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2,886,534

PRODUCTION OF ALKALI METAL
MONOPERSULFATES

Donald B. Lake, Grand Island, and Stephen E. Stephanou, Lewiston, N.Y., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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This invention relates to the manufacture of alkali metal monopersulfates, sodium and potassium monopersulfates in particular.

In co-pending application S.N. 476,607, filed December 20, 1954, now Patent No. 2,802,722, there is disclosed a process for manufacturing the alkali and alkaline earth metal salts of Caro's or monopersulfuric acid, H_2SO_5 . The process of that application results in good yields and products of high active oxygen content and is consequently a great improvement or prior art processes. The salts produced by the direct neutralization technique are, however, hygroscopic and tend to cake very badly. It is, for example, very difficult to dry sodium monopersulfate to a free-flowing powder.

The active oxygen mentioned above and discussed throughout this specification is the oxygen within the molecule in excess of that required to form the corresponding bisulfate. It may be calculated as a percentage from the equation for the decomposition of sodium monopersulfate,



as follows:

$$\text{Percent active oxygen} = \frac{\text{Wt. of } [O]}{\text{Wt. of } NaHSO_5} \times 100$$

where the symbol [O] represents the weight of oxygen liberated by the decomposition, available to oxidize any compound capable of being oxidized, such as potassium iodide, or of combining into molecular oxygen.

An over-all object of this invention is, therefore, provision of an improvement in the manufacture of alkali metal monopersulfates. Another object is provision of an improvement in the method of manufacturing alkali metal monopersulfates shown by the aforesaid co-pending application. A further object is provision of a method for manufacturing dry, free-flowing alkali metal monopersulfates without undue loss of active oxygen. A specific object is provision of a method for manufacturing dry, free-flowing alkali metal monopersulfate composition containing at least around 5% by weight of active oxygen.

The above-mentioned and still further objects may be achieved in accordance with this invention by a process in which a solution of alkali metal monopersulfate is mixed with a diluent or extender before drying. Preferred diluents are boron compounds such as boric oxide or acid or alkali metal borates and perborates. Other alkali metal salts may be used with the boron compounds if it is so desired but these other salts are in general not satisfactory when they are utilized alone.

The percentage of adjuvant employed is not sharply critical. When a boron compound alone is added, a minimum of about 1-2% by weight is desirable. Smaller quantities may be used but with impaired results. The upper limit of the additive is set by the percentage of active oxygen desired, the 5% figure noted above being almost essential if the product is to have practical utility. Consequently the weight of adjuvant should not be above

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about 12%. The weight of the boron compound can be reduced towards the minimal 1-2% limits when other compounds, such as carbonates, phosphates, pyrophosphates, silicates or sulfates are added along with it.

It may be noted that suitable diluents are not limited to those mentioned. Almost any compound that does not act to decompose the monopersulfate and that is compatible with the primary intended utility of the latter, i.e., bleaching, may be supplied along with one of the necessary boron compounds.

For best results the boron compound used as a diluent should be supplied to the monopersulfate while the latter is in solution. It is preferred to add the diluent before the pH of the solution is greater than about 2 or 3. Marked loss of active oxygen results if an alkaline boron compound is added at a higher pH. The diluent may actually be mixed with the neutralizing agent and added during the neutralization. It is, however, more easily added separately, either while the neutralization is being carried out or immediately after it is stopped, the solution pH, of course, not being above about 3.

After the diluent has been added to the monopersulfate drying may be accomplished in a variety of ways. The prior art vacuum drying is satisfactory if sufficient time can be allotted thereto. In this procedure the calculated percentage of diluent is added to the neutralized monopersulfate solution, the pressure reduced on the latter and the solution heated until evaporation to dryness is accomplished. The product is a dry crust which may readily be ground to a free-flowing powder.

In an alternative and preferred drying procedure the diluent is added to the neutralized solution and the solution fed into a spray drier. A Bowen laboratory spray drier can be used for this purpose at an inlet temperature of about 650° F. and an outlet temperature of about 160° F. Ambient pressure is employed. In the drier the material is fed onto a rapidly moving disk and water rapidly evaporated therefrom. A dry, free-flowing powder is thus obtained directly with maximum recovery of active oxygen. About 89% of active oxygen is near the maximum that can be recovered by the older vacuum process. Around 95-96% can easily be obtained by spray drying.

The invention can be understood in more detail from the examples which follow. Unless otherwise noted, the percentages given are by weight. Examples 1-4 show the formation of unsatisfactory products and are included as controls.

Example 1

This example is of interest as showing an unsatisfactory product which contains a high percentage of active oxygen.

