The Role of Organophosphates in Cooling Water Treatment

Introduction:

Cooling Water is used in large industries to remove unwanted process heat with the help of heat exchangers, condensers. Due to the continuous contact of water with the metallic surface corrosion, scale, deposition & fouling of the heat transfer surfaces occur. These cause equipment damage and operating losses and sometimes result in costly shutdown of the plant. Addition of chemical inhibitors in controlling these problems.

Chromate based inhibitors along with polyphosphates, have been in use for long and they have been reasonably effective against both corrosion and scaling. But they have their own limitation. Polyphosphates are hydrolyzed to orthophosphate at higher operating temperature of the cooling water circuit, which lead to orthophosphate scale. Orthophosphate formed is also a nutrient for bacterial growth chromates are toxic to aquatic life and ecological concern has been the primary reason for the search for new substances.

Among the various substance stadius organophosphates have been found to be the best. Organophosphate based formulations give comparable protection with respect to corrosion, scaling and fouling and they are hydrolytically stable. This stability of organophosphates permits greater flexibility, during operation, as they are stable over a greater range of pH and at higher temperature, thereby retaining their activity for longer periods of time. The control on various parameters is more relaxed and they are non – toxic. Phosphonate are compatible with most other chemicals used in

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cooling systems like chlorine, non-oxidizing biocides, silt control chemicals etc. slowly organophosphates are finding more acceptance the world over, primarily because of its freedom from environment problem.

Properties of Organophosphonates: Structurally, organophosphates have the carbon atom directly linked to the phosphorus atom. The two most widely used Organophosphonates in cooling systems are:

"Six phosphate based cooling system corrosion inhibitors were studied for their relative corrosion inhibiting capabilities by an accelerated static test. The static test was standardized by controlling pH and temperature and using an oxidizing accelerator, potassium persulphate. Results indicate that orthophosphate aminotrimethylene phosphonate and hexametaphosphate are the prospective corrosion inhibitors.

Six phosphate based inhibitors selected are Sodium Hexametaphosphate (SHMP), Sodium tripolyphosphate (STPP), tetrasodium pyrophosphate (TSPP), Sodium Orthophosphate (O-PO_4), Aminotrimethylene Phosphonate (ATMP) and Hydroxyethylidene diphosphonate (HEDP), these are frequently used in non-chromate based cooling water treatment.

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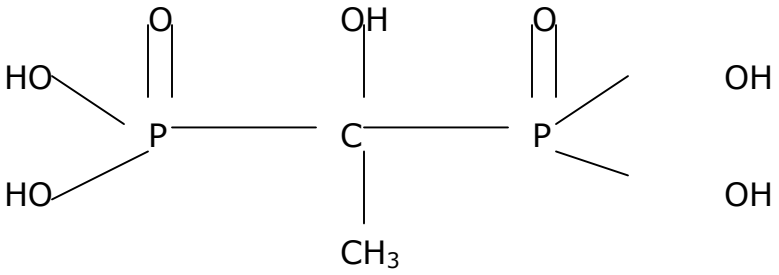
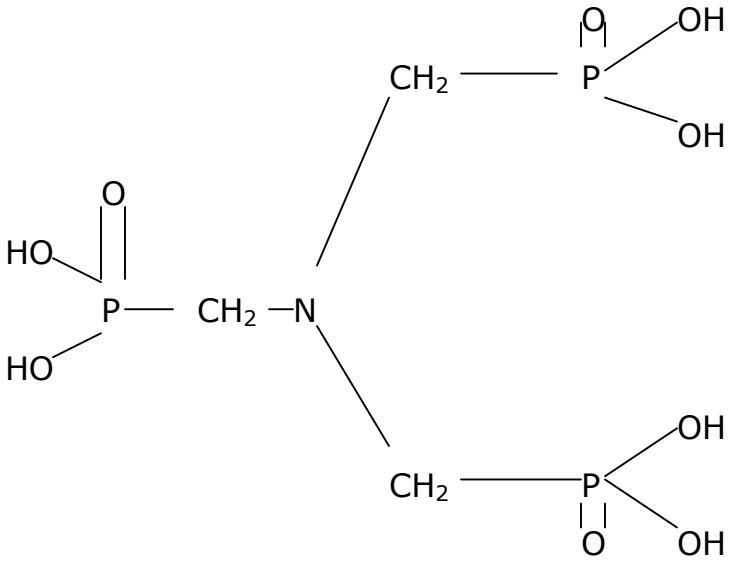
1) 1-Hydroxyethylidene-1, 1-diphosphoric acid (HEDP): -



2) Amino trimethylene phosphoric acid (ATMP):



The key properties of Organophosphonates are:

1. Threshold effect and crystal distortion.
2. Hydrolytic Stability.
3. Sequestration characteristics.
4. deflocculation.
5. Chlorine stability

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These aspects of the Organophosphonates are described in the following paragraphs:

Organophosphonates, in substichiometric amounts prevent or retard the precipitation of scale forming salts. Phosphonate interfere with the nucleation of the hardness crystal causing much higher levels of hardness to stay in solution than would be possible with untreated water. The inhibitor is adsorbed on the surface of scale forming crystals during the process of crystallization. This retards the growth of crystals and when they are formed they are highly distorted preventing orderly lattice type growth. This changes the adherence characteristics of the scales formed leading to a soft sludge rather than an adherent scale, which is easily dispersed by the movement of water.

