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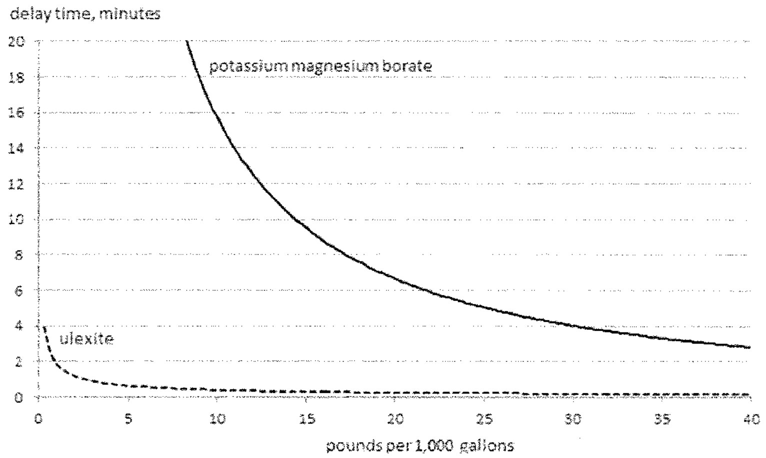


FIG. 6

(57) **Abstract**: This invention relates to methods to produce a potassium magnesium borate and its use in applications. Some applications involve the use of borates in a solution as a crosslinking agent.

POTASSIUM MAGNESIUM BORATE USE FOR DELAYED RELEASE OF BORATE AND METHODS OF MANUFACTURING THE SAME

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority under 35 U.S.C. §119(e) to U.S. Provisional Patent Application Serial No. 62/205,544 filed August 14, 2015, and U.S. Provisional Application Serial No. 62/299,236 filed February 24, 2016. Each of these applications are incorporated herein in their entirety by reference.

FIELD OF THE INVENTION

This invention relates to the use in several applications of a potassium magnesium borate (PMB) compound of the formula $K_2MgB_{12}O_{20}\cdot 10H_2O$ and practical methods for its preparation. Some applications involve the release of borate into solution. The release of borate can be rapid or slow. Slow release of borate can be useful to delay the crosslinking of polyhydroxylated polymers. This invention also relates to a practical method for making the compound and methods to prepare the compound in forms having different dissolution rates in order to fine tune its performance for practical purposes. The invention also includes other uses of the compound.

BACKGROUND

Potassium and magnesium borate chemistries are extensively described in the scientific literature; however, only a small number of potassium-magnesium borates are reported. One of these is $K_2MgB_{12}O_{20}\cdot 10H_2O$, which is a crystalline compound that was first described in 1984 in Sokolova, E.V.; Yamnova, N.A.; Majore, I.V.; Egorov, Tismenko, Yu. K.; Gode, G. K., *Latvijas PSR Zinatnu Akad. Vestis, Khim. Ser.*, 1984, 147-155 ("Sokolova"), which is incorporated by reference in its entirety, with details of its crystal structure. A second determination of the crystal structure of this compound was published in 2005 (Lui, Z.; Li, L.; Li, J.; Hu, M., *J. Alloys and Compounds*, 2005, 394, 277-281, which is incorporated by reference in its entirety), which confirmed the identity and structure of the compound to be the same as that reported two decades earlier. Therefore, the composition of this compound is well established. However, no specific practical uses for this compound were proposed. Methods for the synthesis of this compound described in the literature involve reactions of potassium borates with magnesium salts. For example, Liu et al. describe a method to prepare $K_2MgB_{12}O_{20}\cdot 10H_2O$ involving mixing potassium tetraborate, $K_2B_4O_7\cdot 4H_2O$ (incorrectly written as "$K_2B_4O_7\cdot 5H_2O$"), with magnesium chloride, $MgCl_2\cdot 6H_2O$, in aqueous solution and then adding hydrochloric acid until a pH value of 7.5 was reached. Notably, the $K_2MgB_{12}O_{20}\cdot 10H_2O$ did not begin to crystallize from this solution until after three months. The balanced chemical equation from this method as given by Equation 1.

$$3\ K_2B_4O_7\cdot 4H_2O + MgCl_2\cdot 6H_2O + 2\ HCl \xrightarrow{H_2O} K_2MgB_{12}O_{20}\cdot 10H_2O + 4\ KCl \qquad (1)$$

From this equation it can be seen that four molar equivalents of potassium chloride are produced for each mole of potassium magnesium borate product obtained. Clearly a reaction that requires three months to begin producing product is not a practical commercial process. Furthermore, the production of potassium chloride as a byproduct also presents an added complication from an industrial manufacturing standpoint since the reaction solution cannot be directly recycled to subsequent production batches in a sustainable process.

SUMMARY

Borate compounds are useful as crosslinking agents for polyhydroxylated polymers to produce rheological fluids and gels used in hydraulic fracturing operations for oil and gas recovery. Borate chemistry can be used in alkaline-surfactant flooding enhanced oil recovery, drilling muds, pulsed neutron well logging, and set retarding of downwell cements.

Borate crosslinking can also be used to tackify polymers in the manufacturing of adhesives, films and laminates. Borates can also be used to crosslink polymers to form rheological fluids used to carry proppants in hydraulic fracturing operations. Most refined borates, such as boric acid and potassium borates, dissolve relatively quickly in water and provide no substantial delay before polymer crosslinking occurs. In many cases, it can be advantageous to delay the onset of crosslinking and concomitant development of high viscosity. For example, hydraulic fracturing operations for oil and gas recovery utilize viscous fluids to suspend proppant materials. However, it is advantageous in oilfield operations involving deep subterranean formations to delay the onset of crosslinking until the fluid can be pumped a considerable distance into the well. Ulexite, a mineral borate, is often used in such applications because it dissolves somewhat more slowly and provides delayed crosslinking. However, as a processed mineral, ulexite can be inconsistent in composition and can also contain unwanted impurities. In addition, relatively long delay times are difficult to achieve reliably using ulexite.

Starch and starch-dextrin adhesives are often used in the manufacture of paper goods, such as wound tubes, corrugated boxes, and related products. In this application, starch and/or dextrin are crosslinked using a borate, often borax pentahydrate or borax decahydrate. Such borates provide immediate crosslinking resulting in rapid tackification of adhesives formulations. This immediate crosslinking can be disadvantageous in manufacturing operations involving high speed application of the adhesives and methods to delay the onset of crosslinking would provide a benefit by allowing higher application speeds.

Borates can be used in engineered wood, wood-plastic and agrifiber composites to provide protection against decay, fungi and wood-boring insects. Potassium magnesium borate can provide similar protection.

Borates can also be used to provide fire retardancy to wood, paper and other cellulosic materials. In addition, borates are currently used in the manufacture of fire retardant and intumescent coatings. The potassium magnesium borate disclosed herein can provide such fire retardant benefits when incorporated into cellulosic materials and coatings.

This invention involves practical applications of a potassium magnesium borate compound of the formula $K_2MgB_{12}O_{20}\cdot 10H_2O$ [oxide formula $K_2O\cdot MgO\cdot 6B_2O_3\cdot 10H_2O$] and methods for synthesis of this compound. An advantage of the synthetic methods disclosed herein is the preparation of potassium magnesium borate under mild conditions, from economical and readily available starting materials with relatively short reaction times and without the generation of wasteful byproducts. These methods are thus suitable for industrial scale production of the compound.

The compound can be used to delay crosslinking of polyhydroxylated polymers, which has value for rheological fluids used in oil and gas extraction operations and other applications. Delayed crosslinking results from a controlled rate of solubility and thus a delayed release of borate into aqueous solutions. This controlled rate is advantageous in many applications, including in the manufacture of adhesives, the protection of wood composites and related building materials against insect and microbial attack, and in agriculture for delivery of boron as a crop micronutrient in a controlled fashion. This invention also entails methods to produce potassium magnesium borate having tunable dissolution rates, and therefore controllable crosslinking delay times. Another use of the compound can be as a fire retardant, an advantage of the compound exhibiting fire retardant properties.

