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(54) Process for the manufacture of spray-dried detergent powder.

(57) In a process for preparing a particulate detergent composition containing an anionic detergent-active compound, for example, an alkylbenzene sulphonic acid, a slurry is prepared by incorporating the anionic detergent-active compound in wholly or predominantly acid form when the slurry already contains at least two equivalents of alkaline material per equivalent of the acid, and the slurry is then spray-dried to form a powder.

PROCESS FOR THE MANUFACTURE OF SPRAY-DRIED DETERGENT POWDER

TECHNICAL FIELD OF INVENTION

The present invention relates to a process for the production of detergent powders containing anionic detergent-active compounds, by slurry-making and spray-drying.

BACKGROUND AND PRIOR ART

Spray-dried detergent powders are generally produced by preparing an aqueous slurry of detergent-active compounds, builder and other salts, sodium silicate, fluorescers and other non-heat-sensitive ingredients, and then spray-drying the slurry to form a free-flowing powder. Ingredients unsuitable for spray-drying, such as bleaches, perfumes and enzymes, may be postdosed subsequently to the spray-dried base powder.

Anionic detergent-active compounds such as alkylbenzene sulphonates are incorporated in spray-dried detergent powders via the slurry. Alkylbenzene sulphonates are manufactured by sulphonation of the corresponding alkybenzene to give a sulphonic acid which can then be neutralised with a suitable base, for example, sodium or potassium hydroxide, sodium carbonate, ammonia or triethanolamine, to give the salt of the desired cation. The sodium salt, which is the most commonly used salt in detergent powders, is generally prepared by neutralisation with aqueous sodium hydroxide solution to yield a paste containing 50% or more water, and that material can be incorporated directly in the slurry.

It has already been proposed to omit a separate neutralisation step by dosing the alkylbenzene sulphonic acid directly into the slurry-making vessel and neutralising it there with sodium hydroxide solution: this procedure is disclosed, for example, in GB 1 151 767 (Colgate-Palmolive) and GB 1 355 187 (Unilever). The heat liberated in the neutralisation reaction is useful for heating the slurry to the desired temperature which is generally about 80°C. The alkylbenzene sulphonic acid is conventionally one of the first ingredients introduced into the slurry-making vessel, and is neutralised with sodium hydroxide solution before other ingredients are added. It has hitherto been believed that it is essential to neutralise the sulphonic acid before any sodium silicate is added, in order to prevent those components from interacting to form relatively insoluble siliceous compounds which could seriously affect the solubility of the finished detergent powder and could also lead to jet blocking during the spray-drying operation.

It has now been found that it is possible to delay the addition of sulphonic acid until a later stage in the slurry-making process without encountering this disadvantage. The new procedure gives both product and process benefits, especially in the manufacture of powders containing a relatively high level of anionic detergent-active material.

DEFINITION OF THE INVENTION

The present invention provides a process for the manufacture of a particulate detergent composition, which comprises the steps of:

(i) preparing an aqueous slurry comprising one or more anionic non-soap detergent-active compounds, and one or more alkaline inorganic salts, and

(ii) spray-drying the slurry to form a powder; the process being characterised in that in step (i) an anionic detergent-active compound is incorporated in wholly or predominantly acid form into the slurry after the incorporation of alkaline material in an amount such that a total of at least two equivalents of alkaline material per equivalent of the said acidic detergent-active compound are present.

DESCRIPTION OF THE INVENTION

The characterising feature of the invention is the incorporation of an anionic detergent-active compound wholly or predominantly in its acid form at a relatively late stage in the slurry-making process, when a large reservoir of alkaline material is already present in the slurry.

The invention is applicable to the incorporation of any anionic detergent-active compound having a stable acid form. It is of especial interest in relation to sulphonic acids, especially alkylaryl sulphonic acids, more especially C_8-C_{15} alkylbenzene sulphonic acids, both linear and branched. It may be advantageous for the sulphonic acid to be partially neutralised, for example, up to 10% by weight neutralised, before introduction into the slurry-making vessel: a neutralisation level of about 5% appears to be especially beneficial. This can be helpful in stabilising the sulphonic acid and preventing it from darkening in colour during storage. When the sodium salt of the sulphonic acid is desired, such preneutralisation is conveniently carried out with aqueous sodium hydroxide solution. For convenience, acid or partially neutralised acid added to the slurry will be referred to hereinafter simply as "sulphonic acid".

