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PROCESS FOR THE PRODUCTION OF ALKALI METAL POLYPHOSPHATES

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The present invention relates to a process for the production of alkali metal polyphosphates having a bulk weight lower than that of polyphosphates produced by a known process.

It is known that alkali metal polyphosphates, such as sodium pyrophosphates or sodium triphosphates, are prepared by mixing orthophosphates in an appropriate proportion and treating the resulting mixture by applying heat. Depending on the reaction conditions applied in each particular case, products with considerably varying bulk weights are obtained. Accordingly, processes have been developed to enable the production of polyphosphates having a low bulk weight. Thus, for example, it has been suggested that the aqueous orthophosphate solution necessary for the production of polyphosphates be first spray-dried and then calcined to yield a voluminous pulverulent or granular product, whose bulk weight naturally depends severely on how the spraying operation and calcination have been performed.

It has been found however that the bulk weights obtainable in the manner described above are not sufficiently low to be satisfactory in certain application fields of the polyphosphates. It has also been found that it is extremely difficult to produce a phosphate with a low bulk weight, especially in the case where the phosphate must be completely dehydrated. A sodium triphosphate containing residues of acid pyrophosphates or orthophosphates, for example, has a lower bulk weight than completely dehydrated $Na_5P_3O_{10}$ of 98–100% strength produced in the same manner.

Now we have found that alkali metal polyphosphates having a bulk weight of between about 250 grams/liter and about 600 grams/liter are obtained by heating at least one mono or di-alkali metal orthophosphate to a temperature of between about 200° C. and about 500° C. in the presence of about 0.03 weight percent to about 5 weight percent of an alkali metal salt derived from acids of phosphorus in which the phosphorus has an electropositive valency of less than five. The percentage figures given for these alkali metal salts are calculated upon the quantity of the alkali metal orthophosphate used. It should be noted that the alkali metal polyphosphates produced according to this invention have a bulk weight which is considerably lower than that of a polyphosphate produced by a known process.

In practising the process of this invention there may be used especially sodium orthophosphate and potassium orthophosphate and other alkali metal salts.

As appropriate salts derived from acids of phosphorus in which the phosphorus has an electro-positive valency of less than five, there may be used the alkali metal salts of phosphorous acid or the alkali metal salts of hypophosphorous acid. As alkali metal salt of phosphorous acid it is advisable to use the sodium phosphite and as alkali metal salt of hypophosphorous acid the sodium hypophosphite. The potassium alkali metal salts of this definition, however, are also appropriate salts.

In the process of this invention there may also be used a mixture of alkali metal salts of phosphorous acid and hypophosphorous acid at a ratio of the first to the second component of between about 0% and about 100% or, inversely, between about 100% and about 0%, the first component being represented by the alkali metal salts of phosphorous acid and the second component by the alkali metal salts of hypophosphorous acid.

These salts may be present as already mentioned above in a total amount of between about 0.03 weight percent and about 5 weight percent calculated upon the quantity of alkali metal orthophosphate.

In carrying out the process of this invention on an industrial scale using a mixture of the above type it is advisable that this mixture be composed of sodium phosphite and sodium hypophosphite as alkali metal salts of phosphorous acid or hypophosphorous acid, respectively.

The process of this invention enables for the first time, for example pure sodium triphosphate with a low bulk weight of up to 250 grams/liter to be produced which is used for the production of uniform washing agents not liable to disintegration, for example, by mixing the above substance in a dry state with a spray-dried surface-active substance, for example sulfonates having a similar bulk weight.

According to another feature of this invention, the alkali metal orthophosphates may be used in solution and, more especially in an aqueous solution, i.e., in a saturated or dilute aqueous solution. For economical reasons, however, it is advisable to use a fairly concentrated solution.

The addition of alkali metal salts of phosphorous acid and/or hypophosphorous acid has proved especially effective, if the polyphosphates are prepared in a device which gives rise to the formation of a less heavy substance, i.e. by spraying an aqueous solution of the starting material in the hot at a temperature between about 200° C. and about 500° C. and then calcining at that temperature the resulting solid and only incompletely anhydrous substance.

The spraying operation yields a solid material with a maximum water content of about 20% which is calcined and then completely anhydrous.

