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

(11) Publication number: **0 340 847**
A2

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **89201076.0**

(22) Date of filing: **26.04.89**

(51) Int. Cl.⁴: **C11D 11/00 , C11D 3/39 , C11D 3/36**

(30) Priority: **05.05.88 GB 8810630**

(43) Date of publication of application:
08.11.89 Bulletin 89/45

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

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(54) Process for preparing bodies containing a peroxyacid compound and compositions comprising said bodies.

(57) An improved process for preparing dry particulate bodies containing a solid peroxyacid compound is disclosed, comprising the steps of

(A) forming a water-wet mixture of a solid peroxyacid compound and a hydratable material having a temperature of hydration of up to 40° C, at a temperature which is higher than the temperature of hydration of the hydratable material;

(B) forming the mixture of (A) into particles of the desired shape and size before, during or after cooling the mass to below the temperature of hydration of the hydratable material; and

(C) drying the particles obtained from step (B), the improvement being that in step (A) a film-forming material is incorporated in, and intimately mixed with, the water-wet mixture, forming a mix having a pH of below 7.

The peroxyacid-containing bodies obtainable therefrom are extremely suitable for use as a bleach additive and for the incorporation in bleaching and/or detergent powder compositions.

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PROCESS FOR PREPARING BODIES CONTAINING A PEROXYACID COMPOUND AND COMPOSITIONS COMPRISING SAID BODIES

This invention relates to a process for preparing dry particulate bodies containing a solid organic peroxyacid compound, and to compositions comprising said bodies.

It is known that organic peroxyacids as a class are very effective bleaches, and the use of organic peroxyacid compounds as the bleach system in detergent compositions has been proposed in the art. The solid peroxyacids are of particular importance as they can be handled more easily than the liquid forms for use as a bleach component in bleaching and detergent compositions. Even so, because of their high reactivity, the greatest caution should be exercised in handling and working with peroxyacids, and, especially in the dry solid or highly concentrated state, organic peroxyacids can be very hazardous.

Furthermore, although the efficiency of certain organic peroxyacid compound bleach systems has long been recognized at low to medium wash temperatures, the major problem, which has prevented their exploitation so far, has been their inherent instability in conventional alkaline fabric washing compositions. Unprotected peroxyacid compounds will also attack sensitive ingredients, such as fluorescers, enzymes and perfumes, and can cause severe pin-point spotting during use upon fabrics.

For use as a bleach additive to, or as a bleach component in, bleaching and/or detergent compositions, organic peroxyacids are therefore usually provided in the form of less concentrated, granular compositions or agglomerates, with or without a protective coating.

Both the dry-mixture and wet-mixure peroxyacid granulation processes have been proposed in the art, such as described in EP-A-0200163; EP-A-0256443; US Patent 4,091,544; US Patent 4,497,757 and EP-A-0254331.

As bulk supplies of solid peroxyacids, such as diperoxydodecanedioic acid (DPDA), contain water, i.e. are in the form of an aqueous slurry, the dry-mixture peroxyacid granulation process cannot be used directly.

Wet-mixture peroxyacid granulation has the advantage of being able to handle high moisture content systems. It has the further advantage of being easy to scale up without involvement of any particularly hazardous operations.

The present invention provides an improvement of the wet-mixture peroxyacid granulation process and produces peroxyacid-containing bodies of excellent quality with high grades of homogeneity, mechanical and chemical stability and especially attrition resistance combined with good dispersibility.

The process of the invention comprises the steps of

(A) forming a water-wet mixture of a solid peroxyacid compound and a hydratable material having a temperature of hydration of up to 40 °C, at a temperature which is higher than the temperature of hydration of the hydratable material;

(B) forming the mixture of (A) into particles of the desired shape and size before, during or after cooling the mass to below the temperature of hydration of the hydratable material; and

(C) drying the particles obtained from step (B), and is characterized in that in step (A) a film-forming material is incorporated in, and intimately mixed with, the water-wet mixture, forming a mix having a pH of below 7.

