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METHOD OF PRODUCING A FREE-FLOWING GRANULAR NONSOAP DETERGENT

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This invention relates to detergent compositions and more particularly to substantially dry, solidified compositions composed of substantially homogeneous intimate mixtures of organic detergents and water soluble complex phosphates. The invention also includes methods by which such compositions may be produced. The solidified compositions, on grinding to form small granules or even to a powder, provide particles all, or substantially all of which contain both of the ingredients, the organic detergent being deposited upon and adherent to the crystals of the polyphosphate and encapsulating substantially each of them. In a more limited but important embodiment of the invention, detergency promoter salts, sometimes loosely referred to as "fillers," are included in processes and products, which salts facilitate the production of the products and contribute to their performance in subsequent use.

Detergent compositions containing mixtures of organic and inorganic compounds of the general nature of those within the broad scope of the invention have heretofore been produced, but none of them, as far as can be ascertained, contains the hereinafter described novel combination of properties due not only to the components of the compositions, but also to the homogeneous character of the mass and the intimate bond between the organic detergent and the inorganic salt therein.

In prior practice, cleaning compositions have been produced either by mixing the organic detergent in dried condition (if it can be dried without decomposing) with an anhydrous or dry hydrated phosphate or other inorganic compound, or by mixing solutions of the two compounds and spray drying or otherwise evaporating off the water of the mixture. Each of these procedures has several disadvantages. If the materials are mixed in the dry state, then a careful and comparatively costly or non-commercial method must be preliminarily employed to dry the organic detergent, for many of such materials ordinarily hold on tenaciously to moisture at moderate temperatures and cannot be heated at high temperatures without being in part decomposed. If dry anhydrous inorganic salts are employed in making the dry mix, the particles of the same during subsequent use, tend to ball up and to resist or delay disolution, and if dry hydrated salts are used, then an expensive preliminary crystallizing operation is often required to obtain the salt in that form. Finally, the heterogeneous granules of the dry-mixed compositions have a tendency to separate during transportation, due to differences in particle size or specific gravities of the components. Such masses either require remixing by the purchaser or they result in non-uniformity of successive portions withdrawn from the shipping container.

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If the prior suggested compositions are made by forming solutions of the respective previously dried ingredients and evaporating off the water, the cost to the consumer is prohibitive. Such method, furthermore, is not applicable to a number of the organic detergents due to their heat sensitivity. Other detergents can be successfully dried only when incorporated with some inorganic salt which facilitates evaporation of the water. In view of this heat sensitivity, a number of organic detergents have heretofore been marketable only in the inconvenient or objectionable form of pastes or solutions.

One of the objects of the present invention is to provide substantially dry detergent compositions containing organic detergents and phosphate detergents which are easily and cheaply produced in solid form, are readily and uniformly soluble, and are stable against separation during transportation.

Another object is to provide a method of producing substantially dry, free-flowing granular detergent compositions from heat sensitive organic detergents having a tendency to decompose when heated for the purpose of evaporating off the water invariably present as a result of the production procedures employed.

Broadly considered, the products of the present invention may be defined as compositions of matter comprising granules composed of an organic detergent deposited upon and adhering to particles of a water soluble, hydrated, crystalline polyphosphate, and more particularly such compositions containing tetrasodium pyrophosphate, or sodium tripolyphosphate or mixtures of the same. The invention includes methods by which such compositions are produced, and they involve, basically, the formation of an aqueous slurry of an organic detergent and a substantially non-hydrated alkali metal complex phosphate and solidifying the mixture by causing or permitting the phosphate present to take up all or substantially all of the water present as water of crystallization thereby producing a substantially dry or dry appearing mass capable of being reduced to granular form and then preferably grinding the mass thereby producing a homogeneous non-segregative, free-flowing powder.

The inventions of both the process and the

product include variations of the above compositions and procedures in which a third ingredient is present, namely a detergent promoter salt such as sodium sulphate or sodium carbonate, these salts being the same as those heretofore sometimes incorporated in organic detergents by the producers of such products.

