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PRODUCTION OF FINELY DIVIDED SODIUM TRIPOLYPHOSPHATE

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## ABSTRACT OF THE DISCLOSURE

A process for producing a finely divided sodium tripolyphosphate hexahydrate comprising initially contacting an anhydrous sodium tripolyphosphate material with an aqueous solution containing dissolved therein at least about 90% by weight of the amount of sodium tripolyphosphate required to saturate said aqueous solution and at least about 90% of the weight of the theoretical amount of water required to hydrate said anhydrous sodium tripolyphosphate and allowing the said aqueous solution to intimately contact the anhydrous sodium tripolyphosphate for an amount of time sufficient to hydrate at least about 90% by weight of said anhydrous sodium tripolyphosphate.


This invention relates to the manufacture of sodium tripolyphosphate hexahydrate. More particularly, it relates to the production of extremely finely divided sodium tripolyphosphate hexahydrate.

Sodium tripolyphosphate has heretofore been produced by a variety of processes known to those skilled in the art. These processes generally include a crushing or grinding step. Although the mechanical size reduction of sodium tripolyphosphate using conventional grinders, crushers and the like (in conjunction with conventional screening equipment) provides a product which is acceptable for some uses, such as a builder for dry detergents, these methods of conventional size reduction cannot be used to produce an extremely finely divided sodium tripolyphosphate which is generally required for other uses, such as a builder in some liquid detergents. For example, most conventional means of size reduction equipment cannot be used to produce particles having an average particle size smaller than about 3 microns while in the manufacture of heavy duty liquid detergents, which contain sodium tripolyphosphate dispersed (rather than dissolved) therein and a surface active agent, it is generally preferred to utilize particles of sodium tripolyphosphate smaller than about 5 microns and having an average particle size of less than about 2.0 microns.

It is believed, therefore, that a process which would enable the production of extremely finely divided particles of sodium tripolyphosphate hexahydrate useful in the preparation of heavy duty liquid detergent slurries containing the sodium tripolyphosphate particles dispersed therein would be a significant advancement in the art.

It is therefore an object of this invention to provide a process for producing such extremely finely divided sodium tripolyphosphate hexahydrate.

It is another object of this invention to provide a process for producing an extremely finely divided sodium tripolyphosphate hexahydrate having an average particle size of less than two microns.

It is a further object of this invention to provide an extremely finely divided sodium tripolyphosphate hexahydrate suitable for use in heavy duty liquid detergent slurries.

It is still another object of this invention to provide an extremely finely divided sodium tripolyphosphate hexahydrate having an average particle size of less than two microns.

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Other objects will become readily apparent to one skilled in the art from the detailed description following.

It has been discovered that an extremely finely divided sodium tripolyphosphate hexahydrate can be produced by initially contacting anhydrous sodium tripolyphosphate with a very concentrated aqueous solution of sodium tripolyphosphate and allowing the anhydrous sodium tripolyphosphate to become hydrated. The present invention is surprising because anhydrous sodium tripolyphosphate is ordinarily expected to lump when contacted with water. The term "very concentrated aqueous solution of sodium tripolyphosphate" as used herein means an aqueous solution containing at least 90% by weight of the amount of sodium tripolyphosphate theoretically required to saturate the aqueous solution with sodium tripolyphosphate.

It has also been discovered that crystals formed by the beforementioned process have distinguishing features. The crystals, as identified by an electron microscope, are twinned plates with a ratio of width to length greater than about 1:1.1 and generally in the ratio of from about 1:1.3 to 1:6. The crystals generally have a thickness of at most less than 50% of their width. In accordance with the processes of the present invention, an extremely finely divided sodium tripolyphosphate hexahydrate product can be produced having the ability to remain suspended in aqueous media for prolonged periods of time.

In practicing this invention the sodium tripolyphosphate, that it is desired to convert to the extremely finely divided sodium tripolyphosphate product, should generally contain relatively large amounts of anhydrous sodium tripolyphosphate, e.g. greater than about 70% by weight with amounts greater than about 85% by weight being especially preferred. Furthermore, it is preferred to use an anhydrous sodium tripolyphosphate which has a relatively high content of Form I sodium tripolyphosphate. Anhydrous sodium tripolyphosphate is known to exist in two crystalline forms, commonly designated as Form I and Form II. Form I is also designated as the high temperature form and Form II is referred to as the low temperature form. These two crystalline forms are fully discussed in Van Wazer, J. Phosphorous and Its Compounds, volume I, Interscience Publishers, Inc., New York (1958). Form I sodium tripolyphosphate is also known as the "lumping" variety as disclosed in Van Wazer, supra, pp. 651–652. One industry accepted test for analyzing the "form" content of sodium tripolyphosphate is the X-ray diffraction test. "Relatively high" content of Form I as used herein means sodium tripolyphosphate which has a Form I content of at least about 26%. While anhydrous sodium tripolyphosphate with a Form I content as low as about 20% or even lower can be used in the practice of this invention, it is preferred to use anhydrous sodium tripolyphosphate which has a slightly higher Form I content of about 26% or higher to thereby obtain a relatively large percentage of the desirable extremely finely divided sodium tripolyphosphate hexahydrate product having desirable qualities such as preferred crystal sizes, high purity and resistance to agglomeration. Still further preferred sodium tripolyphosphate raw materials are those that contain about 80 weight percent of their sodium tripolyphosphate in the high temperature (Form I) crystalline form.

