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

(11) EP 0 883 678 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
19.05.2004 Bulletin 2004/21

(21) Application number: **96908611.5**

(22) Date of filing: **29.02.1996**

(51) Int Cl.^{7}: **C11D 11/00**, C11D 17/06,
C11D 3/10, C11D 3/06

(86) International application number:
PCT/US1996/002848

(87) International publication number:
WO 1997/032003 (04.09.1997 Gazette 1997/38)

(54) PROCESS FOR MANUFACTURE OF HIGH DENSITY DETERGENT GRANULES

VERFAHREN ZUR HERSTELLUNG KOMPAKTER WASCHMITTELGRANULATE

PROCEDE DE PRODUCTION DE GRANULES DETERGENTS DE HAUTE DENSITE

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI LU NL PT SE

(43) Date of publication of application:
16.12.1998 Bulletin 1998/51

(73) Proprietor: **THE PROCTER & GAMBLE COMPANY
Cincinnati, Ohio 45202 (US)**

(72) Inventors:
- **ADAMS, Donald, Scott
Cincinnati, OH 45217 (US)**
- **YEAZELL, Burce, Albert
Cincinnati, OH 45231 (US)**
- **RIDDICK, Eric, Fitzgerald
West Chester, OH 45069 (US)**
- **KAO, Junan
Kobe 658 (JP)**

(74) Representative: **Brooks, Maxim Courtney
Procter & Gamble Technical Centres Limited,
Whitley Road,
Longbenton
Newcastle upon Tyne NE12 9TS (GB)**

(56) References cited:
EP-A- 0 351 937
EP-A- 0 555 622
WO-A-95/06109
EP-A- 0 420 317
WO-A-94/02573

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] The invention involves a process for making built high active detergent agglomerates having improved free flow properties.

BACKGROUND OF THE INVENTION

[0002] Laundry detergent granules comprise one or more surfactants (usually of the anionic type) and one or more detergency builders (typically phosphates, carbonates, zeolites, etc.) Detergent granules are typically made by preparing a paste of the detergent ingredients, and spray drying the paste to form granules. Such products also can be made by agglomerating a mixture of the surfactant and builder in a mixer. In an agglomeration process, the anionic surfactant in its neutralized form can be used or it can be introduced into the agglomeration process in its acid form and be neutralized in situ by alkaline materials (e.g. sodium carbonate) as described in EP-A-0 555 622. Optional detergent materials such as brighteners, soil release agents, etc. can be agglomerated along with the surfactant and builder or can be mixed with the agglomerates after they are formed. Generally, agglomeration provides the ability to produce higher density detergent products than those which are produced by spray drying.

[0003] A frequent problem with detergent agglomerates, particularly those having a surfactant level of 20% or more, is a tendency to be somewhat sticky (i.e., poor free flow). To help alleviate this problem, flow aids such as clay, talc, zeolites or silica are typically used.

[0004] Representative examples of prior patents relating to agglomeration processes for the production of detergent granules are: U.S. Pat. 5,133,924 (Appel); U.S. Pat 5,164,108 (Appel); U.S Pat. 5,160,657 (Bartolloti); Brit. Pat. 1,517,713 (Unilever); Euro. Appln. 451,894 (Curtis); U.S.Pat 5,108,646 (Beerse et al.); Euro. Pat. Appln. 351,937 (Hollingsworth et al); and U.S. Pat. 5,205,958.

[0005] The object of the present invention is to provide a process for producing detergent agglomerates having high surfactant levels and improved free flow characteristics.

SUMMARY OF THE INVENTION

[0006] The present invention is directed to a process comprising the steps of:

(a) mixing detergent components in a mixer, the said components comprising:

(1) from 20% to 35% of an acid precursor of an anionic surfactant ;
(2) from 0% to 65% particulate phosphate builder selected from the group consisting of polyphosphate, pyrophosphate, and mixtures thereof,
(3) from 6% to 60% of a particulate carbonate selected from the group consisting of sodium carbonate, potassium carbonate, and mixtures thereof; wherein the amount of carbonate is at least 2 times that which is sufficient to neutralize the said acid precursor;

wherein at least 40% of the total amount of Components (2) and (3) meets a particle size specification of 97% particles less than 40 microns and a median particle size of 5 to 20 μm (microns), and
(b) agglomerating the mixture from Step (a) in a second mixer to produce detergent agglomerates in which the acid precursor has been substantially neutralized.

