

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Agglomeration Process for Making Granular Detergent Compositions

We, THE PROCTOR & GAMBLE COMPANY, a corporation organised under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, Ohio, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for making a granular detergent product and the product of the process. More particularly, the invention relates to a novel process for production of granular cleaning compositions of relatively low bulk density for hard surfaces. As used herein, "granular hard surface cleaning compositions" refers to compositions having utility in cleaning hard surfaces such as floors, furniture, and dishes, but which also have utility in cleaning clothes, other fabrics, etc. These granular hard surface cleaning compositions also have outstanding utility when mixed with other components including detergent materials such as soap and synthetic detergents.

Granular cleaning compositions for hard surfaces normally are produced by mixing dry particulate inorganic salts with minor amounts of a dry organic surface active agent. Due to the relatively high bulk density of the component inorganic salts and the reduction in size of the individual particles thereof as a result of the mixing operation, the bulk density of the usual hard surface cleaning compositions falls in the range of about .85 to 1.0 gm/cc. Products of this bulk density are unsatisfactory if the manufacturer desires to package such a product in cartons of the

volume normally used to package general purpose granular cleaning compositions. If such cartons are filled with a hard surface cleaning granular composition of the normal high bulk density, the amount of product in the carton requires that a price be charged for the filled package that is higher than many consumers are willing to pay for a single package. On the other hand, customers are dissatisfied if cartons of normal volume are used for a granular high density hard surface cleaning composition and, in order to hold the price of the filled package within the range that most customers are willing to pay, a substantial portion of the volume of the carton is left unfilled.

Various methods of production for granular hard surface cleaning compositions of relatively low bulk density have been proposed previously, for example, the process described in United States Patent Specification No. 2,623,856, which discloses the production of a low density granular cleaning composition by heating a mixture of a liquid surfactant and granular tetraborates to a temperature such that the tetraborates evolve steam from their water of hydration and are caused thereby to puff and form hollow spheres, thus lowering the bulk density of the mixture. Such processes in order to obtain a substantial decrease in bulk density require that the tetraborate salt be present in the compositions in major amounts with consequent increase in cost of such products over ones in which less expensive raw materials are used. Another process for obtaining a simulated spray dried granular cleaning composition, not limited to use for hard surface cleaning, and of a bulk density comparable with that of currently

[Price 4s. 6d.]

produced spray dried detergents is described in pending Australian Patent Application, No. 486/61. The products of this invention have bulk densities somewhat reduced from that of the dry particulate starting materials and are formed by agglomeration of dry particulate raw materials, including a hydratable salt, through spraying with relatively small quantities of an aqueous solution of an alkali metal silicate during agitation, with subsequent screening to the final size desired. The bulk density of a finished product so agglomerated, however, is found to be reduced but little below the bulk density of the original dry particulate raw materials because the silicate solution which acts upon partial dehydration as the adhesive producing the interparticulate bonds of the agglomerated granules is a relatively slow setting adhesive, and the particles so bonded are compressed from their original state by mixing subsequent to the instant of their agglomeration and during the period that it takes the silicate bonds to become rigid. It is possible to avoid this compacting action in agglomerating particulate materials by spraying on large quantities of the silicate solution, but in such a case the resultant product is either caked badly as produced or absorbs moisture on standing and becomes badly caked and thus is unacceptable to the consumer. Accordingly the bulk density of a finished product, free from caking, agglomerated by use of practical, low levels of a dehydrated silicate solution spray during mixing is found to be not lower than 80% of the original bulk density of its ingredients at the completion of the process.

Another consequence of the use of even practical levels of a slow setting adhesive to agglomerate a product in the process described in the Australian application is that agitation is required throughout the period during which the adhesive bonds become set to prevent excessive caking and lumping of the final product. Use of a fast setting adhesive according to the present invention reduces markedly the period which agitation is required to produce a free flowing product, and in many instances eliminates the need for any agitation at all after the end of the spray period.

Acid salts, such as alkali metal bicarbonates, are usually used in granular hard surface cleaners to buffer the pH of the water solution of the compositions during use to about 10, for mildness to hands and the washed surfaces. The preferred method of use of such cleaners is one of wiping the soiled surface with a damp cloth containing a solution of the product, and when used in this manner, subsequent rinsing of the washed surface with fresh water or wiping with a dry cloth are not found to be necessary to obtain a clean looking surface after drying. A defect of a product agglomerated by means of an alkali metal silicate spray, which contains an acid

salt such as bicarbonate, either by itself or in the form of sesquicarbonate, is that in an aqueous solution an unsightly silicate flocculate often will appear at the surface of the solution, and a hard surface, allowed to dry after being cleaned in the preferred manner, with a solution of such a composition, will often be found to show a visible deposit or film caused by the flocculate.

An object of the present invention is to provide a process for making granular hard surface cleaning compositions which are relatively low in bulk density and which do not exhibit the defects described above.

