

12

EUROPEAN PATENT APPLICATION

21 Application number: **90304584.7**

51 Int. Cl.⁵: **C11D 3/39**

22 Date of filing: **26.04.90**

30 Priority: **01.05.89 US 345495**

43 Date of publication of application:
07.11.90 Bulletin 90/45

64 Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

71 Applicant: **THE PROCTER & GAMBLE
COMPANY**
One Procter & Gamble Plaza
Cincinnati Ohio 45202(US)

72 Inventor: **Kellner, Charles Edward**
324 Ardon Lane
Cincinnati, Ohio 45215(US)
Inventor: **Alexander, Steven Robert**
1929 Sterling Avenue
Cincinnati, Ohio 45239(US)

74 Representative: **Gibson, Tony Nicholas et al**
Procter & Gamble (NTC) Limited Whitley
Road
Longbenton Newcastle upon Tyne NE12
9TS(GB)

54 **Agglomerated peroxyacid bleach granule and process for making same.**

57 The present invention relates to a dry, peroxyacid bleach granule composition and a novel process for making it comprising: spraying wet peroxyacid bleach onto dry particulate solids in a suitable mixer to form a wet bleach granule product and drying the wet bleach granule product in a fluid bed dryer under controlled conditions.

EP 0 396 341 A2

AGGLOMERATED PEROXYACID BLEACH GRANULE AND PROCESS FOR MAKING SAME

BACKGROUND OF THE INVENTION

5 The present invention is related to a peroxyacid bleach granule and a process for converting a water-wet mixture of materials comprising a peroxyacid bleach and exothermic control materials to a stabilized dry granule.

The prior art contains references which disclose compositions containing mixtures of peroxyacids with exothermic control materials. The use of an agglomeration process to make peroxyacid bleaching granules is suggested generically in U.S. Pat. No. 4,170,453, Kitko, issued Oct. 9, 1979. This reference, however, 10 does not address the favorable or unfavorable aspects, or the specifics, of an agglomeration process.

Preparing low density peroxyacid bleach prills in a spray tower is disclosed in commonly assigned U.S. Pat. No. 4,497,757, Beimesch/Hortel, issued Feb. 5, 1985, incorporated herein by reference. Other background references are U.S. Pat. Nos. 3,703,772, McHugh et al., issued Nov. 28, 1972; and commonly assigned 4,091,544, Hutchins, issued May 30, 1978, both of which are incorporated herein by reference. 15 Such prior art processes require several extra steps to obtain higher density peroxyacid bleach granules.

SUMMARY OF THE INVENTION

20

The present invention relates to a dry, peroxyacid bleach granule composition and a novel process for making it comprising: spraying wet peroxyacid bleach onto dry granular components of the dry bleach composition in a suitable mixer under controlled conditions.

25

DETAILED DESCRIPTION OF THE INVENTION

30 The present invention provides a dry agglomerated bleach granule which comprises a complex mixture of peroxyacid bleach and a stabilizing amount of a solid peroxyacid bleach exotherm control agent. The present invention also provides a process for making the agglomerated bleach granule.

The term "agglomeration" as used herein means forming a particulate by coating, sticking and mixing including forming a dough-like intermediate and combinations thereof.

35 The granule of the present invention has a complex crystalline containing structure as opposed to the spherical particles or flakes as disclosed in the prior art, e.g., U.S. Pat. Nos.: 4,091,544 and 4,497,757, both supra.

The process is an energy saver over the prior art, ensures better bleach granule uniformity, removes water from a wet peroxyacid bleach intermediate without exotherming and with less degradation.

The process of the present invention comprises the following steps:

40 A. Forming a pumpable, preferably sprayable, water-wet slurry of:

- (1) from about 26% to about 55% water;
- (2) from about 20% to about 45% of the peroxyacid bleach; and
- (3) at least about 1/3 of a stabilizing amount of a peroxyacid exotherm control agent;

45 B. Forming wet bleach granules from the wet slurry of Step A via pumping or spraying it onto a dry feed stream of particulate solids containing at least a balance of said exothermic control agent in a mechanical mixer; the wet bleach granules of this step having a free moisture content of from about 10% to about 20%; and

C. Drying the wet bleach granules of Step B at a controlled temperature to a final free moisture content of less than about 0.5%.

