MODULE – 4

Macromolecules for Engineering Applications

CONTENTS

Introduction, definition with examples. **Glass transition temperature (Tg)** - definition, factors affecting Tg and significances of Tg.

Plastics – Compounding of resins in to plastics.

Synthesis, properties and Industrial applications of PMMA and Polyurethane.

Polymer composites- introduction, **fibers**- meaning, synthesis, properties and industrial applications of Kevlar and Polyester.

Adhesives –Meaning, preparation, properties and applications of Epoxy resins & Phenol-formaldehyde resins.

Bio-degradable polymers- Introduction, types of bio-degradable polymers, preparation, properties and applications of polylactic acid (PLA).

Corrosion chemistry

Introduction, electrochemical theory of corrosion, types-differential metal, differential aeration (water line and pitting), factors affecting the nature of corrosion.

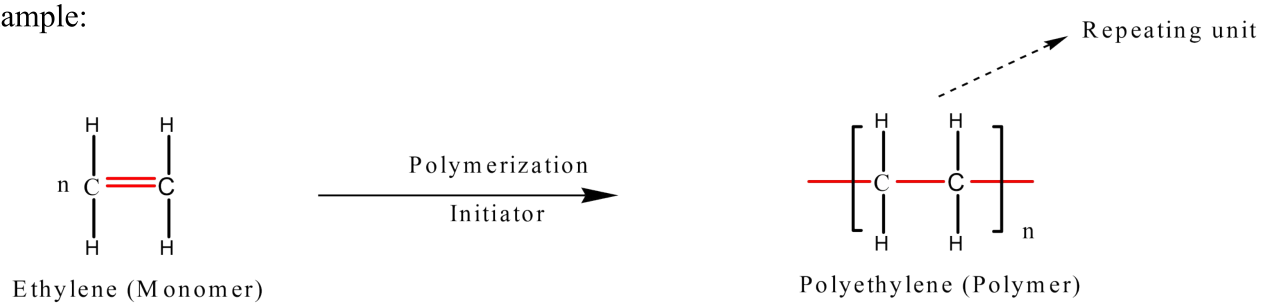
Corrosion control- galvanization, anodization and sacrificial anode method.

10 hours

HIGH POLYMERS

The word polymer is derived from the Greek word: “poly” means ‘many’ and “mers” means ‘units/parts. Thus, polymer is a large molecule formed by repeated linking of small molecules called monomers.

Example:



*The number of repeating units (n) in chain formed in a polymer is known as the “**Degree of polymerization**”.

[There may be thousands to lakhs of molecules (10^4 to 10^6)].

*The polymers with identical monomers are called **Homo polymers** and the polymers with different monomers are called **co-polymers**.

Example: (a) Homo polymer ——A——A——A——A——A——

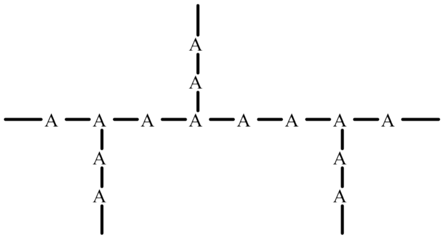
(b) Co-polymer ——A——B——A——B——A——B——

*The monomeric units in a polymer may be present in linear, branched or cross linked (Three dimensions).

Example: 1) ——A——A——A——A——A—— Linear homo polymer

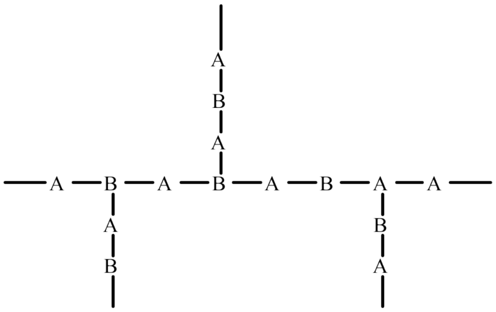
2) —A—B—A—B—A—B— Linear copolymer

3)



Branched chain homo polymer

4)

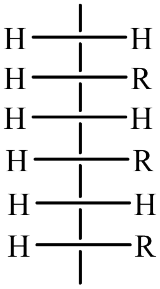


Branched chain copolymer

*The orientation of monomeric units in a polymer molecule can take place in an orderly or disorderly fashion with respect to the main chain.

If the group lies on the same side of the chain then it is called an Isotactic polymer.

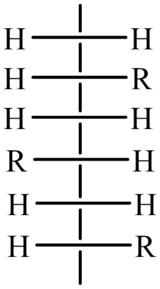
Example:



Natural rubber (cis-arrangements)

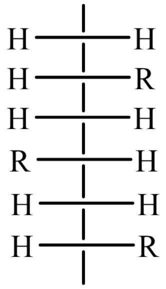
If the monomers have entered the chain in a random fashion, it is called an atactic polymer.

Example: Poly propylene



If the arrangement of side groups is in alternating fashion, it is called a syndiotactic polymer.

Example: Gutta percha



Classification

On the basis of their chemical structures, physical properties, mechanical behavior, thermal characteristics, stereochemistry, polymers can be classified into different types.

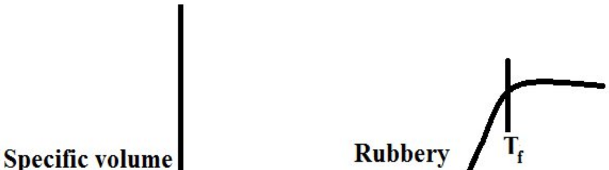
1. Natural and synthetic polymers.
   Ex: Silk, wool, rubber etc., for natural polymers
   Poly ethylene, PVC, Nylon etc., for synthetic polymers.
2. Thermo plastic and Thermo setting polymers.
   Ex: Polythene, PVC, Plexiglass for thermoplastic
   Phenol formaldehyde, epoxy resin, urea formaldehyde for thermosetting polymers
3. Plastics Elastomers Fibres and Liquid resins

Ex; | ↓ ↓ ↓ ↓

PVC Synthetic rubber Nylon Adhesives (Epoxy resins, U-F resins),
PMMA Silicon rubber Terylene Polysulphide Sealants

Glass transition temperature

All amorphous polymers, when cooled below a certain temperature become stiff, hard, brittle and glassy but above this temperature, they become soft, flexible, and rubbery. This transition temperature of a



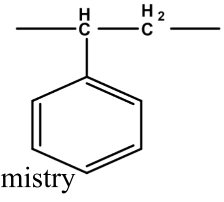
polymer is called glass transition temperature. It is denoted by Tg. The hard, brittle state is known as glassy state and the soft, flexible state as rubbery state.

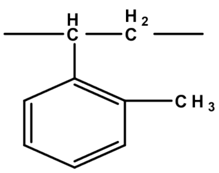
Factors influencing the Tg value

1. Crystallinity: The Tg value of a polymer largely depends on the degree of the crystallinity. Higher the crystallinity larger is the Tg value of a polymer. In crystalline polymer the linear or stereo regular chains are lined up parallel to each other and are held by strong cohesive forces. This leads to a high Tg value of the polymer [Tg value for poly ethylene is -125^{0}C due to absence of cohesive force. On the other hand, Nylon-6 having similar structure has higher Tg value (50^{0}C). This is due to presence of large polar groups in polymer chains. The chains are held together by strong cohesive forces through inter chain hydrogen bonding].

2. Molecular weight: The Tg value of a polymer is also influenced by its molecular weight. The Tg value of all polymers, in general increases with molecular weight up to 20000 and beyond which the effect is negligible.

3.Effects of side groups: Poly methyl styrene has higher Tg value (170^{0}C) while polystyrene has lower Tg value (100^{0}C). The observed higher Tg value of poly methyl styrene is due to the presence of effective methyl side groups. This hinders the free rotation about carbon-carbon bond of chain backbone and restricts the chain mobility and thereby increasing its Tg value.





Polystyrene Poly methyl styrene

Importance/Significances of Tg value

The Tg value is an important parameter of polymer. The polymer above their Tg value are soft and flexible while below Tg, they are hard and brittle. Thus, Tg value is a measure of flexibility of polymers. The use of any polymer at any temperature is decided by its Tg value. Tg value along with Tm (polymer melting point) helps in choosing the right temperature for processing the polymer by different techniques.

