(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 534 525 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
27.12.1996 Bulletin 1996/52

(51) Int Cl.[6]: **C11D 17/06**, C11D 3/10, C11D 3/20, C11D 3/37, C11D 3/39, C11D 3/12

(21) Application number: **92202764.4**

(22) Date of filing: **11.09.1992**

(54) **Detergent powders and process for preparing them**

Waschmittelpulver und Verfahren zu deren Herstellung

Poudres détergentes et leur procédé de préparation

(84) Designated Contracting States:
CH DE ES FR GB IT LI NL SE

(30) Priority: **27.09.1991 GB 9120657**

(43) Date of publication of application:
31.03.1993 Bulletin 1993/13

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EP 0 534 525 B1

Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF THE INVENTION

The present invention relates to detergent powders intended for use in drum-type fabric washing machines. The invention is of especial applicability to detergent powders containing no, or reduced levels of, phosphate builders and to powders of high bulk density, which have a tendency to dispense poorly. The invention also relates to a process for preparing these detergent powders.

BACKGROUND OF THE INVENTION.

In recent years the trend in detergent compositions has been towards reducing or eliminating phosphate builders. The replacement of sodium tripolyphosphate as a builder in detergent powders by its most popular zero-phosphate substitute, crystalline aluminosilicate (zeolite), has led to a number of difficulties with the structure and physical properties of the powder. One such problem that has been encountered is the tendency of zeolite-built powders to dispense less well in automatic washing machines than do their phosphate-built counterparts; a higher proportion of the powder dosed into the washing machine is left behind in the dispenser, leading to product wastage and clogging. The problem is especially marked at low water inlet temperatures.

The tendency towards poor dispensing has been exacerbated by the recent trend in the detergents industry towards higher bulk density powders. Detergent powders of high bulk densities ranging from 650 to 1100 kg/m^3, preferably ranging from 700 to 1100 kg/m^3, are attractive to the customer. A difficulty, however, with these high bulk density powders is that they are not easily flushed from the dispenser drawer of the washing machine: when the powder is wetted by the water flowing through the dispenser, the detergent particles may become stuck together resulting in considerable residues of wetted and adhering powder left behind in the drawer. Similar problems are encountered when applying a detergent dosing device as described in EP-A-253,419, for in-drum dosing of this type of high density detergent powders. From EP-A-329,538 it is known that dispensing from out of an afore-mentioned in-drum dosing device may be improved by incorporating citric acid and sodium bicarbonate in the powder formulation.

The use of mixtures of sodium bicarbonate and citric acid to promote dissolution of pharmaceutical preparations is well known. In order to ensure a uniform distribution of these effervescent materials in these preparations it is essential to utilize sodium bicarbonate and citric acid in the form of fine powders. Furthermore, it is usually necessary to incorporate considerable proportions of these effervescent materials in the preparations in order to obtain the desired effect. A major issue with these mixtures is the poor storage stability when exposed to humid ambient temperatures. Consequently, protective packaging in the form of sealed containers or moisture proof packs is essential.

The idea of using effervescence to promote the dispersion or dissolution of a granular detergent composition is also known. For example, US-A-4,414,130 (Colgate) discloses detergent compositions comprising an effervescent material which promotes dissolution and dispersion of the detergent particles. In this respect it is mentioned that the detergent particles may comprise sodium carbonate or bicarbonate and that the balance of the composition may include citric acid.

We have found that the major problem with such mixtures of citric acid and sodium (bi-)carbonate is that on storage of the detergent powder containing these mixtures deactivation with regard to the effervescent potential occurs. This deactivation is catalysed either by moisture present within the detergent powder or by moisture absorbed from a humid ambient atmosphere.

It is an object of the present invention to provide detergent compositions with high bulk density which dispense well and of which the good dispensing characteristics are not reduced or lost during storage.

It was surprisingly found that a low level of citric acid material is effective in improving dispensing characteristics of the detergent powder and also that good storage stability in respect of the dispensing potential can be obtained provided that the granular detergent composition comprises sodium carbonate and/or -bicarbonate and/or -sesquicarbonate and that the citric acid is a separate granular component with a closely specified particle size range.

DEFINITION OF THE INVENTION

The present invention provides a granular detergent composition having a bulk density of from 650 to 1100 kg/m^3 and comprising anionic and/or nonionic surfactants, from 5 to 30% by weight of sodium carbonate and/or -bicarbonate and/or sesquicarbonate, other builder material, and from 1 to 15% by weight of particulate citric acid, whereby more than 80% by weight of the citric acid has a particle size which is in the range of from 350 to 1500 μm. The invention also provides a process for preparing this composition, wherein the citric acid is added as a separate granular component to a granular detergent base composition.