50 The granule has a free moisture content of less than about 0.5% for stability and flowability. The density of the granules of this invention are at least about 0.5 gm/cc. The preferred density is from about 0.6 to about 0.7 gm/cc. Prior art granules prepared by prilling have densities of 0.35 gm/cc to 0.45 gm/cc, well below 0.5 gm/cc. The preferred free moisture content of the granule of this invention is from about 0.1% to about 0.3%.

The preferred level of water in Step A is from about 30% to about 40%. The preferred moisture content

in Step B is from about 12% to about 18%. The preferred final free moisture content of the granules in Step C is from about 0.1% to about 0.3%.

In a continuous process, the average mixing time of Step B is brief, preferably from about 0.2 seconds to about 5 seconds.

5 The drying time of Step C in a fluid bed dryer is preferably from about 10 minutes to about 60 minutes. The preferred drying inlet air temperature of Step C is from about 35 °C to about 100 °C, keeping the temperature of the wet granules below about 60 °C.

The term "controlled temperature" in Step C means a temperature below a bleach destabilizing temperature.

10 The preferred temperature of the slurry of Step A is from about 30 °C to a maximum of about 40 °C. The more preferred process temperatures for Step A are from about 34 °C to about 38 °C, and for Step C is from about 38 °C to about 82 °C. The drying is preferably conducted in a fluid bed dryer.

The term "pumpable" as used herein means that the slurry can be introduced into a mechanical mixer containing dry particulate components as a stream or a spray.

15 The level of peroxyacid bleach in the dry bleach granule is preferably from about 10% to about 35%, more preferably from about 20% to about 30%, by weight of the granule.

The Peroxyacid Bleach

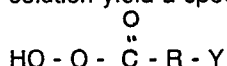
20

The peroxyacid can be any suitable peroxyacid. Examples of suitable organic peroxyacids are disclosed in U.S. Pat. No. 4,374,035, F. P. Bossu, issued Feb. 15, 1983; and U.S. Pat. No. 4,770,666, A. D. Clauss, issued Sept. 13, 1988, both incorporated herein by reference.

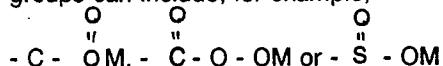
25 The peroxyacid bleach is used at a level which provides an amount of available oxygen (AvO) of from about 0.1% to about 10%, preferably from about 0.5% to about 5%, and most preferably from about 1% to about 4%. A preferred bleach granule comprises 1% to 50% of an exotherm control agent (e.g., boric acid); 3% to 25% of a peroxyacid compatible surfactant (e.g., C₁₃LAS); 0.01% to 10% of one or more chelant stabilizers (e.g., sodium pyrophosphates); and 10% to 50% of a water-soluble processing salt (e.g., Na₂SO₄).

30 A preferred peroxyacid bleach is used at a level which provides an amount of available oxygen (AvO) of from about 1.2% to about 5%, preferably from about 2% to about 4%, and most preferably from about 2.5% to about 3.5%.

A preferred peroxyacid material for use in the present process is a normally solid peroxyacid compound. A compound is "normally solid" if it is in dry or solid form at room temperature. Such peroxyacid compounds are the organic peroxyacids and water-soluble salts thereof which in aqueous solution yield a species containing a -O-O- moiety. These materials have the general formula



40 wherein R is an alkylene group containing from 1 to about 20 carbon atoms or a phenylene group and Y is hydrogen, halogen, alkyl, aryl or any group which provides an anionic moiety in aqueous solution. Such Y groups can include, for example,



45 wherein M is H or a water-soluble, salt-forming cation.

Examples of suitable aromatic peroxyacids and salts thereof include monoperoxyphthalic acid, diperoxyterephthalic acid, 4-chlorodiperoxyphthalic acid, the monosodium salt of diperoxyterephthalic acid, m-chloroperoxybenzoic acid, p-nitroperoxybenzoic acid, and diperoxyisophthalic acid. The most preferred for use in the instant process are diperoxydodecanedioic acid, nonylamideperoxysuccinic acid (NAPSA), and diperazelaic acid.

