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54 **Process for making detergent compositions.**

57 A spray-dried detergent powder free from problems of discolouration and caking can be prepared using a secondary alkane sulphonate as the principal anionic detergent active species if care is taken to select the composition and process features. The secondary alkane sulphonate should be C₁₄-C₁₉ and defined amounts of phosphate and silicate should be present. The moisture content of the crutcher slurry should be at least 35% by weight, and it should be spray-dried at from 85°C to 95°C. The composition may contain nonionic surfactant and a non-soap anti-foam if desired.

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PROCESS FOR MAKING DETERGENT COMPOSITIONS

This invention relates to spray-dried detergent powder and to a process for its production.

Conventionally, the detergent active material in spray-dried detergent powder is sodium alkylbenzene
5 sulphonate. However, manufacturers of detergent powders continue to investigate the viability of alternative detergent active materials and have persisted in research and development despite the fact that in very few compositions is it possible to make a simple substitution
10 for one detergent active compound for another and retain the same essential properties. This latter statement applies both to the processing of the composition and to the properties to be expected from it.

One detergent active compound which we have
15 investigated is sodium secondary alkane sulphonate, but when we have simply substituted it for sodium alkylbenzene sulphonate in a standard formulation which also contained nonionic surfactant and soap we have found that the

resultant spray-dried powder cakes badly and is discoloured. Indeed we have come to associate the presence of nonionic surfactant together with sodium secondary alkane sulphonate with discolouration of the powder during
5 spray-drying.

This discolouration problem is referred to in Belgian patent specification No 866,238 and also in German patent specification No 25 04 276, where it is said to result from interaction between the alkane sulphonate and certain
10 fluorescers or optical brighteners.

We have now discovered that by careful selection of processing, formulation and packaging parameters it is possible to manufacture a detergent powder containing secondary alkane sulphonate as the basic detergent active
15 component without encountering problems in the flow and caking properties of the powder or of discolouration.

Accordingly, the invention provides a process for the production of a soap-free spray-dried detergent powder which comprises forming an aqueous crutcher slurry
20 comprising one or more secondary alkane sulphonates containing from 13 to 19 carbon atoms, optionally a small amount of a nonionic surfactant, from 10-45% by weight, based on the weight of the spray-dried detergent powder of hydrated sodium tripolyphosphate having a number average
25 crystal size of less than 25 microns and from 4-14% by weight of sodium silicate having a molar ratio $\text{SiO}_2:\text{Na}_2\text{O}$ of from 4:1 to 1:1, the process comprising adjusting the temperature of the slurry to from 85 to 95°C and spray-drying it.

30 Preferably, the number average crystal size of the sodium tripolyphosphate is no more than 10 microns.

For sale in humid countries, the detergent composition will be packed in a package manufactured from a substantially vapour-impermeable material, for example a
35 material laminated or coated with polyethylene or with wax.

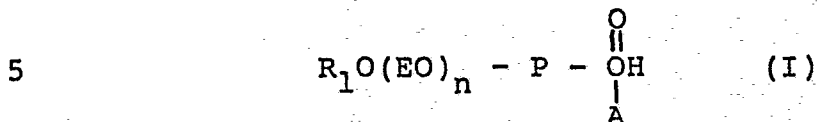
Whilst we consider that detergent powders containing secondary alkane sulphonate are satisfactory across the whole chain length of C_{13} - C_{19} , we prefer to use a C_{14} - C_{17} alkyl material. Whatever the chain length of the alkyl group, the secondary alkane sulphonate may be present in an amount of from 4 to 30%, preferably for economic reasons, from 7 to 25%, and most preferably from 10 to 14% by weight of the composition.

As defined above, the invention relates to spray-dried detergent powders containing only small amounts of nonionic surfactant, typically less than 3.5%. When such small amounts of nonionic surfactant are present, the anti-foaming effect of soap is inadequate and we prefer to use a non-soap anti-foam in order to obtain compositions suitable for use in automatic (front-loading) washing machines. The anti-foams may be incorporated in the slurry and spray-dried with the other crutcher slurry components, or they may be added to the spray-dried powder by a post-dosing technique.

The non-soap anti-foam can be any material not based on soap which exhibits the property of reducing foam produced by anionic surfactants. Typical of non-soap anti-foams are alkyl phosphoric acids and their salts, both used alone and used in conjunction with waxes or hydrophobic oils such as mineral and vegetable oils. Silicone anti-foams and derivatives of nitrogen-containing heterocyclic compounds such as s-triazine may also be used.

