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DETERGENT PROCESSES AND COMPOSITIONS THEREFOR

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This invention relates to novel methods for producing detergent compositions containing alkali metal tripolyphosphates. More specifically, this invention relates to the use of alkali metal trimetaphosphates in the production of heat-dried detergent products.

The benefits that result from the use of alkali metal tripolyphosphates in detergent compositions are well known. The disadvantages which result from such use are perhaps not so well-known, except to the manufacturers of these products. These disadvantages are, nevertheless, very significant. One of the disadvantages which manufacturers of heat-dried detergent products containing hydrated alkali metal tripolyphosphates have heretofore had to contend with is the unpredictable (and undesirable) drastic increases in the viscosities of their aqueous detergent slurries that accompany the hydration of the tripolyphosphates. In addition, the high slurry viscosities that result from such hydration make it practically impossible, using conventional equipment, to spray-dry slurries having more than about 65–70 weight percent of solids (non-volatile materials). Another important disadvantage which results from the use of tripolyphosphates as raw materials in the preparation of detergent slurries that are to be heat-dried is that almost invariably, unless very stringent precautions are taken when the tripolyphosphate is intermixed with the water, undesirable hard, gritty lumps are formed, which interfere with the drying operations, and which are very difficult to eliminate from the slurry. Still another disadvantage which is associated with this use of tripolyphosphates is that during the time in which the slurry is being formulated and ultimately heat-dried, a significant proportion of the tripolyphosphate is hydrolyzed to orthophosphates and pyrophosphates which are not nearly as effective (as sequestrants) in "building" detergent products as is tripolyphosphate and therefore are not nearly as desirable as tripolyphosphate in the final heat-dried detergent product. As a result of these, as well as several other disadvantages which are ordinarily inherent in the use of alkali metal tripolyphosphates as raw materials for heat-dried detergents, a manufacturer of such detergents heretofore had to apply very rigid, practically inflexible, process controls in order to produce a detergent product having acceptable properties at a reasonable processing cost.

The present invention makes it possible to either eliminate or at least alleviate all of the above-described processing difficulties which are ordinarily associated with the use of alkali metal tripolyphosphate in the preparation of heat-dried detergent products. In addition, this invention makes it possible to produce heat-dried detergent compositions at a significantly lower processing cost than was heretofore practicable, and to produce detergent compositions having more desirable qualities, as compared with those produced via conventional procedures.

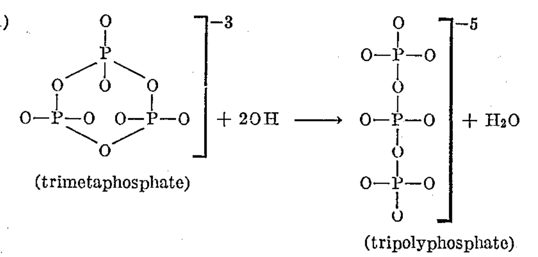
The above-described benefits, as well as others, are obtained in accordance with this invention by substituting for all or part of the alkali metal tripolyphosphate con-

ventionally employed in aqueous detergent slurries used in making detergent compositions a quantity of an alkali metal trimetaphosphate which is at least equivalent [based on the (theoretical) conversion weight ratio of trimetaphosphate to tripolyphosphate] to the amount of tripolyphosphate for which it is substituted, and employing process conditions such that at least a substantial amount or proportion of the trimetaphosphate is transformed to tripolyphosphate during the crutching and/or heat-drying operations.

The invention makes advantageous use of the reaction of alkali metal trimetaphosphates with a base in the presence of alkali metal ions to produce an alkali metal tripolyphosphate. The reaction is believed to be represented by the following series of steps:

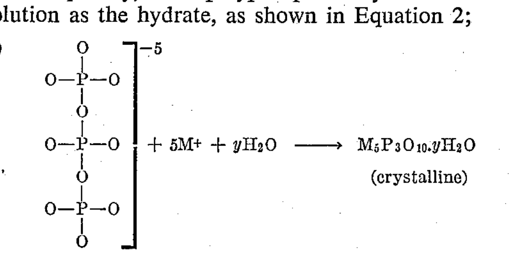
Initially, the trimetaphosphate ring is cleaved by the base, forming the tripolyphosphate anion, as is shown in Equation 1:

(1)



Subsequently, the tripolyphosphate crystallizes from the solution as the hydrate, as shown in Equation 2;

(2)



wherein M is an alkali metal cation and y is an integer which is equal to the whole number of water molecules that are necessary to make a stable hydrated salt of the particular alkali metal tripolyphosphate being produced. Generally, y will be a whole number from 1 to 15, inclusive. Because of economic, as well as other considerations, it is preferred that M represent sodium and that y equal six.

The heat-dried detergent compositions which can be made according to the practice of this invention are those that contain a significant amount of tripolyphosphate; that is, usually at least about 10 weight percent and often as much as 75 weight percent of tripolyphosphate, based on the total weight of the heat-dried composition. Often when these compositions are made conventionally, only part of the tripolyphosphate is hydrated in the compositions which contain the higher levels of tripolyphosphate (for example, compositions containing more than about 20 weight percent of tripolyphosphate). In order for such detergent products to have acceptable flow and non-caking properties, a substantial proportion (for example, at least about 60 weight percent, and preferably at least about 75 weight percent), of the tripolyphosphate in the heat-dried detergent compositions must be in the hydrated state.

