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PROCESS FOR PREPARING DETERGENTS

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The present invention relates to improved detergent compositions and more particularly to novel processes for preparing such compositions. The present invention also relates to novel processes for preparing detergent compositions which have certain, hereinafter defined, improved characteristics and properties and which may be advantageously used in a wide variety of washing operations such as, for example, in dishwashing and laundering operations.

Detergent compositions containing water soluble, inorganic, builder salts such as sodium tripolyphosphate, tetrasodium pyrophosphate, sodium sulfate, sodium carbonate, sodium silicate, etc. and nonionic and/or anionic detergents are well known and have been widely used in washing operations, particularly in washing operations involving the use of automatic dishwashing and laundering machines designed for home use. Such compositions have been conventionally prepared by various known processes. In one such process mixtures of the inorganic builder salts have been mixed with small amounts of water to form granular products consisting of mixtures of hydrated salts. The granular products so-obtained were then mixed with organic surface active agents to form dry detergent compositions containing solid particles of organic surface active agents and particles or granules containing mixtures of the above mentioned salts. Conventional detergent compositions have also been prepared by simultaneously mixing the above mentioned detergent builder salts with water and organic surface active agents to form granules which consist of mixtures of builder salts and organic surface active agents. In some instances, when it has been desired to use large quantities of water, a fluid material is formed which is then conventionally spray dried to form granules, or alternatively is dried on a heated cylinder or drum or dried in an oven and ground to the particle or granular size which it was desired to obtain.

Detergent compositions prepared by the above processes possess a number of distinct disadvantages one of the most important of which is that a portion of the compositions prepared by the above-described conventional methods tend to lose their water solubility and develop "sand-like" residues upon being stored under ordinary conditions for periods of time up to two months or longer. The reason for such partial loss of water solubility and the formation of "sand-like" material in these compositions is not completely understood but it is believed that some of the components such as the water soluble inorganic salts, when processed by previously known methods, tend to form relatively water insoluble complex compounds when stored under ordinary storage conditions. The tendency to form and the formation of such water insoluble complex compounds in the compositions has a tendency to adversely affect the cleaning power of the compositions since the insoluble materials usually adhere to the surface of or become embedded in articles which are being washed in solutions in which the compositions are conventionally employed. Also when such compositions are prepared by processes which require heat drying in the presence of water it has been observed that there is an even greater tendency of such compositions to form such water insoluble materials therein. The previously known processes are also disadvantageous in that the densities of the compositions are difficult to control and compositions prepared by these processes sometimes have densities either below or above the densities necessary for the optimum use in automatic washing machines. Also when the processes involve a heat drying step they tend to become uneconomical due to the cost of heat and the cost of the drying equipment required to obtain the compositions.

Accordingly it is one object of the present invention to provide improved detergent compositions which are useful in washing operations and which do not have the aforementioned disadvantages of previously known compositions.

It is another object of this invention to provide novel processes for preparing detergent compositions.

It is still another object of this invention to provide novel economic processes for preparing stable, free flowing compositions comprising mixtures of previously known ingredients, which compositions remain completely water soluble when stored for prolonged periods of time.

Other objects and advantages of the present invention will become apparent from the following description and the appended claims.

The objects of this invention are attained in general by a process which comprises the steps of (1) partially to completely coating solid particles of a hydratable detergent builder with an organic surface active agent; (2) adding water, with agitation, to the coated particles in an amount at least sufficient to induce agglomeration and insufficient to substantially change the particle character of the particles and sufficient to form a wet fluid mass; (3) ageing the fluid mass until the water is substantially incorporated as water of hydration in the detergent builder and a friable agglomerated product comprising a mixture of hydrated detergent builder and the organic surface active agent is formed. As will be hereinafter evident the agglomerated product may then be readily ground by conventional means to the particle size desired.

The present invention resides in the above-described manipulative steps and particular sequence of steps applied to conventional ingredients of detergent compositions. In accordance with the processes of this invention it has been found possible to economically produce a wide variety of dry, stable compositions which do not form insoluble or difficultly soluble "sand-like" residues on storage and are more efficient in washing operations than detergent compositions prepared by previously known processes.

The term "hydratable detergent builder" as used herein, is intended to refer to and to include anhydrous to partially hydrated inorganic salts conventionally used as builders in detergent formulations. Such hydratable salts are capable of forming crystallized water of hydration upon contact with or in the presence of water.

The term "solid particle" as used herein, is intended to refer to and to include powders having a particle size such that all or substantially all of the particles will pass through a No. 200 mesh U.S. standard screen and granular particles having a particle size such that all or substantially all of the particles will be retained on a No. 200 mesh U.S. standard screen and mixtures thereof. Generally the solid particles which may be coated in accordance with the processes of this invention are powdered to granular particles having a particle size range such that all or substantially all of the particles will pass through a No. 10 mesh U.S. standard screen and all or substantially all of the particles will be retained on a No. 325 mesh U.S. standard screen.

The terms "agglomerate," "agglomeration," "agglomerated particles," as used herein, are intended to refer to

two or more solid particles adhered or bonded to each other upon or after contact or during hydration of the particles with water to form larger particles.