The potassium magnesium borate compound was found to be incongruently soluble and to hydrolyze with release of soluble borate into solution accompanied by precipitation of a sparingly soluble borate, synthetic inderite. In wood preservation and also the protection of biomass derived composite materials, it can be advantageous to dissociate the compound to a more soluble borate and a less soluble borate, so that the borate active ingredient is more rapidly soluble for immediate protection, but a portion of the borate also remain present in the substrate as reservoir for long term protection. By way of example, low solubility of borate offers longer protection in wood applications or delayed crosslinking times in other operations. An advantage of high solubility borates is an increased initial response in wood preservation or low crosslinking time in other operations.

One embodiment of the invention is a method of preparing a compound of a formula of $K_2MgB_{12}O_{20}\cdot 10H_2O$ that includes reacting a potassium source and a boron containing source, with at least one magnesium source. The reaction of the potassium, the boron containing and the magnesium sources does not produce a potassium byproduct.

Another embodiment of the invention is a method of forming a potassium magnesium borate. This method includes reacting a potassium source and a boron containing compound, with at least one magnesium compound. In the reaction, at least one byproduct of the reaction is water.

A further embodiment of the invention is a method to treat a fluid in an oil field application by providing a crosslinking agent to the fluid. The crosslinking agent includes a potassium magnesium borate compound of the formula of $K_2MgB_{12}O_{20}\cdot 10H_2O$.

A still further embodiment of the invention is a method to reduce flammability of an object that includes providing a fire retardant with a potassium magnesium borate compound to the object.

Another embodiment of the invention is a method of crosslinking polymers of a polymer-containing composition that includes contacting the composition with a potassium magnesium borate compound.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates the influence of time and temperature on potassium magnesium borate product yields for reactions carried out at about 65°C, about 80°C and about 95°C;

Figure 2 illustrates product yields for reactions carried out at 80°C for different time periods;

Figure 3 illustrates the general process to form a generic polyhydroxylated polymer;

Figure 4 illustrates a powder X-ray diffraction pattern for potassium magnesium borate produced according to Example 1; and

Figure 5 illustrates vortex closure delay curves for potassium magnesium borate samples prepared at different reaction temperatures and reaction times.

Figure 6 illustrates a comparison of vortex closure delay curves for potassium magnesium borate and ulexite.

DETAILED DESCRIPTION

The invention relates to a potassium magnesium borate of the formula $K_2MgB_{12}O_{20}\cdot10H_2O$ and methods for making the compound. The invention includes the use of potassium magnesium borate to provide advantageous delay times in crosslinking applications. The compound for use in the invention can be prepared by the reaction of potassium borate salts with magnesium salts in aqueous solution, and also by reactions of potassium hydroxide, boric acid and magnesium oxide, magnesium hydroxide or magnesium hydroxy carbonate. The latter processes are a further aspect of the invention and are especially practical because they eliminate the formation of wasteful byproducts.

This potassium magnesium borate is a crystalline compound having a well-defined chemical composition of $K_2MgB_{12}O_{20}\cdot10H_2O$ [oxide formula: $K_2O\cdot MgO\cdot6B_2O_3\cdot10H_2O$]. It was shown by earlier researchers who structurally characterized the compound by single crystal X-ray diffraction analysis to have the structural formula $K_2\{Mg(H_2O)_2[B_6O_7(OH)_6]_2\}\cdot 2H_2O$ (Sokolova, et al.). The observed X-ray powder diffraction data for the compound including approximate diffraction peaks and their approximate intensities are listed in Table 1. These data are in good agreement with the diffraction pattern simulated from the published single crystal data.

Table 1. X-ray powder diffraction data for $K_2MgB_{12}O_{20}\cdot 10H_2O$.

Angle, 2 theta degrees	Relative Intensity	Angle, 2 theta degrees	Relative Intensity
8.6	weak-medium	30.9	weak-medium
11.9	strong	32.4	Weak
13.9	strong	33.6	weak-medium
15.3	medium	33.9	Strong
16.4	medium	34.2	Medium
16.7	medium	35.2	Medium
17.2	medium	36.3	Medium
17.4	medium	37.0	Medium
17.6	medium	37.3	Weak
19.7	strong	37.6	medium
21.9	strong	38.1	medium
23.8	weak	38.6	medium
24.5	medium	39.3	Weak
25.7	medium	39.9	Weak
26.3	medium	40.1	Weak
26.6	medium	41.1	Weak
27.2	strong	41.3	Weak
27.9	strong	41.6	medium
28.8	weak	41.8	Weak
29.4	weak	42.2	medium
29.7	weak	42.6	Weak
30.5	weak-medium	42.8	Weak

Method for forming potassium magnesium borate

An aspect of the invention is a practical method for the preparation of $K_2MgB_{12}O_{20}\cdot 10H_2O$ that, unlike previously described methods, produces this compound in high yields with short reaction times without the production of byproduct salts, in particular byproduct salts of potassium. Therefore, this method is amenable to industrial scale manufacture of potassium magnesium borate and is more sustainable and environmentally acceptable.

This method requires sources of potassium, magnesium and boron. In some embodiments, potassium sources can include, but are not limited to, potassium hydroxide, potassium carbonate, potassium borates, or combinations thereof. Magnesium sources can include, but are not limited to, magnesium oxide, magnesium hydroxide, magnesium carbonate, magnesium hydroxy carbonates, magnesium hydroxy carbonate hydrate, magnesium salts, magnesium sulfate, magnesium chloride, magnesium borates, or combinations thereof. Boron sources can include, but are not limited to, boric acid, boric oxide, potassium borates, magnesium borates, or combinations thereof. In some embodiments, the boron containing compound can be a metaborate compound, a triborate compound, a tetraborate compound, or a pentaborate compound. Suitable potassium borates include potassium pentaborate, potassium triborate, potassium tetraborate, potassium metaborate and combinations thereof. Suitable magnesium borates include magnesium triborates, tetraborates, hexaborates and combinations thereof. In some embodiments, an intermediate compound, potassium pentaborate, can be formed before conversion to potassium magnesium borate.

For example, the potassium magnesium borate compound can be prepared by reaction of a mixture of potassium hydroxide, boric acid and magnesium oxide in water, as given by Equation 2 and described in detail in Example 14.

$$2\ KOH + 12\ B(OH)_3 + MgO \xrightarrow{H_2O} K_2MgB_{12}O_{20}\cdot 10H_2O + 9\ H_2O \qquad (2)$$

In an embodiment of the invention, the potassium magnesium borate compound can be prepared by reactions of aqueous potassium hydroxide, boric acid and a magnesium hydroxy carbonate, such as hydromagnesite, $Mg_5(CO_3)_4(OH)_2\cdot 4H_2O$. The reaction of potassium hydroxide, boric acid and hydromagnesite in water to produce potassium magnesium borate is given by Equation 3 and described in detail in Examples 1 through 12.

$$10\ KOH + 60\ B(OH)_3 + Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O \longrightarrow 5\ K_2MgB_{12}O_{20}{\cdot}10H_2O + 4\ CO_2 + 50\ H_2O \quad (3)$$

The reaction of Equations 2 and 3 can be carried out by combining water, such as deionized water; a potassium source, such as potassium hydroxide or potassium carbonate; a boron source, such as boric acid or potassium borate; and magnesium source, such as magnesium oxide or hydromagnesite; and heating the mixture to between about 40°C to about 100°C for between about two to about 100 hours while mixing using stirring, swirling, agitating or any other suitable mixing method. The heating temperature can be any temperature or sub-range between about 40°C and about 100°C, including about 40°C, about 45°C, about 50°C, about 55°C, about 60°C, about 65°C, about 70°C, about 75°C, about 80°C, about 85°C, about 90°C, about 95°C, or about 100°C. The mixing time can be any time or sub-range of time between about 2 hours and about 100 hours, including about 2 hours, about 4.5 hours, about 5 hours, about 7.8 hours, about 10 hours, about 15 hours, about 18 hours, about 20 hours, about 25 hours, about 30 hours, about 35 hours, about 40 hours, about 45 hours, about 50 hours, about 55 hours, about 60 hours, about 65 hours, about 65 hours, about 70 hours, about 75 hours, about 80 hours, about 85 hours, about 90 hours, about 95 hours, or about 100 hours. Throughout the description, stirring is discussed as the method for mixing, but one skilled in the art would understand that any suitable mixing method can be used. The reagents can be combined in any order.

