TECHNICAL BULLETIN

Borates in industrial cleaning products

Introduction

Borates have been used for more than 150 years as an aid to cleaning and laundering processes. Their value depends on the particular formulation in which they are involved, but a major utility is in pH control. Borates are also useful in aiding in the emulsification of oils and as a soft abrasive. When combined with polyhydroxy materials, borates can be used for viscosity control. Over the years, there have been numerous articles and patents published which cite the use of borates in cleaning formulations. In this bulletin, reference will be made to examples of patents and articles which have employed borates in cleaning formulations.

Borates buffering, building, water-softening, and stain-removal activities collectively deliver added performance to modern laundry detergents and cleaning products and added value to conventional sodium perborate[1,2].

Borax decahydrate, *Neobor*® borax pentahydrate, *Dehybor*® anhydrous borax, *Optibor*® boric acid, and sodium metaborates are the primary borate compounds used for cleaning and laundering formulations. U.S. Borax products are available in a wide range of screen sizes for dry blending, or may be used in solution. *Neobor* offers a more concentrated form and is more convenient to handle and store than borax. Sodium metaborate 4 mol and 8 mol are strong alkalis and more suitable for higher alkalinity cleaners, such as metal cleaners. They provide a high concentration of borate and are readily soluble in water. Boric acid is a very mild acid, and may be called for in some formulations. Further information on these products is available in the product data sheets and specification sheets.

Uses of borates in cleaning products

Metal cleaners

The need to clean the surface of metals subsequent to various metal working operations is well known. For example, parts obtained from machining operations are cleaned to remove metal fines, residual cutting oil, or dirt. Similarly the surface of sheet metal obtained from rolling operations is generally cleaned after the final reduction and prior to the application of slushing oils or coating oils which are employed to protect the surface or the metal sheet during coiling and subsequent storage.

Metal cleaners in powder or liquid form are commonly used to remove oil, grease, rust, and scale from metal surfaces. Highly alkaline detergent solutions (pH 9.5 or higher) are used almost exclusively as metal cleaners.

Due to the problems associated with handling and disposal of highly alkaline metal cleaning materials, there is a need for products which are effective for degreasing and cleaning metal surfaces but which do not include strongly alkaline detergents. Borates improve detergency by offering pH control and contribute to the cleaning process such as enhanced removal of oils and soils. The mild or moderate abrasive properties of borates can also assist in the cleaning process. Borates aid water softening by binding with calcium ions to form soluble complexes. More importantly, borates help promote formation of passivated surface layers on metals and inhibit corrosion. Improved multi-purpose metal cleaning compositions containing boramides (eg, triethanolamine borate), ethoxylated aliphatic alcohol or ethoxylated alkylphenol, alkanolamine salt of a fatty acid, glycol or ether glycol, anti-foaming agent and water were found to be highly effective cleaners for the removal of grease, oil, dirt, scale, and metal fines[3].

For stainless steel that has had previous contact with organic materials, dilute salt solutions, and food products, ferritic particles and oxides as well as corrosion products are likely to form. It can be effectively treated with *Optibor* to remove corrosion and restore passivation. The addition of nitric acid and a thickening agent or other wetting agents should help form an adherent coating. After a period of at least 30 minutes by washing or steaming, the stainless steel surface is restored to its original passivated smooth and bright finish[4]. Various cleaning agents for cleaning stainless steel before applying porcelain enamel were studied[5,6]. It was found that contamination of the surface with borate had no adverse effects on enameling.

Containers used in the foodstuff industry can be made of tin-plated ferrous metals. These containers are ordinarily formed through a process referred to as "drawing and ironing" where the tin-plated metal sheeting is drawn and intentionally thinned to form a sheet providing uniform wall thickness and producing a thin-walled, thick-bottomed container. A number of cleaning compositions were developed for removing lubricants from metal surfaces while providing corrosion resistance to the exposed areas of ferrous metal[7]. Borates—providing detergency and corrosion inhibition—are the major ingredient in this type of metal cleaner (>50 wt %) with the remainder consisting of sodium tripolyphosphate, sodium metasilicate, and nonionic surfactant.

It is known that polyphosphate-based products are used for cleaning solid material and that phosphate/alkali metal borate-based products are used for cleaning workpieces of aluminum and its alloys. These cleaning products are generally marketed as powdered mixtures and are delivered as such to a cleaning batch at intervals. The concentration of cleaning agent in the batch amounting to between 0.1-20% by weight. One of the difficulties of using powdered products is the sensitivity of surfactants to caustic soda. Aqueous alkaline cleaning compositions can be made from strongly alkaline concentrates and acidic concentrates comprising dispersions of boric acid or alkali metal borates in orthophosphoric acid. These liquid products are effective in removing grease from steel sheets, aluminum workpieces, and its alloys.