The solid particles of hydratable, detergent builder can be coated with an organic surface active agent by a variety of methods, such as for example dispersing or dissolving organic surface active agents in an inert non-aqueous liquid which may be contacted with the solid particles after which the liquid is evaporated. The solid particles may also be contacted with the liquid either by immersion in the liquid or by spraying the liquid from an atomizer onto the solid particles. Alternatively, and particularly when the organic surface active agent is a liquid, the particles may be contacted directly with the liquid organic surface active agent. For example the liquid surface active agent may be mixed with the solid particles in a mechanical mixer or may be mixed by tumbling the solid particles with the organic surface active agent.

The amount of surface active agent employed may vary considerably depending upon the particle size of the solid particles which it is desired to coat and generally will be at least 3% by weight and usually in the range of from about 3% to about 25%, preferably about 3% to about 15%, by weight, based on the weight of the final composition. The greater amount of organic surface active agent is generally employed when the solid particles have smaller, hereinafter defined, particle sizes. The particle size of the particles may also vary widely from finely divided powders to particles or granules and mixtures thereof.

In one embodiment of the processes of this invention it has been found advantageous to coat solid particles which are powdered in form and have a particle size such that all or substantially all of the particles pass through a No. 200 mesh U.S. standard screen and all or substantially all of the particles are retained on a No. 325 mesh U.S. standard screen.

In another embodiment of the processes of this invention it has been found advantageous to coat granular solid particles having a particle size such that substantially all of the particles will pass through a No. 10 mesh U.S. standard screen and substantially all of the particles will be retained on a No. 200 mesh U.S. standard screen. As will be hereinafter evident the specific range of particle size of the particles to be coated is not critical and particles having a wide range of particle size and particle size distribution may be coated.

A variety of solid particles of one or more hydratable detergent builder salts conventionally used in detergent formulations may be coated with an organic surface active agent in accordance with the processes of this invention. Such hydratable salts include for example solid particles of hydratable alkaline water soluble alkali metal, inorganic salts for example anhydrous tri-alkali metal phosphates, such as trisodium phosphate and tripotassium phosphate; di-alkali metal hydrogen phosphates such as disodium hydrogen phosphate and dipotassium hydrogen phosphate, anhydrous to partially hydrated alkaline, water soluble, molecularly dehydrated alkali metal phosphate salts such as alkali metal pyrophosphates for example, tetrasodium pyrophosphate, trisodium hydrogen pyrophosphate, and tetrapotassium pyrophosphate and alkali metal tripolyphosphates such as sodium tripolyphosphate ($Na_5P_3O_{10}$) and potassium tripolyphosphate; anhydrous alkaline water soluble alkali metal metaphosphates such as sodium hexametaphosphate, water soluble alkali metal silicates such as sodium silicate having an SiO_2 to Na_2O ratio of from about 1.5:1 to about 3.0:1 and the corresponding potassium silicates; anhydrous water soluble alkali metal borates such as calcined sodium tetraborate or borax, anhydrous water soluble alkali metal carbonates or bicarbonates such as sodium or potassium carbonates or bicarbonates and the like. Solid particles of one or more of these salts can be coated alone or in various combinations with each other. Also solid particles of these salts can be mixed with water soluble neutral inert diluents which may also have some detergent builder properties and solid particles of such mixtures can also be coated with the organic surface active agent. Examples of such neutral inert diluents include solid particles of water soluble anhydrous inert neutral alkali metal sulfates or chlorides for example sodium sulfate and sodium chloride. Solid particles of one or more of the above salts or mixtures thereof can be coated with the organic surface active agent as hereinbefore described and may be in the form of powders or as larger particles having particle sizes within the ranges hereinbefore described.

The organic surface active agent which may be employed to coat the above-described solid particles in accordance with the process of the present invention may by any of a wide variety of organic surface active agents such as foaming agents, emulsifiers, detergents, surfactants or the like. Examples of such organic surface active agents include anionic surfactants such as sulfates and sulfonated alkyl, aryl, alkyl-aryl hydrocarbons and alkali metal salts thereof, for example sodium salts of long chain alkyl sulfates, sodium salts of alkyl naphthalene sulfonic acids, sodium salts of abietenes, sodium salts of alkyl benzene sulfonic acids, particularly those in which the alkyl group contains from about 8 to 24 carbon atoms, sodium salts of sulfonated mineral oils, sodium salts of sulfosuccinic acid esters such as sodium dioctyl sulfosuccinate and the like.

Organic surface active agents which may be used to coat the above-described solid particles are surfactants including products formed by condensing one or more alkylene oxides of 2 to 4 carbon atoms, such as ethylene oxides or propylene oxides, preferably ethylene oxide alone or with other alkylene oxides with a relatively hydrophobic compound such as a fatty alcohol, fatty acid, sterol, a fatty glyceride, a fatty amide, a fatty mercaptan, tall oil fatty acids, etc. Nonionic detergents or surface active agents which may be used also include those products produced by condensing one or more relatively lower alkyl alcohol amines (for example methanolamine, ethanolamine, propanolamine, etc.) with a fatty acid such as lauric acid, cetyl acid, tall oil fatty acid, abietic acid, etc. to produce the corresponding amide. Other typical examples of these categories of anionic and nonionic surface active agents are described in Schwartz and Perry "Surface Active Agents," Interscience Publishers, New York (1949) and The Journal of American Oil Chemists Society vol. 34 No. 4, pages 170–216 (April 1957).