Thus, an important feature of the process is the incorporation and intimate mixing of a film-forming material with the water-wet mixture of step (A). This mix has a pH of below 7.

It is essential that the water-wet mixture of (A) including the film-forming material should have an acid pH of below 7, preferably from 3 to 6.5. This pH can be adjusted by using an acidic, film-forming material and/or by adding a solid, pH-regulating, acid substance, e.g. citric acid, succinic acid, adipic acid, glutaric acid etc.

The film-forming material should preferably be non-oxidizable. Such suitable film-forming materials are, for example, the non-oxidizable polymers, which can be in the acid form or in the form of their alkali metal salts.

Acidic polymers usable in this invention can be any non-cellulosic homo- or copolymeric mono- and polycarboxylic acids having an average molecular weight of from 500 to about 1,000,000, preferably from 2,000 to 250,000, more preferably from 10,000 to 50,000.

Suitable polymers include those derived from acrylic acid, methacrylic acid, maleic acid, citraconic acid, aconitic acid, fumaric acid, mesaconic acid, phenyl maleic acid, benzyl maleic acid, itaconic acid, methylene malonic acid, alpha-C_1-C_4 alkyl acrylic acid, alpha-hydroxy acrylic acid and acetalcarboxylic acid monomers, or from the anhydrides of the above monomers where these exist. The polymers can be homopolymers of the above mono- or polycarboxylic monomers; or copolymers of two or more of the above mono- or polycarboxyl monomers; or copolymers of one or more of the above carboxyl monomers with an unsaturated polymerizable monomer other than the specified mono- and polycarboxyl monomers; or modified homo- or copolymers of the above classes having, for example, a non-oxidizable phosphinic acid or sulphinic acid group.

Preferred acidic, polymeric materials are the polyacrylic acids, phosphinate-modified polyacrylic acids, such as described in GB Patents 1,485,235 and 1,595,688 and EP-A-0182411; copolymers of maleic acid (anhydride) and acrylic or methacrylic acid; and acidic copolymers containing hydrophobic groups, such as copolymers based on polymethacrylic acid and polyacrylic acid esters in which the ratio of free carboxyl groups to ester groups is at least 1:1.

Copolymers of the latter group can be advantageously used for preparing peroxyacid-containing bodies for use in aqueous liquid bleaching compositions, where they could further reduce the solubility of the organic peroxyacid, and hence improve its storage stability.

Other non-acidic, film-forming polymers may also be used, so long as they are sufficiently resistant to oxidation; their selection can be routinely made without difficulty by the skilled artisan.

Although changes in molecular weight did not appear to markedly influence the peroxyacid stability, they are of some influence on the physical properties of the granule, e.g. particle strength, resistance to attrition and film-forming properties. Preferred molecular weights are from 2,000 to 250,000, more preferably from 10,000 to 50,000.

Another suitable class of film-forming materials is that of the so-called glassy or amorphous phosphates having the general formula :

$(M_2O)_x(P_2O_5)_y$

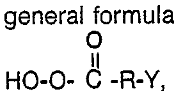
wherein M is hydrogen, alkali metal, ammonium or a substituted ammonium group; Y has a value in the range of from 2 to 50; and the ratio x:y is from 0.7:1 to 1.7:1.

A representative example of a glassy phosphate is sodium hexametaphosphate. - $(Na_2O)_3(P_2O_5)_3$.

The amount of film-forming material which can be added for the purpose of the invention is such that it will give a material level in the final granule of about 0.5-10% by weight. Optimally, this should be within the range of about 2.5-6% by weight.

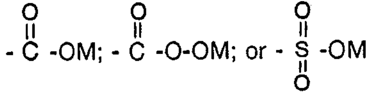
The peroxyacid compound usable in this invention should be solid at room temperature and preferably has a melting point of at least 50 °C.