According to this invention there is provided a process for preparing granular cleaning compositions of a bulk density less than 80% of the average bulk density of the dry particulate raw materials thereof comprising: agitating a mixture of discrete solid particles which will pass a 10 mesh Tyler screen, said mixture essentially comprising inorganic salts, selected from the group consisting of alkali metal orthophosphates, tripolyphosphates, pyrophosphates, carbonates, bicarbonates, sesquicarbonates, tetraborates and mixtures thereof, at least one of said salts having a water of hydration content substantially below its capacity, but which when hydrated forms a crystalline hydrate, and spraying from 70 to 96 parts of said mixture with an aqueous solution of 20% to 50% by weight of an organic adhesive which when dried is resolvable in water, in an amount such that from 1 to 10 parts of organic adhesive solids dissolved in from 3 to 20 parts of water are added to the mixture; removing enough water from the added organic adhesive solution by hydration of the hydratable salts in the agitated mixture to form a dehydrated adhesive, thereby causing agglomeration of the mixture into granules.

The effect of the invention is to produce a mild effective granular hard cleaning composition of a final bulk density less than 80% of the average bulk density of the dry particulate raw materials used therein, by using, as an adhesive to bond individual particles together into an agglomerated granule, materials that, in aqueous solution, are water soluble but which become quick setting on abstraction of water, so that the interparticulate bonds once formed are resistant to substantial rupture or compression during further mixing. Thus, the voids present in the granule as formed are maintained without substantial change during subsequent processing, and the initial low bulk density of the agglomerated granule is preserved. The adhesive used must be water-soluble under the conditions of use of the finished product, for if the adhesive, once it has hardened, will not redissolve, the adhesive will be present in the solution during use in the form of grit, and soiled surfaces will be likely to be scratched during cleaning.

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Preferably, the product is screened, after agglomeration, to the desired particle size.

5 An essential component of the dry particulate raw materials agglomerated by the process is an inorganic salt that is capable of forming a crystalline hydrate and is dry or alternatively has a content of water of hydration so low that the salt has capacity to bind as water of hydration the amount of water that must be removed from the adhesive solution to make the agglomeration possible. When an adhesive solution in an amount and composition as described herein is sprayed onto an agitated mixture of the hydratable inorganic salt and any other ingredients of the composition, or some of them, in a particulate state of reduced moisture content, the water content of the adhesive solution is reduced through the formation of the inorganic salt hydrate, and the resulting sticky adhesive acts as an agglomerating agent in forming granules with interparticulate bonds so strong that they are resistant to further compacting and possess a bulk density less than 80% of that of the particulate raw materials.

25 The steps of the process of this invention are suitably carried out in equipment which essentially comprises a means for reducing the size of the dry ingredients before mixing to at least a size such that all will pass a 10 mesh Tyler screen (if the suppliers do not provide the raw materials of such size), a revolving mixing vessel equipped with means adapted to agitate and uniformly mix dry particulate materials without causing a substantial reduction in size of the particles, (for example, a cement mixer), and a spray system at the mixer through which the adhesive solution can be sprayed onto the agitated dry ingredients. A screening means to recover the desired size range of the finished agglomerated granules also is desirable. It is of course possible to replace the batch mixer with a continuous mixer provided with a feed zone, a spraying zone, and a discharge zone all provided with agitating means. A preferred form of such a continuous mixer is the revolving inclined drum type.

40 The inorganic salt capable of forming a crystalline hydrate to be used may most suitably be any of such salts which are compatible with the other ingredients of the composition and the usual hydrate of which is stable at temperature of at least 120° F., although less stable hydrates can be utilised by maintaining the necessary low temperatures during the process to prevent them from decomposing. Preferably an alkaline phosphate salt or salts, possessing in its hydrate form the required stability, is the hydratable salt as such compounds act not only in this necessary function but also as detergents. Specifically, trisodium orthophosphate which forms octa-, deca- and dodeca-hydrates is the preferred component for use in these compositions. Trisodium ortho-

phosphate octahydrate when fully hydrated contains 46.7% water of hydration and similarly the salt in fully hydrated deca and dodecahydrate forms contains 52.4 and 56.8% water of hydration, respectively. Another inorganic salt useful as the hydratable agent is sodium carbonate which forms both a mono- and a decahydrate (containing respectively when fully hydrated 14.5% and 63.0% water of hydration). Of course the hydratable agent is added to the composition in a dry free-flowing form possessing a moisture content significantly below the maximum that can be bound therein when fully hydrated.

In addition to the alkali metal orthophosphate and carbonate salts, the other inorganic components of such hard surface cleaners may include alkali metal tripolyphosphate, pyrophosphate, tetraborate, bicarbonate or sesquicarbonate salts or mixtures thereof. Some of these salts in addition form crystalline hydrates that are effective for the purposes of this invention.