At the time at which the sulphonic acid is introduced into the slurry-making vessel, there must already be present at least twice as much alkaline material as is required fully to neutralise the sulphonic acid. This will generally be constituted in part by a base such as sodium hydroxide which is especially intended for the purpose, in part by alkaline sodium salts present as builders, and possibly in part by alkaline sodium silicate. It is normally desirable to include in the slurry sufficient sodium hydroxide solution or other alkali to neutralise the sulphonic acid fully but in the manufacture of low-pH detergent powders intended for washing delicate fabrics it may be preferable to use a less than stoichiometric quantity of alkali and allow the neutralisation reaction to be completed by the alkaline builder salts present.
It is even possible for neutralising alkali to be omitted completely and the neutralisation reaction to be effected entirely by means of alkaline salts.

If the detergent composition prepared in accordance with the invention is to include alkaline sodium silicate, the silicate is preferably incorporated in the slurry before the sulphonic acid, and thus contributes to the alkaline material, mentioned previously, that must be present in at least a twofold amount relative to the sulphonic acid at the time when the latter component is added.

Preferred examples of alkaline builder salts present in the slurry when the sulphonic acid is added are sodium tripolyphosphate, sodium carbonate and mixtures of these. These materials are commonly used in detergent powders as builders which sequester or precipitate calcium and magnesium salts in the wash liquor. They generally comprise at least 25% by weight of the detergent powder so that if they are incorporated in the slurry before addition of the sulphonic acid they can serve as a large alkaline buffer to prevent or minimise any adverse interaction between sodium silicate and sulphonic acid. Efficient stirring in the slurry-making vessel also helps to eliminate such adverse interaction.

Any alkali added to the slurry specifically for neutralisation of the sulphonic acid of course makes an additional contribution to the reservoir of alkaline material in the slurry. In the case of alkylbenzenesulphonic acid, the amount of sodium hydroxide required to neutralise the sulphonic acid completely generally ranges from 10 to 20g per 100g sulphonic acid. This relatively large variation occurs because the amount of sulphuric acid present as a by-product in the sulphonic acid can vary quite widely: it is likely to be higher in sulphonic acids prepared by oleum sulphonation than in sulphonic acids prepared by sulphur trioxide sulphonation. Sodium hydroxide solution of specific gravity 1.5 is conveniently used as the neutralising alkali.

When a neutralising alkali is used, it need not be introduced into the slurry before the sulphonic acid, provided that sufficient alkaline material from other sources is present when the sulphonic acid is added. It may be preferable to add the alkali and sulphonic acid simultaneously.

The process of the invention gives several worthwhile advantages. One has already been mentioned: if sodium silicate is present, interaction between sodium silicate and sulphonic acid to form insoluble species can be minimised. Sodium silicate is a desirable ingredient in detergent compositions because it improves powder structure, prevents corrosion of washing machine parts in use, and provides building capacity (towards magnesium ions). The process of the invention is, however, also beneficial for the production of silicate-free powders and gives other advantages applicable both to silicate-containing and to silicate-free powders.

Better control of the slurry temperature during the in-situ sulphonation step can be achieved than in the prior art process when the sulphonic acid is neutralised before addition of the builder salts and other components, because of the larger mass of material present, and available to act as a heat sink, at the time of the addition of the sulphonic acid. This benefit is especially noticeable when spray-dried powders containing 20% by weight or more of alkylaryl sulphonate are prepared: using the prior art procedure, so much heat may be generated under those circumstances that the slurry can boil over.

