

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 373 691
A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 89203023.0

(51) Int. Cl.⁵: C11D 3/39, C11D 3/37

(22) Date of filing: 28.11.89

(30) Priority: 16.12.88 US 285466

(43) Date of publication of application:
20.06.90 Bulletin 90/25(84) Designated Contracting States:
CH DE ES FR GB IT LI NL SE(71) Applicant: UNILEVER NV
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)

(84) CH DE ES FR IT LI NL SE

Applicant: UNILEVER PLC
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ(GB)

(84) GB

(72) Inventor: Foster, Jeffrey Norris
101 Ridgeview
Danville Pennsylvania 17821(US)
Inventor: Karpusiewicz, William Martin
253 Floral Boulevard Floral Park
Nassau New York 11001(US)
Inventor: Irwin, Charles Fraser
15 Dalrymple Street
Randolph Morris New Jersey 07869(US)
Inventor: Pham, Hien Thi
808 Harvard Place Fort Lee
Bergen New Jersey 07024(US)
Inventor: Aronson, Michael Paul
2 Mandarine Lane West Nyack
Rockland New York 10994(US)

(74) Representative: Tan, Bian An, Ir. et al
Unilever N.V. Patent Division P.O. Box 137
NL-3130 AC Vlaardingen(NL)

EP 0 373 691 A2

(54) Stabilized granular bleach compositions.

(57) Granular bleach compositions showing reduced tendency to detonate or decompose are provided which contain an organic peroxycarboxylic acid in intimate contact with a fully neutralized carboxylated polymer or a fully neutralized fatty acid. The granular bleach compositions are useful as bleach ingredients in detergent and cleaning compositions.

STABILIZED GRANULAR BLEACH COMPOSITION

Background of the invention5 FIELD OF THE INVENTION

The present invention relates to granular bleach compositions comprising an organic peroxycarboxylic acid as the active bleaching agent.

10

THE PRIOR ART

Granular bleach compositions which comprise an organic peroxycarboxylic acid as the active bleaching agent are known in the art. Typical representatives of such organic peroxycarboxylic acids as bleaching
15 agents are diperphthalic acid, diperisophthalic acid, diperoxysebacic acid, diperoxytetradecanedioic acid, diperoxydodecanedioic acid, peracetic acid, peroctanoic acid, peradamantoic acid, diperbrassylic acid and so on.

An inherent problem with peroxycarboxylic acids is that they can exhibit an exothermic behaviour due to thermal decomposition. This can result in detonation or explosion of these peroxycarboxylic acids, which
20 makes these products difficult to handle safely. This problem has been recognized in the art, and various proposals have been made to reduce this tendency to detonate and/or explode. Several of these proposals are concerned with the use of inorganic, hydrated or hydratable salts which are brought in intimate contact with the organic peroxycarboxylic acid to form coated granules therefrom; see e.g. US Patent 3,494,787; US Patent 3,770,816 and US Patent 4,091,544.

Several other proposals are directed to the use of organic materials to control the thermal decomposition of these organic peroxycarboxylic acids. Thus, for example, in EP-A-0,254,331, it is proposed to coat
25 diperoxydodecanedioic acid with fatty esters, fatty alcohols or fatty acids, preferably lauric or myristic acid.

In US Patent 4,119,660 it is suggested to use acids, esters, ethers and hydrocarbons to coat organic peroxycarboxylic acids, and in US Patent 4,100,095 various organic acids are suggested as exotherm
30 control agents for organic peroxycarboxylic acids.

Recently, it has been proposed to coat granular peroxycarboxylic acids with polymeric compounds (EP-A-0,200,163 and German Patent Application 3,636,909), or to include polymeric compounds as binder in granular peroxycarboxylic acids (EP-A-0 265,443). These latter proposals concerning the use of polymeric coating or binding materials require the polymeric material to be in unneutralized, acid form or optionally in
35 the form of a partial salt, as long as said salt does not yield a pH of more than 8, preferably not more than 6.5 (1% aqueous solution). The main object of these proposals is to improve the storage-stability of the peroxycarboxylic acids and to prevent their interaction with other components which are sensitive to oxydation.

40

SUMMARY OF THE INVENTION

It has now been found that the tendency of granular organic peroxycarboxylic acids to detonate and/or explode can be significantly reduced by combining them with fully neutralized carboxylated polymers or
45 fully neutralized fatty acids. In comparison with acid carboxylated polymers or fatty acids, the use of the fully neutralized materials prevent autoignition of the granular peroxycarboxylic acids to a satisfactory degree, enabling their safe-handling.

50 DETAILED DESCRIPTION OF THE INVENTION

The invention will be described with particular reference to a preferred peroxycarboxylic acid, namely diperoxydodecanedioic acid (DPDA), it being understood however that this does not imply a limitation, other organic peroxycarboxylic acids as discussed above equally being usable in the present invention. The DPDA used in the present invention is usually in the form of dry granules, containing an inert carrier

material such as sodium sulphate. In general, these granules contain from 5 - 45% DPDA, usually from 10 - 40% and preferably 12 - 37%. The balance of the granules consists mainly of the inert carrier material as well as of minor amounts of surfactants, stabilizing agents and other exotherm control agents. The mean particle size of the granules should be larger than 500 microns, and should preferably range between 800 and 1200 microns.

