Technical Bulletin

Borates in personal care products

1. Introduction

1.1 Oil well cement set retardant

In order to compete in the huge but diverse personal care industry ($25.5 billion in the U.S.), personal care product suppliers have to continually reformulate their products. The objectives are aimed at bringing more value to their customers and reducing their manufacturing costs. As a result of constantly-changing market conditions, personal care companies are forming much closer working relationships with raw material suppliers to utilize their expertise in developing specific chemical ingredients for their products.

Borates and their derivatives such as sodium perborates have been used, recommended for use, and patented for a variety of personal care products, laundry detergents and household/industrial cleaners. The activities of borates collectively deliver added performance to modern laundry detergents and cleaning products and added value to conventional sodium perborate (References 1 and 2). In this bulletin reference will be made to examples of patents and articles that have been issued in recent years which have employed borates in personal care products.

2. Uses of borates in personal care products

2.1 Skin care products

The skin care market in the U.S. ($3.5 billion) continues to grow and should increase at least 30% by the end of the century, reaching $4.6 billion. Creams are the largest segment ($1.8 billion) of the skin care market, followed by deodorants, lotions, and lip and eye preparations. As consumers expectations continue to rise, products are becoming increasingly sophisticated.

In addition to their excellent cleaning functions, borates are used in skin care products for the following reasons:

- pH buffering
- Viscosity or rheology control (crosslinking with starch or polymers)
- Emulsification with oils or waxes
- Enzyme stabilization or inhibition
- Foam stabilization
- Moisture retention
- Active oxygen carrier (as in perborates)

Borates are used in conjunction with beeswax, almond oil, spermaceti, oil, petrolatum, sodium carbonate, stearic acid, glycerin, and perfume in the production of facial creams (Reference 1a). Today, both Borax Decahydrate (Borax 10 Mol) and *Optibor*® boric acid are widely used in the facial creams manufactured by the major and generic cosmetic makers.

For example, cold creams commonly used to remove make-up, frequently contains Borax Dechydrate NF based on its emulsifying property with beeswax. Borax Decahydrate is also used along with stearic acid, petrolatum, lanolin, triethanolamine, and vegetable oil in baby creams. Borax was also used to make borated petroleum jelly for cutting down the urine smell. Moisturizing lotions or creams were prepared from egg white, citrus fruit extract, wax, sugar, vegetable oil, mineral spirit, potassium sorbate and boric acid (Reference 4). Skin creams for rejuvenating the skin comprise a combination of beeswax, a vegetable oil, sorbitol tristearate, methyl paraben, hydroquinone monomethyl ether, water, Borax, preservative, and perfume (Reference 5). Other skin care products such as facial creams or skin lotions containing boric acid or Borax were also developed (References 6 - 22). Today borates can also be found in some products such as shaving creams and bath salts.

Borates in personal care products

Optibor boric acid has been used in various skin cleaners, mainly as a buffer or an antiseptic. Alkali borates such as Borax have been used in skin cleansing preparations as scouring agents in order to increase the cleansing effect or provide a protective ointment layer on the skin. The ability of boric acid to form water-soluble complexes (chelates) with certain water-insoluble substances, specially with dihydrodiols which contain cyclic hydrocarbons, was exploited in skin cleansing agents (Reference 23). *Optibor* boric acid, an essential constituent of the invention and together with a water-containing anionic detergent (e.g., sodium lauryl ether sulfate), provides a possibility of the formation of borate ions in almost neutral conditions. The rate of formation and stability of the water-soluble dithranol borate chelate are optimal for the washing purpose.

Since 1992, alpha-hydroxy acids have been the most popular new ingredients in skin care products. They can make skin shed dead cells more rapidly and increase its moisture content. Such changes can make wrinkles less evident, and can help treat acne or other skin damage. A novel industrial technology was developed for separating hydroxy fatty acids in lanolin fatty acids from the concomitant non-hydroxy acids (Reference 24). The alpha-hydroxy fatty acid fraction can be converted to boric acid ester and is isolated by vacuum distillation. The separated boric acid ester can be hydrolyzed to hydroxy acids. This process will eliminate the animal odor and dark color of lanolin fatty acids to meet the industry's demand. The purified alpha-hydroxy acids are used with beeswax, Borax, perfume and water to produce a cold cream with satisfactory properties.

