TECHNICAL BULLETIN

Borates in industrial fluids

Introduction

Borates are well established and widely used in the manufacture of industrial fluids—antifreeze, brake fluids, lubricants, metalworking and hydraulic fluids, water treatment chemicals, closed system heat exchanger fluids, and fuel additives. In addition to corrosion inhibition for many different alloys, there are numerous benefits of using borates in industrial fluids production:

- Buffering capacity
- Reduction of freezing point
- Increase of boiling point
- Lubrication
- Thermal oxidative stability
- Low sludge formation
- Low moisture sensitivity

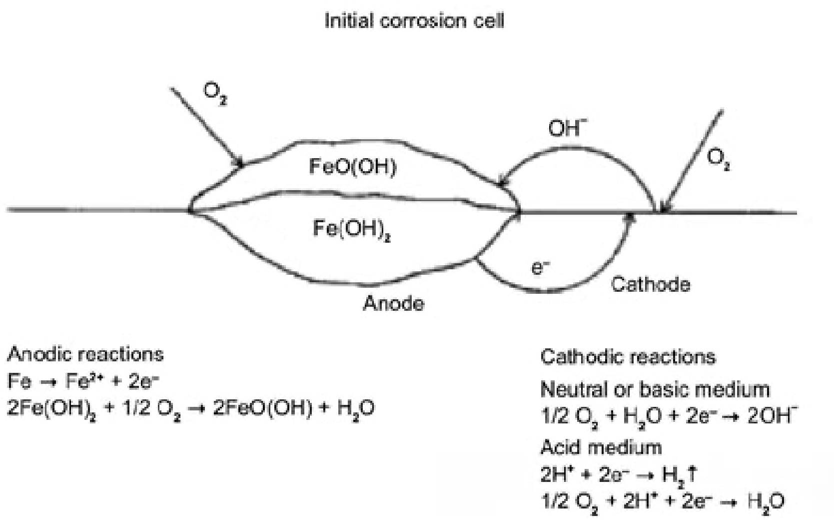
This technical bulletin is intended to provide guidance in the use of borates for the production of industrial fluids.

Corrosion inhibition

In general, corrosion may be defined as a destructive interaction between a metallic surface and its non-metallic environment. It is now generally accepted that metal corrosion is an electrochemical phenomenon. As in any electrochemical cell, oxidation takes place at the anode where the reaction product is metal ions which are released into the surrounding medium. Conversely, at the cathode, oxygen or hydrogen ions are reduced (Figure 1).

Since the rate of anodic and cathodic reactions are equal, it follows that the inhibition of either half-reaction will decrease the overall corrosion rate. Also, the metal in a corrosive medium has many anodic and cathodic sites on its surface. If these sites shift rapidly over the entire surface, the observed corrosion will be of a “general” or uniform type. If, on the other hand, these sites are relatively static, “localized” corrosion will result. Examples of the latter are pitting and crevice corrosion.

Figure 1

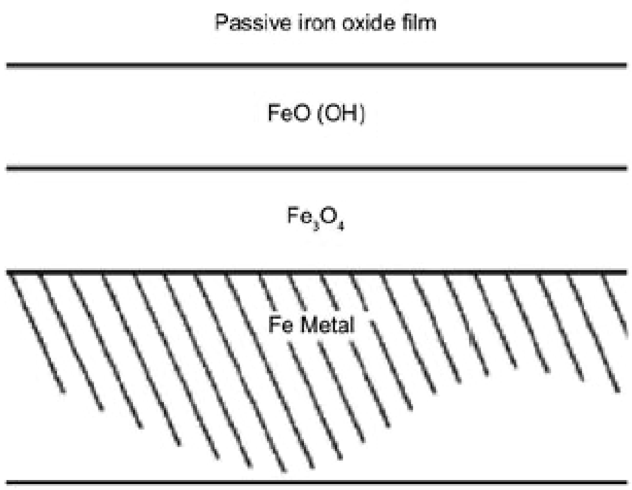


These are two general categories of corrosion inhibition:

1. Cathodic inhibition usually involves some form of barrier film deposited from solution. To be effective, the film must be able to impede the movement of the oxidizing agent (O2 or H+) to the metal surface and must also be an electrical insulator. The rate of film formation has to be carefully controlled or scaling can occur. Examples of cathodic inhibitors are zinc (hydroxide), phosphate (in the presence of calcium or zinc) and mercaptobenzothiazole.
2. Anodic inhibition is accomplished by growing an oxide film on the surface of the metal. This phenomenon is called passivation and is actually a form of controlled general corrosion. A potential drawback related to anodic inhibitors is that if film breaks are not repaired, rapid pitting may occur. Examples of anodic inhibitors in aqueous solution are chromate, nitrite, molybdate, silicate, phosphate, and borate.

