Lecture Notes (Part.)

On

Corrosion and its Prevention

Subject code – MTT604

Prepared By : Goutam Kumar Majhi
Lecturer
Metallurgical Engineering Department
UGIE Rourkela
Email id : majhi.goutam5@gmail.com
Contact No: +91-7899050056

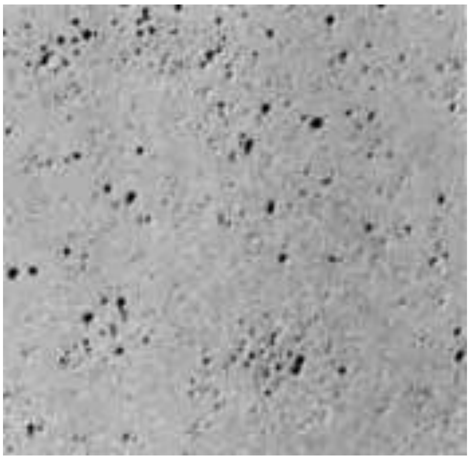
Pitting Corrosion

- Pitting Corrosion is a form of extremely localized attack, the rate of attack being greater at some areas than others.
- Pitting is the most destructive form of corrosion and result in sudden failure of equipment due to formation of holes.

CHARACTERISTICS

Following are the characteristics of pitting corrosion:

1. Active metals are most susceptible to this type of attack, e.g. chromium, aluminium and alloys containing these elements.
2. Pits are usually formed randomly on the surface. They are sometimes isolated or so close together that they look like a rough surface.
3. Pits are, generally, described as a hole or cavity with the surface diameter about the same or less than the depth.
4. It is often difficult to detect pits because of their small size and because they are covered with corrosion products.
5. Pitting is a corrosion process which is autocatalytic, self-stimulating and self-propagating.
6. Pits are usually elongated in the direction of gravity.
7. Pits are generally initiated on the upper surface of the horizontally placed specimens.
8. Pitting usually occurs under stagnant conditions such as crevices, liquid trapped in the part of an inactive pipe system, or liquid stored in a container.



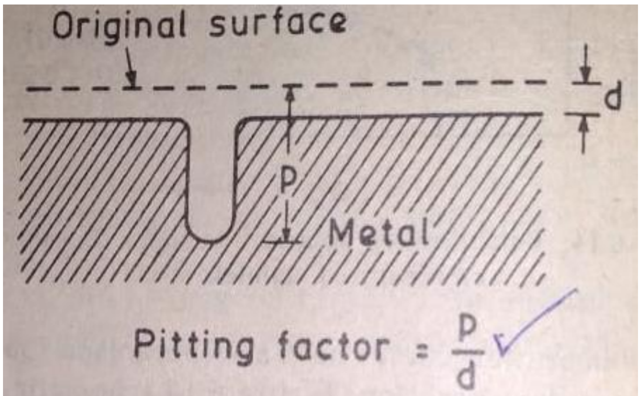
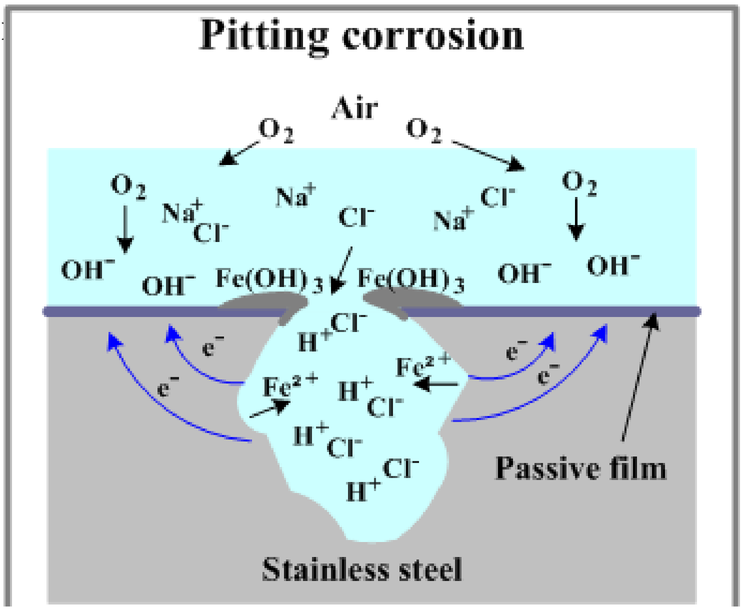


Fig. 6.15. Sketch showing the pitting factor in terms of average metal penetration (d) and depth of deepest pit (p).

