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# HYDRATION OF SODIUM TRIPOLYPHOSPHATE

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This invention relates to methods for hydrating sodium tripolyphosphate. More particularly, this invention relates to novel processes for preparing detergent compositions which contain hydrated sodium tripolyphosphate.

Conventionally, detergent products containing hydrated sodium tripolyphosphate are made by first preparing a fluid mixture of water, detergent substances (surface active agents), and usually certain inorganic salts (such as sodium sulfate, tetrasodium pyrophosphate, sodium carbonate, etc), adding sodium tripolyphosphate to this mixture, allowing the sodium tripolyphosphate to hydrate, and subsequently, generally driving off most of the free water from the resulting slurry by heat-drying (usually by either spray-drying or by drying on a heated steel roll).

In conventional detergent processes, the amount of time which is required to hydrate the sodium tripolyphosphate in a given detergent composition is one of the largest single factors in determining the minimum total processing time which is required in order to produce a final product which will be acceptable to the purchasing public. Since process time is proportional in many respects to process cost, it can readily be seen that if one were able to substantially decrease the amount of time required to hydrate the sodium tripolyphosphate in the detergent composition (other factors being equal), one could by this means substantially reduce one's total processing costs. One could decrease the amount of time required to hydrate the sodium tripolyphosphate, for example, by reducing that part of the total tripolyphosphate in the composition which is hydrated in his process. This procedure, however, is usually undesirable, particularly for the preparation of detergents that contain more than a few percent of water. By decreasing the proportion of the sodium tripolyphosphate in the detergent composition which is in the form of the hexahydrate (for example, by producing a final product having only about half or less of the total sodium tripolyphosphate present in the product in the hexahydrated form), most detergent manufacturers can produce only inferior detergent products which exhibit poor flowability, which cake readily, and, as a result, which are generally considered to be undesirable by the consuming public.

The detergent manufacturer could also reduce the amount of process time required to hydrate the sodium tripolyphosphate in his formulation if he could use sodium tripolyphosphate which is largely in the form of the high temperature crystalline modification, since the high temperature crystalline modification generally hydrates faster than the low temperature crystalline modification. However, the use of sodium tripolyphosphate containing more than about 15–20 weight percent of the high temperature crystalline form is generally not practicable, because, ordinarily, when such a tripolyphosphate is added to the detergent crutcher, many hard, gritty, troublesome lumps form. These lumps are very difficult to redissolve, and unless they are eliminated, often interfere significantly with the subsequent handling of the detergent slurries (e.g., during the pumping, filtering and heat-drying stages of the detergent processes etc.), and also result in inferior detergent products which contain many slowly-soluble lumps.



On the other hand, if there were available a process by which the detergent manufacturer could substantially increase the rate of hydration of the sodium tripolyphosphate, without the formation of undesirable lumps in the detergent slurry, he could by this means produce excellent detergent products, and at the same time show a substantial decrease in process time and expense (as compared to the use of conventional processes), without having to sacrifice any of the desirable properties of the final detergent product. In addition he could obtain products which contain proportionately more of the sodium tripolyphosphate (which was originally added to the aqueous medium) in an undegrated state, and also, as a result of the decrease in total process time per batch of detergent, effectively increase the total capacity of his plant.

Consequently, one of the primary objects of this invention is to substantially increase the rate of hydration of sodium tripolyphosphate in detergent processes, as compared with those rates which are inherent in conventional detergent processes.

Another object of this invention is to utilize sodium tripolyphosphate, a relatively large proportion of which is in the form of the high temperature modification, in the formulation of detergent slurries without the formation of a prohibitive amount of undesirable, hard, gritty lumps in the detergent slurry.

It is another object of this invention to produce detergent compositions containing a maximum amount of the sodium tripolyphosphate which was initially formulated into the detergent process, in an undegraded state.

It is still another object of this invention to provide a method whereby the total capacity of a plant which produces detergents containing hydrated sodium tripolyphosphate can be substantially increased, without a proportionate outlay of money for additional equipment, etc.

