

Borates in oilfield chemical applications



Introduction to borates' uses and benefits

Borates possess a combination of properties and behaviours that make them desirable for use in various oilfield applications. These properties are:

- Polymer cross-linking via borate ester formation: The extent of cross-linking is controllable and reversible, which is not possible with other cross-linkers.
- Wide ranging water solubility and dissolution rates: From highly soluble rapidly dissolving to low solubility or slowly dissolving products. Borate solubility is also strongly temperature dependent.
- Alkalinity and alkaline pH buffering
- Water hardness tolerance: At low concentrations borates will form soluble ion-pair complexes with alkaline earth metal cations present in sea and formation water.
- Oxidizing agent: Perborate releases hydrogen peroxide when dissolved in water.
- Neutron absorption: The ^{10}B nucleus is exceptionally effective at doing this.
- Corrosion inhibition: Borates are anodic inhibitors, promoting the formation of passivating oxide layers on various metal surfaces.
- Anti-microbial action: Borates are used in various industrial and consumer products.
- Benign environmental profile: Borates are considered to pose a low risk.

Technical challenges in the oil and gas industry

Oil has been a dominant primary energy source for more than five decades and is likely to remain so for the next few. High consumption has depleted the most easily exploitable resources. Oil and gas exploration and production projects increasingly operate in geologically and climatically challenging environments, at greater depths below the surface and in more remote regions. This demands more sophisticated engineering solutions, for example the drilling of longer and deeper (hotter) deviated wells and also higher performing oil well fluids and fluid additives. Production from existing fields is being pushed to higher yields through stimulation and enhanced oil recovery (EOR) techniques. The challenges faced by the oil and gas industry, from initial reservoir prospecting to end-of-life production, rely increasingly on bulk and specialty chemicals to ensure continued, affordable supply until alternative renewable and non-renewable primary energy sources are fully developed.

Borate applications

Today, borates are employed in a number of important oil field applications, which can be grouped under the activities "Drilling and Exploration" and "Production and Improved Oil Recovery."

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1. Drilling and exploration

1.1 Oil well cement set retardant

Drilled well bores need to be stabilized before they are operational. A steel casing surrounded by cement reinforces the walls to prevent them from collapsing. The cement properties must be carefully controlled to ensure it can be pumped into the well but set when in place. Prevention of premature setting is particularly challenging when the 300°F temperatures at the bottom of the hole accelerate the process. Set retardants are added to the cement to provide the necessary control. Borates are widely used set retardants in oil well (and many other) cements. Although these are often based on ordinary Portland cement, such as the American Petroleum Industry's class G and H cements, others, for example magnesium oxychloride and calcium aluminate can also be retarded very effectively with borates. The proposed mechanism of action is that borates adsorb onto the surfaces of cement grains where they react with the available calcium ions to form calcium borate coatings that are a barrier to grain hydration and cement setting. Since the goal is to balance pumping and setting of the cement, set retardants must be carefully added to avoid overdosing. Some report that high concentration of borates and other set retardants reduce the early compressive strength of the cement while others see higher strength in the long run (beyond 28 days). Borates are rarely used as stand-alone retardants; but, instead are combined with sugars, gluconates, lignosulphonates, phosphonates, or synthetic polymers.

Borate property: Solubility control through product selection

Borates used: Borax decahydrate, *Neobor*[®]—disodium tetraborate pentahydrate, *Polybor*[®]—disodium octaborate tetrahydrate, *Optibor*[®] boric acid

Borate concentrations: Up to 1% in the cement

1.2 Lost circulation treatments

Drilling operations sometimes encounter fractures in reservoir rock formations. These can be naturally occurring or caused by earlier fracturing operations. Carbonate rocks are particularly susceptible to fracture. Rapid repair is needed to avoid the loss of thousands of barrels of expensive drilling fluids. Although inexpensive materials, such as natural fibres and nut shells, can be used to plug large fractures, more sophisticated products, referred to as solids-free lost circulation pills based on polymer gels are frequently used. Soluble borates are a common component of such products. The borates enhance the gelation of the polymer via cross-linking, a phenomenon described in more detail in section 2.1.1. Borates can be used to cross-link guar and xanthan gums and starch in this application.

