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PROCESS OF MAKING A BLEACHING AGENT

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This invention relates to a process for the manufacture of a solid lithium hypochlorite bleaching material containing a high percent of available chlorine.

Heretofore, the common hypochlorite bleaches manufactured and marketed as apparently dry, solid products have been the commonly known bleaching powder containing about 35% to 38% available chlorine, produced by chlorinating slaked lime; i. e., calcium hydroxide, and the so-called "high test" bleaching powders which contain a higher proportion of calcium hypochlorite and hence contain about 70% available chlorine. Ordinary bleaching powder has a very low solubility in water. When, therefore, it is desired to obtain a clear bleaching solution from this material, it has been the practice to mix the bleaching powder with water, allow the insoluble material to settle out and remove the clear solution for use as a bleaching agent.

It is usual in laundry practice to use a bleaching agent in a washing solution which also contains soap and soluble alkali detergents, such as the carbonates, phosphates, silicates, etc. If a calcium hypochlorite solution, such as might be prepared from ordinary or "high test" bleaching powder, were added to water containing soap or the commonly used alkaline detergents, the calcium of the bleaching powder would be precipitated in an insoluble form; as a calcium soap, calcium carbonate, phosphate, silicate, etc. To avoid the difficulties due to this behavior of calcium bleaches, it has heretofore been the practice to mix the bleaching powder with water and add a carbonate such as sodium carbonate (soda ash) to precipitate the calcium as calcium carbonate and leave, in solution, sodium hypochlorite formed by reaction of the sodium carbonate with the calcium hypochlorite. The precipitated calcium carbonate is settled and the clear solution of sodium hypochlorite decanted off for use in the washing solution. The need for transforming calcium hypochlorite into a solution of sodium hypochlorite to obtain a bleaching solution which could be used with soap and alkali cleansers is a serious disadvantage.

The disadvantages of bleaching powder due to its low solubility and the precipitation of insoluble calcium compounds with alkaline detergents or soap could be avoided by the use of sodium hypochlorite as the bleaching agent. While solutions of sodium hypochlorite and potassium hypochlorite have been prepared and used as bleaching agents (these solutions being known as "Javelle water"), these hypochlorites in the solid form are quite unstable and rapidly lose their available chlorine. It has not heretofore been practicable, therefore, to manufacture and market solid sodium or potassium hypochlorite because of their rapid decomposition and loss of available chlorine in a comparatively short time. Accordingly, solid chlorine bleaches heretofore marketed have been almost exclusively materials containing calcium hypochlorite.

It is an objective of my invention to provide a process for the manufacture of a solid hypochlorite bleach which is soluble in water, even in the presence of alkaline detergents, which contains a high percentage of available chlorine and which is relatively stable so that it may be marketed without rapidly decomposing and losing its available chlorine. It is a further objective of my invention to provide a process for the manufacture of that bleaching agent as a solid product suitable for marketing.

I have found that lithium hypochlorite (LiOCl) is remarkably stable over long periods of time and only very slowly loses available chlorine; so slowly, in fact, that it is suitable for storing and marketing in the usual manner. This stability of solid lithium hypochlorite with respect to its available chlorine content is surprising in view of the fact that both sodium and potassium hypochlorite, when produced in solid form, very quickly decompose. Thus, in an extended experimental investigation of solid sodium hypochlorite bleaches, it was found they decomposed rapidly and, at the end of 40 days, they had lost about 30% of their initial available chlorine content. On the other hand, I have found a solid lithium hypochlorite bleach, which initially contained 102% available chlorine (calculated on the basis of the anhydrous solid), at the end of 53 days contained 100% available chlorine.