Pitting in 18-8 SS by acid chloride solution

Mechanism

- Pitting nucleates by formation of a corrosion cell between a small anodic area and large cathodic area. This small anodic area is known as pit.
- This could be due to heterogeneity in metal, or in the film on metal surface or prese



$$M^+Cl^- + H_2O = MOH\downarrow + H^+Cl^-$$

Prevention

- Select suitable materials that show minimum proneness to pitting in the type of environment being used.
- Control of environment aggressiveness through monitoring chloride concentration level, acidity.
- Use of protective coatings.
- Application of cathodic protection.

CORROSION FATIGUE

- The simultaneous action of cyclic stress and chemical attack is known corrosion fatigue.
- Corrosion fatigue can be defined as the reduction in fatigue strength due to presence of corrosive environment.
- Previously formed pits act as notches and decreases the fatigue strength. The rate o under corrosive environment.

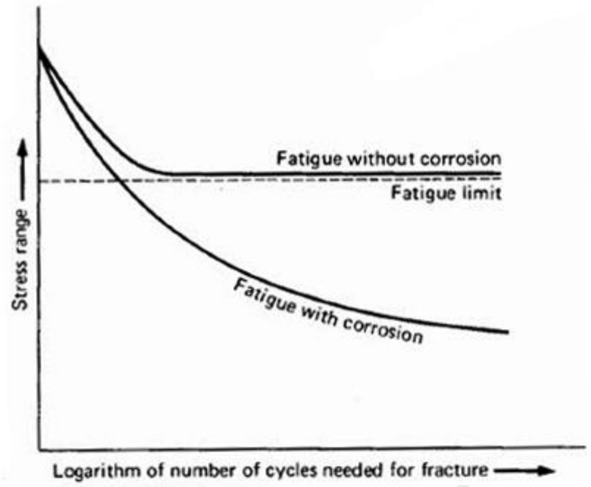


Fig: Fatigue curve(S-N) of ferrous material with and without corrosion

Prevention

- Lowering the tensile strength of the material.
- Reducing stress on the component.
- The choice of material for this type of service should be based on its corrosion resistant properties rather than fatigue properties.
- Nitriding, shot peening is done to avoid corrosion fatigue.
- Application of cathodic protection and inhibitor.

Galvanic Corrosion

- When two or more dissimilar metals/alloys immersed in a corrosive solution(electrolyte) and externally brought in electrical contact with each other, the existence of a potential difference between them results in a flow of current in the external circuit.
- Less corrosion resistant metal acts as anode suffering degradation and the more resistant metal acts as cathode with almost no degradation as compared to their behavior in the same solution if they were not electrically connected or would have been individually immersed in the solution.
- Driving force for the flow of current or corrosion is the developed potential difference between the two metals.

Prevention

- Choose alloys which are close to each other in the Galvanic series.
- Avoid area effect of a small anode and large cathode.
- Electrically insulate dissimilar metals wherever possible.
- Apply coatings with caution and arrange regular maintenance particularly for the anodic portion.
- Using inhibitors to reduce the aggressiveness of the environment.

Stress corrosion cracking (SCC)

- The failure of material by combined action of a tensile stress and corrosive medium is known as stress corrosion cracking.
- Two classic examples of SCC are the season cracking of brass and caustic embrittlement of steel.
- In this type of corrosion, the tensile stress rupture the passivated film which results easy corrosion of the structure , which eventually results in initiation of crack.

Prevention

- Lowering the stress by annealing, or by using thicker section, or by reducing the load.
- Modification or elimination of critical environment by degasification or by adding inhibitors.
- Selection of proper alloy.

- By cathodic protection and by shot-peening.

Cavitation corrosion

- Cavitation damage is a special form of erosion corrosion which is caused due to the formation and collapse of vapour bubbles in a corrosive environment near a metal surface.
- Cavitation damage occurs on surfaces which are in contact with fluids at high velocities and where frequent pressure changes are encountered, e.g., hydraulic turbines, ship propellers, etc.
- Cavitation damage can also occur in the absence of a corrosive environment, but the attack becomes more severe when there is combine action.
- Cavitation corrosion has been attributed to the combined action of mechanical effect and corrosion.
- It is assumed that the collapsing vapour bubbles destroy protective surface films increased corrosion. This mechanism is shown schematically in Fig.