It is preferred, but not necessary, that at least 1%, by weight of the composition, of at least one non-soap organic non-cationic synthetic detergent be present as a minor constituent. A preferred active detergent is a granular sodium alkyl benzene sulphonate having alkyl groups of 9 to 15 carbon atoms, especially one averaging 12 carbon atoms. However, equivalent results are obtained by substituting in whole or in part for the sodium alkyl benzene sulphonate a sodium alkyl sulphate having alkyl groups of 10 to 18 carbon atoms. Moreover, other non-soap organic synthetic detergent active agents may be substituted in whole or in part for the two described above, such as alkyl glyceryl ether sulphonates (particularly those containing at least 10% of alkyl polyglyceryl ether sulphonate), fatty acid monoglyceride sulphates and sulphonates, salts of fatty acid esters of hydroxy alkyl sulphonic acid, acyl taurides, alkyl oxyethylene sulphates or sulphonates, or any other from the class of water-soluble salts of an organic sulphuric reaction product having in its molecular structure an alkyl radical whose carbon atom content is within the range of 8 to 22 carbon atoms and a sulphonic acid or sulphuric acid ester radical.

Nonionic organic synthetic detergent active agents may also be substituted in whole or in part for the anionic detergent agents. Examples of such nonionic agents are alkylated aryl polyether alcohols, polyoxyethylene glycol esters of fatty acids, and polyoxyethylene ethers of fatty alcohols. The nonionic active material may be added in granular solid form or as a liquid.

Among the materials that can be used in accordance with this invention as the organic adhesive in agglomerating the dry particulate raw materials are various starches such as corn starch and tapioca starch; dextrin and

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other partially hydrolysed or so called "water soluble" starches; gums, such as gum tragacanth, quince seed, and other water soluble gums, and water soluble glues.

In known manner the organic adhesive material is prepared by heating it in water, preferably with added borax and mould control agents. For the sake of brevity, these aqueous preparations are referred to as "solutions" although it is recognised that they are usually not true solutions.

The water in the adhesive solution sprayed on the dry mixture of salts and, if desired, detergents does not dissolve the dry mixture, since the adhesive solution is added in amounts and at a rate such that the water is taken up by the hydration of the hydratable salt and the other ingredients. The water of solution of the adhesive acts therefore only as a carrier for the agglomerating agent which is the partially dehydrated adhesive. The adhesives are used in aqueous solutions at a concentration of from 20% to 50% adhesive solids. To obtain the desired degree of agglomeration the adhesive solution is sprayed on the agitated dry mixture in an amount of from 1 part to 10 parts of adhesive solids per 100 parts of the final composition, the solids being dissolved in from 3 to 20 parts of water and thereby adding to the mix from 1 part to 15 parts of water for binding in the inorganic salt hydrate with the remainder of water being absorbed in the product as non-hydrate water. A preferred usage of the aqueous adhesive solution will fall within the range of 0.04 to 0.10 parts per part of the dry ingredient mix with the total water content by analysis in the final composition amounting to less than 40% by weight of said final composition.

The adhesive solution may be sprayed on the agitated mixture of all of the dry particulate raw materials as described above to obtain the desired low density agglomerates, or if desired, certain of the inorganic particulate raw materials including a hydratable salt, such as the orthophosphate, and bicarbonate, may first be agglomerated with the spray of adhesive and then the remaining dry ingredients including other hydratable or non-hydratable salt or salts and the organic non-cationic detergent (if desired) can be added in granular form in a subsequent second mixing step. In such a two step process the reduction in bulk density of the agglomerates alone is sufficiently large than even after the granules at their original density are mixed with the agglomerates, the final bulk density of the whole composition is lower than 80% of the average bulk density of all of the dry raw materials.

Another desirable variation in procedure involves forming a coloured agglomerate. This agglomerate can be coloured by spraying the material with pigment either before or after

agglomeration, to form brightly coloured granules. Pigment, as used herein, refers to any type of colouring material, whether soluble or insoluble. These granules can be used to make a brightly coloured granular composition or they can be mixed with other colourless or lightly coloured granules as, for example, according to British Patent Specification No. 808,668 to obtain a distinctively speckled granular composition. In such a composition from 2% to 30% of the granules are of a hue which is strikingly different from that of the rest of the granules and have a chroma according to the Munsell notation of at least 4 and a Munsell value of substantially 4 to 7. These granules should consist predominantly of granules having a minimum dimension of more than about 0.2 millimeter and the colour is preferably non-toxic, alkali stable and non-substantive to fabrics.

Also, if desired, the coloured granules can be made more quickly soluble than the other granules by preparing them from an inorganic salt or salts having quick solubility. This use of quickly-soluble coloured granules results in the almost immediate disappearance of colour when the speckled detergent composition is added to the wash water. Examples of suitable quick-dissolving inorganic salts include light or heavy density sodium tripolyphosphate in either granular or powdered form, soda ash, pyrophosphates, and ortho phosphates.