Organophosphonates are extremely stable to hydrolysis as compared to polyphosphates at elevated temperature and extremes in pH for extended periods of time. The carbon to phosphorus to oxygen (CPO) bonding in Organophosphonates is more resistant to hydrolysis or cleavage than the COP bond in phosphate esters and the OP bond in polyphosphates.

Organophosphonates form water-soluble complexes with metal ions, thereby preventing their deposition. Many chemicals are capable of exhibiting this property via ligand formation with bivalent and trivalent cations like calcium, magnesium, iron, manganese, aluminum, etc. Stability constant, which is a measure of the thermodynamic stability of the complex formed, can be used to compare sequestering agents. The smaller the stability constant, the larger is the amount of free ions.

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Organophosphonates have also been known as deflocculant and disperse suspensions of colloidal particles. Use of Organophosphonates, added advantages of maintaining the dispersed state for a much longer period as a result of its superior hydrolytic stability.

Suspended particles and dirt in cooling water generally have a negative surface charge. Anionic polymers increase this negative surface charge and keep the particles separated. Cationic dispersant when used should be carefully controlled, since the positive charge might be expected to co-agulate the negatively charged particles, leading to the formation of dense particles. Addition of cationic dispersants also involves greater expense since a higher dosage is required as the charge on the suspended particles would neutralize before sufficient positive charge was built up to keep them separated.

Organophosphonates exhibit good molecules stability towards chlorine, which is commonly used as a biocide in cooling water system. In case where greater molecules stability to chlorine is desired. HEDP is preferable to ATMP since it contains nitrogen and therefore chlorine demand for the formation of chloramines is totally absent.

Corrosion Control: Corrosion Control of metallic surface can be obtained by inhibiting the cathodic, the anodic or both these reaction. A combination of Organophosphonates and zinc works synergistically to give very good corrosion protection by interfering with the cathodic reaction. Polyphosphates, when used as corrosion inhibitor, give rise to excessive orthophosphate sludges whereas Organophosphonates with Zinc give good corrosion protection without leading to any sludge formation.

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Due to the sequestering ability of Phosphonate, the zinc ions are present in a complexed form limiting the rate of reaction of zinc with hydroxyl ions. Therefore, useful concentration of zinc hydroxide allows the formation of a thin hydroxide film at the surface giving the desired corrosion resistance.

Scale and Fouling Control: Organophosphonates are one of the best deposit control agents presently available. The threshold and crystal distortion property of these compounds interferes with the nucleation of the hardness crystals causing much higher levels of hardness to stay in solution. When scales are formed they are so distorted that they are non-adherent and form very soft sludges. Phosphonate also provide excellent

Control of hydrated ferric oxide deposits which are formed as a result of corrosion. They adsorb on the particle surfaces and reduce the attractive forces between individual iron particles. The sequestering ability of phosphonate enables it to control heavy matter (Fe, Cu & Zn) deposits and this control is far superior to other traditional chelants. Phosphonate also help to disperse suspended particles.

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Choice of Phosphonate: From the two most commonly used phosphonate for cooling water treatment HEDP is preferred to ATMP for the following reasons:

1. ATMP is more corrosive to Cu cooling systems involving Cu or Cu alloys, are therefore very sensitive to ATMP. With ATMP one would then have to use Cu corrosion inhibitors like Thiazoles and Trizoles making the treatment more expensive. The corrosivity towards Cu is due to the fact that a very strong complex with Cu is formed, the dissociation constant of the chelate being about 10^{-13}.
2. HEDP has better stability to chlorine than the Nitrogen containing ATMP. Nitrogen containing compound have a tendency to form chloramines. Though, when complexed with Zinc. ATMP exhibits stability towards chlorine it should be used with caution in chlorinated cooling water systems especially when continuous chlorination is used.

   The addition of Zinc to ATMP to a certain extent inhibits the dissolution of copper. In the presence of ATMP, however, the powerful oxidizing potential of chlorine promotes the dissolution of copper, when chlorine is used as a biocide.

   The other phosphonate used to a much lesser extent are, ethylene diamine tetramethylene phosphoric acid, hexamethylene diamine tetramethylene phosphoric acid and diethylene triamine pentamethylene phosphoric acid.

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Compatibility with other Chemicals: Organophosphonates are compatible with most other chemicals used in cooling systems like chlorine, non oxidizing biocides, silt control chemicals, polyphosphates, chromates, zinc, dispersant, etc. Polyanionic dispersants combine with some long chain aliphatic quaternary ammonium compounds and long chain aliphatic amine derivatives to give insoluble salts. Care should be exercised when using these compounds with long chain nitrogen compounds. Poly anionic dispersants are not affected by chlorine or oxidizing biocides under normal conditions of use and are compatible with most other water treatment chemicals.

Summary : Ecological concern has put a considerable restraint on chromate based treatment. As a result of the search for new substitutes, Organophosphonates have been found to be a satisfactory alternative. The multifunctional properties of Organophosphonates in a single active ingredient affords flexibilities of operation. Organophosphonates and Zinc act synergistically giving good corrosion inhibition phosphonate are also effective scale control agents.

The chemical characteristics of Organophosphonates, its temperature stability, antifouling properties, compatibility with other treatment chemicals, the choice of Organophosphonates and analytical procedure to determine its concentration have been briefly described.

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