50

The Peroxyacid Exothermic Control Agent

55

Preparing the peroxyacid wet mix of Step A and reducing the water content of the peroxyacid wet mix in Step B and the drying of the wet bleach granules of Step C, all require care. It is desirable to remove virtually all of the water from the wet granule in the drying Step C so as to improve the available oxygen

stability of the peroxyacid. The mixing temperatures and the mix compositions of Steps A and B and the air temperature of Step C must be controlled and must not be allowed to reach a point where exotherm or substantial degradation occurs. Thus, it is necessary that steps be taken to ensure that the mixing and drying temperatures do not allow the peroxyacid to exothermally decompose. To help control the exotherm problem, an agent is put into the mixture which releases water at about the exotherm point of the bleach and thereby controlling it. Agents of this type will be discussed subsequently.

The time of exposure to the drying temperature is variable depending on the temperature chosen, the materials, the thickness of the individual particles and the drying technique, but will generally be from about several minutes to several hours at a temperature of from about 25 °C to about 100 °C, preferably from about 60 °C to about 70 °C, as long as the temperature of the bleach granule itself does not exceed about 60 °C. Preferably the temperature of the drying bleach granules is kept below about 55 °C.

The actual unit used for this final drying can be any which does not involve the particles pressing together. The term "fluid bed dryer," as used herein, includes moving belt dryers (forced air circulation), and any kind of forced air circulation dryers such as the Wyssmont Turbodryer supplied by Wyssmont Company of Ft. Lee, New Jersey, which can be used to dry the wet bleach granules of the present invention.

It is well documented in the peroxyacid literature that peroxyacids are susceptible to a number of different stability problems, as well as being likely to cause some problems. Looking at the latter first, peroxyacids decompose exothermally and when the material is in dry granular form the heat generated must be controlled to make the product safe. The best exotherm control agents are those which are capable of liberating moisture at a temperature slightly below the decomposition temperature of the peroxyacid employed. U.S. Pat. No. 3,770,816, Nielsen, issued Nov. 6, 1973, incorporated herein by reference, discloses a wide variety of hydrated materials which can serve as suitable exotherm control agents. Included among such materials are magnesium sulfate $\cdot 7H_2O$, magnesium formate dihydrate, calcium sulfate ($CaSO_4 \cdot 2H_2O$), calcium lactate hydrate, calcium sodium sulfate ($CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$), and hydrated forms of such things as sodium aluminum sulfate, potassium aluminum sulfate, ammonium aluminum sulfate, and aluminum sulfate. Preferred hydrates are the alkali metal aluminum sulfates, particularly preferred is potassium aluminum sulfate. Other exotherm control agents include "hydrates" of other suitable salts. The preferred exotherm control agents are those materials which lose water as the result of chemical decomposition such as boric acid, malic acid and maleic acid.

The exotherm control agent is preferably used in a stabilizing amount of from about 70% to about 400%, more preferably of from about 75% to about 200%, and most preferably from about 100% to about 150%, based on the type and weight of the peroxyacid compound and the type of control agent used.

Larger amounts of some of these materials are required to control exotherm than the preferred exotherm control agents.

Other Materials

The other problems faced when peroxyacid compounds are used fall into the area of maintaining good bleach effectiveness. It has been recognized that metal ions are capable of serving as catalyzing agents in the degradation of the peroxyacid compounds. To overcome this problem, chelating agents can be used in an amount ranging from about 0.005% to about 1% based on the weight of the composition to tie up heavy metal ions. U.S. Pat. No. 3,442,937, Sennewald et al., issued May 6, 1969, discloses a chelating system comprising quinoline or a salt thereof, an alkali metal polyphosphate and, optionally, a synergistic amount of urea. U.S. Pat. No. 2,838,459, Sprout, Jr., issued June 10, 1958, discloses a variety of polyphosphates as stabilizing agents for peroxide baths. These materials are useful herein as stabilizing aids. U.S. Pat. No. 3,192,255, Cann, issued June 29, 1965, discloses the use of quinaldic acid to stabilize percarboxylic acids. This material, as well as picolinic acid and 8-hydroxyquinoline would also be useful in the compositions of the present invention. A preferred chelating system for the present invention is a mixture of dipicolinic acid, and an acid polyphosphate, preferably acid sodium pyrophosphate. The acid polyphosphate can be a mixture of phosphoric acid and sodium pyrophosphate wherein the ratio of the former to the latter is from about 0.5:1 to about 2:1 and the ratio of the mixture to dipicolinic acid is from about 0.2:1 to about 5:1.