Borate property: Polymer cross-linking

Borates used: Borax decahydrate, *Neobor*—disodium tetraborate pentahydrate, *Polybor*—disodium octaborate tetrahydrate, *Optibor* boric acid

Borate concentrations: <0.1% of the fluid

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1.3 Non-damaging completion fluids

Fluids used during well completion operations (casing and cementing the well) containing sparingly soluble borates are sometimes employed. They can also act as lost circulation pills. In this instance the borate particles act as bridging agents that help stop the inflow of fluids into the reservoir during these operations. The sparingly soluble borate is suspended in a saturated brine solution that contains a viscosifying polymer and other additives. The dissolved salt prevents the borate particles from dissolving and also gives the fluid the correct density. The fluids are referred to as non-damaging, since the borate particles dissolve cleanly away when they subsequently come into contact with the more dilute reservoir brines at the end of the operation.

Borate property: Low solubility borates

Borates used: Calcium or sodium calcium borates

Borate concentrations: 2-3% of the fluid

1.4 Pulsed-neutron well logging

At various stages in the life of an oil field it is necessary to map the location of oil and water bearing zones and track fluids in the reservoir. Examples of this are: monitoring the progress of an enhanced-oil-recovery flooding trial, diagnosing fluid leaks from the well bore; searching for oil bearing zones; measuring the porosity of regions in the reservoir; and identifying the existence of rock fractures and channels. One tool for this is pulsed neutron logging. This technique exploits differences in the extent that neutrons are trapped by various atomic nuclei. A logging tool emits bursts of high energy neutrons that are slowed by collisions with nuclei as they radiate out into the reservoir. When they have lost sufficient energy they can be captured by the atomic nuclei present in the reservoir materials. Each capture produces a new isotope and generates gamma rays, which can be detected. The acquired signals are used to calculate an average macroscopic value of the neutron capture cross section, which is

dependent on the elements present in the reservoir materials. The 10B isotope has an unusually high neutron capture cross section (100 times greater than that of the 35Cl nucleus). Borates are added as tracers because they dissolve in the water regions in the reservoir and the 10B present then enhances the contrast between the water and oil / rock zones. Borates have further advantages of low cost, availability, ease of handling, and compatibility with the formation rock and water.

Borate property: Neutron absorption, water solubility, water hardness tolerance

Borates used: *Neobor*—disodium tetraborate pentahydrate, borax decahydrate

Borate concentrations: 2-3% of the fluid

1.5 Drilling fluids

Borates fulfill several functions when used in drilling fluids:

- Fluid loss additive: Drilling fluids (muds) contain additives that help form an impervious filter cake on the well bore wall and prevent fluid loss into the formation. Borates enhance the performance of some polymer based fluid loss additives (notably starch) by cross-linking.
- Lubricant: There are instances where borates (or borate esters) have been used to improve the lubricating characteristics of muds.
- pH control: Water-based muds are typically formulated with a mildly alkaline pH. Normally this requires the addition of a pH control agent. Borates can be employed for this purpose as they provide a reserve of alkalinity and buffer pH in the correct region.
- Corrosion inhibitor: Corrosion inhibitors are often employed in drilling fluids to protect steel tubing, casing and pipework. Borates have been used in water based muds often in combination with other corrosion inhibitors.
- Viscosity modifier: In some cases, borates are used to reversibly cross-link viscosity modifying polymers used in water based muds, especially when drilling deviated or horizontal wells where a build up of drill cuttings can be a problem and efficient cuttings removal is critical.

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- Shale stabilizer: Shale or clay strata present in the reservoir formation rock are commonly encountered during well drilling. Water based muds can destabilize this type of rock and result in the erosion of the borehole, weaknesses in the rock formation and jamming of the drill string. Shale stabilizing additives are therefore a necessary ingredient in these muds. Borates exhibit good performance as shale stabilizers when used with salts such as potassium chloride and they can act synergistically with various mono- and oligosaccharides.
- Anti-microbial action: When borates are employed for one of the above properties, a useful secondary benefit is the ability of borates to inhibit the microbial spoilage of organic additives (for example viscosifying gums) that are present in the muds.