It has now been discovered that the aforesaid, as well as other objects of this invention, can be accomplished by hydrating the sodium tripolyphosphate in an aqueous medium which is maintained at a pH above 11.5. For example, it has been found that when one batch of anhydrous sodium tripolyphosphate was added to a typical detergent-base slurry (at a conventional pH of 9.7) in a conventional detergent crutcher, more than 30 minutes were required to hydrate 90% of the sodium tripolyphosphate which was added. By comparison, in a similar test, under identical conditions, except that the pH of the "typical detergent-base slurry" had been raised to 12.0 by the addition of a small amount of sodium hydroxide to the said slurry, less than five minutes were required for 90% of the sodium tripolyphosphate to be converted to the hexahydrate. Please note that in this specification and in the appended claims, the pH to which reference is made means the pH of the slurry after the sodium tripolyphosphate is mixed into the respective aqueous media, measured upon a 1 weight percent solution of the slurry in distilled water.

The fact that the pH of the aqueous medium in which the sodium tripolyphosphate is hydrated can have such an important influence upon the rate at which the sodium tripolyphosphate is hydrated is surprising because pH is

not normally a process variable in the hydration of inorganic salts. In conventional detergent processes the importance of these higher pH's has not been recognized heretofore because the pH's of the aqueous media which have been utilized have been those pH's that simply naturally resulted from mixing the various raw materials together in their respective relative proportions which appeared in the final acceptable detergent products. Even though some relatively alkaline ingredients have heretofore been used in the preparation of detergent slurries, these materials have not been used in amounts which resulted in the aqueous media having pH's of very much higher than about 10.5 after the sodium tripolyphosphate was added—and since, in aqueous media having pH's below about 11, variations in the pH do not significantly affect the rate of hydration of sodium tripolyphosphate, the important effect of the still higher pH's on the hydration of sodium tripolyphosphate according to this invention was not heretofore known.

Apparently, the substantial benefits which can accrue to those who practice this invention result from a combination of (1) the improved dispersion of the sodium tripolyphosphate (in the aqueous media) that occurs when the tripolyphosphate is added to detergent slurries having pH's above about 11.5 along with (2) the relatively low solubility of the sodium tripolyphosphate in the highly alkaline media. Although, theoretically, sodium tripolyphosphate should hydrate in practically any aqueous medium within a very short time after the aqueous medium and the tripolyphosphate are intermixed, such an accomplishment has been impossible to achieve on a practical commercial scale, because at least some small lumps are almost invariably formed when water and sodium tripolyphosphate are intermixed. Since the lumps which do form require time to dissolve and then become hydrated, it can be appreciated that the degree of dispersion (non-lumpiness) of the tripolyphosphate upon its being introduced into the aqueous detergent slurry will have an important effect upon the amount of time required for the tripolyphosphate to become hydrated. In order to achieve the substantial benefits of this invention, it is necessary to hydrate the sodium tripolyphosphate in an aqueous medium which has a pH of at least about 11.5. It is preferred that the pH of the aqueous medium be maintained at between 11.5 and about 12.5 during the hydration of the sodium tripolyphosphate although even stronger alkalinities can be utilized if one desires. As a practical matter, however, one will usually practice the invention in aqueous media which do not contain more than about 8% by weight of such extremely alkaline materials as sodium hydroxide, potassium hydroxide, the very basic silicates, and the like, because in the presence of such extremely high concentrations of these highly alkaline materials the sodium tripolyphosphate hexahydrate which is formed will hydrolyze (decompose) at an undesirably fast rate.

In the practice of this invention, the only requirement with respect to the types of other ingredients that can be present in the aqueous media while the sodium tripolyphosphate is hydrating is that the other ingredients which are present be compatible with the sodium tripolyphosphate. For example, all types of anionic and nonionic surface active agents (detergent "active" ingredients) can be used, as well as any inorganic and organic materials which are or can be conventionally utilized in a detergent composition containing sodium tripolyphosphate. Generally, these ingredients will be preesnt in the aqueous media when the sodium tripolyphosphate is intermixed therewith.

The actual manner by which the aforesaid aqueous media are brought to the higher pH's that are utilized in the practice of this invention has apparently no detrimental effects on either the manner by which the present invention can be practiced or the benefits that can result from the practice of the invention. For example, any material which is compatible with the particular detergent formulation being used, which is acceptable for use in detergents, and which is sufficiently basic in character to raise the pH of an aqueous medium sufficiently high to substantially increase the rate of hydration of sodium tripolyphosphate (which is either dispersed or dissolved in the aqueous medium), as compared to the rate of hydration of sodium tripolyphosphate in conventional aqueous media and in conventional detergent crutching processes (i.e., below 10.5), can be employed without any particular difficulties in the practice of the invention. Examples of materials which can readily be used to accomplish the high pH's at which this invention is practiced are alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, lithium hydroxide etc., sodium silicates, potassium silicates, highly alkaline salts such as trisodium phosphate, and the like.

