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PERBORATE COMPOSITION

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This invention relates to a sodium perborate bleaching composition and method of making it.

The application is a continuation-in-part of our application Serial No. 355,167, filed May 14, 1953, now abandoned.

The use of sodium perborate in bleaching compositions is extensive. While the perborate is sometimes used in the form of the monohydrate, the perborate is ordinarily present as the so-called "tetrahydrate" which may be represented by either one of the following formulae:

- (1) $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$
- (2) $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$

While the latter of these formulae shows the reason for the name "tetrahydrate," the former is perhaps more suggestive of the chemical properties of the material.

The perborate cleansing compositions are characterized not only by their available or active oxygen that gives them value but also by a tendency to absorb moisture with resulting undesired caking of the particles together and final deliquescence when exposed to a moist atmosphere.

These difficulties are increased by spray drying; absorption of moisture increases greatly when the area of surface exposed per unit weight is as large as in the hollow, spray dried particles.

Also, spray drying as practiced in other industries leads to decomposition of perborate. In fact sodium perborate tetrahydrate, when dried to the next lower water level, the monohydrate ($\text{NaBO}_2 \cdot \text{H}_2\text{O}$), becomes unstable at ordinary temperatures.

We have now discovered a perborate composition that contains less water than the tetraborate, does not show the instability characteristic of the perborate monohydrate or anhydrous perborate, and is substantially non-caking. This is the product formed by spray drying incompletely a mixture of sodium perborate tetrahydrate and sodium tripolyphosphate under carefully controlled conditions and then cooling the product.

As an explanation of part at least of the action or relationship of the perborate, tripolyphosphate, and water, the following observation is reported. 100 parts of sodium perborate tetrahydrate were carefully melted in a container in a steam bath and the temperature steadied at approximately 63° C. Then there were introduced and stirred in 50 parts of anhydrous sodium tripolyphosphate. The temperature rose quickly to 71° C. This release of energy as heat is considered to show such transfer of water of hydration or other change as is accompanied by a decrease of free energy, that is, increase of stability of the system.

Briefly stated, our invention comprises the method of and the composition resulting from spray drying a solution of sodium perborate and sodium tripolyphosphate at a pH not substantially above 10.5 and to a total final water content of the codried product corresponding approximately to 2.5–4 moles for 1 atom of retained available oxygen, all the processing being effected at a rela-

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tively low temperature. In one embodiment, the invention comprises introducing a water soluble detergent into the solution before spray drying, the detergent being one that as used does not raise the pH substantially above the value stated when the whole composition is dissolved in water, that is, at usual concentrations for use as a detergent or for spray drying.

Examples of such detergents that may be used and that illustrate satisfactory classes of materials are dodecyl benzene sodium sulfonate, sodium lauryl sulfate, the sodium sulfate of formula $\text{C}_2\text{H}_5\text{CO}_2\text{N}(\text{CH}_3)\text{C}_2\text{H}_4\text{SO}_3\text{Na}$, and polyoxyethylene-modified isooctyl phenol, with 10 ethylene oxide units to the molecule.

Other agents may be and suitably are included in addition to the polyphosphate in the perborate composition. Thus, we may incorporate soluble sodium silicate of low alkalinity, as, for example, the silicate of the following ratio: $1\text{Na}_2\text{O}:2.5\text{SiO}_2$, magnesium silicate powder, a usual blueing agent of which an example is phthalocyanine blue, and an iron sequestering agent. Examples of sequestering agents that may be used are alkali metal derivatives of ethylene diamine tetracetic acid (Versene FE-3, Specific), the sodium salt of nitrilotriacetic acid, and gluconic acid.

As to proportions on the anhydrous basis, we use at least 50 parts of the sodium tripolyphosphate for 100 of sodium perborate on the dry basis, that is at least 50 parts of $\text{Na}_2\text{P}_3\text{O}_{10}$ for 100 of a NaBO_3 . (All proportions are expressed as parts by weight except when specifically shown or stated to the contrary.) When less of the polyphosphate is used, we do not obtain the resistance to deliquescence and the full stabilization features of the invention. The amount of the tripolyphosphate may be increased to larger proportion provided there is still present a proportion of perborate that provides the percentage of available oxygen desired in the finished product, as for example, 1% to 7% of such oxygen on the whole weight of the composition.

