polymerization

Peroxide cross-link

Peroxide — Undergoes isomerization, polymerization and condensation

Highly cross-linked structured macromolecular film

Double bonds of oil film

O_2 absorption

Peroxides, Diperoxides, Hyperperoxides

Isomerization
Polymerization
Condensation

Highly cross-linked structured Macromolecular Film

hard tough   Elastic   Coherent   Insoluble infusible

Varnishes

Varnish : is a homogenous colloidal dispersion solution of natural or synthetic resin in oil, or Thinner or both. It is used as a protective and/or decorative coating of suitable surfaces and Dries by evaporation, oxidation and polymerization of its constituents; leaving behind a hard , transparent, glossy, lustrous, and durable film.

Constituents of Varnish:

1. **Resins:** it can be natural resin (like shellac, kauri, rosin, copal etc) and synthetic resin (like phenol-aldehyde, urea formal dehyde, terpene polymers etc) The resins in general are characterized by high resistance to weathering and chemical conditions. It also provides hardness and durabilty.

2. **Drying Oil:** Principal oils are linseed oil, tung oil, dehydrated castor oil etc. they dry by oxidation and polymerization.
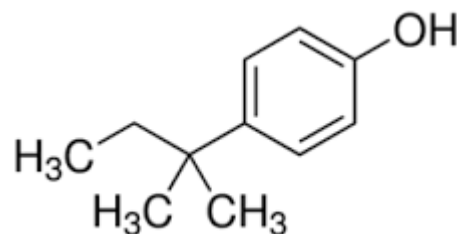
Varnishes

Constituents of Varnish:

3. Solvent or thinners: usually employed are kerosene, xylol, tolyl, ehtyl alcohol, amyl acetate etc.

4. Driers: are added to enhance the drying rate of the oil constituent. These include Pb, Co and

    Mn linoleates, naphthalenes etc.

5. Antiskinning agents: like tert-amyl phenol, guiacol etc.
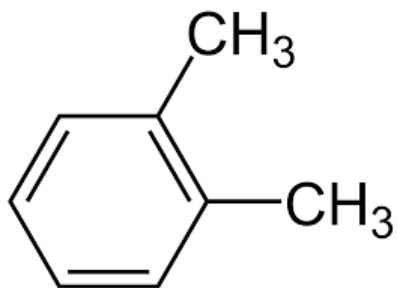
xylol

tert-amyl phenol

Varnishes

There are two main types of varnishes:

1. Oil varnish: is a homogenous solution of one or more natural or synthetic resins in a drying oil and a volatile solvent. The presence of oil reduces the natural brittleness of the pure resin film. This type of varnish dries up by evaporation of the volatile solvent, followed by oxidation and polymerization of the drying oil. An example is copal varnish (prepared by copal in linseed oil and mixing a quantity of turpentine.

2. Spirit Varnish: contains a resin dissolved in a completely volatile solvent. Such a varnish dries by the evaporation of the solvent. Such a varnish dries off rapidly by the evaporation of the solvent and leaving behind a film which has a tendency to crack and peel off. Moreover the film is easily affected by weathering. An example is spirit varnish used for wooden furniture.

Characteristics of a good Varnishes

1. Soft and tender

2. Adapt itself to the contraction/expansion

3. Dry quickly

4. Produce a protective film

5. Produce glossy and shinning film on drying

6. Produce elastic film which does not get crack

7. Color of the film does not fade on exposure to atmosphere

8. Not shrink or crack upon drying

Palm oil

copal

Linseed oil

shellac