In processes for preparing heat-dried detergent compositions, a "slurry" is ordinarily utilized in order to achieve several specific advantages, including the achievement of a better uniformity of ingredients through the final detergent product, and affording to the detergent manufacturer a greater ease of handling the formulation while it is being prepared, etc. In fact, the advantages of using the "slurry" method are so great that the so-called "slurry" method of preparing detergents has become the most important procedure in use today. Detergent "slurries" are well-known in the art, and needn't be detailed here, except to point out that those which relate to this invention contain more than sufficient water to hydrate all of the alkali metal tripolyphosphate in the final detergent composition. On this basis, useful slurries will generally contain at least about 10 weight percent of water, based on the total weight of the slurry before it is heat-dried. In actual practice, however, the minimum amount of water that can be utilized in any of these slurries will be that amount below which the slurry loses some of its fluid properties and becomes too viscous to pump and handle in conventional equipment. For this reason, conventional detergent slurries have heretofore generally contained at least about 35 weight percent of water.

Because of their very low viscosity, however, the slurries that are utilized in the practice of this invention can contain significantly less water than could comparable or equivalent conventional slurries and still be sufficiently fluid to be utilized in conventional crutching and heat-drying facilities. Consequently, it is a preferred embodiment of the processes of the invention to heat-dry detergent compositions containing between about 70 weight percent and 80 weight percent of "solids" (non-volatile at 105° C.) prepared according to the procedures which will be detailed below. Since the slurries within the purview of this invention are to be ultimately heat-dried, cost considerations dictate that those detergent slurries upon which this invention will be practiced will be those containing at least about 25 weight percent of "solids." Some of the benefits which result from practicing this invention, however, will be most apparent when one utilizes slurries containing more than about 45 weight percent of "solids," for it is in the utilization of highly concentrated slurries that conventional procedures are most blatantly disadvantageous. The utilization of the more highly concentrated slurries is additionally advantageous in the practice of the invention because the rate of conversion of alkali metal trimetaphosphate to tripolyphosphate is substantially higher in these systems than it is in those systems which are relatively more dilute.

The bases which can be utilized in the practice of this invention are all of those which can cause the formation of hydroxyl ions, in the aqueous media, for reaction with the alkali metal trimetaphosphate (in order to produce alkali metal tripolyphosphate). Thus, throughout the present specification, and the appended claims, the term "strong base" will be intended to encompass those bases that are sufficiently strong to cause the formation of "excess" hydroxyl ions in aqueous media that contain dissolved alkali metal tripolyphosphate. For purposes of this invention, the "strong bases" that can be utilized are those that yield a solution pH measured at 25° C. of at least about 10.2 when they are dissolved in distilled water at the 1 weight percent level. It will be understood that the term "strong base" encompasses, for example, such basic compounds as for example, alkali metal carbonates, alkali metal silicates, tri-alkali metal orthophosphates, alkali metal and alkaline earth metal oxides, and the like (which compounds do not actually contain hydroxyl anions, but which cause hydroxyl ions [high pH] to result when they are dissolved in water), as well as some of the organic quaternary ammonium hydroxides, the alkali metal hydroxides and the alkaline earth metal hydroxides such as calcium hydroxide, and magnesium hydroxide, etc. Economic considerations will generally dictate that "strong bases" which are inorganic be used. Of these, it is preferred that alkali metal hydroxides, carbonates, and silicates (having SiO_2/M_2O ratios lower than 2.0) be utilized. Still further preferred are the sodium forms of these materials.

The amounts of the various strong bases described above which can be utilized in this invention will vary considerably, depending upon such factors as the molecular weight of the base, its basic strength, rate of dissolution in water, etc. The amount, however, will always be sufficient to furnish enough hydroxyl ions so that at least a substantial amount or proportion (i.e. at least about one third) of the alkali metal trimetaphosphate in the slurry can be converted into the corresponding alkali metal tripolyphosphate. Thus, the amount of the particular inorganic base that can be utilized (in the slurry) in the practice of this invention will generally be at least enough to furnish about ⅔ mole equivalent of hydroxyl ions per mole of trimetaphosphate which is present in the slurry. Because 2 moles of hydroxyl ions are necessary to convert one mole of trimetaphosphate to tripolyphosphate, the term "base conversion unit" will herein be intended to mean the amount of strong base that will generate two mole equivalents of hydroxyl ions per mole of trimetaphosphate in the slurry. Since very high concentrations of base in the detergent slurries will sometimes cause degradation of tripolyphosphate, and also because when a very large excess of base is utilized some of the excess base (that in excess of the amount required to convert the trimetaphosphate) must ordinarily be neutralized with acid before the heat-drying step (in order to maintain a desirable alkalinity in the final detergent product), the amount of strong base present in the detergent slurries which are utilized in the practice of the invention will generally not be more than about 3 "base conversion units."

Although it is appreciated that some inorganic bases are conventionally employed in detergent compositions and processes, the amounts of base with which this invention is concerned will generally be over and above those amounts conventionally employed. For example, two percent solutions of conventional heat-dried detergent composition in distilled water often exhibit alkaline pH's ranging from about 8 to about 10.5 or perhaps even slightly higher than 10.5. These levels of alkalinity are desired to be maintained in the final product because the products often perform better under slightly alkaline washing conditions. In addition, a certain degree of alkalinity is required in the product in order to maintain the silicate corrosion inhibitors in a water-soluble state. The practice of the present invention, however, generally requires that significantly more base be incorporated into the detergent slurries than was heretofore employed.

