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METHOD OF MANUFACTURING STABLE ALKALI HYPOCHLORITE COMPOSITIONS

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The present invention relates to solid stable chlorine-containing preparations, and more particularly to such chlorine-containing preparations comprising sodium hypochlorite associated with a dehydrated or partially dehydrated material which may also function as a detergent or cleansing agent.

At the present time sodium hypochlorite is marketed in the form of its aqueous solution, and in view of its chlorine liberating ability, functions satisfactorily as a bleaching and disinfecting material. This material is particularly useful as a bleach in home and commercial laundries for cotton fabrics as well as other materials not injured by chlorine. In view of the active disinfecting properties of chlorine, sodium hypochlorite solutions are used in dairies, in restaurants, water purification and for many other purposes.

The use of aqueous solutions possesses numerous disadvantages, however, among which are, instability to heat, light, aging, with consequent liberation of chlorine, inconvenience and cost of packaging and handling the large volumes of water in which the hypochlorite is dissolved, and the cost and inconvenience of shipping the dilute and corrosive aqueous hypochlorite solutions. In view of its corrosivity, these solutions must be packaged in glass containers which are fragile, expensive, and bulky. All in all it would be highly desirable to obtain dry, solid compositions containing sodium hypochlorite, in a form which would permit utilization in home and industry as a bleach and disinfectant.

Dry mixtures of alkali metal hypochlorite and hydrated tri-alkali-phosphate, for example of sodium hypochlorite and hydrated trisodium phosphate, have been prepared previously by mixing solutions of sodium hypochlorite with partially or completely dehydrated trisodium phosphate. The amounts of ingredients are so adjusted that the partially or completely dehydrated trisodium phosphate takes up the water of solution of sodium hypochlorite and thus becomes completely or almost completely hydrated. The results of such compounding is a mixture of dry sodium hypochlorite and completely or almost completely hydrated trisodium phosphate. Such a mixture will be stable only if kept dry i. e. when it is not exposed to the atmosphere. However, when exposed to the atmosphere the sodium hypochlorite content of the mixture, being hygroscopic will attract moisture from the atmosphere. In the presence of water sodium hypochlorite decomposes in the following manner:

$$3NaOCl \rightarrow 2NaCl + NaClO_3$$

and thus loses its disinfecting or bleaching

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properties. In the absence of water, the above reaction cannot take place.

It is also known to prepare substantially pure, dry crystalline hydrated sodium hypochlorite, but this product is expensive and difficult to prepare and handle, and is unstable and hence cannot be properly utilized as a solid.

It is an object of the present invention to prepare a solid, stable bleaching and/or disinfectant composition.

It is a further object of the present invention to prepare a solid stable alkali metal hypochlorite composition.

It is an additional object of the present invention to prepare a solid and stable sodium hypochlorite composition associated with a dehydrating agent in a manner which will prevent or minimize hydration on exposure to air.

It is a still further object of the present invention to prepare a solid, stable sodium hypochlorite-trisodium phosphate composition suitable as a bleach, disinfectant and/or detergent.

In accordance with the present invention I have discovered that a solid composition having the desired stability may be obtained in a particular manner to be hereinafter described. This product will, in addition, possess the property of being readily subdivided so that a freely flowing product of the desired particle size and dissolving capacity may be readily obtained, and will retain this free flowing property without the formation of lumps through partial hydration on exposure to moisture-containing air, etc. In the practice of my invention, the water content of a solution of an alkali metal hypochlorite is absorbed as water of hydration in a partially or completely anhydrous alkali metal salt which is capable of holding an appreciable amount of water as water of hydration or crystallization. Such salts include the carbonates, phosphates, silicates, etc. In general sodium hypochlorite and the sodium salts are preferred because of lower cost and greater availability and of these salts, the trisodium phosphate is usually preferred because it has good detergent properties and can retain twelve molecules of water in its hydrated crystalline form. Other alkali metal phosphates such as disodium phosphate which form salts containing several molecules of water of crystallization may be utilized.

