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(54) **Agglomeration process for making granular detergents and composition made thereby.**

(57) Granular detergent compositions resistant to caking in dispenser cups are prepared by the addition of water or an aqueous sodium silicate solution agglomerating agent to particulate ingredients comprising sodium tripolyphosphate followed by the addition of an alkali metal chloride having a particle size such that at least 75% by weight passes through a 35 Tyler mesh screen after at least about 30% of said agglomerating agent has been added to said particulate ingredients.

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# AGGLOMERATION PROCESS FOR MAKING GRANULAR DETERGENTS AND COMPOSITION MADE THEREBY

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## Field of the Invention

This invention relates to a process for making a granular detergent product and the product of the process. More particularly, the invention relates to a process for preparing detergent compositions which are useful in automatic dishwashing machines.

## State of the Art

Detergent compositions comprising in combination an alkali metal polyphosphate such as sodium tripolyphosphate, alkaline salts such as sodium silicate and sodium carbonate, a surfactant and a chlorine containing compound that provides hypochlorite ion in solution have particular utility for machine dishwashing. The production of such compositions made of agglomerates of the ingredients has generally been accomplished by the addition of water or an aqueous sodium silicate solution to a mixture of dry ingredients. Compositions prepared in such manner, however, are characterized by a tendency to cake in their cartons during storage and can also have a tendency to cake in the dispenser cups of automatic dishwashing machines. A number of process modifications have been suggested to reduce the caking tendency of detergent compositions prepared using water or silicate solutions as agglomerating agents. U.S. Patent 2,895,916 discloses an order of addition in which chlorinated trisodium phosphate is added to the composition only after the aqueous silicate has been added to an anhydrous polyphosphate. A carton caking benefit is said to result from a more rapid hydration of the sodium tripolyphosphate in the absence of chlorinated trisodium phosphate.

It has now been found that a substantial reduction in the dispenser cup caking tendency of agglomerated detergent compositions containing sodium tripolyphosphate, an alkali metal silicate and a low-foaming nonionic surfactant can be achieved if from 2% to 20% of certain alkali metal salts are added to the detergent composition after the agglomeration step comprising the addition of water or an aqueous alkali metal silicate solution to a particulate mixture comprising sodium tripolyphosphate has commenced and preferably is substantially complete.

It is an object of this invention to produce agglomerated granular detergent compositions which are resistant to caking in dispenser cups.

Other objects and advantages will be apparent from the following description and examples.

## Summary of the Invention

According to the present invention there is provided a process for preparing agglomerated granular detergent composition comprising from 15% to 50% of sodium tripolyphosphate, from 5% to 25% silicate solids wherein the average $SiO_2:M_2O$ weight ratio is from 1.0 to 3.6, M being an alkali metal, from 2% to 12% of a low-foaming nonionic surfactant and from 2% to 20% of alkali metal chlorides and mixtures thereof, wherein the said agglomerated granular detergent composition is prepared by agitating particulate components comprising anhydrous sodium tripolyphosphate, contacting said particulate components during said agitation with an agglomerating agent comprising water, mixing said agglomerating agent with said particulate components by continuing said agitation, adding a dispenser cup caking inhibitor during said agitation after at least 30% of said agglomerating agent has been added to said particulate components, said dispenser cup caking inhibitor comprising said one or more alkali metal chlorides and being a dry material having a particle size such that at least 80% passes through a screen of mesh size 0.422 mm, and recovering said agglomerated granular detergent composition. The invention also embraces a composition prepared in accordance with the above process.

## Detailed Description of the Invention

The process of the invention is carried out in apparatus suitable for the mixing of dry particulate components and adapted so that liquid components such as water or an aqueous alkali metal silicate solution agglomerating agent can be sprayed on or otherwise added to a bed or falling curtain of one or more particulate components during the mixing operation. Any suitable mixing device such as an inclined pan agglomerator, a rotating drum or any other vessel with suitable means of agitation may be used. Methods of agitating, mixing and agglomerating particulate components are well known to those skilled in the art. The apparatus may be designed or adapted for either continuous or batch operation so long as the essential process steps can be achieved.

Optional process steps include screening of particulate materials before processing, screening or grinding the composition to any desired particle size, addition of optional ingredients such as an alkali metal dichlorocyanurate bleach and sodium carbonate, and allowing the final composition to come to equilibrium with respect to temperature and hydration before packing into cartons.