Additional agents which may be used to aid in giving good bleaching performance include such things as pH adjustment agents, bleach activators and minors such as coloring agents, dyes and perfumes. Typical pH adjustment agents are used to alter or maintain aqueous solutions of the instant compositions within the 5 to 10 pH range in which peroxyacid bleaching agents are generally most useful. Depending

upon the nature of other optional composition ingredients, pH adjustment agents can be either of the acid or base type. Examples of acidic pH adjustment agents designed to compensate for the presence of other highly alkaline materials include normally solid organic and inorganic acids, acid mixtures and acid salts. Examples of such acidic pH adjustment agents include citric acid, glycolic acid, tartaric acid, gluconic acid, glutamic acid, sulfamic acid, sodium bisulfate, potassium bisulfate, ammonium bisulfate, and mixtures of citric acid and lauric acid. Citric acid is preferred by virtue of its low toxicity and hardness sequestering capability.

Optional alkaline pH adjustment agents include the conventional alkaline buffering agents. Examples of such buffering agents include such salts as carbonates, bicarbonates, silicates, pyrophosphates and mixtures thereof. Sodium bicarbonate and tetrasodium pyrophosphate are highly preferred.

Optional ingredients, if utilized in combination with the active peroxyacid/exothermic material system of the instant invention to form a complete bleaching product, comprise from about 50% to about 95% by weight of the total composition. Conversely, the amount of bleaching system is from about 5% to about 50% of the composition. Optional ingredients such as the metal chelating agent is preferably mixed with the peroxyacid and the exothermic control agent in Step A or Step B, thereby becoming a part of the dry units formed in the process. Others such as the pH adjustment agents are added as separate particles in Step B or admixed with the granules of this invention. Such other ingredients may be coated with, for example, an inert fatty material if the ingredients are likely to cause degradation of the peroxyacid.

The bleaching compositions as described above can be added to and made a part of conventional fabric laundering detergent compositions. Accordingly, optional materials for the instant bleaching compositions can include such standard detergent adjuvants as surfactants and builders. Optional surfactants are selected from the group consisting of organic anionic, nonionic, ampholytic and zwitterionic surfactants and mixtures thereof. Optional builder materials include any of the conventional organic builder salts including carbonates.

Water-soluble salts of the higher fatty acids, i.e., "soaps" are useful as the anionic surfactant herein.

Another class of anionic surfactants includes water-soluble salts, particularly the alkali metal, ammonium and alkanolammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 8 to about 22 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.)

Preferred water-soluble anionic organic surfactants herein include linear alkyl benzene sulfonates containing from about 11 to 14 carbon atoms in the alkyl group; the tallow range alkyl sulfates; the coconut range alkyl glyceryl sulfonates; and alkyl ether sulfates wherein the alkyl moiety contains from about 14 to 18 carbon atoms and wherein the average degree of ethoxylation varies between 1 to 6.

Specific preferred anionic surfactants for use herein include: sodium linear C₁₀-C₁₂ alkyl benzene sulfonate; triethanolamine C₁₀-C₁₂ alkyl benzene sulfonate; sodium tallow alkyl sulfate; sodium coconut alkyl glyceryl ether sulfonate; and the sodium salt of a sulfated condensation product of tallow alcohol with from about 3 to about 10 moles of ethylene oxide.

It is to be recognized that any of the foregoing anionic surfactants can be used separately herein or as mixtures.

The instant granular compositions can also comprise those detergency builders commonly taught for use in laundry compositions. Useful builders herein include any of the conventional inorganic and organic water-soluble builder salts, as well as various water-insoluble and so-called "seeded" builders.