- The steps are as follows: (i) cavitation bubble forms on the protective film; (ii) the bubbles collapse and destroy the film; (iii) the newly exposed metal surface corrodes and the film is reformed; (iv) cavitation bubble forms at the same spot; (V) the new bubble collapses and destroys the film (vi) the exposed area corrodes and the film reforms. Repetition of this process results in deep

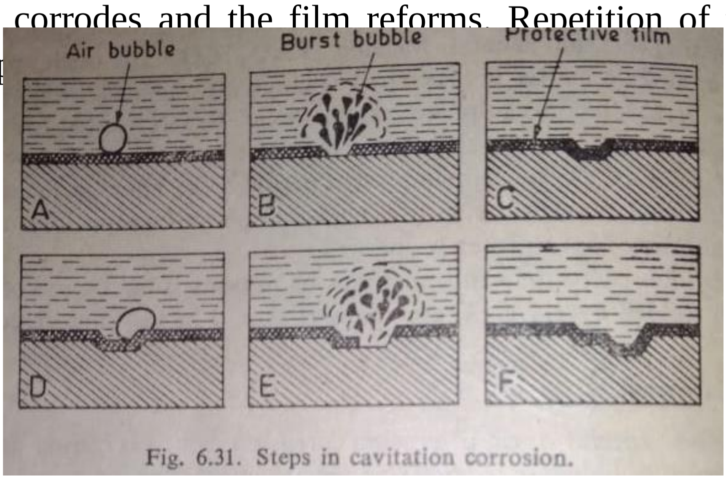


Fig. 6.31. Steps in cavitation corrosion.

Prevention

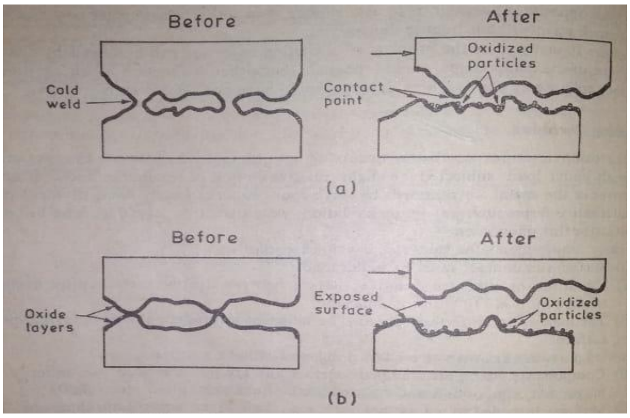
- Proper selection of material.
- Use of cathodic protection.
- Application of coatings.
- By changing the design of structures.

Fretting Corrosion

- It is a type of corrosion occurring at contact areas between two surfaces under load subjected to vibration and slip.
- The basic requirements for this type of corrosion are: the surface in contact must be under load, vibration or repeated relative motion and plastic deformation.
- There are two mechanisms which have been proposed to explain damage due to Fretting corrosion:

1. *Wear Oxidation Mechanism*: According to this mechanism, the two surfaces make contact at only a small number of high points, where cold welding or fusion occurs due to applied load. These contact points are ruptured during subsequent relative motion and as a result fragments of metal are removed. These fragments immediately get oxidized due to their small size and frictional heat (Fig. a). This process repeats itself.

2. *Oxidation Wear Mechanism*: According to this mechanism, metal surfaces are protected from atmospheric Oxidation by an adherent oxide film. When metals are placed in contact under load and are subsequently subjected to repeated motion, the oxide layer ruptures at high points and results in oxide particles (Fig. b). The exposed metal surface re-oxidizes, and the process repeats itself.



Prevention

- Using hard-metals, or even cold-worked or shot-peened metals reduce Fretting-corrosion.
- Use of gaskets to absorb vibrations and exclude oxygen at surfaces.
- Increase the load on surfaces to prevent slip of surfaces.
- Lubricate the parts with low viscosity oils and grease.

High temperature oxidation corrosion

- Corrosion of metal can occur in the absence of a liquid electrolyte when it is exposed to an oxidizing gas, e.g.-, oxygen, Sulphur, or halogens, at ambient or elevated temperatures. This is sometimes called scaling, tarnishing, dry corrosion, or high temperature oxidation.