Any amount of alkali metal trimetaphosphate can be used in formulating detergent compositions according to the processes of this invention. However, the amount of alkali metal trimetaphosphate that is actually utilized will usually be dependent upon basically two requirements of the detergent manufacturer: the amount of tripolyphosphate which he desires in his final detergent product, and the proportion of this amount of tripolyphosphate that should be in the hydrated state. Because the products which result from the practice of this invention will almost invariably contain at least about 10 weight percent of hydrated tripolyphosphate, the slurries contemplated herein will ordinarily contain at least about 5 weight percent initially (based on the weight of the slurry "solids") of one of the alkali metal trimetaphosphates. On the other hand, because of the presence of water, strong base, and other detergent ingredients in the slurries, generally not more than about 60 weight percent of any of the alkali metal trimetaphosphates can be utilized therein, if relatively complete conversion of the trimetaphosphate to tripolyphosphate is desired before the slurry is heat-dired.

It is preferred that the amount of alkali metal trimetaphosphate which is initially intermixed with the aqueous medium in the practice of this invention be from about 10 to about 50 percent by weight, based on the total weight of the slurry just before it is heat-dried (i.e., after the slurry has been completely formulated).

Although the conversion of trimetaphosphate to tripolyphosphate apparently takes place largely in the aqueous phase of the slurries involved, the actual size of the particles of trimetaphosphate that can be utilized in the practice of this invention is not critical. For example, the alkali metal trimetaphosphates can be utilized in any of the particle sizes and physical forms (i.e., flake, powder, granular, etc.) in which the alkali metal tripolyphosphates can be employed in conventional processes for preparing heat-dried detergent products. Typically, the granular form is sometimes desired because of its free-flowing, ease of handling, characteristics. However, when one desires optimum results, it is preferred that the alkali metal trimetaphosphates be in a finely divided state before they are mixed into the aqueous media in order to form the desired detergent slurries. By "finely divided" is meant that the trimetaphosphate granules, flakes or power etc. should be small enough so that at least about 80 (weight) percent of them will pass through a U.S. Standard 100 mesh screen. In some applications of the invention it will be advantageous if the particles of the phosphate are small enough so that at least about 80 (weight) percent of them could pass through a U.S. Standard 200 mesh screen.

The ingredients (such as water, surface active agents, bases, and "builders" such as alkali metal trimetaphosphate, etc.) from which the slurries described herein are produced, can be blended together in any manner which is conventient to the slurry formulator without detracting appreciably from the benefits that can result from practicing the invention. Usually it will be most convenient to utilize conventional detergent heat-drying plant facilities including crutchers, pumps, spraying facilities, etc., although no particular types of equipment are critical. All that is basically required is a vessel, fitted with a means for blending the various materials which will be formulated into the detergent slurry, and a conventional heat-drying facility such as, for example, a steam or hot flue-gas heated drum-drier, or a conventional spray-drying facility. It is also generally most convenient to prepare the slurry first by charging into the mixing vessel the water, followed by the remainder of the materials from which the slurry is made. For optimum results in the practice of certain embodiments of the invention, either the alkali metal trimetaphosphate or the strong inorganic bases (described above) should be added to the slurry during the latter stages of its preparation.

One of the more important elements involved in the processes of this invention relates to the temperature of the detergent slurry containing the alkali metal trimetaphosphates and strong bases described herein. It has been found, for example, that when the temperatures of concentrated detergent slurries containing the proper ingredients are raised significantly above about 50° C., and particularly, when their temperatures are raised to above about 75° C., the rate of conversion of the alkali metal trimetaphosphates is extremely high. In one instance, for example, more than 85% of the sodium trimetaphosphate in a slurry containing 60% of the "solids" at about 75° C. is converted to sodium tripolyphosphate in less than 7 minutes. At a temperature below about 50° C., the rate of conversion of these trimetaphosphates is reduced. However, the benefits of reduced slurry viscosity, along with the concomitant benefits of reduced detergent processing costs, improved properties of the resulting detergent product, etc. are readily attainable by practicing the invention, even if the temperature of the detergent slurries are kept fairly low up until the time they are heat-dried. This is because there is usually sufficient exposure of the slurries to high temperatures in the heat-drying step alone to force the conversion to tripolyphosphates of substantially all of the alkali metal trimetaphosphate in the detergent slurries that has not been converted to alkali metal tripolyphosphate during the time in which the slurry is being formulated (for example, prior to its being introduced into the heat-drying step of the process). It has presently been found, for example, that more than 98% of the sodium trimetaphosphate contained in a slurry having 2.1 moles of NaOH/mole of trimetaphosphate was converted into sodium tripolyphosphate in less than 9 seconds on a steam-heated conventional drum-drier. Ordinarily the time-temperature relationship during the heat-drying step of the processes of this invention is such that, at any temperature that is practical for drying slurries such as those contemplated herein, practically complete conversion of trimetaphosphate to tripolyphosphate can be made. For example, the slurries can be dried at a temperature of 75° C. or even of 40° C. However, the use of such low temperature is not ordinarily practical because of the greater amount of time that is required to dry a detergent slurry under these conditions. Usually they are dried at from about 120° C. to about 375° C.