DETAILED DESCRIPTION OF THE INVENTION

The first aspect of the invention is a granular detergent composition having a bulk density of from 650 to 1100 kg/m^3, preferably from 700 to 1100 kg/m^3. The composition comprises a base composition to which particulate citric acid, and optionally a foam depressing agent, has been added. The base composition may be prepared by spray-drying and dry-mixing/agglomeration. For obtaining high bulk densities, it is preferably prepared by dry-mixing/agglomeration.

As essential ingredients,the base composition contains one or more anionic and/or nonionic surfactants, and builder material. The base composition preferably also comprises sodium carbonate and/or sodium bicarbonate and/or sodium sesquicarbonate.

The granular composition of the invention may further contain any of the materials conventionally included in detergent compositions. These are described in more detail below.

The surfactant component

The total amount of surfactant present in the composition of the invention will generally range from 5 to 40 % by weight, more preferably from 10 to 30% by weight, and especially from 12 to 20% by weight. These figures are typical for fully formulated detergent compositions, and as a spray-dried or dry-mixed/agglomerated base forms only part of such a composition the surfactant content of that base, as a percentage, may of course be higher.

The invention is of especial applicability to compositions containing anionic and nonionic surfactants.

The amount of anionic surfactant present is desirably at least 3% by weight, and may suitably be in the range of from 3 to 30% by weight, these figures again being based on the fully formulated composition. Anionic surfactants are well known to those skilled in the art. Examples of suitable anionic surfactants include alkylbenzene sulphonates,particularly sodium linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15}; primary and secondary alkyl sulphates, particularly sodium C_{12}-C_{15} primary alkyl sulphates; sodium salts of fatty acids (i.e. soaps); olefin sulphonates; alkane sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates.

Suitable nonionic surfactants that may be used include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic surfactants are alkyl (C_6-C_{22}) phenols-ethylene oxide condensates, generally with 5 to 25 units of ethylene oxide (i.e.: 5-25 EO) per molecule, and the condensation products of aliphatic (C_8-C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, generally 3-40 EO. Furthermore, alkyl polyglycosides and glucose ethers and esters may be effectively used as nonionic surfactants.

The sodium (bi)carbonate and/or -sesquicarbonate and citric acid

The sodium carbonate and/or bicarbonate and/or - sesquicarbonate may be added to the base composition but is preferably present in it.

The amount of this material present in the composition of the invention is in the range of from 5 to 30% by weight based on a fully formulated detergent composition. In zeolite built detergent powder according to the invention this amount is preferably in the range of from 5 to 15% by weight, whereas in detergent powder including a calcite/sodium carbonate builder system this amount is preferably in the range of from 15 to 30% by weight.

The citric acid is a separate granular component and needs to be added to the base composition.

The amount of particulate citric acid needed to obtain the desired good dispensing characteristics and storage stability is in the range of from 1 to 15% by weight, preferably from 2 to 12% by weight, more preferably from 3 to 10% by weight, based on a fully formulated composition.

For the same purpose, more than 80% by weight of the particulate citric acid has a particle size of from 350 to 1500 μm, preferably from 350 to 1000 μm, a particle size range of 350-750 μm being most preferred.

The detergency builder

In addition to the above-mentioned sodium (bi)carbonate and/or -sesquicarbonate, the composition according to the invention includes at least one further builder material capable of reducing the level of free calcium ions in the wash liquor and preferably providing the composition with other beneficial properties such as the generation of an alkaline pH and the suspension of soil removed from the fabric. The total level of the detergency builder may be from 10% to 70% by weight, preferably from 25% to 50% by weight of the detergent composition.

Preferred builders are ion exchange builders such as the crystalline (zeolite) or amorphous alkali metal alumino-silicates. Optionally, organic and inorganic polymers may be present, for example, polycarboxylate polymers such as polyacrylates, acrylic-maleic copolymers such as SOKALAN types of polymers may be present. Other preferred builder

systems are precipitant builders such as those containing calcite and sodium carbonate as described in EP-A-267,042. The detergent composition according to the invention is preferably essentially free of phosphates-containing builders such as orthophosphates and alkali metal tripolyphosphates.

