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DRY-MIXED DETERGENT COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Dry-mixed, built detergent compositions which are resistant to formation of objectionable fines, are provided by blending a granular sodium tripolyphosphate prepared from sodium orthophosphate and adjusted to a water content of 0.4 to 8%, and at least one of a water-soluble, non-soap, organic synthetic anionic or nonionic detergent, a sodium silicate, a chlorocyanuric compound, chlorinated trisodium phosphate, an alkali metal carbonate and an inert water-soluble inorganic filler.

This invention relates to dry-mixed built detergent compositions, and particularly to such compositions which contain a granular sodium tripolyphosphate produced by heating sodium orthophosphate and modified by a special treatment to render it resistant to breaking down into fines on handling.

Built detergent compositions useful in automatic washing machines, dishwashers, sanitizing applications, bleaching applications and the like are available in tablet, granular and liquid forms. The tablet and granular forms have particular advantage because they are easily handled and stored as compared with the liquid materials, and because with them it is not necessary to ship and store water as is the case with liquid compositions. This invention is concerned with the dry compositions, namely the tablet and granular varieties.

These dry compositions generally contain sodium tripolyphosphate as a builder and any or all of an anionic or nonionic surfactant, an anti-corrosion agent such as sodium silicate, a chlorinated cyanuric compound such as trichlorocyanuric acid, dichlorocyanuric acid or a salt of dichloro cyanuric acid, chlorinated trisodium phosphate, an alkali carbonate, and an inert inorganic filler such as sodium sulfate, sodium chloride, sodium orthophosphate and the like. The surfactant and the sodium tripolyphosphate are the principal cleaning components, while the sodium silicate prevents the alkaline detergent from attacking metallic parts of washing machines and the like with which it comes into contact when dissolved in water in use. The chlorinated cyanuric compound serves as a sanitizing and bleaching agent and the filler is employed as an extender to obtain the desired bulk density and to provide smoother tablets and more uniform compositions. The makeup of the compositions depends on the ultimate use to which they will be put.

There are basically two methods of preparing these dry compositions. One method involves forming an aqueous slurry of the sodium tripolyphosphate and other ingredients, while the other simply involves dry-blending the ingredients and either using them directly as granular compositions or tableting them. The dry-blending system has the obvious advantage of ease of operation in not requiring drying, for example spray-drying to provide the final product.

The dry-blending method has a serious drawback, however. Granular sodium tripolyphosphate prepared by the common method of heating sodium orthophosphate having an Na/P mole ratio of 1.67 to 1 at a temperature of about 300° to 550° C., reducing the product in size and screening out the desired granular fraction having a particle size of about 20 to 100 mesh, has a tendency to break down into fines (particles smaller than about 100 mesh) on typical handling in manufacture and bulk storage or shipment, as well as in compounding. The fines produced are objectionable in production of tablets which they frequently cause to be non-uniform and/or weak and friable, and in compounded granular compositions, in which they segregate from the remainder of the composition and provide objectionable dustiness.

It therefore has been desired, and it is an object of our invention, to provide uniform dry-mixed built detergent compositions containing a granular sodium tripolyphosphate which is especially resistant to breakdown into fines.

We have now found it possible to provide such uniform dry-mixed built detergent compositions by dry-mixing (a) a granular sodium tripolyphosphate produced by heating sodium orthophosphate at a temperature of about 300° to 550° C., cooling the sodium tripolyphosphate produced thereby to less than about 70° C., providing about 0.4 to 8%, and preferably 0.7 to 4%, of water into the resulting sodium tripolyphosphate (the sodium tripolyphosphate being crushed and screened to granular size particles at any stage of the above process following the heating of the orthophosphate), with (b) at least one of a water soluble, non-soap organic synthetic anionic or nonionic detergent, sodium silicate, a chlorocyanuric compound, chlorinated trisodium phosphate, an alkali carbonate and an inert inorganic filler. The compositions may be provided in their mixed granular form, or they may be tableted. Throughout the specification and in the claims appended hereto, reference to compositions as being "dry-mixed" means compositions which are not slurried or dissolved in a liquid in compounding, and which are free-flowing, solid compositions. The 0.4 to 8% of water in our improved granular sodium tripolyphosphate does not cause compositions prepared from it to fall outside the category of dry-mixed compositions.