Work with aluminum cleaners has shown that cleaners based on borate-polyphosphate systems with surfactants are very effective before anodizing, brightening, adhesive bonding, welding, enameling, chromating, and phosphating[8].

A silver-cleaning compound comprising borax decahydrate, soda ash, ammonium chloride, and potassium cyanide was found to be effective in removing the tarnish and brightening silver or silver-plated articles[9]. A cleaning composition comprising sodium perborate, an alkali monopersulfate, and a bleach promoter selected from alkali metal and alkaline earth halides was developed to clean dental appliances having metal parts[10]. Sodium perborate in this cleaning solution exhibited improved tarnish and corrosion resistance.

Perborates promote the development of a passivated surface layer of metals, leading to corrosion resistance. The antibacterial activity of perborate also reduces corrosion by discouraging the growth of microorganisms in water in contact with metals[11]. The use of tetraacetylethylenediamine (TAED) under alkaline conditions to activate peroxide and produce effective low-temperature bleaching and biocidal activity is well known. Research at Warwick International Ltd has shown that reacting TAED with sodium perborates under acidic conditions provides a means of generating peracetic acid solutions. Peracetic acid is an effective oxidizing agent and a broad spectrum biocide. Products used as a biocide need to have proper U.S. Environmental Protection Agency (EPA) registrations.

Corrosion inhibition of carbon steel by perborates was established by electrochemical and gravimetric methods[12]. A copper-based corrosion inhibitor for metal in contact with acid gas solutions in alkanolamines functions by having an oxidant (eg, perborates) present which provides polysulfide species at the metal surface[13]. After oxidative pickling, steel surfaces are brightened using a strong solution of sodium perborate and sodium oxalate[14], or potassium titanium oxide oxalate[15]. The latter can replace chromating for passivation. Copper-containing scale in pipes is removed by alternatively heating with ammoniacal perborate solutions and 5% HCl with corrosion inhibitor[16].

Aluminum is chemically machined using a mixture of H_3PO_4, HNO_3, KHF_2, $FeCl_3$, and sodium perborates[17]. Aluminum surfaces are etched to give low reflectance by exposure to a caustic solution of a chelating agent (eg, sorbitol) and perborates[18].

A scale remover formulation is claimed containing sodium perborate, $NaHCO_3$, Na_2CO_3, EDTA, and anionic surfactant[19]. Cleaning and corrosion protection of metallic surfaces is claimed[20] for a nonionic detergent containing sodium perborate, carboxymethylcellulose, formatin, and aqueous ammonia. Cooling water containing oxidants such as perborates is protected against growth of ferrobacteria which cause biocorrosion[21]. This application requires EPA registration. Aluminum cleaned with perborates/phosphate is corrosion resistant[22]. This aluminum bathtub cleaner with reduced corrosion is patented containing sodium perborate and a sodium phosphate.

Tin cans are rendered corrosion resistant for 2+ years after sterilization at pH 9 with a solution of perborates, Na_2HPO_4, triethanolamine phosphate, anionic detergent, and sodium silicate[23]. Crude silver is freed of copper and other impurities by melting, contacting with oxygen from perborates, and treating with a caustic flux containing *Optibor* and borax[24,25]. A solution for fast corrosion testing contains up to 300g/l of NaCl and is saturated in perborates as a cathodic depolarizer[26]. Adhesion of polymer films to steel is improved by having perborates present in the polymer emulsion during dip coating[27].

Hard surface cleaners

Aqueous based alkaline cleaners consisting of surfactants, sodium tripolyphosphate, silicate, sodium hydroxide, and sodium borates are used to remove oil, grease, rust, scale, and other particulate from hard surfaces in the industrial and institutional (eg, hospitals, schools, and restaurants) markets. Borate solutions have moderate oil and soil removal characteristics but they also promote formation of passivated surface layers on metals and inhibit corrosion. An all-purpose liquid detergent for the industry and institutional industry is made from borax, surfactant, alkylarylsulfonic acid, tetrapotassium pyrophosphate, sodium hydroxide, and water[28].

The brewery and soft drink industries utilize equipment that is in constant contact with water, such as soakers, conveyor chains, spray nozzles, pasteurizers, and sterilizers. Rust and corrosion in these industries lead to higher maintenance costs by decreasing the workable life of equipment, increasing frequency of repairs, and requiring closer maintenance checks. In this industry, the use of strong alkalis is prohibited due to their harmful effects such as softening glass, deterioration of lithographed colors, and corrosive action on contact with skin. Hence, a moderate alkali is needed and is available in borates, as evidenced by its resistance to change over a concentration range of 0.1-5.0%, in terms of its alkali strength. It is less strong than caustic, and as such, is more suitable for this application. The ability of borates in solution to maintain a constant pH over a wide concentration makes it an excellent buffering and anti-corrosive agent.