The theoretical basis for the unexpected improvement in dispenser cup caking resistance provided by incorporation of the dispenser cup caking inhibitor is believed to be at least partially related to the complex hydration characteristics of anhydrous sodium tripolyphosphate. This compound has different hydration characteristics depending on its method of manufacture. A so-called Form I is produced if the process of manufacture includes a relatively high temperature calcination step. A Form II results when lower temperatures are employed. Form I is characterized by relatively rapid hydration characteristics. Form II, particularly in the absence of any substantial level of Form I material, is slow to hydrate, but has a greater immediate solubility. Commercially available sodium tripolyphosphate is generally a mixture of Form I and Form II. U.S. Patents 2,622,068, 2,961,409 and 2,961,410, disclose the hydration characteristics of Form I and Form II sodium tripolyphosphate in the manufacture of spray-dried detergents.

The process and product of this invention apply to granular detergent compositions comprising the following essential ingredients: (1) sodium tripolyphosphate; (2) alkali metal silicate; (3) a low-foaming nonionic surfactant; and (4) an alkali metal salt dispenser cup caking inhibitor.

Sodium Tripolyphosphate

The detergent compositions of the invention contain sodium tripolyphosphate at a level of from 15% to 50% and preferably from 25% to 45% by weight.

Anhydrous sodium tripolyphosphate comprises all or a part of the particulate components contacted with the agglomerating agent in the process aspect of the invention. The sodium tripolyphosphate can be in granular form such that at least 90% is retained on a 100 Tyler mesh screen or in powdered form such that at least 90% passes through a 100 Tyler mesh screen..

Optional polyphosphates useful in the practice of the invention are the water-soluble sodium and potassium salts of pyrophosphoric acid ($H_4P_2O_7$) and polymeric metaphosphoric acid ($(HPO_3)n$). The value of n is typically below 50 in the interest of water solubility. The sodium and potassium salts of metaphosphoric acid are often designated "glassy" phosphates and exist as a series of polymers. Glassy phosphates may also be represented by the formula $(M_2O)m(P_2O_5)n$ wherein M is an alkali metal, n is in the range of from 5 to 50 and m:n is in the range of 1:1 to 1:1.5 on a molar basis. An example of a glassy phosphate is sodium hexametaphosphate ($Na_6P_6O_{18}$).

The Alkali Metal Silicate

The compositions made by the process of this invention contain alkali metal silicate solids at a level of from 5% to 25% on an anhydrous weight basis and having an average $SiO_2:M_2O$ weight ratio of from 1.0 to 3.6, M being an alkali metal. Particularly preferred is a sodium silicate having a weight ratio of $SiO_2:Na_2O$ of from 1.6 to 3.3, most preferably from 2 to 3.2. Lower ratio silicates which are relatively more alkaline provide good cleaning performance but in order to provide protection to materials such as aluminum and china, it is desirable to have at least 10% and up to 75% of the $SiO_2$ present at a $SiO_2:Na_2O$ ratio above 3.0. It is possible to add all of the silicate in the form of aqueous solutions typically containing from 35% to 55% silicate solids but all or a portion may be part of the particulate components comprising sodium tripolyphosphate or added in dry form at some other point in the process. Aqueous alkali metal silicate solutions used as agglomerating agents preferably contain at least 45% water.

Silicate solids in the compositions of the invention can be added dry in anhydrous or hydrous form. Preferably at least a portion of the total silicate is hydrous silicate mixed with sodium tripolyphosphate before the addition of an agglomeration agent.

Low-Foaming Nonionic Surfactant

The compositions of this invention contain from 2.0% to 12% of a low-foaming nonionic surfactant by weight. A preferred level of surfactant is from 3.0% to 8.0%. Preferably the surfactant is an alkoxylated nonionic surfactant and preferably the composition is essentially free of sulfonated or sulfated anionic surfactants.

Examples of nonionic surfactants include:

(1) the condensation product of 1 mole of a saturated or unsaturated, straight or branched chain, alcohol or fatty acid containing from 10 to 20 carbon atoms with from 4 to 50 moles of ethylene oxide. Specific examples of such compounds include a condensation product of 1 mole of coconut fatty acid or tallow fatty acid with 10 moles of ethylene oxide; the condensation of 1 mole of oleic acid with 9 moles of ethylene oxide; the condensation product of 1 mole of stearic acid with 25 moles of ethylene oxide; the condensation product of 1 mole of tallow fatty alcohols with about 9 moles of ethylene oxide; the condensation product of 1 mole of oleyl alcohol with 10 moles of ethylene oxide; the condensation product of 1 mole of $C_{19}$ alcohol and 8 moles of ethylene oxide; and the condensation product of one mole of $C_{18}$ alcohol and 9 moles of ethylene oxide.