Although it is preferred that at least about 90% by weight of the anhydrous sodium tripolyphosphate pass through a U.S. Standard 100 mesh screen and about 100% pass through a U.S. Standard 40 mesh screen, satisfactory results can be achieved with larger particle sizes. For example, anhydrous sodium tripolyphosphate having at least 60% by weight passing through a U.S. Standard 60 mesh screen and 100% by weight passing through a U.S. Standard 30 mesh screen can be satisfactorily converted by this invention into extremely finely divided sodium tripolyphosphate hexahydrate. Materials having even a larger particle size can be used if desired.

Although the aqueous solution used to initially contact the anhydrous sodium tripolyphosphate can consist essentially of water and at least 90% by weight of the theoretical amount of sodium tripolyphosphate required to saturate said water with sodium tripolyphosphate, it is preferred to use an aqueous solution that is approximately saturated with sodium tripolyphosphate, that is a solution which contains from about 95% to about 100% by weight of the sodium tripolyphosphate required to saturate it at 25° C. In addition an aqueous solution supersaturated with sodium tripolyphosphate can be used and, if desired and in addition, those containing crystals of sodium tripolyphosphate hexahydrate can also be advantageously used. In addition certain soluble inorganic sodium salts, such as sodium chloride can be used in the aqueous solution if it is desired to depress the solubility of sodium tripolyphosphate.

In the practice of this invention the aqueous solution should generally contain at least the amount of water theoretically required to hydrate at least about 90 weight percent of the anhydrous sodium tripolyphosphate in the material that is initially contacted with the aqueous solution. It is preferred, however, in the practice of this invention to use an aqueous solution containing enough excess water so that the slurry of sodium tripolyphosphate hexahydrate and excess aqueous solution that is formed in the present invention can be handled by the conventional agitators, pumps, and separation equipment. Therefore, for practical reasons it is generally preferred to use an aqueous solution which contains at least about 110% by weight of the theoretical amount of water required to hydrate the anhydrous sodium tripolyphosphate to thereby form a slurry. For the before-mentioned reasons it is still further preferred to use an aqueous solution which contains enough water so that the molar ratio of water to anhydrous sodium tripolyphosphate is from about 10:1 to about 100:1 with ratios of from about 15:1 to 30:1 being especially preferred.

It is essential for the successful practice of this invention that to convert anhydrous sodium tripolyphosphate to extremely finely divided sodium tripolyphosphate hexahydrate that said anhydrous sodium tripolyphosphate be initially contacted with a very concentrated aqueous solution as previously described. Initial contact as used herein means contact with an aqueous solution of the foregoing description before contact with significant amounts of any other aqueous solution.

Although in the practice of this invention it is necessary for the aqueous solution to contact the anhydrous sodium tripolyphosphate for a measurable time to enable some hydration to occur, generally the time of contact is not critical. The time required for the hydration to occur will be dependent upon several factors such as temperature, the amount of Form I sodium tripolyphosphate present, the amount and the concentration of aqueous solution used, the amount of recycled sodium tripolyphosphate suspended in the aqueous solution, and size of the particles of anhydrous sodium tripolyphosphate. Complete hydration of sodium tripolyphosphate at temperatures below 100° C. can be completed rapidly, for example in about 1 minute, because lump formation, which conventionally prevents complete hydration of material in the center of a lump, is minimized by the use of concentrated aqueous solutions in accordance with the processes of this invention. Inefficient mixing of the tripolyphosphate with the solution, however, will result in somewhat longer times for hydration, though usually less than about 2 hours; but in cases of highly inefficient mixing may result in still longer times, that is, up to about 4 hours or even longer, such as about 24 hours, in some cases where relatively small amounts of water and essentially no agitation are used. An effective method to determine if hydration is complete (which will not be influenced by the buffering action of any contaminants which may be present) is to measure the temperature rise of slurry produced. Since the heat liberated in the hydration of anhydrous sodium tripolyphosphate is known, it is a relatively simple matter to calculate the theoretical temperature rise for a given slurry.