The reaction described above produces a slurry containing a solid reaction product. The slurry can be filtered to remove the solid product, which can then be washed with water, for example, deionized water, distilled water, tap water, or combinations thereof. Washing the solid product can displace the adhering reaction liquor and the amount of wash water can be estimated. In some embodiments, the minimum amount of water can be used to wash the product. The solids can then be dried in an oven at a temperature between about 50ºC and about 100ºC until the samples reached a constant weight (in some embodiments, between about 2 hours and about 12 hours). The drying temperature can be any temperature or sub-range between about 50°C and about 100°C, including about 50°C, about 55°C, about 60°C, about 65°C, about 70°C, about 75°C, about 80°C, about 85°C, about 90°C, about 95°C, or about 100°C. One skilled in the art would understand that many other drying methods can be employed, such as rotary dryers, tray dryers, fluid bed dryers and so forth, without deviating from the invention.

The amount of the potassium compound in the reaction can be stoichiometrically balanced such that no excess potassium remains to produce a byproduct containing potassium, for example a potassium salt such as potassium chloride. The amount of the boron compound and/or the magnesium compound can also be stoichiometrically balanced.

The boron compound, the potassium compound and the magnesium compound can be selected to prevent the formation of a potassium byproduct in the reaction to form the potassium magnesium borate. For example, a magnesium compound can be selected to prevent the formation of potassium chloride as a byproduct. Other suitable examples of potassium byproducts that are not formed with the invention include potassium chloride, potassium sulfate, potassium bromide, potassium acetate, potassium phosphate, or combinations thereof. The reaction of the boron compound, the potassium compound and the magnesium compound can form water as a byproduct as illustrated by way of example in Equations 2 and 3. While the specific reactions are illustrated in Equations 2 and 3, one skilled in the art would understand the potential for other reactions with similar starting compounds to form the potassium magnesium borate with a byproduct that can include water.

The molar ratio of B/Mg in the reactants can be about between about 10 to about 14, in some embodiments between about 11 and 13, and in some embodiments about 12, but can be varied by a considerable amount from this ratio, generally with some loss in yield.

The concentration of the solids in the slurry following the reaction can be any amount or sub-range between about 5% and about 70% in water. For example, the concentration of the solids can be about 30% by volume with the remaining 70% by volume as water.

Although not required, in some embodiments, a seed of potassium magnesium borate can be included to facilitate the reaction forming the PMB product. The amount of seed can range from as little as a single seed crystal up to a large amount. The seed can be added after the magnesium source is added to the reaction and the reaction is at the reaction temperature or added before or together with the other reagents. In some embodiments, the amount of the seed can be from about 0.01 wt. % to about 10 wt. % of the reaction, from about 0.5 wt. % to about 1 wt. %, from about 5 wt. % to about 10 wt. %. In one embodiment, the potassium magnesium borate seed can be about 0.84 weight percent of the combined weight of the reagents.

Product yield in the production of potassium magnesium borates according to the present invention varies with time and temperature with longer reaction times resulting in somewhat higher yields and higher reaction temperatures resulting in somewhat lower yields. Results of experiments given in Examples 1 and 3 through 9 are plotted in Figure 1. Figure 1 illustrates the effects of reaction times and for given temperatures (65°C, about

80°C and about 95°C) on product yield. At longer reaction times, the yield continues to increase slightly. The effect of reaction times on product yields is further illustrated in Figure 2 for reactions carried out at 80°C for different time periods, as given by Examples 1-4 and 10. In various embodiments, the reaction can be conducted for at least about 1 hours, at least about 2 hours, at least about 3 hours, at least about 4 hours, at least about 5 hours, at least about 10 hours, at least about 15 hours or at about 20 hours. In various embodiments, the reaction can be conducted at a temperature of less than about 100°C, less than about 95°C, less than about 85°C, less than about 75°C, less than about 65°C, less than about 50°C, less than about 40°C, or less than about 35°C. In still further embodiments, the reactions can be conducted at combination of any one time parameter described above with any one temperature parameter described above. The product yield can be between about 55% and about 85%, in some embodiments between about 60% and about 80%, or 65% and about 75%.

It can be seen from the data illustrated in Figures 1 and 2 that product yield on a per batch basis can be controlled by adjusting reaction time and temperature. In addition, the methods described herein can be carried out in a semi-continuous process in which the filtrate from each batch is recycled to the following batch (as shown in Example 13). In this way, the overall yield becomes essentially about 100% and process feed reagents are completely converted to useable product. These methods can be further adapted to a fully continuous process.

Use of the potassium magnesium borate

Potassium magnesium borate displays a slow rate of dissolution that can be exploited for the controlled or delayed release of borate into a solution. Thus, potassium magnesium borate can be used as a delayed crosslinking agent in oilfield applications, such as in a fracturing fluid. An advantage of the invention is that the dissolution rate of the potassium magnesium borate as reflected by crosslinking delay time remains relatively constant regardless of the temperature of the reaction during formation, for example, as illustrated in Figure 5. Crosslinking delay times can be controlled by vary the amount of potassium magnesium borate used, as well as other factors, such as pH, temperature, and the type of polymer to be crosslinked. Crosslinking delay times can be controlled over a wide range. In some embodiments the range can be from less than 3 minutes to more than 40 minutes at room temperature. This advantage compared to the production of other crosslinking compounds allows for greater tolerance on the reaction temperature which results in lower costs.

When used as a crosslinking agent, the amount of PMB added to solution can vary. In some embodiments, about 1 pound of PMB per thousand gallons of solution can be used. In some embodiments, between about 1-5 pounds of PMB per thousand gallon of solvent can be used. In still other embodiments, between about 4-5 pounds of PMB per thousand gallon of solvent can be used.

Another aspect of the invention is the use of the potassium magnesium borate as a fire retardant. In other aspects of the invention, the potassium magnesium borate can be used as a fungicide, an insecticide, a microbicide, a fertilizer, and/or in the manufacture of adhesives.

In order to be effective, between about 0.1-0.5 wt. % of the PMB can be used in biocidal applications. In some embodiments, the amount of about 1-10 wt. % of the PMB is used when the application is as a fire retardant.

The manufacture of glass and other vitreous materials is an important industrial use of borates where they provide B_2O_3 as a glass forming component of vitreous compositions. Potassium oxide, K_2O, and magnesium oxide, MgO, are also important components in vitreous formulations. The formula for the potassium magnesium borate

$K_2MgB_{12}O_{20}\cdot10H_2O$ can be written so as to factor out these components as $K_2O\cdot MgO\cdot6B_2O_3\cdot10H_2O$. Thus, this borate compound can contain about 12.9 wt. % K_2O, about 5.5 wt. % MgO and about 57 wt. % B_2O_3 by weight, and is useful as a raw material for use in glass making.

Control of dissolution rates and crosslinking delay times using potassium magnesium borate

Borate crosslinking is believed to be based on the reversible formation of borate ester linkages between chains of polyhydroxylated polymers. The addition of borate to a polyvinyl alcohol solution forming what is often referred to as “slime” is a familiar classroom demonstration of this dynamic process. Figure 3 illustrates the general process to form a generic polyhydroxylated polymer. The reaction illustrated in Figure 3 is both reversible and pH dependent, with increasing pH shifting the equilibrium toward higher concentrations of crosslinked species. The reaction is illustrated for simplicity here using boric acid as the boron source.

In the context of oil and gas recovery operations, borates can be used to crosslink polyhydroxylated polymers in order to form gels that are employed to suspend proppant materials. Guar gum and modified guar gums are polymers commonly used for this application. Other polyhydroxylated polymers, such as xanthan gum and hydroxylated polyacrylamides can also be used. Combinations of multiple crosslinking polymers can also be used. Crosslinking delay times are often measured using a vortex closure test carried out with a laboratory blender. The procedure is described in G. J. Rummo, *Oil & Gas Journal*, 1982, *80* (September 13), 84-89 (“Rummo”), which is incorporated by reference in its entirety. This test involves adding guar gum, modified guar gum or other suitable polymer to a salt solution in a blender and mixing at high speed in order to produce a vortex. The crosslinking agent is then added to the blender and the elapsed time until the viscosity of the mixture becomes high enough to close the vortex is recorded. Crosslinking delay times are a function of the amount of crosslinking agent used. By measuring the vortex closure times for different amounts of added crosslinking agent a delay curve can be produced that one can use to calculate the amount of crosslinking agent required to achieve a desired delay time. Processed ulexite mineral is often used in oilfield applications to provide crosslinking delay and a commercial grade of ulexite used in the oilfield industry was used for comparative purposes. Since solid crosslinking agents can be often suspended in oil or other liquid medium to allow for liquid handling, they are generally supplied as fine powders that can readily form suspensions.