The present invention is particularly applicable to those organic detergents which because of their sensitivity to heat cannot be satisfactorily dried on a commercial scale or can be dried satisfactorily only if admixed with sodium sulfate or other salt. The invention, however, in its broader aspects is also applicable to other organic detergents and compositions hereinafter described.

Among the organic detergents tested and found successful in the compositions of the invention are various sodium alkyl sulphates such as sodium tetradecyl sulphate, sodium lauryl sulphate and mixtures of sulphates of lower and higher molecular weight organic radicals. Sodium alkyl sulphonates may also be employed, such as sodium keryl sulphonate. There also may be mentioned sodium alkyl aryl sulphonates of which sodium dodecyl benzene sulphonate (Nacconols) and sodium isopropyl naphthalene sulphonate (Nekals) are examples. Sodium alkyl dicarboxylate detergent compounds are also suitable, such as those having 15 carbon atoms, more or less, in the hydrocarbon radical. Finally there may be mentioned the sodium alkyl phosphates such as sodium di-(2-ethylhexyl) phosphate. The foregoing compounds may be described more specifically as surface active, anionic, non-soap, water-soluble salt, organic detergents.

In preparing the compositions of the present invention, it is essential that the proportions of the ingredients be correlated such that the amount of the substantially nonhydrated phosphate salt is sufficient to take up the amount of the water used in making the homogeneous slurry. With this qualification the proportions of organic detergent and phosphate can be adjusted to suit the particular purpose for which the ultimate composition is intended.

The amount of phosphate required to accomplish chemical absorption of the water depends not only upon the maximum hydration capacity of the phosphate selected, but also upon the degree of hydration, if any, of the phosphate at the time it is introduced into admixture with the organic detergent. The amount of hydrated complex phosphate required in the compositions is ordinarily more than about 50% or more than about two times the amount of organic detergent. During the solidifying or aging step, the polyphosphates in becoming substantially hydrated take up water to an extent amounting to 70–100% of the highest stable hydrate at room temperature.

Maximum capacity for the chemical absorption of water by the phosphate is obtained when the phosphate is used in anhydrous condition and the phosphate ordinarily is employed in this form. However, where the amount of phosphate in relation to the organic detergent can be extremely high in view of the intended use of the produced composition, partially or slightly hydrated polyphosphates can be employed.

Since compositions containing substantial proportions of organic detergents are particularly efficient in certain fields of use, the present invention includes as one of its preferred embodiments a process whereby a larger or maximum amount of organic detergent is incorporated in the polyphosphate compositions. These compositions are prepared by the use of elevated temperatures for the formation of the slurry preferably above 50° C. but not sufficiently high to decompose the organic detergent. By the use of such temperatures the amount of water required to form the homogeneous slurry is at a minimum and hence the amount of polyphosphate necessary to take up the water is also at a minimum. Therefore, larger proportions of organic detergents are contained in the final compositions than would otherwise be obtained. Also, the elevated temperature results in more homogeneity in the compositions.

This elevated temperature method of production has the additional advantage that a substantially dry, grindable mass can often be obtained simply by cooling to room temperature thereby causing solidification. Some compositions, however, may require an additional aging period in order that the free water be adequately taken up by the polyphosphate.

The hot slurry may be cooled and solidified by any suitable method and then ground to provide the homogeneous granules of the present invention. One satisfactory method of cooling and granulation employs a drum cooler in which the slurry is spread on the drum, cooled and scraped off in the form of flakes which may be subsequently ground to a powder, if desired. In this treatment, the water present is taken up by the phosphate as water of crystallization. In a variation of this process, some of the water may be removed from the composition on the drum by evaporation, but in this procedure the water is likewise taken up primarily by combination with the polyphosphate as water of crystallization.

In another alternative process, the slurry is simultaneously cooled during stirring, and as a result a granular mass is obtained. Where aging of the composition is required in order to permit granulation, the composition may be poured out on any suitable cold surface and permitted to cool and age, after which the solidified substantially dry mass may be introduced into a suitable pulverizing apparatus.