In carrying out the process of my invention, lithium hypochlorite is formed by reacting a solution of lithium hydroxide with chlorine, preferably supplied as gaseous chlorine. The reaction taking place may be expressed by the following equation:

$$2LiOH+Cl_2=LiCl+LiOCl+H_2O$$

Lithium hydroxide has a relatively low solubility in water as compared with other alkali metal hydroxides so that by chlorinating with chlorine a solution substantially saturated with LiOH at ordinary room temperatures, a solution containing about 10% lithium hypochlorite, about 7% lithium chloride, and slightly less than 1% residual unreacted lithium hydroxide may be pre-

pared. If such a solution is cooled to about −20° C., ice crystals will form. However, by first concentrating the lithium hypochlorite solution until it contains about 20% or more lithium hypochlorite, the solid hypochlorite may be recovered by crystallization from the solution at temperatures below 55° C. For example, by concentrating the above solution until it contains about 25% lithium hypochlorite, 18% lithium chloride and about 1¼% lithium hydroxide, and bringing the concentrated solution to a temperature of about 20° to 25° C., I have discovered a crop of crystals of a hydrated lithium hypochlorite is obtained. By merely filtering the crystals from the mother liquor, a product wet with mother liquor and containing 49.6% lithium hypochlorite, 8.6% lithium chloride, 0.7% lithium hydroxide, 0.1% lithium chlorate and 41% H_2O may be obtained. I have thus discovered that lithium hypochlorite is less soluble than lithium chloride so that by crystallization from solution containing both the hypochlorite and chloride a product may be obtained containing an increased proportion of hypochlorite to chloride over that of the solution itself.

The crystals, wet with mother liquor, may be dried to obtain an apparently dry, solid bleaching material which is highly stable with respect to its available chlorine content for long periods of time. The apparently dry solid contains a little more than 100% available chlorine on the anhydrous basis. It is unnecessary to remove all the water from the material to obtain a product which is suitably dry for marketing. I have discovered that lithium hypochlorite combines with water to form a hydrate which, in crystallizing the salt from solution in the manner described above, appears to be the monohydrate ($LiOCl.H_2O$). Accordingly, when the material wet with mother liquor was dried, it became an apparently dry, solid product while it still contained about 26% water.

The high available chlorine content of the products of my invention is an important characteristic. They contain 75% or more available chlorine based on the total content of lithium compounds in the product calculated as the anhydrous compounds. They may be further characterized by their high ratio of available chlorine to total chlorine. Thus, even though the dried product described above contains a substantial proportion of lithium chloride, it contains a high ratio (about 1.65 to 1) of available chlorine to total chlorine. The total chlorine content of the product is derived from lithium hypochlorite and whatever lithium chloride and lithium chlorate is present.

It is particularly advantageous to prepare the lithium hypochlorite by reaction of chlorine with lithium hydroxide solution. This reaction forms equal molecular proportions of lithium chloride and lithium hypochlorite. In view of my discovery that lithium hypochlorite is less soluble in water than is lithium chloride, by crystallizing the hypochlorite from a solution containing it together with lithium chloride, the lithium hypochlorite may be separated in large part, or substantially completely, if desired, from the lithium chloride. Even though the final product contains most of the lithium chloride produced by this chlorination reaction, the ratio of available chlorine to total chlorine in the products of my invention is above 1 to 1. It is preferred, however, in crystallizing the lithium hypochlorite from solution to separate it from a substantial proportion of the chloride so as to obtain a product containing higher ratios, about 1.5:1 to 2:1, of available chlorine to total chlorine as, for example, the product described hereinabove. Furthermore, by washing mother liquor from the lithium hypochlorite crystals prepared as described above, a material containing 60.6% lithium hypochlorite, less than 0.2% each of lithium chloride and lithium chlorate, and about ½% of lithium hydroxide, may be prepared. This material may be dried to remove excess moisture, for example, until it contains about 21% or less H_2O. It will contain about 117% available chlorine on the anhydrous basis and its ratio of available chlorine to total chlorine is substantially 2:1.