DETAILED DESCRIPTION OF THE INVENTION

[0007] In accordance with the present invention, it has been found that in the preparation of anionic detergent agglomerates having high anionic surfactant content, (i.e., 20% or above) and containing carbonate and, optionally, phosphate builders, improved free flow characteristics can be achieved if at least 40% of the total (i.e., combined) amount of particulate carbonate/phosphate used in preparing the agglomerates meets a specification of 97% particles less than 40μm (microns) and a median particle size of 5 to 20 μm (microns)

Raw Materials

[0008] Anionic surfactant is an essential component of compositions prepared by the present process. Such surfactants are well known in the art. The anionic surfactants useful in the subject invention are preferably the alkali metal (i.e., sodium and potassium) salts of alkylbenzene sulfonates or alkyl sulfates or mixtures thereof. Examples of other anionic surfactants which are also useful are the alkali metal salts of paraffin sulfonates, alkyl glyceryl ether sulfonates and alkyl ether sulfates, all having 8 to 1.8 carbon atoms in their alkyl chains. The anionic surfactant raw materials preferably have a moisture content of less than 1.0%, more preferably less than 0.5%. Based on the total weight of raw materials added during the process of the subject invention, the amount of anionic surfactant is from 20% to 35%, preferably from 20% to 30%.

[0009] Preferred alkylbenzene sulfonates useful in the subject process include those with an alkyl portion which is straight chain or branched chain, preferably having from 8 to 18 carbon atoms, more preferably from 10 to 16 carbon atoms. The alkyl chains of the alkylbenzene sulfonate preferably have an average chain length of from about 11 to about 14 carbon atoms. Alkylbenzene sulfonate which includes branched chain alkyl is termed ABS. Alkylbenzene sulfonate which is all straight chain is preferred because it is more easily biodegraded; it is termed LAS.

[0010] Preferred alkyl sulfates useful in the subject process include those with an alkyl portion which is straight chain or branched chain, preferably having from 8 to 24 carbon atoms, more preferably from 10 to 20 carbon atoms, more preferably still from 12 to 18 carbon atoms. The alkyl chains of the alkyl sulfates preferably have an average chain length of from 14 to 16 carbon atoms. The alkyl chains are preferably linear. Alkyl sulfates are typically obtained by sulfating fatty alcohols produced by reducing the glycerides of fats and/or oils from natural sources, especially from tallow or coconut oil.

[0011] Preferred anionic surfactants useful in the subject invention process may also be combinations of alkylbenzene sulfonates and alkyl sulfates, whether mixed together or added during the process separately. Combinations having a ratio of alkylbenzene sulfonate to alkyl sulfate of from 20:80 to 80:20 are preferred; those having a ratio of from 40:60 to 60:40 are more preferred. Additional disclosure of anionic synthetic surfactants can be found in U.S. Pat. 3,664,961, Norris, issued May 23, 1972. In practicing the process herein the anionic surfactant can be introduced in its neutralized (i.e., alkali metal) form or it can be introduced in its unneutralized acid precursor form, in which case it is neutralized by excess alkali metal carbonate, as discussed later herein.