The last four are called “nonoxidizing anodic inhibitors” because they have insufficient oxidizing power of their own to effect passivation (ie oxygen must be present). The passivation process is shown in Figure 2.

Figure 2



Applications

Antifreeze (automotive engine coolants)

The vast majority of passenger cars and trucks use a mixture of water and antifreeze to remove approximately 50% of the heat generated by an internal combustion engine. The requirements for the antifreeze solutions used in the radiator systems are: Low freezing point, high boiling point, efficient heat transfer medium, corrosion inhibition, chemical stability, and low toxicity. An aqueous solution of ethylene glycol or propylene glycol meets most of these requirements. However, ethylene glycol or propylene can oxidize to corrosive organic acids in an automobile cooling systems. To counteract this, buffers and corrosion inhibitors must be added. Borax decahydrate or borax pentahydrate (*Neobor*®), together with other components, serves this purpose. The buffering action of borax decahydrate or *Neobor* maintains the pH above 7, where acidic compounds cannot form. It is readily soluble in glycols, is non-toxic and can be handled with safety. Borax inhibits corrosion by minimizing the rate of oxidation at the surface of the metal and is classified as an anodic inhibitor. The anodic inhibitors are believed to form a sparingly soluble salt with the metal, retarding further corrosion.

Brake fluids

Brake fluid specifications are defined by the U.S. Department of Transportation (DOT). They are generally made from triethylene glycol monoalkylethers. These types of brake fluids are moisture sensitive and the presence of water can significantly reduce the boiling points. As a result, vapor is produced and that causes locking of the brakes. The borate ester of the glycol ethers is a good partial replacement for glycol ethers. This product is made by reacting triethylene monoalkylethers and *Optibor*® boric acid under proper conditions. The absorption of moisture into the brake fluid converts the borate esters back to boric acid and glycol ethers. The released boric acid remains dissolved in the fluid and therefore has a minimum effect on the boiling point.

The development of higher performance vehicles has involved reducing weight of components including those of the braking system. Thus more heat is dissipated in smaller volume systems. This has led to increasingly high boiling point specifications for brake fluids and the progression from DOT 3 to DOT 4 and DOT 5 specifications. DOT 4 brake fluids generally contain about 2–3.5% B_2O_3 (or 29–51% triethylene glycol monomethyl borate). With the borate ester content increasing to 63% (or 4.4% B_2O_3), brake fluids can meet DOT 5 specification.

Lubricants

More than 45% of lubricating oils are consumed in automotive (motor oil and transmission fluids) and aviation applications with about 30% used in industrial applications (greases, gearbox, and metal forming lubricants). The remaining 2% is consumed in nonlubricating uses, such as working fluid in hydraulic pumps. Lubricants are made by blending additives, viscosity modifiers, ashless dispersants, detergents, inhibitors, anti-wear agents, friction modifiers, and flow enhancers into a base oil stock to meet certain performance characteristics or specifications. Ideal lubricants should have the following properties:

- Excellent thermal oxidative stability
- Reduced friction
- High temperature anti-corrosion,
- Low sludge
- Pumpability at low temperatures
- Good elastomer compatibility
- Good storage stability
- No sulfur odor

Borates are used fairly widely in the manufacture of additives for lubricating oils. Extreme pressure additives have been developed based on the stable dispersion of alkali borate microspheres. Hydrated potassium and lithium borates have received much attention in this area. These inorganic borate spheres interact with metal load-bearing surfaces to form a film of extraordinary resilience. This tenacious film provides outstanding load-carrying capacity and wear protection. The small size and low density of dispersed borate make the lubricant very stable.

A number of nitrogen-boron-containing additives have been proposed for lubricating oil compositions. They are prepared by reacting polyamines, carboxylate esters, or amine/ester mixtures with boric acid or boric oxide at elevated temperatures.

In addition to their corrosion inhibitive properties, boron-containing additives have detergent and anti-rust properties, lubrication, reduction of carbonaceous deposits, anti-knocking, and low sludge formation.

Metalworking fluids

Metalworking fluids are primarily used in metal cutting and grinding applications to remove metal chips, reduce friction, and cool the cutting zone. Industrial machinery, transportation equipment, and fabricated metal applications are important markets, accounting for almost 90% of the demand. The properties of metalworking fluids containing borates are rust inhibition, reduction of friction and wear, efficient cooling capability, and as a biocide.