The granular sodium tripolyphosphate employed in the compositions of our invention is prepared by drying conventional orthophosphate liquors having an Na/P ratio of about 1.67 to 1, and calcining the resulting dried material at about 300° to 550° C. in conventionl equipment, preferably a rotary drier, a spray drier, a fluid bed system or the like. The sodium tripolyphosphate produced thereby normally is crushed and screened to the desired granular particle size of about −16 +100 mesh, at any stage following heating of the orthophosphate, and normally during or after cooling of the product to 70° C. or below. Sodium tripolyphosphate produced by this means normally contains less than about 0.2% of water, and is subject to breakdown into fines on mechanical handling such as airveying or other commonly used operations. The fines produced on such handling are particles having a size smaller than about 100 mesh; they sometimes are extremely fine, being smaller than 400 mesh.

The granular sodium tripolyphosphate produced as described above is prepared for use in our compositions by incorporation into it of sufficient water to provide a water content of about 0.4 to 8% by weight, and preferably about 0.7 to 4% by weight. The water is incorporated by exposing the sodium tripolyphosphate to a humid atmosphere, preferably while the sodium tripolyphosphate is in fluidized state, by spraying water into the material while it is undergoing agitation, or the like. The water is added when the sodium tripolyphosphate is at a temperature of less than about 70° C., and preferably at less than about 50° C., in order to avoid hydrolytic degradation of the tripolyphosphate to ortho- or pyrophosphate, which sometimes occurs upon addition of water to hot sodium tripoly phosphate.

The amount of water present in sodium tripolyphos-

phate is determined conveniently by heating the material at 150° C. for one hour and observing the weight loss produced thereby.

Granular sodium tripolyphosphate treated as described above, and containing the indicated 0.4 to 8% of water, has a greatly reduced tendency to form fines, that is particles having a size smaller than 100 mesh. Granular sodium tripolyphosphate not treated to contain our 0.4 to 8% of water often powders to the extent of about 10 to 20% or even more under actual use conditions, for example in shipment or storage of the sodium tripolyphosphate, and in bulk handling of the material for example in pneumatic and mechanical systems frequently employed in handling the material in shippers' and users' facilities. Products which powder, or produce fines, to the extent of much more than about 6% are objectionable, so that a real improvement in the ordinary granular sodium tripolyphosphate of commerce is required for the material to be made entirely suitable for use in manufacture of granular and tableted detergent compositions.

The susceptibility of the granular sodium tripolyphosphate to particle breakdown, its so-called "friability value" is readily determined by measuring the percentage increase in —100 mesh material produced by subjecting the granular material to a high velocity jet of air in a fluid bed. The test method, described as follows correlates well with the actual results obtained when sodium tripolyphosphate is transferred from a truck or railroad car into a user's storage facility by means of typical pneumatic and mechanical equipment, an operation quite representative of the kind of handling encountered by the material in actual use. A fifty-gram sample of the sodium tripolyphosphate having a particle size within the range of—20 +100 U.S. Standard mesh is fluidized for 10 minutes in a one inch diameter, two-foot high glass tube fitted at the top with a Soxhlet extraction thimble and at the bottom with an air inlet and orifice plate having a 0.016 inch hole in its center at an air flow of 0.25 standard cubic feet per minute which is achieved at an air pressure of 50 p.s.i.g. The sample is then removed from the glass tube and its content of particles smaller than 100 U.S. standard mesh is determined by screening on an appropriate sieve. The weight percentage of the material which is smaller than 100 mesh, and therefore which passes through the 100 mesh screen is taken as the friability value. A product having a friability value of up to about 6% is satisfactory for use. Before being subjected to the friability test, all samples are screened to remove material already smaller than 100 mesh.

In preparing the dry-mixed built detergent compositions of our invention, the principal ingredient, the granular sodium tripolyphosphate containing the herein 0.4 to 8% of water, is measured into a mixer in an amount sufficient to provide about 20 to 90% by weight of the composition. A surface active agent, which may be either anionic or nonionic, also is desirable in many compositions. Certain cationic surfactants cannot be employed because they are incompatible with sodium tripolyphosphate. When used the surfactant is added to the mixture in the amount of about 0.5 to 50% by weight of the composition.