The above-described solid particles can be coated with any of the above-described organic surface active agents by a variety of methods hereinbefore described.

As noted hereinbefore, the amount of organic surface active agent which may be employed to coat the aforedescribed solid particles may vary considerably depending upon the size of the coated particles, the particular organic surface active agent employed and the end uses for which the detergent is intended. Generally, it has been found advantageous to employ from about 3% to about 25%, preferably 3% to about 15% by weight based on the weight of the composition, of the surface active agent. When the solid particles have a particle size such that all or substantially all of the solid particles will pass through a No. 10 mesh U.S. standard screen and all or substantially all of the particles will be retained on a No. 200 mesh U.S. standard screen from about 3% to about 10% by weight, based on the weight of the composition, of surface active agents may usually be employed to partially to completely coat the solid particles. When the solid particles have a particle size such that all or substantially all of the particles pass through a No. 200 mesh U.S. standard screen and all or substantially all of the particles are retained on a No. 325 mesh U.S. standard screen from about 8% to

about 15% by weight, based on the weight of the composition, of surface active agent will normally be sufficient to coat the particles to the extent that substantially all of the particles will have at least a partial coating thereon of the surface active agent. When less than 3% by weight of organic surface active agent is employed such amount would usually be insufficient to coat the solid particles to an extent which would attain the advantages of the processes of the present invention. Although amounts as large as 30% by weight, or even more, of organic surface active agent may be employed to coat the solid particles there is usually no advantage and 15% by weight of organic surface active agent is usually more then sufficient to satisfactorily coat the solid particles of the hydratable detergent builder.

In accordance with one embodiment of this invention it has been found advantageous to coat the solid particles of a powered to granular, anhydrous to partially hydrated alkali metal tripolyphosphate, preferably solid particles of a powered to granular substantially anhydrous sodium tripolyphosphate with from about 3% to about 15% by weight, based on the weight of the composition, of a nonionic surface active agent such as a condensation product of a hydrophobic compound having at least one active hydrogen atom and a lower alkylene oxide (for example the condensation product of an aliphatic alcohol containing from about 8 to about 18 carbon atoms) and from about 3 to about 30 mols of ethylene oxide per mol of the alcohol, or the condensation product of an alkyl phenol containing from about 8 to about 18 carbon atoms in the alkyl group and from about 3 to about 30 mols of ethylene oxide per mol of alkyl phenol. Other nonionic detergents which may be suitably employed include for example condensation products of ethylene oxide with a hydrophobic compound formed by condensing propylene oxide with propylene glycol.

As noted hereinbefore, water is added, with agitation, in an amount at least sufficient to induce agglomeration and to form a wet fluid mass and insufficient to substantially change the particle character of the particles, in other words to dissolve substantial amounts of the coated particles. If the amount of water is insufficent to form a wet fluid mass or is an amount large enough to dissolve or destroy the particle character of substantial quantities of the particles, the composition will tend to develop "sand-like" materials on storage. The amount of water added to the coated particles will in general depend upon the degree of hydratability of the hydratable detergent employed and the amount of detergent builder employed. For example if the detergent builder is incapable of consuming large amounts of water either inherently or due to partial hydration of the builder a small amount usually about 10% will be sufficient to induce agglomeration and to form a wet fluid mass. On the other hand, if the detergent builder is capable of incorporating large amounts of water as water of hydration up to 35% by weight of water may be required to induce agglomeration and to form a wet fluid mass. The water may be added to the coated particles per se or in the form of an aqueous solution of any of the previously described detergent builders so long as such aqueous solution is added in an amount sufficient to provide from about 10% to about 35%, based on the weight of the composition, of water.

By way of illustration, if water is added per se or in the form of an aqueous solution of detergent builder to coated particles consisting essentially of a substantially anhydrous alkali metal tripolyphosphate for example substantially anhydrous sodium tripolyphosphate or alternatively to a mixture of coated particles comprising a major proportion of coated particles of substantially anhydrous alkali metal tripolyphosphate for example substantially anhydrous sodium tripolyphosphate and a minor proportion of coated particles of substantially anhydrous alkali metal sulfate for example substantially anhydrous sodium sulfate, the amount of water per se, or in the form of an aqueous solution of detergent builder will be from about 20 to about 35% by weight, based on the weight of the composition. On the other hand, if the solid coated particles consist of particles of partially hydrated alkali metal tripolyphosphate and/or alkali metal sulfates or if the solid particles include a significant amount of an inert diluent such as for example solid particles of sodium chloride the amount of water added per se or in the form of an aqueous solution may be in the range of from about 5 to about 25%. When it is desired to add water in the form of an aqueous solution of detergent builder salt it has been found particularly advantageous to employ an aqueous solution of an alkali metal silicate for example an aqueous solution containing from about 5% to about 50% of sodium silicate having an SiO_2 to Na_2O ratio of from about 1.5:1 to about 3.4:1. The coated particles of detergent builder are agitated, preferably by well known mechanical means, such as for example in a bladed mechanical mixer during the addition of water to intimately contact all or substantially all of the particles with the water. In general it has been found desirable to add the water as rapidly as possible so that appreciable agglomeration of the coated particles and hydration of the hydratable detergent builder salt does not occur during the addition of the water.