A novel skin lotion or moisturizer consisting of Borax, castor oil, oleic acid, sodium thiosulfate, and calcium hydroxide was developed (Reference 25). This product was claimed to have therapeutic values such as removing the "piled up" hyperkeratotic scales in seborrheic capitis and psoriasis vulgaris as well as expediting the involution of the lesions of acute herpes simplex. A skin lotion for treating blemished skin with acne was developed (Reference 26). The lotion contains boric acid or Borax, ammonium hydroxide, hydrogen peroxide, salicylic acid and other common additives used in the cosmetics industry. Stable emulsifiable compositions useful for preparing personal care products such as skin creams comprise a mineral oil, a refined oxidized petrolatum, and sodium borates for neutralizing the acidic functionality of the oxidized petrolatum (Reference 27). Skin lotions including a vasoconstrictor for reducing blemish redness were developed (Reference 28). This skin lotion comprises an effective amount of phenylephrine hydrochloride and boric acid as an antiseptic (not FDA approved). In a preferred embodiment, Borax is combined with a substantial amount of an alkyleneoxy sulfate ester salt or tauride salt and a small amount of water. The cleaner aids in the treatment of oily skin, acne and scalp conditions (Reference 29).

In the 1980s, retinoids revolutionized the skin care market as a miracle treatment for lines and wrinkles. During the recent years, alpha-hydroxy acids (derived from fruit, milk, and sugarcane) have been the popular new ingredient for improving skin texture. Producers of skin care ingredients are searching for next-generation additives that will surpass alpha-hydroxy acids or provide new therapeutic benefits. Starches are gaining many new uses in skin care and they can improve the aesthetics and performance of color cosmetics, skin creams, lotions and baby care products. The interactions between starches and borates are the basis for many industrial applications such as adhesives. Borates can provide many benefits to starch or dextrin derived products (Reference 30).

Sunscreen cream can be made from Borax Decahydrate, beeswax, silicone fluid, octyl stearate, sorbitol, and water (Reference 31). Rouge-emulsified cream can be made from Borax, mineral oil, petrolatum, beeswax, pigment, methyl p-hydroxybenzoate, and perfume. An emollient cleansing cream for makeup removal incorporates Velsans as a moisturizer. This water-in-oil product, containing Borax, mineral oil, beeswax and propylene glycol is designed to be wiped away with a tissue. Another cleansing cream formulation contains lanolin oil, stearic acid, beeswax, glyceryl stearate, and Borax in a smooth, creamy emulsion. It will remove facial makeup and environmental contaminants such as dust. One of the most common cosmetic emollients used today is a cold cream. Mixing mineral oil, beeswax

and Borax in water will produce a cold cream. Another formulation of cold cream consists of Borax, beeswax, mineral oil, glycerin, propylene glycol, and preservative. The pH of this product is 7.8 with 28% solids. A moisturizing lotion is made from Borax, mineral oil, cetyl esters, cetyl alcohol, stearyl alcohol, and stearic acid as well as perfume, dye and preservative. A skin care lotion contains boric acid, glyceryl stearate, propylene glycol isostearate, lanolin oil, dimethicone, glycerin and lanolin quaternary.

2.2 Soaps

Traditional bar soaps are still the sales leaders, but new introductions mainly in the form of body washes and shower gels are gaining popularity ($0.3 billion). The annual sales of bar and liquid soaps is about $2 billion.

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 is the most widely used soluble scrubber (Reference 32). The advantages of Borax Decahydrate used in powdered hand soaps are:

- Borax, available in a range of particle sizes, enables the formulator to tailor the abrasive quality of the formulation to meet the demands of the market.
- Borax improves detergency by offering pH control and contributes to the cleaning process such as enhanced removal of pigment and oily soils.
- Borax aids water softening by binding with calcium ions to form soluble complexes.
- Borax provides quick cleaning and free rinsing because it is soluble.
- Borax is gentle to the skin yet highly effective in removing embedded dirt.
- Borax is not a skin sensitizer.
- Borax is not susceptible to insect or microorganism attack.
- Borax is soluble, and therefore will not clog drains.