- As the temperature increases, Oxidation resistance of most metals decreases. This type of attack is a serious problem in many major industries, such as an aircraft, automobile, chemical, electrical, metallurgical, paper and pulp, and power

- In one of the earliest studies on oxidations, Piling and Bedworth proposed that the oxidation resistance is related to the volume ratio of oxide and metal. This ratio is called *Pilling-Bed- worth ratio*.
  The ratio R indicates the volume of oxide formed from a unit volume of metal.
  If the value of R is close to unity (1) then the oxide layer is supposed to be a protective layer.

Prevention

The loss due to high temperature oxidation can be minimized by using
High temperature alloys like Ni-alloys, use of coatings.

Stray Current Corrosion

- Stray current corrosion refers to type of corrosion resulting from stray current- the current flowing through paths other than the intended circuit.
- All metallic structures buried underground are susceptible to this type of corrosion. Ex: DC railways, tunnels, underground pipe lines etc.
- This corrosion is independent of the environmental factors .

Prevention

- Identification of the stray current source.
- Maintaining good electrical connection and insulation.
- Installation of impressed current cathodic protection.

Chapter - 6

Corrosion Prevention

Corrosion occurs when metals come in contact with a corrosive atmosphere. Thus, corrosion can be prevented by:

1. Change of metal/alloy
2. Design improvement
3. *Change of metal electrode potential*
4. *Use of coating*
5. *Change of environment*

Cathodic Protection

It is a method of reducing or preventing corrosion of a metal by making it cathode in the electrolytic cell. There are two methods available for cathodic protection:

(i) Sacrificial anode method
(ii) Impressed current method

Sacrificial anode method

- In this method, another metal, which has more negative electrode potential than the structure to be protected, is connected electrically to the structure, which now acts like a cathode.
- The structure is protected at the sacrifice (corrosion) of another metal, and that is why, this name is given to the method.
- Mg and Mg alloy are widely used. Zn is also often used. Sacrificial anodes are replaced as soon as consumed.
- This method is used for protection of under-water parts of ships, underground pipes, steel water-tanks, water heaters, condenser-tubes, oil-cargo-ballast tanks etc. Galvanised sheet is basically sacrificial-protection of steel, where Zn is sacrificed.

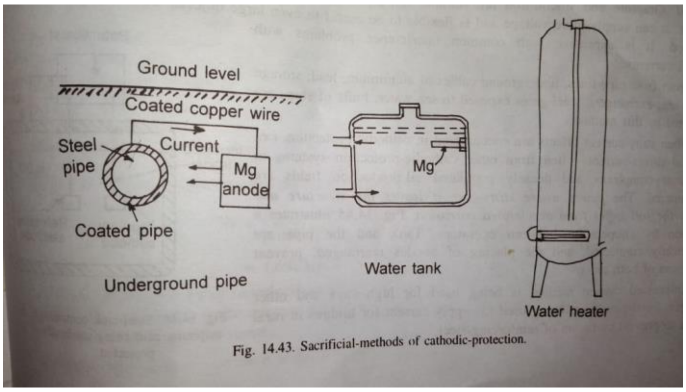


Fig. 14.43. Sacrificial-methods of cathodic-protection.

Impressed current method

- In this method, the given metallic structure is made the cathode by the use of external current by connecting the negative terminal of the external power-supply source to the metallic structure, and the positive is connected to an inert anode of scrap steel, aluminium, graphite, or silicon-iron.
- Apart from pipe-lines, underground cables of aluminium, lead; storage tanks, heat-exchangers, steel-gates exposed to sea-water, hulls of ships are protected by this method.
- Often stray-current effects are encountered in this type of cathodic protection.

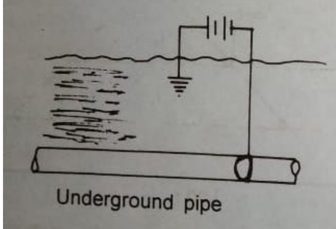


Fig. 14.44. Impressed-voltage makes the pipeline a cathode.

