Corrosion Inhibitors for Cooling water system:-

Chromate: -

The anodic inhibitor is functions by oxidizing ferrous hydroxide to gamma Fe$_2$O$_3$. Reduced chromate, Cr$_2$O$_3$ is incorporated into the protective film and the film consists of 75% gamma Fe$_2$O$_3$ and 25% Cr$_2$O$_3$. In contrast to the use of chromate alone, the use of zinc/chromate provides Cathodic inhibition. The combination is synergistic, which requires far less inhibitor dosage than chromate alone. Due to the environment aspect now a days Chromate is not used as corrosion inhibitors.

Zinc: -

Zinc is a very effective cathodic inhibitor, at low dose. Cathodic inhibitors function by forming a barrier film that inhibits the formation of hydroxyl ions in the presence of dissolved oxygen. The barrier films prevent dissolved oxygen from reaching the metal surface and receiving electrons. The barrier films are formed by the precipitation of the cathodic inhibitors as a result of the localized, high pH at the cathode. However; environmental restrictions on zinc discharge have begun to limit the use of zinc.

Zinc/phosphate products are very effective in general application and considered by some to be the products of choice in soft water, when zinc discharge limitations do not preclude their use. The reason for using zinc products in soft water is that zinc hydroxide and zinc phosphate/phosphonate can form and provide cathodic inhibition in the absence of calcium ion. Phosphate based programs require calcium for the formation of calcium salt formation, and therefore are not effective at very low calcium concentrations.

The Synergistic treatment of phosphonate along with zinc gives good protection to cast steel. The good control range in the pH range of 6.5 to 9.0. Sometimes degradation of phosphonate to ortho-phosphate takes place due to presence of chlorine.
Molybdate: -

Molybdate is non-toxic and can be used substitute of chromate. Molybdate is usually fed at 200 to 300 mg/L as molybdate ion, at a pH of 7.0 to 9.0. As with other anodic inhibitors, the effectiveness of molybdate is reduced by chloride ions. Consequently, the higher the chloride concentration, the higher the molybdate concentration required. At a chloride concentration of 200 mg/L, 800 mg/L of molybdate ion is needed. When the chloride concentration exceeds 500 mg/L, molybdate is not an effective treatment. When combined with nitrite, the molybdate concentration can be reduced in water having a moderate chloride concentration, since nitrite enhances the performance of molybdate.

Azole: -

To protect copper and copper alloy surfaces from corrosion, the azoles, such as benzotriazole or tolyltriazole, have to form a protective layer on the surface of the metal and capture any dissolved free copper ions. Mainly used as antirust and anticorrosion agent for metals such as copper, silver, zinc, lead, and copper alloys. Also widely used in the antirust oil products as gas phase corrosion inhibitor for copper and copper alloy, as treating agent for recycling water, as antifreeze for cars, antifogging for photograph, stabilizer for macromolecular compound growth regulator for plant, lubricant additive, ultraviolet absorbent etc. As a general rule of thumb, the azole concentration in the recirculating water should be at least 2.0 ppm, or (Total Copper residual x 2) + 2 ppm whichever is higher.

Phosphonate: -

Phosphonate used in conjunction with poly phosphates or zinc. The mode of inhibition is Cathodic. The key to the success of cathodic inhibitors is the formation of a protective film at the metal surface while at the same time preventing bulk precipitation of scale, usually with the use of polymers. Phophonate acts as mild corrosion inhibitor when used alone. Phosphonate having a greater hydraulic stability than poly phosphate. Threshold inhibition property of phosphonate provides good control on calcium carbonate scale. The antagonistic effects of chloride and sulfate ions are subdued by poly phosphate – phosphonate treatment. An effective inhibitor for steel and aluminum metals.
Poly Phosphate :-
The evolution of modern, open system corrosion inhibitor treatments began with the of glassy polyphosphates. The glassy polyphosphates are commonly called sodium hexametaphosphate, but generally are not exactly 6 units in length, but rather 6 to 12 units in length, depending on the production process variables. Other polyphosphates used for controlling corrosion include sodium tripolyphosphate, and sodium or potassium pyrophosphate. Poly phosphate can be used with phosphonate, zinc or azoles for synergistic treatment. Poly phosphates can revert to some degree into ortho phosphate. In general, polymers are being introduced with poly phosphate to control ortho phosphate i.e calcium phosphate deposition in system.

Nitrite :-
Nitrite is excellent anodic corrosion inhibitor have wide use in closed systems, where oxygen concentrations are low and waters tend to have low ionic strengths. Additionally, the high required doses of anodic inhibitors could be tolerated in closed systems, since make-up requirements are small. Historically, chromate was fed at a maintenance dose of about 200 mg/L, at a pH of 8.0 to 9.0, whereas nitrite is fed at 600 to 1500 mg/L as NaNO$_2$ at a pH above 7.5. For further detail on treatment please please article on closed recirculating cooling system and product literature of Altret –806 CS & Altret 816 CS.

All Organic treatment: -
The interest in all-organic programs spurred the development of new phosphonate, such as phosphonobutanetricarboxylic acid, (PBTC) and hydroxypropylacetic acid. All-organic programs usually contain combinations of phosphonate, since combinations were found to function better than individual phosphonate, perhaps due to better surface coverage with varying size molecules. AMP/HEDP, ATMP/HEDP, HEDP-HPA and HEDP/PBTC or other Phosphonates combination used as all organic corrosion inhibitors.

Apart from above treatment polydiols, poly ether phosphonates, poly amino acid such as poly asphertic acid are widely introduce as corrosion inhibitor for cooling water system.

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Source:-
1. Hollander et al., 1982
3. Susan P. Rey, The National Colloid Company
4. Water treatment Service manual – RCRPMS
5. ALTRET Hand Book.