Resins and plastics

Resins: Resins are linear, low molecular weight, soluble and fusible polymers. They are also called as pre-polymers or binding materials. These pre-polymers during curing undergo further polymerization or extensive cross linking, resulting in hard and rigid three-dimensional network.

Example: Urea-formaldehyde resins, Phenolic resins, epoxy resins, etc.

Plastics: Plastics are high polymers which can be moulded into any shape by the application of heat and pressure in the presence of catalyst. Example: Polyethylene, polystyrene, PVC, nylons etc.,

Differences between Thermoplastics and Thermosetting plastics

No.	THERMOPLASTICS	THERMOSETTING PLASTICS
1	They are formed by addition polymerization.	They are formed by condensation polymerization.
2	They consists of long chain linear polymer	They have three-dimensional network structure, joined by strong covalent

		bond.
3	They soften on heating and hard on cooling.	They are fusible on initial heating, but become permanently hard, regid and infusible product on further heating.
4	They can be reshaped by heat cycle.	They cannot be reshaped by heat cycle.
5	They are soluble in organic solvents.	They are insoluble in organic solvents (due to strong bond and cross linking)
6	They are soft and flexible.	They are hard, rigid and infusible.
7	They can be reclaimed from wastes	They cannot be reclaimed from wastes.
	Example: Polyethylene, polypropylene, polystyrene, PVC, Plexi glass etc	Example: Phenol-formaldehyde resin, urea-formaldehyderesin, epoxy resins,etc,.

Compounding of resins and plastics

The process of mixing various additives to the polymer is called compounding of plastic and resins. The additives get incorporated into the polymer to give homogeneous mixture.

The functions of additives are as follows:

- To modify the properties of the polymer.
- To introduce new properties into the fabricated article.
- To assist polymer processing.
- To make the polymer products more pleasing and colorful.

Compounding materials:

1. Fillers
2. Plasticizers
3. Stabilizers

4. Accelerators
5. Colorants
6. Flame retarders

1. Fillers

Filler is an organic or inorganic compound added into polymer to transform a non-serviceable polymer into a serviceable one. The main functions of the fillers are:

- To reduce the cost of the fabricated plastic articles.
- To impart certain specific properties to the product.

There are two types of fillers used in the compounding of plastics, they are,

(a) Particulate fillers

(b) Fibrous fillers

(a) Particulate fillers:

The important fillers are wood flour, asbestos, mica, limestone, clay, silica, talc, etc. These are all inert fillers and are added as diluents, mainly to reduce the cost of the product. They also impart hardness and dimensional stability, but do not improve tensile strength.

(b) Fibrous fillers:

The most commonly used fillers are cotton flocks, fabric scraps, nylons, polyesters, glass fibres, carbon block, etc. These fillers are called reinforcing fillers. They greatly enhance the tensile strength, impart resistance and abrasion resistance.

(2) Plasticizers

A plasticizer is a substance incorporated into plastic to increase its workability and flexibility. The added plasticizer lowers the polymer melt viscosity and glass transition temperature. This helps in converting a hard, brittle, glass and difficult to process polymer into a soft, flexible and tough material. Thus, the process ability of polymer is greatly enhanced by plasticizers. The main requirements of a good plasticizers are---

- It should be miscible with the polymer.
- It should be inert.
- It should be high molecular weight, high B.P. and non-volatile substance.

Example: Phosphate esters (Tri crystal phosphate, Tri phenyl phosphate), phthalicesters (Di-Octyl Phthalates), fatty acid esters (natural), etc.

3. Stabilizers

Many polymers in service or during processing undergo degradation by the action of air, UV-rays and heat. This can be avoided by incorporating the polymer with certain compounds. A stabilizer is a compound incorporated onto the polymer to retard degradation of polymers.

Example:

(1) Elastomers have a tendency to undergo degradation by air and light. This can be prevented by adding anti- oxidants like alkyl phenols and napthols.

(2)The polymers such as polystyrene, PVC, polyesters, polypropylene are easily undergone degradation by UV light. This can be prevented by adding phenyl salicylate.

4. Colourant

A substance incorporated into a polymer to give a specific color to the product is called a colorant. Most of commercial plastic products come in highly attractive and more pleasing colours. Thus, the colourants are mainly used for decorative purpose. They do not influence the properties of polymer product.

There are two types of pigments.

1. Organic pigments
2. Inorganic pigments.

The color imparted to the product depends upon the nature of the pigments used. The organic colors are brighter, less dense and more transparent. But the color imparted by the inorganic pigments is less bright and more opaque.

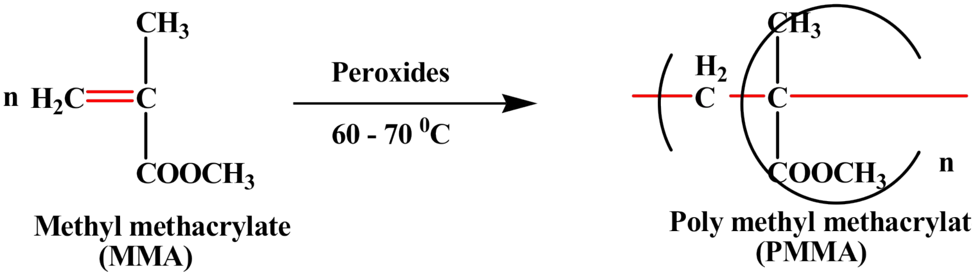
Ex: Organic pigments: carbon block, Azo dye stuff, anthraquinones, etc.

Ex: Inorganic pigments: Titanium oxide, Barium sulphate, lead chromate, Zinc chromate, Iron oxide, etc.

Preparation, Properties and applications of some Synthetic polymers

PMMA (Poly MethylMeth Acrylate) or Plexi glass (trade name)

PMMA is obtained by polymerization of methyl methacrylate (ester of methyl acrylic acid) in presence of acetyl peroxide or hydrogen peroxide. It is an acrylic polymer.

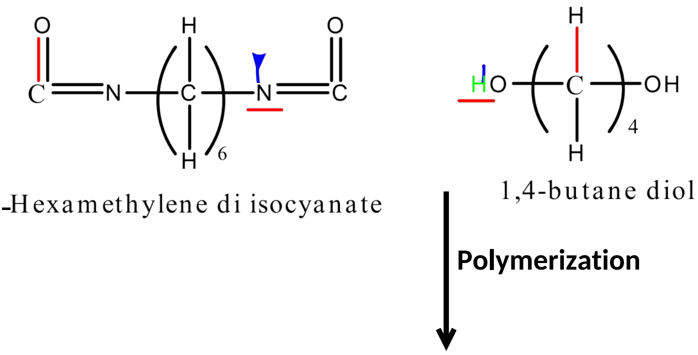


Properties: PMMA is a white transparent thermo plastic. It is amorphous in nature due to bulky groups. It has excellent optical clarity which is not affected by sun light but poor scratch resistant. It has low chemical resistance to hot acids and alkalis.

Uses: It is used for making lenses, air craft windows, light fixtures, artificial eyes, dentures (set of artificial teeth), wind screens and used as paints, adhesives etc.,

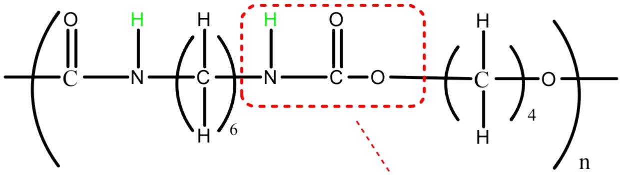
POLYURETHANES (PU)

These are obtained by poly addition reaction between di-iso cyanate and diol.



1,6-Hexamethylene di isocyanate

1,4-butane diol



Poly Urethane
(Perlon U)

Properties

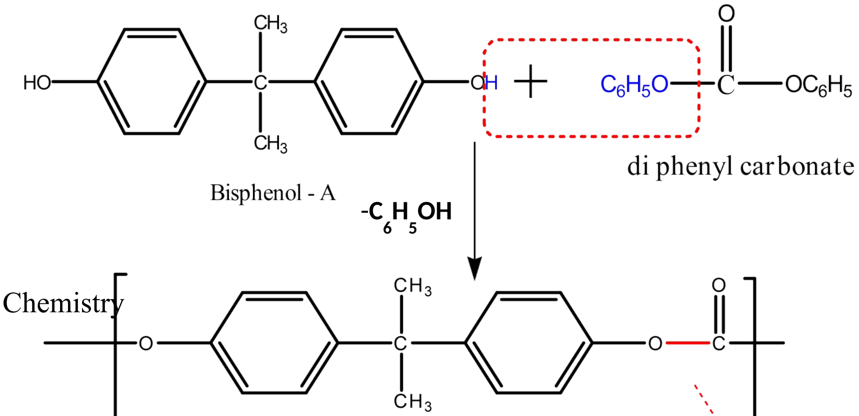
The presence of additional oxygen in the chain increases its flexibility. This is the cause for its much lower melting point than polyamides. (Polyurethane m.p. =150^0C and nylon-6 (polyamide) m.p=250^0C) (Less stable at high temperature). They resist abrasion and chemical attack.