One preferred embodiment of the invention requires that the slurries (prepared according to the processes of this invention as herein described) be heat-dried within about 2 hours, and preferably within about 30 minutes, of the time the alkali metal trimetaphosphate is intermixed with the inorganic base in the aqueous medium, or within about 1 hour, and preferably within about 20 minutes of the time at which the aqueous slurry (containing the trimetaphosphate plus base) is heated to a temperature above about 75° C. By practicing this aspect of the invention it is possible to produce final (heat-dried) detergent products that contain almost all of the tripolyphosphate which was theoretically charged into the formulation (presuming that all of the trimetaphosphate charged to the slurry is converted to tripolyphosphate) in an undegraded state. By comparison, almost 20% (and sometimes even more) of the tripolyphosphate that is initially formulated into slurries that are prepared according to conventional processes for manufacturing heat-dried detergent slurries, is degraded (hydrolyzed) in the conventional processes, and effectively "lost" in the form, for example, of orthophosphates from the resulting heat-dried detergent composition. This increase in tripolyphosphate "savings" in the detergent products that are manufactured according to the processes of this invention is additionally advantageous in that, since the "extra" tripolyphosphate is present as the hydrate, it is possible for the final detergent product to contain proportionately more water, and thus on a pound for pound basis, be proportionately less costly to produce. It should be noted here that the increase in the water content of the detergent products produced in this manner can be accomplished without any of the disadvantages (such as increased caking, poorer flow properties, etc.) that would ordinarily be expected to result from increasing the water content of the detergent product without substantially changing its intended formula.

The cost of processing detergent slurries can also be significantly reduced by utilizing still another embodiment of the invention. This embodiment relates to the use of slurries having extremely high "solids": actually higher "solids" than was heretofore possible using conventional detergent processing techniques. Useful slurries having such extremely high "solids" result from the unexpectedly low viscosities that are developed (as compared to similar slurries containing tripolyphosphate) in slurries in which more than about 25 weight percent of the tripolyphosphate is replaced by its equivalent of trimetaphosphate. Table I below, illustrates the decrease in slurry viscosities which can result from practicing the invention.

TABLE I.—APPARENT VISCOSITIES OF DETERGENT SLURRIES [1]—57% "SOLIDS"

Phosphate	Time,[2] minutes	Apparent Viscosity
100% Sodium Tripolyphosphate (85% Form II).	0	400
	7	5,500
	15	19,000
	30	18,000
50% Sodium Trimetaphosphate+50% Sodium Tripolyphosphate (85% Form II).	0	430
	7	520
	15	560
	30	5,600
100% Sodium Trimetaphosphate	0	460
	7	380
	15	460
	30	470

[1] Prepared according to Example I, below. Only the phosphate has been changed. Viscosity measured at 40° C. by a Bendix Ultraviscoson.
[2] After addition of phosphate. Phosphate was added last to the slurry.

Since the viscosities of detergent slurries are ordinarily important limiting factors in determining the minimum amount of water which must be present in these slurries, and because removing water from the slurries during the heat-drying step is expensive, it can readily be appreciated that the relatively lower viscosities of slurries prepared according to the processes of this invention make it possible, as well as advantageous, for detergent manufacturers to handle detergent slurries containing more "solids" than they could conventionally handle heretofore.

Convenient methods for utilizing alkali metal trimetaphosphates in the practice of this invention are shown in the following specific examples. Note that in all of the examples, "parts" shown are parts by weight unless otherwise specified.

Example I

In a conventional detergent crutcher are charged 4,000 parts of water, 1,340 parts of sodium dodecylbenzene sulfonate, 1,040 parts of sodium sulfate, 540 parts of sodium silicate (dry basis) having an SiO_2/Na_2O ratio of 2.40, and 40 parts of detergent grade sodium carboxymethylcellulose. The resulting mixture is stirred for about 5 minutes, during which time 1,600 parts of a 50% aqueous solution of NaOH are also blended into the mixture, after which the temperature of the blend is about 40° C. Then 3,070 parts of sodium trimetaphosphate is added to the blend. Stirring is continued for about 20 minutes, during which time the viscosity of the slurry is continuously monitored. The apparent viscosity of the slurry after 20 minutes (measured with a Bendix Ultraviscoson probe) is only about 460 units, which viscosity can be described as very fluid. About 60 percent of the trimetaphosphate is converted into tripolyphosphate during this time.

At the end of the 20-minute "hold" time, the slurry is pumped (continuously) into heat-exchange relationship with a heater, so that the temperature of the slurry is quickly raised to about 85° C. From the heater, the slurry is quickly transferred to a conventional pressure pump, and from there to a conventional spray-drying tower where it is heat-dried. The amount of time (prior to the drying step) during which the temperature of the slurry is about 80° C. is only about 3 minutes. Yet more than 95 weight percent of the sodium trimetaphosphate initially added to the slurry is converted into tripolyphosphate by the time the slurry is sprayed. No difficulty is encountered with the viscosity of the slurry, during either the crutching or the spray-drying operations.

By comparison, if commercial sodium tripolyphosphate is utilized (in place of the trimetaphosphate in Example I) in the formulation of a similar detergent slurry (other conditions being the same), the viscosity of the slurry would be almost too high to stir and pump using conventional equipment (i.e. >15,000 units apparent viscosity) after only 10 minutes of the "hold" time have transpired. In addition, several of the hard, gritty lumps described heretofore, can be observed in the slurry prepared using sodium tripolyphosphate as a raw material. (No such lumps result from the use of trimetaphosphate, as in Example I, above.) It will be noted that conventional processes for manufacturing detergents that contain hydrated sodium tripolyphosphates require a "hold" time such as that described in Example I (particularly when the Form II modification is utilized) in order for the sodium tripolyphosphate in the slurry to hydrate before it is heat-dried. By comparison, when optimum processing conditions are utilized in the practice of this invention, such a "hold" time is not required. However, under most conditions, at least a short "hold" time such as that illustrated above, has been found to be advantageous in the practice of the invention.

