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DRY-MIXED DETERGENT COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Dry-mixed built detergent compositions of a granular, compacted sodium tripolyphosphate having a specified density and particle size and having distributed on it 2.5 to 7% of water, together with at least one of a water-soluble, non-soap synthetic anionic or nonionic detergent, a sodium silicate, a chlorocyanuric compound, chlorinated trisodium phosphate, an alkali carbonate and an inert organic filler, are provided.

This invention relates to dry-mixed built detergent compositions, and particularly to such compositions which contain as an essential component fast-hydrating, dense sodium tripolyphosphate builder in a form in which it is readily soluble without caking under adverse dissolving conditions.

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 dichlorocyanuric 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 method 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.

A serious problem is inherent in dry-blending compositions, however, which is not as aggravated in forming the compositions from slurries. Sodium tripolyphosphate, an essential constituent of these compositions, is erratic in its dissolving characteristics. Its dissolution in water in end use or in some cases in subsequent processing sometimes is slowed, and the material even cakes into insoluble, adhesive masses if entrapped temporarily in a piece of clothing or if not properly agitated, such as might occur in a washing machine or upon pouring the granular composition into a container of water without agitation. Even absent such a condition, compositions containing more than about 75% of sodium tripolyphosphate frequently cake in water. This problem is particularly aggravated in dry-mixed compositions, whose preparation does not expose them to water. When the compositions are prepared in water, a tendency in the sodium tripolyphosphate to give serious trouble in dissolving on use of the composition, often shows up during preparation of the composition.

In an attempt to overcome this unpredictable and serious dissolving problem, as well as to provide a dense sodium tripolyphosphate of regular particle size, H. L. Marschall et al., provided a method of producing a sodium tripolyphosphate having a density of about 1.0 to 1.25 g./cc., and a desirable hydration and dissolving rate. Their method comprises compacting the sodium tripolyphosphate at a high pressure into a large, dense mass of the material, and grinding this mass to the proper particle size. This is taught in the Marschall et al. U.S. patent application, Ser. No. 289,315, filed June 20, 1963 and assigned to the assignee of this invention.

The dense, granular sodium tripolyphosphate provided by Marschall et al., referred to hereinafter as "compacted" sodium tripolyphosphate, has a faster rate of dissolution in water under normal conditions, than does sodium tripolyphosphate not produced by their method. However, it has not been found in practice to solve all problems relative to dissolving. While under normal conditions it dissolves in water more readily than does non-compacted sodium tripolyphosphate, there are certain adverse conditions, for example when a composition contains on the order of 75% or more of sodium tripolyphosphate or when the composition is not agitated when added to water or is temporarily entrapped such as in a piece of clothing in a washing machine or in a dispenser of the kind used for example in a home dishwasher, which cause it to cake and not dissolve despite its normally fast dissolving characteristic.

It therefore has remained desirable, and it is an object of this invention, to provide a sodium tripolyphosphate which not only has a fast dissolving rate under normal dissolution conditions, but also which dissolves readily without caking under adverse conditions.

I have now found it possible to provide an improved form of compacted sodium tripolyphosphate which produces dry-mixed built detergent compositions which dissolve readily without caking under normal, and also under adverse, dissolving conditions. The improved compacted sodium tripolyphosphate of my invention is provided by uniformly distributing on a compacted sodium tripolyphosphate containing 0 to 0.7% by weight of water, an amount of water to increase the amount of water in the tripolyphosphate to 2.5 to about 7%, and preferably 2.5 to 4%, by weight. This improved material is then dry-mixed in a composition containing by weight about 20 to 90% of my sodium tripolyphosphate and any or all of 0 to 50% of a water-soluble, non-soap organic synthetic detergent which may be an anionic or nonionic detergent, about 0.5 to 50% of sodium silicate, 0.5 to 20% of a chlorocyanuric compound, 0.5 to 50% of chlorinated trisodium phosphate, 0.5 to 50% of an alkali carbonate and 0.5 to 60% of an inert inorganic filler. The components present in a given composition vary as the composition's end use varies, and a variety of combinations of these added ingredients in practice are used with my improved sodium tripolyphosphate. These compositions may be granular, in which case they are produced by simply mixing the components together, or in tableted form, in which

case the granular compositions are tableted under pressure. 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 2.5 to 7% of water in my improved compacted sodium tripolyphosphate obviously does not cause compositions prepared from it to be removed from this dry-mixed category.