In general, the non-soap anti-foams of this invention may be present in the compositions in amounts from 0.05%, which would be the minimum amount which could possibly be effective, to 5%, which would be the practical maximum having regard to the extreme efficacy of the majority of non-soap anti-foams, to their expense and to the necessity for keeping as much room in the composition as possible for other components.

In greater detail, the alkyl phosphoric acids which may be used, optionally in sodium, potassium, calcium or magnesium salt form, have the following general formula:



where A is -OH or $R_2O(EO)_m-$, R_1 and R_2 are the same or different $C_{12}-C_{24}$, preferably $C_{16}-C_{22}$, straight or branched chain, saturated or unsaturated alkyl groups, especially $C_{16}-C_{18}$ linear saturated groups and m and n are the same or different and are 0 or an integer of from 1 to 6. Preferably, A is -OH and n is 0, so that the compounds are the monoalkyl phosphoric acids, preferably with linear alkyl groups.

15 In practice, the alkyl phosphoric acids are commonly mixtures of both mono- and di-alkyl phosphoric acids, with a range of alkyl chain lengths. Predominantly monoalkyl phosphoric acids are usually made by phosphorylation of alcohols or ethoxylated alcohols, when n or m is 1 to 6, 20 using a polyphosphoric acid. Phosphorylation may alternatively be accomplished using phosphorus pentoxide, in which case the mixed mono- and di-alkyl phosphoric acids are produced. Under optimum reaction conditions only small quantities of unreacted materials or by-products are 25 produced, and the reaction products can advantageously be used directly in the detergent compositions.

When a mixture of alkyl phosphoric acid and wax is to be used as the non-soap anti-foam compound the wax may be of synthetic, mineral, vegetable or animal origin.

30 The waxes should normally melt at a temperature between about $20^{\circ}C$ and about $120^{\circ}C$, preferably not more than about $90^{\circ}C$ and especially in the range of about $30^{\circ}C$ to about $70^{\circ}C$, i.e. lower than the maximum intended wash temperatures for the detergent compositions. 35 When waxes having melting points above the maximum intended

wash temperatures are used they should be adequately dispersed in the wash liquor by suitable incorporation in the original detergent compositions.

The preferred waxes are of mineral origin, especially those derived from petroleum, including microcrystalline and oxidised microcrystalline petroleum waxes, petroleum jelly ("Vaseline") and paraffin waxes. Petroleum jelly is correctly a semi-solid wax, usually having a pour point about 40-45°C, but is for convenience here grouped with other solid waxes. Synthetic waxes such as Fischer-Tropsch and oxidised Fischer-Tropsch waxes, or Montan waxes, or natural waxes such as beeswax, candelilla and carnauba waxes may be used if desired. Any of the waxes described may be used alone or in admixture with other waxes. The waxes should be readily dispersible in the detergent liquor but not soluble therein and, preferably, they should not have very high saponification values, e.g. not in excess of about 100. It is advantageous to include emulsifying or stabilising agents for the waxes in the detergent compositions.

Examples of suitable oils which may be used if desired are vegetable oils such as sesame oil, cottonseed oil, corn oil, sweet almond oil, olive oil, wheat germ oil, rice bran oil, or peanut oil, or animal oils such as lanolin, neat's foot oil, bone oil, sperm oil or cod liver oil. Any such oils used should of course not be highly coloured, of strong odour or otherwise unacceptable for use in a detergent composition.

It is an essential feature of the compositions of this invention that they contain from 10-45% by weight of hydrated sodium tripolyphosphate and that the number average crystal size of this material is less than 25 microns, preferably less than 10 microns. When compositions containing lower amounts of sodium tripolyphosphate, or in which the average crystal size is greater than 25 microns, are prepared, they are found to

have a soft appearance and to have unsatisfactory flow properties in that there is an unacceptably high "threshold" before they begin to flow at all. Similarly, compositions containing lesser amounts of silicate than 4-14% have also been found to cake badly.

A discovery we have made which is relevant to the processing aspect of this invention is that by correct choice of the appropriate composition parameters specified above, it is possible to reduce the water content of the crutcher slurry to as little as 35% by weight, typically 35-40% by weight. Lower amounts of water have resulted in a slurry which is not easily atomised, but in view of the fact that the normal slurry water content would be 40-45% by weight, reduction of up to 25% in the amount of water which has to be evaporated during spray-drying represents a very substantial saving.