When a detergent promoter is to be included in the compositions of the invention, the relative proportions of the ingredients generally present in the final product may be indicated by the following: up to 25% active organic detergent, up to 25% hydrated or partially hydrated salts such as sodium sulfate and sodium carbonate and the balance (50% or more) of the complex phosphate or phosphates hydrated to the extent of 70–100% of the highest stable hydrate at room temperature.

Example 1

Into a make-up tank there was charged 12,800 pounds of anhydrous tetrasodium pyrophosphate, 3,200 pounds of Nacconol HG (56.3% active sodium alkyl aryl sulphonate with sodium suphate) and 7,860 pounds of water. The resulting mixture was agitated and heated to 75–80° C. until a fluid, uniform, solution-slurry was obtained. This mixture was then solidified by cooling on a drum and the flakes thereby obtained were, after aging, ground to a dry powder.

Another mixture containing 57% tetrasodium pyrophosphate, 10% Nacconol NR (37.5% sodium alkyl aryl sulphonate and sodium sulphate) and 33% water was made, solidified and ground in

the same manner as described above and a dry free-flowing powder was also obtained.

According to the manufacturer, the alkyl aryl part of the Nacconol molecules is made up of a benzene ring substituted by the hydrocarbon radicals of paraffin, such products being described in United States Patents Nos. 2,387,572 and 2,393,526.

Example 2

A make-up tank was charged with 6,440 pounds of Ultrawet 30–SD (27.5% sodium alkyl benzene sulphonate in which the alkyl content aggregates ten carbon atoms, in aqueous solution) and 3,820 pounds of water. The mixture was heated to 80–90° C. and then 13,600 pounds of tetrasodium pyrophosphate was introduced and agitated until a homogeneous slurry was obtained. The hot slurry was then cooled and solidified on a drum and after the flakes had aged sufficiently they were ground to provide a homogeneous, dry-appearing, free-flowing powder.

Example 3

A mixture of 73 pounds of anhydrous tetrasodium pyrophosphate, 49 pounds of a 25% aqueous solution of Santomerse TIB

$$\left(\begin{array}{c} COONa \\ | \\ C_{11}H_{23}CHCH_2COONa \end{array}\right)$$

and 6 pounds of water was heated in a metal drum during agitation to a temperature of about 70° C. The fluid mixture obtained was then introduced onto a drum flaker and the flakes obtained were substantially homogeneous in composition. On standing the flakes hardened and gave the appearance of being completely dry.

A similar mixture may be made by mixing 80 pounds of anhydrous tetrasodium pyrophosphate to which 36% water has been added and 20 pounds of dry 100% Santomerse TIB. Upon continuance of the heating and mixing, a smooth fluid solution-slurry is obtained. The slurry is then rapidly chilled, and as a result it solidifies immediately to a substantially dry product capable of being ground to a powder.

Example 4

A number of mixtures were prepared containing between 55% and 60% tetrasodium pyrophosphate in anhydrous condition, between 17 and 18% of a 57% Tergitol (sodium salt of 7-ethyl 2-methyl undecanol-4 sulfate in aqueous paste form) and the balance water. The mixtures were produced at elevated temperatures higher than the solidification point of the mixtures and well below 100° C. A portion of each of the solution-slurries obtained were poured on a water cooled drum flaker and after solidification thereon the material was separated from the drum as substantially dry flakes. Other portions of the slurries were slowly cooled in a mixer during continuous stirring and produced free-flowing granular products.

Example 5

A mixture of 51 pounds of anhydrous tetrasodium pyrophosphate with 19 pounds of MP 189 SX (DuPont) comprising a 52% aqueous sodium keryl sulphonate, and 30 parts of water is heated to yield a uniform solution-slurry and is introduced onto a cold surface. As soon as the mixture has cooled and solidified, it is scraped off in the form of damp flakes. These flakes subsequently harden on standing.