Today, hand soaps in powdered or liquid forms also contain builders to improve detergency, fatty materials to impart softness, and perfumes and dyes for aesthetic reasons. Synthetic liquid hand soaps can be made with Borax, surfactants, triethanolamine, dodecyl benzene sulfonic acid and water (Reference 31). The pH is between 8 and 8.6 and the solid content is around 8%. Several formulations have been developed for hand and skin cleaning. A system of skin cleaning compounds has been claimed which involves a mixture of polydimethylsiloxanes and the reaction product of liquid polydimethylsiloxanes with Boric oxide (Reference 33). Another system for cleaning and softening hands is a composition containing powdered Borax, an aqueous biodegradable anionic and nonionic surfactant, and a starch paste. This system is claimed to be capable of removing grease and oils, inks and carbon deposits from the hands (Reference 34). Abrasive cleaners containing small quantities of Borax along with anionic surfactants and foam stabilizers for use in removal of dead skin, excess oil and comedones of acne from the face (Reference 35). Another hand cleaner with a mild abrasive action is based on 30 to 80% Borax along with ethoxylated alcohol and a fatty amide (Reference 36). A novel abrading cream skin cleanser is based on a Borax/water mixture (Reference 37). One example of this cleanser contains 40% Borax, surfactants, cetyl alcohol and water. This product is stable for long periods at room temperature.

Bar soaps are made by both the major producers and a multitude of specialty soap manufacturers. A conventional bar soap is made from distilled fatty acids, plant oils and animal tallow. Other ingredients such as fillers, perfumes, antioxidants, optical brighteners, etc. are added to improve the product characteristics. Non-soap detergents such as synthetic surfactants can substitute for natural fatty acids to enhance the cleaning function of the soap. The surfactant improves the wetting ability of water, loosens and removes soil with the aid of wash action, and emulsifies, solubilizes, or suspends soils in the wash solution.

Technical Bulletin

Borates in personal care products

Borates were used in the production of laundry soap chips and bar soaps for personal care. However, this was discontinued in the 1960s. Recently, enzymes were included in the bar soaps to enhance the cleaning function (Reference 38). Enzymes aid in breaking down complex soils, especially proteins such as grass and blood, so that they can be more easily removed by other detergent ingredients. The enzymes that are incorporated in the bar soaps are the usually proteolytic enzymes such as protease, amylases, cellulases and oxidases. Incorporation of enzyme in bar soaps requires the stabilizing agents due to the presence of significant amounts of water. A mixture of a boron compound, a polyol, an organic acid or its alkali metal salt can effectively stabilize the enzymes contained in the bar soaps. The boron compound can be either boric acid or Borax, and the polyol an aliphatic polyol such as propylene glycol. The organic acid is an aliphatic carboxylic acid such as formic acid, succinic acid, adipic acid, glutaric acid or citric acid. Examples of the alkali metal salts of inorganic acids are sodium sulfate, sodium chloride, sodium carbonate, sodium bicarbonate, or sodium phosphate.

In general, the intimate contact between the bleach and soap would lead to decomposition of the bleach. It was found that some commercial bleaching agents such as sodium perborates could be incorporated into a bar soap under certain conditions (Reference 39). A bleach stabilizer such as magnesium silicate can substantially improve the perborate stability.

A recent invention pertains to applying an adhesive to form a bar soap for ease of use (Reference 40). This adhesive agent is made from wheat flour, glue, alcohol, boric acid, and fragrance. These ingredients are mixed and kneaded in optional proportions in hot water to produce a paste. The resulting paste can be used to produce a bar soap. Boric acid is chosen for its antiseptic (FDA approval required) and antioxidant properties. Also, the crosslinking reaction between boric acid and starch is the basis for developing the adhesive effect.

The builder in bar soap enhances the cleaning efficiency of the surfactant by inactivating water hardness minerals. Builders soften water by sequestration, precipitation, or ion exchange. Most builders provide a desirable level of alkalinity, which aids in cleaning, and disperse and suspend soils to prevent their re-deposition. Carbonate and silicate systems have a predominant role as builders in today's detergent formulations. Citrate has reappear in some products to support building, dispersion, and solubility. However, its cost and limited sequestration ability have confined it to a supporting role in the laundry detergent marketplace.