In order to prepare the product of my invention, mere absorption of the water from the sodium hypochlorite as water of hydration is not sufficient, since the resulting material is unstable, and becomes partially hydrated and lumpy and will not form a suitably finely divided product, nor will it retain its freely flowing properties. Mere provision of an excess of dehydrating

salt in the ordinary manner, or by mixing the hypochlorite with an excess of the salt over that required to absorb the water, is also not completely satisfactory.

I have discovered that if the composition is formed in a sequence of two separate steps, in which the water of the solution is absorbed as water of hydration or crystallization by the dehydrating salt in the first step, and the resulting hydrated material is then intimately mixed with an additional quantity of the anhydrous or partially anhydrous salt, a suitably stable, dry and free-flowing product is obtained. Apparently the advantageous properties are the result of the formation of a novel product which comprises a mixture of two types of particles one of which is composed of sodium hypochlorite associated with the salt such as trisodium phosphate together with water of hydration taken from the hypochlorite solution. The other type of particle consists of the excess of dehydrated salt which is free from association with sodium hypochlorite. In accordance with the present invention the hypochlorite containing particles are coated and/or surrounded by particles of anhydrous or partially dehydrated salt free from sodium hypochlorite which serves as a protective barrier to pick up any moisture which may contact the mixture on exposure to air.

In explaining the mechanism of the behavior of the product of my invention by comparison with that formed in the ordinary way, the addition of an excess of trisodium phosphate to a hypochlorite solution, or the addition of the hypochlorite solution to an excess of trisodium phosphate will result in all of the granules of the solid salt participating in the dehydration with resultant association of each solid particle with at least some hypochlorite. This is facilitated by the observed fact that the solid particle, after first absorbing water on its surface, appears to resist further penetration or absorption of water in the center of the particle, apparently due to the formation of a film of hydrated salt on its surface. Therefore complete hydration will necessarily be delayed until the interior of the granules has been penetrated and as a result all of the dehydrating salt particles will become associated with some sodium hypochlorite. On the other hand, in the two step process of my invention, after complete absorption of the water of solution as water of hydration, an excess of dehydrated trisodium phosphate free from any association with sodium hypochlorite, is incorporated with the hypochlorite-containing material in a separate step so that the resulting product comprises a mixture of hydrated trisodium phosphate having sodium hypochlorite associated therewith, intimately admixed with dehydrated trisodium phosphate free from hypochlorite as a protective material.

More specifically, in illustrating my invention, I admix, for example, a solution of sodium hypochlorite with partially or completely dehydrated trisodium phosphate in such proportions that all of the water of solution of the hypochlorite becomes water of hydration of the trisodium phosphate. The mixing is carried out in such a manner that the heat of hydration which develops during the mixing is dissipated by cooling to avoid overheating.

In general it is preferred to utilize water absorbing salts in as complete a state of dehydration as possible, but some salts are fairly difficult to completely dehydrate. In the case of trisodium phosphate, the monohydrate is readily formed from the dodecahydrate, but the last molecule of water is not as readily removed. Economic factors also come into play since some salts are relatively expensive. Disodium phosphate, sodium pyrophosphate, sodium carbonate and the silicates such as sodium metasilicate may also be used. The corresponding dehydrating salts of the other alkali metals may also be used, but are not economically feasible due to their greater cost.

Example I

100 parts of a solution of sodium hypochlorite containing 10% NaOCl were admixed with 67 parts of trisodium phosphate monohydrate, $Na_3PO_4.1H_2O$, in granular form. A fairly dry mixture was obtained and this was ground to about 50 mesh. After grinding, the mixture was then thoroughly mixed with 20 parts of monohydrated trisodium phosphate of the same mesh size. The product was a dry, free-flowing and stable material containing about 5.3% NaOCl.

In a single step process carried out according to the prior art, 100 parts of sodium hypochlorite solution containing 10% NaOCl were admixed with 87 parts of monohydrated trisodium phosphate, and a dry product was obtained which was ground to 50 mesh. After standing in the open air for a period of one week, the product of the single step process had become somewhat lumpy and did not flow as freely as that of the two step process. Furthermore, the content of the NaOCl or available chlorine had declined appreciably whereas no significant decrease had occurred in the product of the two step process.