A second discovery, which is also relevant to the processing aspect of this invention, is that the higher the temperature of the crutcher slurry, the more free-flowing the spray-dried powder produced. Consequently, we specify a temperature of from 85 to 95°C, preferably 90 to 95°C, for the slurry. As sodium tripolyphosphate is present in the slurry it is essential to ensure that the temperature does not rise above 95°C, since above that temperature hydration is prevented and hydrolysis is accelerated, possibly resulting in powders which flow poorly and are prone to caking. Sodium ortho- and pyrophosphates are amongst several suitable detergency builders which are well known and are suitable for use with tripolyphosphates. Many more have been described in the literature, especially in recent patent specifications, on replacements for these phosphate based materials. Other detergency builders which may be mentioned by way of example are alkali metal carbonates, especially sodium carbonate, alkyl methyl polyphosphonates, e.g. sodium ethane-1-hydroxy-1,1-diphosphonate, alkyl metal amine

carboxylates such as sodium nitrolotriacetate and sodium ethylenediamine tetraacetate, alkali metal ether carboxylates, such as sodium oxydiacetate, sodium carboxymethyloxysuccinate, sodium carboxymethyloxy-
5 malonate and homologues thereof, alkali metal citrates, alkali metal mellitates and salts of polymeric carboxylic acids, such as sodium polymaleate, copolyethylenemaleate, polyitaconate and polyacrylate. When sodium carbonate is used as a detergency builder, it is advantageous to have
10 present some calcium carbonate having a surface area of at least about $10\text{m}^2/\text{g}$, as described in UK Patent 1,437,950.

Another type of detergency builder which can be used, either alone or in admixture with other builders, is a cation exchange material, especially a sodium aluminosilicate such as described in UK Patent 1,429,143 or in
15 Netherlands Patent Application 7403381. Preferred materials of this type have the formula:

$(\text{Na}_2\text{O})_{0.7-1.1} \cdot \text{Al}_2\text{O}_3 (\text{SiO}_2)_{1.3-3.3}$
and may be amorphous or crystalline, with some bound water
20 usually in an amount of about 10-30% depending on the drying conditions used. Such sodium aluminosilicate materials should, of course, be very finely divided so as to minimise deposition on the fabrics during washing.

The amount of the detergency builder which is used is
25 normally from about 10% up to about 80% by weight of the composition, preferably about 10% to about 60%, and the ratio by weight of the detergency builders to the detergent active compounds which are used is generally from about 10:1 to about 1:5 parts by weight.

30 The detergent compositions of the invention may also include any of the conventional optional additives in the amounts usually employed in detergent compositions. Examples of these additives include powder flow aids such as finely divided silicas and aluminosilicates, anti-
35 redeposition agents such as sodium carboxymethylcellulose and the cellulose ethers, oxygen-releasing bleaching agents

such as sodium perborate and sodium percarbonate, per-acid bleaches and precursors thereof such as tetraacetyl-ethylenediamine, chlorine-releasing bleaching agents such as trichloroisocyanuric acid and alkali metal salts of
5 dichloroisocyanuric acid, fabric softening agents such as clays of the smectite and illite types, anti-ashing aids, starches, slurry stabilisers such as copolyethylenemaleic anhydride and copolyvinylmethylether maleic anhydride, usually in salt form, slurry hydrotropes such as sodium
10 toluene sulphonate, inorganic salts such as sodium sulphate and, usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases and amylases, germicides and colourants. The detergent compositions usually have an alkaline pH, generally in the region of pH
15 9-11, which is achieved by the presence of alkaline salts.

The invention is illustrated by the following Example in which parts and percentages are by weight except where otherwise indicated.

Example

20 Three detergent powders A, B and C were prepared by slurry making, spray-drying and dry-dosing techniques and under the spray-drying conditions described below. Their formulations were as follows:

	<u>% by weight</u>		
	<u>A</u>	<u>B</u>	<u>C</u>
Sodium C ₁₄₋₁₇ secondary alkane sulphonate	14.0	14.0	7.5
Tallow alcohol 18EO	-	-	3.5
5 Sodium salt of C ₁₈₋₂₂ saturated and unsaturated fatty acids	-	-	4.0
Sodium tripolyphosphate	33.0	33.0	33.0
Sodium silicate (alkaline)	6.0	6.0	8.0
Sodium sulphate	17.0	19.0	7.0
10 Sodium carboxymethyl cellulose	0.5	0.5	1.0
Ethylene diamine tetraacetic acid	0.1	0.1	0.1
Coconut monoethanolamide	2.0	-	-
Sodium toluene sulphonate	1.0	1.0	1.0
Fluorescer	0.37	0.37	0.3
15 Sodium perborate tetrahydrate	19.0	19.0	27.0
Calcium salt of C ₁₆₋₁₈ monoalkyl phosphate mixed with petroleum jelly (20:80)	-	1.5	-
Moisture	-	-	-
Sodium tripolyphosphate crystal size (microns)	- balance to 100 - 10-20	< 10	< 10

