Corrosion inhibitors

- Inhibitors are chemicals – inorganic or organic – which react with corroding surfaces or the environment, to give the surface a level of protection.
- This may be by forming a film thereon or forming an inert compound.
- Inhibitors are used in a wide variety of applications such as oil pipelines and industrial water cooling systems.
- Advantage of using inhibitors is that it can be implemented or changed without disrupting the process in which it is being implemented.

Classifications of inhibitors

- Organic & Inorganic
- Organic inhibitors function by adsorbing on metallic corroding surfaces
- Examples are benzotriazole, mercaptans etc. they usually contain N, S or O in their structures
- Inorganic inhibitors, further divided into oxidising (chromates & nitrates) and non oxidising(phosphates &silicates) function by reacting with metallic surfaces forming adherent passivating layers

Cathodic and anodic inhibitors

- Add cathodic inhibitor to a corroding system, the geometry of the Evan's diagram changes with a reduction in i_{corr} and E_{corr}
- Add anodic inhibitor, the geometry of the Evan's diagram changes as well but, the corrosion potential, E_{corr} increases, while I_{corr} drops.
- Describe with E/logi diagram
- They interfer with the reaction in one manner or the other
- Increase in anodic or cathodic polarization reaction.
- By forming resistance in movement or diffusion

ions to or from the metal surface.

Cathodic inhibitors- safe inhibitors

- In natural environments, the cathodic reactions driving corrosion processes are:

$H^+ + 2e \rightarrow H_2$ & $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

- Both rxns consume H^+ thus OH^- increases
- Add Mg^{2+} or Zn ions, as inhibitors, these rxns occur,

$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$ & $Zn^{2+} + 2O \rightarrow Zn(OH)_2$

- With the deposition of the corresponding metal hydroxides at the cathode sites; which eventually cover the surface of the metal.
- Thus, Mg^{2+} and Zn^{2+} are cathodic inhibitors which are widely used in practice.

Safe inhibitors

- In a bicarbonate environment.
- $HCO_3^- + OH^-$ ⌖ $CO_3^{2-} + H_2O$
- $Ca^{2+} + CO_3^{2-}$ ⌖ $CaCO_3$
- So, freely corroding steel in natural water will be protected by scales of $CaCO_3$ formed initially, at the cathode sites. Total coverage with the $CaCO_3$ occurs over a period time.
- Cathodic inhibitors are called 'safe' inhibitors for these reasons
- in practice are As_2O_3, referred to as cathodic poison.
- For iron corroding freely as:3Fe $3Fe^{2+} + 6e^-$
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- On adding As_2O_3 to the system the cathodic reaction is:
- $2As^{3+} + 6e^-$ As - - - - 3.8
- Arsenic, will deposit on the surface of iron to stifle corrosion reactions on the metal.
- However, great care should be taken in the use of As_2O_3, Arsenic is a **POISON**

Vapour phase inhibitors

- These are organic compounds with vapours which have inhibitive effects.
- They are usually used for temporary protection of critical machinery parts (such as bearing) against rusting by moisture during shipment
- A good example of vapour phase inhibitors is dicyclohexylammonium nitrite.
- It decomposes slowly, however, in a well packaged environment it has been shown to protect steel for many years.
- Other examples are ethanolamine carbonate, cyclohexylamine carbonate. A mixture of urea and sodium nitrate have been used in practice with great success

Inhibition efficiency

- The efficiency of inhibitor can be expressed by the measure of improvement in corrosion rates.
- Thus, inhibitors efficiency % = $\underline{100 \times (CR_U - CR_I)} / CR_U$

  where CR_u is corrosion rate in uninhibited solution, and CR_I is corrosion rate in inhibited solution.
- The efficiency of corrosion inhibitors increases with increase in inhibitor concentrations.
- good inhibitor should have 95% inhibition at a conc in the region of 0.008% while 90% efficiency may be observed at a conc of about 0.004%. For most good inhibitors, a parabolic curve for a plot of % efficiency versus inhibitor concentration should be obtained.

Selection of inhibitors

- There are no fast and hard rules or equations & theories to guide the choice which are very limited.
- The choice of inhibitor use in the field is a major challenge because synergism is often present between different inhibitors and the environment to be controlled.
- However, mixtures of inhibitors are the usual choice in commercial formulations.
- Efforts are still being carried on by corrosionists to formulate and compound more effective inhibitors for varied environments.

Inhibitors for aqueous corrosion

- Neutral solutions: Where Ferrous materials are employed, Benzoates are preferred. Benzoates are also suitable and tolerated where Zinc and Aluminum alloys are the materials employed.
- Tannins, which have variable compositions, being a natural product are suitable for Aluminum materials as well as ferrous materials.
- Amines, Quaternary ammonium compounds are suitable inhibitors for ferrous materials in neutral solutions as well. However, for $[R_4N]^+X$, a hypothetical quaternary amine, where R is between C_{12} and C_{18}, inhibitor efficiency is much better if the halide, X is iodine, I.
- For copper based alloys in neutral solutions, the preferred inhibitor species are benzotriazole and mercaptobenzotriazole.

Inhibitors for acid solutions

- For ferrous materials corroding in acidic systems, choice of inhibitors are,
- substitued thioureas, $H_2N - CS - NH_2$, which are good for aluminum alloys as well.
- Pyridine and quinoline, however, this should not be used where copper is present.
- Quaternary ammonium compounds are equally good for ferrous materials corroding in acidic solutions. However a synergistic effect is obtained when a mixture of quaternary ammonium compounds and substituted thiourea is employed as the inhibitor of choice. However, it is dangerous to make the mixture alkaline.
- Long chain amines are also good inhibitors for ferrous materials corroding in acidic solutions.

Corrosion control in industrial water systems

- Two major problems generally encountered with water systems.
- Microbial corrosion, and blocking of heat exchange surfaces causing reduction of efficiency and lack of uniformity in trickling over cooling tower timbers.
- Three types of industrial water systems can be identified: Once through, open recirculation and closed cooling water systems

Problems and solutions with cooling water systems

- Once through-Limited problems. Source of water to use should have low microbe population.
- Closed system- no problem. System can be filled with deionised water. Although thermophilic srb can cause problem.
- Open recirculation system- most problematic. Evaporation loss, blow downs concentrates nutrients for microbes to thrive.
- Use biocides- initial slug treatment followed by intermittent doses of e.g chlorine etc