A solution containing around 60% of monopersulfuric acid and 25% of sulfuric acid was neutralized to pH 3 with powdered sodium carbonate at 0° C. A small amount of water was added to keep the slurry mobile. Glauber's salt, $Na_2SO_4 \cdot 10H_2O$, precipitated under the conditions employed and was removed by filtration. The filtrate was then evaporated to some extent and additional sodium sulfate frozen out. This process was repeated. The final filtrate was evaporated to dryness in 10 minutes at 4 mm. of mercury pressure and 110° C. The product contained 8.4% of active oxygen but was tacky and hygroscopic and could not be ground to a free-flowing powder.

Example 2

A solution containing around 60% monopersulfuric acid and 25% sulfuric acid was neutralized to pH 3 with 80 mesh sodium carbonate at 0° C. A small amount of water was again added to keep the slurry mobile. Glauber's salt, $Na_2SO_4 \cdot 10H_2O$, in the crystalline form

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was removed by filtration. The filtrate was then mixed with 1 g. of sodium sesquicarbonate and dried for six minutes at 112° C. and 6 mm. of mercury pressure. The product, which contained 4.9% of active oxygen, was very gummy and hygroscopic.

Example 3

A solution containing around 60% monopersulfuric acid and 25% sulfuric acid was neutralized to pH 3 with 80 mesh sodium carbonate at 0° C. Water was added to keep the slurry mobile. Glauber's salt, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, precipitated and was removed by filtration. The filtrate was then mixed with 0.5 g. of a mixture of equal parts of sodium sulfate and sodium carbonate and was dried for 12 minutes at 113° C. and 6 mm. of mercury pressure. The product, analyzed to contain 3.6% of active oxygen, was gummy and could not be scraped from the reaction vessel.

Example 4

This example shows that the preferred boron additives cannot satisfactorily be added if the pH of the monopersulfuric acid rises above about 2 or 3.

Fifteen grams of borax were added to 500 g. of an aqueous solution of sodium monopersulfate. The pH of the solution was initially 2.4 but rose to 5.5 during the addition of borax. The change in pH was accompanied by the vigorous evolution of gas. Spray drying of the mixture was begun immediately upon completion of the borax addition. During the 12 minutes required to feed the mixture to the spray drier a total of 18% of the active oxygen was lost. Analyses of samples going to the drier are as follows:

Time in Minutes.....	0	2	5	11
Percent Sodium Monopersulfate.....	17.2	16.5	14.9	14.4

Example 5

This example shows the production of a desirable free-flowing product by one embodiment of the invention.

(a) Ten grams of monopersulfuric acid containing 37% of sulfuric acid was neutralized to pH 3.0 at around -5 to -10° C. with 6.3 g. of 80 mesh sodium carbonate. The slurry was filtered to yield 7.3 g. of filtrate having a pH of 2.0 and 14 g. of filter cake.

The filtrate was mixed with 1 g. of a mixture of equal parts of tetrasodium pyrophosphate, anhydrous borax, sodium carbonate, and sodium tripolyphosphate. The resulting slurry was dried for 15 minutes at 112° C. and 6 mm. of mercury pressure. The solid was pulverized to a free-flowing material which contained 5.1% of active oxygen.

(b) The run of (a) was essentially repeated except that 0.5 g. of the adjuvant mixture was added to 5.9 g. of filtrate. The vacuum dried product, which could readily be ground to a fine, free-flowing powder, contained 6.3% of active oxygen.

Example 6

This example shows a second embodiment of the invention.

Ten grams of monopersulfuric acid containing 37% of sulfuric acid was neutralized to pH 3.0 at -5 to -10° C. with 6.3 g. of 80 mesh sodium carbonate. The slurry was filtered giving 7.2 g. of filtrate having a pH of 1.5. The filtrate was mixed with 1.0 g. of a mixture of equal parts of sodium sesquicarbonate and anhydrous borax and the resulting slurry dried in 10 minutes at 110° C. and 6 mm. of mercury pressure. The product was pulverized to a dry power containing 5.6% active oxygen.

Example 7

This example shows the use of the preferred boron compounds alone.

(a) Two hundred sixty-five grams of monopersulfuric

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acid containing 39% of sulfuric acid was neutralized with 220 g. of sodium carbonate to a pH of about 3. The slurry formed was filtered and 8.0 g. of the filtrate, containing 49% of sodium monopersulfate, was mixed with 1.0 g. of anhydrous borax and was dried for 15 minutes at 115° C. under 6 mm. of mercury pressure. The product was pulverized to a dry powder which contained 6.8% of active oxygen.

(b) Eight grams of aqueous filtrate obtained as described in (a) was mixed with 1.0 g. of a mixture of equal parts of anhydrous borax and boric oxide and dried at 110° C. and 6 mm. of mercury pressure for 18 minutes. The dry powder contained 6.7 of active oxygen.