As to silicates, we use at least 5% and ordinarily not more than 20% for 50 parts anhydrous weight of the perborate, the silicate being either magnesium silicate or in part magnesium silicate and in part the sodium silicate of low alkalinity.

Example 1

Sodium perborate 4 moles (328 parts on the anhydrous basis) and sodium tripolyphosphate 1 mole (368 parts anhydrous) are dissolved in warm water in excess of 14 moles, actually 400 parts of water being used, the water being warmed sufficiently to prevent crystallization of either the perborate or the tripolyphosphate from the solution.

The solution is then sprayed into spray drying equipment through which warm air is being passed in accordance with usual spray drying technique.

The conditions selected were such that, in spray drying four representative runs of about 50,000 pounds each of product, the total moisture content in the final bead product varied from 4.5%–11.3% and the available oxygen from 1.94%–4.56%. The moles of total water as calculated from data for the individual runs are 2.54–3.5 for 1 atom of the available oxygen.

The dried, hollow solid particles of product were collected in and then removed from the spray drier in the usual manner.

During the spray drying operation there was substantially less loss of available or active oxygen than when a perborate solution was dried in comparable manner in the absence of the tripolyphosphate.

In this example, the temperature of the perborate was maintained at all times during the dissolving and spray drying at a temperature below 100° C.

The product is in the form of hollow, generally spheri-

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cal particles that are free flowing and non-caking and non-deliquescent on reasonable exposure.

In a modification of this example any one of the detergents listed above is introduced into the said solution before spray drying, in the proportion of 10%–40% of the combined weight of the perborate and tripolyphosphate on the anhydrous basis. Although organic and oxidizable the detergent does not decrease appreciably the available oxygen in the perborate.

In another modification of this example, there were incorporated also magnesium silicate and soluble sodium silicate in about equal amounts and in total proportion corresponding to 10% of the combined weight of the perborate ($\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$) and anhydrous tripolyphosphate and 1–5% of one of the iron sequestering agents (Versene FE-3, Specific) on the said combined weight. These additional additives further stabilized the composition.

Example 2.—Perborate preparation

A slurry of perborate crystals forming no part of the present invention is made as follows: $\frac{1}{4}$ mole borax (decahydrate, 95.25 parts) and $\frac{1}{2}$ mole sodium hydroxide (20 parts) are dissolved in 175 parts water and the resulting solution cooled to 10°–11° C. 1 mole hydrogen peroxide (68 parts of 50% H_2O_2) is next added very gradually with cooling to maintain the temperature within the range about 0°–11° C. until crystallization of the tetrahydrate begins. This occurs when about half the peroxide has been added. The addition of H_2O_2 is stopped while the crystallization is allowed to proceed with cooling. Additional peroxide is added gradually while the temperature is maintained within the said range. A fluid slurry of granular perborate will result only if the subsequent H_2O_2 additions are made gradually and at 10°–11° C. or lower but not below the freezing point of water in contact with the perborate. An increase in the crystallization temperature will produce slurries of high viscosity and of very fine crystals which do not lend themselves well to building into complete detergents with suitable additional components.

The resultant slurry of 154 parts of $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ in a total of 358.25 parts (i. e. 43%) is fluid when properly made and the supernatant mother liquor is practically free of H_2O_2 . A small amount of a known stabilizer, such as magnesium silicate or magnesium sulfate, is added preferably as soon as the crystallization of the perborate has started, to avoid any unnecessary breakdown.

Such a perborate slurry has been spray-dried, but the resulting beads or dried particles have a very strong tendency to become liquefied at high humidity. The deliquescent tendency of the perborate is even more pronounced when it is made above 40° C., as has been proposed, without allowing the formation of the tetrahydrate.

Example 3.—Built perborate

To make a spray-dried perborate bleach of the desired active oxygen content, it was necessary to build the perborate with other materials. For this purpose the slurry of perborate tetrahydrate crystals was made as in Example 2.