Borate property: Polymer cross-linking, alkalinity and alkaline pH buffering, corrosion inhibition, anti-microbial action, lubrication

Borates used: Borax decahydrate, *Neobor*—disodium tetraborate pentahydrate, *Polybor*—disodium octaborate tetrahydrate

Borate concentrations: Up to 6%, based on weight of fluid

2. Production and improved oil recovery

2.1 Hydraulic fracturing fluids

The rate of production of oil and gas can be increased by enhancing the permeability of the reservoir; this is known as stimulation. There are two types of stimulation treatment: acidization and hydraulic fracturing. The latter technique involves the deliberate

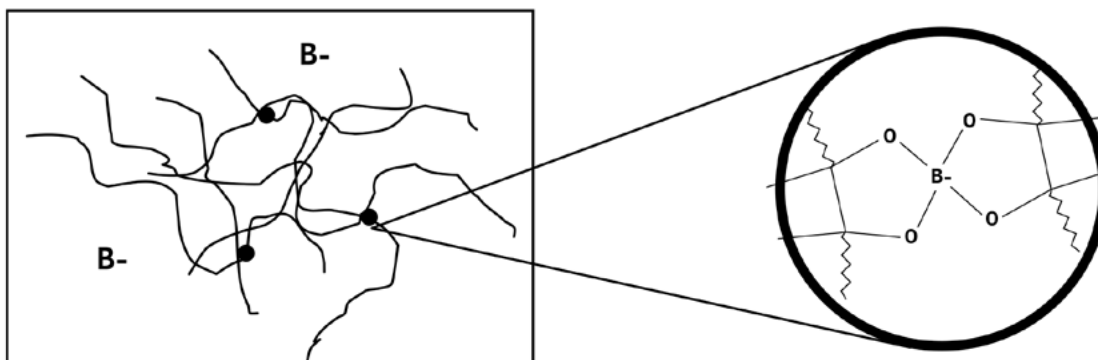
fracturing of the reservoir rock around an injecting well. This is achieved by rapidly pumping large quantities (100,000 gallons on average) of a gelled water based fluid containing suspended particles of sand or other “proppants” into the reservoir and pressurizing the fluid until fracturing occurs. The particles enter the fractures and remain there propping them open when the pressure is relieved and the components of the suspending fluid are broken down and flushed away. The open fractures increase permeability and improve fluid flow through the reservoir. Two different types of borates are added for different purposes in hydraulic fracturing.

2.1.1 Fluid gelation

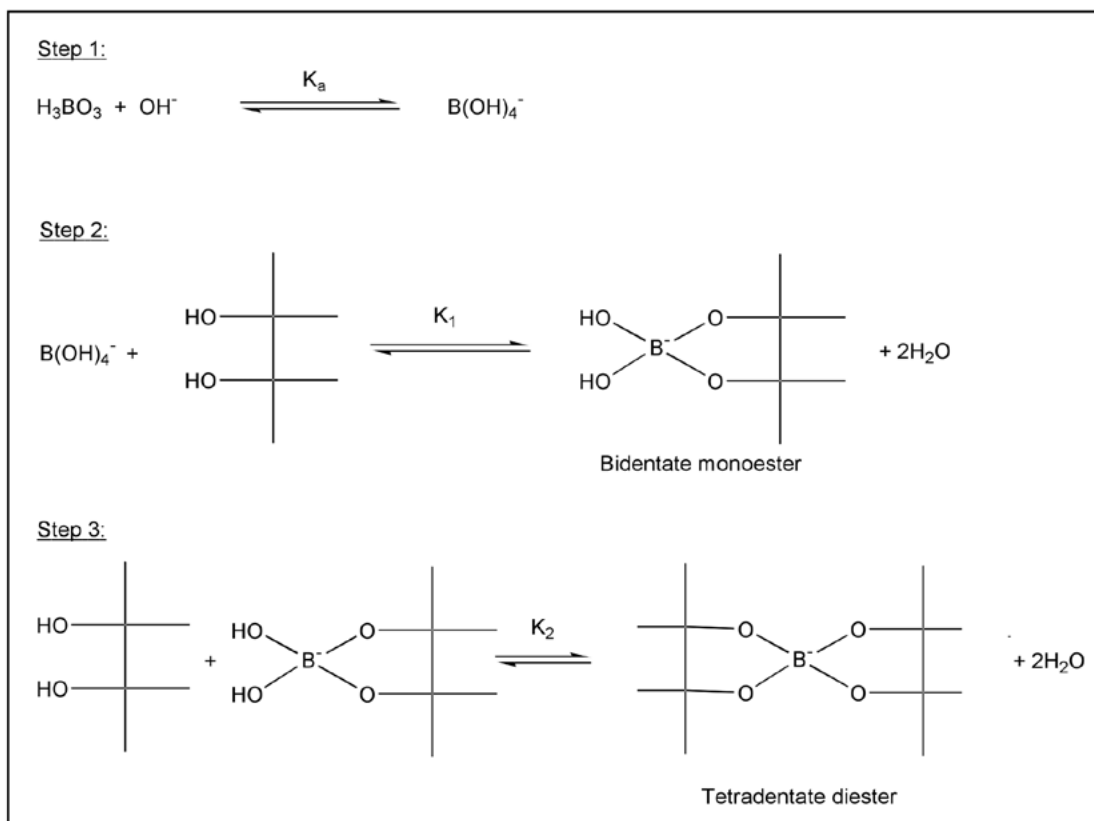
Gelation of the fracturing fluid prevents the suspended particles from settling before they enter the fractures. The gel is formed by a water soluble polymer, guar gum, or hydroxypropyl guar with a cross-linking agent to provide sufficient gelation to prevent settling of the particles.