[0012] Optionally, phosphates are used as builders in compositions made according to the process herein. The phosphate builder raw materials useful in the subject invention process are in particulate form and consist essentially of the water-soluble salts (e.g., the sodium and potassium salts) of polyphosphates (e.g., tripolyphosphate, hexametaphosphate, etc.) or pyrophosphates or mixtures thereof. The phosphate builder raw materials preferably have a moisture content of less than 2%, more preferably less than 1%. Based on the total weight of raw materials added during the process of the subject invention, the amount of phosphate builder is typically from 5% to 65%, preferably from 15% to 55%, more preferably from 25% to 45%. Phosphate builder raw materials are typically supplied from their manufacturers in powder form, usually having a median particle size of from 25 μm (microns) to 50 μm (microns). Carbonate raw materials are typically supplied from their manufacturers in granular form, usually having a particle size of from 25 μm (microns) to 150 μm (microns) "As is" median particle size for polyphosphate and carbonate varies for supplies obtained in different geographies as well as by supplier. For use in the present invention the polyphosphate builder and/or carbonate are ground to a particle size such that at least 40% of the total amount of particles of phosphate/carbonate used in the process meet a particle size specification of 97% of particles less than 40 μm (microns) and median particle size of 5 to 20 μm (microns) preferably 10 to 20 μm (microns). Either the carbonate, phosphate or both can be ground to achieve the specified amount of total phosphate/carbonate particles within the required size requirements. Preferably at least 70% of the particles should meet the required specification. Typically, all of the particles of phosphate and carbonate used in the process will be within an overall size range of 5 to 300μm (microns). Grinding can be accomplished in conventional powder grinding equipment such as an ACM Classifier Mill (Hosokawa Micron Powder Systems). During grinding, or after grinding, if necessary, the particles are classifed to assure that the ground particles to be used are within the required specification. For classification, a Micron Pulsaire Classifier (Hosokawa Powder Systems) can be used.

[0013] A preferred phosphate builder useful in the subject process is sodium tripolyphosphate (STPP); STPP can be obtained commercially from, for example, FMC Corp. Another preferred phosphate builder is tetrasodium pyrophosphate (TSPP); TSPP can be obtained commercially from, for example, FMC Corp.

[0014] The subject invention process utilizes particulate alkali metal carbonate preferably consisting essentially of sodium carbonate or potassium carbonate or a mixture thereof as builders. An acid precursor of anionic surfactant is used in the process and the carbonate also functions as a neutralizing agent to convert the acid precursor to the alkali metal salt. The alkali metal carbonate raw materials preferably have a moisture content of less than 2%, more preferably less than 1%. Based on the total weight of raw materials added to the process of the subject invention, the amount of alkali metal carbonate is from 6% to 60%, preferably from 10% to 50%, more preferably from 30% to 40%.

[0015] To neutralize the acid precursor of anionic surfactant, each carbonate ion ($CO_3^{=}$) reacts with two acidic hydrogens (H^+). From this reaction, the amount of carbonate needed to theoretically neutralize acid precursor of anionic surfactant can be determined. When an acid precursor of anionic surfactant is used in the process, the amount of carbonate fed to the process is at least 2 times that theoretically needed to neutralize the acid. Preferably the amount of carbonate will be from 4 times to 12 times, more preferably still from 6 times to 12 times, the amount needed to neutralize the acid precursor.

[0016] In the subject invention process, substantially the only water present in the materials as they go through the process is the minor amounts of moisture present in the raw materials and the water generated by neutralization of acid precursor of anionic surfactant. Throughout the process, the maximum amount of water in the materials being processed is preferably 10%, more preferably 7%, more preferably still 5%, still more preferably 3%. The detergent agglomerates produced by the process may be somewhat hygroscopic and pick up moisture from the atmosphere.

[0017] The detergent agglomerates from the process of the subject invention typically have an average particle size of from 200 μm (microns) to 800 μm (microns), more preferably from 300 μm (microns) to 700 μm (microns), more preferably still from 400 μm (microns) to 600 μm (microns).

[0018] An advantage of the process of the invention is that the use of flow aids such as silicas, clays, diatomaceous earth, aluminosilicates (e.g., zeolites), perlite, and calcite can be substantially reduced or eliminated.

Process Steps

[0019] The subject invention can be carried out in a continuous or batch manner. Continuous processing is preferred. A description of the subject process conducted in a continuous manner is as follows:

[0020] The first step of the process is preferably carried out in a high-speed, high-shear mixer. Suitable mixers for this step include, for example, the Loedige CB®, the Shugi Granulator®, and the Drais K-TTP®. The preferred mixer for the first step is the Loedige CB®. Typically, the high-speed mixer has a substantially cylindrical mixing chamber which is from 0.3m to 1m in diameter and from 1m to 3.5m in length. Preferred mixers for the first step have a central shaft, with mixer blades attached, which preferably rotates at a speed of from 300 rpm to 1800 rpm, more preferably from 350 rpm to 1250 rpm, more preferably still from 400 rpm to 1000 rpm, the speed generally being lower for larger mixers. The high-speed mixer preferably is water-jacketed to permit cooling water to flow through the mixer jacket, in order to remove heat generated by the neutralization reaction.