Uses

Polyurethanes are very light. Therefore, they are used in light weight garments and swimming suits (due to stretching). They are used as coatings (flour), films, foams, adhesives ,etc. (Cushions for furniture and automobiles).

POLY CARBONATES

Poly carbonates are prepared by interaction of bisphenol-A with di phenyl carbonate



Properties

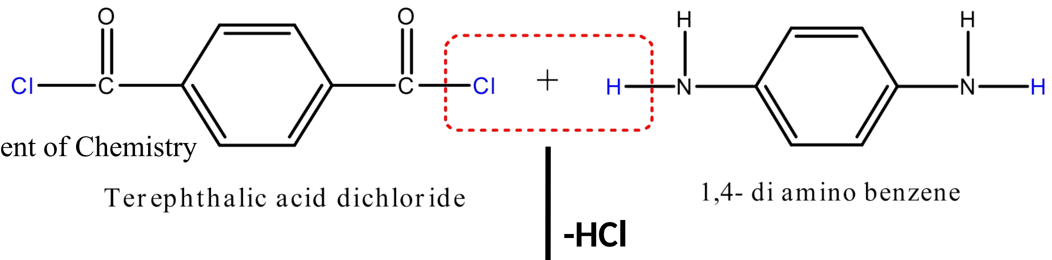
Polycarbonates melt at about 265^0C and are characterized by high impact and tensile strength over a wide range of temperature. They are also resistant to water and many other organic compounds, but they are soluble in organic solvents and alkalies.

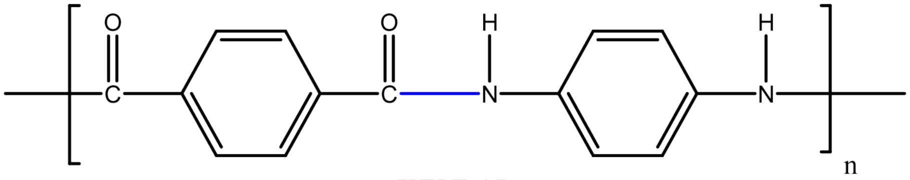
Uses

It is mainly used for preparing moulded domestic wares, housing for apparatus and electrical insulator in electronics and electrical industries. Polycarbonate is a white transparent plastic, hence they are used in sun glass lenses, automotive heat lamp lenses, C.D., DVDs, and also they can be laminated to make bullet-proof glass.

KEVLAR

Kevlar is an aromatic polyamide similar to nylons, but with benzene rings rather than aliphatic chains linked to the amide groups –CONH-. It is prepared by poly condensation between aromatic dichloride and aromatic di amines.





KEVLAR

It is an aromatic polyamide.

<u>Properties</u>

Kevlar is exceptionally strong (5times stronger than steel and 10times stronger than aluminum). It has high heat stability and flexibility. The unique properties to Kevlar are due to the delocalized bonding which causes the benzene rings to be inflexible. Therefore, Kevlar is for more rigid than nylons. The high electron density in the chains of Kevlar also results in relatively stronger Wander walls inter molecular forces between neigh boring polymer molecules.

<u>Uses</u>

Kevlar is used extensively in the aerospace and air craft industries, car parts(brakes, clutch,linings, etc) ropes, cables, protective clothing's, bullet proof vests, motor cycle helmets and other high-performance materials.

ADHESIVES

Adhesive is a non-metallic compound, which can hold firmly two materials together by surface attachment.

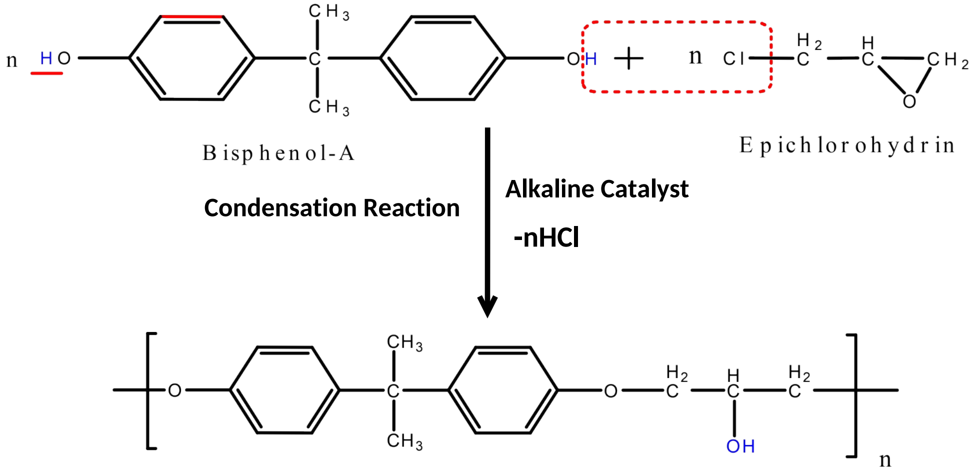
Ex: 1) Natural– Gum, glue, starch etc.

2) Synthetic – Phenol-formaldehyde, urea-formaldehyde, epoxy resins, silicones, etc.

SYNTHESIS, PROPERTIES AND APPLICATIONS OF SOME POLYMER

EPOXY RESINS (ARALDITE)

Epoxy resins are prepared by the condensation of Bisphenols&epichlorohydrin excess in presence of alkaline catalyst.



Epoxy resin

Properties

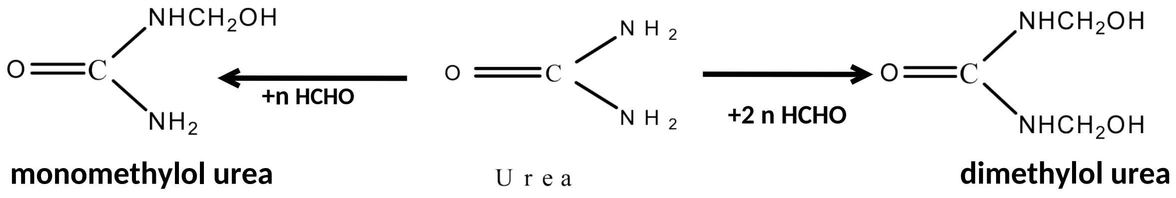
Epoxy resin is a linear, low molecular weight polymer. It is insoluble in organic solvents. During curing, they form cross linking with diamines, dicarboxylic acid, etc. After adhesion, they are highly resistant to water, solvents, acids, alkalies and weather.

Applications

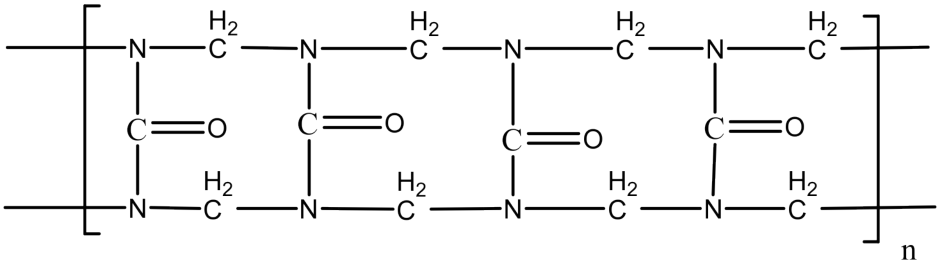
1. They are used for laminating materials.
2. As surface coatings
3. Adhesives like araldite (for joining glass, metals, etc.)
4. Epoxy resins are applied over cotton, rayon and bleached fabrics to impart grease resistance and shrinkage control.