The rate of addition of the adhesive solution in the form of a spray should be rapid enough to wet the particles of the agitated dry ingredient mixture sufficiently for agglomeration to occur during continued agitation, but not so rapid that the agitated dry mixture forms into balls or other large masses thus losing its desired particulate characteristics. The degree of atomization of the adhesive spray is important in obtaining the best agglomerating performance. Poor atomization results in excessive lumping and non-agglomeration of some of the dry ingredients. Proper atomization is achieved by use of spray nozzles of the two fluid type, with air or steam at or above about 20 p.s.i.g., as the second material fed to the nozzles or if desired by the use of nozzles which atomize the liquid being sprayed solely as a result of its pressure, as for instance nozzles supplied by The Spraying Systems Company, Whirljet or LN Series. It may be desirable to heat the adhesive solution to reduce its viscosity. For best results the agglomerating spray must be finely atomized and the desired particle size of the droplets of the spray should be no larger than the size of the average of the particles to be agglomerated, with even smaller droplet sizes being preferable.

In order to obtain the proper agglomerating performance from the addition of such relatively small amounts of the agglomerating

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agent the dry ingredient mix must be uniformly contacted by the spray and thus must be in constant motion which is provided by the agitator of the mixer during the spraying operation. Instead of a relatively level agitated bed of the dry ingredients during the spraying operation, a tumbling bed may be provided by rotating the mixer about an axis substantially different than the vertical for a preferred method of obtaining proper agglomeration.

If the process is carried out on a batch basis the dry ingredients of proper size are charged to the mixer preferably with the agitator running during charging in order to produce a mix of maximum uniformity, the aqueous adhesive solution spray is then started at the prescribed rate and continued until finished. However, the agitator may be started after charging is completed but prior to the start of the spray.

After the agglomeration step, either batch or continuous, the product may be screened at once to recover the desired range of particle sizes for packaging purposes, and the oversize particles are returned for regrinding and addition to any separated dust for reworking. Alternatively the agglomerated mixture may be allowed to age in bulk, preferably thinly spread, for a few hours prior to screening. Such an aging period is desirable if the product, as discharged from the mixer, is merely in character rather than crisp and free flowing.

The preferred size range of the agglomerated low-density final product is from a particle that will just pass a 10 mesh Tyler screen to a particle that will just be retained on a 100 mesh Tyler screen. In addition, it is desired to control the particle size of the dry particulate raw materials and the operation of the agglomeration process such that at least 75% of the agglomerates formed are sized within a size range of from 20 to 100 mesh (Tyler Scale). All dry particulate raw materials thus should be of size at least to pass a 10 mesh Tyler screen and preferably to pass a 20 mesh Tyler screen. As the size of the particulate raw materials decreases it is necessary to increase the usage of the adhesive solution to obtain a final product of a constant particle size distribution. Thus it is preferable to set a minimum size limit for the dry particulate raw materials at about 100 mesh (Tyler) to hold the usage of the adhesive solution to an economical amount of 9% or less, though finer raw materials can be agglomerated with amounts of the adhesive solution in excess of 9%.

EXAMPLE I

The following dry particulate ingredients all of which passed a 10 mesh screen were added to a cement mixer of 3.5 cubic feet capacity while it was agitating.

38 lb. trisodium orthophosphate (containing 50.6% water of hydration) 65
19 lb. anhydrous sodium carbonate
19 lb. sodium bicarbonate
5.6 lbs. anhydrous sodium tripolyphosphate
7.8 lb. synthetic detergent composition (containing 21.6% sodium alkyl benzene sulphonate having alkyl groups of an average of 12 carbon atoms, 38.4% sodium tripolyphosphate, 18.8% sodium sulphate, with the remainder being other ingredients or water). 70 75

0.6 lb. of a mixture of minor ingredients

The minor ingredients were pigments, a pigment emulsifier, perfume, and a dust suppressant. On to the agitated mixture of dry ingredients which possessed an average density of 0.81 grams/cc. was sprayed at a temperature of 150° F., 10 lbs. of an aqueous adhesive solution containing 38% of dextrin, 1.9% of sodium tetraborate pentahydrate, and .095% of sodium salt of orthophenylphenol, a mould control agent (Dowicide A from the Dow Chemical Co.) prepared by heating in known manner. The adhesive solution was sprayed onto the agitated dry ingredients at the rate of .25 lb. of adhesive solids per minute through a two fluid nozzle made by Spraying Systems Company, Chicago, Illinois, of 60/100 120's size (Set-up No. 4) with air at 60 p.s.i.g. as the second fluid. Crisp free-flowing granules were formed by the end of a three minute period of agitation following the end of the adhesive addition. The granules were found to have a bulk density of 0.65 grams/cc constituting a reduction in density to below 80% of the original average bulk density of the component dry raw materials. The granules were screened and found to have 1.0% retained on a 20 mesh screen and 6% passing a 100 mesh screen, the remainder of 93% being between these two sizes. Analysis of the finished product showed that it contained 27.3% water. An aqueous solution of 1% of the composition was found to have a pH of 10.4 and when used in a no-rinse, no-wipe, method was found to clean soiled hard surfaces efficiently. Similar results are obtainable by substituting in whole or in part for the sodium alkyl benzene sulphonate as the organic detergent active ingredient, sodium alkyl sulphate having alkyl groups of 8 to 18 carbon atoms and in a preferred instance, containing a predominance of alkyl groups of 12 carbon atoms. 80 85 90 95 100 105 110 115