For some reason which is unknown to me, sodium tripolyphosphate which has not been compacted by the process of the Marschall et al. patent application referred to above to produce a uniform sodium tripolyphosphate product having a density of about 1.0 to 1.25 g./cc., does not respond to addition of moisture in the above amounts at all in the same fashion as does the compacted material. It is most surprising, therefore, that it is possible to effect the herein improvement of dry-mixed built detergent compositions by employing in them compacted sodium tripolyphosphate treated in accordance with my invention.

The improved sodium tripolyphosphate employed in preparing the compositions of my invention is produced from the Marschall et al. compacted material in accordance with my invention by exposing it to a humid atmosphere, preferably while the sodium tripolyphosphate is in fluidized state, by spraying water into the tripolyphosphate while the latter is undergoing agitation or the like. The amount of water present in the sodium tripolyphosphate is analyzed by heating the sodium tripolyphosphate at 150° C. for one hour and observing the weight loss produced thereby. Normally the moisture content of the compacted sodium tripolyphosphate before treating is about 0 to 0.7% depending on conditions encountered in preparing the material and in storing it.

I have found the minimum amount of water required to be present in the compacted sodium tripolyphosphate to provide a material useful in providing the herein highly soluble compositions to be quite critical, as shown by a so-called "caking" test. This test involves placing a 10-gram sample of the sodium tripolyphosphate in granular form in a porcelain crucible (Coors No. 2) and carefully adding 6 ml. of distilled water to completely cover the tripolyphosphate. The tripolyphosphate is then probed gently with a dissecting needle at 10 second intervals, and the time at which caking (the formation of a hard mass of material) occurs is noted.

The dependence on its water content of the ability of compacted, granular sodium tripolyphosphate to withstand caking and the specificity of this property to compacted tripolyphosphate are demonstrated in Tables 1 and 2 which follow:

TABLE 1.—CAKING TIME OF COMPACTED GRANULAR SODIUM TRIPOLYPHOSPHATE

[Particle size −20 +100 mesh, U.S. Standard]

Water content, percent:	Caking time, seconds
Anhydrous	10
0.5	10
1	10
2.0	10
2.1	10
2.2	10
2.5	300+
3.0	300+
4	300+
5	300+
7	300+

TABLE 2.—CAKING TIME OF NON-COMPACTED GRANULAR SODIUM TRIPOLYPHOSPHATE[1]

Water content, percent:	Caking time, seconds
Anhydrous	20
0.5	15
1.0	15
2.0	20
3.0	40
4.0	65
5.0	90

[1] −20 +100 mesh, produced by rotary calcining.

Caking times of on the order of 300 seconds or more are indicative of a product which will dissolve readily in use, regardless of the existence of adverse conditions.

In preparing the dry-mixed, built detergent compositions of my invention, the principal ingredient, the compacted sodium tripolyphosphate containing the herein amount of water, is measured into the detergent formulation in amount sufficient to constitute about 20 to 90% by weight of the composition. Preferably it has a particle size of about −16 to +100 mesh with no more than about 20% being −70 mesh.