UREA- FORMALDEHYDE RESIN

Urea formaldehyde is prepared by the reaction between two parts of urea and one part of formaldehyde in basic medium in stainless steel vessel at about 50^0C.The primary products formed are mono and dimethylolurea.



For moulding the methylol derivatives are compounded (with fillers, plasticizers, pigments and catalyst) and then cured (by applying heat and pressure). During curing long –C-N-C-N bonds chains are formed.



Cross link U-F resin

Properties

Urea formaldehyde resin is a clear white product of good tensile strength, good electrical insulation, good chemical resistance, great hardness, great light stability and good abrasion resistance.

Uses

1. For bonding grinding wheels.
2. For bonding glass fibers, rock wool etc.
3. For binding foundry cores.
4. For bonding plywood.
5. Used in cat-ion exchanger
6. Used in electrical insulation.
7. Used for decorative articles like plates, drinking glasses, dishes etc.

ELASTOMERS (RUBBERS)

Elastomers are high polymers which undergo very large elongation (300-1000%) under stress and regain original shape and size fully on release of stress (force). This property of elastomers is called elasticity. This arises due to coiled structure of elastomers. Example: - Rubber band.

Types of rubber:

There are two types of rubber.

1. Natural rubber and2. Synthetic rubber

Natural rubber

Natural rubber consists of basic material latex, which is dispersion of isoprene. During the treatment, these isoprene molecules polymerize to form long coiled chains of cis-polyisoprene.

PREPARATION OF NATURAL RUBBER FROMLATEX

The latex is collected by making small cuts or trapping in the trees in such a manner so as to allow the latex (milky liquid or sap) to accumulate in small cups. The percentage of rubber in it is 25-35%. The average composition of the latex is water 60%, rubber 35%, proteins, enzymes and nucleic acid is 3%, fatty acids and esters is 1% and inorganic salts is 0.5%, (In these trees the rubber is formed from polymerization of isoprene to produce poly-isoprene by a biochemical reaction in which a particular type of enzyme acts as catalyst).

The latex is first sieved (filter) to remove the impurities such as leaves, barks, dirt, etc. present in it. It is then diluted from 25-35% dry rubber content of the latex to about 15-20% of rubber content. The rubber is then separate from the latex by the process of coagulation. The acetic acid or formic acid is added as coagulants and the rubber is coagulated to soft white mass. This coagulated mass is called crude rubber and it contains about 90-95% rubber, 2-4% proteins and 1-2% resins. The crude rubber is washed and treated for producing smoked rubber, crepe rubber etc.

Deficiencies of natural rubber

The origin rubber is as useless as 24 carat gold. As such it has virtually no practical utility value. It is mainly because of its many inherent deficiencies.

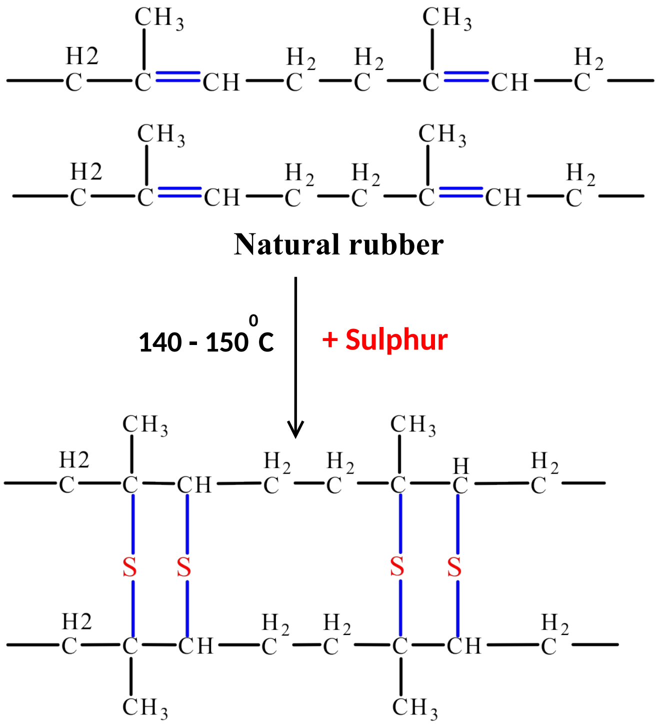
1. It is hard and brittle at low temperature and soft and sticky at high temperature.
2. It has poor keeping qualities as it develops obnoxious odour on storage.
3. It is soft and soluble in many hydrocarbon solvents and carbon disulphide.
4. It has high water absorption power.
5. It is a sticky substance rather difficult to handle
6. It is readily attacked by acids and alkalies.
7. It has low tensile strength.
8. It has poor abrasion resistant.
9. It is sensitive to oxidative degradation.

Compounding

The process of mixing various ingredients or chemicals such as fillers, plasticizers, stabilizers, colorants, vulcanizing agents etc. in to the rubber is known as compounding of the rubber.

Vulcanization of rubber: - (Good year in 1839)

Vulcanization is a process of heating natural rubber with sulphur and other compounding agents like Zinc oxide, hydrogen sulphide, benzoyl chloride, etc. at 140-150^{0}C temperature to improve the hardness and other mechanical properties like tensile strength, elasticity and resistance to swelling etc. is called vulcanization. The extent of stiffness of vulcanized rubber depends on the amount of sulphur added. For soft vulcanized rubber 1-5% of sulphur is used while for hard vulcanized rubber it is about 40%



Vulcanized rubber

The added Sulphur combines chemically at the double bonds of different layers (spring) of rubber molecules.

SYNTHETIC RUBBER (OR) ARTIFICIAL RUBBER

Synthetic rubber is a vulcanizable man made rubber like polymer which can be stretched to at least twice its length, but it returns to its original shape and dimension as soon as stretching force is released.

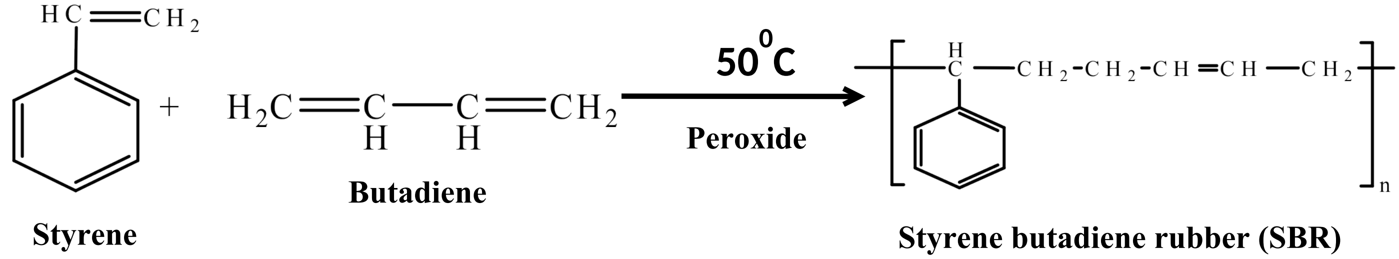
Advantages of synthetic rubber over natural rubber

1. They are produced from petrochemical raw materials in abundant amounts
2. Their production cost is less.
3. They are not only replacement, but are superior to natural rubber in certain cases.
4. They are tailor made elastomers with diverse applications.
5. They have high abrasion resistance and high tensile strength.
6. Certain elastomers like silicones have low temperature (-80^0C) flexibility and high temperature (250^0C) stability.

7. They are used for the manufacture of motor tyres, floor tiles, shoe soles, foot wear components, wire and cable insulations, tank linings etc.

SBR rubber or Buna 'S'

Styrene-butadiene rubber (SBR) is the first commercially made synthetic rubber. It is produced by co-polymerization of butadiene (75%) and styrene (25%) in presence of peroxide (cold polymerization take place at 5^{0}C and hot polymerization is carried out 50^{0}C temperature).