The condensation product of a fatty alcohol containing from 17 to 19 carbon atoms, and being substantially free of chain lengths above and below these numbers, with from 6 to 15 moles, preferably 7 to 12 moles, most preferably 8 moles, of ethylene oxide is particularly preferred. This can be capped with a low molecular weight ($C_{1-5}$) acid or alcohol moiety, so as to minimize or eliminate the need for a suds-suppressing agent.

(2) Polyethylene glycols having molecular weights of from 1,400 to 30,000, e.g., 20,000; 9,500; 7,500; 6,000; 4,500; 3,400; and 1,450. All of these materials are waxlike solids which melt between 49°C and 93°C.

(3) The condensation products of 1 mole of alkyl phenol wherein the alkyl chain contains from 8 to 18 carbon atoms and from 4 to 50 moles of ethylene oxide.

Specific examples of these nonionics are the condensation products of 1 mole of decylphenol with 40 moles of ethylene oxide; the condensation product of 1 mole of dodecylphenol with 35 moles of ethylene oxide; the condensation product of 1 mole of tetradecylphenol with 25 moles of ethylene oxide; the condensation product of 1 mole of heptadecylphenol with 30 moles of ethylene oxide, etc.

(4) Polyoxypropylene, polyoxyethylene condensates having the formula

$$HO(C_2H_4O)x(C_3H_6O)y\ (C_2H_4O)x\ H$$

where y equals at least 15 and $(C_2H_4O)x+x$ equals 20% to 90% of the total weight of the compound and the molecular weight is from 2,000 to 10,000, preferably from 3,000 to 6,000. These materials are, for example, the PLURONICS which are well known in the art.

(5) The compounds of (1) which are capped with propylene oxide, butylene oxide and/or short chain alcohols and/or short chain fatty acids, e.g., those containing from 1 to 5 carbon atoms, and mixtures thereof.

(6) Condensation products of ethylene oxide and propylene oxide with a low molecular weight trifunctional alcohol such as glycerine or trimethylolpropane. These materials are, for example, the PLURADOT polygols made by the BASF Wyandotte Corporation.

Preferred surfactants are those having the formula $RO-(C_2H_4O)_xR^1$ wherein R is an alkyl or alkylene group containing from 17 to 19 carbon atoms, x is a number from 6 to 15, preferably from 7 to 12, and $R^1$ is selected from hydrogen, $C_{1-5}$ alkyl groups, $C_{2-5}$ acyl groups and groups having the formula $-(C_yH_{2y}O)_nH$ wherein y is 3 to 4 and n is a number from 1 to 4.

Also preferred are the low sudsing compounds of (4), the other compounds of (5), and $C_{17-19}$ materials of (1) which have a narrow ethoxy distribution.

In addition to the above mentioned surfactants, other suitable surfactants can be found in the disclosure of U.S. Patents 3,544,473, 3,630,923, 3,888,781 and 4,001,132.

## Alkali Metal Salt Dispenser Cup Caking Inhibitor

The compositions of the invention contain from 2% to 20%, preferably from 4% to 15%, of a dispenser cup caking inhibitor selected from alkali metal chlorides and mixtures thereof.

Operative dispenser cup caking inhibitors are in the form of dry powders having a particle size such that at least 80% passes through a 35 Tyler mesh screen (mesh size 0.422 mm). The dispenser cup caking inhibitor is added during the process of the invention after at least 30%, preferably 75%, and most preferably 90%, of the water or aqueous sodium silicate agglomerating agent has been added to the particulate components comprising sodium tripolyphosphate.

An especially preferred material is sodium chloride having a particle size such that at least 80% passes through a 100 Tyler mesh screen (mesh size 0.152 mm).

## Water

The compositions of the invention are made by a process in which either water or an aqueous sodium silicate solution is used as the agglomerating agent.

The finished compositions will contain water in the form of hydrated salts, preferably from 9% to 12% by weight.

## Alkali Metal Dichlorocyanurate

Sodium or potassium dichlorocyanurate is optionally but preferably incorporated in the compositions of the invention in an amount sufficient to provide available chlorine equal to from 0.75% to 2.5% by weight of the composition. A preferred material is sodium dichlorocyanurate dihydrate as disclosed in U.S. Patent 3,936,386, which provides 56% available chlorine by weight. The ability of a compound to provide hypochlorite ion in solution is generally measured as "available chlorine". The available chlorine reflects the method of producing an inorganic hypochlorite (e.g., $2\ NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$). Available chlorine is the chlorine liberated by acidification of a solution of hypochlorite ions and at least a molar equivalent amount of chloride ions. The usual analytical method of determining available chlorine in a solution is addition of an excess of an iodide salt and titration of the liberated free iodine with a reducing agent.