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 the compacted 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 amount of about 0.5 to 50% by weight may be included in the formulation also 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. Ratios below 1:3.2, for example 1:4, dissolve too slowly and are not 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 and are available in granular form. When used they generally are employed in amounts of about 0.5 to 20% by weight. Another useful chlorinated compound is chlorinated trisodium phosphate which may be used in an amount of 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 in these compositions. Typical fillers include sodium sulfate, sodium chloride, sodium orthophosphates 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 carboxymethyl cellulose, normally in an amount of 0.2 to 1.5%, foam stabilizers such as lauroyl diethanolamide, tarnish inhibitors, fluorescent brighteners, perfumes, bacteriostats, coloring matter and the like may be employed in my compositions. Where it is desired to employ the compositions 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 my 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 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 (commercially 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 or above 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 of this invention only, and are not to be considered as limiting the scope thereof in any way. All amounts are present by weight.

Example 1.—Tablets

A compacted sodium tripolyphosphate having a density of 1.2 g./cc. and a particle size of −20 +100 mesh was treated with water by spraying while the sodium tripolyphosphate was being agitated to provide a material having a water content of 3%. This material was stirred together with an amount of anionic spray dried beads to provide a 90–10% by weight tripolyphosphate-anionic spray dried bead granular mixture. The beads were composed of 41.9% of sodium tridecyl benzene sulfonate, 0.9% of carboxymethyl cellulose, 36.4% of sodium sulfate, 8.2% of sodium metasilicate and 12.6% of sodium chloride. This mixture of the sodium tripolyphosphate and the beads was then compacted into tablets having a diameter of 1¾ inches and a thickness of 1 inch, and weighing 50 grams.

A corresponding tablet was prepared in the same way from compacted sodium tripolyphosphate which had not been provided with the 3% of water, but rather was used with its initial amount of 0.5% of water.

The two tablets were placed in one-half inch wire mesh cages placed in a fixed position in a top-loading automatic home washing machine containing 16 gallons of agitated 100° F. tap water. The tablet containing my water-treated compacted sodium tripolyphosphate disintegrated in 71 seconds and entirely escaped from the cage, while a 9.9 gram core or cake of the tablet containing the compacted sodium tripolyphosphate not treated in accordance with my invention remained after 5 minutes in the washer.

The same kind of comparative results was obtained when samples containing 78% of sodium tripolyphosphate and the balance the anionic spray dried bead were tested, thus demonstrating that my water treatment of compacted sodium tripolyphosphate is effective in compositions containing both amounts of tripolyphosphate. These amounts are in the range in which sodium tripolyphosphate dissolution is erratic.

Example 2.—Tablets

Tablets containing 55 parts by weight of sodium tripolyphosphate and 45 parts of the anionic spray dried bead composition used in Example 1 were prepared and tested in the same way as were the tablets of Example 1. The tablets prepared with my water-treated compacted sodium tripolyphosphate disintegrated completely and left the cage in 115 seconds. The tablet prepared with the compacted sodium tripolyphosphate which was not water treated in accordance with my invention required 167 seconds to disintegrate and leave the cage.

Examples 3 to 6

Granular compositions having the formulations shown in Table 3 which follows, were prepared by dry mixing the indicated ingredients until homogeneous mixtures had been obtained. The examples identified by the letters A through D are comparative examples run with ordinary compacted sodium tripolyphosphate not treated in accordance with my invention. The compositions are given in Table 3 together with results of dissolution tests run with them, under conditions which would normally lead to caking. The test involved dropping a 10-gram sample of each composition into an individual beaker containing one liter of water at the indicated temperature. The composition was permitted to sit in the water for one minute

before agitation with a magnetically-operated stirrer was commenced. The ease of dispersion was noted. The granular compositions normally were of a particle size to pass through a 20 mesh screen and be retained on a 200 mesh screen, with the individual components varying within this range.