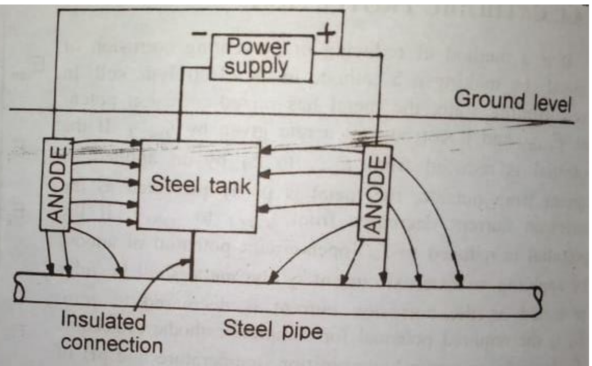


Fig. 14.45. Cooperative proper design to prevent stray-current corrosion.

Anodic Protection

- It is a technique to control the corrosion of a metal surface by making it anode of an electrochemical cell by controlling the electrode potential in a zone where the metal is passive.
- This technique is only applicable to those metals which exhibit passivation (protective film).
- This technique is mostly used for steel and stainless steel in extreme corrosive conditions.

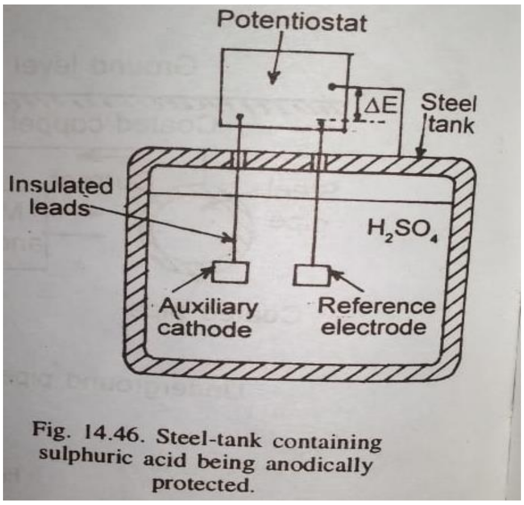


Fig. 14.46. Steel-tank containing sulphuric acid being anodically protected.

Coatings

Cost is a very important factor while choosing an engineering material. Instead of using a costly non-corroding material an easily corrodible alloy like steel can be used by protecting it from environment. By far the most important protective mean is one kind of thin coating. *The chief function of such a coating is to provide an effective barrier between the metal and its environment*. The coat itself should have good resistance to corrosion, should be adherent and cover the metal completely. The coatings are broadly classified as

i. Metallic Coatings

ii. Non-metallic coatings

METALLIC COATINGS

Protecting the metals by metal-coating is an old and very widely used practice as they are more durable, more decorative and provide better protection against corrosion.

Metallic coatings are classified as:

i. Cathodic Coatings

In such a case the coating metal is cathodic with respect to the base metal. Coatings of tin, nickel and chromium are cathodic coatings as these are higher than steel in the galvanic series . These coatings provide a physical barrier between the metal and the environment. When the coating is dense. nom-porous, continuous corrosive medium did not come in contact with base metal, and the base metal does not corrode. Coating being cathodic does not corrode. Ex- Nickel and chromium plating on steel for automobile, coating on tin plate tube used as food container.

ii. Anodic Coatings

The coating metal is anodic as compared to the underlying metal. The anodic coating provide galvanic protection to the base metal, in addition to acting as a physical barrier between the base metal and the environment. This type of coatings offers a sacrificial type cathodic protection.

Ex: Galvanised corrugated steel sheets used for roofing, automobile parts etc.

METHODS OF APPLYING METALLIC COATINGSs

Some common methods of applying metal coatings are:

1.Electroplating/ Electrodeposition: The part is made cathode by dipping it in a solution of metal to be plated by passing direct current between the part and another electrode. The coats give thin and uniform coat. Cadmium and decorative Ni and Cr coatings are almost always produced by electroplating.

2. Metallizing or Flame Spraying: the metal wire or its powder is fed through a melting-flame (oxy-acetylene) to blow finely divided liquid particles on to the surface. Metal particles solidify in air. Zinc, tin or lead are flame-sprayed. Coatings are porous and non-protective in severe wet corrosive conditions. Tank cars, vessels, bridges, ship-hulls, fabricated steel products, refrigerators are flame-sprayed. This method produces thick coats and any metal can be spray-coated.

3. Hot-Dipping: Clean steel plates are immersed in a molten metal bath of low melting-point metals mainly zinc, tin, lead and aluminium. Galvanised sheet is produced by hot-dipping. Thin coats are difficult to produce by this method.