## Optional Alkali Metal Carbonates

Optionally, the process and composition of the invention utilize alkali metal carbonate to provide the alkalinity needed for optimum cleaning performance.

Alkali metal carbonates, particularly sodium carbonate, can be present in the compositions at levels up to 25%, preferably from 2% to 12% by weight.

## Other Optional Ingredients

In addition to the above ingredients it can be desirable, if the product sudses too much, to incorporate one of the many suds-suppressing ingredients disclosed in the above mentioned patents at a level of from 0.01% to 10%, preferably from 0.05% to 3%. The preferred suds suppressing materials are mono- and distearyl acid phosphates; the self-emulsified siloxane suds suppressors of U.S. Patent 4,126,045, and mixtures thereof.

Organic sequestering builders such as citrates and nitrilotriacetates can be present in the compositions, but preferably at levels no greater than 10% by weight. The presence of organic builders tends to hurt the performance of these compositions by leaving visible spots and filming on glassware.

China protecting agents including aluminosilicates, aluminates, etc., can be present in amounts up to 5%, preferably from 0.2% to 2%.

Filler materials, sodium sulfate in particular, to control product density and other physical characteristics can also be present in amounts up to 60%, preferably not more than 30% by weight.

Dyes, perfumes, crystal modifiers and the like can also be added in minor amounts.

As used herein, all percentages, parts and ratios are by weight unless otherwise stated.

The following Examples illustrate the invention and facilitate its understanding.

## EXAMPLE I

A. 33.1 Parts by weight of powdered anhydrous sodium tripolyphosphate and 8.0 parts by weight of hydrous sodium silicate (82% solids, $SiO_2$:$Na_2O$ weight ratio of 2.4) were added to a ribbon mixer. With the mixer in operation the following ingredients were added during a cycle time of 180 seconds.

a) <u>from 0 seconds to 165 seconds--added as a spray</u>

blend of 13.8 parts of an aqueous sodium silicate solution containing 47.3% silicate solids with a $SiO_2$:$Na_2O$ weight ratio of 2.0 and 4.7 parts of an aqueous sodium silicate solution containing 37.5% silicate solids with a $SiO_2$:$Na_2O$ weight ratio of 3.2. This solution also contained minor amounts of perfume and dye.

b) <u>at 60 seconds--added dry</u>

19.4 parts of sodium sulfate and 10.0 parts of sodium carbonate.

c) <u>from 60 seconds to 165 seconds--added as a spray</u>

4.0 parts of a polyoxyalkylene nonionic surfactant (condensation product of $C_{18}$ alcohol with average of 8.25 moles ethylene oxide).

d) <u>at 145 seconds--added dry</u>

5.0 parts of sodium chloride having a particle size such that at least 80% passed through a 100 Tyler mesh screen (mesh size 0.152 mm).

e) <u>after 180 seconds</u>

Product is discharged from mixer.

f) 2.5 parts of sodium dichlorocyanurate dihydrate was added and mixed in after drying and aging of the product discharged from the mixer at step e).

B. The process of A was repeated with the elimination of step d). 24.4 Parts sodium sulfate added at step b) replaced the sodium chloride of step d).

The compositions were packed in airtight containers pending evaluation. Resistance to automatic dishwasher dispenser cup caking was measured as indicated in the table below.

| Composition | Dispenser Cup Caking Grade[1] A | B |
|---|---|---|
| Automatic Dishwasher | | |
| Hotpoint | | |
| end of main wash | 0.6 | 3.0 |
| middle of rinse | 0.1 | 1.1 |
| end of rinse | 0.0 | 0.5 |
| Frigidaire | | |
| end of main wash | 0.1 | 2.8 |
| middle of rinse | 0.0 | 1.6 |
| end of rinse | 0.0 | 0.6 |

[1] scale of 0-8. 0 indicating complete removal of product from cup, 8 indicating cup full of product.

Composition A was superior to Composition B in resistance to dispenser cup caking. No Composition A remained in the dispenser cup at the end of the rinse cycle, the point of principal notice of dispenser cup caking.

## EXAMPLE II

The process of Example I-A was repeated with the substitution of NaCl having a particle size such that 80% passed through a 35 Tyler mesh screen (mesh size 0.422 mm) and less than 20% passed through a 100 Tyler mesh screen (mesh size 0.152 mm). The resultant composition was superior to Composition B of Example I but slightly inferior to Composition A of Example I.