A less aerated slurry is also obtained by the process of the invention, especially when other, high-foaming anionic, surfactants such as alkyl sulphates or alkyl ether sulphates are absent. A less aerated slurry gives a spray-dried powder of higher particle density, and allows high bulk density powders to be prepared without the need for a separate deaeration step. A less aerated slurry is also less bulky so that larger batches of slurry can be processed in a given slurry-making vessel: for powders containing high levels of alkylbenzene sulphonate (20% or more) an increase in batch size of up to 20% has been achieved, leading to a corresponding increase in the output of the slurry making plant. Pumping of a less aerated slurry is also easier because its viscosity is lower and cavitation problems are less likely to occur.

Another benefit of the process of the invention is seen when sodium tripolyphosphate is a major building and structuring component of the powder: in a preferred embodiment of the invention, all sodium tripolyphosphate is added before the addition of the sulphonic acid. The temperature of the slurry at the time at which the sodium tripolyphosphate is added is then lower than in the prior art process in which the sulphonic acid neutralisation step has already occurred and raised the slurry temperature. The sodium tripolyphosphate can dissolve and hydrate more quickly at a lower temperature: this ensures that less degradation of the tripolyphosphate occurs during spray-drying, and also favours the growth of very small sodium tripolyphosphate hexahydrate crystals in the slurry, thus giving spray-dried powders of improved structure and absorptivity. Advantageously, a period of at least 2 minutes may be allowed to lapse between addition of the sodium tripolyphosphate and addition of the sulphonic acid to the slurry, in order to maximise hydration of the sodium tripolyphosphate before any temperature increase due to the neutralisation reaction occurs.

In a typical slurry-making plant, the finished slurry is pumped, first via low-pressure pipes and then via high-pressure pipes, to a distribution manifold for the atomising nozzles of a spray-drying tower. As an alternative to incorporating the sulphonic acid in the slurry-making vessel itself, it may be injected either into the low-pressure pump or pipes, or into the high-pressure pump or pipes. It has been found especially beneficial to inject the sulphonic acid into the high-pressure pump or pipes, very shortly before the slurry arrives at the spray-nozzle distribution manifold.

In this procedure slurry aeration and interaction with other materials in the slurry, particularly other detergent-active materials, are minimised: this is of especial advantage if nonionic surfactants are present, since alkylbenzene sulphonates can form viscous phases with nonionic surfactants in slurries, especially when the weight ratio of alkylbenzene sulphonate to nonionic surfactant is within the range of from 1:5 to 5:1. Furthermore, the slurry viscosity is lower before the addition of the sulphonic acid, and this lower viscosity can be exploited to the full, in easier pumping operations, if the sulphonic acid addition is delayed as long as possible.

Alkylbenzene sulphonic acids are fairly viscous liquids at ambient temperatures but can be pumped without too much difficulty using positive displacement pumps. It has been found that sulphonic acid can be used at ambient temperature if it is to be added to the slurry-making vessel. When the alternative procedure of injection into a slurry transfer pump or pipe is to be used, however, the sulphonic acid is preferably heated to a temperature of about 50 to 60°C to lower its viscosity to a value at which accurate metering with a pump of the piston type is possible. An alternative method of reducing the viscosity of the sulphonic acid is to premix it with a viscosity-lowering ingredient, especially a nonionic surfactant, but this method is suitable only for preparing powders in which the viscosity-lowering ingredient is required.

The process of the invention may be used with advantage to prepare any spray-dried detergent powder containing an anionic detergent-active compound having a stable acid form. This will normally be a sulphonate-type anionic detergent, especially an alkylaryl sulphonate and more especially a C_8-C_{15} linear alkylbenzene sulphonate. Other anionic detergent-active compounds may also be present, for example, primary and secondary alkyl sulphates, olefin sulphonates, alkane sulphonates, alkyl ether sulphates, and fatty acid ester sulphonates.

Nonionic surfactants may also be used in detergent powders prepared according to the invention. These include the primary and secondary alcohol ethoxylates, especially the C_{12}-C_{15} primary and secondary alcohols ethoxylated with an average of from 3 to 20 moles of ethylene oxide per mole of alcohol.

It may also be desirable to include one or more soaps of fatty acids. The soaps which can be used are preferably sodium soap derived from naturally occurring fatty acids, for example, the fatty acids from coconut oil, beef tallow, sunflower or hardened rape seed oil.