The "aqueous medium" referred to in this specification and claims means water, either with or without reasonable amounts of other materials which are conventionally utilized or can be utilized in the preparation of detergent compositions. For example, the aqueous media will usually contain materials such as organic detergent surface active agents, sodium carboxymethylcellulose, silicates, sodium sulfate, sodium carbonate, tetrasodium pyrophosphate, etc. The aqueous media that are utilized in the processes of this invention will generally contain more than sufficient free water (i.e., water not otherwise bound as water of crystallization, water of composition, etc.) to hydrate the sodium tripolyphosphate. It is preferred, however, that during the manufacture of detergent compositions (slurries) which are to be heat-dried ultimately, between about one-half and about 10 times as much water by weight, be present (in the aqueous media before the tripolyphosphate is added thereto) as the amount of sodium tripolyphosphate which is utilized in the formulation.

The temperature of the aqueous medium, when the sodium tripolyphosphate is added thereto according to the processes of this invention can be varied through a relatively wide range. Ordinarily, conventional detergent slurry temperature practices will be utilized and conventional precautions should be observed. For example, one would not expect the low temperature crystalline form or modification of sodium tripolyphosphate to hydrate at temperatures above about 80° C. Yet, one would expect the high temperature form to hydrate at temperatures as high as about 105° C., or even higher under certain conditions. As a general rule, however, the hydration of the sodium tripolyphosphate which is accomplished according to the processes of this invention will be carried out at temperatures within the range of from about 25° C. to about 70° C.

Nor does the particular physical or crystalline form of the tripolyphosphate which is utilized have any noticeably detrimental effect on the beneficial practice of the invention. Generally, any of the varieties or forms of sodium tripolyphosphate (e.g., granular, powdered, flake, low or high temperature crystalline modification, etc.) which can be used in the production of detergent products can be used in the practice of this invention, without any special requirements whatever, other than those usually observed in the conventional handling and processing of these types or forms of sodium tripolyphosphate. Actually, the hydration of sodium tripolyphosphate according to this invention makes it possible to accomplish certain things which cannot ordinarily be accomplished conventionally. For example, conventionally one cannot hydrate sodium tripolyphosphate in an aqueous medium without the formation of hard, gritty, undesirable lumps, unless there is present in the aqueous medium (before the sodium tripolyphosphate is added thereto) a substantial amount of the organic surface active agent. However, when the aqueous media are

maintained at the high pH's which are utilized in the practice of this invention, sodium tripolyphosphate can be hydrated without forming any of the aforesaid undesirable lumps, even in the complete absence of detergent "active" material.

The invention will be illustrated by the following specific examples in which all parts are by weight unless otherwise specified.

*Example I*

Into a conventional detergent crutcher are charged the following ingredients.

| Ingredients: | Parts |
|---|---|
| Sodium dodecylbenzene sulfonate (44.5% "active," 48.0% $H_2O$, 7.5% $Na_2SO_4$) | 460 |
| Sodium sulfate | 41 |
| Sodium silicate solution (63% $H_2O$, $Na_2O/SiO_2=1/2.5$) | 225 |
| Sodium carboxymethylcellulose | 7 |
| Fluorescent dye | 1 |
| Water | 258 |

The resulting blend is mixed for about 5 minutes after all of the above ingredients have been added to the crutcher. During this time the blend is warmed to about 60° C. Then 100 parts of 50% sodium hydroxide solution is added to the blend in order to bring its pH to 11.8. Over the next 6 minutes, 470 parts of sodium tripolyphosphate (containing 88 weight percent of the low temperature crystalline form and 0.35 weight percent of moisture) are added to the crutcher. After only 10 minutes of additional stirring in the detergent crutcher, 90% of the sodium tripolyphosphate has been hydrated. Then 62.5 parts of sulfuric acid (98% $H_2SO_4$) are added to bring the pH of the resulting slurry to 9.6.

By comparison, if a similar slurry is made up and maintained at a pH of 9.6 during the hydration of the sodium tripolyphosphate, at least about 30 minutes would be required in order for 90 percent of the sodium tripolyphosphate to become hydrated.