EXAMPLE II

The following dry particulate ingredients, 100% of which passed a 10 mesh screen, were added to a cement mixer of 2 cubic feet capacity while it was agitating:

30.0 lbs. sodium tetraborate decahydrate 125
6.4 lbs. anhydrous sodium carbonate
6.3 lbs. sodium bicarbonate

Onto the agitated mixture of the dry ingre-

dients which possessed an average bulk density of 0.85 grams/cc. was sprayed at a temperature of 150° F., 4.0 lbs. of an aqueous adhesive solution containing 1.29 lbs. of dextrin and 0.104 lbs. of sodium tetraborate pentahydrate with .1% of Dowicide A prepared by heating in known manner. The rate of addition of the adhesive solution in spray form to the agitated mixture was .33 lb. of solids/minute with air at 40 p.s.i.g. as the second fluid through the spraying system of Example I.

Following the addition of the adhesive solution, and while the mixer continued to be agitated the following dry particulate materials at an average bulk density of 0.85 grams/cc. were added, all of which passed a 10 mesh screen.

11.0 lbs. anhydrous granular sodium tripolyphosphate

2.0 lbs. sodium alkyl benzene sulphonate granular detergent having alkyl groups of 9 to 15 carbon atoms and averaging 12 carbon atoms (40% ABS-60% Na₂SO₄)

0.3 lbs. minor ingredients as in Example I.

The complete mixture was agitated for three minutes and at the conclusion of that period crisp free-flowing granules were obtained. The granules were found to have a bulk density of .60 grams/cc., and thus the density of the product had been reduced to below 71% of the average density of the starting dry raw materials. The granules were screened and found to have therein 1.5% coarser than 20 mesh and 15.6% finer than 100 mesh, for a total of 82.9% between these two sizes. Analysis of the product revealed that it contained 21.8% H₂O. An aqueous solution of 1% of the composition was found to have a pH of 9.42, and when used to wash soiled black tiles in a no-rinse, no-wipe manner was found to clean the tiles efficiently, and the tiles were free from a visible deposit thereon after drying.

Similar results are obtained if the mixture of minor ingredients is added in dry form or as a solution sprayed on the final composition, although minor ingredients as the dust suppressant and perfume, if used, are preferably added as solutions, and if a nonionic organic synthetic detergent active ingredient, for example, of the type of an alkyl aryl ether (Triton—Trade Mark—CF 10 from the Rohm & Haas Co.) is substituted in whole or in part for the anionic synthetic detergent of this Example. Similar results are also obtained if sodium tetraborate decahydrate or sodium metaborate pentahydrate are substituted in whole or in part for the sodium tetraborate pentahydrate used in the adhesive solution of this Example.

EXAMPLE III

The following dry particulate ingredients,

both of which passed a 20 mesh screen, were added to the cement mixer of Example II.

7.4 lbs. of trisodium orthophosphate (60.6% H₂O)

5.3 lbs. of granular sodium bicarbonate

Onto the agitated mixture thereof, which had an original bulk density of 0.92, was sprayed at a temperature of 150° F. 1.5 lbs. of an aqueous solution containing 0.43 lbs. of dextrin (containing 7.6% water), 0.04 lbs. of sodium tetraborate pentahydrate and .1% Dowicide A prepared by heating in known manner. The adhesive solution was sprayed onto the agitated mixture at a rate of .16 lbs. of solids content/minute with air at 40 p.s.i.g. as the second fluid in the spraying system of Example I. Immediately following completion of the addition of the adhesive solution, and while the mixer continued to be agitated the following dry particulate materials at an average bulk density of 1.02 grams/cc. were added, both of which passed a 10 mesh screen:

5.3 lbs. of granular anhydrous sodium carbonate

0.6 lbs. of the detergent of Example II

The complete mixture was agitated for three minutes and at the conclusion of that period crisp free-flowing granules of a bulk density of 0.64 grams/cc. were obtained, which on screening were found to have 93.9% by weight in a size range that passes a 20 mesh but is retained on a 100 mesh screen. A reduction in bulk density to less than 67% of the original density of the dry raw materials was achieved.

