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(54) Title: CALCIUM HYPOCHLORITE OF REDUCED REACTIVITY

(57) Abstract: The present invention describes a calcium hypochlorite product formulation, including a polymeric alkali salt. The formulation exhibits improved environmental stability and shelf-life while simultaneously inhibiting scale in dispensing equipment, as well as in and on feed equipment used for delivering a calcium hypochlorite solution to a water stream which is to be treated.

CALCIUM HYPOCHLORITE OF REDUCED REACTIVITY

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

This invention relates to calcium hypochlorite blends; particularly to blends of calcium hypochlorite with an alkali salt form of anti-scaling polymers, wherein the polymer(s) are present in an alkali salt form effective at reducing the hygroscopic characteristics of the solid polymer(s), and subsequent calcium hypochlorite blend. This invention also relates to a means of reducing the reactivity of solid calcium hypochlorite with the said polymer(s) by applying a coating of the polymer(s) to the solid calcium hypochlorite.

2. DESCRIPTION OF THE RELEVANT ART

U.S. Patent No. 4,146,676 describes calcium hypochlorite particles coated with about 4 to 45 percent by weight of a low melting inorganic salt, e.g. aluminum sulfate hydrates, to reduce dusting during handling and to increase stability of calcium hypochlorite contacted with lighted cigarettes or reactive organic materials such as glycerine.

U.S. Patent No. 4,965,016 describes a granular calcium hypochlorite composition comprising a particle of calcium hypochlorite, the surface of which has been covered with a double decomposition product of calcium hypochlorite and an alkali metal hydroxide. It was shown the granular strength and stability was enhanced.

None of the prior art describes addition of an alkali salt of an organic polymeric anti-scaling agent to provide improved deposit control, while reducing the stability and reactivity of the solid calcium hypochlorite.

U.S. Patent Nos. 5,112,521 and 5,004,549 disclose the blending of phosphono-butane-tricarboxylic acid (PBTC) with calcium hypochlorite to produce a solid calcium hypochlorite blend that inhibits scale formation associated with the reconstitution and dispensing of the calcium hypochlorite solution.

U.S. Patent No. 6,146,538 discloses the use of polymaleic acid (PMA) and/or polyepoxysuccinic acid (PESA) in an alkali salt form that is blended with calcium hypochlorite to reduce or eliminate scale formation associated with the reconstitution and dispensing of the calcium hypochlorite solution.

PBTC, disclosed in U.S. Patent Nos. 5,112,521 and 5,004,549, when combined with calcium hypochlorite as an anti-scaling agent, can compromise manufacturing safety and solid product stability, due to its inherent hygroscopic characteristics.

SUMMARY OF THE INVENTION

Increased moisture, especially localized moisture, can increase the rate of decomposition of calcium hypochlorite. During decomposition, oxygen is typically released, with chlorides and chlorates typically being the resulting byproducts. In the presence of sufficient moisture, exothermic reactions can result, oxygen release can increase, and a potential fire hazard increases when fuel sources are available, e.g. cloth, hydrocarbons and the like.

The alkali salt forms of PMA, PESA, and similar polymeric salts, which are commonly employed as deposit control agents, can significantly reduce the hygroscopic characteristics of calcium hypochlorite when combined therewith, in addition to providing enhanced anti-scaling properties. A coating of these polymers or blends thereof can significantly reduce the reactivity of the solid calcium hypochlorite blend.

Thus, a step forward in the art is realized via provision of a solid calcium hypochlorite combination which simultaneously exhibits anti-scaling properties and reduced hygroscopic and reactivity characteristics. Such a composition can yield improvements in both manufacturing safety and product stability by reducing moisture adsorption and subsequent decomposition of the calcium hypochlorite, as well as improved safety by reducing the reactivity of the solid calcium hypochlorite.

According to one or more embodiments, the present invention provides a composition comprising calcium hypochlorite and a polymeric alkali salt.

According to other embodiments, the present invention provides a method of preparing a composition. The method comprises the step of coating calcium

hypochlorite with at least one polymeric alkali salt in an amount sufficient to reduce reactivity of said calcium hypochlorite.

DETAILED DESCRIPTION OF THE INVENTION

The instant invention is directed toward a calcium hypochlorite product formulation and a method for its production. The product can exhibit improved environmental stability and shelf-life while inhibiting scale in dispensing equipment, as well as in and on feed equipment used for delivering a calcium hypochlorite solution to a water stream which is to be treated.

A calcium hypochlorite composition with improved hygroscopic and reactivity characteristics can be formulated comprising hydrated calcium hypochlorite and an alkali salt of polymaleic acid, polyepoxysuccinic acid or mixtures thereof, having between 0.01 and 10% by weight of said alkali salts, an available chlorine concentration of at least 30% and water in the range of about 2% to about 20% by weight.