Especially suitable additions as already described above are alkali metal phosphites or alkali metal hypophosphites, for they are most readily accessible. The same effect may, however, be brought about using alkali metal salts of an acid other than phosphorous acid or hypophosphorous acid, in which the phosphorus has an electropositive valency of less than five; in other words, in addition to the aforesaid alkali metal salts of phosphorous acid and hypophosphorous acid there may also be used the alkali metal salts of pyrophosphorous acid or diphosphorous acid. These latter acids appear, for example in the hydrolysates of phosphorus trihalides in addition to phosphorous acid and it has been found that all reducing phosphorus compounds present in such hydrolysates play an essential part in bringing about a bulk weight reducing effect.

A suitable addition may be prepared in simple manner from a technical and economical point of view by reacting yellow phosphorus with a boiling solution of sodium hydroxide. The concentration of this solution may vary within wide limits, a solution of about 30% strength being, however, preferred. During this reaction, sodium phosphite and sodium hypophosphite are formed side by side in the solution. In addition, gaseous phosphorus hydride is evolved. The reaction proceeds in an especially favorable manner when the sodium hydroxide solution is used in an excess quantity.

In order to bring about a complete reaction of the phosphorus with the sodium hydroxide solution, it is necessary to use the latter component in an excess quantity of at least 20%. The higher the excess quantity, the more

rapidly proceeds the reaction. The sodium hydroxide solution in excess may be neutralized with the use of phosphoric acid after the reaction is complete.

The mixture of sodium phosphite and sodium hypophosphite optionally in admixture with the sodium phosphate obtained by neutralizing the sodium hydroxide solution in excess with phosphoric acid, is added in a desired proportion to the ortho-phosphates which serve to yield the polyphosphates. It is understood that a mixture of salts of reducing acids of phosphorus naturally has the same effect as a uniform addition, such as phosphite or hypophosphite.

All these compounds which serve to reduce the bulk weight according to this invention are heated together with the acid orthophosphates to form salts of pentavalent phosphorus. The polyphosphate obtained as end product is free from reducing ingredients.

The process of this invention offers the particular advantage of enabling the same industrial apparatus and the same operating procedures to be applied in the production of polyphosphates whose bulk weights may vary within wide limits depending on the quantity of the substances added.

It has been found that already the addition of the above substances in an amount of 0.03% to the orthophosphates may involve a minor reducing effect on the bulk weight. Larger amounts than 0.03% reduce the bulk weight further; an amount exceeding 5% involves however no further noteworthy effect.

The following examples serve to illustrate the invention but they are not intended to limit it thereto. These examples clearly evidence the advance achieved in the art by this new process especially with reference to the conventional working method.

Example 1

For the production of sodium trimetaphosphate 500 grams of pulverulent dry and mono sodium orthophosphate are slowly heated to 480° C. in a rotary drum and kept at that temperature for 7 hours. The reaction yields 420 grams of a loose agglomerate which consists of 95% of sodium trimetaphosphate and can be comminuted to give a powder with a bulk weight of about 570 grams/liter.

When the same reaction is carried out according to this invention, i.e. with the addition of 1% of sodium phosphite, the bulk weight is considerably reduced to about 460 grams/liter. The yield is about 99%.

Example 2

To produce sodium triphosphate, a solution is prepared at 80–100° C. which contains per liter of water 600 grams of Na_2HPO_4 and 253.5 grams of NaH_2PO_4. The solution so prepared is spray-dried at a rate of 200 liters/hour; the dry powder is then calcined for 10 minutes at 350° C. in a rotary drum. Sodium triphosphate is obtained in a yield of 150–160 kg./hour with a relatively high bulk weight of 650–700 grams/liter. The yield is 99–100%.

The reaction conditions are the same with the exception, however, that per liter of the above orthophosphate solution 6 grams of sodium phosphite ($Na_2HPO_3.5H_2O$) are added in accordance with this invention. The addition corresponds to about 0.7%. Triphosphate is obtained in a quantity of 150–160 kg./hour with a bulk weight of only 450–500 grams/liter. The triphosphate is free from reducing agents and obtained in a yield of 99–100%.