By so proceeding a pourable water wet fluid mass is formed which is aged, usually from about several seconds to several hours, until the water is substantially incorporated as water of hydration and a friable continous agglomerated solid product or mass is formed. The agglomerated product, upon inspection, is heterogeneous in appearance and consists of large and smaller bonded agglomerates in which the larger agglomerates are composed of loosely bonded smaller agglomerates. The hydration of the detergent builder with water during ageing is usually accompanied by a rise in the temperature of the wet fluid mass or agglomerated product. Such temperature rise is due to the heat of hydration of the detergent builder. The amount of temperature rise generally depends upon the size of the mass, the inherent heat of hydration of detergent builder employed and is usually an increase of from about 10° to about 50° C.

Generally the temperature is not critical in carrying out any of the process steps of this invention. However, although the temperature of the coated particles and the water is not generally critical it is preferred that the temperature of the wet fluid mass and/or the agglomerated product formed therefrom be kept below about 105° C. and this can almost always be accomplished by carrying out the water addition step of the process under substantially ambient conditions, e.g. from about 20° C. to about 40° C. The ageing time required to form the agglomerated product is preferably from about 5 minutes to several hours and generally depends upon the size of the mass, the hydratability of the detergent builder and the amount of water employed, the greater amount of water usually corresponding to longer ageing time. Generally the ageing time tends to be shortened when hydratable detergent builders having an appreciable heat of hydration are employed.

As noted hereinbefore, the product formed by the above procedure comprises a mixture, usually a heterogeneous mixture in form and appearance, of one or more hydrated detergent builders and the organic surface active agent. The product so prepared is friable, that is, it can be readily broken or ground to any desired particle size with minimum mechanical force, such as for example brushing the mass through a screen. By way of contrast, products containing identical ingredients prepared by previously known methods are non-friable and usually require substantial mechanical grinding to achieve the particle size desired.

Generally it has been found that the grinding steps may often be eliminated by agitating the wet fluid mass and/or agglomerated products during ageing. Such agita-

tion is generally and preferably carried out employing the same mechanical mixing means employed during the addition of water to the coated solid particles, Such mechanical mixing may be continuous or intermittent. The product formed by the above procedure is a granular product in which the granules consist of agglomerates comprising a mixture of one or more hydrated detergent builders and the organic surface active agent. The size of the granules or the granular product so obtained depends upon the particular mixing means, the amount of water and the detergent builder employed. As will be hereinafter evident the granules are usually substantially larger than the coated powdered to granular particles initially employed in the process. Generally and regardless of the size of the coated particles initially employed granular products having a particle size such that all or substantially all of the granules will pass through a No. 10 mesh U.S. standard screen and all or substantially all of the granules will be retained on a No. 100 mesh U.S. standard screen may be readily obtained. These granular products may be used as such in a wide variety of automatic washing machines or alternatively and surprisingly may be compressed into tablet form without further processing. On the other hand granular products obtained by conventional processes require extensive further treatment before they can be incorporated into tablet form. Generally although the compositions prepared by the processes of this invention contain the same or similar ingredients of well known detergent compositions the compositions prepared by the processes of this invention differ markedly in their physical behavior than properties from the compositions prepared by previously known processes.

One embodiment of the processes of this invention comprises the steps of partially to completely coating solid particles of powdered to granular substantially anhydrous sodium tripolyphosphate with from about 3% to about 15% based on the weight of the composition of a condensation product of a hydrophobic compound having at least one active hydrogen and a lower alkylene oxide to form coated particles of the tripolyphosphate having at least a partial coating thereon of the condensation product. Thereafter and with agitation there is added to the coated particles water or an aqueous solution containing from about 5% to about 50% by weight of sodium silicate having an SiO_2 to Na_2O ratio of from about 1.5:1 to about 3.0:1. The amount of water either per se or in the form of the sodium silicate solution is an amount sufficient to provide from about 10% to about 35% by weight, based on the weight of the composition, of water. By so proceeding there is formed a wet fluid mass consisting of an aqueous slurry comprising agglomerates of the coated particles dispersed in the aqueous phase of the slurry. Thereafter the fluid mass is aged with or without agitation until the water is substantially incorporated as water of hydration in the sodium tripolyphosphate and a composition comprising hydrated agglomerates of the coated particles and consisting essentially of a mixture of hydrated sodium tripolyphosphate, sodium silicate (where an aqueous solution of sodium silicate is used) and the condensation product is formed.

In accordance with another embodiment of this invention, solid particles of a mixture comprising a major proportion of the solid particles of substantially anhydrous sodium tripolyphosphate and a minor proportion of solid particles of substantially anhydrous sodium sulfate are coated and treated as above-described. The product thus formed comprises hydrated agglomerates of the coated particles, the agglomerates consisting essentially of a mixture of hydrated sodium tripolyphosphate, sodium sulfate and, when an aqueous solution of sodium silicate is employed, sodium silicate as well as the aforementioned condensation product.