Example 6

A mixture of 44 pounds of 50% aqueous solution of sodium di-(2-ethylhexyl) phosphate, 156 pounds of sodium tripolyphosphate in anhydrous condition and 22 pounds of water is heated until a uniform fluid mass is obtained. This fluid is then slowly cooled during strirring and gives a free-flowing granular product.

A similar composition may be produced from 47.2 pounds of a 50% aqueous solution of sodium di-(2 ethylhexyl) phosphate, 150 pounds of anhydrous tetrasodium pyrophosphate and 26.4 pounds of water. A fluid mass is obtained in this instance during mixing at elevated temperatures, but it is too thick for satisfactory solidifying in a drum flaking treatment. The mass may be solidified by cooling in a mixing apparatus.

Example 7

Several mixtures were made with a 10% Gardinol ME, composed substantially wholly of sodium lauryl sulphate, with tetrasodium pyrophosphate containing 9 molecules of water. The mixture was heated until a fluid mass was obtained. Part of the mass was cooled during agitation and another part was cooled on a drum flaker. In both instances an apparently dry free-flowing mass of particles was obtained.

Example 8

A mixture containing 54% sodium tripolyphosphate, 11% Nacconol NR and 35% of water was heated to about 90° C. in a suitable mixer and then cooled during mixing. Although some evaporation of water occurred, the solidification was due primarily to the water being taken up by the polyphosphate as water of crystallization. A free-flowing product was obtained.

With some exceptions, the hereinbefore mentioned organic detergents employed in the products and processes of the present invention cannot practically be produced as free-flowing solids with the common detergent promoter salts such as sodium carbonate, sodium sulphate or with disodium phosphate. The action of the complex phosphate salts with reference to such detergents in the compositions of the present invention is therefore unique. When mixtures containing Tergitol, for example, and sodium sulfate are heated together with water in an attempt to form a slurry, the Tergitol separates out as a gummy mass on top of the hot fluid and the undissolved inorganic salt tends to settle out rapidly. Furthermore, when these mixtures are cooled, they result in the formation of very wet sticky solids of non-uniform composition. If the water is reduced in an attempt to avoid this condition in the solidified mass, then a fluid mixture of required homogeneity cannot be obtained during the agitation at an elevated temperature. The present invention is particularly valuable in its applicability to this type of detergent, that is the soluble salts of sulfated higher molecular secondary alcohols.

The products of the present invention have a number of advantages in use in addition to the high wetting, dispersing and cleansing properties, which are far superior to the activity of either of the ingredients when used separately. The products go into solution in water quickly and do not develop any undesirable heat of solution. The granular forms of the products are non-segregative during transportation and storage and when they are introduced into the water there is no

balling up or caking and the components go into a solution uniformly or at more even rates. With reference to the Tergitols and some of the other organic detergents which are of such sensitive character that they have not in the past been marketed in other than solution or paste form, the invention is advantageous in providing solid, free-flowing, granular compositions containing such organic materials in combination with phosphates which enhance the cleansing properties.

It should be understood that the present invention is not limited to the specific details herein given but that it extends to other materials and procedures which will occur to those skilled in the art upon consideration of the scope of the claims appended hereto.

We claim:

1. The method of producing a free flowing homogeneous granular detergent composition which comprises heating a mixture of a surface active, anionic, non-soap, water-soluble salt, organic detergent with a substantially non-hydrated alkali metal polyphosphate in a quantity adequate to take up as water of hydration substantially all of the water to be added, and with water added in a quantity sufficient to form a slurry at the temperature to which the mass is heated, said elevated temperature being below that at which decomposition of the detergent will occur, agitating the resulting mass until a homogeneous slurry is obtained, then solidifying the mixture merely by cooling the same without vaporizing off substantially any of the water whereby the water is left to be taken up as water of crystallization in the polyphosphate and reducing the solidified material to granular form whereby as a result the granules obtained are homogeneously constituted with the organic detergent intimately bound to the crystals of the polyphosphate in hydrate form.