Dispensing behaviour

It is an essential feature of the detergent powder of the invention that the incorporation as specified above of citric acid and sodium (bi)carbonate and/or sodium sesquicarbonate should bring about an improvement in dispensing behaviour. Dispensing is assessed by means of a standard test using a Philips (Trade Mark) AWB 126 washing machine using a 100 gram powder dose and a water fill of 5 litres at 20°C flowing in over a period of 1 minute. The dry weight of powder remaining in the dispenser, in grams, then represents the weight percentage of powder not dispensed into the machine (the residue).
It will be appreciated that this test is stringent, using a low water inlet temperature and flow rate, and a machine with a drawer-type dispenser which is particularly vulnerable to high residues and clogging.

The incorporation of citric acid and sodium (bi)carbonate and/or sodium sesquicarbonate preferably results in a reduction in the residue of at least 10 percentage points, most preferably at least 20 percentage points. Clearly, an improvement of this magnitude can only be observed if the control powder exhibits poor dispensing properties. The present invention is therefore especially applicable to powders which, without citric acid and sodium (bi)carbonate and/or -sesquicarbonate, give dispenser residues of at least 20% by weight. That is especially likely to be the case if the powder is a zero-phosphate composition built with amorphous or crystalline (zeolite) sodium alumino-silicate; and/or if it has a bulk density of at least 650, preferably of at least 700 kg/m^3.

Other components

The granular detergent composition of the invention preferably also contains one or more foam depressing agents. Silicone oil based compositions containing high or low viscosity silicone oil, particularly high viscosity silicone oil, may be effectively used as antifoaming agents.

Preferably, there is also a bleach present in the composition of the invention. Preferred bleaches are the oxygen bleaches, for example in the form of an inorganic persalt, preferably with a precursor, or as a peroxy acid compound. From an environmental point of view, the most preferred bleach compound is percarbonate.
Effective amounts of these bleach compounds present in the detergent composition of the invention range from 5 to 20% by weight, preferably from 10 to 20% by weight.

If desired, the powder of the invention may contain sodium silicate. High levels of silicate can in themselves have a beneficial effect on dispensing, as well as on powder structure and prevention of machine corrosion, but are undesirable in powders containing alumino-silicate because the two components react together to form insoluble siliceous species. The present invention enables the dispensing behaviour of zeolite-built powders to be improved without a corresponding increase in the level of insoluble material. Accordingly, the invention is of especial applicability to powders containing less than 10% by weight, more especially less than 5% by weight, of sodium silicate.

Other materials that may be present in the powder of the invention include fluorescers, antiredeposition agents, inorganic salts such as sodium sulphate, enzymes, bleach activators, and bleach stabilizers. These may be included in the spray-dried base powder or postdosed according to their known suitability for undergoing spray-drying processes and their compatibility with other slurry ingredients.

The invention is further illustrated by the following Examples, in which parts and percentages are by weight unless otherwise stated. In the Examples the following abbreviations are used:

LAS:	sodium C_{12}-C_{15} alkyl benzene sulphonate, ex Manro Products Ltd, England
Nonionic EO :	Nonionic surfactant (ethoxylated alcohol), 1.7:1 mixture of Synperonic A3 and A7 (containing 3 and 7 EO groups), ex ICI
Soap :	sodium salt of fatty acids
Zeolite 4A :	amorphous alumino-silicate, Wessalith A4 (trade mark) ex Degussa
Sokalan CP5 :	Copolymer of maleic and acrylic acid having a molecular weight of 70,000, ex BASF
Carbonate :	Sodium carbonate
Percarbonate :	Sodium percarbonate, ex Interox
Perborate :	Sodium perborate tetrahydrate
Silicone :	DB 100 poly dimethyl siloxane, ex Dow
TAED :	Tetra acetyl ethylene diamine

EXAMPLES 1-4

A phosphate-free detergent base powder was prepared, by slurry-making, spray-drying and subsequently densifying in a Lödige "Recycler/ploughshare", as described in EP-A-367,339, to form the following nominal composition:

	Parts
LAS	8.3
Nonionic EO	6.7
Soap	1.8
Zeolite 4A	28.0
Sokalan CP5	4.5
Carbonate	8.5
Minor ingredients + moisture	14.8

To this base powder, the following components were postdosed:

	Parts
Silicone	0.4
Percarbonate	20.0
TAED	5.0
Carbonate	2.0

The bulk density of the detergent powder obtained was 850 kg/m^3.
To 100 parts of this densified powder, citric acid of which more than 80% by weight has a particle size in the range of 350-1000 μm was added at four different levels. The dispensing properties of the thus obtained compositions were tested in a Philips (trade mark) AWB 126 washing machine using 100 g powder, and 5 litres of water at 20°C flowing in over a period of 1 minute. Other samples were stored during 6 weeks in wax-laminated cartons at 28 °C and 70% RH, and thereafter tested in the Philips washing machine.
Table 1 shows the resulting dispenser residues.