While the practice of this invention can be conducted at temperatures as high as 100° C. or even higher and at any temperature above the freezing point of the saturated solutions described above, it is preferred to practice the invention at temperatures below about 70° C. because of the tendency of sodium tripolyphosphate to degrade to other phosphate with higher temperatures, particularly at the pH levels which will normally be present during the practice of this invention, that is, from about 8.5 to about 10.5. However, lower pH (to about 6.5) and higher pH values up to about 12.5 or even higher may be used in some instances. The temperature range of from about 20° C. to about 70° C. is especially preferred to give more desirable hydration rates and very low degradation rates.

Because the hydration rate, among other things, is beneficially influenced by agitation, it is preferred in the practice of this invention to use agitation to aid the initial contacting of the anhydrous sodium tripolyphosphate with the "very concentrated" aqueous solution. Therefore, as previously stated, it is preferred to use enough water so that the ratio of water to anhydrous sodium tripolyphosphate is from about 15:1 to about 30:1 to thereby enable conventional agitators to be used.

Conventional equipment can be used in the practice of this invention. For example, a suitable batch process is to charge a tank equipped with a conventional agitator with one of the very concentrated aqueous sodium tripolyphosphate solutions of the present invention. Enough anhydrous sodium tripolyphosphate is charged to the tank to produce a slurry of sodium tripolyphosphate hexahydrate which can be agitated and pumped satisfactorily. After agitating for a sufficient time to enable the anhydrous sodium tripolyphosphate to be converted to the hexahydrate form, the extremely finely divided sodium tripolyphosphate hexahydrate is separated from the aqueous solution by any convenient conventional solid-liquid separation means. The aqueous solution separated from the solids can then be supplemented with fresh very concentrated aqueous solution and reused in a subsequent batch. The heat liberated from the hydration of anhydrous sodium tripolyphosphate is about 16 to about 19 kcal. per gram mol of sodium tripolyphosphate hydrated. The amount of heat liberated varies depending upon the relative amounts of Form I or Form II sodium tripolyphosphate present in the anhydrous sodium tripolyphosphate. Since in the practice of this invention it is preferred to hold the temperature during hydration below about 70° C., it is sometimes desirable to remove the heat liberated during the hydration. If a jacketed tank is used for heat removal whereby the heat is transmitted to a coolant in the jacket, such as water, agitation is preferred for an adequate heat removal rate. Another excellent means of removing heat is by evaporative cooling whereby a conventional means for creating a negative pressure and a stream of air are used thereby enabling the heat that is liberated to be consumed as heat to vaporize part of the water present in the tank. As can be appreciated, if evaporative cooling is used, an adjustment in the water content of the aqueous solution can be made to give a slurry of desired solids concentration if a final product in the form of a slurry is desired. Generally less than 1 pound of water will be evaporated for pound mol of anhydrous sodium tripolyphosphate hydrated. In addition, if desired to produce sodium tripolyphosphate hexahydrate which is free of excess water, conventional evaporative methods, such as rotary driers, spray towers and the like, can be used to effectively remove the excess water.

If in the practice of this invention the starting sodium tripolyphosphate raw material is a relatively impure anhydrous sodium tripolyphosphate containing an inorganic heavy metal salt impurity selected from the group consisting of inorganic iron salts, inorganic aluminum salts, inorganic iron and aluminum complex salts and mixtures thereof and at least some of the aqueous solution is removed after hydration as a liquid, an additional advantage of at least partial purification of the impure sodium tripolyphosphate can be achieved. This, however, is the subject matter of a separate patent application; co-pending patent application, Ser. No. 449,289, filed concurrently herewith.

To illustrate the invention, the following examples are presented. All parts, percentages and proportions are by weight unless otherwise indicated.

## EXAMPLE I

One thousand parts of anhydrous sodium tripolyphosphate analyzing 25% Form I, 65% Form II, 8% $Na_4P_2O_7$, 1.5% $NaPO_3$-I and less than 0.5% of other impurities as measured by X-ray diffraction are gradually charged within about 40 minutes into a tank which contains 2,300 parts of an aqueous solution nearly saturated with sodium tripolyphosphate and is equipped with a conventional agitator. Essentially 100% of the anhydrous sodium tripolyphosphate passes through a U.S. Standard 40 mesh screen and about 90% passes through a U.S. Standard 100 mesh screen.

The temperature is maintained at about 60° C. with a water-cooled jacket.