## EXAMPLE III

The materials listed in the table below were added to Composition B of Example I at the levels and process cycle time indicated. 300 grams of each resultant composition was mixed with 100 grams of 37°C distilled water and stirred in a 400 ml beaker. Viscosity of the product slurries was measured by a Brookfield spindle viscometer (No.4 spindle/6 rpm) after seven minutes.

The reduction in viscosity for each additive was found to be predictive of the improvement in resistance to dispenser cup caking.

| Dispenser Cup Caking Inhibitor | Viscosity (cps) |
|---|---|
| None | 28,000 |
| 1% NaCl--added at 165 sec. | 22,500 |
| 2% NaCl--added at 165 sec. | 14,000 |
| 5% NaCl--added at 165 sec. | 6,000 |
| 10% NaCl--added at 165 sec. | 1,400 |
| 10% NaCl--added at 60 sec. | 2,700 |
| 3% NaCl (granular)--after end of cycle | 25,000 |
| 4% NaCl (granular)--after end of cycle | 8,000 |
| 10% NaCl (granular)--after end of cycle | 4,800 |
| 1% LiCl--added at 165 sec. | 15,000 |
| 3% KCl--added at 165 sec. | 16,000 |
| 10% $Li_2SO_4$--added at 165 sec. | 15,000 |
| 10% $Na_3PO_4$--added at 165 sec. | 8,000 |
| 9% $Na_2SO_4$--added at 165 sec. | $>$28,000 |
| 9% $Na_2CO_3$--added at 165 sec. | $>$28,000 |
| 9% sodium citrate--added at 165 sec. | 12,500 |
| 3% sodium acetate--added at 165 sec. | 18,000 |

All dispenser cup caking inhibitor materials listed above had a particle size such that at least 80% by weight passed through a 100 Tyler mesh screen (mesh size 0.152 mm) except granular NaCl for which 80% passes through a 35 Tyler mesh screen (mesh size 0.422 mm) and 50% is retained on a 65 Tyler mesh screen (mesh size 0.211 mm).

## CLAIMS

1. A process for preparing agglomerated granular detergent composition comprising from 15% to 50% of sodium tripolyphosphate, from 5% to 25% silicate solids wherein the average $SiO_2:M_2O$ weight ratio is from 1.0 to 3.6, M being an alkali metal, from 2% to 12% of a low-foaming nonionic surfactant and from 2% to 20% of alkali metal chlorides and mixtures thereof, characterised in that the said agglomerated granular detergent composition is prepared by agitating particulate components comprising anhydrous sodium tripolyphosphate, contacting said particulate components during said agitation with an agglomerating agent comprising water, mixing said agglomerating agent with said particulate components by continuing said agitation, adding a dispenser cup caking inhibitor during said agitation after at least 30% of said agglomerating agent has been added to said particulate components, said dispenser cup caking inhibitor comprising said one or more alkali metal chlorides and being a dry material having a particle size such that at least 80% passes through a screen of mesh size 0.422 mm, and recovering said agglomerated granular detergent composition.

2. A process according to Claim 1 wherein the dispenser cup caking inhibitor is sodium chloride.

3. A process according to either one of Claims 1 and 2 wherein the dispenser cup caking inhibitor has a particle size such that at least 80% passes through a screen of mesh size 0.152 mm.

4. A process according to any one of Claims 1-3 wherein the dispenser cup caking inhibitor is added after at least 75% of said agglomerating agent has been added to said particulate components.

5. A process according to any one of Claims 1-4 which additionally comprises an alkali metal dichlorocyanurate to provide an available chlorine level of from 0.5% to 3.0%.

6. A process according to any one of Claims 1-5 wherein the low-foaming nonionic surfactant comprises a condensation product of an alcohol or a fatty acid containing from 10 to 20 carbon atoms with from 4 to 50 moles ethylene oxide.

7. A process according to any one of Claims 1-5 wherein the low-foaming nonionic surfactant comprises a compound having the formula $RO-(CH_2H_4O)_xR^1$ wherein R is an alkyl or alkylene group containing from 17 to 19 carbon atoms, x is a number from 6 to 15 and $R^1$ is selected from hydrogen, $C_{1-5}$ alkyl groups, $C_{2-5}$ acyl groups, and groups having the formula $-(C_yH_{2y}O)_nH$ wherein y is 3 to 4 and n is from 1 to 4.

8. An agglomerated granular detergent composition when prepared according to the process of any one of Claims 1-7.