Borates contribute to the functions of a builder in basic detergency processes (References 41 and 42). Borates provide alkalinity and pH buffering. The sequestration of calcium by borate is sufficient to inhibit the precipitation of surfactant in hard water. In addition, it is shown that borate can boost oily soil detergency through a lowering of the interfacial tension. Due to the higher negative zeta potentials of common pigment soils such as iron oxide when suspended in dilute borate solutions, pigment deposition onto cotton in washing tests is consequently reduced. The combination of effects makes borate a better performer than some of the more traditional detergent builders. The advantages of borates in bar soap for laundry or personal care products are:

- Enzyme stabilization
- pH buffering and control
- Antioxidation
- Water softening
- Enhanced stain removal
- Accelerated grease or oil removal
- Gentle to skin
- Corrosion inhibition
- Low toxicity
- Active oxygen carrier as in perborate bleach

Borates in personal care products

2.3 Oral hygiene

The U.S. oral care industry has approximately $2.4 billion annual sales with $1.6 billion of dentifrice sales and $0.8 billion of mouthwash sales. Toothpaste based on baking soda, hydrogen peroxide, and fluorine-containing chemicals as tooth whiteners have generated impressive sales for the past few years. The combination of two incompatible ingredients, baking soda and hydrogen peroxide, can be done through use of a dual-chamber pump or microencapsulation. Several major toothpaste producers have introduced their own versions of this popular product in recent years.

Borates are used in some specialty toothpaste and mouthwash products today. Aqueous sodium perborate can be used for the bleaching of discolored non vital teeth (Reference 43). A toothpaste formulation uses a mixture of calcium peroxide and sodium perborate as oxidizing agents to remove stains and plaque from natural teeth as well as composite filling material (Reference 44).By far, the largest use of borate today is in the denture cleaning products. Denture cleansing is generally carried out by soaking dentures overnight in an aqueous cleansing solution. Multiple oxidizing and bleaching agents are used together to remove visible stains from hard surfaces, while at the same time effecting the removal of scale or plaque build-up. Sodium perborate monohydrate and its derivative, sodium oxoborate, are commonly included in the denture cleaning formulations for their cleaning, bleaching, disinfecting and effervescing properties (References 45 - 49). Sodium oxoborate in particular effervesces on contact with water and is widely used in denture cleaners. This effervescent property results in the removal calculus and plaque deposits as well as the removal of stains.

A simple example of denture cleaner contains sodium perborate monohydrate, sodium oxoborate, Oxone (potassium persulfate), and builder (sodium carbonate and sodium phosphate) (Reference 50). It has been proposed that the persulfate is the oxidant and the perborate provides the effervescence. Enzymes have been incorporated such as protease and amylase to enhance the cleaning function (Reference 51). A denture cleaner based on a mixture of perborate and borax also contains silica gel, some surfactant, thymol and a deodorizer (Reference 52).

2.4 Hair care products

Annual sales in the hair care market are around $5 billion with 5% projected annual growth rate. According to a recent survey, the three principal segments in the hair care market are shampoo ($1.7 billion), conditioners and treatment ($925 million), and styling products ($2.4 billion).

Borates have been used in a variety of powdered and liquid shampoos as well as conditioners (Reference 53). In shampoos, Borax is used in conjunction with soda ash, Fuller's earth, talc, perfume, castor oil, petrolatum, wax, and preservative. In conditioners, Borax is used in conjunction with methylparaben, mineral oil, lantrol, lanogel, lanolin, petrolatum, and beeswax.

A hair shampoo consisting of Borax Decahydrate, colorant and perfume was developed (Reference 54). This shampoo also can provide conditioning and make hair manageable and attractive. When peroxy compounds such as sodium perborate are included or used in the preparation of selenium sulfide-containing shampoo compositions, these compositions provide anti dandruff efficacy and color stability without requiring the use of a buffer system (Reference 55).

Rinse-free shampoos gain their property from a high water content and an absorbent gel which entraps the dirt without leaving residue. This high water content means that the shampoo and the entrapped dirt are easily removed by toweling and/or combing the hair (Reference 56). This shampoo is based on he use of a cross-linked, carboxylated cellulosic material which acts as an absorbent. The carboxylated cellulosic material is cross-linked by the aluminum acetate/boric acid and sells with the aqueous solution.

A neutralizing rinse comprising an acid (e.g., boric acid), a hydroxyalkylcellulose thickener, a wetting agent and a color indicator was developed (Reference 57). The product aids in the chemical relaxation of hair so as to allow hair to be straightened, curled or waved. It also helps reduce the swelling and subsequent damage to the hair and scalp caused by the rinsing products and process.