Example II

Into a conventional detergent crutcher are charged 7,400 parts of a condensation product of tridecyl alcohol with ethylene oxide (containing an average of 30 moles of ethylene oxide per mole of alcohol), 3,800 parts (dry basis) of sodium silicate (having an SiO_2/Na_2O ratio of 4.0), 50 parts of sodium carboxymethylcellulose, 22,280 parts of water (including that from the silicate), 25,300 parts of sodium sulfate, and 29,500 parts of sodium trimetaphosphate. The resulting slurry is stirred for 5 minutes. Its apparent viscosity is only about 2,000 units. It contains no "lumps." This slurry is then pumped from the mixer to a high-pressure pump which is part of a conventional spray-drying facility. Just before it enters the high-pressure pump, a 50% solution of sodium hydroxide is metered into the slurry at the rate of 22 parts per 100 parts of the slurry (approximately 2.5 moles of NaOH per mole of sodium trimetaphosphate present therein). From the high-pressure pump, the slurry is then pumped directly to a conventional spray tower, where it is heat-dried. The amount of time that a given portion of the slurry remains in the conduit between the high-pressure pump and the spray nozzles is only about 2 minutes.

The resulting detergent product contains 38.2 weight percent of sodium tripolyphosphate hexahydrate (about 92% of that theoretically possible from the trimetaphosphate) and only about 3 weight percent of unconverted sodium trimetaphosphate. Note that in this example, only about 22,200 parts of water have to be evaporated in the heat-drying step. This amounts to only about 20 weight percent of the total weight of the detergent slurry, just before it is heat-dried.

Although in the foregoing discussion and examples alkali metal trimetaphosphates have been discussed as though they were present and handled as a pure material, it is not the inventors' intention that the invention be so limited. As a matter of fact, it has been found to be distinctly advantageous in some instances, to utilize inorganic phosphate salt blends in the practice of the invention, which are composed only partly of alkali metal trimetaphosphate. The remainder of the inorganic phosphate (generally at least about 5 weight percent) can be composed of any or several of a number of water-soluble phosphate salts, especially those which have been found to be useful in detergents, such as, for example, alkali metal pyrophosphate, alkali metal tripolyphosphate, alkali metal tetrapolyphosphtae, alkali metal hexametaphosphate, alkali metal orthophosphates, and the like, particularly when the alkali metal is either sodium or potassium, or a mixture of them. Often the phosphate salts that are present in these blends with the trimetaphosphate are there because of economic and other considerations during the manufacture of the trimetaphosphate. Sometimes, in order to achieve a given result, or even simply for convenience, they can be deliberately intermixed with the trimetaphosphate after it has been manufactured. But, because in the detergent art clear solutions of the final detergent products are desired, it is preferred that the inorganic phosphate salt blends described above be substantially (i.e., at least about 97, and preferably more than 99 weight percent) soluble in water. In addition, when such phosphate salt blends as those described above are utilized in the practice of this invention, they will preferably be in a finely divided state (i.e., at least about 80 percent by weight of the particles thereof will ordinarily be small enough to pass through a U.S. Standard 80-mesh screen).

Generally, when an alkali metal trimetaphosphate is used as a part of one of these phosphate salt blends in the practice of this invention, the trimetaphosphate comprises at least about 10 weight percent of the phosphate salt blend, and preferably, will represent more than about 25 weight percent of the phosphate salt blend. The blend of phosphate salts can be prepared (before they are added to the aqueous medium) either as simple physical blends of the individual crystalline (or amorphous) powders, granules, or flakes, etc., if desired, or as part of a mixture with other of the ingredients that will be utilized in the detergent slurries. Also, the phosphate blend can be an intimate blend of phosphates that is prepared from a common melt, for example, which, after being cooled has been ground to produce the phosphate blend.

A particularly preferred phosphate blend, which can be utilized in another of the specific embodiments of this invention is one which contains both sodium trimetaphosphate and sodium tripolyphosphate. The tripolyphosphate part of this preferred blend usually consists almost entirely of the Form II crystalline modification. In this particular blend, the sodium trimetaphosphate can represent any proportion of the blend which is more than about 10 weight percent. By utilizing such a blend in slurries that are maintained at temperatures above about 85° C., and preferably above about 90° C., at all times after the phosphate blend is intermixed therewith, it is possible to produce heat-dried detergent compositions that contain a predetermined and readily controlled proportion of the sodium tripolyphosphate contained therein in the hydrated state. For this particular application, it is preferred that the sodium trimetaphosphate fraction or portion of the phosphate blend be at least about 75 weight percent. The actual practice of this aspect of the invention will be illustrated by Example III.

Example III

Into a conventional detergent crutcher are charged 4,000 parts of water, 2,168 parts of sodium sulfate, 330 parts (dry basis) of sodium silicate having a SiO_2/Na_2O ratio of 2.0, 1,135 parts of Na_2CO_3, 42 parts of sodium carboxymethylcellulose, and 635 parts of an alkyl phenol-ethylene oxide condensation product (containing an average of 15 moles of ethylene oxide per mole of dodecylphenol). The temperature of the resulting mixture is then raised to 85° C. Then the resulting slurry is metered continuously into a separate mixing vessel into which is also continuously metered a finely divided phosphate blend which contains about 45.5 weight percent of sodium trimetaphosphate and about 54.0 weight percent of Form II sodium tripolyphosphate. The rates of adding slurry and phosphate blend into the mixing vessel are adjusted so that the phosphate blend is intermixed with the slurry at a rate which is proportionate to the desired total tripolyphosphate content of the final detergent product; i.e. at a ratio of "slurry" to phosphate blend of 8,310/1,808 in this case, to yield a product containing 30.0 weight percent (dry basis) of sodium tripolyphosphate. Sojourn time in the mixing vessel is about 1 minute.