TABLE 3.—DISSOLVING PROPERTIES OF GRANULAR DETERGENT FORMULATIONS CONTAINING SODIUM TRIPOLYPHOSPHATE WITH AND WITHOUT THE WATER TREATMENT OF THIS INVENTION

	Type							
	Laundry Detergent		Hard Surface Cleaner		Machine Dishwashing Detergent		Hand Dishwashing Detergent	
	Ex. 3	Ex. A [1]	Ex. 4	Ex. B [1]	Ex. 5	Ex. C [1]	Ex. 6	Ex. D [1]
Composition, Wt. Percent:								
Compacted Sodium Tripolyphosphate (3% water)	40		28		30		30	
Compacted Sodium Tripolyphosphate (anhydrous)		40		28		30		30
Anionic Spray Dried Beads of Example 1	60	60						
Disodium Phosphate			10	10				
Sodium Sesquicarbonate			48	48				
Sodium Carbonate			12.5	12.5	26	26		
Spray Dried Beads (40% alkyl benzene sulfonate, 60% sodium sulfate)			1.5	1.5			40	40
Sodium Metasilicate					30	30		
Sodium Dichlorocyanurate					2.5	2.5		
Low-foaming Nonionic Surfactant (Polyethoxylated isooctyl phenol with terminal isobutyl groups)					1.5	1.5		
Sodium Sulfate							30	30
Dissolving Properties:								
Water temperature, ° F	120	120	90	90	140	140	90	90
Dissolving Properties	[2]	[3]	[2]	[4]	[2]	[4]	[2]	[4]

[1] Comparative.
[2] No cake.
[3] Soft cake.
[4] Hard cake.

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 dry-mixed, built detergent composition containing compacted sodium tripolyphosphate and being readily soluble in water without caking under adverse dissolving conditions, essentially containing 20 to 90% of a granular compacted sodium tripolyphosphate having a density of 1.0 g./cc. to 1.25 g./cc. and a particle size of about —16 to +100 mesh, said compacted sodium tripolyphosphate having uniformly distributed thereon 2.5% to 7% of water, and the balance of said composition essentially containing at least one of 0.5 to 50% of a water-soluble, non-soap organic synthetic detergent from the group consisting of water-soluble anionic detergents and water-soluble nonionic detergents, 0.5 to 50% of 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 chlorocyanuric compound from the group consisting of chlorocyanuric acids, an alkali metal or alkaline earth metal salt of dichlorocyanuric acid and mixtures thereof, 0.5 to 50% of chlorinated trisodium phosphate, 0.5 to 50% of an alkali metal carbonate and 0.5 to 60% of an inert inorganic filler.

2. The composition of claim **1** in which the sodium tripolyphosphate has distributed thereon 2.5% to 4% of water.

3. The composition of claim **1** in which the dry-mixed, built detergent composition is in the form of a tablet.

4. The composition of claim **1** in which the dry-mixed, built detergent composition is in the form of a granular composition.

5. A method of producing dry-mixed built detergent compositions essentially containing compacted sodium tripolyphosphate and being readily soluble in water without caking under adverse dissolving conditions, which essentially involves dry-mixing 20 to 90% of a granular compacted sodium tripolyphosphate having a density of 1.0 g./cc. to 1.25 g./cc. and a particle size of about —16 to +100 mesh, said compacted sodium tripolyphosphate having uniformly distributed thereon 2.5% to 7% of water, and the balance of said composition which essentially contains at least one of 0.5 to 50% of a water-soluble, non-soap organic synthetic detergent from the group consisting of water-soluble anionic detergents and water-soluble nonionic detergents, 0.5 to 50% of 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 chlorocyanuric compound from the group consisting of chlorocyanuric acids, an alkali metal or alkaline earth metal salt of dichlorocyanuric acid and mixtures thereof, 0.5 to 50% of a chlorinated trisodium phosphate, 0.5 to 50% of an alkali metal carbonate and 0.5 to 60% of in inert inorganic filler.

6. The method of claim **5** in which the sodium tripolyphosphate has distributed thereon 2.5% to 4% of water.

7. The method of claim **5** in which the dry-mixed, built detergent composition is compressed into tablets.

8. The method of claim **5** in which the dry-mixed, built detergent composition is granular.

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