Potassium magnesium borate of the invention provides advantageous delay times in the onset of polymer crosslinking and these delay times can be controlled by changing the conditions used to prepare this compound. Samples of potassium magnesium borate were prepared under different reaction conditions in which the reaction times and temperatures were varied. The resulting products, after screening to -325 U.S. mesh (<44 μm), were tested for delayed crosslinking using a vortex closure test described in Rummo. An advantage of using particles of this size is that they can be in suspension in oil. Particles that are larger than this amount may settle quickly. These tests showed that samples of potassium magnesium borate prepared under specific conditions provide crosslinking delay times that are reproducible. In general, it was found that preparing potassium magnesium borate with longer reaction times leads to somewhat slower dissolution rates and thus greater crosslinking delay times.

Samples of potassium magnesium borate prepared at about 80°C (Example 1) and at about 95°C (Example 4) gave similar dissolution rates when measured by the vortex closure test as described in Example 14. In each case the delay times were substantially longer than found for ulexite mineral. Crosslinking delay times longer than about three to four minutes are difficult to achieve reliably using ulexite, whereas delay times in the approximately 4-30-minute timeframe are easily achieved using potassium magnesium borate.

Dispersability in non-aqueous solvents.

Potassium magnesium borate was found to readily disperse in non-aqueous solvents, such as hydrocarbons. This property is important as it provides utility in applications including oil field use since it is common practice to disperse crosslinking agents in oils, such as those that are low in benzene, toluene, ethylbenzene and xylenes (low BETEX) or other non-aqueous carrier fluids so they can be handled and added as liquids.

These reactions described herein can occur under mild non-hydrothermal conditions with relatively short reaction times. A notable feature of the various synthetic routes and compounds that do not produce byproducts of salts.

Ranges have been discussed and used within the foregoing description. One skilled in the art would understand that any sub-range within the stated range would be suitable, as would any number within the broad range, without deviating from the invention.

EXAMPLES

Example 1

This example illustrates the preparation of potassium magnesium borate using potassium hydroxide, boric acid, and hydromagnesite. A flask was charged with about 175 g of deionized water, 90% potassium hydroxide (about 15.6 g, 0.25 mole KOH) and boric acid (about 93.0 g, 1.504 moles) with stirring, mindful that the *reactions of KOH with both water and boric acid are exothermic*. The mixture was heated to about 80°C with stirring. Hydromagnesite, $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$, (about 11.69 g, 0.025 mole) was added to the mixture with stirring. Mild effervescence ensued. About 1.0 g of potassium magnesium borate seed was added and the mixture was maintained at about 80°C with stirring for about 4.5 hours after which time the slurry was filtered and the filtered solids were washed with about 50 mL deionized water and dried in an oven at about 60°C to give

$K_2MgB_{12}O_{20}\cdot 10H_2O$ (about 66.38g (after subtracting the 1.0 g of seed), 71.9% recovered yield) as a white fine powder identified by chemical analysis and by X-ray powder diffraction, as illustrated in Figure 4. The product after drying easily passed through a -325 U.S. mesh (44 μm opening) screen.

The XRD pattern can identify the compound and illustrate its purity. The more intense peaks are referenced in Table 1. The pattern also illustrates that the compound is substantially pure.

Example 2

This example illustrates the preparation of potassium magnesium borate using potassium hydroxide, boric acid, and hydromagnesite. The same procedure to form the product given in Example 1 was followed, except the reaction mixture was maintained at 80°C with stirring for 6.0 hours. The product yield was 66.84 g $K_2MgB_{12}O_{20}\cdot 10H_2O$ (after subtracting the 1.0 g of seed) (about 73.0% recovered yield) as a white fine powder identified by chemical analysis and by X-ray powder diffraction. The X-ray diffraction pattern of the product was substantially the same that illustrated in Figure 4. The product after drying easily passed through a -325 U.S. mesh screen.

Example 3

This example illustrates the preparation of potassium magnesium borate using potassium hydroxide, boric acid, and hydromagnesite. The same procedure to form the product given in Example 1 was followed, except the reaction mixture was maintained at 80°C with stirring for 7.88 hours. The product yield was 67.55 g $K_2MgB_{12}O_{20}\cdot 10H_2O$ (after subtracting the 1.0 g of seed) (about 73.8% recovered yield) as a white fine powder identified by chemical analysis and by X-ray powder diffraction. The X-ray diffraction pattern of the product was substantially the same that illustrated in Figure 4. The product after drying easily passed through a -325 U.S. mesh screen.

Example 4

This example illustrates the preparation of potassium magnesium borate using potassium hydroxide, boric acid, and hydromagnesite. The same procedure to form the product given in Example 1 was followed, except the reaction mixture was maintained at 80°C with stirring for 18 hours. The product yield was 70.48 g $K_2MgB_{12}O_{20}\cdot 10H_2O$ (after subtracting the 1.0 g of seed) (about 77.0% recovered yield) as a white fine powder identified by chemical analysis and by X-ray powder diffraction. The X-ray diffraction pattern of the product was substantially the same that illustrated in Figure 4. The product after drying easily passed through a -325 U.S. mesh screen.

Example 5

This example illustrates the preparation of potassium magnesium borate using potassium hydroxide, boric acid, and hydromagnesite. The same procedure to form the product given in Example 1 was followed, except the reaction mixture was maintained at 95°C with stirring for 4.5 hours. The product yield was 57.56 g $K_2MgB_{12}O_{20}\cdot 10H_2O$ (after subtracting the 1.0 g of seed) (about 62.9% recovered yield) as a white fine powder identified by chemical analysis and by X-ray powder diffraction. The X-ray diffraction pattern of the product was substantially the same that illustrated in Figure 4. The product after drying easily passed through a -325 U.S. mesh screen.

Example 6

This example illustrates the preparation of potassium magnesium borate using potassium hydroxide, boric acid, and hydromagnesite. The same procedure to form the product given in Example 1 was followed, except the reaction mixture was maintained at 95°C with stirring for 7.88 hours. The product yield was 61.54 g $K_2MgB_{12}O_{20}\cdot 10H_2O$ (after subtracting the 1.0 g of seed) (about 66.6% recovered yield) as a white fine powder identified by chemical analysis and by X-ray powder diffraction. The X-ray diffraction pattern of the product was substantially the same that illustrated in Figure 4. The product after drying easily passed through a -325 U.S. mesh screen.

Example 7

This example illustrates the preparation of potassium magnesium borate using potassium hydroxide, boric acid, and hydromagnesite. The same procedure to form the product given in Example 1 was followed, except the reaction mixture was maintained at 95°C with stirring for 18 hours. The product yield was 64.34 g $K_2MgB_{12}O_{20}\cdot10H_2O$ (after subtracting the 1.0 g of seed) (about 70.3% recovered yield) as a white fine powder identified by chemical analysis and by X-ray powder diffraction. The X-ray diffraction pattern of the product was substantially the same that illustrated in Figure 4. The product after drying easily passed through a -325 U.S. mesh screen.

Example 8

This example illustrates the preparation of potassium magnesium borate using potassium hydroxide, boric acid, and hydromagnesite. The same procedure to form the product given in Example 1 was followed, except the reaction mixture was maintained at 65°C with stirring for 7.88 hours. The product yield was 70.09 g $K_2MgB_{12}O_{20}\cdot10H_2O$ (after subtracting the 1.0 g of seed) (about 76.6% recovered yield) as a white fine powder identified by chemical analysis and by X-ray powder diffraction. The X-ray diffraction pattern of the product was substantially the same that illustrated in Figure 4. The product after drying easily passed through a -325 U.S. mesh screen.

Example 9

This example illustrates the preparation of potassium magnesium borate using potassium hydroxide, boric acid, and hydromagnesite. The same procedure to form the product given in Example 1 was followed, except the reaction mixture was maintained at 65°C with stirring for 18 hours. The product yield was 72.30 g $K_2MgB_{12}O_{20}\cdot10H_2O$ (after subtracting the 1.0 g of seed) (about 78.8% recovered yield) as a white fine powder identified by chemical analysis and by X-ray powder diffraction. The X-ray diffraction pattern of the product was substantially the same that illustrated in Figure 4. The product after drying easily passed through a -325 U.S. mesh screen.