The total amount of detergent-active material (surfactant), excluding soap, in detergent powders prepared according to the invention is generally within the range of from 5 to 40% by weight. For low-sudsing powders intended for use in European front-loading automatic washing machines the preferred range is from 5 to 20% by weight, with a weight ratio of anionic surfactant to nonionic surfactant not exceeding 10:1, and preferably not exceeding 6:1. As indicated above, however, the present invention is especially applicable to the manufacture of medium-and high-sudsing powders containing higher levels of anionic surfactant and/or higher ratios of anionic surfactant to nonionic surfactant.

Detergent powders prepared in accordance with the invention will also comprise one or more detergency builders, suitably in an amount of from 10 to 60% by weight. Detergency builders are very well known to those skilled in the art and include sodium tripolyphosphate, orthophosphate and pyrophosphate;

crystalline and amorphous sodium aluminosilicate; sodium carbonate; and monomeric and polymeric polycarboxylates, for example, sodium citrate, nitrilotriacetate and polyacrylate, and acrylic copolymers. As mentioned above, at least some of the builders incorporated in the powder must be alkaline salts.

Other inorganic salts without a detergency building function, for example, sodium sulphate, may also be included in detergent powders prepared according to the invention.

Detergent powders prepared according to the invention will also generally contain various additives to enhance the efficiency of the product, notably bleach systems, antiredeposition agents, fluorescers, lather suppressors, enzymes and perfumes. These may be added to the slurry or postdosed into the spray-dried powder in accordance with their known suitability for undergoing spray-drying processes.

EXAMPLES

The invention will now be illustrated in further detail by the following non-limiting Examples.

Example 1

A slurry was prepared in a batch slurry-making apparatus from the following ingredients, added in the order listed:

	parts by weight
Water	1814
Sodium silicate solution (1.6 S.G.)	529
EDTA 40% solution	13
Fluorescer premix slurry	38
Sodium carboxymethyl cellulose	19
Sodium tripolyphosphate	1475
Sodium hydroxide solution (1.5 S.G.)	64
Sodium sulphate	540
Linear alkylbenzene sulphonic acid (Petrelab (Trade Mark) 550 ex Petresa)	241
	4733

The contents of the slurry-making vessel were stirred continuously during the preparation of the slurry. During addition of the sulphonic acid, which was at ambient temperature, the temperature of the slurry rose from about 80°C to about 85°. It was noticeable that much less air than usual was entrained in the slurry during its preparation.

It will be noted that at the time of addition of the alkylbenzene sulphonic acid (746 equivalents) to the slurry, 16782 equivalents of alkaline material (16033 equivalents from the sodium tripolyphosphate and 749 equivalents from the sodium hydroxide) were available in the slurry-making vessel, that is to say, the equivalent ratio of alkali to sulphonic acid was 22:1 without counting the sodium silicate and minor ingredients.

The slurry was transferred via low and high-pressure transfer pipes to a spray-drying tower, 162 parts of a nonionic surfactant being injected into the high-pressure slurry transfer pipe just before it entered the spray jet distribution manifold.

The solubility of the powder was assessed by stirring 4g into 400 ml of water at a temperature of 40°C for 2 minutes and then filtering the undissolved material. The weight of undissolved material under these test conditions should be less than 0.16g for a detergent powder, equivalent to 4% undissolved powder: the weight of undissolved material is greatly affected by the amount of insoluble siliceous material present.

Under the above testing conditions, the level of undissolved material in the detergent powder of Example 1 was very satisfactory at 1.1%. The sulphonic acid used in Example 1 had been prepared by sulphonating an alkylbenzene with sulphur trioxide and air on a falling film reactor. It was of very good quality and contained only 0.9% by weight of free sulphuric acid.

Example 2

This Example describes the preparation of a high-sudsing detergent powder containing 20% by weight of alkylbenzene sulphonate. The alkylbenzene sulphonic acid used had been prepared by reacting the corresponding alkylbenzene directly with 20% oleum and then allowing the resulting mixture of sulphonic and sulphuric acids to separate into two layers; its sulphuric acid content was 6.9% by weight.

