

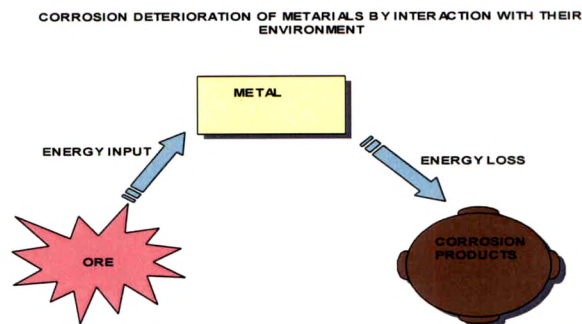
INTRODUCTION

1. INTRODUCTION

The science of corrosion prevention and control is highly complex, exacerbated by the fact that corrosion takes many different forms and is affected by numerous outside factors. Corrosion professionals must understand the effects of environmental conditions such as soil resistivity, humidity, and exposure to salt water on various types of materials, the type of product to be processed, handled, or transported, required lifetime of the structure or component, proximity to corrosion-causing phenomena such as stray current from rail systems, appropriate mitigation methods, and other considerations before determining the specific corrosion problem and specifying an effective solution.

The first step in effective corrosion control, however, is to have a thorough knowledge of the various forms of corrosion, the mechanisms involved, how to detect them, and how and why they occur.

Corrosion is a nature process and is a result of the inherent tendency of metals to revert to their more stable compounds, usually oxides. Most metals are found in nature in the form of various chemical compounds called ores. In the refining process, energy is added to the ore, to produce the metal. It is this same energy that provides the driving force causing the metal to revert back to the more stable compound.



Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals. The most widely used metal is iron (usually as steel) and alloys. Corrosion of metals in cooling and boiler water systems occurs in differing forms depending on the condition of the water temperature flow rate .etc

Copper alloys represent an important category of non ferrous alloys which are widely used as materials in various cooling water system. Brass has been widely used for shipboard condensers, power plant condensers and petrochemicals heat exchangers. Copper and its alloys are widely used in industry because of their excellent Electrical and thermal conductivity, Strength, Ductility, hardness, Machinability, Wear resistance, Color and Recyclability. Due to these characters Brass is usually the first choice of materials for many of the components for equipment made in the general electrical and all precision engineering industries.

CAUSE FOR CORROSION, AND CORROSION MITIGATION

When found in nature, most engineering metals are generally in their oxidized state. During the smelting and refining processes they are reduced to an inherently unstable metallic state. Metals corrode to return to their natural form, achieving a lower energy state. In order to control the corrosion, the current loop must be broken by stopping the electron flow using various means. One ways to control corrosion is the addition of corrosion inhibitor.

THE CONSEQUENCES OF CORROSION (Why Monitor Corrosion?)

The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than the simple loss of a mass of metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small. Some of the major harmful effects of corrosion can be summarized as follows.

1. Reduction of metal thickness leading to loss of mechanical strength and structure failure or breakdown. When the metal is lost in localized zones so as to give a crack like structure, very considerable weakening may result from quite a small amount of metal loss.
2. Hazards or injuries to people arising from structural failure or breakdown (e.g bridges, cars, aircraft).
3. Loss of time in availability of profile-making industrial equipment.
4. Reduced value of goods due to deterioration of appearance.
5. Contamination of fluids in vessels and pipes (e.g. beer goes cloudy when small quantities of heavy metals are released by corrosion).
6. Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings. For example a leaky domestic radiator can cause expensive damage to carpets and decorations, while corrosive sea water may enter the boilers of a power station if the condenser tubes perforate.
7. Loss of technically important surface properties of a metallic component. These could include frictional and bearing properties, ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.
8. Mechanical damage to valves, pumps, etc, or blockage of pipes by solid corrosion products.
9. Added complexity and expense of equipment which needs to be designed to withstand a certain amount of corrosion, and to allow corroded components to be conveniently replaced.

CHEMISTRY OF CORROSION

Common structural metals are obtained from their ores or naturally-occurring compounds by the expenditure of large amounts of energy. These metals can therefore be regarded as being in a meta stable state and will tend to lose their energy by reverting to compounds more or less similar to their original states. Since most metallic compounds, and especially corrosion products, have little mechanical strength a severely corroded piece of metal is quite useless for its original purpose. Virtually all corrosion reactions are electrochemical in nature, at anodic sites on the surface the iron goes into solution as M^{n+} ions, this constituting the anodic reaction.