A sodium silicate having an Na_2O to SiO_2 mole ratio of about 1:1 to about 1:3.2 in an amount of about 0.5 to 50% by weight may be included in the formulation as an anti-corrosion agent and for its building and alkaline properties. The mole ratio of Na_2O to SiO_2 in the silicate determines its alkalinity; as the ratio approaches 1:1 the sodium silicate becomes more alkaline. At Na_2O to SiO_2 ratios below 1:3.2, for example about 1:4, the materials dissolve too slowly and are not normally effective.

Another ingredient which is often useful in these formulations is a chlorocyanuric compound which may be trichlorocyanuric acid, dichlorocyanuric acid or the alkali metal or alkaline earth metal salts of dichlorocyanuric acid exemplified by sodium dichlorocyanurate, potassium dichlorocyanurate, calcium dichlorocyanurate and the like. These materials, which serve as sanitizing and bleaching agents, are solids available in granular form. When used they generally are employed in amounts of about 0.5 to 20% by weight. Another useful chlorinated compound which may be used is chlorinated trisodium phosphate, useful in amounts of about 0.5 to 50% as a sanitizing agent.

The alkali carbonates are also useful additives for many formulations. Typical carbonates are sodium sesquicarbonate and sodium carbonate which are useful in an amount of about 0.5 to 50%. Inert inorganic fillers also may be employed to advantage in these compositions. Typical fillers include sodium sulfate, sodium chloride, sodium orthophosphate and the like. Where used they control the bulk density of the composition and improve the surface appearance and strength of tablets containing them.

In addition, small amounts of auxiliary compounds such as sodium carboxymethylcellulose, normally in an amount of 0.2 to 1.5% foam stabilizers such as lauroyl diethanolamide, tarnish inhibitors, fluorescent brighteners, perfumes, basteriostats, coloring matter and the like may be employed in our compositions. Where it is desired to employ them as granular mixes they are merely packaged in their mixed form. Where it is desired to form them into tablets, they are uniformly mixed and then compressed into tablets. The pressing normally is carried out at a pressure of on the order of 100 to 350 p.s.i. and the finished tablet has a bulk density in the range of about 0.8 to 1.3. The tablets normally have strengths (when pressed on edge) of about 10 to 15 pounds or more. If the tablets are suitably aged for at least 24 hours, they have a strength (when pressed on edge) of up to about 25 pounds.

Anionic surface active agents are useful in our formulation in amounts of from about 0.5% to about 50% by weight. These anionic surface active agents are non-soap synthetic detergents made up of water soluble salts of organic sulfuric reaction products having from about 8 to about 18 carbon atoms in the form of a straight-chain or branched chain alkyl radical or an acyl radical within the molecular structure and containing sulfuric or sulfonic acid ester radicals. Typical examples of these anionic surface active agents are sodium or potassium alkyl benzene sulfonates or sodium or potassium alkyl sulfates or sulfonates in which the alkyl group, which may be straight or branched chained, contains from about 8 to about 18 carbon atoms, e.g. sodium dodecyl benzene sulfonate, sodium tridecyl benzene sulfonate; the sodium and potassium alkyl glycerol ether sulfonates, including ethers of higher fatty alcohols derived from the reduction of coconut oils; the reaction products of isethionate; sodium or potassium alkyl sulfonates and sulfates obtained by sulfonation of coconut or tallow fatty alcohols and mixtures of such alkyl sulfates; dialkyl esters of sodium or potassium salts of sulfosuccinic acid; sodium or potassium salts of sulfates or sulfonated monoglycerides, e.g. those derived from coconut oil; sodium or potassium salts of higher fatty alcohol esters of sulfocarboxylic acids, e.g. sodium salt of lauryl alcohol ester of sulfoacetic acid; and other anionic agents set forth in U.S. Patent 2,486,921 issued to Byerly on Nov. 1, 1949. If desired, the anionic surfactant can be added in the form of a dense, dry bead or as a flake admixed with sodium sulfate. In this latter case, the sodium sulfate constitutes a portion of the total sodium sulfate used in making up the entire mixture.