An aqueous solution of 1% of the composition had a pH of 10.4 and was an efficient cleaner of soiled hard surfaces when used thereon in a no-rinse, no-wipe manner.

EXAMPLE IV

To the mixer of Example II were added the following dry particulate ingredients, both of which passed a 20 mesh screen:

11.4 lbs. of trisodium orthophosphate (47.0% H₂O)

6.5 lbs. of sodium bicarbonate

Onto the agitated mixture thereof, which had a bulk density of 0.964 grams/cc. was sprayed at a temperature of 140° F., 1.35 lbs. of an aqueous solution containing a total of 42% of dextrin, sodium tetraborate, and mould control agent in the proportions of Example I. The adhesive solids were sprayed on the agitated mixture at a rate of 0.18 lb./minute with air at 50 p.s.i.g. as the second fluid in the spraying system of Example I. The original moisture content of the trisodium orthophosphate was low enough that sufficient of the water added thereto in the solution of the adhesive solids was taken up as water of constitution in crystalline Na₃PO₄·10 H₂O and Na₃PO₄·12 H₂O, to produce the requisite sticky adhesive and agglomerates of .543 grams/cc. bulk density were formed.

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Immediately following the completion of the addition of the adhesive solution, and while the mixer continued to be agitated the following dry particulate materials at an average bulk density of 0.697 grams/cc. were added, all of which passed a 10 mesh screen:

5 6.5 lbs. of anhydrous granular sodium carbonate

10 1.7 lbs. of granular anhydrous sodium tripolyphosphate

2.4 lbs. of the detergent of Example II

12 lbs. of an aqueous solution of the minor ingredients of Example I

15 was added to the mixture, and the entire mixture was agitated for four additional minutes. At the conclusion of the period of agitation crisp free-flowing granules of a bulk density of 0.598 grams/cc. were obtained, which when screened were found to have 88.6% by weight within a size range that will pass a 20 mesh screen and be retained on a 100 mesh screen. The bulk density of the final product had been reduced to less than 69% of the composite bulk density of the particulate raw materials (.87 grams/cc.). An aqueous solution of 1% of the composition had a pH of 10.4 and was an efficient cleaner of soiled hard surfaces when used thereon in a no-rinse, no-wipe method.

30 Similar results are obtained when corn starch or gum tragacanth are substituted for dextrin in the adhesive solution of this example.

EXAMPLE V

35 To the mixer of Example II were added the following dry particulate ingredients, both of which passed a 20 mesh screen:

9.24 lbs. of anhydrous sodium carbonate

9.24 lbs. of sodium bicarbonate

40 Onto the agitated mixture which had a bulk density of 0.813 grams/cc. was sprayed at a temperature of 120° F., 5.4 lbs. of the aqueous adhesive solution of Example I. The adhesive solids were sprayed on the agitated mixture at a rate of 0.26 lb./minute, with air at 50 p.s.i.g. as the second fluid in the spraying system of Example I. Agglomerates of a bulk density of 0.449 grams/cc. were formed by the end of the spray period.

50 Immediately after the end of the spray period, to the agglomerated particles in the agitated mixer were added the following dry particulate materials which passed a 10 mesh screen and had a bulk density of 0.485 grams/cc.:

55 5.4 lbs. granular anhydrous sodium tripolyphosphate

2.4 lbs. of the detergent of Example II

12 lbs. of an aqueous solution of the minor ingredients of Example I

60 was added to the agglomerates and the entire mixture was agitated for four additional minutes. Mealy granules resulted which after aging for two hours were found to be crisp and free-flowing and of a bulk density of 0.451 grams/cc., and thus the final composition

had been reduced in density to less than 64% of the bulk density of the original particulate raw materials (.715 grams/cc.). The composition was screened and 79.6% was found to be within a size range that passes a 20 mesh screen and is retained on a 100 mesh screen. An aqueous solution of 1% of the composition had a pH of 10.2 and proved to be an efficient cleaner of soiled hard surfaces when used thereon in a no-rinse, no-wipe method.

Similar results are obtained by substituting potassium pyrophosphate for the sodium tripolyphosphate of this Example.

EXAMPLE VI

To the mixer of Example II were added the following dry particulate raw materials, all of which passed a 20 mesh screen:

11.4 lbs. trisodium orthophosphate (47.0% H₂O)

4.5 lbs. sodium bicarbonate

4.5 lbs. anhydrous sodium carbonate

1.7 lbs. anhydrous sodium tripolyphosphate

Onto the agitated mixture which had a bulk density of 0.839 grams/cc. was sprayed at a temperature of 100° F. 5.4 lbs. of an aqueous adhesive solution containing 28% of ingredients in the proportions of the solution of Example III.