Such peroxyacid compounds are the organic peroxyacids and water-soluble salts thereof having the general formula:



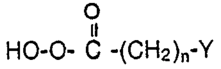
$$\mathrm{HO{-}O{-}\overset{\overset{O}{\|}}{C}{-}R{-}Y},$$

wherein R is an alkylene or substituted alkylene group containing 1 to 20 carbon atoms or an arylene group containing from 6 to 8 carbon atoms, 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 :



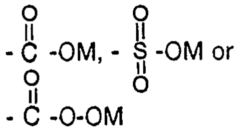
$$\mathrm{-\overset{\overset{O}{\|}}{C}{-}OM;\ -\overset{\overset{O}{\|}}{C}{-}O{-}OM;\ or\ -\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}OM}$$

wherein M is H or a water-soluble, salt-forming cation. They can contain either one, two or more peroxy groups and can be either aliphatic or aromatic. When the organic peroxyacid is aliphatic, the unsubstituted acid can have the general formula :



$$\mathrm{HO{-}O{-}\overset{\overset{O}{\|}}{C}{-}(CH_2)_n{-}Y}$$

wherein Y can be H, $-CH_3$, $-CH_2Cl$,

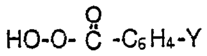


$$\mathrm{-\overset{\overset{O}{\|}}{C}{-}OM,\ -\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}OM\ or\ -\overset{\overset{O}{\|}}{C}{-}O{-}OM}$$

and n can be an integer from 6 to 20.

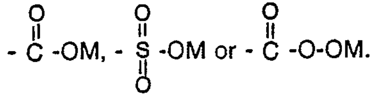
Peroxydodecanoic acids, peroxytetradecanoic acids and peroxyhexadecanoic acids are preferred compounds of this type, particularly 1,12-diperoxydodecanedioic acid (DPDA), 1,14-diperoxytetradecanedioic acid and 1,16-diperoxy- hexadecanedioic acids. Examples of other suitable compounds of this type are diperoxyazelaic acid, diperoxyadipic acid and diperoxysebacic acid.

When the organic peroxyacid is aromatic, the unsubstituted acid can have the general formula :



$HO\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_6H_4\text{-}Y$

wherein Y is, for example, hydrogen, halogen, alkyl,



$-\overset{O}{\overset{\|}{C}}\text{-OM}, -\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}\text{-OM or} -\overset{O}{\overset{\|}{C}}\text{-O-OM}.$

The percarboxy and Y groupings can be in any relative position around the aromatic ring. The ring and/or Y group (if alkyl) can contain any non-interfering substituents, such as halogen or sulphonate groups. Examples of suitable aromatic peroxyacids and salts thereof include monoperoxyphthalic acid, diperoxyterephthalic acid, 4-chlorodiperoxyphthalic acid, diperoxyisophthalic acid, peroxy benzoic acids and ring-substituted peroxy benzoic acids, such as peroxy-alphanaphthoic acid. A preferred aromatic peroxyacid is diperoxyisophthalic acid.

The hydratable material usable in the present invention will have a hydration temperature of up to 40° C, so as to allow working at relatively low temperatures, thereby minimizing peracid decomposition. It should also preferably be non-alkaline.

Hydration temperature is the transition temperature for dehydration of the hydrate to its anhydrous state. A preferred hydratable material is sodium sulphate, which is neutral and has a hydration temperature to the decahydrate of about 32.4° C. (see International Critical Tables, Volume IV, published by McGraw Hill).

When sodium sulphate is used as the hydratable material, the convenient working temperatures are about 40° C in step (A) and from 10 to about 20° C in step (B).

Drying of the particles in step (C) should preferably be carried out under dynamic conditions, such as in a fluidized bed drier. Drying in a static bed, such as e.g. using a tray drier, is not recommended since the solid particles will tend to revert to a slurry or pasty mass, due to dehydration of the hydrates at the high drying temperature. In order to maximize peroxyacid stability, the granules are preferably dried to a state in which all hydratable material has been converted to its anhydrous form.

The amount of water in the water-wet mixture of step (A) is not critical and may amount to about 10-35% by weight.

The amount of hydratable material in the water-wet mixture, however, is dependent upon the water content and should be such that it is sufficient to take up a substantial amount of the free water as water of hydration.