Properties

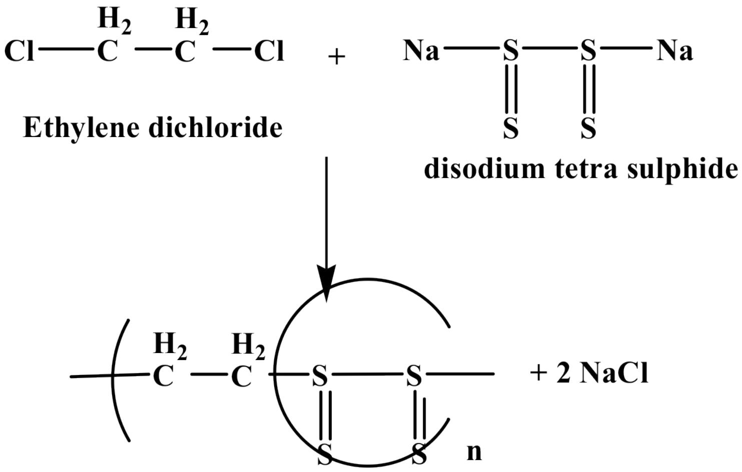
SBR possesses high abrasion and high load bearing capacity. The weather ability of SBR is better than that of natural rubber. SBR gets easily oxidized in presence of traces of ozone present in atmosphere and also it undergoes swelling in presence of oils and solvents.

Applications

SBR rubber is mainly used for making light duty tyres, conveyor belts, shoe soles, floor tyres, gaskets, wires and cable insulation, adhesives, tank linings, carpet baking etc.

THIOKOL RUBBER (POLY SULPHIDE RUBBER)

Thiokol is the condensation polymer, which is obtained by the reaction between disodium tetra sulphide and ethylene dichloride. This reaction results in a bond being formal between the Sulphur and carbon atoms and a long chain molecule is formed.



Properties

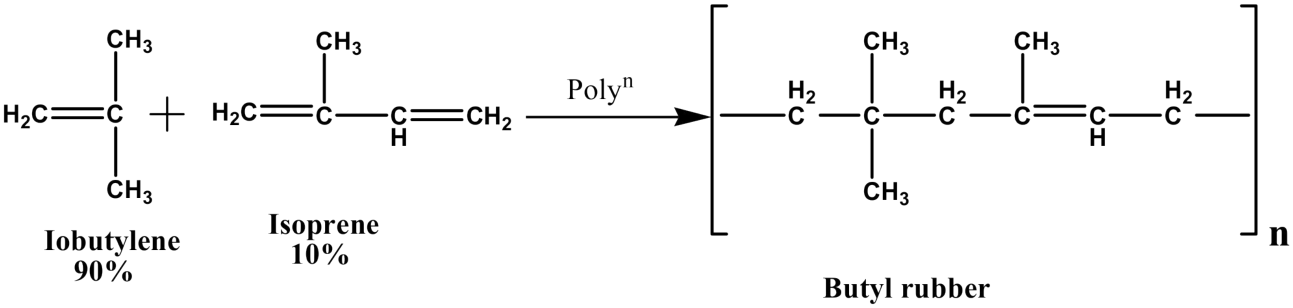
Vulcanization of the Thiokol is not carried with Sulphur because polymer chain is not unsaturated (Sulphur will not react with the polymer). Hence it is not a hard rubber. For vulcanization active metal oxides like ZnO are used. (Sulphur has the ability to react with ZnO and as a result interlinks the chains in to a network). Thiokol's are chemically most oil resistant and solvent resistant and practically unaffected by gasoline, kerosene, etc. They have good resistant to oxygen, ozone, and sunlight, because of low gas permeability. They are advantages in balloon fabrics.

Applications

Thiokol's are used for seals, gaskets, cable insulations, oil tank linings, etc. It is also used as a solid propellant fuel for rocket motors.

BUTYL RUBBER

Butyl rubber is prepared by co-polymerization of isobutene (90%) in presence of small amounts of isoprene (5-10%).



Properties

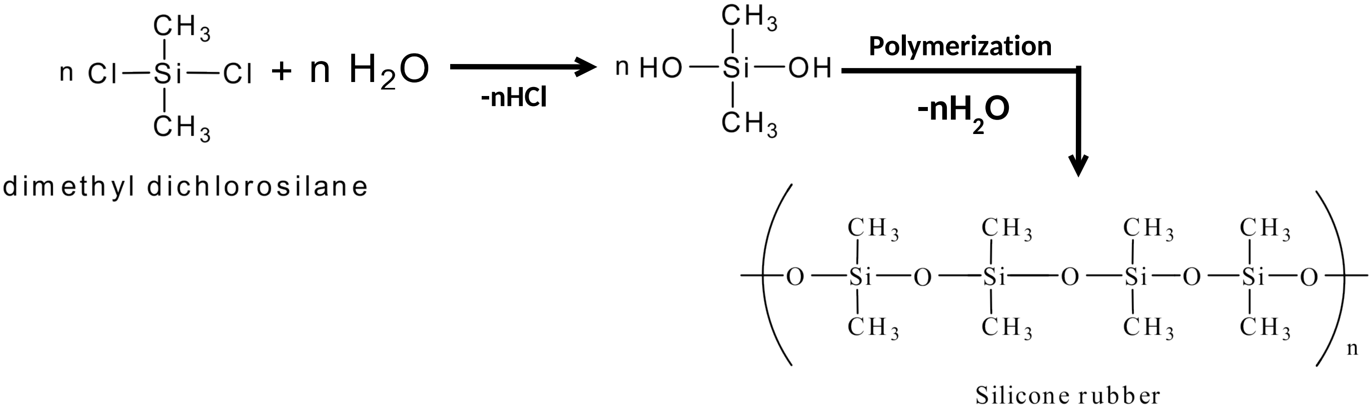
It has excellent resistance to heat, abrasion, chemicals, (H_2SO_4, HNO_3, HCl, HF) and polar solvents (alcohol, acetone) but is soluble in hydrocarbon solvents like benzene. It has high resistance to ozone and good electrical insulating properties. It can be vulcanized, but it cannot be hardened much, due to very low unsaturation.

Uses

For making cycle and automobile tubes, automobile parts, hoses, tank linings, insulation for high voltage wires and cables etc.

SILICONE RUBBER

Silicone rubbers are prepared by mixing high molecular weight linear di methyl silicone polymers with fillers [like finely divided silicon dioxide (SiO_2)] and a peroxide as curing agent. Peroxide helps to form bridges (cross-link) between methyl groups of adjacent chains.



$$n\,Cl-\underset{CH_3}{\overset{CH_3}{Si}}-Cl + n\,H_2O \xrightarrow[-nHCl]{} n\,HO-\underset{CH_3}{\overset{CH_3}{Si}}-OH \xrightarrow[-nH_2O]{Polymerization} \left(-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O- \right)_n$$

Properties

They possess exceptional resistance to prolonged exposure to sunlight, weathering, most common oils, dilute acids and alkalies. They remain flexible in the wide range of temperature (90-250^0C) and hence, find use in making tyres of fighter air craft's since they prevent damage in landing. Ordinary rubber tyre becomes brittle and hence disintegrates.

Uses

1. As a sealing material in air craft engines.
2. For manufacture of tyres for fighter air craft's.
3. For insulating the electrical wiring in ships.

CORROSION

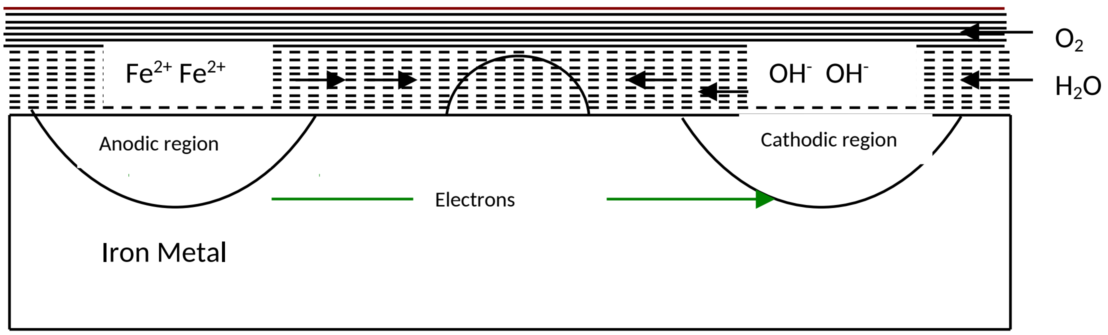
Definition of corrosion: "Corrosion is defined as the destruction of metals or alloys by the surrounding environment through chemical or electrochemical reactions."

Dry corrosion is the direct chemical attack in the absence of moisture by dry gases like SO_2, CO_2, Cl_2, H_2S etc.

Wet corrosion: It is common in nature & which occurs by electrochemical attack on the metal with the moisture and oxygen present in the atmosphere.