Inorganic detergency builders useful herein include, for example, water-soluble salts of phosphates, pyrophosphates, orthophosphates, polyphosphates, phosphonates, carbonates, bicarbonates, borates and silicates. Examples of these and other phosphorus builder compounds are disclosed in U.S. Pat. Nos. 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148, incorporated herein by reference. Sodium tripolyphosphate is an especially preferred, water-soluble inorganic builder herein.

Non-phosphorous containing sequestrants can also be selected for use herein as detergency builders. Specific examples of non-phosphorous, inorganic builder ingredients include water-soluble inorganic carbonate, bicarbonate, borate and silicate salts. The alkali metal, e.g., sodium and potassium, carbonates, bicarbonates, borates (Borax) and silicates are particularly useful herein.

Water-soluble organic builders are also useful herein.

Highly preferred non-phosphorous builder materials (both organic and inorganic) herein include sodium carbonate, sodium bicarbonate, sodium silicate, sodium citrate, sodium oxydisuccinate, sodium mellitate, sodium nitrilotriacetate, and sodium ethylenediaminetetraacetate, and mixtures thereof.

Another type of detergency builder material useful in the present compositions and processes comprises a water-soluble material capable of forming a water-insoluble reaction product with water hardness cations in combination with a crystallization seed which is capable of providing growth sites for

said reaction product.

Another type of builder useful herein includes various substantially water-insoluble materials which are capable of reducing the hardness content of laundering liquors, e.g., by ion-exchange processes.

The complex aluminosilicates, i.e., zeolite-type materials, are useful presoaking/washing adjuvants herein in that these materials soften water, i.e., remove Ca⁺⁺ hardness. Both the naturally occurring and synthetic "zeolites", especially zeolite A and hydrated zeolite A materials, are useful for this builder/softener purpose. A description of zeolite materials and a method of preparation appears in Milton, U.S. Pat. No. 2,882,243, issued April 14, 1959, incorporated herein by reference.

The bleach granules of this invention can be used with soil release agents. Any suitable soil release agent can be used including those disclosed in U.S. Pat. No. 4,770,666, supra, incorporated herein by reference.

Any dry materials used in Step B as part of the "dry feed," including excess exothermic control agent materials, builders, etc., are referred to herein as "fillers" unless otherwise specified.

The peroxyacid bleach granules of the present invention can be admixed with other compatible granular bleach and/or detergent composition materials. The particle sizes of the bleach containing granules or optional granular material are not critical. However, commercially acceptable flow properties having certain granule size limitations are highly preferred. Thus, the granules of the instant compositions preferably range in size from about 100 microns to 3,000 microns, more preferably from about 100 microns to 1,300 microns, and most preferably from about 250 microns to about 1,000 microns.

Bleaching compositions of the present invention are utilized by dissolving them in water in an amount sufficient to provide from about 1.0 ppm to 100 ppm available oxygen in solution. Generally, this amounts to from about 0.01% to 0.2% by weight of composition in solution. Fabrics to be bleached are then contacted with such aqueous bleaching solutions.

The dry granular peroxyacid bleach composition of the instant invention and the process for making same are illustrated by the following examples, but not limited thereto. Percentages and parts are by weight.

EXAMPLE 1

A dry granular peroxyacid bleach composition is prepared using the following:

Wet Peroxyacid Bleach Slurry	Parts
Diperoxydodecanedioic acid (DPDA) 22.9%; water 46%; boric acid 25.2%; surfactant paste + minors 5.9%	0.93
Dry Feed Solids	
Anhydrous sodium sulfate	0.35
Recycled dry DPDA fines	2.95
	Total
	4.23

The equipment used is a Bepex 8" TC8 Turbulizer mixer and an Aeromatic batch type, fluid bed dryer Model STREA-1 made by Aeromatic AG, Muttentz.

Step A -

The wet peroxyacid bleach slurry is prepared by adding the boric acid and the surfactant paste + minors to the aqueous solution of diperoxydodecanedioic acid.