The adhesive solids were added to the agitated mixture at a rate of 0.18 lbs./minute with air at 20 p.s.i.g. as the second fluid in the spraying system of Example III. Agglomerates of a bulk density of 0.547 grams/cc. were formed by the end of the spray period. Immediately after the spray has ended 2.4 lbs. of the granular dry detergent of Example II of a bulk density of 0.29 grams/cc. were added to the agitated agglomerates, followed by 12 lbs. of the aqueous solution of minor ingredients of Example I. After three minutes of additional agitation the composition was found to be mealy and formed soft lumps. After aging for 16 hours the product was screened and found to be free-flowing and had 94.2% by weight of a size range which passes a 20 mesh screen and is retained on a 100 mesh screen. The product was found to have a total moisture content of 34.0% by analysis. The final product had a bulk density of 0.517 grams/cc. and thus had been reduced in density to less than 66% of the composite bulk density of the particulate raw materials (.784 grams/cc.). An aqueous solution of 1% of the composition had a pH of 10.4 and was an excellent cleaner for soiled hard surfaces when used thereon in a no-rinse, no-wipe method.

Similar results are obtained when the particulate ingredients of this Example are varied within the following amounts: trisodium orthophosphate—from 30 to 45%, sodium bicarbonate—from 10 to 24%, sodium carbonate—from 8 to 48%, sodium tripolyphosphate—from 1 to 3%.

phate—from 3 to 7%, and detergent from 3 to 20% (i.e., from 1 to 8% for the detergent active ingredient).

EXAMPLE VII

5 One hundred pounds of granular light-density (0.65 grams/cc. hard pack density) sodium tripolyphosphate with a granule size smaller than 20 mesh was the dry ingredient. The spray-on technique of Example I was used and 20 pounds of dextrin glue was sprayed on to the sodium tripolyphosphate. This glue contained 12 pounds water, 7.36 pounds dextrin, 0.14 pounds $\text{Na}_2\text{B}_4\text{O}_7$, and 0.50 pounds NaBO_2 . The completed granules were coloured by spraying on 15 pounds of a dye slurry consisting of 14.548 pounds water, 0.395 pounds phthalocyanine blue, and 0.057 pounds of Geigy Polar Brilliant Blue. The last ingredient is substantive to clothing. This gave 20 135 pounds of blue speckles with a density of 0.45 grams/cc. When 5% by weight of these coloured granules are mixed with white granules, either spray dried or agglomerated according to the process of this invention, a distinctive speckled product results.

The granules prepared in the preceding Examples and the granules of this invention in general can be either packaged and sold as such or may be compressed to form tablets.

WHAT WE CLAIM IS:—

30 1. A process for preparing granular cleaning compositions of a bulk density less than 80% of the average bulk density of the dry particulate raw materials thereof comprising: 35 agitating a mixture of discrete solid particles which will pass a 10 mesh Tyler screen, said mixture essentially comprising alkali metal salts, selected from the group consisting of alkali metal orthophosphates, tripolyphosphates, pyrophosphates, carbonates, bicarbonates, sesquicarbonates, tetraborates and mixtures thereof, at least one of said salts having a water of hydration content substantially below its capacity, but which when hydrated forms a crystalline hydrate, and spraying from 70 to 96 parts of said mixture with an aqueous solution of 20% to 50% by weight of an organic adhesive which when dried is resoluble in 50 water, in an amount such that from 1 to 10 parts of organic adhesive solids dissolved in from 3 to 20 parts of water are added to the mixture; removing enough water from the added organic adhesive solution by hydration of the hydratable salts in the agitated mixture to form a dehydrated adhesive, thereby causing agglomeration of the mixture into granules.

2. The process of claim 1 in which the product is subsequently screened to the desired particle size.

3. The process of claim 1 or 2 in which the

mixture contains an organic non-cationic detergent ingredient.

4. The process of any of the preceding claims in which the mixture contains at least the orthophosphate and bicarbonate salts which are mixed and sprayed with 0.04—0.10 parts of the aqueous solution of the organic adhesive per part of the total dry ingredients to the finished composition to form agglomerates thereof and, in a second mixing step, other ingredients of the composition are added.

5. The process of any of the preceding claims in which the size of the dry particulate raw materials is 10 to 100 mesh Tyler screen.

6. The process of any of claims 3 to 5 in which the organic detergent ingredient is sodium alkyl benzene sulphonate having alkyl groups of 9—15 carbon atoms.

7. The process of claim 6 in which the alkyl groups have an average of 12 carbon atoms.

8. The process of any of claims 3 to 5 in which the organic detergent ingredient is sodium alkyl sulphate having alkyl groups of 10—18 carbon atoms.

9. The process of any of the preceding claims in which the hydratable salt comprises at least trisodium orthophosphate.

10. The process of any of claims 1 to 9 in which the hydratable salt comprises at least sodium carbonate.

11. The process of any of the preceding claims in which the organic adhesive is a starch, a partially hydrolysed starch, a gum, or a glue.