Borates have two main advantages as cross-linkers. First, cross-links through boron form, break, and re-form so that the gels are not irreversibly degraded under the extremely high shear conditions caused by pumping through the reservoir tubulars and perforations. Second, because borates are water soluble, the gels they form are easier to clean-up than ones containing other cross-linkers, such as zirconates and titanates.

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Borate cross-linking mechanism



Chemical equilibria giving rise to reversible borate cross-linking reaction

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In addition borates are considered to be more environmentally friendly than the competing transition metal cross-linkers.

Borates were first employed in this application more than 40 years ago. Their use was originally restricted to low temperature reservoirs (150°F). This is because at higher temperatures changes in the chemical equilibria mean that less of the boron in the fluid is available in the form of the tetrahydroxyborate ion, the active cross-linking agent, and it is therefore less effective. Since then, due to fluid technology advances, borates have evolved for use in much hotter reservoirs with temperatures up to 300°F. These advances have centered on:

- Increasing the pH ultimately attained by the fluid in the reservoir—from the original range (7.5-9) to 9.5-12. This pushes the equilibrium in favor of the active borate ion.
- Delaying the release of the borate and in some cases also the separately added alkaline agent, until the fluid is in place. The objective is to avoid the premature development of a highly viscous gel as this causes unacceptably high friction pressures during the pumping operations.

Where delayed borate release is required, several approaches have been employed:

- Use of borates that are slowly dissolving or sparingly soluble at surface temperatures (*Dehybor* anhydrous borax, boric oxide). Some use is made of mineral borates, but they can pose problems of clean-up after the operation due to associated impurities.
- Preparation of diesel oil suspensions of borates
- Use of borate esters that hydrolyse when the fluid is in the reservoir

Where a delay is not required, then more rapidly dissolving and more intrinsically soluble borates are employed in this application.

Similar methods for delaying the development of alkaline pH have been proposed, for example by using a calcined magnesium oxide, also delivered as slurries in diesel.

Borates are highly effective and only required at a level of a few hundred ppm in the fluid, typically less than 10% of the weight of gum employed.

Recently there has been a substantial increase in the number of hydraulic fracturing operations carried out worldwide. Much of this has been in the United States, where it has been associated with a corresponding rise in gas production. In general it is linked with the economic imperative to extract as much oil and gas as possible from existing reservoirs, before investing in new ones that are increasingly hard and expensive to find. Outside the United States, there are significant opportunities for this technology in other regions, notably the CIS. Borates are very popular for this application and half of the 30,000 to 40,000 hydraulic fracturing operations conducted worldwide every year involve their use. Borates are anticipated to remain the preferred cross-linker for the foreseeable future.