When the sodium tripolyphosphate which is utilized in Example I, above, is composed largely of the high temperature crystalline modification, the results from practicing this invention are even more striking, because, conventionally, when the high temperature crystalline form of sodium tripolyphosphate is hydrated under the above-described conditions (pH=9.6, temperature=65° C., tripolyphosphate contains 0.35% moisture), many troublesome, gritty lumps are formed in the detergent slurry, often making the slurry unfit for use in some applications. For example, slurries containing many of the undesirable, gritty lumps are generally unfit for use in conventional spray-drying facilities because the lumps readily plug the screens and spray-nozzles. However, by practicing the present invention, a detergent manufacturer can use even the high temperature crystalline modification of sodium tripolyphosphate without having to be particularly concerned about such troublesome lumps. For example, when sodium tripolyphosphate, which is largely composed of the high temperature form, is hydrated in an aqueous medium having an initial pH of about 11.1, the number of gritty lumps which are formed in the slurry (as compared to the number which are formed when the sodium tripolyphosphate is hydrated in a similar aqueous medium having a conventional pH) is substantially reduced. When the pH of the said aqueous medium is within the preferred range (between 11.5 and about 12.5), practically none of the undesirable lumps are formed. Thus another advantage of the present invention can readily be appreciated by those in the detergent art.

Generally, when detergent products or solutions containing them will possibly come into contact with human skin, it is preferred that their solutions have pH's no higher than about 10.5 or even lower, in order to avoid undesirable reactions and irritation of the skin which can sometimes result from the application to skin of materials which are highly alkaline. Since solutions of detergent products which result from the heat-drying of slurries containing sodium tripolyphosphate which has been hydrated according to this invention (without any further adjustment of the pH of said slurries having been made) will have generally undesirably high pH's (insofar as their use where they will come into contact with human skin is concerned), it is usually advantageous to lower the pH of said slurries to a more desirable level (i.e., to between about pH 5 and pH 10.5), if necessary, before they are subjected to the usual heat-drying step. In order to lower the pH of the slurry after the tripolyphosphate has been hydrated to a desirable extent according to the hydration processes of this invention (i.e., from about 50% to 100% and preferably from about 70% to 98% of the tripolphosphate has been hydrated), any convenient, relatively acidic material which will lower the pH of the slurry to the desired level can be added to the slurry. For example, any of the mineral acids such as $H_2SO_4$, HCl, $HNO_3$, and $H_3PO_4$, can be used, as well as many other relatively acidic materials. If the pH of the slurry is lowered to a conventional level before it is subjected to the heat-drying step of the detergent process, the resulting detergent product will be substantially identical in physical appearance to a product which has been formulated similarly, but which is produced conventionally. In addition, because of the decreased time during which the sodium tripolyphosphate is exposed to the hazards of hydrolysis in the aqueous media, the products which result from the application of this invention will generally contain proportionately more of the sodium tripolyphosphate (which was originally added to the aqueous medium) in an undegraded state.

*Example II*

Into a conventional detergent crutcher are charged the following ingredients.

| Ingredients: | Parts |
|---|---|
| Water | 7000 |
| Sodium sulfate, anhydrous | 2500 |
| Sodium carboxymethylcellulose | 100 |
| Optical bleach | 10 |

The resulting blend is stirred for five minutes in order to achieve a uniform distribution of the ingredients through the blend. The pH of this blend is 7.2. Then 280 parts of 50% sodium hydroxide solution are added to the blend in order to bring the pH of the blend to 12.0. At this point the temperature of the blend is 65° C. Over the next seven minutes, while the blend in the crutcher is being stirred, 4500 parts of sodium tripolyphosphate (containing 35 weight percent of the high temperature crystalline modification and 0.25 weight percent of water) are added to the blend. Within eight minutes more than 95 percent of the sodium tripolyphosphate is converted to the hexahydrate.

In a similar mixture (but at a conventional pH of 7.2) sodium tripolyphosphate from the same lot is hydrated. This batch requires more than about 45 minutes to hydrate 95 percent of the tripolyphosphate. The presence of many of the heretofore-described undesirable, gritty lumps in the slurry (due at least partially to the absence of any surface active agent in the slurry while the tripolyphosphate was being hydrated) contributes substantially to the amount of time that is required to hydrate the sodium tripolyphosphate. It will be noted that the beneficial results which can accrue to those who practice this invention are practically unaffecteed by either the presence or absence of the surface active agent from the aqueous medium during the hydration of the sodium tripolyphosphate.