In one or more embodiments, the composition is a solid having greater than about 50% active calcium hypochlorite which exhibits anti-scaling characteristics and reduced hygroscopicity and reactivity.

The solid calcium hypochlorite may be coated and/or encapsulated with at least one polymeric alkali salt selected from within the group including polymaleate, polyacrylate, polyacrylamide, polycarboxylate, carboxylate-sulfonate copolymer, maleic anhydride copolymer, polyepoxysuccinate, maleate-sulfonate copolymer, maleate-phosphonate copolymer, carboxylate-phosphonate copolymer, and/or mixtures thereof.

The alkali salt may be selected from at least one of the group including sodium, potassium, lithium, calcium, or magnesium salts and mixtures thereof. Additionally, the polymeric alkali salt may be in a liquid, slurry, or solid form.

At some point in the manufacturing process the calcium hypochlorite may be formulated/treated with a deposit control agent including at least one alkali salt(s), e.g. sodium, potassium, lithium, calcium, magnesium and/or mixtures thereof, of polymaleic acid, polyepoxysuccinic acid, maleic anhydride copolymer, phosphinopolycarboxylic acid, carboxylic-sulfonic acid copolymer, maleic-sulfonic

acid copolymer, maleic-phosphonic acid copolymer, carboxylic-phosphonic acid copolymer, and/or mixtures thereof. The weight percent of deposit control agent can be within the range of about 0.01% to about 10% of the final weight of the formulated calcium hypochlorite product.

These polymers and copolymers should exhibit similar hygroscopic characteristics in the desired salt forms while providing deposit control capability. Furthermore, they are typically hydrophilic and can possess high thermal stability. Therefore they should reduce reactivity of the solid calcium hypochlorite product.

While not wishing to be bound to any particular physical form, the combination of calcium hypochlorite and polymer may be in the form of a homogeneous mixture, may alternatively take the form of an outer layer or covering which coats or encapsulates the calcium hypochlorite for increased stability and reduced reactivity, or a combination thereof.

Accordingly, it is an objective of the instant invention to provide a calcium hypochlorite product and a method for its production, wherein the resultant product exhibits reduced hygroscopic characteristics thereby improving the manufacturing safety and shelf-life and anti-scaling properties of the solid product.

It is a further objective of the instant invention to provide a coated or encapsulated solid calcium hypochlorite product having reduced reactivity and anti-scaling properties.

The function and advantage of these and other embodiments of the present invention will be more fully understood from the example below. The following example is intended to illustrate the benefits of the present invention, but does not limit the full scope of the invention.

Example

As illustrated in Table 1, embodiments disclosed in U.S. Patent Nos. 5,112,521 and 5,004,549 as well as an alkali salt form of the polymaleic acid disclosed in U.S. Patent No. 6,146,538 were tested for their hygroscopic properties by exposing similar quantities of each to a controlled atmospheric environment consisting of the following approximate conditions: 70°F, and 50% humidity.

The samples were weighed before and after exposure to the controlled environment.

The increase in weight is associated with the increased moisture. The NaPBTC increased moisture through adsorbing moisture from the surrounding environment.

It is understood that based upon the known reactivity of calcium hypochlorite, which is a Class 3 oxidizer, and its known increased decomposition with increased moisture, that the addition of an anti-scaling agent that increases hygroscopicity will lead to a potentially dangerous situation.

The instant invention provides a combination of ingredients which simultaneously reduces the hygroscopic characteristics of the final solid product, thereby improving the manufacturing safety and final product stability, while ensuring chemical feed reliability through improved deposit control.

Table 1

	Weight Before	Weight After 2 hr.	w/w % Change 2 hr.
Dry polymaleate	0.99 grams	1.01 grams	2.02%
Polymer BAYHIBIT® (PBTC)	1.09 grams	1.27 grams	16.51%
		Weight After 24 hr.	w/w % Change 24 hr.
Dry polymaleate		1.06 grams	7.07%
Polymer BAYHIBIT® (PBTC)		1.93 grams	77.06%

Adsorption of localized moisture creates the greatest concern. While the % weight increase to a 1.5% blend would appear to be minimal, localized moisture increase should correlate to the data exemplified in Table 1, reducing shelf life and chlorine activity, as well as a potential increased risk of combustion especially when fuel sources are contacted, as outlined in Table 2, below.

Table 2 illustrates the reaction of 68% calcium hypochlorite shock, sold under the brand name HTH® SHOCK®, with and without a coating of a calcium polymaleate salt, upon exposure to oil.