2. The method of producing a free flowing homogeneous granular detergent composition which comprises heating a mixture of a surface active, anionic, non-soap, water-soluble salt, organic detergent with a substantially non-hydrated alkali metal polyphosphate in a quantity adequate to take up as water of hydration substantially all of the water to be added, and with water added in a quantity sufficient to form a slurry at the temperature to which the mass is heated, said elevated temperature being below that at which decomposition of the detergent will occur, agitating the resulting mass until a homogeneous slurry is obtained, then solidifying the mixture by flowing the mixture on to a cooling surface whereby solidification is effected without vaporizing off substantially any of the water, scraping the solidified material from the surface and after the resulting flakes have hardened through taking up the water as water of crystallization in the polyphosphate, grinding the same to a powder, the particles of which are homogeneously constituted with the organic detergent intimately bound to the crystals of the polyphosphate in hydrate form.

3. The method of producing a free flowing homogeneous granular detergent composition which comprises heating a mixture of a higher molecular alkyl sulphate water-soluble salt with a substantially non-hydrated alkali metal polyphosphate in a quantity adequate to take up as water of hydration substantially all of the water to be added, and with water added in a quantity sufficient to form a slurry at the temperature to which the mass is heated, said elevated temperature being below that at which decomposition of the detergent will occur, agitating the resulting mass until a homogeneous slurry is obtained, then solidifying the mixture merely by cooling the same without vaporizing off substantially any of the water whereby the water is left to be taken up as water of crystallization in the polyphosphate and reducing the solidified material to granular form whereby as a result the granules obtained are homogeneously constituted with the organic detergent intimately bound to the crystals of the polyphosphate in hydrate form.

4. The method of producing a free flowing homogeneous granular detergent composition which comprises heating a mixture of a water soluble salt of a sulphated higher molecular secondary alcohol with a substantially non-hydrated alkali metal polyphosphate in a quantity adequate to take up as water of hydration substantially all of the water to be added, and with water added in a quantity sufficient to form a slurry at the temperature to which the mass is heated, said elevated temperature being below that at which decomposition of the detergent will occur, agitating the resulting mass until a homogeneous slurry is obtained, then solidifying the mixture merely by cooling the same without vaporizing off substantially any of the water whereby the water is left to be taken up as water of crystallization in the polyphosphate and reducing the solidified material to granular form whereby as a result the granules obtained are homogeneously constituted with the organic detergent intimately bound to the crystals of the polyphosphate in hydrate form.

5. The method of producing a free flowing homogeneous granular detergent composition which comprises heating a mixture of a surface active, anionic, non-soap, water-soluble salt, organic detergent with a substantially non-hydrated tetrasodium pyrophosphate in a quantity adequate to take up as water of hydration substantially all of the water to be added, and with water added in a quantity sufficient to form a slurry at the temperature to which the mass is heated, said elevated temperature being below that at which decomposition of the detergent will occur, agitating the resulting mass until a homogeneous slurry is obtained, then solidifying the mixture merely by cooling the same without vaporizing off substantially any of the water whereby the water is left to be taken up as water of crystallization in the pyrophosphate and reducing the solidified material to granular form whereby as a result the granules obtained are homogeneously constituted with the organic detergent intimately bound to the crystals of the pyrophosphate in hydrate form.

6. The method of producing a free flowing homogeneous granular detergent composition which comprises heating a mixture of a surface active, anionic, non-soap, water-soluble salt, organic detergent with a substantially non-hydrated sodium tripolyphosphate in a quantity adequate to take up as water of hydration substantially all of the water to be added, and with water added in a quantity sufficient to form a slurry at the temperature to which the mass is heated, said elevated temperature being below that at which decomposition of the detergent will occur, agitating the resulting mass until a homogeneous slurry is obtained, then solidifying the mixture merely by cooling the same without vaporizing off substantially any of the water whereby the water is left to be taken up as water

of crystallization in the polyphosphate and reducing the solidified material to granular form whereby as a result the granules obtained are homogeneously constituted with the organic detergent intimately bound to the crystals of the polyphosphate in hydrate form.

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