[0021] For the first step of the subject process, the essential raw materials (i.e., surfactant acid precursor; carbonate; and phosphate, if used) are typically fed to the high-speed mixer near one end of the cylindrical chamber and intimately mixed as they proceed through the chamber; the mixture is discharged near the other end of the cylindrical chamber. The typical average throughput rate is from 0.2 kgs^{-1} (kg/sec) to 17 kgs^{-1} (kg/sec), especially from 2 kgs^{-1} (kg/sec) to 13 kgs^{-1} (kg/sec), the higher throughput rates generally being achieved using larger mixers. The average residence time of materials in the first-step mixer is preferably from 2 seconds to 30 seconds, more preferably from 5 seconds to 20 seconds, more preferably still from 10 seconds to 15 seconds.

[0022] Much of the neutralization of the acid by the carbonate occurs in the first step of the process. Preferably, substantially all of the neutralization takes place in the first step. However, the neutralization reaction may be completed after the mixture discharges from the first-step mixer. The acid is substantially completely neutralized during the process. Cooling water at a temperature of from 5°C to 25°C is preferably fed to the water jacket of the high-speed mixer. The temperature of the mixture at the discharge from the high-speed mixer is typically from 35°C to 70°C, preferably from 45°C to 55°C.

[0023] The materials discharged from the first-step mixer are typically fed substantially immediately into the second-step mixer. The average residence time for materials between the mixers is preferably less than 5 minutes, more preferably less than 1 minute.

[0024] The second step of the process of the subject invention is preferably carried out in a moderate-speed mixer. Suitable mixers for this step include plowshare mixers, for example, the Loedige KM® and the Drais K-T®. The Loedige KM® is the preferred mixer for the second step of the subject invention process. Typically, the moderate-speed mixer has a substantially cylindrical mixing chamber which is from 0.6m to 2m in diameter and from 2m to 5m in length. The preferred mixers have a central shaft, with mixer blades attached, which preferably rotates at a speed of from 40 rpm to 160 rpm, more preferably from 45 rpm to 140 rpm, more preferably still from 50 rpm to 100 rpm, the speed generally being lower for larger mixers. The moderate-speed mixer preferably is water-jacketed to permit water to flow through the mixer jacket, in order to maintain the temperature of product in the moderate-speed mixer at about its incoming temperature.

[0025] For the second step of the subject process, the mixture of materials discharged from the first-step mixer is typically fed to the moderate-speed mixer near one end of the cylindrical chamber, mixed as it proceeds through the chamber, and discharged near the other end of the cylindrical chamber. Typically, the throughput rate for the second step is the same as for the first step. The average residence time of the materials in the second-step mixer is preferably from 0.5 minutes to 10 minutes, more preferably from 0.5 minutes to 5 minutes, more preferably still from 1 minute to 4 minutes.

[0026] The temperature of the mixture at the discharge of the moderate-speed mixer is typically from 35°C to 70°C, preferably from 45°C to 55°C.

[0027] The agglomerates produced by the process herein can be used "as is" for detergent purposes. However other materials normally included in detergent compositions can be included in the agglomerates per se or combined with the agglomerates in one or more subsequent mixing steps. Such materials include organic polymeric builders such as polycarboxylates (see U.S.Patent 4,144,226 Diehl), phosphonic acid builders such as disclosed in U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,442,137; 3,400,176; and 3,400,148, alkali metal silicates, zeolite builders as disclosed in U.S. Patent 4,605,509, bleaches, bleach activators, soil suspending agents, enzymes, perfumes, chelating agents, and additional surfactants such as alkyl polyethoxylates, ethoxylated fatty amines, etc.

[0028] All percentages and ratios set forth in this document are "by weight" unless specified otherwise.