Example 10

This example illustrates the preparation of potassium magnesium borate using potassium hydroxide, boric acid, and hydromagnesite. The same procedure was followed as given in Example 1 except the reaction mixture was maintained at 80°C with stirring for 64 hours. The product yield was 73.78 g $K_2MgB_{12}O_{20}\cdot 10H_2O$ (after subtracting the 1.0 g of seed) (about 80.6% recovered yield) as a white fine powder identified by chemical analysis and by X-ray powder diffraction. The X-ray diffraction pattern of the product was substantially the same that illustrated in Figure 4. The product after drying easily passed through a -325 U.S. mesh screen.

Example 11

This example illustrates the preparation of potassium magnesium borate using potassium hydroxide, boric acid, and hydromagnesite. Example 11 describes the preparation of potassium magnesium borate without the addition of seed. A flask was charged with about 175 g of deionized water, about 90 wt.% potassium hydroxide (about 15.6 g, 0.25 mole KOH) and boric acid (about 93.0 g, 1.504 moles) with stirring. The mixture was heated to about 80°C with stirring. Hydromagnesite, $Mg_5(CO_3)_4(OH)_2\cdot 4H_2O$, (about 11.69 g, 0.025 mole) was added to the mixture with stirring. Mild effervescence (i.e. bubbles gently released) ensued. The mixture was maintained at about 80°C with stirring for about 4.5 hours after which time the slurry was filtered and the filtered solids were washed with about 50 mL deionized water and dried in an oven at about 75°C to give $K_2MgB_{12}O_{20}\cdot 10H_2O$ (about 66.7 g, 72.9% recovered yield) as a white fine powder identified by chemical analysis and by X-ray powder diffraction. The X-ray diffraction pattern of the product was substantially the same that illustrated in Figure 4. The product after drying easily passed through a -325 U.S. mesh (44 μm opening) screen.

Example 12

This example illustrates the effect of temperature and time on reaction yield. Example 12 illustrates the effect of reaction temperature and time on the reaction yield, as listed in Table 2. Experiments were conducted using potassium hydroxide, boric acid and hydromagnesite as reagents to prepare potassium magnesium borate. All of the values in Table 2 are approximate.

Table 2. Product yield data for reactions carried at different temperatures for different durations.

Experiment	Reaction Temperature (°C)	Reaction Time (hours)	Product Yield (wt. % based on Mg)
A (Example 8)	65	7.88	76.6
B (Example 9)	65	18.0	78.8
C (Example 1)	80	4.50	71.9
D (Example 11)	80	4.50	72.9
E (Example 2)	80	6.00	73.0
F (Example 3)	80	7.88	73.8
G (Example 10)	80	64.0	80.6
H (Example 4	80	18.0	77.0
I (Example 5)	95	4.50	62.9
J (Example 6)	95	7.88	66.6
K (Example 7)	95	18.0	70.3

It can be seen by comparing the product yields in Table 2 for reactions carried out for the same durations at different temperatures, for example experiments A, F and J, that yield decreases with increasing temperature. It can also be seen from the data in Table 2 that yields increase as a general trend with increasing reaction time, for example experiments C, E, F, H and G.

Example 13

This example illustrates the preparation of potassium magnesium borate using recycled filtrate liquor. Example 13 demonstrates the utility of the methods for making potassium magnesium borate described herein for the efficient and sustained production of potassium magnesium borate using a semi-continuous process in which the filtrate from each production batch is recycled to the following batch. These methods can be further adapted to a fully continuous process.

A batch of potassium magnesium borate was prepared from potassium hydroxide, boric acid and hydromagnesite according to Example 2. Hot filtrate solution collected from this batch (150 mL) was transferred to a flask and potassium hydroxide (11.2 g, 0.20 moles) and boric acid (74.5 g, 1.2 moles) were added with stirring. The mixture was heated to 80°C and hydromagnesite (9.37 g, 0.02 moles) was added with stirring along with 1.0 g of potassium magnesium borate seed. The mixture was maintained at 80°C with stirring for 6 hours after which time it was filtered. The filtered solids were washed with 50 mL deionized water and dried at 75°C to give 49.49 g $K_2MgB_{12}O_{20}\cdot10H_2O$ after subtracting the 1.0 g of seed (about 67.6% recovered yield) as a white fine powder identified by chemical analysis and by X-ray powder diffraction. The X-ray diffraction pattern of the product was substantially the same that illustrated in Figure 4.

Example 14

This example illustrates the preparation of potassium magnesium borate from potassium hydroxide, boric acid and magnesium oxide. A flask was charged with about 150 mL deionized water, about 186 g boric acid (3.08 moles $B(OH)_3$) and about 31.2 g of 90% potassium hydroxide (about 0.50 mole KOH) and the mixture was heated to about 80°C with stirring. About 10.08 g magnesium oxide (about 0.25 mole MgO) was added along with 1.0 g of potassium magnesium borate seed and the mixture was maintained about 80°C with stirring for about 6 hours after which time the slurry was filtered and the filtered solids were washed with about 50 mL deionized water and dried in an oven at about 75°C to give $K_2MgB_{12}O_{20}\cdot 10H_2O$ (about 125.3g after subtracting the 1.0 g of seed, 72.1% recovered yield) as a white powder identified by chemical analysis and by X-ray powder diffraction. The X-ray diffraction pattern of the product was substantially the same that illustrated in Figure 4.

Example 15

This example illustrates the preparation of potassium magnesium borate from magnesium sulfate, potassium pentaborate, and potassium tetraborate. A flask was charged with about 150 g deionized water and heated to about 80°C. About 58.64 g (about 0.2 mole) $KB_5O_8\cdot 4H_2O$, about 30.55 g (about 0.10 moles) $K_2B_4O_7\cdot 5H_2O$, and about 24.65 g (about 0.10 moles) $MgSO_4\cdot 7H_2O$ were added to the heated water. About 1.0 g of potassium magnesium borate seed was added and the resulting mixture was maintained at about 80°C with stirring. After about 5 hours the slurry was filtered and the filtered solids were dried at 75°C. The resulting product was a free flowing fine granular material identified as potassium magnesium borate by X-ray powder diffraction as $K_2MgB_{12}O_{20}\cdot 10H_2O$. The X-ray diffraction pattern of the product was substantially the same that illustrated in Figure 4. The yield was 54.4 g (after subtracting the 1.0 g of seed) or 74.3%.

Example 16

This example illustrated delayed crosslinking using potassium magnesium borate prepared under different conditions. Two batches of potassium magnesium borate were prepared at about 80°C (Example 1) and about 95°C (Example 5) with set reaction times of about 4.5 hours. Crosslinking delay data were measured for samples from each batch after screening to -325 U.S. mesh (<0.44 μm) using a standard vortex closure method described in Rummo. These data gave good linear regression fits to power functions of the form $t =$

ax^p, where t is the crosslinking delay time (vortex closure time), x is the amount of potassium magnesium borate added, and a and p are constants. The crosslinking delay data and their respective power function curves are illustrated in Figure 5. It can be seen that samples of potassium magnesium borate prepared at about 80°C and 95°C (Examples 1 and 5) gave similar crosslinking delay curves, indicating that the dissolution rates of samples remain relatively constant regardless of the reaction temperature prepared over this temperature range. It can also be seen that samples of potassium magnesium borate prepared with reaction times of about 4.5, 6, and 18 hours give similar crosslinking delay times and thus have similar dissolution rates. These data demonstrate the methods for making potassium magnesium borate described herein can be suitable for the manufacture of a product having consistent attributes for use in practical application.

Example 17

For the $M_2MgB_{12}O_{20}\cdot xH_2O$ family of compounds, the dissolution rates can change as M, the monovalent cation, is varied. In addition, synthesis conditions can be used to further tailor dissolution rates and thus crosslinking delay times. Several compounds were studied by first screening the compounds in the family to about -325 U.S. mesh and then examining the dissolution rates by conductivity vs. time measurements and vortex closure tests. The vortex closure tests were performed pursuant to Rummo. Vortex closure times were compared to those obtained for a sample of commercial about -325 U.S. mesh ulexite mineral. Figure 6 illustrates the room temperature vortex closure delay curves for ulexite and a sample of PMB of the formula of $K_2MgB_{12}O_{20}\cdot 10H_2O$ that was prepared at about 80°C. For any given addition rate, the latter compound provided a substantially longer delay in crosslinking time compared to ulexite. PMB achieved delay times of about 3 minutes to more than 40 minutes. This delay curve was reproducible for multiple batches of PMB prepared under the same conditions.