Spray-drying conditions

Air inlet temperature		<u>300-320°C</u>		
		<u>A</u>	<u>B</u>	<u>C</u>
	Slurry water content	38	40	43
5	Slurry temperature	80	90	80
	Moisture content of spray-dried powder (%)	5	11	13

Properties of spray-dried powder

	Dynamic flow rate (ml/sec)	71	100	92
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- 10 Powder C, which contains a relatively large amount of nonionic surfactant and which is consequently not within the scope of this invention was yellow in colour.

- Powder A, which is free of nonionic surfactant, but which was spray-dried at a slurry temperature of only
 15 80°C was not discoloured but had an unsatisfactory dynamic flow rate.

Powder B, which is in accordance with the invention was white and had satisfactory dynamic flow rate and caking characteristics.

20 Storage behaviour of spray-dried powder

After storage in wax laminated cartons the caking characteristics of the spray-dried powders were assessed visually, with the following results:

			<u>% of powder caked</u>		
25	<u>Temperature</u>	<u>Relative Humidity</u>	<u>A</u>	<u>B</u>	<u>C</u>
	20 °C	90%	25	0	50
	28 °C	70%	25	0	25

These results show the clear superiority of powder B in accordance with the invention.

CLAIMS:

1. A soap-free composition comprising from 4-20% by weight of a C_{14} - C_{19} secondary alkane sulphonate salt, from 10-45% by weight of hydrated sodium tripolyphosphate having a number average crystal size of less than 25 microns, and from 4-14% by weight of sodium silicate having a molar ratio $SiO_2:Na_2O$ from 4:1 to 1:1.
2. A detergent composition according to claim 1 comprising up to 25% by weight, based on the weight of the secondary alkane sulphonate salt, of a nonionic surfactant.
3. A detergent composition according to claim 2 wherein the nonionic surfactant is present in an amount of from 2 to 5% by weight, based on the weight of the composition.
4. A detergent composition according to any one of the preceding claims comprising a non-soap anti-foam or a mixture thereof.
5. A detergent composition according to claim 4 wherein the non-soap anti-foam comprises an alkyl phosphoric acid, or a salt thereof.
6. A detergent composition according to claim 4 or claim 5 wherein the non-soap anti-foam is present in an amount of 0.05 to 5% by weight of the composition.
7. A detergent composition according to any one of claims 4,5 or 6, wherein the non-soap anti-foam comprises a mixture of an alkyl phosphoric acid or salt thereof and a wax.

8. A detergent composition according to any one of the preceding claims wherein the secondary alkane sulphonate salt is a C₁₄₋₁₇ secondary alkane sulphonate salt.

9. A detergent composition in accordance with any one of the preceding claims, packed in a package which is manufactured from a moisture impermeable material.

10. A process for the production of a spray-dried detergent powder which comprises forming an aqueous crutcher slurry comprising a C₁₄₋₁₉ secondary alkane sulphonate, optionally a nonionic surfactant, sodium tripolyphosphate, sodium silicate and at least 35% by weight of water, adjusting the temperature of the slurry to form 85 to 95°C and spray-drying it.

11. A process in accordance with claim 10 wherein the aqueous crutcher slurry comprises a nonionic surfactant.

12. A process in accordance with claim 10 or claim 11 wherein a non-soap anti-foam is incorporated into the aqueous crutcher slurry and spray-dried.

13. A process in accordance with any one of claims 10 to 12 wherein the non-soap anti-foam is added to the spray-dried powder by a post-dosing technique.

14. A process in accordance with any one of claims 10 to 13 wherein the aqueous crutcher slurry comprises 34-40% by weight of water.

15. A process in accordance with any one of claims 10 to 14 wherein the aqueous crutcher slurry is adjusted to, or spray-dried at, a temperature of from 90-95°C.

16. A process as claimed in claim 10 and substantially as hereinbefore described.

17. A process for the production of a spray-dried detergent powder comprising a C₁₄-C₁₉ secondary alkane sulphonate substantially as hereinbefore described in any one of the accompanying Examples.

18. A spray-dried detergent powder produced by a process in accordance with any one of claims 10 to 17.

19. A spray-dried detergent powder as claimed in claim 1 and substantially as hereinbefore described.

20. A spray-dried detergent powder comprising a C₁₄-C₁₉ secondary alkane sulphonate substantially as hereinbefore described in any one of the Examples.