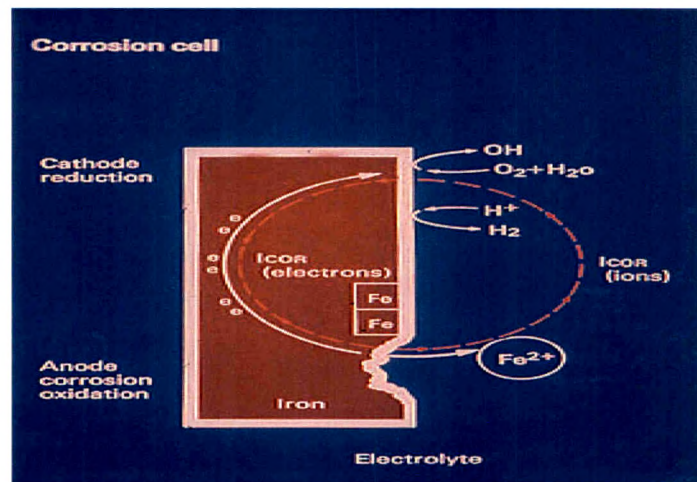
The rates of the anodic and cathodic reactions must be equivalent according to Faraday's Laws, being determined by the total flow of electrons from anodes to cathodes which is called the "corrosion current", I_{corr} . The corroding piece of metal is described as a "mixed electrode" since simultaneous anodic and cathodic reactions are proceeding on its surface. The mixed electrode is a complete electrochemical cell on one metal surface.



This cathodic reaction is most common in acidic medium.



Most important reaction is oxygen reduction. (Common in alkaline or neutral medium) Dissolution will only continue if the electrons released can pass to a site on the metal surface where a cathodic reaction is possible. At a cathodic site the electrons react with some reducible component of the electrolyte and are themselves removed from the metal.



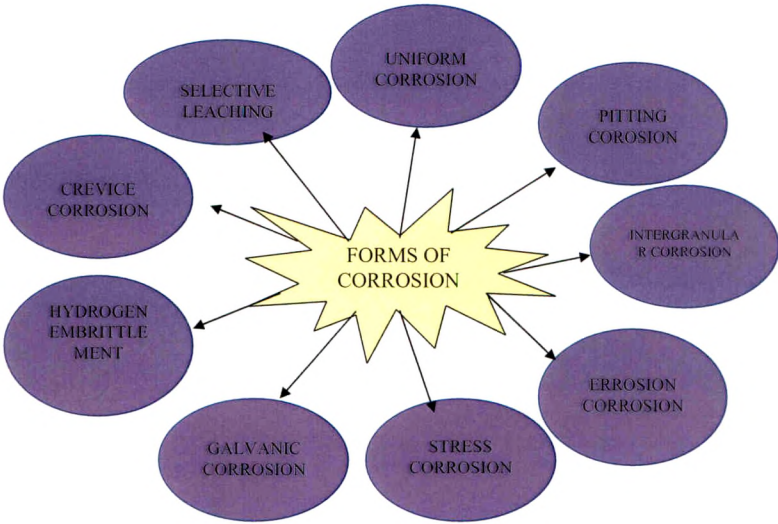
NECESSARY TO CONCENTRATE ON THE METALLIC CORROSION

- Increasing use of metals in all fields of technology.
- Use of new high strength alloys which are usually more susceptible to certain type of corrosion attack.
- Increasing pollution of air and water resulting in a more corrosive environment.
- Strict safety standards of operating equipment, which may fail in a catastrophe manner due to corrosion.

BASIC FORMS OF CORROSION AND ITS CONCEPTS

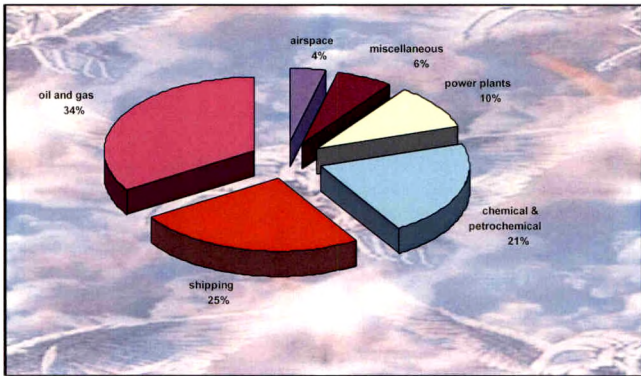
There are 10 primary forms of corrosion, but it is rare that a corroding structure or component will suffer from only one. The combination of metals used in a system and the wide range of environments encountered often cause more than one type of attack. Even a single alloy can suffer corrosion from more than one form depending on its exposure to different environments at different points within a system.