A slurry was prepared in a batch slurry-making vessel by adding the following ingredients with mixing, in the order stated:

	Parts by weight
Water	1210
Sodium silicate solution (1.6 S.G.)	980
Fluorescer premix	52
Sodium carboxymethyl cellulose	24
Sodium tripolyphosphate	1162
Sodium hydroxide solution (1.5 S.G.)	301
Alkylbenzene sulphonic acid (as Example 1)	825
Sodium sulphate	689
	5243

It will be noted that at the time of addition of the alkylbenzene sulphonic acid (3525 equivalents) to the slurry, 16155 equivalents of alkaline material from the sodium tripolyphosphate and the sodium hydroxide were available, that is to say, the equivalent ratio of alkali to sulphonic acid was 4.6:1.

The slurry temperature before addition of the sodium tripolyphosphate was 56°C and this rose to 72°C after a 2-minute period to allow the sodium tripolyphosphate to hydrate: this temperature rise indicated that 93% hydration has been achieved. During addition of the alkylbenzene sulphonic acid the temperature rose by a further 22°C to a final value of 94°C; at no time during the slurry-making process was heat from an external source applied to the vessel.

The degree of aeration of the slurry after all the slurry ingredients had been added was significantly less than normal. The slurry was easy to pump.

Without deaeration the slurry was transferred to a spray-drying tower and spray-dried to give a free-flowing powder having a bulk density of 413 g/litre.

The standard dissolution test described in Example 1 established that the dissolving properties of the detergent powder were very good. The amount of undissolved material remaining after 2 minutes' stirring was only 0.1%. This result confirmed that no adverse reaction between the sulphonic acid and the sodium silicate had occurred in the slurry.

Comparative Example A

The same ingredients as in Example 2, in the same proportions, were dosed into an identical slurry-making vessel in the following order:

	Parts by weight
Water	990
Sodium hydroxide solution	247
Alkylbenzene sulphonic acid (as Example 1)	674
Sodium silicate solution	802
Fluorescer premix	42
Sodium carboxymethyl cellulose	20
Sodium tripolyphosphate	950
Sodium sulphate	563
	4288

During addition of the sulphonic acid the temperature in the slurry-making vessel rose by 42°C. The extent of hydration of the sodium tripolyphosphate was 83%. The slurry was considerably more aerated than that of Example 2, so that a smaller batch size (about 80% of that of Example 2) had to be used. The slurry was spray-dried to form a powder having a bulk density of 390 g/litre.

Example 3

This Example illustrates an alternative procedure according to the invention, in which alkylbenzene sulphonic acid was injected continuously into the slurry immediately before the slurry reached the distribution menifold for the spray nozzles of the spray-drying tower.

In a batch slurry-making vessel a slurry was prepared from the following ingredients, added with thorough mixing in the order listed:

	Parts by weight
Water	2510
Sodium silicate solution (1.6 S.G.)	940
EDTA solution (40%)	25
Sodium carboxymethyl cellulose	35
Fluorescer premix	23
Polyacrylate polymer solution (25%)	490
Nonionic surfactant	77
Sodium tripolyphosphate	1685
Sodium hydroxide solution (1.5 S.G.)	183
	5968

The slurry was pumped through low and high-pressure pipes to the distribution manifold. The alkylbenzene sulphonic acid used in Example 1 (689 parts) was injected continuously at a pressure of 50 bar into the slurry just before it entered the manifold: the slurry pressure at this point was 45 bar. A simple static in-line mixer installed after the injection point ensured that the sulphonic acid mixed well with the slurry. Further and more intense local mixing also took place in the high shear swirl type of spray jets in the spray-drying tower.

At the point of injection of the sulphonic acid (2110 equivalents) to the slurry, 20457 equivalents of alkaline material (18315 equivalents from the sodium tripolyphosphate and 2142 equivalents from the sodium hydroxide) were present in the slurry, that is to say, the equivalent ratio of alkali to sulphonic acid was 9.7:1, without counting the alkali present in the sodium silicate solution and minor ingredients.