Example 3

A solution of Na_2HPO_4 saturated at 80° C. which contains per liter 690 grams of di-sodium phosphate is dehydrated at 350–400° C. at a rate of 145 liters/hour by hot-spraying in a spray-tower to produce sodium pyrophosphate in the form of hollow balls. Spraying is effected using a pressure nozzle at a pressure of liquid of 6 atmospheres (gauge). The yield per hour is 94 kg. of hollow balls of sodium pyrophosphate having a purity of 98–100%. The grain size of the individual particles is about 0.2–0.5 mm. The yield is 100% and the pyrophosphate obtained has a bulk weight of about 530 grams/liter.

While the conditions are otherwise identical, the di-sodium phosphate solution is mixed with 0.5% of sodium phosphite (Na_2HPO_3) according to this invention; the pyrophosphate is obtained with the same degree of purity and yield.

The reduced bulk weight is only 400 grams/liter. If, however, 0.5% of sodium hypophosphite

($NaH_2PO_2.H_2O$)

is used instead of sodium phosphite, the sodium pyrophosphate is obtained in the form of hollow balls with the same degree of purity and in the same yield. The reduced bulk weight is in this case only 380 grams/liter.

Example 4

For the production of sodium tripolyphosphate a solution is prepared at 80–100° C. which contains per liter 600 grams of Na_2HPO_4 and 253.5 grams of NaH_2PO_4. This solution is sprayed in the hot at 400–450° C. at a rate of about 300 liters/hour to be converted into sodium tripolyphosphate which is obtained in a yield of about 230 kg./hour with a bulk weight of 600–620 grams/liter. The yield is 99–100%.

While the conditions are identical, 0.25 gram of Na_2HPO_3 is added per liter of the orthophosphate solution; the addition corresponds to 0.03%. The tripolyphosphate obtained has a bulk weight of 580–600 grams/liter; in spite of this minor addition the bulk weight is lower than that of a tripolyphosphate produced without such addition.

While the conditions are identical, the starting solution of orthophosphates is mixed per liter with 42.7 grams of Na_2HPO_3 corresponding to an addition of 5%. The tripolyphosphate obtained has a bulk weight of only 250–270 grams/liter.

While the conditions are the same, the starting orthophosphate solution is mixed per liter with 50.0 grams of Na_2HPO_3 corresponding to an addition of about 6%. The tripolyphosphate obtained again has a bulk weight of 250–270 grams/liter.

The above example clearly evidences that already a very small addition of Na_2HPO_3 reduces the bulk weight, while the upper limit of such additions is about 5% outside which no further reduction of the bulk weight which is as low as 250 grams/liter can be achieved, so that an addition of more than 5% of substances reducing the bulk weight is useless.

Example 5

A solution of sodium phosphite (Na_2HPO_3) and sodium hypophosphite suitable as addition may be prepared as follows:

3 kg. of yellow phosphors are introduced into 17.5 kg. of a boiling 30% sodium hydroxide solution. A vigorous reaction sets in with evolution of phosphorus hydride which is calcined with air to form phosphorus pentoxide; the phosphorus pentoxide is then introduced into an apparatus suitable for use in the production of ortho-phosphoric acid.

The water evaporating upon boiling is replaced. The reaction is complete within about 90 minutes. In the aqueous phase there are obtained 7240 grams of sodium phosphite in addition to 795 grams of sodium hypophosphite and an excess quantity of sodium hydroxide solution. The reaction product obtained in the form of an aqueous solution has about the following composition after the sodium hydroxide solution present in excess has been neutralized with about 430 grams of a 85% phosphoric acid: 7240 grams of Na_2HPO_3, 795 grams of NaH_2PO_2, 510 grams of Na_2HPO_4 and 10,055 grams of H_2O. The solution so obtained is then added under the conditions described in Example 2 to 2400 liters of an

orthophosphate solution and the whole is processed as described in that example. The sodium triphosphate is obtained in the same yield and has a reduced bulk weight of only 450–500 grams/liter.

We claim:

1. A process for the production of alkali metal polyphosphates having a bulk weight of between about 250 grams and about 600 grams per liter, which comprises heating at least one alkali metal orthophosphate selected from the group consisting of mono-alkali metal orthophosphate and di-alkali metal orthophosphate to temperatures between about 200° C. and about 500° C. in the presence of about 0.03 to about 5 percent of an alkali metal salt of at least one acid of phosphorus selected from the group consisting of phosphorous acid and hypophosphorous acid, the percentage amount of alkali metal salt being calculated upon the quantity of alkali metal orthophosphate present, and recovering alkali metal polyphosphates having a bulk weight of between 250 and about 600 grams per liter.