All forms of corrosion, with the exception of some types of high-temperature corrosion, occur through the action of the electrochemical cell. The elements that are common to all corrosion cells are an anode where oxidation and metal loss occur, a cathode where reduction and protective effects occur, metallic and electrolytic paths between the anode and cathode through which electronic and ionic current flows, and a potential difference that drives the cell. The driving potential may be the result of differences between the characteristics of dissimilar metals, surface conditions, and the environment, including chemical concentrations. There are specific mechanisms that cause each type of attack, different ways of measuring and predicting them, and various methods that can be used to control corrosion in each of its forms.



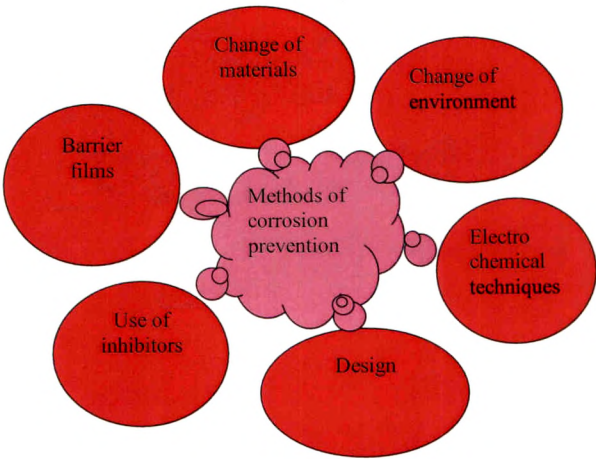
Industrial application

Corrosion in different types of industries

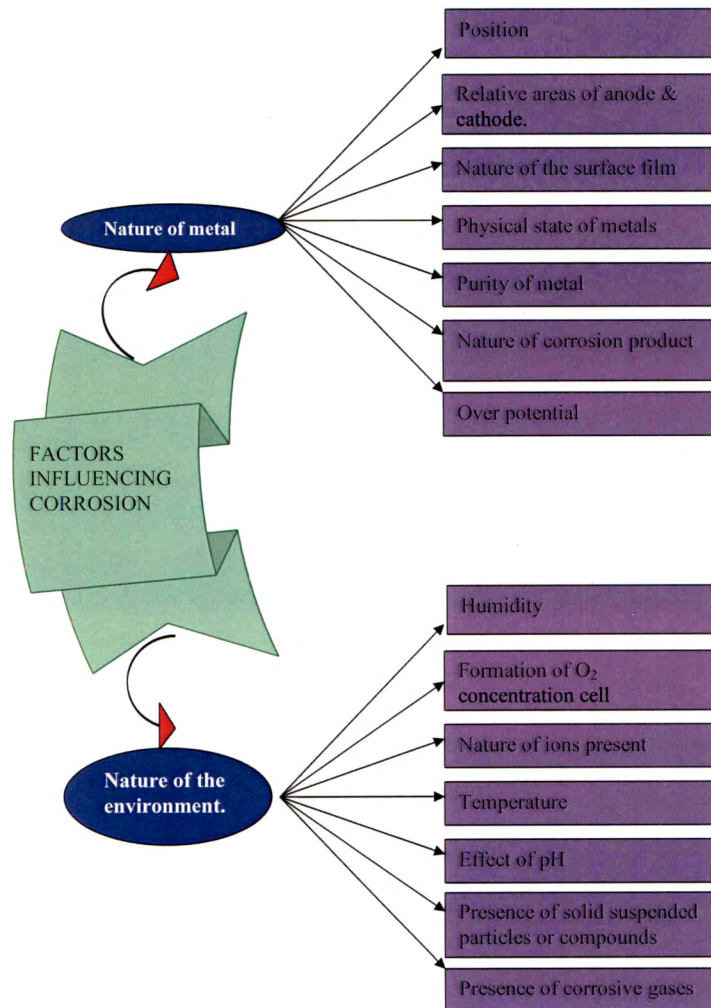


METHODS OF CORROSION PREVENTION

Corrosion is a process very harmful for the metal or alloys. Since the metals and alloys disintegrated or wasted every year through corrosion cost a huge amount. It is necessary to protect the metal or alloys corrosion is an one of the serious problems for industry and its control has been done in different methods such as.