Of the inorganic builders tried, sodium tripolyphosphate was found to be effective in imparting non-deliquescence to the perborate bead. The mix was made wet and spray dried as described. For instance, a bead containing 42.9% $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$, 45.7% tripolyphosphate, 8.8% silicate ($1:2.4 \text{ Na}_2\text{O}/\text{SiO}_2$), 2.2% magnesium silicate, 0.5% of an iron sequestrant (Versene Fe_3 , i. e. with 3% of anhydrous H_2O_2), and initial water content of 17.6% (in addition to 5.6% H_2O in the H_2O_2) absorbed 28.64% by weight of additional water in 139 hours, at 75% relative humidity, without deliquescence and with only slight surface caking. Another sample which had an initial water content of only 8% absorbed 48.6% moisture

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in 67 hours at 75% relative humidity without deliquescence and with only slight surface caking. To inhibit caking, the presence of the silicates (in addition to the polyphosphate) was found to be most effective. Silicates alone were not able to overcome deliquescence. However, the silicate content of these bleaches was limited to about 10% of the total weight, so as to avoid the detrimental effect of its high pH and of the insolubles it forms on contact with CO_2 or on reduction of the pH value.

Example 4.—Built perborate slurry

(a) Starting with a perborate made as in Example 2, a slurry is made by adding, to 358.25 parts of 43% perborate tetrahydrate slurry, 5 parts of magnesium silicate, 43 parts of a 47% sodium silicate solution, and then gradually adding sodium tripolyphosphate, 117 parts, while allowing the exothermic hydration and crystallization to raise the slurry temperature from 10° C. to about 33° C. The slurry thickens while the crystallization progresses and may require additional water to maintain fluidity, depending upon the agitation available. It is spray dried, as described.

(b) Starting with dry perborate tetrahydrate, the order is preferably reversed: Into 225 parts of water (or water-ice) and 43 parts of 52° Bé. sodium silicate, 117 parts of granular sodium tripolyphosphate are introduced with good agitation. The temperature rises from 1° C. to 170° C. Upon completing the hydration as shown by no further temperature rise, the slurry is completed by adding 5 parts magnesium silicate and 154 parts of sodium perborate tetrahydrate.

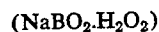
The formulation has been varied in the ratio of its three major ingredients: The perborate content may be varied to adjust the final active oxygen content to compensate for moisture content of the product and for oxygen losses which should normally be between 5 and 10%. The silicate content may be varied to impart a lower pH and lower content of water-insoluble material or to give greater protection against caking. The tripolyphosphate content would then be adjusted accordingly but never substantially below 50 parts for 100 of the tetraborate calculated as $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$.

Among other conventional builders, sodium sulfate, borax, sodium metaborate, salt, and sodium pyrophosphate, when used instead of tripolyphosphate, gave gummy or adherent particles after spray drying. Tripolyphosphate increases decomposition of the perborate. We consider that the stabilizing effect of the tripolyphosphate is due to the substantially uniform blending of the tripolyphosphate, of its desirable properties including pH, with the perborate within and throughout the fine, hollow, thin-walled spherical particles resulting from spray drying.

It will be understood that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purpose of illustration which do not constitute departures from the spirit and scope of the invention.

What is claimed is:

1. A stabilized perborate composition of improved resistance to caking together and deliquescence of the particles, the composition being in the form of fine, hollow, free flowing, spray dried particles comprising partially hydrated sodium perborate and partially hydrated sodium tripolyphosphate, the proportions on the anhydrous basis being at least about 50 parts of the tripolyphosphate for 100 parts of the perborate



2. the perborate and tripolyphosphate being in intimate association and codried condition throughout the said particles, and the total water content in the spray dried particles being about 2.5–4 moles for each atom of available oxygen in the perborate.

2. The composition of claim 1 including 10-40 parts of water soluble detergent for 100 parts of combined weight of perborate and tripolyphosphate on the anhydrous basis, the detergent being one that, in the said composition, gives a pH not substantially above 10.5 5 when the composition is dissolved in water.

3. In making sodium perborate composition, the method which comprises forming an aqueous slurry of sodium perborate and sodium tripolyphosphate in the proportion of at least about 50 parts of the tripolyphosphate for 100 parts of the perborate, both on the anhydrous basis, spraying the slurry into heated air at a temperature approximately within the range 100°-315° C., so as to effect spray drying, and separating the resulting solid particles comprising partially hydrated sodium perborate and partially hydrated sodium tripolyphosphate from the air when the remaining total water content of the particles corresponds to approximately 2.5-4 moles for each atom of available oxygen in the perborate, the perborate being maintained at all times during the forming of the slurry and the spray drying 10 15 20

at a temperature not substantially above 100° C. and at a pH not above about 10.5.

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