The spray dried detergent powder had very good physical properties and a bulk density of 490 g/litre. The level of undissolved material remaining after 2 minutes' stirring in water at 40°C was 0.1%. This very low result confirmed that no unusual adverse reaction had occurred between the injected sulphonic acid and the silicate in the slurry leading to the formation of high levels of insoluble siliceous material.

Claims

1. A process for the manufacture of a particulate detergent composition, which comprises the steps of:

(i) preparing an aqueous slurry comprising one or more anionic detergent-active compounds, and one or more alkaline inorganic salts, and

(ii) spray-drying the slurry to form a powder;

the process being characterised in that in step (i) an anionic detergent-active compound is incorporated in wholly or predominantly acid form into the slurry after the incorporation of alkaline material in an amount such that a total of at least two equivalents of alkaline material per equivalent of the said acidic detergent-active compound are present.

2. A process as claimed in claim 1, wherein the anionic detergent-active compound incorporated into the slurry in wholly or predominantly acid form is a C_8-C_{15} alkylbenzene sulphonic acid.

3. A process as claimed in claim 1 or claim 2, wherein the alkaline material incorporated in the slurry before the incorporation of the anionic detergent-active compound in wholly or predominantly acid form includes sodium hydroxide.

4. A process as claimed in any one of claims 1 to 3, wherein the alkaline material incorporated in the slurry before the incorporation of the anionic detergent-active compound in wholly or predominantly acid form includes one or more alkaline builder salts.

5. A process as claimed in claim 4, wherein the alkaline builder salts comprise sodium tripolyphosphate, sodium carbonate or a mixture thereof.

6. A process as claimed in claim 5, wherein the detergent-active compound in wholly or predominantly acid form is incorporated in the slurry after the incorporation of any sodium tripolyphosphate.

7. A process as claimed in any preceding claim, wherein the alkaline material incorporated in the slurry before the incorporation of the anionic detergent-active compound in wholly or predominantly acid form includes alkaline sodium silicate.

8. A process as claimed in any preceding claim, wherein the anionic detergent-active compound in wholly or predominantly acid form is incorporated in the slurry in an amount corresponding to 20% by weight or more of the neutralised detergent-active material in the spray-dried powder.

9. A process as claimed in any preceding claim, wherein the anionic detergent-active compound is incorporated in the slurry in 0 to 10% by weight neutralised form.

10. A process as claimed in any preceding claim, wherein the slurry is prepared in a slurry-making vessel and then pumped through pipes to a spray-drying tower, characterised in that the anionic detergent-active compound in wholly or predominantly acid form is injected into a pipe or pump between the slurry-making vessel and the spray-drying tower.

11. A process as claimed in claim 10, wherein the anionic detergent-active compound in wholly or predominantly acid form is premixed with a liquid nonionic detergent-active compound before incorporation in the slurry.

12. A process as claimed in claim 10, wherein the anionic detergent-active compound in wholly or predominantly acid form is heated to a temperature within the range of from 50 to 60°C before incorporation in the slurry.

13. A process for the manufacture of a particulate detergent composition, carried out substantially as hereinbefore described in any one of Examples 1 to 3.

14. A particulate detergent composition whenever prepared by a process as claimed in any preceding claim.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 87 31 1311

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	FR-A-2 204 684 (PROCTER & GAMBLE CO.) * example 2, claims 1, 3 *	1,4,5,7	C 11 D 11/02 C 11 D 17/02
A	GB-A-2 170 217 (UNILEVER PLC) * examples 1-3, claims 1, 3 *	1,4,5,7	
A	FR-A-2 124 410 (UNILEVER N.V.) * example 3, claims 1, 2, 4 *	1,3-5,7	
D,A	GB-A-1 355 187 (UNILEVER LTD.) * example 1, claims 1, 5 *	1,3-5,7	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 11 D 11/00
C 11 D 17/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	10-03-1988	SCHULTZE D

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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& : member of the same patent family, corresponding document