In the above embodiment the solid particles are preferably coated with from about 3% to about 15% by weight, based on the weight of the composition of a condensation product of an aliphatic alcohol containing from about 8 to about 18 carbon atoms and from about 3 to about 30 mols of ethylene oxide per mol of alcohol or a condensation product of an alkyl phenol containing from about 8 to about 18 carbon atoms in the alkyl group and from about 3 to about 30 mols of ethylene oxide per mol of the alkyl phenol.

The particles are preferably coated by mechanical mixing of one or more of the condensation products with the solid particles in a conventional mixer such as for example a standard paddle type detergent crutcher until the condensation product is thoroughly admixed and the particles are at least partially coated with the condensation product. Thereafter, and with agitation, water and/or the previously described solution of sodium silicate is added in an amount sufficient to provide from about 10 to about 30% by weight, based on the weight of the composition of water to form the wet fluid mass. The water is preferably added relatively rapidly over a time period of from several seconds to several minutes depending upon the size of the batch of the composition which it is desired to prepare. The fluid mass is then preferably agitated until a granular agglomerated product having the general composition hereinbefore described is formed.

When desired it is also possible to add small amounts of other conventional ingredients of detergent compositions to the solid particles before or after the coating step. Thus for example small amounts of brightening agents such as fluorescent dyes and anti-redeposition agents such as carboxymethyl cellulouse can be added to the solid particles prior to or after the coating steps.

The following specific examples are intended to illustrate the invention but not to limit the scope thereof, parts and percentages being by weight unless otherwise specified.

Example I

Thirty parts of substantially anhydrous powdered sodium tripolyphosphate having a particle size such that all of the particles pass through a No. 200 mesh screen and all of the particles are retained on a No. 325 mesh screen were placed in a paddle type mixer. Seven parts of a dispersion of acetone containing 10% by weight of sodium alkyl benzene sulfonate were sprayed through an atomizer over the powdered sodium tripolyphosphate while the powders were being mixed with the liquid. Thereafter the liquid was evaporated and a dry mass of fine coated particles of substantially anhydrous sodium tripolyphosphate coated with sodium dodecyl benzene sulfonate was obtained. To these particles there was added while mixing was continued 13 parts of water. During and after the addition of water agglomerated particles having a size larger than the powder initially coated formed and the temperature of the contents in the mixer rose from 25° C. to about 35° C. Mixing was continued for about 15 seconds after the water had been added and a wet fluid mass formed which was poured from the mixer into a shallow drying pan having a depth of about 1 inch. The wet fluid mass containing the agglomerates was aged in the pan for about 15 minutes after which a solid cake had formed. The cake was permitted to further age until the mass returned to a temperature of 25° C. The solid cake or mass had a grainy dry appearance and could be readily broken up into granules by brushing the mass through a No. 10 mesh U.S. standard screen with a soft camel hair brush. The granules were then stored in an oven at 37° C. for five months in an atmosphere of air. After this period the granular composition was tested for its ability to launder clothes using an automatic machine. The composition proved to be readily soluble in water and to effectively clean soiled textiles. On the other hand a granular composition containing the same ingredients which had been prepared by mixing an aqueous solution of sodium dodecyl benzene sulfonate and which had been granulated by grinding in

a hammer mill and stored for a similar period was dispersed in water about 6% of the granules were difficultly soluble to insoluble and gave the appearance of grains of sand.

Example II

The procedure of Example I was repeated except that the wet fluid mass was permitted to remain in the mixer and mixing was continued intermittently during the hydration of the sodium tripolyphosphate, for about 30 minutes. After this time a dry, free flowing composition had formed in the mixer. The composition was stored and tested as described in Example I and proved to be an excellent detergent composition which was readily soluble in water, before and after storage.

Example III

Sixty-five parts of substantially anhydrous granular sodium tripolyphosphate, having a particle size such that the particles passed through a No. 10 mesh screen and were retained on a No. 200 mesh screen, was mixed with eight parts of the condensation product of an aliphatic alcohol containing about 12 carbon atoms and about 15 mols of ethylene oxide per mol of alcohol were mixed in a paddle type mixer for about 20 minutes until the granular sodium tripolyphosphate was substantially coated with the condensation product. To the mixer, and while mixing was continued, there was added 27 parts of water until a pourable water wet fluid mass was formed. The temperature in the mixer rose from about 25 to about 32° C. at the time the water was totally dispersed through the solid particles of the granules of sodium tripolyphosphate. The mixture was aged while the mixing operation was intermittently continued until the temperature of the contents in the mixer fell from 32° C. to 27° C. A granular composition dry and free flowing in appearance was obtained and consisted of particles in which each particle substantially contained hydrated sodium tripolyphosphate and the above mentioned condensation product.

The composition was found to have excellent washing characteristics before and after storage for 5 months in air in an oven at 37° C. However, compositions prepared using granular sodium tripolyphosphate hexahydrate mixed with the condensation product developed 4% insoluble substance when stored for the same period of time.