The nonionic surface active agents useful in the present invention are non-soap synthetic detergents made up of a water solubilizing polyoxyethylene group in chemical combination with an organic hydrophobic compound. Among the hydrophobic compounds which can be used are polyoxypropylene, the reaction product of propylene oxide and ethylene diamine, aliphatic alcohols, etc.

Examples of the nonionic synthetic detergents useful

in the present invention are, condensation products of 6 to 30 moles, and preferably 7 to 11 moles, of ethylene oxide with 1 mole of an alkyl phenol containing 6 to 12 carbon atoms in the alkyl group; condensation products of 6 to 30 moles of ethylene oxide with 1 mole of an aliphatic straight or branch chained alcohol containing 8 to 18 carbon atoms; condensation products of ethylene oxide and the reaction product of propylene oxide and ethylene diamine; nonyl phenol polyethoxy ethanol (commercially known as "Triton N" series); isooctyl phenol polyethoxy ethanol (commerically known as "Triton X" series). Another well known group of nonionic detergents is marketed as "Pluronic" series. These compounds are the reaction products obtained by condensing ethylene oxide with a hydrophobic base produced by the condensation of propylene oxide with propylene glycol, and have molecular weights on the order of about 1800. The addition of polyoxyethylene radicals to the hydrophobic base increases the water solubility of the nonionic detergent and concurrently increases the foaming properties of the detergent in aqueous solution in proportion to the mole ratio of polyoxyethylene radicals to the hydrophobic base. In general, a surfactant which has a mole ratio of 7.5 moles of ethylene oxide per mole of an alkyl phenol, e.g. nonyl phenol, is low-foaming while one with a mole ratio of 10:1 foams moderately. The molecular weight of these nonionic synthetic detergents will range from as low as 800 up to about 11,000.

Nonionic surfactants should be employed in the herein compositions in the amount of about 0.5 to 15% by weight of the total composition in order for the surfactant to be completely effective. Amounts over 15% should be avoided because the nonionic surfactant tends to exude or "oil out" of the detergent formulation when it is pressed into tablets. Within the range of 0.5 to 15% the nonionic surfactant gives effective washing action, and has been found to be effective as a binder for the remainder of the detergent formulation without "oiling out" of the pressed tablet.

The following examples are presented by way of illustration only, and are not intended to limit the scope of our invention in any way. All percentages are given by weight.

Example 1.—Preparation of sodium tripolyphosphate

Sodium tripolyphosphate was prepared by a typical commercial rotary drier process in which soda ash and phosphoric acid were added to water in sufficient quantities to provide a mole ratio of Na/P of about 1.67:1 and a density of 53° Baume. The heat of reaction was sufficient to increase the temperature of the solution to about 100° C. and drive off most of the carbon dioxide formed. The resulting solution was fed to a drier to remove the free water and the dry orthophosphate salts were further heated by exposure to hot gases in a rotary kiln till the temperature of the product was about 500° to 520° C. The product was then removed from the kiln, partially cooled, crushed and screened to separate a −20+100 mesh granular fraction which was used in the following examples. The friability value of this material as prepared was 12% Another sample of granular sodium tripolyphosphate was prepared, having a friability of 8%. These samples of sodium tripolyphosphate were employed in the examples which follow.

Example 2.—Incorporation of water in the granular sodium tripolyphosphate

A. Five hundred and fifty grams of the granular product as produced in Example 1, and having a friability value of 8%, were placed in a 3-inch I.D., one foot high glass column, and a stream of humid air having a water vapor pressure of 24 mm. Hg was passed up through the bed at a flow rate sufficient to give a slow turn-over of the granules in the bed. The temperature within the bed was 50° C. Samples were taken after 15 and 50 minutes and tested for moisture content and friability. Another 550 gram portion was treated in the same manner, but in this case the humid air had a water vapor pressure of about 92 mm. Hg. Water contents and friability values of the treated materials are given in Table 1 which follows:

Humid Air Treatment		Product Analysis	
Time, min.	H_2O Vapor, mm. Hg	Percent H_2O	Friability Value, Percent
None	----------	0.05	8
15	24	0.15	8
60	24	0.4	5.3
15	92	1.15	2.5
30	92	1.55	2.4
60	92	2.14	3.1
120	92	4.20	4.3

B. A sample of rotary calcined granular sodium tripolyphosphate prepared as described in Example 1, and having a friability value of 12%, was subjected to the same humid air treatment as used in Example 2A above with the results reported in Table 2 which follows:

TABLE 2

Humid Air Treatment		Product Analysis	
Time, min.	H_2O Vapor, mm. Hg	Percent H_2O	Friability Value, Percent
None	----------	0.05	12
15	24	0.15	7.3
30	24	0.4	5.6
5	92	0.4	3.8
15	92	1.25	3.7
60	92	2.30	5.1
90	92	3.30	2.5
120	92	4.03	3.9

Example 3.—Incorporation of water in the granular sodium tripolyphosphate

A sample of rotary calcined granular sodium tripolyphosphate prepared as described in Example 1, and having a friability of 8% was moisturized by addition of liquid water. About 15 pounds of the product was agitated in a laboratory ribbon blade mixer while water was added as a fine spray. Samples were removed and analyzed for moisture content and friability with the results shown in Table 3 which follows:

TABLE 3

	Percent H_2O	Friability Value, Percent
Sample 3A	0.09	8
	0.39	5.5
	0.83	3.7
	3.4	3.6
	4.4	2.7
	6.3	3.2
	7.4	4.2
Sample 3B	0.01	8
	0.71	2.5
	1.80	2.3

Example 4.—Granular compositions

Granular compositions having the formulations shown in Table 4 which follows, were prepared by dry-mixing the indicated ingredients in a laboratory ribbon blade mixer until homogeneous mixtures were obtained. The sodium tripolyphosphate used was first subjected to simulated handling conditions, as described above with reference to the friability value test. The compositions were examined for possible segregation and dustiness. None of the formulations prepared with the granular sodium tripolyphosphate treated in accordance with the moisture

addition method of our invention demonstrated any substantial segregation of ingredients or objectionable dustiness.

Formulations were prepared with granular sodium tripolyphosphate not treated with moisture in accordance with the method of our invention but otherwise the same as samples 4*a*, 4*b*, 4*c* and 4*d*, segregated bady and were quite dusty.

TABLE 4.—GRANULAR BUILT DETERGENT FORMULATIONS CONTAINING SODIUM TRIPOLYPHOSPHATE TREATED WITH WATER IN ACCORDANCE WITH THIS INVENTION

Ingredient, Weight Percent	Type			
	Laundry Detergent	Hard Surface Cleaner	Machine Dishwashing Detergent	Hand Dishwashing Detergent
	Example No.			
	4*a*	4*b*	4*c*	4*d*
Granular sodium tripolyphosphate (.5% water, 2.5 friability value)	40		30	
Granular sodium tripolyphosphate (4% water, 3.9 friability value)		28		30
Anionic spray dried beads [1]	60			
Disodium phosphate		10		
Sodium sesquicarbonate		48		
Sodium carbonate		12.5	26	
Spray dried beads (40% alkyl benzene sulfonate 60% sodium sulfate)		1.5		40
Sodium metasilicate			30	
Sodium dichlorocyanurate			2.5	
Low-foaming nonionic surfactant [2]			1.5	
Sodium sulfate				30

[1] The beads were composed of 41.9% of sodium tridecyl benzene sulfonate, 0.9% of a carboxymethyl-cellulose, 36.4% of sodium sulfate, 8.2% of sodium metasilicate and 12.6% of sodium chloride.

[2] Polyethoxylated isooctyl phenol with terminal isobutyl groups.

Example 5.—Tablets

A granular sodium tripolyphosphate prepared in accordance with the process of Example 1 and having a friability value of 12% was treated with water in accordance with the process of Example 2, employing humid air to provide 1% of water on the tripolyphosphate thereby improving its friability value to 4%. Products from the herein described friability test were used as the sodium tripolyphosphate ingredients; these products have the characteristics of sodium tripolyphosphate samples handled in commercial pneumatic and mechanical bulk handling equipment.