[0029] The invention will be illustrated by the following example which is not to be construed as limiting the invention in any way.

EXAMPLE I

[0030] In this Example, the following agglomerated compositions were prepared.

	A	B
Sodium alkylbenzene sulfonate	27.5%*	27.5%*
Sodium carbonate	40.0**	32.0***
Tripolyphosphate	21.9	19.6
Sodium sulfate	0.6	0.7
Zeolite	7.2	15.2
Moisture	1.9	4.7
Miscellaneous	to 100	to 100.

*26.5% as unneutralized alkylbenzene sulfonic acid.

**44% prior to neutralization of alkylbenzene sulfonic acid.

***36% prior to neutralization of alkylbenzene sulfonic acid.

[0031] Compostion A was made according to the process of the present invention, utilizing acid precursor of the alkylbenzene sulfonate surfactant. A Loedige CB mixer was used in Step 1 and a Loedige KM mixer in Step 2. All materials were added in Step 1, except that 20% of the zeolite (i.e., 1.44 parts) was added in Step 2. All of the sodium carbonate which, "as received" had a particle size of 97% less than approximately 200 μm (microns) and a median particle size of 50 μm (microns) was ground and classified to meet a specification of 97% less than 40 μm (microns) and a median particle size of 10 μm (microns). The tripolyphosphate had an "as received" particle size of 97% less than 200 μm (microns) and a median particle size of 50 μm (microns). The tripolyphosphate was not ground and classified prior to use. Thus, 44 parts carbonate which is 67% of the total amount phosphate and carbonate used to prepare the composition was pretreated to meet the particle size specification required by the invention.

[0032] Composition B was made in the same manner as Composition A, except that both the carbonate and phosphate were used with their "as received" particle size. Also, in Composition B, 90% of the zeolite was added in Step 1 and 10% (i.e., 1.52 parts) was added in Step 2.

[0033] Composition A had excellent free flow characteristics, whereas Composition B had poor free flow characteristics.

[0034] Both compositions were subjected to an "arch test". In this test the ability of an agglomerate product to form an arch under pressure can be used to determine potential flowability problems in conveying equipment and storage silos. In this test the agglomerate product is pressed into the form of an arch in a cylindrical vessel, and the stickiness of the product is assessed by measuring the force required to break the arch. The stickier the product, the greater the force required. 1.5 kg force was required for Composition A and 3-5 kg was required for Composition B.

Claims

1. A process for preparing detergent agglomerates comprising the steps of:

(a) mixing detergent components in a mixer, the said components comprising:

(1) from 20% to 35% of an acid precursor of an anionic surfactant,
(2) from 0% to 65% of a particulate phosphate builder selected from the group consisting of polyphosphate, pyrophosphate, and mixtures thereof; and
(3) from 6% to 60% of a particulate carbonate selected from the group consisting of sodium carbonate, potassium carbonate, and mixtures thereof; wherein the amount of carbonate is at least 2 times that which is sufficient to neutralise the surfactant acid; and

(b) agglomerating the mixture from Step (a) in a moderate speed mixer to produce detergent agglomerates in which the acid precursor has been substantially neutralised,

characterised in that at least 40% of the total amount of Components (2) and (3) meets a particle size specification of 97% of particles less than 40 µm (microns) and median particle size of 5 to 20 µm (microns).

2. A process according to claim 1 in which at least 67% of the total amount of components (2) and (3) have the particle size specification stated in claim 1.

3. A process according to claim 1 or claim 2 in which the amount of component (3) is from 4 to 12 times the amount needed to neutralise component (1).

4. A process according to any preceding claim in which the amount of component (2) is from 5 to 65%.

5. A process according to any preceding claim in which the amount of component (2) is 15 to 55% and the amount of component (1) is 20 to 30%.