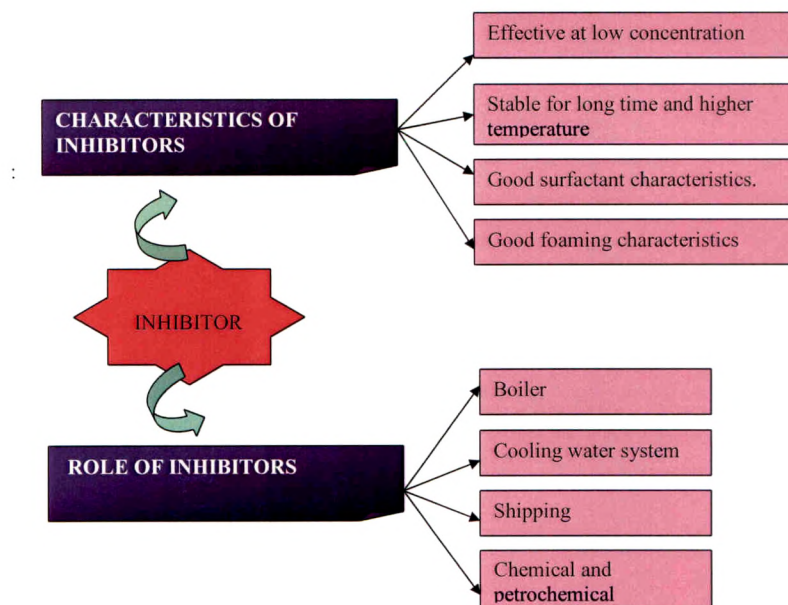
FACTORS INFLUENCING CORROSION



INHIBITOR

One of the most important ways in the protection of metallic surface against corrosion is the use of corrosion inhibitors. The study of organic corrosion inhibitors in – NaCl medium is an attractive field of research due to its useful in several industries. The hetero cyclic compounds containing nitrogen sulfur or oxygen like pyra azole tetra zole derivatives have been studied earlier. There are best known widely used inhibitors. New organic inhibitors especially benzotriazole, nitrated benzotriazole and brominated benzotriazole have been synthesized and corrosion inhibiting effect were assessed. In general corrosion inhibiting means the reduction in the oxidation rate of the metal by the addition of a chemical compound to the system in contact with the solution.

A corrosion inhibitor is a substance which when added in small quantity to a corrosive environment lowers the corrosion rate (Raj Narayanan 1988).



Inhibitors often play an important role in the industries, where they have always been considered to be the first line of defence against corrosion.

TYPES OF CORROSION INHIBITOR

- Anodic inhibitors
- Cathodic inhibitors
- Mixed inhibitors
- Volatiles corrosion inhibitors.

ANODIC INHIBITOR

Anodic inhibitors usually act by forming a protective oxide film on the surface of the metal causing a large anodic shift of the corrosion potential. This shift forces the metallic surface into the passivation region. They are also sometimes referred to as passivators. Chromates, nitrates, tungstate, molybdates are some examples of anodic inhibitors.

CATHODIC INHIBITORS

Cathodic inhibitors act by either slowing the cathodic reaction itself or selectively precipitating on cathodic areas to limit the diffusion of reducing species to the surface. The rates of the cathodic reactions can be reduced by the use of cathodic poisons. However cathodic poisons can also increase the susceptibility of a metal to hydrogen induced cracking since hydrogen can also be absorbed by metal during aqueous corrosion or cathodic charging.

The corrosion rate can also be reduced by the use of oxygen scavengers that react with dissolved oxygen. Sulfite and bisulfite ions are examples of oxygen scavengers.