Electrochemical theory of corrosion: According to electrochemical theory, when a metal such as iron is exposed to corrosive environment, following changes occur.

A large number of tiny galvanic cells with anodic and cathodic regions are formed.



1. Oxidation of metal takes place at the anodic region. e.g. Fe ® $Fe^{2+} + 2e^-$

   The Fe^{2+} ions dissolve, so corrosion takes place at the anodic region.

2. The electrons travel through the metal from the anodic region to cathodic region.
3. Reduction takes place at the cathodic region. The metal is unaffected at the cathodic region.
4. Fe^{2+} and OH^- ions travel through the aqueous medium and form corrosion product.

5 The corrosion product may undergo further oxidation to form rust.

Reactions

Anodic reaction: As mentioned above, oxidation of metal takes place at anode.

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

<u>Cathodic reaction</u>: At cathode, the reaction is either a) liberation of hydrogen or b) absorption of oxygen.

a) <u>Liberation of hydrogen</u> (in the absence of oxygen)

In acidic medium the reaction is

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

In neutral, the reaction is

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2$$

b) <u>Absorption of oxygen</u> (in the presence of oxygen)

In acidic medium, the reaction is

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

In neutral, the reaction is

$$O_2 + 2H_2O + ne^- \longrightarrow 4OH^-$$

Overall reaction:

$$2Fe^{2+} + 4OH^- \longrightarrow 2Fe(OH)_2$$

$$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 2Fe_2O_3\ 3H_2O$$

Brown rust hydrated ferric oxide

Galvanic Series: The metals are arranged in the order of their corrosion tendencies or corrosion resistance.

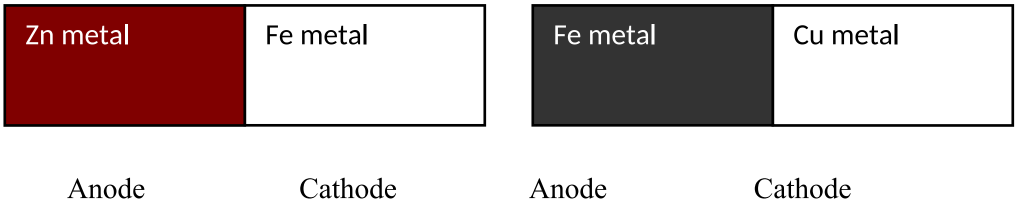
According to galvanic series,

1. The metal/alloy higher up in the series corrodes faster than the metal/alloys in the bottom of the series.
2. Metals like Ti (placed below Ag in galvanic series but above in emf series) and Al (placed below Zn in galvanic series but above in emf series) exhibit resistance to corrosion due to phenomenon called passivation.

3. Passivation: It is the phenomenon of protection of metals against atmospheric corrosion due to formation of a thin layer of non-porous film of metal oxide. The film forms a barrier between the corrosive medium and metal.

Different types of corrosion:

1. <u>Differential metal corrosion</u>:



This type of corrosion occurs when two dissimilar metals are in contact with each other and are exposed to a corrosive environment. The two metals differ in their electrode potentials. The metal with lower electrode potential acts as anode and the other metal with higher electrode potential acts as cathode.

The anodic metal undergoes oxidation and gets corroded. A reduction reaction occurs at the cathodic metal. The cathodic metal does not undergo corrosion.

Example: When iron is in contact with zinc, iron acts as cathode and zinc acts as anode because zinc has lower electrode potential compared to iron. Therefore zinc undergoes corrosion. On the other hand, when iron is in contact with tin, iron acts as anode because iron has lower electrode potential compared to tin. Hence iron undergoes corrosion.

The reactions may be represented as follows:

Cell reactions:

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

At cathode : $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ (Reduction)

Higher the potential difference between the anodic and cathodic metals, higher is the rate of corrosion.

Other examples:

1. Steel screws in copper sheet.
2. Steel screws with copper washer.
3. Bolt and nut made of different metals.

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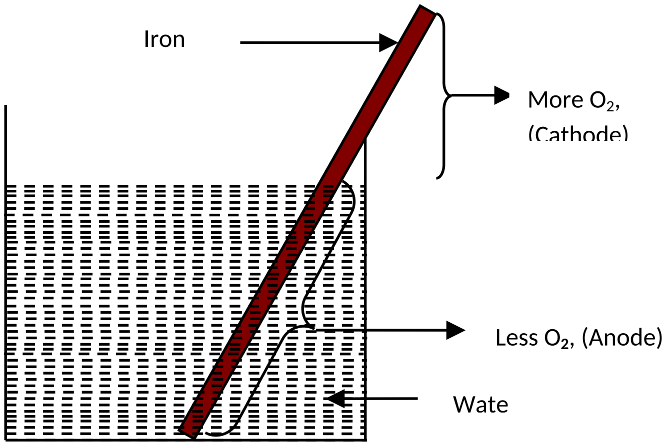
2. Differential aeration corrosion



This type of corrosion occurs when two different parts of the same metal are exposed to different oxygen concentrations. (e.g. An iron rod partially dipped in water.) The part of the metal which is exposed to less oxygen concentration acts as anode. The part which is exposed to more oxygen concentration acts as cathode. The anodic region undergoes corrosion and the cathodic region is unaffected.

The reactions may be represented as follows:

Cell reactions:

At anode : $M \longrightarrow M^{n+} + ne^-$ (Oxidation of metal M)

At cathode : $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ (Reduction of oxygen)

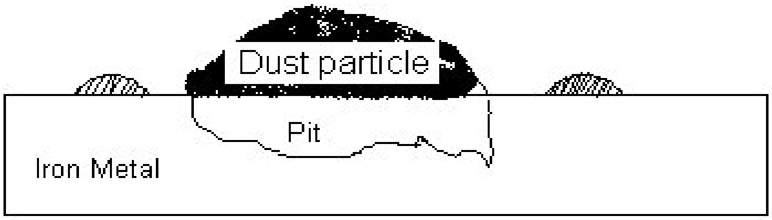
Other examples:

1. Part of the nail inside the wall undergoes corrosion.

2. When a dirt particle sits on a metal bar, the part under the dirt undergoes corrosion.
3. Partially filled iron tank undergoes corrosion inside water.

i) Pitting corrosion: This is an example of differential aeration corrosion.

When a small dust particle gets deposited on a steel surface, the region below the dust particle is exposed to less oxygen compared to the remaining part. As a result, the region below the dust particle acts as anode undergoes corrosion and forms a pit. The remaining region of the metal acts as cathode and is unaffected.



The reactions may be represented as follows:

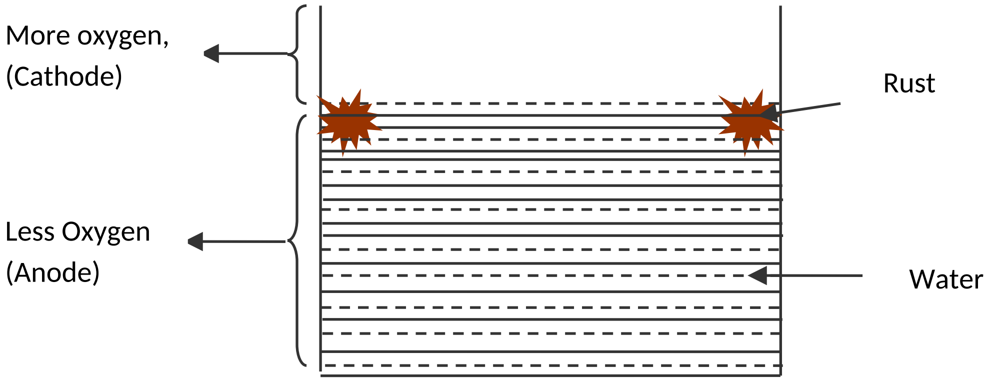
Cell reactions:

At anode : $M \xrightarrow{\hspace{2cm}} M^{n+} + ne^-$ (Oxidation of metal M)

At cathode : $O_2 + 2H_2O + 4e^- \xrightarrow{\hspace{2cm}} 4OH^-$ (Reduction of oxygen)

Formation of a small anodic area and a large cathodic area results in intense corrosion below the dust particle.

ii) Water line corrosion: This is an example of differential aeration corrosion.