Step B -

The recycled dry feed DPDA fines and sodium sulfate are blended in the proportions shown and

EP 0 396 341 A2

introduced into the Turbulizer mixer. The dry feed solids temperature is about 18 °C. The size of the DPDA fines is under 250 microns and the size of the sulfate is between about 180 microns and 285 microns. The wet slurry (30 °C) is metered from a tank and sprayed using an air atomized nozzle onto the dry feed solid components in the Turbulizer mixer. The exiting material, in the form of wet granules, is collected and transferred to the Aeromatic dryer. The temperature of the wet granules out of the Turbulizer mixer is about 30 °C.

Step C -

10

The wet granules are therein dried and the dried bleach granules are cooled down in the dryer.

15

The final bleach granules are then analyzed for density, particle size and chemical composition. The speed, blade angle, and clearance in the Turbulizer mixer are adjusted during the experiments to optimize granule size. The wet granules are dried with about 65 °C air for about 30 minutes and then cooled to about 18 °C in the dryer.

20

A description of the dried peroxyacid bleach granules of Example 1 follows: moisture about 0.2%; density about 0.64 gm/cc; percent DPDA about 25%; percent boric acid about 27%; and sodium sulfate about 46%. About 90% of the granules have a particle size in the range of from about 250 microns to about 1,750 microns; and an average particle size of about 500, ±75 microns.

25

The surfactant paste and minors composition for Example 1 is as follows:

Ingredient	Parts
LAS (Linear alkylbenzene sulfonate 28%; sulfate 22%; water 50%)	34.26
Dipicolinic acid (DPA)	0.09
Phosphoric acid (H ₃ PO ₄)	0.2
Trisodium phosphate (TSPP)	0.11
Total	34.46

30

35

The three minors (DPA, H₃PO₄ and TSPP) are premixed with the LAS paste in the proportions shown. The anhydrous sodium sulfate acts as a filler and also serves as a secondary exothermic control agent/heat sink.

EXAMPLE 2

40

The following ingredients are used:

45

Wet Peroxyacid Bleach Slurry	Parts
Diperoxydodecanedioic acid 25.55%; water 46.5%; boric acid 19.68%; surfactant paste + minors 8.27%	3.01
Dry Feed Solids	
Anhydrous sodium sulfate	1.28
Boric acid powder	0.25
Recycled dry DPDA fines (250 microns)	5.46
Total	10.00

50

55

The equipment used is a Bepex 8" TC8 Turbulizer Mixer and a Bepex 1 sq. meter continuous fluid bed

EP 0 396 341 A2

dryer. The process and equipment are similar to those of Example 1, except that a continuous fluid bed dryer is used.

5 Step A -

The wet peroxyacid bleach slurry (30° C) is prepared by adding the boric acid and the surfactant paste + minors to the aqueous solution of diperoxidodecanedioic acid.

10

Step B -

The wet slurry (30° C) is metered from a tank and sprayed using an air atomized nozzle onto the dry solid components (ambient temperature) in the Turbulizer mixer.

15

Step C -

20 Wet granules from the Turbulizer mixer are fed continuously to the Bepex fluid bed dryer. The drying air to the first two zones of the Bepex fluid bed is about 65° C. The temperature of the drying granules is controlled and kept to less than about 30° C during the drying. A third zone of the Bepex is supplied with ambient air to cool the dried bleach. Final dried bleach granules have a moisture of about 0.3%; a density of about 0.61 gm/cc; DPDA 24%; boric acid about 28%; and sodium sulfate about 42.5%.

25 The sulfate and boric acid solids of Example 2 are fed separately using volumetric feeders. The recycled dry bleach fines, which are produced in the fluid bed dryer (Step C), are separated from the desired particle size granules and recycled to the mixer of Step B as dry feed solids. The bleach granules in the dryer which are below about 250 microns in size are continuously removed from the dryer. The dry bleach granular particles over about 1,750 microns in size are screened out and ground up to less than about 250 microns and then recycled as dry solid fines in Step B in the dry feed.