Each sample used approximately 7.5 grams of solid calcium hypochlorite. The treated sample was mixed with 4.7 grams of polymer salt (slurry weight), followed by convective drying. Each sample was placed in a dish where 1 oz. of oil (brake fluid) was added as a fuel source.

The results clearly illustrate that coating the solid calcium hypochlorite with a polymeric salt(s) of polymaleic acid or PESA as described in U.S. Patent No. 6,146,538 dramatically reduces the reactivity of calcium hypochlorite. Even in the case of extended exposure to combustible materials, the formulation described has the ability to significantly reduce the rate of decomposition of the calcium hypochlorite and prevent ignition when ignition would otherwise occur without treatment. It is therefore also reasonable to extrapolate from the data that further improvement would be achieved by encapsulation of the solid calcium hypochlorite.

Table 2

	Time to Fuming	Time to Combustion	Residue
HTH® SHOCK®	58 seconds	62 seconds	Charred, light weight, ash like residue
Treated HTH® SHOCK®	525 seconds	Not applicable	No charred, heavy, polymer cal-hypo mix

Additional tests were performed using various polymeric salts with known anti-scaling abilities. These polymers all possess thermal stability sufficient to prevent their decomposition during exposure to exothermic reactions from the decomposition of exposed calcium hypochlorite as well as hot fuming fuels. The thermal stability ensures the polymer coating prevents exposure of coated calcium hypochlorite thereby preventing a self-sustaining decomposition or runaway reaction.

Salt samples of polyacrylate and polymaleate were produced for reactivity testing as illustrated in Table 3.

Table 3

Sample	Polymer Salt Form	Grams 68% Cal-Hypo	Grams Polymer (solids)
1	Na/Ca polyacrylate	45	Approx. 2
2	Ca polyacrylate	45	Approx. 2
3	Na/Ca polymaleate	45	Approx. 2

These polymer salt samples were applied in either the form of a slurry or foam to 45 gram samples of >68% calcium hypochlorite sold under the brand name HTH. Table 4 illustrates the results of the testing. Foam was used to enhance the distribution of the polymer. After drying, the treated samples were compared to blank samples for reactivity. 10ml of brake oil fluid was used as a fuel source, and the time from addition to fuming and ignition was measured, along with their weights. Table 4 illustrates the results of the testing.

Table 4

Sample	Cal-hypo wt. (gm)	Total wt. (gm)	Fuming (sec)	Ignition (sec)	Final Weight (gm)	Appearance	Polymer applied
Untreated							
1	7.72	9.99	spilled	n/a	n/a	n/a	n/a
2	7.84	10.02	12	14	10.13	Charred Ash	n/a
3	7.81	9.99	13	15	9.74	Charred Ash	n/a
4	7.86	10.03	13	15	9.37	Charred Ash	n/a
Treated							
	7.88	9.95	100	n/a	15.97	Cal-hypo residue	Slurry
	7.77	10.03	105	n/a	16.8	Cal-hypo residue	Slurry
	7.89	9.99	45	n/a	14.67	Cal-hypo residue	Slurry
	7.88	9.92	195	n/a	18.83	Cal-hypo residue	Foam

The results of these tests illustrate that treating the >68% calcium hypochlorite with an alkali salt form of hydrophilic polymer with thermal stability exceeding 300°F significantly reduces the reactivity of the calcium hypochlorite.

The reaction can be self-limiting in that only exposed (untreated) calcium hypochlorite is involved in the reaction and once consumed in the reaction, residual fuel remains in contact with the stabilized (treated) calcium hypochlorite.

These test results further illustrate that by limiting exposure of calcium hypochlorite to the fuel source, the rate of reaction is significantly reduced, and ignition is avoided altogether.

Yet another result of these tests is that increased coverage of the calcium hypochlorite yields further reduction in reactivity of the treated calcium hypochlorite. In this example, application of the polymer by use of an expanded foam to increase its volume improved coverage and distribution, correlating to improved performance at reducing the samples' reactivity.

Improving the hygroscopic characteristics of the calcium hypochlorite can improve the manufacturing safety and shelf-life of the solid product. This should be true regardless of whether the solid product is in a granular, pellet, tablet or briquette form. By adding an anti-scaling agent with improved hygroscopic characteristics, the potential for compromising safety and shelf-life is reduced.

By reducing the surface area of the calcium hypochlorite by coating the solid material with a hydrophilic polymeric salt with thermal stability exceeding 300°F, the reactivity of the calcium hypochlorite can be reduced, while allowing rapid dissolution of the calcium hypochlorite when diluted with water, as in the case of a calcium hypochlorite dispenser. To further improve the hygroscopic characteristics of the hydrophilic salt, divalent salts, or increased percentages thereof, should be included in the final salt form of the polymer.

