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Molybdate-Based Cooling Water Treatment
New Developments Which Expand Their Applications Areas

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Molybdate-Based Corrosion Inhibitor programs for cooling water systems have been commercially applied for many years. Due to increasing environmental constraints on the use of chromate treatments, molybdate represents a logical, environmentally acceptable alternative. Other "chrome alternatives" like inorganic phosphate, zinc, and all-organic treatments have been far more popular, however, relegating molybdate-based treatments to be attractive curiosities for use in isolated applications. A survey of non-toxic cooling tower water inhibitors published in 1981, indicated only about 4 percent of the respondents made use of some type of molybdate technology in their cooling water systems.

Although more recent developments in technology have spurred increased interest in molybdate-based corrosion inhibitors, their widespread use has been limited by a number of key factors:

*Molybdate when used alone as a corrosion inhibitor must be carried at high concentration levels in the cooling water to maintain acceptable corrosion rates, making the program extremely costly.

*Improved corrosion protection can be achieved at lower concentrations of molybdate when blended with organic inhibitors, however film formation remains relatively weak, and in corrosive environments the level of protection is marginal.

*Low levels of zinc dramatically improve the film formation of blended molybdate products, however increasing environmental pressures are curtailing or eliminating the use of zinc.

*Blended products that allow for low levels of molybdate in the treated system, at times, remain uneconomical to use when compared with inorganic phosphate or zinc-based corrosion inhibitor programs.

*The technology of molybdate-based corrosion inhibitors has advanced significantly over the years and recently, a number of developments have overcome many of these limitations.

New Developments in Molybdate Technology

Molybdate/Orthophosphate/Aromatic Azole - A new formulation, recently made available, takes advantage of molybdate's anodic film-forming properties but reinforces this film with another known anodic film former, i.e. orthophosphate.

Laboratory evaluations, as well as field experience, have shown the combination of these two mild steel inhibots, along with an aromatic azole for yellow metal corrosion protection, has the ability to give extremely low corrosion rates even in highly aggressive environments.

The primary difference between a formulation of this type lies in its mild steel film-forming properties. The mechanism of molybdate's mild steel corrosion inhibition has already been discussed and that mechanism occurs in this formulation.

However, a drawback of previously low-level molybdate formulations has been their relatively weak inhibitory properties and their resulting poor performance in highly corrosive waters.

The inclusion of low levels of orthophosphate into the formulation overcomes this historic drawback. Orthophosphate alone has been found to be an effective anodic corrosion inhibitor for mild steel and forms a passive iron-phosphate film at those surfaces. When used in conjunction with molybdate, it is speculated that a combination phospho-molybdate ferric oxide film is essentially generated which is extremely strong and resistant to breakdown in aggressive waters. This allows products of this type to be used in a far wider pH range (6.5-8.5) and in the presence of high temperature, high chloride and sulfate, with continuous chlorination without sacrificing corrosion protection.

A major factor that makes a molybdate/orthophosphate corrosion inhibitor viable is the recent advances in polymer technology associated with calcium orthophosphate control. Even the low levels of orthophosphate associated with this product could be a problem in systems experiencing high calcium, elevated pH and temperature, and high iron concentration. These situations tend to cause precipitation problems of either tricalcium orthophosphate or iron phosphate generating increased corrosion from non-uniform film formation as well as heat insulating deposit problems. The polymer present in this new formulation is specifically incorporated to minimize these negative effects and maintain orthophosphate totally in solution where it is available for corrosion inhibition.

Molybdate/Phosphonate Blend! Aromatic Azole - One area of molybdate application that holds a bright future is in alkaline, no-pH control cooling water systems. Most of the traditional molybdate formulations are used with HEDP alone, or in combination with zinc and an aromatic azole to control corrosion. As stated earlier, high levels of alkalinity and calcium can cause precipitation of both the zinc and HEDP portions of the product. New technology, which makes use of organophosphorus compounds specifically designed for use in alkaline waters make excellent companions for molybdate. The combination of these components have been shown to control corrosion in water with pH levels between 8.0-95 even when high levels of aggressive ions like chloride and sulfate are present. Naturally, a primary concern in the treatment of highly alkaline waters is the control of calcium

carbonate scale. This aspect can be controlled by the combination of organophosphorous compounds in this new formulation, as well as a carboxylated polymer. Formulations of this type, which use molybdate, aromatic azole, and specific organophosphorus compounds designed for alkaline waters, are ideal for applications that want to improve plant safety and eliminate acid feed to the cooling water system.

Economic Considerations

To successfully operate in today's competitive business environment, it is imperative that newly developed water treatment programs provide plants with cost-effective results. Historically, however, corrosion control programs based upon molybdate have been relatively expensive, when compared with traditional chromate/zinc and high phsophate treatments. During the past several years, a series of favorable technological developments have enabled water treatment suppliers to formulate molybdate-based corrosion inhibitors that rival even inorganic phosphate programs in terms of cost-effectiveness.