After about 25 minutes a slurry is formed which contains about 40 weight percent of extremely finely divided sodium tripolyphosphate crystals. A sample of the crystals is analyzed by electron miscroscope by substantially following the procedures and recommendations in the preparation of specimens as described in Zworykin, V., G. Morton, E. Ramberg, J. Hillier, and A. Vance, Electron Optics and the Electron Microscope, Section 8.1, New York: John Wiley and Sons, 1945. The crystals, as determined by the electron microscope, are twinned plates with a ratio of width to length of from about 1:1.3 to 1:6 and have a thickness appreciably smaller than the width, generally less than about 50% of the width. About 80% of the crystals have a length of less than about 5 microns and a width less than about 3 microns and a thickness less than about 50% of their width. Although the exact width and length of the smallest particles cannot be determined to a high degree of accuracy, the small particles are in the submicron range but are above the colloidal size, e.g., about 0.01 micron, as judged from the electron microscope photographs and from the behavior of the slurries containing them. These crystals are special objects of this invention and in the examples following the particles produced have the same general shape with only the size of crystals varying but still within the general dimensions given in this example.

The resulting slurry is pumped to a conventional solid bowl centrifuge to remove the extremely finely divided particles from the aqueous phase. The solid sodium tripolyphosphate hexahydrate is dried in a vacuum drier and can be used as a builder in form of a suspension in a nonaqueous liquid detergent.

## EXAMPLE II

Five hundred parts of anhydrous sodium tripolyphosphate with an analysis similar to the anhydrous sodium tripolyphosphate used in Example I is mixed with 1,110 parts of an aqueous solution containing about 12.5% of sodium tripolyphosphate. Essentially 100% of the anhydrous sodium tripolyphosphate passes through a U.S. Standard 30 mesh screen and about 60% passes through a U.S. Standard 60 mesh screen.

The temperature of the aqueous solution before the addition of the sodium tripolyphosphate is about 50° C. The temperature will rise after the addition. When the temperature reaches about 58° C. and remains constant for about 13 minutes, the hydration is complete.

A slurry of finely divided sodium tripolyphosphate hexahydrate is formed which contains about 40% by weight of the sodium tripolyphosphate hexahydrate crystals. The particle size of the sodium tripolyphosphate hexahydrate is measured by the sedimentation technique. The average size is determined to be about 1.5 microns with less than 5% of the particles having a size larger than about 5 microns. The resulting solids can be separated using conventional techniques and used in a nonaqueous liquid detergent or may be used directly in a slurry type detergent by adding to the slurry enough desirable detersive surfactants to produce a slurry containing about 20% by weight of the detersive surfactant.

## EXAMPLE III

One thousand parts of anhydrous sodium tripolyphosphate having 3% Form I and 60% Form II and 9% other sodium phosphate salts and less than 1% of minor impurities are added to about 400 parts of an aqueous solution saturated with sodium tripolyphosphate. Essentially 100% of the anhydrous sodium tripolyphosphate passes through a U.S. 40 mesh screen and about 90% passes through a U.S. 100 mesh screen.

The temperature of saturated aqueous solution is about 40° C. Complete hydration occurs in less than 2 hours. The finely divided sodium tripolyphosphate has an average particle size of about 1.0 micron and about 98% smaller than about 3.0 microns. The crystals are found to be twinned plates with a ratio of width to length from about 1:1.3 to about 1:6. About 80% of the crystals have a length of less than about 2 microns and a width of less than about 0.5 micron. The particles are noncolloidal and samples of the material produced remain uniformly suspended in the aqueous medium for about 3 days without settling. The remaining material can be vacuum dried and be used in form of a suspension as a builder in a nonaqueous liquid detergent.

## EXAMPLE IV

To five hundred parts of the aqueous solution containing 6.5% sodium tripolyphosphate and about 1% NaCl, about 1,000 parts of anhydrous Form I sodium tripolyphosphate analyzing by X-ray analysis 88.6% Form I, 8.7 Form II, 1.8% $Na_4P_2O_7$ and 0.9% $NaPO_3$-I were added. Essentially 100% of the sodium tripolyphosphate will pass through a U.S. Standard 100 mesh screen. The average particle size of the finely divided sodium tripolyphosphate hexahydrate is determined to be about 0.6 micron with a maximum particle size of about 2 microns and has the same general rectangular twinned plate shape with only the size of crystals being slightly smaller.