As described elsewhere herein, PMB was found to have substantially slower dissolution rates than ammonium magnesium dodecaborate resulting in longer delay times. Thus, the potassium magnesium borate of the invention provides the art with an alternative compound for use in delayed crosslinking having characteristics from known compounds allowing for increased and improved options in the field.

Example 18

Example 18 illustrates the dispersability of potassium magnesium borate in oils, a property that provides utility in applications such as oil field use where handling of crosslinking agents as liquid dispersions is commonly practiced. A 1.0-g sample of potassium magnesium borate that had been screened to -325 U.S. mesh to give a particle size less than about 44 μm was dispersed in 25 g mineral oil and placed in a glass test tube. A 1.0-g sample of commercial ulexite, which was specified by the supplier to also be -325 U.S. mesh, was dispersed in 25 g mineral oil and placed in a glass test tube. The two tests were placed side by side to observe the settling behavior of each material. It was observed that the potassium magnesium borate dispersed more readily than the ulexite and after being dispersed exhibited a settling rate that was no greater than that of the ulexite, remaining suspended for an extended period of time.

The foregoing description of the present invention has been presented for purposes of illustration and description. Furthermore, the description is not intended to limit the invention to the form disclosed herein. Consequently, variations and modifications commensurate with the above teachings, and the skill or knowledge of the relevant art, are within the scope of the present invention. The embodiment described hereinabove is further intended to explain the best mode known for practicing the invention and to enable others skilled in the art to utilize the invention in such, or other, embodiments and with various modifications required by the particular applications or uses of the present invention. It is intended that the appended claims be construed to include alternative embodiments to the extent permitted by the prior art.

Claims

1. A method of preparing a compound of a formula of $K_2MgB_{12}O_{20}\cdot 10H_2O$, comprising: reacting a potassium source and a boron containing source, with at least one magnesium source, wherein the reaction of the potassium source, the boron containing source and the magnesium source does not produce a potassium byproduct.

2. The method of Claim 1, wherein the potassium source is selected from the group consisting of potassium hydroxide, potassium carbonate, potassium salt and combinations thereof.

3. The method of Claim 1, wherein the boron containing source is selected from the group consisting of boric acid, boric oxide, potassium borate, magnesium borate and combinations thereof.

4. The method of Claim 1, wherein the boron containing source is selected from the group consisting of a triborate compound, a tetraborate compound, a metaborate compound, and a pentaborate compound.

5. The method of Claim 1, wherein the at least one magnesium source is selected from the group consisting of magnesium oxide, magnesium hydroxide, magnesium salt, magnesium sulfate, magnesium carbonate, magnesium hydroxy carbonate, magnesium borate, and combinations thereof.

6. The method of Claim 1, wherein the potassium source is potassium hydroxide, the boron containing source is boric acid and the magnesium compound is magnesium oxide.

7. The method of Claim 1, wherein the potassium source is potassium hydroxide, the boron containing compound is boric acid and the magnesium compound is a magnesium hydroxy carbonate.

8. The method of Claim 7, wherein the magnesium hydroxy carbonate is hydromagnesite.

9. The method of Claim 1, wherein the potassium source is potassium carbonate.

10. The method of Claim 1, wherein the step of reacting comprises adding the boron containing source to the potassium source to form a first mixture, heating the first mixture to a first temperature between about 40 °C and about 100 °C while stirring the first mixture.

11. The method of Claim 10, wherein the first temperature is one of about 65°C, about 80°C, about 95°C or about 100°C.

12. The method of Claim 1, wherein the reaction of the potassium source, the boron containing source, and the at least one magnesium source is conducted in a slurry, and further comprising filtering the slurry to remove to a solid of the formula of $K_2MgB_{12}O_{20}\cdot 10H_2O$.

13. The method of Claim 12, further comprising recycling a filtrate from the step of filtering.

14. The method of Claim 1, further comprising adding a potassium magnesium borate seed added to the reaction to facilitate preparation of the potassium magnesium borate.

15. A method of forming a potassium magnesium borate, comprising:

reacting a potassium source and a boron containing compound, with at least one magnesium compound, wherein at least one byproduct of the reaction is water.

16. The method of claim 15, wherein a second byproduct of the at least one byproduct of the reaction is carbon dioxide.

17. The method of claim 15, wherein the reaction does not produce a potassium salt.

18. The method of claim 15, wherein the potassium source is at least one of a potassium chloride, a potassium bromide, and a potassium sulfate.

19. The method of Claim 15, wherein the potassium source is selected from the group consisting of potassium hydroxide, potassium carbonate, potassium salt and combinations thereof.

20. The method of Claim 15, wherein the boron containing source is selected from the group consisting of boric acid, boric oxide, potassium borate, magnesium borate and combinations thereof.

21. The method of Claim 15, wherein the boron containing source is selected from the group consisting of a triborate compound, tetraborate compound, a metaborate compound, and a pentaborate compound.

22. The method of Claim 15, wherein the at least one magnesium source is selected from the group consisting of magnesium oxide, magnesium hydroxide, magnesium salt, magnesium sulfate, magnesium carbonate, magnesium hydroxy carbonate, magnesium borate, and combinations thereof.

23. The method of Claim 15, wherein the potassium source is potassium hydroxide, the boron containing source is boric acid and the magnesium compound is magnesium oxide.

24. The method of Claim 15, wherein the potassium source is potassium hydroxide, the boron containing compound is boric acid and the magnesium compound is a magnesium hydroxy carbonate.

25. The method of Claim 24, wherein the magnesium hydroxy carbonate is hydromagnesite.

26. The method of Claim 15, wherein the potassium source is potassium carbonate.

27. The method of Claim 15, wherein the step of reacting comprises adding the boron containing source to the potassium source to form a first mixture, and heating the first mixture to a first temperature between about 40 °C and about 100 °C while stirring the first mixture.

28. The method of Claim 27, wherein the first temperature is one of about 65°C, about 80°C, about 95°C or about 100°C.

29. The method of Claim 15, wherein the reaction of the potassium source, the boron containing source, and the at least one magnesium source is conducted in a slurry, and further comprising filtering the slurry to remove to a solid of the formula of $K_2MgB_{12}O_{20}\cdot10H_2O$.

30. The method of Claim 15, further comprising recycling a filtrate from the step of filtering.

31. The method of Claim 15, further comprising adding a potassium magnesium borate seed added to the reaction to facilitate preparation of the potassium magnesium borate.

32. A method to treat a fluid in an oil field application, comprising:

providing a crosslinking agent to the fluid, wherein the crosslinking agent comprises a potassium magnesium borate compound of the formula of $K_2MgB_{12}O_{20}\cdot10H_2O$.

33. The method of Claim 32, wherein the fluid is a fracturing fluid.

34. A method to reduce flammability of an object, comprising:

providing a fire retardant comprising a potassium magnesium borate compound to the object.

35. A method of crosslinking polymers of a polymer-containing composition comprising contacting the composition with a potassium magnesium borate compound.

36. The method of Claim 34, wherein a formula of the potassium magnesium borate compound is $K_2MgB_{12}O_{20}\cdot10H_2O$.