30 In the continuous fluid bed drying step of Example 2 or Example 3, the bed is seeded with either recycled peroxyacid bleach fines or ground bleach granules from a previous run. The seeding fines, granules and other dry bleach solid components have particle sizes preferably below 250 microns. The process is preferably started up using formulated proportions of particulate boric acid and sulfate as dry feed and mixing the dry feed with the peroxyacid slurry. The first bleach granules are recycled from the
35 dryer discharge until the target material balance is reached. Drying air temperature is from about 60° C to about 70° C.

40 EXAMPLE 3

The ingredients used in this example are as follows:

45

50

55

Wet Peroxyacid Bleach Slurry	Parts
Diperoxidodecanedioic acid 28.6%; water 52.2%; boric acid 11%; surfactant paste + minors 8.2%	2.99
Dry Feed Solids	
Anhydrous sodium sulfate	1.52
Boric acid powder	0.61
Recycled dry DPDA fines	6.88
	Total
	12.00

The equipment used is a Bepex 8" TC8 Turbulizer Mixer and a Bepex 3 sq. meter continuous fluid bed

dryer.

5 Step A -

The wet peroxyacid bleach slurry is prepared by adding the boric acid and the surfactant paste + minors to the aqueous solution of diperoxydodecanedioic acid. The temperature of the wet slurry is about 30 ° C.

10

Step B -

The wet slurry is metered from a tank and sprayed using an air atomized nozzle onto the dry feed solids in the Turbulizer mixer.

15

The anhydrous sodium sulfate and boric acid solids are fed separately using volumetric feeders. Recycled dry DPDA fines which are produced in the fluid bed dryer and separated from the desired particle size granules are added to the Turbulizer mixer as dry feed solids.

20 Step C -

Wet granules from the Turbulizer mixer are fed continuously to the fluid bed dryer. The drying air temperatures are as follows:

25

- Zone 1 - 70 ° C
- Zone 2 - 55 ° C
- Zone 3 - 50 ° C
- Zone 4 - 10 ° C

30

Dryer residence time for the drying bleach granules is about 30 minutes. The temperature of the dry bleach granules leaving the dryer is about 22 ° C. Their free moisture content is about 0.3%. Their density is about 0.63 gm/cc. DPDA content is about 26%. Their boric acid content is about 28.4%; and their sodium sulfate content is about 42.5%. Their average particle size is about 500.

The product yield for Example 3 is about 34% on a dry basis.

The target peroxyacid concentration in Example 3A is about 10% dry basis (using sulfate as a dry diluent). The yield is about 81.9% on a dry basis (See Table 1, Example 3A).

35

The target peroxyacid concentration of Example 3B is 24% on a dry basis. The peroxyacid slurry moisture content is 32%. The product yield is 78.95% on a dry basis (See Table 1, Example 3B).

40

45

50

55

TABLE 1

		Example 3	Example 3A	Example 3B
	Ingredient	Parts	Parts	Parts
	Peroxyacid slurry	2.99	2.99	4.87
	(Slurry % moisture)	(52.2)	(52.2)	(32)
	Anhydrous sodium sulfate	1.52	6.51	3.52
	Boric acid	0.61	0.61	1.41
	Recycled fines/overs*	6.88	1.89	2.20
	Totals	12.00	12.00	12.00
	Dry yield parts	10.44	10.44	10.44
	Yield (dry basis)	34.1%	81.9%	78.95%
	% Peroxyacid	24	10	24

* The drying process when in equilibrium typically produces 15% to 25% recycle as fines/oversize material.

An appropriate recycled DPDA fines composition for Examples 1, 2 and 3 is:

Diperoxydodecanedioic acid (DPDA)	24%
Sodium sulfate	43%
Boric acid	26%
LAS paste	5.2%
Minors (includes Na ₂ SO ₄ in paste)	1.3%
Free moisture	0.5%

Surfactant paste and minors compositions for Examples 2 and 3 are as follows:

Ingredient	Parts
LAS (Linear alkylbenzene sulfonate 50%; sulfate 1%; water 49%)	19.58
Dipicolinic acid (DPA)	0.09
Phosphoric acid (H ₃ PO ₄)	0.2
Trisodium phosphate (TSPP)	0.11
Total	19.98

The three minors (DPA, H₃PO₄ and TSPP) are premixed with the LAS paste in the proportions shown. The DPA, TSPP and H₃PO₄ are added to the formulation as chelating agents to tie up heavy metal ions. The LAS is used as a processing aid. The temperatures of the wet granules in Step C for all examples are estimated to be below about 30 °C.