The process of the invention can be conveniently applied directly to 1,12-diperoxydodecanedioic acid (DPDA) suspensions as obtained from the usual process of manufacturing DPDA from the reaction of 1,12-dodecanedioic acid with hydrogen peroxide under the influence of sulphuric acid in an aqueous medium. Such usual preparation methods are described, among others, in US Patent 4,119,660, US Patent 4,314,949 and DE-A-2,930,546.

Such suspensions as supplied from manufacturers usually comprise from 25-35% DPDA, 50-70% water, and 5-15% sodium sulphate.

A convenient way of using these suspensions as the starting material is by heating the suspension to about 40° C and adding sufficient anhydrous sodium sulphate for binding the water upon hydration and thereafter adding the film-forming material, whilst ensuring that the slurry is well agitated. This is then followed by the cooling and shaping step (B) and subsequently the drying step (C), which can be further followed by screening to the desired particle size range, if necessary. The resultant granules exhibit good stability in detergent bases.

Any optional ingredient, including sequestering agents, solid organic acids and surfactants, can be incorporated in the first mixing step (A).

A desirable particle size range for peroxyacid-containing bodies usable in detergent and bleaching compositions is between 150 µm and 2,000 µm, particularly between 350 µm and 1700 µm.

With the process of the invention, particulate bodies can be obtained containing from about 15% to about 30% by weight of peroxyacid compound. Preferably, the process is suitably used for preparing particulate bodies containing from 17% to 25% by weight of peroxyacid, the balance being formed by one or more hydratable material(s), film-forming material and minor amounts of any optional ingredients as desired.

The peroxyacid-containing bodies (particles or granules) obtained by the process of the invention are extremely suitable for use as a bleach additive and for the incorporation in bleaching and/or detergent powder compositions.

Accordingly, detergent compositions comprising the peroxyacid-containing bodies as described herein are within the purview of the present invention. Such detergent compositions will usually also contain surface-active materials, detergency builders and other known ingredients of such formulations.

The surface-active material may be naturally derived, such as soap, or a synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof. Many suitable actives are commercially available and are fully described in literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. The total level of the surface-active material may range up to 50% by weight, preferably being from about 1% to 40% by weight of the composition, most preferably 4% to 25%.

The detergent compositions of the invention will normally also contain a detergency builder. Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate; nitrilotriacetic acid and its water-soluble salts; the alkali metal salts of carboxymethyloxy succinic acid, ethylene diamine tetraacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, citric acid; and polyacetal carboxylates as disclosed in U.S. patents 4,144,226 and 4,146,495.

Examples of precipitating builder materials include sodium orthophosphate, sodium carbonate and long-chain fatty acid soaps.

Examples of calcium ion-exchanging builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives.

In particular, the compositions of the invention may contain any one of the organic or inorganic builder materials, such as sodium or potassium tripolyphosphate, sodium or potassium pyrophosphate, sodium or potassium orthophosphate, sodium carbonate, the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethyl malonate, carboxymethyloxy succinate and the water-insoluble crystalline or amorphous aluminosilicate builder materials, or mixtures thereof.

These builder materials may be present at a level of, for example, from 5 to 80% by weight, preferably from 10 to 60% by weight.

Apart from the components already mentioned, the detergent compositions of the invention can contain any of the conventional additives - if not already included in the instant peroxyacid granules - in the amounts in which such materials are normally employed in fabric-washing detergent compositions. Examples of these additives include lather boosters, such as alkanolamides, particularly the monoethanol amides derived from palmkernel fatty acids and coconut fatty acids, lather depressants, such as alkyl phosphates and silicones, anti-redeposition agents, such as sodium carboxymethyl cellulose and alkyl or substituted alkyl cellulose ethers, peroxide stabilizers, such as ethylene diamine tetraacetic acid and preferably phosphonates, e.g. ethylene diamine tetra-methylene phosphonic acid and diethylene triamine penta-methylene phosphonic acid or their salts, fabric-softening agents, inorganic salts, such as sodium sulphate, and, usually present in very small amounts, fluorescent agents, perfumes, enzymes, such as proteases, cellulases, lipases and amylases, germicides and colourants.