MIXED INHIBITORS

Mixed inhibitors work by reducing both the cathodic and anodic reactions. They are typically film forming compounds that cause the formation of precipitates on the surface blocking both anodic and cathodic sites indirectly. The most common inhibitors of this category are the silicates and phosphates. Sodium silicate for example, is used in many domestic water softeners to prevent the occurrence of rust water

VOLATILES CORROSION INHIBITORS

Volatile corrosion inhibitors (VCI) also called vapor phase inhibitors (VPI) are compounds transported in a closed environment to the site of corrosion by volatilization from a source.

When these inhibitors come in contact with the metal surface the vapor of these salts condenses and is hydrolyzed by moisture to liberate protective ions. It is desirable for an efficient VCI, to provide inhibition rapidly while lasting for long periods. Both qualities depend on the volatility of these compounds, fast action wanting high volatility while enduring protection requires low volatility.

ORGANIC INHIBITORS

These materials are characterized by high molecular weight structures. Incorporating nitrogen or phosphorous groups. They are usually high polar molecules. Examples: phosphate ester

INORGANIC INHIBITORS

Salt of some metals and amphoteric elements act as corrosion inhibitors quite often these materials have tenacious film forming or passivation effects some instances they react with the metal surface.

Examples: chromate salts.

SELECTION OF INHIBITORS AND MEDIUM

Their choice is especially based on their structure having 3 nitrogen atoms in the cyclic rings and the various substituents which are the major active centers of adsorption. The selection of appropriate inhibitor for a given system depends mainly on the type of an inherent stability of medium concentration, temperature the extent of dissolved organic or inorganic substance in solution and the nature of the metal, the magnitude of the charge of the metal solution interface and the anodic and cathodic reaction. The use of organic inhibitors in NaCl solution is very common nitrogen containing organic compounds have been widely used as effective and efficient metallic corrosion inhibitors. Easy to obtain benzotriazole compounds are non toxic and find a wide applications in NaCl fields.

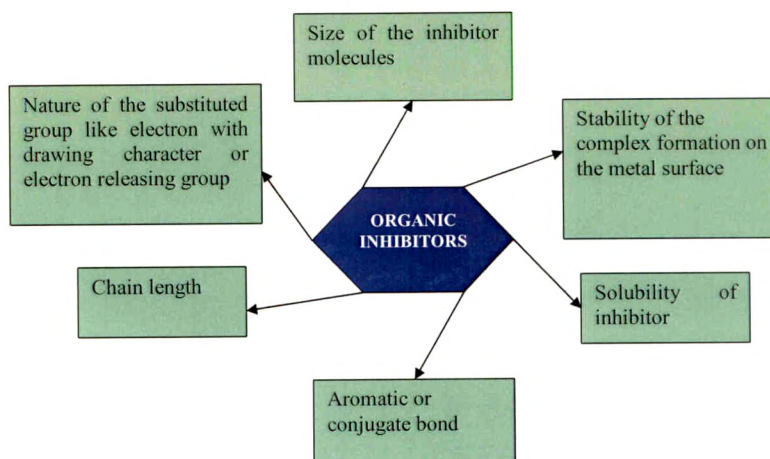
NATURE OF THE INHIBITOR

The inhibitive action of these organic compounds has been explained in terms of mobile electron pairs (lone pair e^-) and π electrons around the nitrogen and aromatic rings system. The inhibitive action of an organic compound depends on its adsorption mechanism like chemisorption and physisorption on the metal surface. The adsorption of these materials is influenced by the presence of functional groups such as $\text{CH}_2\text{-CH}_2\text{-OH}$, Br, and NO_2 in the inhibitor molecules.

The molecular structure of organic compounds used as inhibitors has been found to exert a major influence on the extent of inhibition of corrosion. In addition to this other different characteristics such as the molecular size and nature of substitutions groups in the organic compound have also been found to have a significant influence on the extent of corrosion inhibitor.

EFFECTIVENESS OF ORGANIC INHIBITORS

Effectiveness of the organic inhibitors depends upon the following character such as



CORROSION PROTECTION OF BRASS IS ESSENTIAL BECAUSE....

Screw machine products made from Free-Cutting Brass, UNS C36000, can be significantly less expensive than identical parts made from leaded AISI Type 12L14 steel. This is possible for three reasons.

- Brass turnings are a valuable commodity, and automatic screw machines usually produce more turnings than parts by weight.
- Brass parts can be machined much faster than leaded steel (theoretically, almost five times as fast), which translates into significantly lower production costs.
- Brass screw machine products don't require expensive electroplating to resist corrosion or preserve their usefulness or appearance.