In reacting lithium hydroxide with chlorine to produce lithium hypochlorite, it is preferred to discontinue the treatment with the chlorinating agent short of complete exhaustion of the lithium hydroxide, so that the lithium hypochlorite will contain some residual alkaline material. If chlorination is carried to the point at which all the alkaline material is reacted, the lithium hypochlorite which is formed may decompose more rapidly than when it contains residual alkaline material. On the other hand, it is undesirable to leave undue amounts of unreacted lithium hydroxide in the product because this represents a waste of material. Accordingly, the products of my invention preferably contain not more than 10 parts residual alkaline material, calculated as LiOH, to every 100 parts of lithium hypochlorite.

As pointed out hereinabove, it is preferred to produce lithium hypochlorite by chlorinating a solution of lithium hydroxide. Due to the relatively low solubility of this hydroxide, however, the hypochlorite solutions which may be prepared by chlorinating a liquid in which the lithium hydroxide is completely in solution are relatively dilute and are not suitable without concentration for crystallizing the lithium hypochlorite from the solution merely by cooling it. The concentration of the lithium hypochlorite solution preparatory to crystallizing the solid therefrom may be accomplished by evaporation, particularly by evaporating under a high vacuum and at the reduced temperatures at which the vacuum makes it possible to evaporate the water. For example, the evaporation of the solution may be carried out under pressures of about 4 to 12 mm. absolute, at temperatures ranging from about 10° C. to about 40° C., to produce solutions containing about 25% lithium hypochlorite which, at temperatures of about 20° C. to 25° C. or lower, produce a crop of lithium hypochlorite crystals.

I have discovered, however, a procedure whereby a solution may be prepared containing a sufficiently high percentage of lithium hypochlorite to permit crystallization merely by cooling and without evaporation of water. I have found that when a slurry or suspension of solid lithium hydroxide in a saturated solution thereof is treated with a chlorinating agent, the reaction to form lithium hypochlorite goes smoothly and, as it proceeds, the solid lithium hydroxide dissolves and is converted into lithium hypochlorite. By thus chlorinating a solution of lithium hydroxide which contains solid lithium hydroxide, a solution of lithium hypochlorite may be produced of the desired high concentration suitable for crystallizing the solid hypochlorite at temperatures of, for example, about 20° to 25° C., without undue decomposition of hypochlorite during the chlorination treatment of the hydroxide.

While I have described the production of lith-

ium hypochlorite by chlorination of lithium hydroxide using chlorine as the chlorinating agent, my invention is not limited thereto. For example, the chlorinating reagent may be chlorine monoxide. When this is used, its reaction with lithium hydroxide may be expressed by the equation:

$$2LiOH+Cl_2O=2LiOCl+H_2O$$

Since this reaction does not involve the formation of lithium chloride, the use of chlorine monoxide simplifies the recovery from the resulting solution of a lithium hypochlorite bleaching material of high purity containing substantially all of its chlorine as available chlorine.

While I have illustrated my invention by describing the production of lithium hypochlorite from lithium hydroxide, the invention is not limited to the chlorination of this material but comprises the chlorination of any suitable alkaline lithium compound.

While the preferred method of producing the bleaching material of this invention involves the chlorination of a solution of lithium hydroxide, the invention is not limited thereto. Lithium hypochlorite mixed with lithium chloride, lithium chlorate, etc. prepared by any suitable method may be dissolved in water and the hypochlorite crystallized from the solution.

When, in this specification and in the appended claims, I refer to available chlorine, that term is used as customary in the bleaching art. In that art, the available chlorine in a material is determined by usual analytical procedures such as that involving the liberation of iodine from potassium iodide by reaction with the bleaching material and titration of the liberated iodine with standard thiosulfate solution. As is well known in this art, one mol of lithium hypochlorite is equivalent to two gram atoms of available chlorine. Accordingly, for a pure lithium hypochlorite, its available chlorine content would be 121.1%, although its actual chlorine content is only one-half of that or 60%. Total chlorine, on the other hand, means the actual amount of combined chlorine present in the material, in the form, for example, of chloride, chlorate and hypochlorite.