6. A process according to any preceding claim in which the amount of the particulate carbonate is at least 10%.

7. A process according to any preceding claim in which the amount of the particulate carbonate is at least 30%.

Patentansprüche

1. Verfahren zur Herstellung von Detergensagglomeraten, umfassend die Schritte:

(a) Mischen von Detergenskomponenten in einem Mischer, wobei die Komponenten umfassen:

(1) 20% bis 35% eines Säurevorläufers eines anionischen Tensids,
(2) 0% bis 65% eines teilchenförmigen Phosphatbuilders, gewählt aus der Gruppe, bestehend aus Polyphosphat, Pyrophosphat und Mischungen hiervon; und
(3) 6% bis 60% eines teilchenförmigen Carbonats, gewählt aus der Gruppe, bestehend aus Natriumcarbonat, Kaliumcarbonat und Mischungen hiervon; wobei die Menge an Carbonat mindestens das zweifache derjenigen beträgt, welche ausreichend ist, um die Tensidsäure zu neutralisieren; und

(b) Agglomerieren der Mischung aus Schritt (a) in einem Mäßiggeschwindigkeitsmischer zur Erzeugung von Detergensagglomeraten, in denen der Säurevorläufer im Wesentlichen neutralisiert worden ist,

dadurch gekennzeichnet, dass mindestens 40% der Gesamtmenge der Komponenten (2) und (3) eine Teilchengrößenspezifikation erfüllen, gemäß der 97% der Teilchen kleiner als 40 µm (microns) sind und die mittlere Teilchengröße 5 bis 20 µm (microns) beträgt.

2. Verfahren nach Anspruch 1, wobei mindestens 67% der Gesamtmenge der Komponenten (2) und (3) die in Anspruch 1 angegebene Teilchengrößenspezifikation aufweisen.

3. Verfahren nach Anspruch 1 oder Anspruch 2, wobei die Menge an Komponente (3) das 4- bis 12-fache der Menge beträgt, welche erforderlich ist, um Komponente (1) zu neutralisieren.

4. Verfahren nach mindestens einem vorangehenden Anspruch, wobei die Menge an Komponente (2) 5 bis 65% beträgt.

5. Verfahren nach mindestens einem vorangehenden Anspruch, wobei die Menge an Komponente (2) 15 bis 55% beträgt und die Menge an Komponente (1) 20 bis 30% beträgt.

6. Verfahren nach mindestens einem vorangehenden Anspruch, wobei die Menge des teilchenförmigen Carbonats mindestens 10% beträgt.

7. Verfahren nach mindestens einem vorangehenden Anspruch, wobei die Menge des teilchenförmigen Carbonats mindestens 30% beträgt.

Revendications

1. Procédé de préparation d'agglomérats détergents comprenant les étapes consistant à :

(a) mélanger des composants détergents dans un mélangeur, lesdits composants comprenant :

(1) 20 % à 35 % d'un précurseur acide d'un tensioactif anionique ;
(2) 0 % à 65 % d'un adjuvant phosphate particulaire choisi dans le groupe constitué par le polyphosphate, le pyrophosphate, et leurs mélanges ; et
(3) 6 % à 60 % d'un carbonate particulaire choisi dans le groupe constitué par le carbonate de sodium, le carbonate de potassium, et leurs mélanges ; dans lequel la quantité de carbonate est au moins deux fois celle qui est suffisante pour neutraliser l'acide tensioactif ; et

(b) agglomérer le mélange de l'étape (a) dans un mélangeur à vitesse modérée pour produire des agglomérats détergents dans lesquels le précurseur acide a été sensiblement neutralisé,

caractérisé en ce qu'au moins 40 % de la quantité totale des composants (2) et (3) satisfait à une dimension de particule de 97 % de particule inférieures à 40 µm (microns) et une dimension moyenne de particule de 5 à 20 µm (microns).

2. Procédé selon la revendication 1, dans lequel au moins 67 % de la quantité totale des composants (2) et (3) a la dimension de particule mentionnée dans la revendication 1.

3. Procédé selon la revendication 1 ou 2, dans lequel la quantité de composant (3) est de quatre à douze fois la quantité nécessaire pour neutraliser le composant (1).

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel la quantité de composant (2) est de 5 à 65 %.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel la quantité de composant (2) est 15 à 55 % et la quantité de composant (1) est 20 à 30 %.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel la quantité du carbonate particulaire est au moins 10 %.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel la quantité de carbonate particulaire est au moins 30 %.