The resulting mixture is continuously withdrawn from the mixing vessel through a conventional high-pressure pump and then spray-dried conventionally within 3 minutes of the time that the phosphate blend is added to the "slurry," yielding a detergent product having excellent physical and functional properties, and containing 27.0 weight percent (dry basis) of sodium tripolyphosphate, about 50 weight percent of which is hydrated.

It will be noted that the proportion of sodium tripolyphosphate in the final product which is hydrated is substantially the same as the proportion of tripolyphosphate which would theoretically result from the trimetaphosphate in the phosphate blend. Under these conditions, sodium trimetaphosphate is almost completely converted to tripolyphosphate, Form II sodium tripolyphosphate does not hydrate significantly, and, because of the extremely short period of time between the mixing of the phosphate blend into the aqueous medium and its actually being heat-dried, the tripolyphosphate has had little opportunity to degrade (hydrolyze).

Ordinarily, if one desires optimum results from such a process the slurries should be heat-dried within about 5 minutes of the time the phosphate blend is intermixed therewith. However, beneficial results can still be noted if the slurry is sprayed within about 20 minutes of this time. It is also not necessary, in the practice of this aspect of the invention for the trimetaphosphate and tripolyphosphate to be added to the aqueous medium simultaneously.

Variations of the specific manipulative processes of the various aspects of the invention can be readily appreciated by those skilled in the art. For example, the slurry can be prepared by first heating the mixtures of materials in the absence of the base or the phosphate blend, for example, then mixing the phosphate blend into the hot aqueous medium in the crutcher, and subsequently transferring the resulting mixture to the pump (from which the slurry is transported to the spray nozzles) and intermixing the Na_2CO_3 at a point just before the pump. The CO_2 gas which is produced by the reaction of sodium trimetaphosphate with Na_2CO_3 can aid in developing pressure for use in the spraying operation, as well as to make possible the production of a lighter density heat-dried detergent product.

The processes of this invention can also be advantageously applied as continuous processes for the preparation of heat-dried detergents containing hydrated alkali metal tripolyphosphates. Such continuous processes were generally not practicable heretofore, because of the relatively long periods of aging which conventional detergent slurries had to undergo in order for most of the tripolyphosphates contained therein to hydrate prior to the heat-drying step. Typically, during the continuous operations wherein this invention is practiced, there is no particularly critical preferred order of addition of the various ingredients from which the detergent slurry is manufactued. All that is essential is that, prior to the time the slurry is submitted to the heat-drying step, the alkali metal trimetaphosphate and strong base be well-blended. Usually, sufficient blending of these ingredients can be accomplished within a pump and conduit (if spray-drying is utilized in the process, for example). In addition, sufficient blending of trimetaphosphate and strong base can be accomplished within a transporting vessel such as a pipe or a conduit by properly placed baffles, screens, etc. (the placement and specific design of which are well within the ability of anyone skilled in the art), or even by the turbulence which normally occurs in such vessels. Example IV exemplifies the substantial benefits that can result from utilizing the invention as a continuous process for preparing heat-dried detergents. In this example the figures in parenthesis after the names of the various ingredients that are employed in the process represent the rate (in parts by weight per minute) at which the respective ingredients are utilized.

Example IV

The following dry ingredients are continuously metered onto a belt conveyor; detergent grade sodium carboxymethylcellulose (20), a commercial blend of 60 weight percent sodium sulfate plus 40 weight percent of sodium dodecylbenzene sulfonate (1,625), and sodium trimetaphosphate (1,550). The mixture is then dropped into a mixing tank (fitted with a fairly efficient anchor-type stirrer), and continuously intermixed at this point with water (825) at a temperature of about 80° C., sodium silicate solution (625) containing 40 weight percent of "solids", and having an SiO_2/Na_2O ratio of 3.0, and a 35 weight percent solution of sodium hydroxide (200). The mixing tank is designed so that the amount of time the materials are blended therein is about two minutes, after which the resulting slurry is withdrawn, transported immediately into the high-pressure pump of a conventional spray-drying facility, and spray-dried, utilizing conventional spraying techniques (i.e. dried countercurrently at a rate of 20,000 pounds of slurry per hour with an initial air temperature of about 270° C). The resulting detergent contains only about 4 weight percent of unconverted trimetaphosphate.

It will be noted from Example IV that by utilizing the invention under optimum processing conditions it is no longer necessary for a detergent manufacturer to build and maintain large expensive crutching tanks and storage ("hold") tanks in his detergent plant. Detergent manufacturers can readily appreciate this particular advantage of the invention.