Borate property: Polymer cross-linking, high and low solubility borates, fast and slow dissolving borates

Borates used: *Neobor*—disodium tetraborate pentahydrate, borax decahydrate, *Polybor*—disodium octaborate tetrahydrate, *Dehybor*—anhydrous borax, *Optibor* boric acid, boric oxide

Borate concentrations: 0.01 to 0.05% based on the gel weight

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2.1.2 Fluid breaker

At the end of the fracturing operation, clean-up and removal of the gelled polymer solution residues is required to realise the full value of the permeability improvements achieved through this process. Breakdown of the high molecular weight polymer chains can be achieved either with enzymes or with chemical oxidants.

Perborate is an oxidising breaker, supplying hydrogen peroxide. It is considered to have a favourable environmental profile in this application. The breaker particles can be coated to delay release of the perborate. The perborate can also be made more water soluble by blending with polyols. Borate cross-linked fluids clean-up better than those employing other cross-linkers, regardless of the breaker system employed.

Borate property: Oxidizing agent

Borates used: Sodium perborate monohydrate or sodium perborate tetrahydrate

Borate concentrations: 0.001 to 0.06% based on the fracture fluid weight employed

2.2 Water flooding profile control

The overall efficiency of water flooding processes in recovering oil from reservoirs is a function of both microscopic and macroscopic oil displacement efficiencies. Microscopic efficiencies refer to the ease of displacement of oil at the rock pore scale, and are influenced by amongst other things oil / water interfacial tension and the preference for the rock surface to be wetted by oil or water. Macroscopic efficiency, or conformance control, is a measure of how efficiently the injected water flood sweeps the reservoir volume. Reservoir engineers try to prevent 'fingering' of the injected water flood through or around the oil front via more permeable paths. Instead they strive to push all the trapped oil ahead of an even front of injected water, without by-passing any regions in the oil bank. This is often achieved by adding high molecular weight polymers to the water flood, which are then more accurately referred to as polymer flooding processes. The addition of polymer increases the water viscosity and provides a

more favourable match to that of the oil, which in turn improves the macroscopic oil recovery efficiency.

Borates can be used in this application in two distinctly different ways to block off high permeability thief zones:

- The viscosity control method uses cross-linking and viscosity delay mechanisms to improve performance. With the development of more responsive and intelligent fluids, the use of borates is projected to increase. Borax, slow release systems based on borate glasses and borate esters are used.
- The "thermal precipitation" process exploits the marked dependence of solubility with temperature for sodium borates such as borax. A hot nearly saturated solution of borax is pumped into the reservoir, migrating into the high permeability zones, where it precipitates borate compounds on cooling to cause pore blocking.

Borate property: Polymer cross-linking, water solubility—strong temperature dependence

Borates used: *Neobor*—disodium tetraborate pentahydrate, borax decahydrate, *Optibor* boric acid (esters)

Borate concentrations: 0.1-1% of fluid weight (polymer cross-linking); up to 50% of fluid weight (thermal precipitation)

2.3 Alkaline flooding

A developing application for borate is as an alkaline agent in several enhanced oil recovery (EOR) processes, for example alkali-polymer and alkali-surfactant-polymer (ASP) flooding. Laboratory data has revealed the following about borates when they substitute or partially replace existing alkalis:

- They offer the possibility of extending the use of this technology to a large number of reservoirs containing water with very high salinities and levels of hardness ions. Studies have demonstrated that unlike the conventional alkali, sodium carbonate, that forms precipitates with hard water, sodium metaborate can tolerate reservoir brines containing up to 6,000 ppm of these ions (Ca^{2+} , Mg^{2+}), without precipitation and alkali loss.

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- In the absence of EOR surfactants and polymers, uptake of borate solutions (through capillarity driven natural imbibition) by oil wet limestone rock and associated oil recoveries are substantially greater than are obtained with solutions of the alternative alkalis, sodium carbonate or sodium hydroxide. Sodium tetraborate (eg from *Neobor* or borax decahydrate) promotes excellent oil recovery despite its lower pH; an effect attributed to its strong pH buffering capacity and pH maintenance over a wide concentration range.
- The necessary ultra-low oil / water interfacial tensions in this application are readily obtained using borates in combination with conventional EOR surfactants and polymers, particularly with lighter (high API gravity) crude oils. Tertiary oil recovery from borate-based ASP core floods is comparable to that obtained with similar formulations containing conventional alkalis. Borate-based formulations exhibit no injectivity problems in coreflood trials. As with conventional alkalis, borates assist in reducing EOR surfactant adsorption and in the in situ generation of surfactants by the saponification of crude oil components.
- Flooding compositions containing borates benefit from a substantial reduction in alkali consumption on certain rock types, notably those rich in anhydrite (calcium sulphate) and dolomite (calcium magnesium carbonate). Consumption can be less than 10% of the level encountered with conventional agents and even in the case when borate substitutes only 10% of the existing alkali, a 50% drop in overall consumption is observed. This surprising result can have a significant positive impact on the economics of the tertiary flooding process.