These materials were stirred together with amounts of anionic spray dried beads having a particle size of about 30 to 70 mesh to provide 60 to 40% by weight tripolyphosphate-anionic spray dried bead-granular mixtures. The beads employed were composed of 41.9% of sodium tridecyl benzene sulfonate, 0.9% of carboxymethylcellulose, 36.4% of sodium sulfate, 8.2% of sodium metasilicate and 12.6% of sodium chloride. These mixtures of the sodium tripolyphosphates and the beads were then compacted into tablets having a diameter of 1¾ inches and thicknesses of 1 inch, and weighing 50 grams.

The tablets made with our improved sodium tripolyphosphate containing the herein amount of water were uniform in strength and dissolving characteristics. On the other hand, the composition of the sodium tripolyphosphate not treated as herein, and containing the above described 12% of fines was difficult to tablet uniformly because of the difficulty of maintaining a uniform feed, without segregation of the fines, to the tableting machine. Thus, the resulting tablets tended to be less uniform in strength, density and dissolving characteristics.

Pursuant to the requirements of the patent statutes, the principle of this invention has been explained and exemplified in a manner so that it can be readily practiced by those skilled in the art, such exemplification including what is considered to represent the best embodiment of the invention. However, it should be clearly understood that within the scope of the appended claims the invention may be practiced by those skilled in the art, and having the benefit of this disclosure otherwise than as specifically described and exemplified herein.

What is claimed is:

1. A process of producing uniform dry-mixed built detergent compositions free of objectionable amounts of fines, which essentially involves dry-mixing (a) 20 to 90% of a granular sodium tripolyphospate having a particle size of −16 to +100 mesh produced by heating sodium orthophosphate having an Na to P ratio of about 1.67 to 1 at a temperature of about 300° to 550° C. to produce essentially anhydrous sodium tripolyphosphate, cooling said sodium tripolyphosphate to below 70° C. and providing 0.4 to 8% of water in said cooled sodium tripolyphosphate; and (b) at least one member from the group consisting of 0.5 to 50% of a water-soluble, non-soap organic synthetic water-soluble anionic or water-soluble nonionic detergent, 0.5 to 50% of a sodium silicate having a molar ratio of Na_2O to SiO_2 of about 1:1 to 1:3.2, 0.5 to 20% of a water-soluble chlorocyanuric compound, 0.5 to 50% of chlorinated trisodium phosphate, 0.5 to 50% of an alkali metal carbonate and an inert water-soluble inorganic filler.

2. The process of claim 1 in which the sodium tripolyphosphate has in it 0.7 to 4% of water.

3. The process of claim 1 in which the dry-mixed composition is compressed into tablets.

4. The process of claim 1 in which the dry-mixed composition is in the form of a granular composition.

5. A uniform dry-mixed built detergent composition free of objectionable amounts of fines, essentially containing (a) 20 to 90% of a granular sodium tripolyphosphate having a particle size of about −16 to +100 mesh produced by heating sodium orthophosphate having an Na to P ratio of about 1.67 to 1 at a temperature of about 300° to 550° C. to produce essentially anhydrous sodium tripolyphosphate, cooling said sodium tripolyphosphate to below 70° C. and providing 0.4 to 8% of water in said cooled sodium tripolyphosphate; and (b) at least one member from the group consisting of 0.5 to 50% of a water-soluble, non-soap organic synthetic water-soluble anionic or water-soluble nonionic detergent, 0.5 to 50% of a sodium silicate having a molar ratio of Na_2O to SiO_2 of about 1:1 to 1:3.2, 0.5 to 20% of a water-soluble chlorocyanuric compound, 0.5 to 50% of chlorinated trisodium phosphate, 0.5 to 50% of an alkali metal carbonate and an inert water-soluble inorganic filler.

6. The composition of claim 5 in which the sodium tripolyphosphate has in it 0.7 to 4% of water.

7. The composition of claim 5 in which the dry-mixed built detergent composition is in the form of a tablet.

8. The composition of claim 5 in which the dry-mixed built detergent composition is in the form of a granular composition.

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