Formulation of a slowly dissolving block based on a gelled or solidified borate suspension softens flush water (and thus prevent limescale), deodorize, and remove or inhibit the build-up of stains. Placed in the toilet, it could be manufactured either from an aqueous borate suspension converted into a hydrogel polymer, or alternatively by preparing and cooling a molten borate-in-polyethylene glycol suspension. Slow release or dissolution of the borate would be the feature of the product. The presence of small amounts of boron was found to be capable of controlling the microbial growth[29]. A composition specifically designed to remove urine from soiled fibers or sand contains perborates plus other peroxide salts coated with a water-soluble synthetic glue, organic acids, builder salts, and surfactant[30]. A cleaning/bleaching product for flush toilets consists of two solid blocks, one comprising neutral salt, detergents, dye, and perfume while the other contains neutral salt, detergents, and perborates[31]. Tablets with perborates, a chemiluminecent compound, and a halogen source give a strong blue light with every flush[32]. Tablets for cleaning food such as vegetables are formulated with perborates, potassium peroxymonosulfate, and other ingredients[33]. Paper, fabric, or foam can be impregnated with compositions containing surfactants, builders, and perborates as a gas-forming agent for cleaning pads for glass, skin, and dentures[34].

Biocidal properties of sodium perborates, as well as its powerful stain removing properties, recommend it for use in hard surface cleaners[35]. An effective perborate-based cleaner for circulatory bath tubs contains sodium sulfate, sodium percarbonate, a chelating agent, and a small amount of surfactant[36]. A hard surface, foaming cleaner is formulated with perborates and a metal ion or other decomposition catalyst, builders, and surfactant[37]. Good cleaning and corrosion protection are provided by a perborate-based cleaner with carboxymethylcellulose, formaldehyde, and ammonia[20]. A scouring agent for hard surfaces is formulated with perborates, an acylated activator, detergent, and powdered quartz[38]. A composition for cleaning carbonized residues from PTFE-coated cookware comprises perborates plus sodium lauryl sulfate or disulfonaphthylmethane[39]. Self-heating scouring powders containing perborates use calcium or magnesium chloride to generate heat on contact with water[40].

Removal of pesticide residues from metal surfaces is improved by adding nonionic detergent, perborates, and triethanolamine to a soap/alkyl succinate cleaner[41]. Perborate is a detoxicant for hazardous organophosphates[42] and is even more effective in the presence of organic onium salts[43]. A detergent for cleansing daily equipment contains fatty acid, perborates, caustic, STPP, nonionic surfactants, and soda ash[44]. A bleach for solid surfaces at 60-100°C is a simple mixture of perborates, crystalline aluminosilicate, and detergent[45]. Stabilized, near neutral perborate concentrated aqueous solutions which increase in pH on dilution may find application in hard surface cleaners[46].

Drain cleaners based on perborates can be made with nonionic detergent, tripolyphosphate, powdered silica, and Glauber's salt[47]. An aluminumcaustic type also contains cobalt carbonate, surfactant, potassium salts, and perborates[48]. Another formulation uses coated caustic granules, a hypochlorite generator, and perborates[49].

Redox® drain cleaning compositions contain perborates, reducing agents such as sodium thiosulfate, reducing sugar, thiourea, and caustic soda[50]. These produce greater than 230 cal/g of heat and turbulence when dissolved in water. An example is sodium perborate tetrahydrate plus sodium sulfite[51]. A two-component system uses caustic soda and a second component made up of perborates, sodium bisulfate, and BIO-TERGE®[52]. Semi-permeable membranes used in wastewater treatment are cleaned with a solution of sodium perborate tetrahydrate and EDTA, which gives better results than acid washing[53]. A hand washing paste with oxidizing and reducing effects is formulated with perborate granules coated with silicone oil dispersed in a paste comprising sodium dithionite plus soap, pumice, and other ingredients[54].

Powdered hand soaps

Powdered hand soaps enjoy a considerable share of the industrial hand cleaning market. Their primary purpose is to remove medium to heavy soils such as are encountered in industrial operations. In addition to a high-grade soap, borax decahydrate is the most widely used soluble scrubber[55]. Insoluble scrubbers contain either vegetable or mineral materials such as ground cornmeal, corncob flour, wood flour, rice hulls, peanut hulls, pumice, silica, or finely ground sand. The last three mentioned scrubbers are minerals which may abrade the skin and eventually clog plumbing. The former group are vegetable in nature and susceptible to insect and microorganism attack and may also cause plumbing difficulties. Borax, an inorganic soluble scrubber, possesses none of these difficulties.