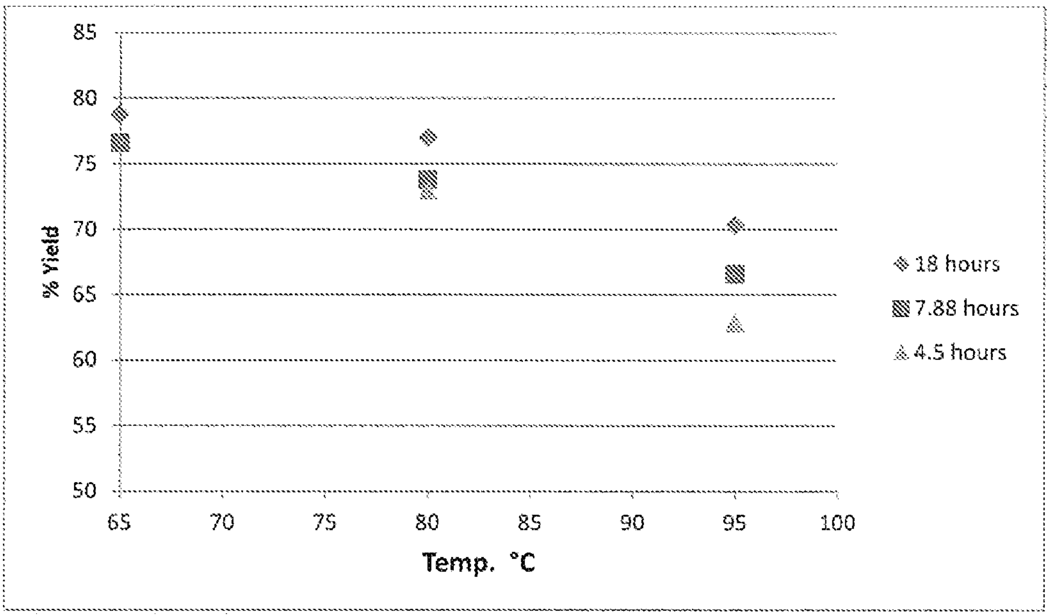
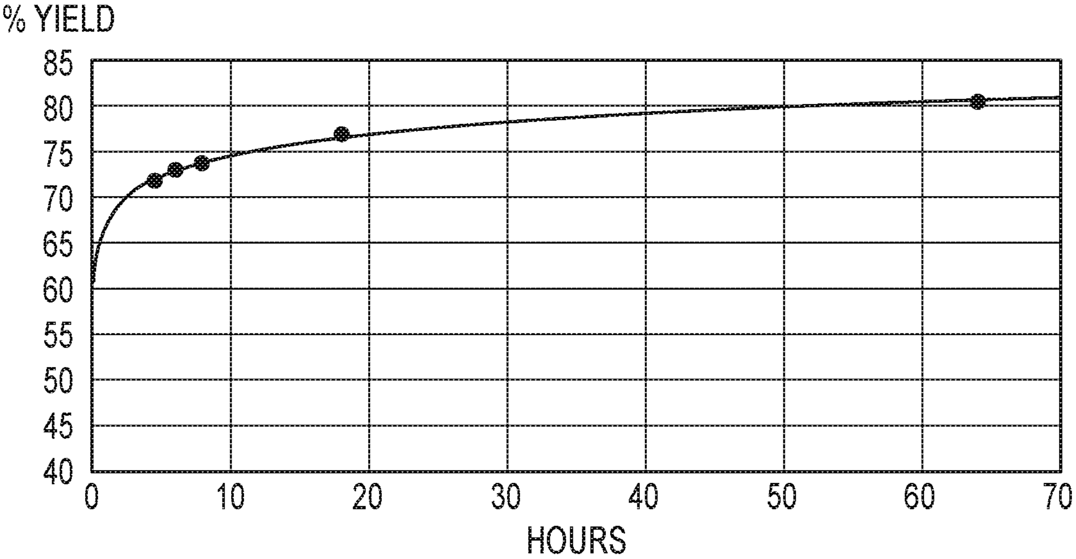

85
80
75
70
65
60
55
50
% Yield
65
70
75
80
85
90
95
100
Temp. °C
18 hours
7.88 hours
4.5 hours

FIG.1


% YIELD
85
80
75
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65
60
55
50
45
40
0
10
20
30
40
50
60
70
HOURS

FIG.2

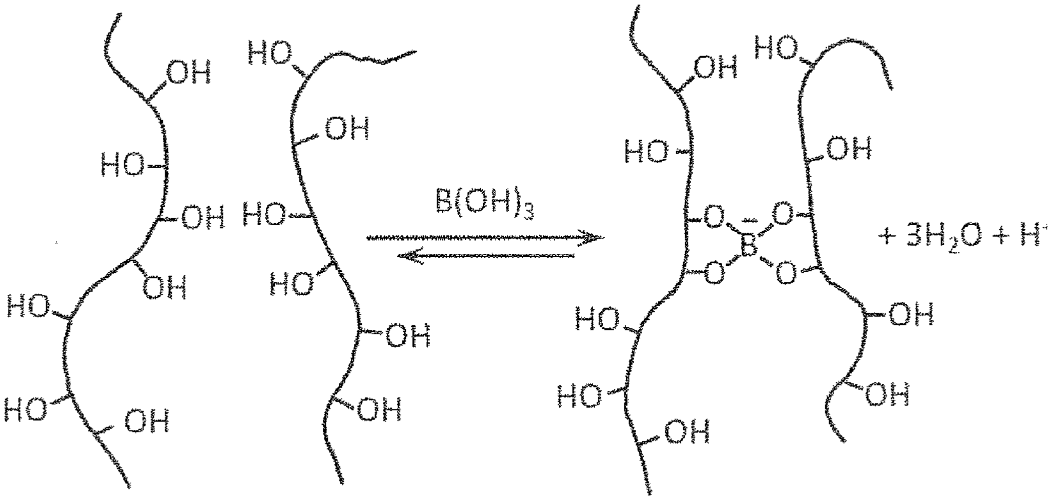
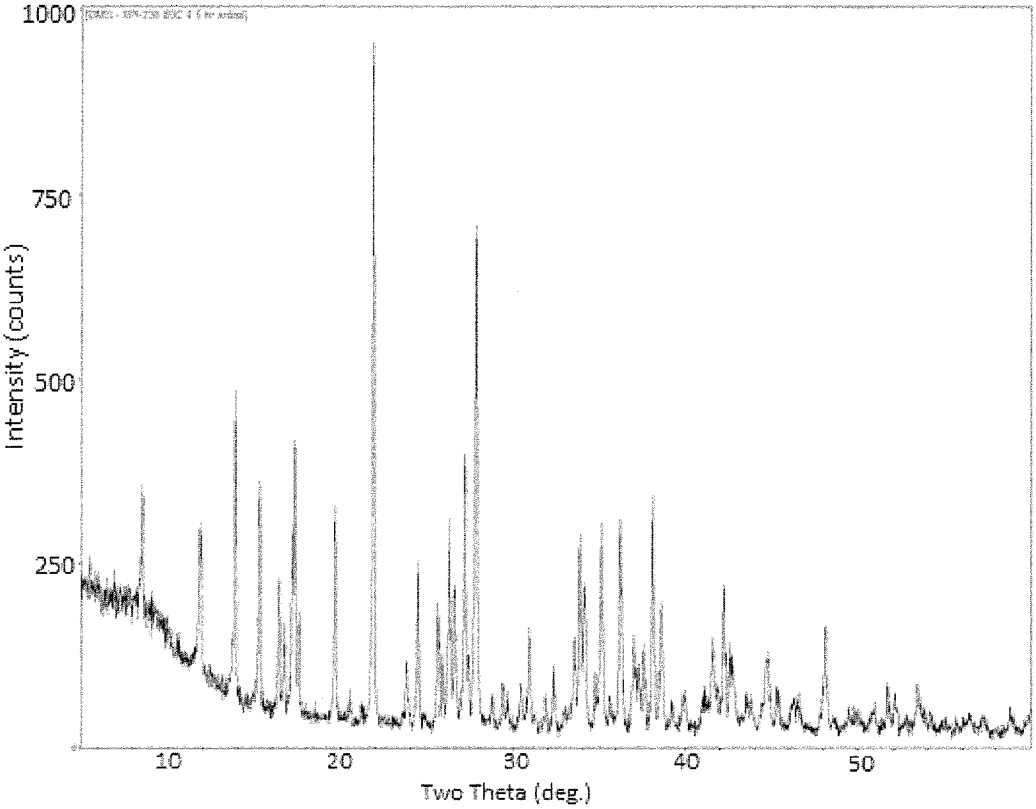