Hair dye can be formulated with sodium perborates as the oxidizing agent (Reference 58). Long lasting hair wave setting formulations which also dye the hair contain a reducing agent such as thioglycolate or cysteine, a metallic salt (FeSO4), a metal-activated dye, and a perborate salt (References 59 and 60). Dry hair bleaching compositions use perborates in conjunction with guanidine derivatives and peroxydisulfate salts (Reference 61). The two-component hair dye consists of the oxidation dye and the oxidizing agent such as perborate (Reference 62). The powdered hair dye and the oxidizing agent are mixed just prior to their use to prepare a tinting mixture.

Aqueous mixtures containing a precondensate of glyceraldehyde and resorcinol with *Optibor*® boric acid impart excellent and lasting set holding to hair, exhibit multi-stylability, and improve the resistance to humid conditions and removal by normal shampooing (Reference 63). Borates were also used with sodium bicarbonate, starch, ammonia, sodium hydroxide, sodium pyrophosphate, and oil in the production of permanent wave solutions (Reference 53).

A hair-growing agent or hair tonic for developing and growing terminal hair on a hairless or bald scalp area was developed (Reference 64). An oxidizing agent such as perborates was found to be capable of controlling or suppressing an enzymatic activity of 5-alpha-reductase present in sebaceous glands. It prevents 5-alpha reductase from converting testosterone to 5-alpha dehydrotestostevene, which can inhibit nitrosis of hair follicle matrix cells. Hair-setting creams can be made from Borax, lanolin, mineral oil, sorbitol sesquioleate, beeswax, perfume and water (Reference 31). They can also be made from Borax, petrolatum, mineral oil, beeswax, spermaceti wax, preservative, sorbitan stearate, and fragrance.

2.5 Eye care products

Eye drops or artificial tears are used to moisturize irritated eyes, remove redness or relieve itching associated with allergies and colds. Both Borax Decahydrate NF and *Optibor* NF are frequently added in small quantities to these eye care products for providing pH control and moisture retention. The active ingredients in these products are oxymetazoline hydrochloride, tetrahydrozoline hydrochloride, pheniramine maleate, naphzoline hydrochloride or hydroxypropyl methylcellulose. Common preservatives are benzalkonium chloride, edetate disodium, or sobic acid.

Sterile saline solutions for contact lenses are often buffered with small quantities of Borax Decahydrate NF and *Optibor* NF. These solutions with or without preservatives are used for daily cleaning and rinsing of contact lenses before wearing and weekly removal protein residues during disinfection. The lens rewetting drops, containing Borax Decahydrate NF and *Optibor* NF, make contact lens wear more comfortable.

Cleaning and sterilization of contact lenses without eye irritation can be accomplished with a solution of thimerosal and sodium perborates (Reference 65). Simultaneous cleaning and disinfecting also are accomplished using perborate-activated proteolytic enzyme (Reference 66). A 2-package product for the same use has aqueous or granular perborates in one compartment and an aqueous metal ion-surfactant combination in the other (Reference 67). Discolored contact lens are restored by boiling in an acid peroxygen solution followed by alkaline perborates (Reference 68). Lenses which have absorbed preservatives from cleaning solutions are restored by soaking in a perborate solution containing ethylene oxide-propylene oxide copolymer. Dyed plastic lenses can be bleached with perborate solution containing anionic surfactant (References 69 and 70).

Borates in personal care products

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Technical Bulletin

Borates in personal care products

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 500 customers with more than 1,700 delivery locations globally. We supply 30% of the world's need for refined borates from our world-class mine in Boron, California, about 100 miles east of Los Angeles. We pioneer the elements of modern living, including:

- Minerals that make a difference: Consistent product quality secured by ISO 9000:2001 registration of its integrated quality management systems
- People who make a difference: Experts in borate chemistry, technical support, and customer service
- Solutions that make a difference: Strategic inventory placement and long-term contracts with shippers to ensure supply reliability

About *20 Mule Team*® products

20 Mule Team borates are produced from naturally occurring minerals and have an excellent reputation for safety when used as directed. Borates are essential nutrients for plants and key ingredients in fiberglass, glass, ceramics, detergents, fertilizers, wood preservatives, flame retardants, and personal care products.