The following example will more fully illustrate the embodiments of the invention. All parts, percentages and proportions referred to herein are by weight unless otherwise illustrated.

Example

Granules containing 1,12-diperoxydodecanedioic acid are prepared and processed in the following manner :

A suspension containing :

28% by weight of 1,2-diperoxydodecanedioic acid (DPDA);
7% by weight of sodium sulphate; and
65% by weight of water
was heated to a temperature of about 40 °C.

To this suspension was added sufficient sodium sulphate to give a homogeneous slurry with a DPDA:sulphate weight ratio of about 20/80.

Polyacrylic acid of MW 30,000 was added in an amount to give a final polyacrylic acid level of about 5% in the final granule, whilst ensuring that the slurry was well agitated and the temperature of 40 °C was maintained.

The slurry was then transferred to a mixer/cooler (a Lodige ® mixer with cooling jacket) and the temperature was reduced to 10 °C. A granule/crumb was slowly formed from the mixture, which was then discharged to a fluidized bed drier for drying.

The dry granules from the fluidized bed drier were screened to a particle size range of between 150 µm and 2,000 µm. Any oversize (>2,000 µm) and undersize (<150 µm) were collected for recycling to the mixer/cooler. The following granule composition was obtained :

DPDA	19%
Na_2SO_4	76%
Polyacrylic acid	5%.

The granules have a bulk density of 600 kg/m^3 and show good attrition resistance, good stability on storage and an excellent dispersibility, showing no sign of high local concentration of DPDA.

Claims

1. A process for preparing dry particulate bodies containing a solid peroxyacid compound comprising the steps of

(A) forming a water-wet mixture of a solid peroxyacid compound and a hydratable material having a temperature of hydration of up to 40° C, at a temperature which is higher than the temperature of hydration of the hydratable material;

(B) forming the mixture of (A) into particles of the desired shape and size before, during or after cooling the mass to below the temperature of hydration of the hydratable material; and

(C) drying the particles obtained from step (B), characterized in that in step (A) a film-forming material is incorporated in, and intimately mixed with, the water-wet mixture, forming a mix having a pH of below 7.

2. A process according to Claim 1, characterized in that the process comprises heating an aqueous suspension of solid peroxyacid compound, adding thereto the hydratable material and thereafter the film-forming material, whilst ensuring that the slurry is well agitated and the temperature is maintained, followed by cooling and gentle milling of the mixture to form a granule/crumb, which is then dried and optionally screened to the desired particle size range.

3. A process according to Claim 1 or 2, characterized in that the hydratable material is added in sufficient amounts for binding a substantial amount of the free water upon hydration.

4. A process according to Claim 1, 2 or 3, characterized in that the hydratable material is sodium sulphate.

5. A process according to any of the above Claims 1-4, characterized in that the drying step is carried out under dynamic conditions.

6. A process according to any of the above Claims 1-5, characterized in that the film-forming material is selected from the group consisting of non-oxidizable polymeric materials, and glassy or amorphous phosphates having the general formula

$(M_2O)_x(P_2O_5)_y$

wherein M is hydrogen, alkali metal, ammonium or a substituted ammonium group; y has a value in the range of from 2 to 50; and the ratio of x:y is from 0.7:1 to 1.7:1.

7. A process according to Claim 6, characterized in that the film-forming material is selected from polyacrylic acids, copolymers of maleic(anhydride) and (meth)acrylic acid and salts thereof.

8. A process according to Claim 6 or 7, characterized in that the amount of film-forming material is such that it will give a material level in the final particulate bodies of about 0.5-10% by weight.

9. A process according to any one of the above Claims 1-8, characterized in that the pH of the mix in step (A) is from 3 to 6.5.

10. A process according to any one of the above Claims 1-9, characterized in that the peroxyacid compound is 1,12-diperoxy-dodecanedioic acid.

A bleaching and/or detergent powder composition comprising dry particulate bodies as obtainable from the process according to any one of the aforementioned Claims 1-10.