Example 8

This example shows a fourth embodiment of the invention.

Eight grams of aqueous filtrate obtained as described in Example 7 was mixed with 1.0 g. of a mixture of equal parts sodium tripolyphosphate, tetrasodium pyrophosphate and boric oxide. The slurry was dried at 110° C. under 6 mm. of mercury pressure for 18 minutes. The flaky product was ground to a fine powder that contained 7.3% of active oxygen.

Example 9

This example shows the spray-drying of a sample of monopersulfate containing boron compounds alone.

(a) A mixture containing 60% of monopersulfuric acid and 23% of sulfuric acid was neutralized to pH 2.5 with 50% potassium carbonate solution. Solids were filtered from the slurry to give a 20% solution of potassium monopersulfate. Solid boric acid was then added to a concentration of 1%. The resultant mixture was spray-dried at ambient pressure and 324° C. to give a free-flowing powder containing 7.2% active oxygen.

Storage of this powder in a vented bottle at room temperature for four weeks produced no caking. Similar preparations containing no boric acid caked badly and could not be poured from the bottle after standing for one day at room temperature in a bottle.

(b) Monopersulfuric acid containing 40% of sulfuric acid was neutralized to pH 3.0 with aqueous sodium carbonate. The slurry was filtered and the filtrate diluted until the concentration of sodium monopersulfate amounted to 15.1%. Sodium sulfate was added to the solution to give a total concentration of 11.5% sodium sulfate. Borax and boric acid were added to the respective concentrations of 2.9% and 1.5%. This mixture was spray-dried at ambient pressure and an inlet temperature of 323° C., to give a free-flowing powder containing 5.1% of active oxygen.

Example 10

This example shows the spray-drying of potassium monopersulfate containing a borate.

A mixture containing 59% of monopersulfuric acid and 24% of sulfuric acid was neutralized to pH 0.8 with 50% potassium carbonate solution. Anhydrous sodium borate was added to a concentration of 3%. The pH of the mixture was then adjusted to 2 by means of further additions of potassium carbonate solution. The slurry was filtered and spray-dried as in Example 9. No caking of the dried sample occurred during storage for four weeks in a vented bottle at room temperature. The active oxygen content of the powder was 7.0%.

Having described our invention, we claim:

1. In a method for producing a dry, free-flowing monopersulfate product, the steps of adding to an aqueous solution of an alkali metal monopersulfate at least 1% by weight, based upon the weight of the solution, of a boron compound of the group consisting of boric oxide, boric acid, borax and sodium perborate, said solution having a pH not exceeding 3 before, during and after the addition thereto of said boron compound, and drying the resulting solution.

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2. The method of claim 1 in which there is added along with the boron compound a compound of the group consisting of carbonates, sesquicarbonates, phosphates, sulfates and silicates of the alkali metals and mixtures thereof.

3. The method of producing a dry, free-flowing monopersulfate product comprising forming an aqueous solution of a compound of the group consisting of sodium and potassium monopersulfates, adding to said solution 1 to 12% by weight, based upon the weight of said solution, of a boron compound of the group consisting of boric oxide, boric acid, borax and sodium perborate, said solution having a pH not exceeding 3 before, during and after the addition of said boron compound, drying the resulting solution and comminuting the solid obtained thereby.

4. The method of claim 3 in which there is added to the solution, in addition to the boron compound, a compound of the group consisting of alkali metal carbonates, sesquicarbonates, phosphates, sulfates and silicates of the alkali metals and mixtures thereof.

5. The method of producing a dry, free-flowing powder comprising a major proportion of an alkali metal monopersulfate which comprises neutralizing in solution monopersulfuric acid to a pH not greater than about 3 with a member of the group consisting of alkali metal carbonates and hydroxides, adding to the solution about 1-12% by weight thereof of a boron compound, said addition being made without increasing the pH of said solution to a value exceeding 3, and subsequently drying said solution and obtaining said powder therefrom.

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6. The method of claim 5 in which the solution is dried in a vacuum to produce a solid crust and the crust is comminuted to free-flowing powder.

7. A comminuted composition of matter which yields an acidic solution when dissolved in water, said composition consisting essentially of at least 5% by weight of active oxygen comprising sufficient of a member of the first group consisting of sodium and potassium monopersulfates to supply said active oxygen admixed with a sufficient quantity of a member of the second group consisting of boric oxide, boric acid, borax and sodium perborate to impart free-flowing characteristics thereto.

8. A composition according to claim 7 which also contains at least one member of the group consisting of the carbonates, sesquicarbonates, phosphates, sulfates and silicates of the alkali metals.

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