As pointed out above, the product of this invention may contain residual alkaline material. This is determined by first decomposing the hypochlorite by treatment with hydrogen peroxide and then titrating the solution with a standardized acid solution to determine the total alkalinity using methyl orange as the indicator. While this residual alkalinity of the material may be due solely to lithium hydroxide, some of it may be present as lithium carbonate. Accordingly, when in this specification and appended claims, reference is made to the residual alkaline material in a lithium hypochlorite bleach, I mean the total alkalinity of the material as determined by the above method and calculated as LiOH.

I claim:

1. The process for the production of a soluble, stable, solid chlorine bleach which comprises reacting chlorine and lithium hydroxide in the presence of sufficient water to dissolve the lithium chloride and substantially chemically equivalent amount of lithium hypochlorite formed by the reaction of said chlorine and lithium hydroxide, crystallizing at a temperature below 55° C. said lithium hypochlorite as solid from solution in said water of a concentration of at least 20% lithium hypochlorite while maintaining in the solution sufficient water to retain lithium chloride in solution and separating from the crystallized lithium hypochlorite mother liquor containing dissolved lithium chloride in amount such that the mixture of solid crystals and residual mother liquor left therewith contains a substantially higher ratio of lithium hypochlorite to lithium chloride than the 1 to 1 mol ratio of these salts which is formed by the reaction of said chlorine and lithium hydroxide.

2. The process for the production of a soluble, stable, solid chlorine bleach which comprises reacting chlorine and lithium hydroxide in the presence of sufficient water to dissolve the lithium hypochlorite and lithium chloride formed in equal molecular proportions by the reaction of said chlorine and lithium hydroxide, bringing the concentration of lithium hypochlorite in the resulting solution to at least 20%, crystallizing from said solution at a temperature below 55° C. solid lithium hypochlorite while maintaining in the solution sufficient water to dissolve the lithium chloride therein, and separating from the crystallized lithium hypochlorite mother liquor containing dissolved lithium chloride in amount such that the mixture of solid crystals and residual mother liquor left therewith contains at least 75% available chlorine based on its total content of lithium compounds calculated as the anhydrous compounds.

3. The process for the production of a soluble, stable, solid chlorine bleach which comprises reacting chlorine with a solution of lithium hydroxide, thereby forming a solution of equal mol ratios of lithium chloride and lithium hypochlorite in which the ratio of available chlorine to total chlorine is substantially 1:1, evaporating the solution of lithium chloride and hypochlorite until the concentration of lithium hypochlorite in the solution is at least 20%, crystallizing from the resulting solution at a temperature below 55° C. solid lithium hypochlorite while maintaining in the solution sufficient water to dissolve the lithium chloride, and separating from the crystallized lithium hypochlorite mother liquor containing lithium chloride in solution therein in amount sufficient to increase the ratio of available chlorine to total chlorine in the crystallized hypochlorite and mother liquor left therewith to at least 1.5:1.

4. The process for the production of a soluble, stable, solid chlorine bleach which comprises reacting chlorine with a slurry of solid lithium hydroxide in a saturated aqueous solution of lithium hydroxide, whereby lithium hypochlorite and lithium chloride are formed in substantially equal mol ratios, maintaining present in said slurry an amount of water which dissolves the lithium chloride and gives a solution in which the concentration of lithium hypochlorite is at least 20%, crystallizing from the resulting solution at a temperature below 55° C. solid lithium hypochlorite while retaining in solution the lithium chloride, and separating from the crystallized lithium hypochlorite mother liquor containing dissolved lithium chloride in amount such that the mixture of solid, crystallized lithium hypochlorite and residual mother liquor left therewith contains at least 75% available chlorine based on its total content of lithium compounds calculated as the anhydrous compounds.

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