As many of the original programs relied almost exclusively upon molybdate to establish inhibitory films, it was generally necessary to carry molybdate residuals up to 20 mg/I (as MoO4) to insure adequate corrosion control in open recirculating cooling water systems. By having to maintain such elevated residuals of the relatively expensive molybdate inhibitor in the system, such programs were usually considered unattractive from a cost perspective.

The development of synergistic blends incorporating additional inhibitors such as orthophosphate, phosphoneate and zinc, however, has allowed water treatment suppliers to significantly reduce the concentration of molybdate needed to obtain desired levels of corrosion control. As such, newer molybdate-based inhibitors are designed to operate with molybdate residuals of 4-6 mg/I (as MoO4), thereby providing improved cost over older programs.

As presented in Table 4,chemical costs have been calculated on a dollar per million pounds of blowdown basiv~ so comparisons can be made between the economics of newer molybdate programs and commonly used alternative treatments. Although it may initially appear that zinc/chromate inhibitors offer substantial cost advantages over alternative treatments, it must be noted that to properly operate these programs, many plants must use acid to control pH levels and feed supplemental dispersants to inhibit deposit formation. Therefore, as these calculations do not take into account additional expenses associated with acid purchases, ancillar feed equipment or manpower requirements, discrepancies in operating costs between zinc/chromate treatments and alternative programs would not actually differ by such a degree.

Furthermore, as comprehensive one-drum approaches to cooling water treatment, molybdate formulations incorporate sequesterants and dispersants to minimize

fouling by metal oxides and hardness salts. The inclusion of these antifoulants also extends the product's optimum pH range and allows systems to operate at higher cycles of concentration, thereby minimizing water and chemical consumption rates and further reducing overall operating cost.

Based upon these economics and operating factors, it is apparent that recent changes in product technology have allowed for the development of new molybdate-based corrosion inhibitors that can provide cost-effective results. As such, the use of molybdate-based corrosion inhibitors in cooling water applications by even the most cost-conscious plants should no longer be limited by economic considerations.

Technical Article Review Quiz

Molybdate Based Cooling Water Treatment

The Questions for the exam may be answered by reading and understanding the **Spring 1988** Analyst Article titled "**Molybdate Based Cooling Water Treatment"** by **Kenneth F. Soeder** and **Joseph R. Roti.** The correct answers are derived from that article and any disputed answers will be referred back to that article for justification.

1. A drawback of low level molybdate formulations has been their relatively weak inhibitory properties. The inclusion of low levels of _____ overcomes this historic drawback.
    a. zinc.
    b. orthophosphate
    c. sulphite
    d. erythorbate.

2. Molybdate when used alone as a corrosion inhibitor must be carried at _____ in the cooling water system to maintain acceptable levels of corrosion.
    a. Low levels
    b. High levels
    c. Less than 2ppm with chlorine present
    d. Less than 2ppm with zero chlorine present

3. Improved corrosion protection can be achieved at lower concentrations of molybdate when blended with _____.
    a. chlorine
    b. bromine
    c. organic inhibitors
    d. Carbohydrazide

4. Molybdate/orthophosphate/azole combinations can be used in a pH range of 6.5-8.5 and in the presence of
    a. erythorbate
    b. hydroquinone
    c. Carbohydrazide
    d. Continuous chlorination

5. Molybdate/orthophosphate/azole combinations could be a problem with systems containing
    a. low levels of hardness
    b. non-oxidizing biocides
    c. Low levels of iron
    d. High calcium

6. Blended products that allow for low levels of molybdate in the treated system, at times, remain uneconomical to use when compared with
    a. Molybdate only based inhibitor programs
    b. nonvolatile oxygen scavenger programs
    c. Inorganic phosphate inhibitor programs
    d. Diethylhydroxylamine (DEHA) inhibitor programs

7. Molybdate/phosphonate/azole blends have a bright future with systems containing _____.
    a. a minimum 5.0ppm chlorine
    b. soft water only (less than 50ppm)
    c. tight pH control (7.0-7.5)
    d. high levels of calcium

8. Molybdate/phosphonate/azole blends have been shown to control corrosion in water with pH levels between _____.
    a. 9.0 - 12.0
    b. 6.5 – 7.5
    c. 8.0 - 9.5
    d. 5.0 - 7.0

9. A primary concern in treating high alkaline waters with Molybdate/phosphonate/azole blends is the control of calcium carbonate scale. This can be controlled adding _____ to the formulation
    a. Chlorine
    b. Muriatic acid
    c. Organophosphorous compounds
    d. bromine

10. Molybdate/phosphonate/azole blends designed for alkaline waters _____.
    a. require acid feed to control pH below 8.0
    b. generally do not require acid feed to control pH.
    c. do not require the addition of biocides.
    d. must use high levels of chlorine