*Example III*

Into a convention detergent crutcher are charged the following ingredients.

| Ingredients: | Parts |
|---|---|
| Water | 4500 |
| Sodium sulfate, anhydrous | 2500 |
| Sodium carbonate | 500 |
| Sodium silicate solution | 1000 |
| Nonionic surface active agent [1] | 1000 |
| Sodium carboxymethylcellulose | 100 |
| Optical bleach | 10 |

[1] Condensation product of 12.5 moles of ethylene oxide per mole of dodecylphenol.

The resulting blend is stirred for 6 minutes. The pH of this blend is 10.6. Then 300 parts of 50% potassium hydroxide are added to bring the pH of the blend to 11.8. Over the next 5 minutes, while the blend is continuously stirred, 3000 parts of sodium tripolyphosphate (90 weight percent of which is in the form of the low temperature modification) are added to the blend. Within 12 minutes, while the pH of the aqueous medium remains between 11.6 and 11.8, more than 90 percent of the sodium tripolyphosphate is hydrated.

By comparison, a similar detergent slurry which is maintained at a pH of 10.6 requires more than 60 minutes to hydrate 90% of the sodium tripolyphosphate.

What is claimed is:

1. A process for the preparation of a detergent composition containing hydrated sodium tripolyphosphate, which process comprises the steps of slurrying sodium tripolyphosphate into an aqueous medium containing an amount of water equal to at least about one-half of the weight of said sodium tripolyphosphate, the resulting aqueous slurry having a pH after said sodium tripolyphosphate is intermixed with said aqueous medium of at least about 11.5, maintaining the pH of said resulting slurry after said slurrying step between about 11.5 and about 12.5 until at least about 50% of said sodium tripolyphosphate has been converted to the hexahydrate, and thereafter reducing the pH of the resulting slurry to below about 10.5.

2. A process for the preparation of a heat-dried detergent composition containing hydrated sodium tripolyphosphate, which process comprises the steps of slurrying sodium tripolyphosphate into an aqueous medium containing an amount of water more than sufficient to hydrate said sodium tripolyphosphate to the hexahydrate, the resulting aqueous slurry having a pH after said sodium tripolyphosphate is intermixed with said aqueous medium of at least about 11.5, maintaining the pH of said resulting slurry between about 11.5 and about 12.5 from immediately after said slurrying has been completed until said sodium tripolyphosphate has been converted to the hexahydrate, thereafter reducing the pH of the resulting slurry to less than about 10.5, and subsequently heat-drying said resulting slurry.



3. A process as in claim 2, wherein at least about 20 weight percent of the sodium tripolyphosphate is in the form of the high temperature crystalline modification.

4. A composition suitable for use in the preparation of a heat-dried detergent containing hydrated sodium tripolyphosphate, which comprises sodium tripolyphosphate, an aqueous medium and an amount of a highly alkaline material which is compatible with sodium tripolyphosphate, said amount being less than that which causes excessive decomposition of sodium tripolyphosphate hexahydrate in said composition, said aqueous medium having a pH above about 11.5, and the weight ratio of water to sodium tripolyphosphate in said composition being at least about 1 to 2.

5. A composition as in claim 4 wherein the weight ratio of water to sodium tripolyphosphate in said composition is between about 1 to 2 and about 10 to 1.

6. A composition suitable for use in the preparation of a heat-dried detergent containing hydrated sodium tripolyphosphate, which comprises sodium tripolyphosphate, an organic surface active agent selected from the group consisting of anionic and nonionic surface active agents, and water, said composition having a pH between about 11.5 and about 12.5, and the weight ratio of water to sodium tripolyphosphate in said composition being between about 1 to 2 and about 10 to 1.

7. A composition which can be heat-dried in the manufacture of a solid, particulated detergent which composition consists essentially of sodium tripolyphosphate, an organic surface active agent selected from the group consisting of anionic and nonionic surface active agents, and water, said composition having a pH between about 11.5 and about 12.5, and the weight ratio of water to sodium tripolyphosphate in said composition being between about 1 to 2 and about 10 to 1.

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