2. The process of claim 1 wherein sodium orthophosphate and a sodium salt of at least one acid of phosphorus selected from the group consisting of phosphorous acid and hypophosphorous acid are heated.

3. The process of claim 1 wherein potassium orthophosphate and a potassium salt of at least one acid of phosphorus selected from the group consisting of phosphorous acid and hypophosphorous acid are heated.

4. The process of claim 1 wherein an aqueous solution of at least one alkali metal orthophosphate selected from the group consisting of mono-alkali metal orthophosphate and di-alkali metal orthophosphate and about 0.03 to about 5 percent of a dissolved alkali metal salt of at least one acid of phosphorus selected from the group consisting of phosphorous acid and hypophosphorous acid are heated.

5. The process of claim 4 wherein the aqueous solution is atomized at a temperature between about 200° C. and about 500° C. and the resulting solid product is calcined at a temperature between about 200° C. and about 500° C.

6. A process for the production of alkali metal polyphosphates having a bulk weight of between about 250 grams/liter and about 600 grams/liter which comprises heating at least one alkali metal orthophosphate selected from the group consisting of mono-alkali metal orthophosphate and di-alkali metal orthophosphate to a temperature of between about 200° C. and about 500° C. in the presence of about 0.03 to about 5 percent of sodium phosphite, the amount of alkali metal salt being calculated upon the quantity of the alkali metal orthophosphate present, and recovering alkali metal polyphosphates having a bulk weight of between 250–600 grams/liter.

7. A process for the production of alkali metal polyphosphates having a bulk weight of between about 250 grams/liter and about 600 grams/liter which comprises heating at least one alkali metal orthophosphate selected from the group consisting of mono-alkali metal orthophosphate and di-alkali metal orthophosphate to a temperature between about 200° C. and about 500° C. in the presence of about 0.03 to about 5 percent of sodium hypophosphite, the percentage amount of alkali metal salt being calculated upon the quantity of the alkali metal orthophosphate present, and recovering alkali metal polyphosphates having a bulk weight of between about 250–600 grams/liter.

8. A process for the production of alkali metal polyphosphates having a bulk weight of between about 250 grams/liter and about 600 grams/liter which comprises heating at least one alkali metal orthophosphate selected from the group consisting of mono-alkali metal orthophosphate and di-alkali metal orthophosphate to a temperature of between about 200° C. and about 500° C. in the presence of about 0.03 to about 5 percent of a mixture of sodium phosphite and sodium hypophosphite, the percentage amount of the mixture of alkali metal salts being calculated upon the quantity of alkali metal orthophosphate present, and recovering alkali metal polyphosphates having a bulk weight of between about 250–600 grams/liter.

9. A process for the production of alkali metal polyphosphates having a bulk weight of between 380 grams/liter and about 400 grams/liter which comprises heating at least one alkali metal orthophosphate selected from the group consisting of mono-alkali metal orthophosphate and di-alkali metal orthophosphate to a temperature between about 200° C. and about 500° C. in the presence of about 0.5 percent of an alkali metal salt of at least one acid of phosphorus selected from the group consisting of phosphorous acid and hypophosphorous acid, the percentage amount of alkali metal salt being calculated upon the quantity of alkali metal orthophosphate present, and recovering alkali metal polyphosphates having a bulk weight between 380 and 400 grams/liter.

10. A process for the production of alkali metal polyphosphates having a bulk weight of between about 380 grams/liter and about 400 grams/liter which comprises heating a solution containing at least one alkali metal orthophosphate selected from the group consisting of mono-alkali metal orthophosphate and di-alkali metal orthophosphate to a temperature between about 200° C. and about 500° C. in the presence of about 0.5 percent of a dissolved alkali metal salt of at least one acid of phosphorus selected from the group consisting of phosphorous acid and hypophosphorous acid, the percentage amount of alkali metal salt being calculated upon the quantity of the alkali metal orthophosphate present, atomizing resulting solution at a temperature of between about 200° C. and about 500° C., and calcining resulting solid material at a temperature of about 200° C. to about 500° C., and recovering alkali metal polyphosphates having a bulk weight of between about 280–400 grams/liter.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 47, for "280-400" read -- 380-400 --.

Signed and sealed this 14th day of November 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

USCOMM-DC