FIG. 3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750
500
250
0
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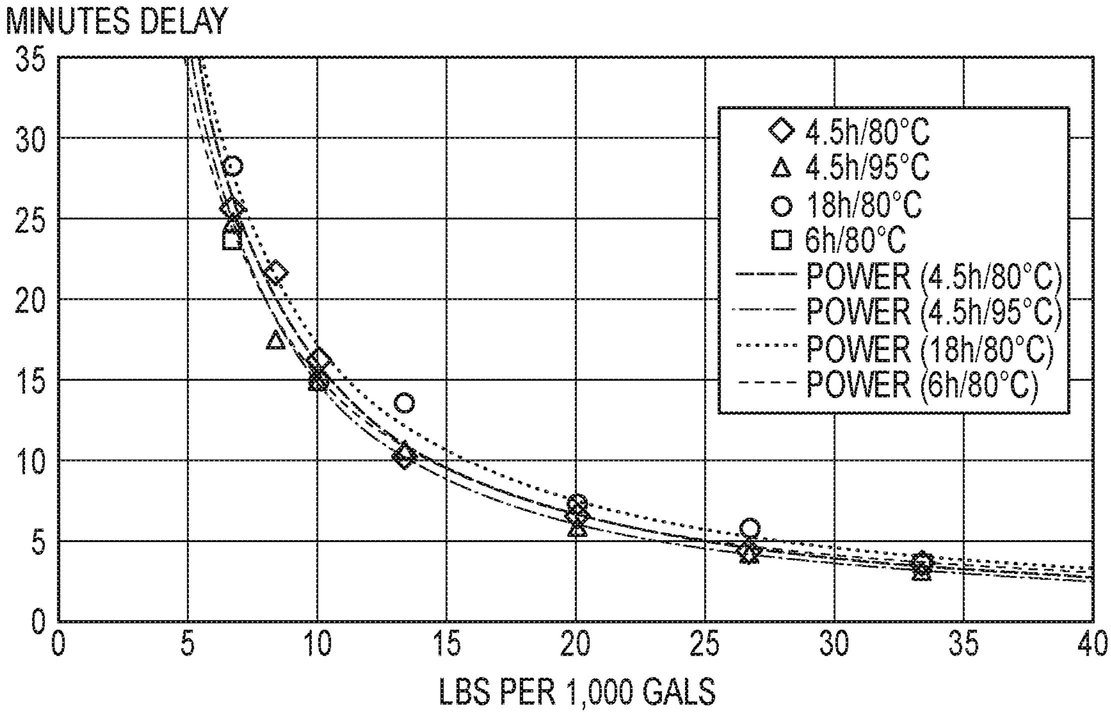
20
30
40
50
Two Theta (deg.)

FIG. 4


MINUTES DELAY
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30
25
20
15
10
5
0
0
5
10
15
20
25
30
35
40
LBS PER 1,000 GALS
◇ 4.5h/80°C
△ 4.5h/95°C
○ 18h/80°C
□ 6h/80°C
POWER (4.5h/80°C)
POWER (4.5h/95°C)
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POWER (6h/80°C)

FIG.5

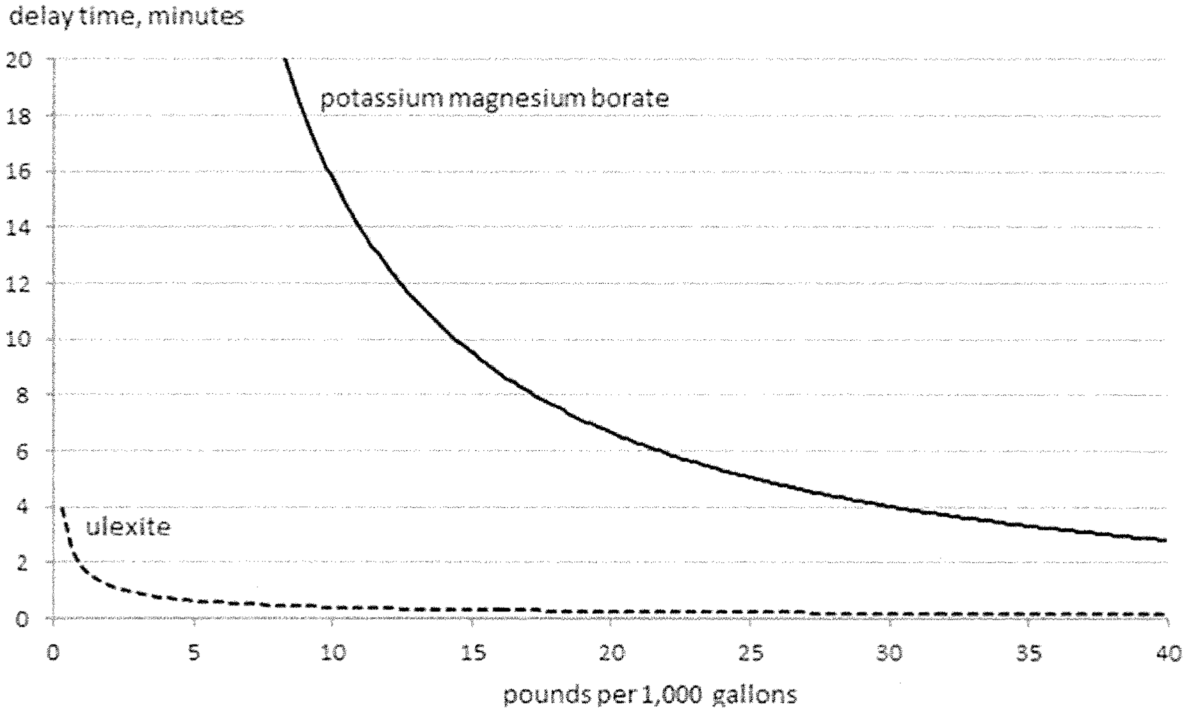
delay time, minutes
20
18
16
14
12
10
8
6
4
2
0
potassium magnesium borate
ulexite
0
5
10
15
20
25
30
35
40
pounds per 1,000 gallons

FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 16/46822

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C10M 163/00 (2016.01)
CPC - C10M 159/24
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8): C10M 163/00 (2016.01)
CPC: C10M 159/24

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 508/186 (key word limited; see search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase, Google Patents, Google Scholar
Search terms used: K2MgB12020 potassium source boron containing source

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 2006/0257578 A1 (ZHANG et al.) 16 November 2006 (16.11.2006); para [0013], [0036]	34 --- 36
X -- Y	EP 0,594,363 A1 (HALLIBURTON COMPANY) 27 April 1994 (27.04.1994); pg 2 ln 39-40; pg 3 ln 6-7, 10-12; pg 4 ln 32	35 ---- 32-33
Y	LIU Z. et al., "Crystal structure, vibrational spectroscopy, and thermal behavior of K2Mg[B6O7(OH)6]2*4H2O", Journal of Alloys and Compounds [online], 17 May 2005 (17.05.2005) [retrieved on 2016-10-06], volume 394, issue 1-2, retrieved from the Internet: <DOI: 10.1016/j.jallcom.2004.10.039>, pp. 277-281; see entire document, especially pg 277-278	1-33, 36
Y	KURBATOV R. V. et al., "Phase equilibria in the K2O-MgO-B2O3 system", Inorganic Materials [online], February 2010 (02.2010) [retrieved on 2016-10-06], volume 46, issue 2, retrieved from the Internet: <DOI: 10.1134/S0020168510020111>, pp. 151-153; see entire document, especially pg 151 and 153	1-31
Y	CN 101,941,709 A (JIANGXI LVYUE BIOENGINEERING CO LTD) 12 January 2011 (12.01.201 ar 1);pa [0020]-[0021]	6-8, 10-11, 23-25, 27-28
Y	US 5,785,939 A (SCHUBERT) 28 July 1998 (28.07.1998); col 3 ln 41-43; col 4 ln 35-37, 52	12-13, 29-30
Y	US 2,395,567 A (HENDERSON et al.) 26 February 1946 (26.02.1946); pg 1 col 2 ln 48-54; col 3 ln 57-58	14, 18, 31
Y	US 2011/0147682 A1 (BOWN et al.) 23 June 2011 (23.06.2011); para [0018], [0031]	7-8, 24-25

☒ Further documents are listed in the continuation of Box C. ☐

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search 06 October 2016 (06.10.2016)	Date of mailing of the international search report 28 OCT 2016
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 16/46822

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	VAN'T HOFF J. H., "Formation of oceanic salt deposits. XXXVII. Potassium pentacalcium sulphate and a double compound analogous to kaliborite", in: Journal of the Chemical Society, Abstracts [online], 1904 (1904) [retrieved on 2016-10-06], volume 86, issue 2, part 1, retrieved from the Internet: <DOI: 10.1039/CA9048605556>, pp. B556-B570; see entire document, especially pg 561	1-36