Example IV

Forty parts of substantially anhydrous granular sodium tripolyphosphate having a particle size such that substantially all of the particles pass through a No. 10 mesh U.S. standard screen and substantially all of the particles were retained on a No. 200 mesh U.S. standard screen and 20 parts of a substantially anhydrous sodium sulfate, having a particle size in the same range as the sodium tripolyphosphate, were placed in a paddle type mixer and mixed for several minutes. To the mixture there was added 6 parts of the condensation product of an alkyl phenoy containing about 12 carbon atoms in the alkyl group and about 15 mols of ethylene oxide per mol of alcohol and 2 parts of sodium dodecyl benzene sulfonate. The mixing was contained until the particles of the sodium tripolyphosphate and sodium sulfate were coated with the condensation product and the sodium dodecyl benzene sulfonate. To the mixer there was added while mixing was continued 32 parts by weight of an aqueous solution of sodium silicate containing 6.68% by weight of a sodium silicate having an SiO_2 to Na_2O ratio of 2.8:1. The sodium silicate solution was added to the mixer over a period of about 30 seconds and the mixing was continued until a "mush" or wet fluid mass containing agglomerates of the coated particles dispersed in the aqueous phase of the sodium silicate solution was formed. During and immediately after the addition of the sodium silicate solution the temperature of the contents in the mixer rose from 24° C. to 33° C. The contents were permitted to remain in the mixer, while the mixing was continued, and the anhydrous sodium tripolyphosphate and anhydrous sodium sulfate had completely incorporated the water as water of hydration into the agglomerates of the solid particles. The mixing operation was continued until the temperature of the contents of the mixer fell to about 26° C. A dry, free flowing granular composition was obtained which was evaluated for washing and cleaning ability in an automatic dishwashing machine. The composition proved to be readily soluble in water and to effectively clean metalware and dinnerware. A portion of the composition was stored in an oven at 37° C. for six months in an atmosphere of air and re-evaluated for its cleansing ability. The composition again proved to be readily soluble in water and to effectively clean dinnerware and metalware. On the other hand a granular composition containing the same ingredients but which had been prepared by adding an aqueous solution of dodecyl benzene sulfonate and the condensation product to particles of sodium tripolyphosphate and sodium sulfate, both of which were anhydrous and had the same particle size and crystalline sodium silicate and which had been granulated by grinding in a hammer mill and stored for a similar period of time, was dispersed in water about 10% of the granules were "sand-like" and substantially insoluble in water. Such insoluble particles adhered to the surfaces of the metalware and dinnerware giving them a blotched unclean appearance.

Example V

The process of Example IV was repeated except that anhydrous powdered sodium tripolyphosphate, having a particle size such that all of the particles passed through a No. 200 mesh U.S. standard screen and were retained on a No. 325 mesh U.S. standard screen, was employed instead of the anhydrous granular sodium tripolyphosphate employed in Example IV. By so proceeding a product similar to the product obtained in Example IV was obtained. The product was equally as efficient when evaluated in washing operations as the product of Example IV. Also after storage for 6 months the detergent composition was readily soluble in water.

What is claimed is:

1. A process for preparing a stable, water-soluble composition which comprises the steps of (1) partially to completely coating solid particles of a hydratable inorganic detergent builder salt selected from the group consisting of alkali metal phosphates, silicates, borates, carbonates, bicarbonates, sulfates, chlorides, and mixtures thereof with from about 3% to about 30% by weight, based upon the weight of said composition, of a nonsoap synthetic surface active agent selected from the group consisting of nonsoap synthetic anionic surface active agents and nonsoap synthetic nonionic surface active agents; (2) adding to the resulting coated solid particles from about 10% to about 35% by weight, based on the weight of said composition, of water sufficient to induce agglomeration of the particles and to form a pourable wet fluid mass consisting of an aqueous slurry comprising agglomerates of said coated particles dispersed in the aqueous phase of said slurry but insufficient within said 10 to 35% range to dissolve said coated particles, said water being added over a period of from about two seconds to about two minutes to prevent appreciable agglomeration of said particles and hydration of said builder salt during said addition of water; and (3) aging the resulting fluid mass until said water is substantially completely incorporated as water of hydration in said builder salt and a friable, agglomerated product comprising a mixture of the hydrated builder salt and said organic surface active agent is formed.

2. A process for preparing a stable, dry, free flowing, detergent composition which comprises the steps of (1) coating solid particles of a hydratable inorganic de-

tergent builder salt selected from the group consisting of alkali metal phosphates, silicates, borates, carbonates, bicarbonates, sulfates, chlorides, and mixtures thereof, and having a particle size such that substantially all of the particles pass through a No. 10 mesh U.S. Standard screen and substantially all of the particles will be retained on a No. 325 mesh U.S. Standard screen with from about 3% to about 15% by weight, based on the weight of the composition, of a nonsoap synthetic nonionic surface active agent to form coated solid particles of said detergent builder salt having at least a partial coating thereon of said nonionic surface active agent; (2) adding to the resulting coated solid particles, with agitation, from about 10% to about 30% by weight, based on the weight of the composition, of water sufficient to induce agglomeration of the particles and to form a pourable wet fluid mass consisting of an aqueous slurry comprising agglomerates of said coated particles dispersed in the aqueous phase of said slurry but insufficient within said 10 to 30% range to dissolve said coated particles, said water being added over a period of from about two seconds to about two minutes to prevent appreciable agglomeration of said particles and hydration of said builder salt during said addition of water; and (3) aging said fluid mass until the water is substantially completely incorporated as water of hydration in said builder salt and a friable, agglomerated granular composition comprising a mixture of the hydrated builder salt and said nonionic surface active agent is formed.