TABLE 1

	1	2	3	4
Parts citric acid added	0	1	2	3
Dispenser Residue (%)	80	50	0	0
Dispenser Residue after After storage for 6 weeks	80	65	10	0

It can be seen that the incorporation of the above-described type of citric acid effectively reduces the level of dispenser residue. Furthermore, the incorporation of 3 parts or more of this citric acid in the detergent powder appeared to be effective at eliminating dispenser residues.

EXAMPLES 5-9

To the base powder of Examples 1-4, the following components were postdosed:

	Parts
Silicone	0.4
Perborate	20.0
TAED	5.0
Carbonate	2.0

The bulk density of the detergent powder obtained was 850 kg/m^3.
To 100 parts of the above mixed powder, citric acid of which more than 80% by weight has a particle size in the range

of 350-1000 μm was added at four different levels. Samples of the thus obtained compositions were tested in a Philips (trade mark) AWB 126 washing machine, as described above. Other samples were stored during 6 weeks in wax-laminated cartons at 28°C and 70% RH, and thereafter tested in the Philips washing machine.

Table 2 shows the resulting dispenser residues.

TABLE 2

	5	6	7	8	9
Parts citric acid added	0	2	4	6	8
Dispenser Residue (%)	80	70	40	0	0
Dispenser Residue after Storage for 6 weeks (%)	80	70	40	10	0

It can be seen that addition of 6 parts or more of citric acid resulted in acceptable dispenser residues.

COMPARATIVE EXAMPLES A-E

To 100 parts of the detergent powder of Examples 1-4 (having a bulk density of 850 kg/m^3), citric acid of which more than 80% by weight has a particle size in the range of 50-100 μm was added at several levels. Samples of the thus obtained compositions were tested in a Philips (trade mark) AWB 126 washing machine, as described above. Other samples were stored during 4 weeks in wax laminated cartons at 37°C and 70% RH, and thereafter tested in the Philips washing machine. Table 3 shows the resulting dispenser residues.

TABLE 3

	A	B	C	D	E
Parts citric acid added	0	0.5	1	2	4
Dispenser Residue (%)	80	15	0	0	0
Dispenser Residue after Storage for 4 weeks (%)	80	80	80	80	80

From the results shown in table 3 it can be concluded that particulate citric acid of which more than 80% by weight has a smaller particle size than according to the present invention, is very effective at improving dispensing immediately after the detergent powder has been prepared. However, it can also be concluded that the storage stability in respect of the dispensing properties particularly with regard to storage of the detergent powder at high humidity, is poor when this type of citric acid is incorporated in the detergent powder.

COMPARATIVE EXAMPLES F-I

To 100 parts of the detergent powder of Examples 1-4 (having a bulk density of 850 kg/m^3), citric acid of which more than 80% by weight has a particle size in the range of 1500-2000 μm was added at several levels. Samples of the thus obtained compositions were tested as described above for Comparative Examples A-E. Table 4 shows the resulting dispenser residues.

TABLE 4

	F	G	H	I
Parts citric acid added	0	2	4	8
Dispenser residue (%)	80	70	53	35
Dispenser residue after Storage for 4 weeks (%)	80	80	80	80

From these results it can be derived that particulate citric acid of which more than 80% by weight has a larger partical size than according to the present invention, is not very effective at improving dispensing, neither immediately after preparation of the detergent powder nor after storage for 4 weeks.

Claims

1. Granular detergent composition having a bulk density of from 650 to 1100 kg/m^3 and comprising anionic and/or nonionic surfactants, from 5 to 30% by weight of sodium carbonate and/or -bicarbonate and/or -sesquicarbonate, other builder material, and from 1 to 15% by weight of particulate citric acid, whereby more than 80% by weight of the citric acid has a particle size which is in the range of from 350 to 1500 μm.

2. Composition according to claim 1, wherein more than 80% by volume of the citric acid has a particle size which is in the range of from 350 to 1000 μm.

3. Composition according to claim 2, wherein more than 80% by weight of the citric acid has a particle size which is in the range of from 350 to 750 μm.