## EXAMPLE V

One thousand parts of anhydrous sodium tripolyphosphate, essentially Form I variety, are charged into a tank equipped with a conventional agitator that contains 2,000 parts of a supersaturated solution which has contained therein about 1% by weight excess sodium tripolyphosphate. Essentially 100% of the anhydrous sodium tripolyphosphate passes through a U.S. Standard 40 mesh screen and about 90% through a U.S. Standard 100 mesh screen. During the hydration period the mixture is controlled at about 60° C. by using evaporative cooling and by passing a stream of room temperature air through the tank. The heat liberated vaporizes part of the water present. About one pound of water is evaporated per pound mol of anhydrous sodium tripolyphosphate hydrated. The slurry of finely divided sodium tripolyphosphate hexahydrate is pumped to a conventional solid bowl centrifuge to remove the extremely finely divided particles from the aqueous phase. The particle size of sodium tripolyphosphate hexahydrate crystal is essentially below about 1.0 micron and is subsequently dried in a conventional air rotary dryer and incorporated as a builder in the heavy duty detergent.

What is claimed is:

**1.** A process for producing extremely finely divided sodium tripolyphosphate hexahydrate, having at least about 80% of the particles smaller than about 5 microns, comprising initially contacting an anhydrous sodium tripolyphosphate material with an aqueous solution containing dissolved therein at least about 90% by weight of the amount of sodium tripolyphosphate required to saturate said aqueous solution; said aqueous solution containing at least about 90% by weight of the theoretical amount of water required to hydrate said anhydrous sodium tripolyphosphate; and allowing said aqueous solution to intimately contact said anhydrous sodium tripolyphosphate material for an amount of time sufficient to hydrate at least about 90% by weight of said anhydrous sodium tripolyphosphate.

**2.** The process of claim **1** wherein said aqueous solution contains at least about 95% by weight of the amount of sodium tripolyphosphate required to saturate said aqueous solution.

**3.** A process for producing extremely finely divided sodium tripolyphosphate hexahydrate comprising initially contacting a sodium tripolyphosphate material containing at least about 70% by weight of anhydrous tripolyphosphate with an aqueous solution containing dissolved therein at least about 90% by weight of the amount of sodium tripolyphosphate required to saturate said aqueous solution and said aqueous solution containing at least about 110% by weight of the theoretical amount of water required to hydrate said anhydrous sodium tripolyphosphate; allowing said aqueous solution to intimately contact said sodium tripolyphosphate material for an amount of time sufficient to hydrate said anhydrous sodium tripolyphosphate; to thereby produce a slurry containing finely divided sodium tripolyphoshate hexahydrate crystals in amounts up to about 90% by weight of said slurry and at least about 80% by weight of said particles are smaller than 5 microns.

**4.** The process of claim **3** wherein the hydration of said anhydrous sodium tripolyphosphate is conducted at a temperature of from about 20° C. to about 70° C.

**5.** The process of claim **4** wherein said aqueous solution contains at least about 95% by weight of the amount of sodium tripolyphosphate required to saturate said aqueous solution.

**6.** The process of claim **4** wherein said anhydrous sodium tripolyphosphate contains at least about 20% by weight of Form I sodium tripolyphosphate.

**7.** A process for producing a slurry containing finely divided sodium tripolyphosphate hexahydrate crystals having a maximum particle size of less than about 5 microns and with an average particle size of less than about 3 microns; comprising initially contacting an anhydrous sodium tripolyphosphate raw material containing at least about 85% by weight of anhydrous sodium tripolyphosphate and at least about 26% by weight of Form I sodium tripolyphosphate; said aqueous solution containing dissolved therein at least about 12.5% by weight of sodium tripolyphosphate; said aqueous solution containing from about 10 mols to about 40 mols of water per mol of anhydrous sodium tripolyphosphate in said raw material and being at a temperature of from about 30° C. to about 70° C.; and allowing said aqueous solution to intimately contact said raw material for at least about one minute to thereby hydrate substantially all of the anhydrous sodium tripolyphosphate present in said raw material at a temperature from about 30° C. to about 70° C.

**8.** The process of claim **7** wherein at least about 90% by weight of said anhydrous sodium tripolyphosphate raw material will pass through a U.S. Standard 100 mesh screen and about 100% by weight will pass through a U.S. Standard 40 mesh screen.

**9.** The process of claim **7** wherein the aqueous solution contains at least about 95% by weight of the amount of sodium tripolyphosphate required to saturate said aqueous solution.

**10.** The process of claim **7** wherein at least about 80% by weight of the sodium tripolyphosphate present in said raw material is Form I sodium tripolyphosphate.

**11.** The process of claim **10** wherein the hydration of said hydrous sodium tripolyphosphate is conducted at a pH of from about 6.5 to about 12.5.

**12.** The process of claim **11** wherein said intimate contact is from about 1 minute to about 4 hours.

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