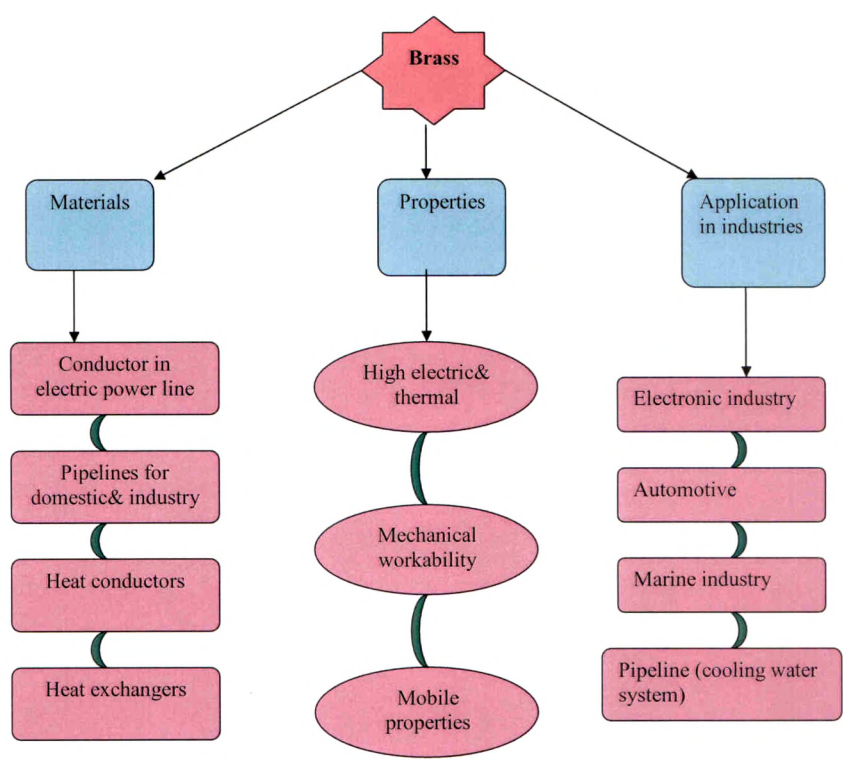
Brass parts can cost less whether or not electroplating is a factor; however, environmental concerns have driven the cost of electroplating up significantly in recent years, and brass is becoming a better value than ever before.

CORROSION BEHAVIOURS OF BRASS

Brass doesn't require extra corrosion protection because **it inherently resists attack**. While brass may be less corrosion resistant than other copper alloys, its performance is quite adequate for the conditions encountered in under hood applications.

Brass tarnishes. Exposed to the atmosphere, it quickly forms a brown or gray-green protective corrosion product film. The rate of film formation (the corrosion rate) soon diminishes as oxygen is excluded from the metal's surface. Under certain conditions, brass can also dezincify (lose the zinc constituent of its composition). Dezincification is associated with submerged or stagnant exposure conditions, often in acidic media. Under atmospheric exposure, this form of corrosion is usually limited to superficial attack. Brass are widely used in industry due to its excellent characters.

INDUSTRIAL IMPORTANCE OF BRASS

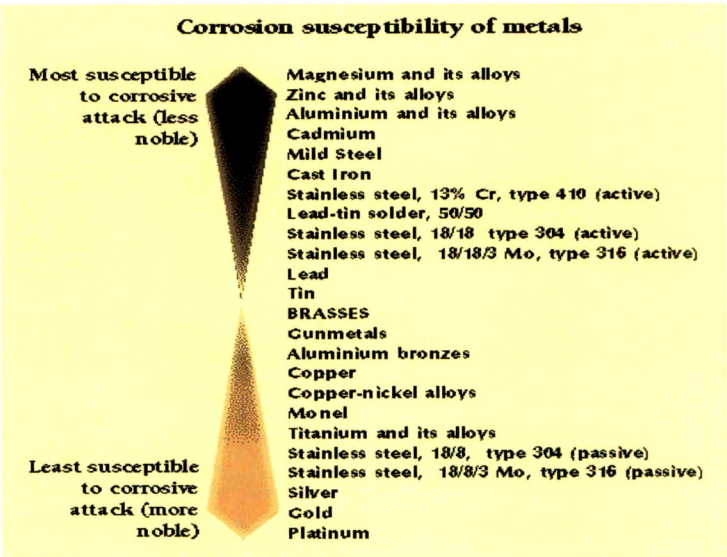


GALVANIC CORROSION OF METALS:

When different metals or alloys are in contact with one another in an electrolyte (sea water, fresh water, rain, dew, condensation, etc.) they affect one another's resistance to corrosion. Usually one - the more "noble" - will cause some degree of accelerated attack (galvanic corrosion) on the other and will itself receive a corresponding degree of protection. Figure 1 show lists a number of common metals and alloys in their order of nobility in sea water and may be used to give some indication of the possible galvanic corrosion effects of coupling brasses to other metals.

In general the further the other metal is from the brasses in the electrochemical series the greater the effect will be.

Fig 1: Galvanic series for common metals and alloys in sea water



It can be seen from this general table that **brasses are more noble than other commonly used engineering materials**. The table represents the galvanic behaviour of metals are in bimetallic contact the one high in the table will corrode preferentially. Actual performance depends on the surface film formed under conditions of service. On exposed surfaces the free oxygen in the water ensures a passive film on many metals

The relative positions of the different metals indicated in Figure (1) are different in a different environment or even under prolonged stagnant conditions in sea water, where the passive films on stainless steels could break down and sulphide films could form on the copper alloys. The series shown can however be taken as representing the majority of service conditions. Among the brasses themselves there are small differences of electro chemical potential, those of highest copper content being more noble. In particular, the alpha brasses are somewhat more noble than the beta brasses,

this shows itself in the tendency for the beta phase in alpha-beta brasses to suffer preferential attack but the difference between the two is not great.

BRASS THE YELLOW METAL.....

The generic term "brass" covers a wide range of copper-zinc alloys with differing combinations of properties, including:

- * Excellent machinability
- * Good electrical and thermal conductivity
- * Cost Effective and Recycled without loss of properties
- * Easily joined
- * Ductile and malleable
- * Non-sparking
- * Readily finished/plated
- * Available in many forms
- * Good corrosion resistance
- * Good strength
- * Impact resistant
- * Attractive colour
- * Wear resistant
- * No loss of properties below 200°C
- * No degradation by sunlight
- * Cost-effective material

Brass is a cost-effective engineering material ideally suited for the manufacture of machined and stamped items. The need for plating or painting to prevent corrosion in normal circumstances is eliminated, but when required for cosmetic purposes or to give additional protection against corrosion it is easily plated. Brass is readily recycled without loss of properties and the infrastructure to do so has been proven over many years. Brasses have excellent resistance to corrosion that makes them a natural, economic first choice for many applications.

Benzotriazole is a synthetic auxiliary that offers many advantages. It is inexpensive, odourless and stable. A benzotriazole group is easily introduced activates molecules towards numerous transformations and can be removed easily at the end of the reaction sequence. This concept provides some recent examples of the synthetic application of benzotriazole methodology and intended to draw attention to the versatile application of benzotriazole in all fields of chemistry.

Perfluoropoly ether benzotriazole compounds can be attached to a substrate having a metal or metal oxide containing surface to provide at least one of the following characteristics: antisoiling, anti-staining, ease of cleaning, repellency, hydrophobicity or oleophobicity.

OBJECTIVES

The objective of this investigation is to assess the corrosion rate of brass and to find out the effectiveness of the selected organic inhibitors to protect metals from corrosion.

- * To synthesis the organic inhibitors by standard procedures.
- * To examine the protection of brass from corrosion by 2- hydroxyl ethyl benzotriazole (HEBTA), nitro benzotriazole (NBTA), and bromo benzotriazole (BBTA).
- * To investigate the effect of organic inhibitors HEBTA, NBTA and BBTA. By varying its concentration.
- * To find out the stability of the inhibitor at high temperatures.
- * To fit the observed data in various isotherms and to locate the appropriate adsorption isotherms.
- * To determine thermodynamic parameters such as change in free energy, change in enthalpy, change in entropy.
- * To use cyclic voltammetry technique to understand the electrochemistry of brass with and without inhibitors.
- * To propose a possible mechanism for inhibition process.
- * To analyse the surface of brass after inhibition using surface analytical technique and to study the surface morphology of the brass and inhibitors layers.