Water-based metalworking fluid formulations generally include a corrosion inhibitor component. Traditionally, a combination of sodium nitrite and an alkanolamine has been the inhibitor of choice for ferrous metal systems. However, concern over potential health hazards of the nitrite component has reduced or eliminated nitrite in the formulations. One replacement for nitrite is an adduct of *Optibor* and alkanolamine plus a triethanolamine (10%), biocide (1%), and water (54%) used for light metal removal operations. It is designed to be diluted 80:1 before use. Another formulation which has been shown to be an effective inhibitor for ferrous metal systems contains 0.4% sodium nitrite, 0.3% sodium molybdate and 0.1% borax decahydrate. The presence of nitrite in this formulation is not considered hazardous since no amine containing component is used.

The major components in cutting fluids are fatty acids, alkanolamines, *Optibor*, and water. Typically, cutting fluids have approximately 25% of the reaction product between boric acid and alkanolamine. The B_2O_3 content in cutting fluids averages about 2.6%. Boric acid alkanolamine esters act as bacteriostatic agents in cutting emulsions. They are also corrosion inhibitors. The use of boric acid alkanolamine esters has led to the development of high quality water-miscible cutting fluids, longer emulsion charge life, and better workplace conditions.

Water treatment chemicals

In heat exchange devices utilizing aqueous solutions, corrosion to metals or alloys could result in deterioration of heat transfer and a shorter service life. This problemis of particular concern in central heating systems, cooling towers, and circulating water devices. Metal or alloy corrosion is an electrochemical phenomenon. Oxidation takes place at the anode where the reaction product is metal ions which are released into the surrounding medium.

The inhibition of this reaction by growing an oxide film on the surface of the metal (passivation) will decrease the overall corrosion rate. Chromate, nitrite, nitrate, molybdate, silicate, phosphate, and borate are used for the anodic passivation. The first three are oxidizing inhibitors because they have sufficient oxidizing power of their own to effect passivation The rest can promote the oxidation of iron thereby passivating the surface of the metals.

In the presence of oxygen, borate can promote the passivating growth of ferric oxide film. In addition, borates have a buffering ability to make the solutions less aggressive. Borax decahydrate or *Neobor* are widely used as a corrosion inhibitor and pH buffer in heat exchangers. Exact formulations depend on the metals present in the system. However, they are generally similar to inhibitor compositions used in automotive coolants. The synergism between borate and other inhibitors often decreases the concentrations of other components required in the formulation.

Borates provide protection for ferrous metals under mildly corrosive conditions, and acts as a buffer and neutralizer of acidic materials. The minimum concentration of 0.6% borax was found necessary to afford protection.

The optimal pH for closed heat exchange systems is generally in the 9.8-10.5 range. It can be maintained by using borax decahydrate and sodium hydroxide (or sodium metaborate). It is preferred that the initial pH of the water treatment chemicals be relatively high, ie, about 10-10.5, because the pH decreases in use. The additional alkalinity is provided to neutralize the carbonic acid due to the carbon dioxide of the air which is absorbed on standing. Ammonium pentaborate is also used in small quantities for protecting steel in contact with polyvinyl acetate aqueous emulsions.

The corrosion inhibiting effects of *Optibor* was reported by Electric Power Research Institute in 1987. Boric acid has been shown to inhibit stress corrosion cracking and intergranular attack in steam generators in the nuclear power plants. As a result of the outstanding inhibition shown by boric acid in the field, plants are now using boric acid to control the corrosion problem in the steam generators. Boric acid is being applied via crevice flushing, low power soaks, or using a combination of these methods. Recently, potassium borate was also recommended for corrosion inhibition of closed cooling water auxiliary system for nuclear power plants. It has been found that the potassium-based inhibitor, kept virtually without sodium, will not produce secondary radiation in any significant amount, and at the same time results in prevention of corrosion in the closed cooling water systems.

Fuel additives

Two borate esters were used as gasoline additives and were claimed to assist in stopping pre-ignition and leaving a much cleaner carburetor. There has been a renewed interest in adding borate esters to gasoline for improving fuel efficiency.

Aviation fuel will pick up moisture from the air and this water slowly settles to the bottom of the storage tank or use tanks. The interface, the area of contact between the hydrocarbon fuel and the water bottoms, is a breeding ground for bacterial and fungus growth. Biobor®, dioxaborinanes (glycol borates), is an active microbicide and prevents such growth from occurring thus yielding a clean burning fuel. In 1991, U.S. Borax Inc. sold the Biobor business to Hammond Fuel Additives. This product has approximately 7.2% boron, 0.5% water, and 4.5% naphtha.