It is to be understood that while a certain form of the invention is illustrated, it is not to be limited to the specific form or arrangement of parts herein described and shown. It will be apparent to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is shown and described in the specification.

One skilled in the art will readily appreciate that the present invention is well adapted to carry out the objects and obtain the ends and advantages mentioned, as well as those inherent therein. The compounds, compositions, and any related compounds, methods, procedures and techniques described herein are presently representative of the preferred embodiments, are intended to be exemplary, and are not intended as limitations on the scope. Changes therein and other uses will occur to those skilled in the art, which are encompassed within the spirit of the invention and are defined by the scope of the appended claims.

Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are obvious to those skilled in the art are intended to be within the scope of the following claims.

What is claimed is:

CLAIMS

1. A composition comprising calcium hypochlorite and a polymeric alkali salt.

2. The composition of claim 1, wherein said calcium hypochlorite is in the form of a granule, a pellet, a tablet or a briquette.

3. The composition of any one of claims 1-2, wherein the composition comprises about 0.01 to about 10% by weight of said polymeric alkali salt.

4. The composition of any one of claims 1-3, wherein said polymeric alkali salt is in the form of a liquid, a slurry, or a solid.

5. The composition of any one of claims 1-4, wherein said polymeric alkali salt is selected from the group consisting of a polymaleate, a polyacrylate, a polycarboxylate, a polymethacrylate, a phosphinopolycarboxylate, a carboxylate-sulfonate copolymer, a maleic anhydride copolymer, a polyepoxysuccinate, maleate-sulfonate copolymer, maleate-phosphonate copolymer, carboxylate-phosphonate copolymer, and mixtures thereof.

6. The composition of any one of claims 1-4, wherein the polymeric alkali salt is a polyepoxysuccinic acid salt.

7. The composition of any one of claims 1-4, wherein said polymeric alkali salt is a polymaleic acid salt.

8. The composition of any one of claims 1-4, wherein said polymeric alkali salt is a maleic anhydride copolymer salt.

9. The composition of any one of claims 1-4, wherein said polymeric alkali salt is a phosphinopolycarboxylate salt.

10. The composition of any one of claims 1-4, wherein said polymeric alkali salt is a polyacrylate salt.

11. The composition of any one of claims 1-4, wherein said polymeric alkali salt is a polyacrylamide salt.

12. The composition of any one of claims 1-4, wherein said polymeric alkali salt is a carboxylic-sulfonic acid copolymer.

13. The composition of any one of claims 1-4, wherein said polymeric alkali salt is a maleic-sulfonic acid copolymer.

14. The composition of any one of claims 1-4, wherein said polymeric alkali salt is a maleic-phosphonic acid copolymer.

15. The composition of any one of claims 1-4, wherein said polymeric alkali salt is a carboxylic-phosphonic acid copolymer.

16. A method of preparing a composition comprising coating calcium hypochlorite with at least one polymeric alkali salt in an amount sufficient to reduce reactivity of said calcium hypochlorite.

17. The method of claim 16, wherein the amount of said polymeric alkali salt is about 0.01 % to about 10% by weight of the composition.

18. The method of any one of claims 16-17, wherein the composition comprises at least about 68% by weight calcium hypochlorite.

19. The method of any one of claims 16-18, wherein said polymeric alkali salt is in the form of a liquid, slurry, solid, or foam.

20. The method of any one of claims 16-19, wherein said polymeric alkali salt at least partially encapsulates at least some particles of said calcium hypochlorite.

21. The method of any one of claims 16-20, wherein the polymeric alkali salt is a polyepoxysuccinic acid salt.

22. The method of any one of claims 16-20, wherein said polymeric alkali salt is a polymaleic acid salt.

23. The method of any one of claims 16-20, wherein said polymeric alkali salt is a maleic anhydride copolymer salt.

24. The method of any one of claims 16-20, wherein said polymeric alkali salt is a phosphinopolycarboxylate salt.

25. The method of any one of claims 16-20, wherein said polymeric alkali salt is a polyacrylate salt.

26. The method of any one of claims 16-20, wherein said polymeric alkali salt is a polyacrylamide salt.

27. The method of any one of claims 16-20, wherein said polymeric alkali salt is a carboxylic-sulfonic acid copolymer salt.

28. The method of any one of claims 16-20, wherein said polymeric alkali salt is a maleic-sulfonic acid copolymer salt.

29. The method of any one of claims 16-20, wherein said polymeric alkali salt is a maleic-phosphonic acid copolymer salt.

30. The method of any one of claims 16-20, wherein said polymeric alkali salt is a carboxylic-phosphonic acid copolymer salt.