These results can be readily explained on the following basis: The 100 parts of NaOCl solution contains about 10 parts of NaOCl and about 8 parts of NaCl, so that the amount of water present is 82 parts. When this is mixed with 87 parts of the trisodium phosphate in one step, each molecule of Na_3PO_4 takes up

$$\frac{82}{18}+\frac{87}{164}$$

or 8.6 molecules of water. This is due to the fact that the water is relatively uniformly distributed among the trisodium phosphate particles. The saturation point for water of crystallization of Na_3PO_4 is 12 molecules of H_2O. NaOCl is considerably more hygroscopic than $Na_3PO_4.9.8H_2O$, and on exposure to an atmosphere containing moisture will not be protected by the trisodium phosphate.

On the other hand, in the two step process of the present invention, where 67 parts of anhydrous trisodium phosphate are added in the first step, each molecule of Na_3PO_4 will absorb

$$\frac{82}{18}+\frac{67}{164}=11.1 \text{ molecules of } H_2O$$

The 20 parts of $Na_3PO_4.H_2O$ added in the second step remain in the dehydrated form and will serve to absorb any moisture contained in air to which the mixture is exposed and will thus protect the hypochlorite from reaction with H_2O and resultant decomposition.

The product of the process described herein may be utilized in the same manner as the conventional aqueous sodium hypochlorite solution, for bleaching and sterilizing purposes. Various chlorine concentrations may be obtained by utilizing aqueous solutions of the desired strength. Usually solutions containing 5–30 percent of

NaOCl are readily available. The product mixes well with powdered or granulated soaps and with synthetic detergents, such as the sulfonated alkyl aromatics or sulfated higher fatty alcohols, etc., to form a detergent having good washing, bleaching, and sterilizing properties. The product may be ground to any desired size, but generally, a particle size of 20–100 mesh is satisfactory.

I claim:

1. A process for the preparation of a solid, stable, crystalline composition comprising an alkali metal hypochlorite, which comprises contacting an aqueous solution of the hypochlorite with a sufficient quantity of an at least partially dehydrated inorganic alkaline salt to absorb all of the water of solution of the hypochlorite as water of crystallization of the salt and forming a substantially dry granular mixture, and then intimately admixing the resultant hydrated material with at least 10% by weight of an additional quantity of the said salt to serve as a protectve medium to prevent decomposition of the hypochlorite by selective absorption of moisture.

2. A process according to claim 1 wherein the hypochlorite is sodium hypochlorite.

3. A process according to claim 1 wherein the hypochlorite is sodium hypochlorite and the alkaline salt is trisodium phosphate.

4. A process for the preparation of a relatively stable, solid composition comprising sodium hypochlorite, which comprises contacting an aqueous solution comprising sodium hypochlorite with sufficient at least partially dehydrated trisodium phosphate to absorb all of the water of solution of the hypochlorite solution as water of hydration and forming a substantially dry granular mixture, and intimately admixing the resultant hydrated solid material with at least 10% by weight of additional at least partially dehydrated trisodium phosphate to provide a dry, stable, solid product.

5. A process for the preparation of a relatively stable crystalline product comprising sodium hypochlorite which comprises intimately mixing an aqueous solution of sodium hypochlorite with monohydrated trisodium phosphate in such proportions and for a period of time such that all of the water of solution is absorbed by the trisodium phosphate as water of crystallization and forming a substantially dry granular mixture, intimately mixing with the resultant addition product from about 10 to 100 percent by weight of additional trisodium phosphate monohydrate to serve as a protective agent against moisture in the air to minimize decomposition of the sodium hypochlorite on exposure thereto.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,965,304	Adler	July 3, 1934
1,988,991	Albertshauser	Jan. 22, 1935
2,097,517	Durgin	Nov. 2, 1937
2,145,015	Seaton	Jan. 24, 1939