The advantages of borax in powdered hand soaps are:

- Availablity in a range of particle sizes which enables the formulator to tailor the abrasive quality of the formulation to meet market demands
- Improves detergency by offering pH control and contributes to the cleaning process such as enhanced removal of pigment and oily soils
- Aids water softening by binding with calcium ions to form soluble complexes
- Provides quick cleaning and free rinsing because it is soluble
- Gentle to the skin yet highly effective in removing embedded dirt
- Not a skin sensitizer
- Not susceptible to insects or microorganisms
- Soluble, therefore, does not clog drains

Glass cleaners

Borate's improved glass-cleaning composition is particularly adapted for use in cleaning windshields and other glass surfaces exposed to the external environment during motor vehicle operation. The compositions consist essentially of aminopolycarboxylic acid chelating agent, amine sulfonate, corrosion inhibitor, methanol, and boric acid[56]. It is preferred that boric acid be included in the compositions where the cleaning composition is used at low temperatures. A cleaning compound for glasses especially for use in cold water was developed[57]. One example of this system consists of *Neobor*, sodium tripolyphosphate, sodium hydrogen sulfate, urea, sodium dichloroisocyanurate, and sodium dodecylbenzene sulfonate. Other glass cleaning formulations contain borax dechydrate, *Neobor*, sodium hexametaphosphate, sodium bisulfate, sodium sulfate, nonionic surfactant, chlorine releasing agent, and protease enzyme[58,59].

Automatic dishwashing detergents

Traditional dishwashing detergents are largely based on sodium metasilicate and sodium tripolyphosphate and contain chlorine-releasing chemicals—such as sodium choroisocyanurate—to remove stains and kill bacteria. The high solution pH is necessary to saponify fat and grease. Alkaline silicates have the ability to suspend the detached soil and prevent its reposition while maintaining a high level of alkali reserve. Silicates are also effective anti-corrosion agents and provide adequate protection to all internal parts of the washing machine. Sodium tripolyphosphate provides a water softening property and acts as an additional soil suspension agent. Sodium choroisocyanurate is effective in removing stains and small quantities of residual protein and fatty matter. In the United States, the slightly less alkaline sodium disilicate is used with additional sodium carbonate due to the adverse effect of strong alkalinity on glazes. Today, surfactants are typically incorporated into dishwash preparations[60]. Due to the corrosive nature of sodium silicates and chlorine-release agents as well as the reduction of phosphate due to environmental concern, new powder and liquid automatic dishwashing detergents have been developed. The newer formulations consist of sodium tripolyphosphate, sodium silicates, sodium carbonate, sodium citrate, surfactants, and oxygenated stain-removing agents either with or without an activator. Enzymes (protease, amylase, and lipase) are another important ingredient in dishwashing products. They are more efficient in stain removal at lower temperatures than the previous versions[61].

The bleach function in automatic dishwash detergents is introduced as hydrogen peroxide or in chloride form as hypochlorite, N-chloro compounds, and chlorinated trisodium phosphate. Most recently, dichloroisocyanurates and trichloroisocyanuric acids have been used. Incompatibility with organic components such as fragrance, color, and enzymes, required an alternative bleaching system provided by peroxygen compounds[62-64]. Perborate also showed extended shelf life[65].

Bleach stabilizers and activators also exist in automatic dishwashing detergents formulations (eg TAED), providing excellent bleach performance at the lower temperature washes that are becoming the rule rather than the exception. Borates and perborates will find an increasing use in automatic dishwashing detergent compositions due to the following reasons[66]:

- Perborates function as alternative bleaching agents to chlorine releasing compounds
- Borates are china-glaze protectors
- Borates provide a moderate alkaline buffering
- Perborates have biocidal property (EPA registration required)
- Borates are known to have many cleaning functions

In the past, the main functions of borates in automatic dishwashing detergents were peroxy bleaching, glaze protection, and to a lesser extent anti-caking. Whereas the use of perborates has flourished under the new system of enzymatic automatic dishwashing detergents, the use of boric acid and boric oxide as glaze protectors and anti-caking agents has all but disappeared. A phosphate-free automatic dishwashing formula consists of zeolite, polyacrylate polymer, metal silicate, surfactant, sodium toluene sulfonate, perborate or percarbonate, and a peroxygen activator[67-70].

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About U.S. Borax

U.S. Borax, part of Rio Tinto, is a global leader in the supply and science of borates—naturally-occurring minerals containing boron and other elements. We are 1,000 people serving 650 customers with more than 1,800 delivery locations globally. We supply around 30% of the world's need for refined borates from our world-class mine in Boron, California, about 100 miles northeast of Los Angeles.

About 20 Mule Team products

U.S. Borax produces the *20 Mule Team*® borates family of products from naturally occurring minerals and have an excellent reputation for purity and safety when used as directed. Borates are key ingredients in a number of industrial applications including fiberglass, glass, ceramics, batteries and capacitors, wood preservatives, and flame retardants.

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