3. A process for preparing a stable, dry, free-flowing detergent composition which comprises the steps of (1) partially to completely coating solid particles of a hydratable inorganic detergent builder salt selected from the group consisting of alkali metal phosphates, borates, carbonates, bicarbonates, sulfates, chlorides, and mixtures thereof, with from about 3 to about 30% by weight, based upon the weight of said composition, of a nonsoap synthetic surface active agent selected from the group consisting of nonsoap synthetic anionic surface active agents and nonsoap synthetic nonionic surface active agents; (2) adding to the resulting coated solid particles an aqueous solution containing from about 5% to about 50% by weight of an alkali metal silicate in an amount sufficient to provide from about 10% to about 30% by weight, based on the weight of the composition, of water sufficient to induce agglomeration of said particles and to form a pourable wet fluid mass consisting of an aqueous slurry comprising agglomerates of said coated particles dispersed in the aqueous phase of said slurry but insufficient within said 10 to 30% range to dissolve said coated particles, said solution being added over a period of from about two seconds to about two minutes to prevent appreciable agglomeration of said particles and hydration of said builder salt during said addition of said solution; and (3) aging the resulting fluid mass until said water is substantially completely incorporated as water of hydration in said builder salt and a friable, agglomerated product comprising a mixture of the hydrated builder salt, alkali metal silicate and said nonsoap synthetic surface active agent is formed.

4. A process for preparing a stable, dry, free flowing detergent composition which comprises the steps of (1) partially to completely coating solid particles of a hydratable inorganic detergent builder salt selected from the group consisting of alkali metal phosphates, borates, carbonates, bicarbonates, sulfates, chlorides, and mixtures thereof with from about 3% to about 30% by weight, based on the weight of the composition, of a nonsoap synthetic nonionic surface active agent; (2) adding, with agitation, to the resulting coated solid particles an aqueous solution containing from about 5% to about 50% by weight of an alkali metal silicate in an amount sufficient to provide from about 10% to about 30% by weight, based on the weight of the composition, of water which is sufficient to induce agglomeration of the particles and to form a pourable wet fluid mass consisting of an aqueous slurry comprising agglomerates of said coated particles dispersed in the aqueous phase of said slurry but insufficient within said 10 to 30% range to dissolve said coated particles, said aqueous solution being added over a period of from about 2 second to about two minutes to prevent appreciable agglomeration of said particles and hydration of said builder salt during said addition of said aqueous solution; and (3) aging the resulting fluid mass, with agitation, until said water is substantially completely incorporated as water of hydration in said builder salt and a friable, agglomerated, granular product in which the granules consist of agglomerates comprising a mixture of the hydrated builder salt, the alkali metal silicate, and said nonionic surface active agent is formed.

5. A process for preparing a stable, dry, free flowing detergent composition which comprises the steps of (1) coating solid particles of substantially anhydrous sodium tripolyphosphate with from about 3% to about 15% by weight, based on the weight of the composition of a condensation product of an alkyl phenol containing from about 8 to about 18 carbon atoms in the alkyl group and from about 3 to about 30 mols of ethylene oxide per mol of said alkyl phenol to form coated solid particles of said tripolyphosphate having at least a partial coating thereon of said condensation product; (2) adding to the said coated particles, with agitation, an aqueous solution containing from about 5% to about 50% by weight of a sodium silicate having a SiO_2 to NaO_2 ratio of from about 1.5:1 to about 3.0:1 in an amount sufficient to provide from about 10% to about 35% by weight, based on the weight of the composition, of water which is sufficient to induce agglomeration of the particles and to form a pourable wet fluid mass consisting of an aqueous slurry comprising agglomerates of said coated particles dispersed in the aqueous phase of said slurry but insufficient within said 10 to 35% range to dissolve said coated particles, said solution being added over a period of from about 2 seconds to about 2 minutes to prevent appreciable agglomeration of said particles and hydration of said builder salt during said addition of said aqueous solution; and (3) aging the resulting fluid mass, with agitation, until the water is substantially completely incorporated as water of hydration in the sodium tripolyphosphate and a friable, agglomerated, granular composition comprising hydrated agglomerates of said coated particles and consisting essentially of a mixture of the hydrated sodium tripolyphosphate, sodium silicate and said condensation product is formed.