When a steel tank is partially filled with water for a long time, the inner portion of the tank below the water line is exposed only to dissolve oxygen, whereas, the portion above the water line is exposed to more oxygen. Thus, the portion below the water line acts as anode and undergoes corrosion. The upper portion acts as cathode and is unaffected.

A distinct brown line is formed just below the water line due to the deposition of rust.
The reactions may be represented as follows:

Cell reactions:

At anode : $M \longrightarrow M^{n+} + ne^-$ (Oxidation of metal M)

At cathode : $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ (Reduction of oxygen)

Other example: Ships which remain partially immersed in sea water for a long time undergo water line corrosion.

3. Stress corrosion:

Stress corrosion occurs when stressed region of metals are exposed to corrosive environments. The stressed region acts as anode and undergoes corrosion. The unstressed region acts as cathode and is unaffected.

Stress corrosion is highly specific in nature. Stress may due to the mechanical operations such as bending, quenching, pressing and poor design.

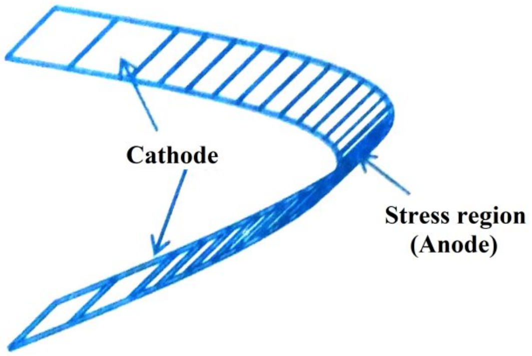
Example: Caustic embrittlement in Mild steel boilers

Factors affecting the rate of corrosion:

1. Nature of the metal: Metals with lower electrode potentials are more reactive and are more susceptible to corrosion. For example, elements such as Mg and Zn, which have low electrode potentials, are highly susceptible to corrosion. Noble metal such as gold and platinum, which have higher electrode potentials, are less susceptible to corrosion.

Exceptions: Metals and alloys which show passivity are exceptions for this general trend. Such metals form a protective coating on the surface which prevents corrosion.

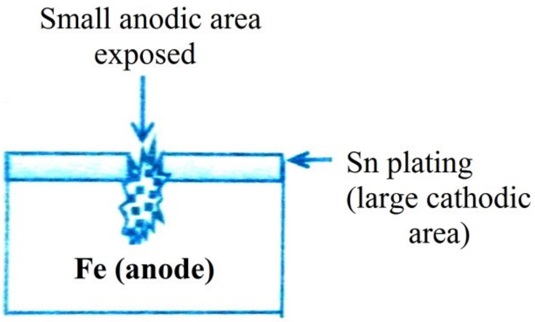
2. Nature of corrosion product: If the corrosion product is insoluble, stable and non-porous, then it



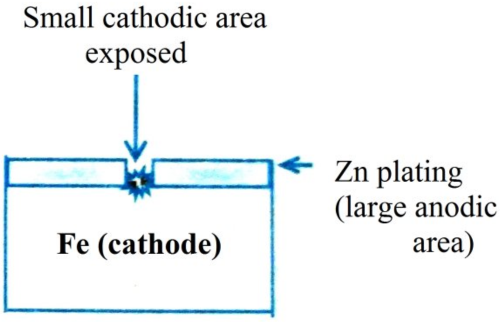
acts as a protective film which prevents further corrosion. The film acts as a barrier between the fresh metal surface and the corrosive environment. On the other hand, if the corrosion product is soluble, unstable and porous, then the corrosion process continues even after the formation of corrosion product.

Example: Aluminium, titanium and chromium form a protective film of metal oxide on the surface. Stainless steel forms a protective film of Cr_2O_3 on the surface. But in the case of Zn and Fe, the corrosion products formed do not have protective value.

3. Anodic and cathodic areas: Smaller the anodic area and larger the cathodic area, more intense and faster is the corrosion. For example, a broken coating of tin on iron surface results in intense corrosion at the broken region. Iron is anodic to tin. Exposed region of iron acts as anode with small area. Tin acts as cathode which has large area.



(a) Rapid corrosion at small anodic area



(b) Slow corrosion at small cathodic area

4. pH of the medium: In general, lower the p^H of corrosion medium, higher is the corrosion rate. (Exception: Metals like Al, Zn etc. undergo fast corrosion in media with high pH)
Iron does not undergo corrosion at p^H greater than 10. This is due to the formation of protective coating of hydrous oxides of iron.

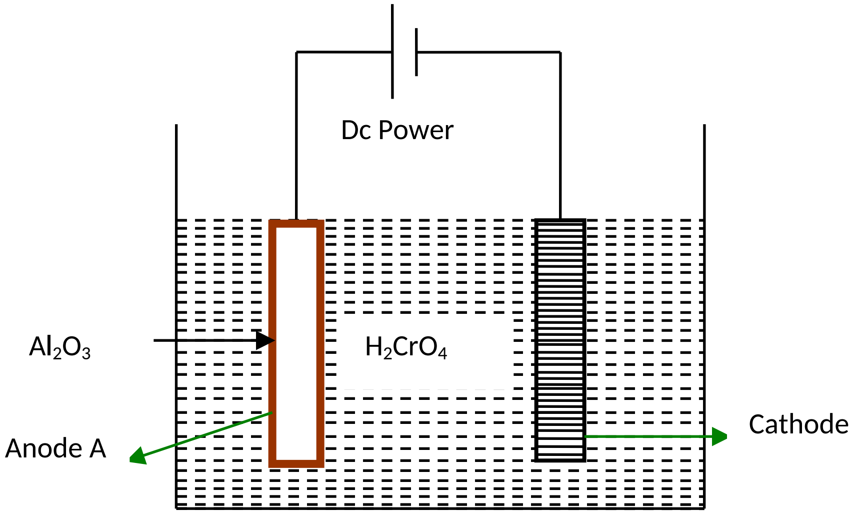
5. Temperature: Higher the temperature, higher is the rate of corrosion.
In general, the rate of a chemical reaction increases with increase in temperature. Corrosion is one such chemical reaction. Therefore, the rate of corrosion increases as the temperature increases.
Increase in temperature increases the ionic conductivity of the corrosive medium. This also contributes to the increase in corrosion rate.

6. Conductance: As the conductivity of the corrosion medium increases, the corrosion rate also increases. Higher the conductivity of the medium, faster the ions can migrate between the anodic and cathodic regions of the corrosion cell, in turn, faster will be the change of electrons at the electrode surfaces. This facilitates higher corrosion rate.

Corrosion control

Inorganic coating

1. Anodizing (Anodizing of aluminum): When aluminum metal is made anodic in an electrolytic bath with sulphuric acid or chromic acid as the electrolyte, a thin layer of aluminium oxide (Al_2O_3) is formed on the surface. This process is called anodizing of aluminium or anodic oxidation of aluminum.



When anodized aluminium is exposed to a corrosive environment, the Al_2O_3 layer on the surface acts as a protective coating, hence corrosion is prevented.

Other metals such as Mg, Ti etc. can also be anodized.

Electrolyte	5 - 10 % of chromic acid

Temperature	35 °C
Thickness of oxide layer	2 – 8 µm

(Note: On anodizing, Al_2O_3 is formed on the surface as a porous layer. The layer may be made compact by sealing, which involves heating with boiling water or steam. During sealing, Al_2O_3 is converted into $Al_2O_3.H_2O$ which occupies higher volume. Therefore, the pores are sealed.)

Applications: Metals such as Al, Mg, Ti etc. are anodized to control corrosion.

2. Phosphating: Converting the surface metal atoms into their phosphates by chemical or electrochemical reactions is called phosphating

The phosphating bath contains three essential components:

(i) free phosphoric acid,
(ii) a metal phosphate such as Fe, Mn phosphate and
(iii) An accelerator such as H_2O_2, nitrites, nitrates.