When a continuous process of the present invention reaches an equilibrium, the yield out of the dryer is from about 75% to about 85%. About 5% to about 10% are overs which are ground to DPDA fines and recycled. About 10% to about 15% of the wet granules are pulled out of the dryer as fines via an exhaust bag house collection system.

5

Claims

1. A dry bleach granule product comprising a complex agglomerated mixture of peroxyacid bleach and a stabilizing amount of a peroxyacid bleach exothermic control agent; wherein said dry bleach granule is prepared by:

(I) continuously mechanically mixing:
 (A) a stream of pumpable water-wet slurry of peroxyacid bleach containing from 26% to 55% water and at least one-third of said stabilizing amount of said exothermic control agent; and
 (B) a dry feed of particulate solids selected from recycled dry bleach fines and powdered exothermic control agent salts, fillers, and mixtures thereof,
 wherein said stream of water-wet slurry is pumped onto said dry feed to form moisture-wet bleach granules having a free moisture content of from 10% to 20%; and

(II) drying said wet bleach granules at a controlled temperature to a free moisture content of less than 0.5% in a fluid bed dryer to provide said dry bleach granule product.

2. A dry bleach granule product according to Claim 1 wherein said exothermic control agent is selected from boric acid, malic acid, maleic acid, sodium sulfate, magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), magnesium formate dihydrate, calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcium lactate hydrate, calcium sodium sulfate ($\text{CaSO}_4 \cdot 2\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$), and hydrated forms of sodium aluminum sulfate, potassium aluminum sulfate, ammonium aluminum sulfate, aluminum sulfate, and mixtures thereof.

3. A dry bleach granule product according to either one of claims 1 and 2, wherein said exothermic control agent is present at a level of from 70% to 400%, preferably from 75% to 200% by weight of the peroxyacid bleach.

4. A dry bleach granule according to any one of claims 1-3 wherein said granule has a density of at least 0.59%/cal, preferably from 0.6 to 0.7 g/ml, and from 100% to 150% of said exothermic control agent by weight of the bleach.

5. A dry bleach peroxyacid bleach granule product according to any one of claims 1-4 wherein said exothermic control agent is a mixture of sodium sulfate and boric acid having a weight ratio of from 1:1 to 6:1 and wherein said boric acid is present at a level of at least 70% by weight of said peroxyacid bleach.

6. A process of making a dry peroxyacid bleach granule product according to Claim 1 comprising the following steps:

A. forming said pumpable water-wet peroxyacid bleach slurry containing:

- (1) 20% to 45% by weight of said peroxyacid bleach, and
- (2) 26% to 55% by weight of water, together with
- (3) said 1/3 of said stabilizing amount of said exothermic control agent;

B. forming wet granules having a moisture content of from 10% to 20% by spraying said pumpable, water-wet slurry of Step A onto said dry feed of dry bleach solid components; and

C. drying said wet granules with forced air having a temperature of from 35° C to 100° C.

7. A process according to claim 6 wherein the amount of water in the water-wet slurry is from 30% to 40%; the moisture content of said wet granule is from 12% to 18%, and the final moisture content of the dried granule is from 0.1% to 0.3%.

8. A process according to either one of claims 6 and 7 wherein the temperature of the slurry is from 30° C to a maximum of 40° C, preferably from 34° C to 38° C, the fluid bed temperature is from 38° C to 81° C preferably from 60° C to 70° C while the drying temperature of the wet granules of Step C is controlled at not more than 60° C.

9. A process according to any one of claims 6-8 wherein the level of peroxyacid bleach of said dry granule is from 10% to 35%, preferably from 20% to 30% by weight.

10. A process according to any one of claims 6-9 wherein said Step B has a mixing residence time to form the wet granule of from 0.2 seconds to 5 seconds, and said drying time of Step C is from 10 minutes to 60 minutes.