12. The process of claim 11 in which the organic adhesive is dextrin.

13. The process of any of the preceding claims in which a pigment is included in the mixture so that the resulting granules are brightly coloured having a chroma according to the Munsell notation of at least 4 and a Munsell value of substantially 4 to 7.

14. A process for preparing granular cleaning compositions substantially as hereinbefore described in any of the Examples.

15. A granular cleaning composition prepared according to the process claimed in any of the preceding claims.

16. A speckled granular cleaning composition which is a mixture of from 98% to 70%, by weight, of a composition prepared by the process claimed in any of claims 1 to 12 and from 2% to 30%, by weight, of a composition prepared according to claim 13.

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phate—from 3 to 7%, and detergent from 3 to 20% (i.e., from 1 to 8% for the detergent active ingredient).

EXAMPLE VII

5 One hundred pounds of granular light-density (0.65 grams/cc. hard pack density) sodium tripolyphosphate with a granule size smaller than 20 mesh was the dry ingredient. The spray-on technique of Example I was used and 20 pounds of dextrin glue was sprayed on to the sodium tripolyphosphate. This glue contained 12 pounds water, 7.36 pounds dextrin, 0.14 pounds $\text{Na}_2\text{B}_4\text{O}_7$, and 0.50 pounds NaBO_2 . The completed granules were coloured by spraying on 15 pounds of a dye slurry consisting of 14.548 pounds water, 0.395 pounds phthalocyanine blue, and 0.057 pounds of Geigy Polar Brilliant Blue. The last ingredient is substantive to clothing. This gave 20 135 pounds of blue speckles with a density of 0.45 grams/cc. When 5% by weight of these coloured granules are mixed with white granules, either spray dried or agglomerated according to the process of this invention, a distinctive speckled product results.

The granules prepared in the preceding Examples and the granules of this invention in general can be either packaged and sold as such or may be compressed to form tablets.

WHAT WE CLAIM IS:—

1. A process for preparing granular cleaning compositions of a bulk density less than 80% of the average bulk density of the dry particulate raw materials thereof comprising: 35 agitating a mixture of discrete solid particles which will pass a 10 mesh Tyler screen, said mixture essentially comprising alkali metal salts, selected from the group consisting of alkali metal orthophosphates, tripolyphosphates, pyrophosphates, carbonates, bicarbonates, sesquicarbonates, tetraborates and mixtures thereof, at least one of said salts having a water of hydration content substantially below its capacity, but which when hydrated forms a crystalline hydrate, and spraying from 70 to 96 parts of said mixture with an aqueous solution of 20% to 50% by weight of an organic adhesive which when dried is resolvable in water, in an amount such that from 1 to 10 parts of organic adhesive solids dissolved in from 3 to 20 parts of water are added to the mixture; removing enough water from the added organic adhesive solution by hydration of the hydratable salts in the agitated mixture to form a dehydrated adhesive, thereby causing agglomeration of the mixture into granules.

2. The process of claim 1 in which the product is subsequently screened to the desired particle size.

3. The process of claim 1 or 2 in which the

mixture contains an organic non-cationic detergent ingredient.

4. The process of any of the preceding claims in which the mixture contains at least the orthophosphate and bicarbonate salts which are mixed and sprayed with 0.04—0.10 parts of the aqueous solution of the organic adhesive per part of the total dry ingredients to the finished composition to form agglomerates thereof and, in a second mixing step, other ingredients of the composition are added.

5. The process of any of the preceding claims in which the size of the dry particulate raw materials is 10 to 100 mesh Tyler screen.

6. The process of any of claims 3 to 5 in which the organic detergent ingredient is sodium alkyl benzene sulphonate having alkyl groups of 9—15 carbon atoms.

7. The process of claim 6 in which the alkyl groups have an average of 12 carbon atoms.

8. The process of any of claims 3 to 5 in which the organic detergent ingredient is sodium alkyl sulphate having alkyl groups of 10—18 carbon atoms.

9. The process of any of the preceding claims in which the hydratable salt comprises at least trisodium orthophosphate.

10. The process of any of claims 1 to 9 in which the hydratable salt comprises at least sodium carbonate.

11. The process of any of the preceding claims in which the organic adhesive is a starch, a partially hydrolysed starch, a gum, or a glue.

12. The process of claim 11 in which the organic adhesive is dextrin.

13. The process of any of the preceding claims in which a pigment is included in the mixture so that the resulting granules are brightly coloured having a chroma according to the Munsell notation of at least 4 and a Munsell value of substantially 4 to 7.

14. A process for preparing granular cleaning compositions substantially as hereinbefore described in any of the Examples.

15. A granular cleaning composition prepared according to the process claimed in any of the preceding claims.

16. A speckled granular cleaning composition which is a mixture of from 98% to 70%, by weight, of a composition prepared by the process claimed in any of claims 1 to 12 and from 2% to 30%, by weight, of a composition prepared according to claim 13.

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