4.Vapour Deposition: In high vacuum chamber, the coating metal is vapourised by heating electrically and ne vapour deposits on the parts to be coated. Steel is vapour-coated by aluminium. As it is an expensive method, critical part such as high-strength parts for missiles and rockets are vapour-coated.

5. Diffusion-Coating or Surface Alloying: The parts to be coated are packed in powdered solid metal, (or exposed to gaseous atmosphere containing the metal) to be coated. High temperature treatment causes the diffusion and may form the alloy. The coatings are relatively thick. Ex: Alonized Al_2O_3 on steel plate.

6. Cladding: It is the joining of two metal or alloys by forming a strong bond between them. The bond is generally formed by casting a liquid metal on another solid metal or could be by any other method. The coats are thick. Ex- alclading.

2. NON-METALLIC COATINGS

These coatings can further be divided into two types

(i) Organic coatings (ii) Inorganic coatings

(i) Organic coatings

These are the inert organic barriers applied on materials as a barrier to corrosion.

Ex: Paints, varnishes, enamel etc.

These types of coatings required surface preparation, primary coating (primer) before application of organic coating.

(i) Inorganic Coatings

Various inorganic coatings on metal surface are:

Vitreous coating or glass-steel- Steels with glass coatings, where glass linings act as the barrier.

Portland cement – It also known as concrete which saves the TMT bars getting corroded.

Chemical conversion coating – These are some chemicals which on application on the metal surface, reacts with the metal and creates a passivated layer.

INHIBITORS

- These are the substances which when added to the corrosive environment decreases the rate of corrosion by reducing the severity of the environment.
- Inhibitors either act as a barrier by forming a adsorbed layer or retard the cathodic or anodic reaction.

Types of Inhibitors

1. **Chemical Passivators:** Certain substances while added to the corrosive medium results in formation of passivated layer on the metal surface.
   Ex: Chromate, Nitrate and ferritic salts.
2. **Absorption Inhibitors:** These are organic compounds which get absorbed on the entire anodic as well as cathodic surfaces to act as a blanket and thus affect the reactions. Inhibitors doesn’t allow the acids to react with base metal.
   Ex: Hexamethylene tetramine and thiourea etc.
3. **Film-Forming Inhibitors:** These are the inhibitors which stop corrosion by forming a blocking or barrier film of a material other than the actual inhibiting species.
   Ex: Calcium salt, zinc salt, benzoate etc.
4. **Vapour-phase Inhibitors:** When these types of inhibitors are added a vapour, phase is created. This vapour gets condensed onto the metal surface and it is spread throughout. The condensed phase is hydrophobic (water repellent) so saves the metal from getting corroded.
   Ex: Dicyclohexylamine, benzotiazole etc.

Model Questions

1.

(a) Express corrosion rate with an empirical formula.

(b) Write down one example each of oxidation and reduction reaction.

(c) Define electrode potential.

(d) Write the working principle of electrochemical cell with its examples.

(e) Sea water or normal water which one is more corrosive and why?

(f) Define current density and its unit.

(g) Write the various causes for atmospheric corrosion.

(h) What is stray current corrosion?

(i) Give four examples of organic coating.

(j) Define process of Cladding.

(k)What is enamel?

2.

(a) Broadly classify corrosion and briefly explain them.

(b) Discuss Faraday’s laws of electrolysis.

(c) Briefly describe concentration cell with a neat sketch.

(d) With a suitable example explain the phenomena of passivation.

(e) Explain mechanism of Fretting corrosion and its prevention.

(f) Define grain boundary corrosion. Explain the phenomena of sensitization in steel.

(g) What are inhibitors? Briefly explain various type of inhibitors.

(h)Describe the methods used for metallic coatings.

(i) Describe in detail, the various factors that affect corrosion.

3.Define Corrosion. Discuss about the direct and indirect losses that occur due to corrosion.

4.Explain the construction, application and limitation of EMF series. How Galvanic series is better than EMF series?

5.Discuss about the various metallurgical factors that affects corrosion of metals.

6.Write short notes on

(a)Galvanic corrosion (b)Pitting corrosion (c) Fretting Corrosion (d) Galvanic Corrosion (e)Corrosion Fatigue (f) Pitting Corrosion

7.Explain cathodic and anodic protection with suitable diagram and their applications.