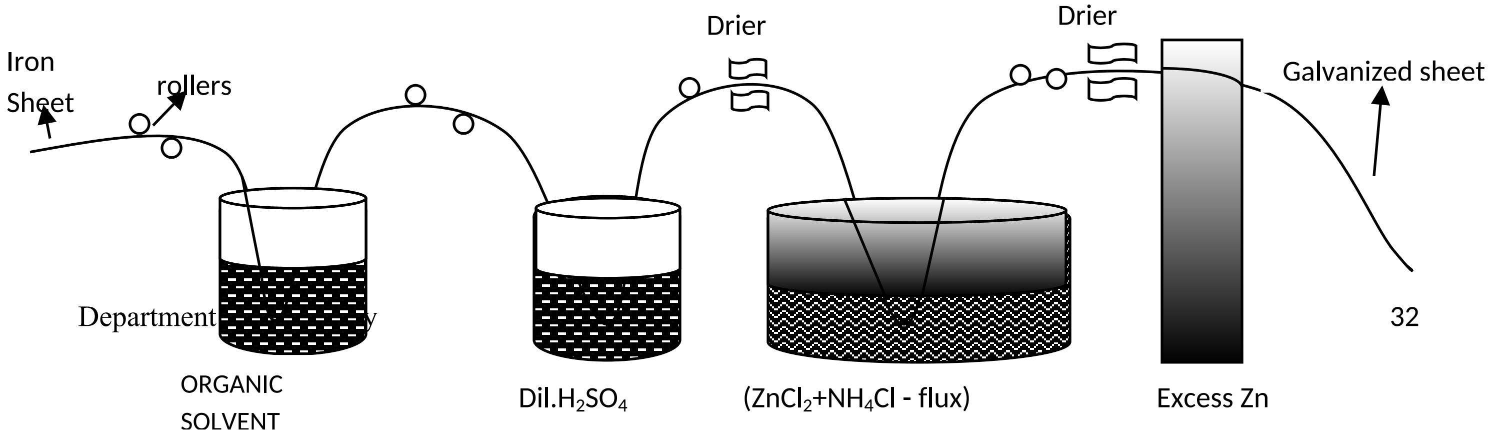
Phosphating not only improves the corrosion resistance but also imparts good paint adhesion quality to the surface.

Applications: Phosphate coating is given as an under layer before painting the car bodies, refrigerators and washing machines.

Metal coating

1. Galvanizing: Galvanizing is the process of coating a metal surface such as iron with zinc metal. Galvanizing of iron is an example of anodic metal coating on the surface of a cathodic metal.

Galvanization is carried out by hot dipping method. It involves the following steps.



1. The metal surface is washed with organic solvents (CCl_4, toluene) to remove organic matter on the surface.
2. Rust is removed by washing with dilute sulfuric acid.(Pickling process)
3. Finally, the article is washed with water and air-dried.
4. The article is then dipped in a bath of molten zinc. (Molten zinc is covered with a flux of ammonium chloride to prevent the oxidation of molten zinc.)
5. The excess zinc on the surface is removed by passing through a pair of hot rollers.

Application: Galvanization of iron is carried out to produce roofing sheets, fencing wire, buckets, bolts, nuts, pipes etc.

Corrosion inhibitors

Corrosion inhibitors are chemical substances which are added in small quantities to the corrosive environment to decrease the rate of corrosion. Inhibitors slow down the anodic reaction or the cathodic reaction generally by forming a protective film on the anodic region or the cathodic region. There are two types of corrosion inhibitors namely,

1. Anodic Corrosion Inhibitors

2. Cathodic Corrosion Inhibitors

1. Anodic corrosion inhibitors

Compounds such as chromates, molybdates and tungstates are used as anodic corrosion inhibitors. They react with the surface atoms at the anodic region and form a protective film of oxide or metallate. This protective film acts as a barrier between the metal surface and the corrosive environment. Anodic corrosion inhibitors must be added in sufficient quantities. If insufficient quantity is added, then a part of the anodic region is covered with the protective film leaving the remaining anodic region exposed to the environment. Formation of small anodic area results in intense corrosion.

2. Cathodic Corrosion Inhibitors

The cathodic reaction may be

i) Liberation of Hydrogen

ii) Absorption of Oxygen

When the cathodic reaction is liberation of Hydrogen, the cathodic reaction may be retarded by

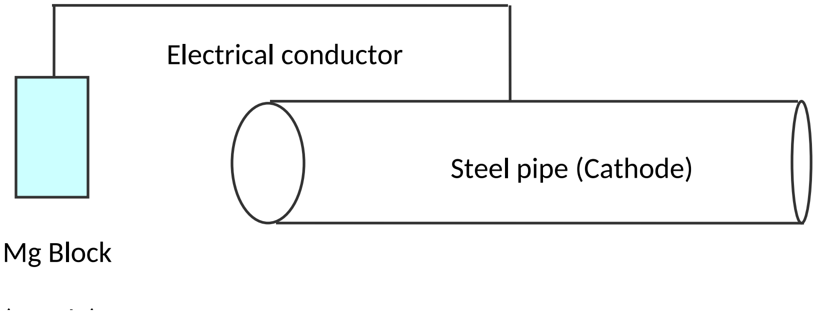
i) By forming an adsorbed layer on the cathode surface

ii) By increasing the hydrogen over voltage

When compounds such as amines, urea and thiourea are added to the corrosion medium, they are adsorbed on the cathodic region forming a protective film. This film prevents the migration of H^+ ions on to cathodic surface.

Cathodic protection:

1. Sacrificial anode method:



In cathodic protection, the metal to be protected is completely converted into a cathode. Since cathodes do not undergo corrosion, the metal is protected against corrosion.

In sacrificial anode method, the metal to be protected is electrically connected to a more active metal. For example, when steel is to be protected, it may be connected to a block of Mg or Zn. In such a situation, steel acts as cathode and is unaffected. Mg and Zn act as anode and undergo sacrificial corrosion. When the sacrificial anode gets exhausted, it is replaced with new ones.

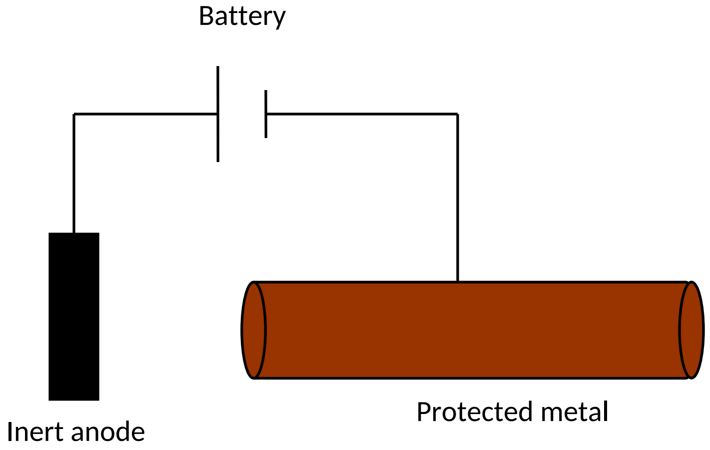
Other examples: i) Mg bars are fixed to the sides of ships to act as sacrificial anode.

ii) Mg blocks are connected to buried pipe lines.

Impressed current method (impressed voltage method)

In cathodic protection, the metal to be protected is completely converted into a cathode. Since cathodes do not undergo corrosion, the metal is protected against corrosion.

In impressed current method, the metal to be protected is connected to the negative terminal of an external d.c. power supply. The positive terminal is connected to an inert electrode such as graphite. Under these conditions, the metal acts as cathode and hence does not undergo corrosion. The inert electrode acts as anode; but it does not undergo corrosion because it is inert.



TEXT BOOKS

1. Engineering Chemistry by M.M.Uppal, Khanna Publishers (2001 edition).
2. A text Book of Engineering Chemistry- by P C Jain and Monica Jain, Dhanapatrai Publications, New Delhi.(2015 edition)

REFERENCE BOOKS

1. Principles of Physical Chemistry B.R.Puri, L.R.Sharma & M.S.Pathania, S.Nagin Chand &Co., (2008 edition).
2. Industrial Chemistry by B. K. Sharma, GOEL Publishing House (2014 edition).
3. Industrial Electrochemistry, Second Edition by Derek Pletcher & Frank C. Walsh publisher: Chapman & Hall, USA (1993 edition).

TEXT BOOKS

1. Engineering Chemistry by M.M.Uppal, Khanna Publishers (2001 edition).
2. A text Book of Engineering Chemistry- by P C Jain and Monica Jain, Dhanapatrai Publications, New Delhi.(2015 edition)

REFERENCE BOOKS

1. Text Book of Polymer Science by V. R. Gowarikar, N.V. Viswanathan and J. Sreedhar, Wiley-Eastern Ltd (2006 edition).