4. Composition according to any of claims 1-3, wherein the composition comprises a foam depressing agent.

5. Composition according to claim 4, wherein the foam depressing agent is a high viscosity silicone oil.

6. Composition according to any of claims 1-5, wherein the composition comprises a bleach component.

7. Composition according to claim 6, wherein the bleach component is sodium percarbonate.

8. Composition according to any of claims 1-7, wherein the other builder material comprises sodium alumino-silicate.

9. Composition according to any of claims 1-8, wherein the composition is essentially free of phosphates.

10. Process for preparing the composition of claim 1, wherein the citric acid is added as a separate granular component to a granular detergent base composition.

Revendications

1. Composition détergente en granulés présentant une masse volumique comprise entre 650 et 1 100 kg/m^3 et comprenant des agents tensioactifs anioniques et/ou non ioniques, 5 à 30 % en masse de carbonate et/ou de bicarbonate et/ou de sesquicarbonate de sodium, une autre matière d'édificateur de détergence, et 1 à 15 % en masse d'acide citrique particulaire, dans laquelle plus de 80 % en masse de l'acide citrique présente une taille de particules qui se situe dans la gamme comprise entre 350 et 1 500 μm.

2. Composition selon la Revendication 1, dans laquelle plus de 80 % en volume de l'acide citrique présente une taille de particules qui se situe dans la gamme comprise entre 350 et 1 000 μm.

3. Composition selon la Revendication 2, dans laquelle plus de 80 % en masse de l'acide citrique présente une taille de particules qui se situe dans la gamme comprise entre 350 et 750 μm.

4. Composition selon l'une quelconque des Revendications 1 à 3, dans laquelle la composition comprend un agent dépresseur de mousse.

5. Composition selon la Revendication 4, dans laquelle l'agent dépresseur de mousse est une huile de silicone présentant une viscosité élevée.

6. Composition selon l'une quelconque des Revendications 1 à 5, dans laquelle la composition comprend un composant de blanchiment.

7. Composition selon la Revendication 6, dans laquelle le composant de blanchiment est du percarbonate de sodium.

8. Composition selon l'une quelconque des Revendications 1 à 7, dans laquelle l'autre matière d'édificateur comprend de l'aluminosilicate de sodium.

9. Composition selon l'une quelconque des Revendications 1 à 8, dans laquelle la composition est essentiellement

exempte de phosphates.

10. Procédé de préparation de la composition de la Revendication 1, dans lequel on ajoute l'acide citrique comme composant granulaire séparé à une composition de base détergente en granulés.

Patentansprüche

1. Körnige Reinigungsmittelzusammensetzung einer Schüttdichte von 650 bis 1100 kg/m^3, die anionische und/oder nichtionische grenzflächenaktive Mittel, 5 bis 30 Gew.-% Natriumcarbonat und/oder -bicarbonat und/oder -sesquicarbonat, weitere Buildermaterialien sowie 1 bis 15 Gew.-% teilchenförmige Citronensäure umfaßt, wobei mehr als 80 Gew.-% der Citronensäure eine Teilchengröße im Bereich von 350 bis 1500 µm aufweisen.

2. Zusammensetzung nach Anspruch 1, wobei mehr als 80 Vol.-% der Citronensäure eine Teilchengröße im Bereich von 350 bis 1000 µm aufweisen.

3. Zusammensetzung nach Anspruch 2, wobei mehr als 80 Gew.-% der Citronensäure eine Teilchengröße im Bereich von 350 bis 750 µm aufweisen.

4. Zusammensetzung nach einem der Ansprüche 1 bis 3, wobei die Zusammensetzung ein schaumunterdrückendes Mittel umfaßt.

5. Zusammensetzung nach Anspruch 4, wobei das schaumunterdrückende Mittel ein hochviskoses Siliconöl ist.

6. Zusammensetzung nach einem der Ansprüche 1 bis 5, wobei die Zusammensetzung eine Bleichmittelkomponente umfaßt.

7. Zusammensetzung nach Anspruch 6, wobei die Bleichmittelkomponente Natriumpercarbonat ist.

8. Zusammensetzung nach einem der Ansprüche 1 bis 7, wobei das weitere Buildermaterial Natriumalumosilicat umfaßt.

9. Zusammensetzung nach einem der Ansprüche 1 bis 8, wobei die Zusammensetzung im wesentlichen keine Phosphate enthält.

10. Verfahren zur Herstellung der Zusammensetzung nach Anspruch 1, wobei die Citronensäure als getrennte körnige Komponente einer körnigen Reinigungsmittelgrundlagenzusammensetzung zugesetzt wird.