6. A process for preparing a stable, dry, free flowing detergent composition which comprises the steps of (1) coating solid particles of a mixture comprising (a) solid particles of substantially anhydrous sodium tripolyphosphate and (b) solid particles of substantially anhydrous sodium sulfate with from about 3% to about 15% by weight, based on the weight of the composition of a condensation product of an aliphatic alcohol containing from 8 to about 18 carbon atoms and from about 3 to about 30 mols of ethylene oxide per mol of said alcohol to form coated solid particles of said mixture wherein said particles have at least a partial coating thereon of said condensation product; (2) adding to said coated solid particles, with agitation, an aqueous solution, containing from about 5% to about 50% by weight of a sodium silicate, sufficient to provide from about 10% to about 35% by weight, based on the weight of the composition, of water which is sufficient to induce agglomeration of the particles and to form a pourable wet fluid mass consisting of an aqueous slurry comprising agglomerates of said coated particles dispersed in the aqueous phase of said slurry but insufficient within said 10 to 35% range to dissolve said coated particles, said aqueous solution being added over a period of from about 2 seconds to about 2 minutes to prevent appreciable agglomeration of said particles and hydration of said mixture during said addition of

the aqueous solution; and (3) aging the resulting fluid mass, with agitation, until said water is substantially completely incorporated as water of hydration in the sodium tripolyphosphate and the sodium sulfate, and a friable, granular composition comprising hydrated agglomerates of said coated particles and consisting essentially of a mixture of hydrated sodium tripolyphosphate, sodium sulfate, sodium silicate and said condensation product is formed.

7. A process for preparing a stable, water soluble dishwashing composition which comprises the steps of (1) partially to completely coating solid particles of substantially anhydrous, powdered sodium tripolyphosphate, having a particle size such that all of the particles pass through a No. 200 mesh U.S. Standard screen and are retained on a No. 325 mesh U.S. Standard screen, with sodium dodecyl benzene sulfonate contained in an acetone dispersion, said acetone dispersion containing about 10% by weight of said sulfonate and being present in an amount sufficient to provide a coating of from about 8% to about 15% by weight, based on the weight of the composition, of said sulfonate on the said tripolyphosphate particles; (2) evaporating the acetone from the above mixture and thereby forming a dry mass of coated solid particles of substantially anhydrous sodium tripolyphosphate coated with sodium dodecyl benzene sulfonate; (3) adding, with agitation, from about 20% to about 35% by weight, based on the weight of the composition, of water sufficient to induce agglomeration of the particles and to form a pourable wet fluid mass consisting of an aqueous slurry comprising agglomerates of said coated particles dispersed in the aqueous phase of said slurry but insufficient within said 20 to 35% range to dissolve said coated particles, said water being added over a period of from about 2 second to about 2 minutes to prevent appreciable agglomeration of said particles and hydration of said sodium tripolyphosphate during addition of the water; and (4) aging the resulting fluid mass, without agitation, until the water is substantially completely incorporated as water of hydration in the sodium tripolyphosphate and a granular composition comprising hydrated agglomerates of said coated particles and consisting essentially of a mixture of hydrated sodium tripolyphosphate and said sulfonate is formed.

8. A process as in claim 1 wherein the solid particles of the hydratable inorganic detergent builder salt have a particle size such that substantially all of the particles pass through a No. 10 mesh U.S. standard screen and substantially all of the particles are retained on a No. 325 mesh U.S. standard screen.

9. A process as in claim 1 wherein the solid particles of the hydratable inorganic detergent builder salt have a particle size such that substantially all of the particles pass through a No. 200 mesh U.S. standard screen and substantially all of the particles are retained on a No. 325 mesh U.S. standard screen.

10. A process as in claim 1 wherein the solid particles of the hydratable inorganic detergent builder salt have a particle size such that substantially all of the particles will pass through a No. 10 mesh U.S. standard screen and substantially all of the particles will be retained on a No. 200 mesh U.S. standard screen.

11. A process as in claim 2 wherein the solid particles of the hydratable inorganic detergent builder salt are solid particles of an anhydrous to partially hydrated alkali metal tripolyphosphate.

12. A process as in claim 2 wherein the solid particles of hydratable inorganc detergent builder salt comprise a mixture of solid particles of anhydrous to partially hydrated alkali metal tripolyphosphate and of solid particles of anhydrous to partially hydrate alkali metal sulfate.

13. A process as in claim 2 wherein the nonionic surface active agent is a condensation product of an aliphatic alcohol containing from about 8 to about 18 carbon atoms and from about 3 to about 30 mols of ethylene oxide per mol of said alcohol.

14. A process as in claim 4 wherein the solid particles of the hydratable inorganic detergent builder salt consist essentially of solid particles of substantially anhydrous sodium tripolyphosphate having a particle size such that substantially all of the particles pass through a No. 10 mesh U.S. standard screen and substantially all of the particles are retained on a No. 325 mesh U.S. standard screen.

15. A process as in claim 4 wherein the solid particles of hydratable inorganic detergent builder salt comprise a mixture of solid particles of substantially anhydrous sodium tripolyphosphate and of solid particles of substantially anhydrous sodium sulfate and the particle size of the particles of said mixture is such that substantially all the particles pass through a No. 10 mesh U.S. standard screen and are retained on a No. 325 mesh U.S. standard screen.

16. A process as in claim 4 wherein the alkali metal silicate in the aqueous solution of alkali metal silicate is a sodium silicate having an SiO_2 to Na_2O ration of from about 1.5:1 to about 3.4:1.

17. A process as in claim 4 wherein the nonionic surface active agent is a condensation product of an aliphatic alcohol containing from about 8 to about 18 carbon atoms and from about 3 to about 30 mols of ethylene oxide per mol of said alcohol.

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