In the foregoing examples and discussion, it has been convenient to specifically describe only a few of the ingredients other than the alkali metal trimetaphosphates, alkali metal tripolyphosphate, and bases that can be used to prepare the detergent slurries that are useful in practicing the invention. Actually, the invention can be practiced by utilizing in the slurries any material that can conventionally be employed in the preparation of heat dried detergents which contain alkali metal tripolyphosphates. Typical examples of other materials that can be included in the slurries contemplated herein include those organic (detergent) surface active agents which are conventionally present in detergent compositions (and which are compatible with tripolyphosphate), such as the anionic, nonionic, as well as some of the ampholytic surfactants, including for example, such individual detergent active ingredients as the well-known water-soluble soap (i.e. the sodium and/or potassium salts of coconut fatty acids, oleyl fatty acids, etc.), water-soluble alkylaryl sulfonates (i.e. sodium dodecylbenzene sulfonate, etc.), water soluble alkyl sulfates (i.e. sodium and potassium lauryl sulfate, sodium and potassium alkyl glyceryl ethers such as those derived from tallow and coconut oil, sodium coconut oil fatty acid monoglyceride sulfate, etc.), fatty alkylamides (i.e. N-dodecyl monoethanolamide, N-octadecyl diethanolamide, etc.), alcohol-alkylene oxide condensates (i.e. alcohols having from 8–20 carbon atoms, in either straight chain or branched chain configuration having from about 6–30 moles of ethylene oxide and/or propylene oxide per mole of alcohol, etc.), alkylphenol-alkylene oxide condensates (i.e. those made by condensing alkylphenol, having an alkyl group with from about 6 to about 20 carbon atoms in the chain, with from about 6 to about 30 moles of ethylene oxide and/or propylene oxide per mole of alkylphenol), and the like. In addition, other conventional detergent "builders" can be present in these compositions. For example, such materials as the alkali metal phosphates such as the soluble hexametaphosphates, etc. can be utilized. So also can alkali metal sulfates, alkali metal silicates, as well as anti-redeposition agents such as the carboxymethylcelluloses and the polyvinylalcohols and small amounts of organic "optical bleaches." Also, chemical bleaches such as the alkali metal perborates and chlorinated organic bleaches can be used in the slurries and heat-dried detergent compositions with which this invention is concerned.

It is also significant that the invention need not be limited to being practiced with slurries that contain all of the ingredients usually found in conventional heat-dried detergent compositions. For example, it is advantageous in some instances to heat-dry a blend of materials for the preparation of compositions such as bleach-bases, wherein the final bleach-base may or may not contain an organic surface active agent. For such applications the invention is of great value, because of the extremely low levels of tripolyphosphate degradation products that can be present in heat-dried products made according to this invention, as compared to the large amount of tripolyphosphate degradation that "normally" occurs when conventional processes are utilized for their preparation.

What is claimed is:

1. A process for manufacturing a heat-dried composition containing hydrated penta alkali metal tripolyphosphate, which process comprises the steps of preparing an aqueous slurry containing at least about 10 weight percent, based on the total weight of said slurry, of water, at least about 5 weight percent based on the total weight of said slurry of an alkali metal trimetaphosphate, and an alkali metal base, said alkali metal base being one which provides at 1 weight percent concentration in distilled water a solution pH measured at 25° C. of at least about 10.2 and said alkali metal base being present in said aqueous slurry in an amount at least sufficient to convert at least about one third of said alkali metal trimetaphosphate to said hydrated penta alkali metal tripolyphosphate, and thereafter heat-drying said aqueous slurry.

2. A process for manufacturing a heat-dried detergent composition containing hydrated penta alkali metal tripolyphosphate, which process comprises the steps of preparing an aqueous slurry containing at least about 10 weight percent of water from about 8 to about 64 weight percent, based on the weight of said detergent composition, of an alkali metal trimetaphosphate; and a base selected from the group consisting of alkali metal hydroxides, alkali metal carbonates, alkali metal silicates having an SiO_2/M_2O ratio, where M is an alkali metal cation, lower than 2, and mixtures thereof in an amount sufficient to convert at least about one third of said alkali metal trimetaphosphate to said hydrated penta alkali metal tripolyphosphate, and thereafter heat-drying the resulting mixture.

3. A process for manufacturing a heat-dried composition, which process comprises the steps of preparing an aqueous slurry containing at least about 20 weight percent, based on the total weight of said slurry, of water, a mixture of at least two substantially water soluble inorganic polyphosphate salts and a base selected from the group consisting of alkali metal hydroxides, alkali metal carbonates, alkali metal silicates having an SiO_2/M_2O ratio, wherein M is an alkali metal cation, lower than 2, and mixtures thereof, said mixture of polyphosphate salts containing between about 5 and about 95 weight percent of alkali metal trimetaphosphate and being present in said slurry in an amount such that said slurry contains between about 5 and about 60 weight percent of said alkali metal trimetaphosphate, and said base being present in said slurry in an amount sufficient to furnish from about 1.5 to about 4 mole equivalents of hydroxyl ion per mole of said alkali metal trimetaphosphate, and thereafter heat-drying said slurry, whereby at least about one third of said alkali metal trimetaphosphate is converted to hydrated penta alkali metal tripolyphosphate.

4. A process for manufacturing a heat-dried detergent composition containing hydrated sodium tripolyphosphate, which process comprises the steps of preparing an aqueous slurry containing a mixture of at least two substantially water soluble sodium polyphosphate salts and sodium hydroxide, said sodium polyphosphate salts containing from about 10 to about 95 weight percent of sodium trimetaphosphate and being present in said

slurry in a substantially water soluble amount such that at least about 5 weight percent of said sodium trimetaphosphate, based on the weight of said slurry, is present in said slurry, and the weight ratio of said sodium hydroxide to said sodium trimetaphosphate in said slurry being between about 1:4 and about 2:1; and thereafter heat-drying said slurry, whereby at least about one third of said sodium trimetaphosphate is converted to said sodium tripolyphosphate.

5. A process for the manufacture of a heat-dried detergent composition containing hydrated penta alkali metal tripolyphosphate, which process comprises the steps of mixing together in at least about 10 percent based on the weight of the resulting mixture, of water, at least about 10 weight percent, based on the weight of said resulting mixture, of alkali metal trimetaphosphate; and a base; said base being selected from the group consisting of alkali metal hydroxides, alkali metal carbonates, alkali metal silicates having an SiO_2/M_2O ratio lower than 2, wherein M is an alkali metal cation, and mixtures thereof, and being present in the resulting mixture in an amount sufficient to furnish at least about 2 mol equivalents of hydroxyl ions per mol of said alkali metal trimetaphosphate, holding the resulting mixture at a temperature above about 50° C. until at least about 30 weight percent of said alkali metal trimetaphosphate has been converted to tripolyphosphate, and thereafter heat-drying the resulting aqueous mixture.