Borate property: Alkalinity and pH buffering, water hardness tolerance

Borates used: *Neobor*—disodium tetraborate pentahydrate, borax decahydrate, sodium metaborate 4 mol—sodium metaborate dihydrate, sodium metaborate 8 mol—sodium metaborate tetrahydrate

Borate concentrations: 0.5 to 2% of ASP or alkali-polymer slug

2.4 H₂S scavenger

The presence of hydrogen sulphide gas in crude oils and reservoirs can present significant problems during drilling and production operations. During drilling encounters with hydrogen sulphide rich strata are referred to as “sour gas kicks.” Hydrogen sulphide is highly toxic and in addition can cause pitting and corrosion of steel structures (drill casings, pipelines). Its origins are multiple; from sulphate ions present in seawater, pyrite rock and the organo-sulphur compounds in crude oil that provide a source of nourishment for sulphide producing bacteria.

Sodium perborate, a solid oxidant, is claimed to be effective in this application acting not only to oxidize sulphide to elemental sulphur and sulphate, but also to destroy the sulphide producing bacteria. It can easily be dissolved in for example water-based drilling fluids when a sour gas kick is encountered.

Borate property: Oxidizing agent, antimicrobial activity

Borates used: Sodium perborate monohydrate, sodium perborate tetrahydrate

Borate concentrations: 0.15 to 0.6% based on the weight of the injected oil well fluid

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About borates

Borates are naturally occurring minerals that have an excellent reputation for safety when used as directed. Borates are essential nutrients for plants, part of a healthy diet for people, and key ingredients in fiberglass, glass, ceramics, detergents, fertilizers, wood preservatives, flame retardants, and personal care products.

Borates are regarded as safe for the environment. For example in relation to their specific use in offshore drilling and production activities in the North Sea, most of the commercially available forms of sodium borate are found on the “OSPAR List of Substances Used and Discharged Offshore which are Considered to Pose Little or No Risk to the Environment (PLONOR).”^{*} Those currently listed include:

Disodium tetraborate, anhydrous ($\text{Na}_2\text{B}_4\text{O}_7$)—*Dehybor*[®]
Disodium tetraborate pentahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$)—*Neobor*[®]
Disodium tetraborate decahydrate / Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)—Borax decahydrate
Sodium pentaborate, anhydrous ($\text{Na}_2\text{B}_{10}\text{O}_{16}$)
Sodium pentaborate pentahydrate ($\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 5\text{H}_2\text{O}$)
Disodium octaborate, (anhydrous) ($\text{Na}_2\text{B}_8\text{O}_{13}$)
Disodium octaborate tetrahydrate - *Polybor*[®] ($\text{Na}_2\text{B}_8\text{O}_{13} \cdot 4\text{H}_2\text{O}$)
Disodium tetraborate / Boron sodium oxide, hydrated ($\text{Na}_2\text{B}_4\text{O}_7 \cdot x\text{H}_2\text{O}$)

Borates naturally occur in seawater at a level of 5 ppm expressed in terms of boron concentration.

^{*}OSPAR – Oslo Paris Convention for the Protection of the Marine Environment of the North-East Atlantic; PLONOR list – 2008 Update

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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 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.

The recommendations in this bulletin are based upon information believed to be reliable. As the use of our products is beyond the control of the manufacturer, no guarantee, expressed or implied is made as to the effects of such or the results to be obtained if not used in accordance with directions of established safe practice. Nor is there any warranty of fitness for a particular purpose which extends beyond the described uses in this bulletin. Furthermore, nothing herein shall be construed as permission or recommendation to practice a patented invention without authorization of the patentee.