6. A process for manufacturing a heat-dried detergent composition containing hydrated sodium tripolyphosphate, which process comprises the steps of mixing together in at least about 10 percent, based on the weight of the resulting mixture, of water, at least about 10 weight percent, based on the weight of said heat-dried detergent composition, of sodium trimetaphosphate and an amount of sodium hydroxide sufficient to furnish between about 1.5 and about 8 mole equivalents of hydroxyl ions per mole of said sodium trimetaphosphate, subjecting the resulting mixture to a temperature above about 50° C. while at least about 30 weight percent of said sodium trimetaphosphate is converted to tripolyphosphate, and heat-drying the resulting reaction product within about 2 hours of the time said resulting mixture is prepared.

7. A process for manufacturing a heat-dried detergent composition that contains sodium tripolyphosphate, a predetermined proportion of which is hydrated, which process comprises the steps of intermixing sodium trimetaphosphate, Form II sodium tripolyphosphate and from about 2 to about 8 mol equivalents, based on the amount of said sodium trimetaphosphate, of sodium hydroxide in an aqueous medium at a temperature above about 75° C., the initial weight ratio of said sodium trimetaphosphate to said sodium tripolyphosphate being about 1/1.2 times said predetermined proportion; maintaining the temperature of the resulting mixture above about 85° C. until it is heat-dried; and heat-drying said resulting mixture within about 20 minutes after said sodium trimetaphosphate and said base are intermixed.

8. A continuous process for manufacturing a spray-dried composition containing hydrated sodium tripolyphosphate, which process comprises the steps of making a fluid aqueous slurry by blending together in a flowing stream of material at least about 5 percent, based on the weight of resulting blend, of a sodium trimetaphosphate, at least about 10 percent, based on the weight of the resulting blend, of water, sodium hydroxide, the amount of said sodium hydroxide in said slurry being sufficient to furnish between about 1.5 and about 8 mol equivalents of hydroxide ions per mol of said sodium trimetaphosphate in said slurry, and thereafter transforming said stream of material into a spray in a drying atmosphere, whereby said spray-dried composition is produced.

9. A process as in claim **7**, wherein said sodium hydroxide is replaced by sodium carbonate.

10. A process as in claim **7**, wherein said sodium hydroxide is replaced by sodium silicate having an SiO_2/Na_2O ratio below 2.

11. A process for manufacturing a heat-dried detergent composition containing penta sodium tripolyphosphate, which process comprises the steps of preparing an aqueous slurry containing at least about 20 weight percent of water, from about 8 to about 64 weight percent, based on the weight of said detergent composition, of sodium trimetaphosphate, and at least about 1.2 moles of sodium hydroxide per mole of said sodium trimetaphosphate, and thereafter heat-drying the resulting mixture.

12. A process for manufacturing a heat-dried detergent composition containing penta sodium tripolyphosphate, which process comprises the steps of preparing an aqueous slurry containing at least about 20 weight percent of water, from about 8 to about 64 weight percent, based on the weight of said detergent composition, of sodium trimetaphosphate, and at least about 1.2 mole equivalents of sodium carbonate per mole of said sodium trimetaphosphate, and thereafter heat-drying the resulting mixture.

13. A process for manufacturing a heat-dried detergent composition containing hydrated pentasodium tripolyphosphate and a water-soluble surface active agent which is compatible with said pentasodium tripolyphosphate, said surface active agent benig selected from the group consisting of organic synthetic nonionic and non-soap anionic surface active agents, which process comprises the steps of (a) preparing an aqueous slurry containing at least about 20 weight percent, based on the weight of the resulting mixture, of water; said water-soluble surface active agent; at least about 10 weight percent, based on the weight of the resulting mixture, of sodium trimetaphosphate; and sodium hydroxide; said sodium hydroxide being present in said aqueous slurry in an amount sufficient to furnish about 2 mole equivalents of hydroxyl ions per mole of said sodium trimetaphosphate; (b) holding said aqueous slurry at a temperature above about 50° C. until at least about 30 weight percent of said sodium trimetaphosphate has been converted to tripolyphosphate; and (c) thereafter heat-drying the resulting aqueous slurry.

14. The detergent product obtained by (a) reacting together in a fluid aqueous slurry at a temperature above about 50° C. and in the presence of a surface active agent selected from the group consisting of anionic and nonanionic surface active agents, sodium trimetaphosphate and a base selected from the group consisting of alkali metal hydroxides, alkali metal carbonates, alkali metal silicates having an SiO_2/M_2O ratio, where M is an alkali metal cation, lower than 2, and mixtures thereof; said slurry initially containing at least about 20 weight percent of water and at least about 10 weight percent of said sodium trimetaphosphate, and the amount of said base being sufficient to furnish between about 1.5 and about 8 mole equivalents of hydroxyl ions per mole of said sodium trimetaphosphate; and (b) thereafter heat-drying said fluid aqueous slurry.

References Cited by the Examiner

UNITED STATES PATENTS

2,019,665	11/1935	Fiske et al.	23—106
2,244,158	6/1941	Hubbard et al.	
2,365,190	12/1944	Hatch	252—135
2,622,068	12/1952	Huzer	252—135 XR
2,947,701	8/1960	Ruff	252—109

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