The fully neutralized carboxylated polymers of the invention are alkali-soluble carboxylated polymers or copolymers of which the carboxy groups have been neutralized with a suitable neutralizing agent to the corresponding salts. Suitable salts are the alkalimetal, the alkaline earth metal and the aluminum salts. The alkalimetal salts are preferred. Suitable examples of carboxylated polymers, copolymers and homopolymers useful in the present invention when in their fully neutralized form are given in US Patent 4,759,956. Particularly suitable fully neutralized carboxylated polymers are alkalimetal polyacrylates, alkalimetal polymethacrylates, alkalimetal salts of copolymers of acrylic acid or methacrylic acid with maleic anhydride or styrenic monomers or alkylacrylates or mixtures thereof. Typical examples are sodium polyacrylate; copolymers of alkylacrylates, such as butylacrylate, styrenic monomers such as styrene and alkalimetal-(meth) acrylates, fully neutralized copolymers of alkalimetal (meth)acrylates with maleic anhydride, and so on. Representative examples are the commercial products A-1N, a sodium polyacrylate ex. Rohm and Haas; WS-24 ex. Rohm and Haas, a fully neutralized acrylic copolymer dispersion resin; fully neutralized NSC 78-6312 ex. National Starch, an acrylate copolymer latex, and Sokalan CP7 ex BASF, which is the sodium salt of a copolymer of maleic and acrylic acid with an average molecular weight of 50,000 and a viscosity of 1200 mPa s at 23 °C.

Mixtures of the various fully neutralized carboxylated polymers can also be used in the present invention.

The fully neutralized fatty acids, used in the present invention, are the alkalimetal, alkaline earth metal or aluminium salts of C₁₀-C₃₂, preferably C₁₂-C₂₂ saturated or unsaturated, natural or synthetic fatty acids. Preferred are the alkalimetal, particularly the sodium salts of C₁₂-C₁₈ saturated fatty acids. Polymerized fatty acids can also be used.

The amount of fully neutralized carboxylated polymer or fatty acid to be used in the present invention is dependent upon the level of the organic peroxycarboxylic acid, present in the granule.

In general, the weight ratio of the organic peroxycarboxylic acid to the fully neutralized carboxylated polymer or fatty acid ranges from 5:1 to 1:5, preferably from 2:1 to 1:2. The organic peroxycarboxylic acid and the fully neutralized carboxylated polymer or fatty acid should be in intimate contact in order to get the maximum reduction of the tendency of the peroxycarboxylic acid to undergo thermal decomposition. Such intimate contact can be achieved by simply dry-blending the ingredients, or dusting the granular peroxycarboxylic acid with the fully neutralized carboxylated polymer or fatty acid. A preferred way of achieving the intimate contact is coating the granular peroxycarboxylic acid with a layer of the fully neutralized carboxylated polymer or fatty acids in manners, known per se., e.g. by spraying the fully neutralized carboxylated polymer or fatty acid onto a fluidized bed of the granular peroxycarboxylic acid. If the fully neutralized carboxylated polymer or fatty acid is sprayed in the form of an aqueous solution or dispersion, it may be advantageous to pre-mix the granular peroxycarboxylic acids with an alkaline, hydratable inorganic salt which will then take up the water of the aqueous solution or dispersion as water of hydration. The granular bleach compositions of the invention can be used as such or as ingredients in detergent cleaning and bleaching compositions for fabrics. Such cleaning and bleaching compositions incorporating the granular bleach compositions in an amount of up to 50%, usually contain one or more detergent-active materials, builders and other adjuvants commonly present in such compositions. Thus, they may contain from 1 to 40, usually from 2 to 35 and preferably from 5 to 30% by weight of an anionic, a nonionic, a cationic and/or zwitterionic detergent-active material, all of which are well-known in the art. Suitable examples thereof are fully described in Schwartz, Perry and Berch, "Surface-Active Agents and Detergents", Vol. I (1949) and Vol. II (1958). The compositions may furthermore comprise up to 55% of one or more organic and/or inorganic builders, such as alkalimetal carbonates, alkalimetal citrates, alkalimetal nitrilotriacetates, zeolites, mixtures of alkalimetal carbonates with calcites, alkalimetal ortho-, pyro- and polyphosphates and so on.

The compositions may furthermore comprise optional other detergent ingredients in amounts, commonly used in detergent compositions, such as lather boosters, foam depressors, anti-corrosion agents, soil-suspending agents, sequestering agents, anti-soil redeposition agents, perfumes, dyes, enzymes such as proteases, amylases, cellulases and lipases, bleach precursors, etc.

The compositions are preferably formulated in particulate forms, but other forms such as pastes, liquids, bars, cakes, etc. can also be used. The granular bleach compositions of the invention are added to the particulate detergent composition by simply admixing them with the particulate composition.

The invention will be further illustrated by way of the following Examples.

Example I

The thermal stability of various granular bleach compositions containing various levels of DPDA, with or without a carboxylated polymer or fatty acid, neutralized or unneutralized, was assessed by an autoignition temperature test to measure the Autoignition Temperature (AT).

The apparatus used in measuring the Autoignition Temperature consisted of a 31.5 O.D. mm by 175 mm capped steel pipe inserted into a heating mantle (Type 0-610, 325 Watt) containing sand. The sample was placed into a 25 x 200 mm Pyrex glass tube and a thermocouple, shielded inside in a 6.25 O.D. mm glass tube, was inserted into the center of the sample. The glass tube containing the sample was then placed into the steel pipe. The heating mantle, controlled with a Powerstat (Type 3PN117C) to give a 2°C/min heating rate, was turned on. The temperature of the sample versus time was recorded. The autoignition temperature was taken as the point at which the sample ignited, as indicated by the sharp change in sample temperature.

The Table below shows the results of the autoignition test of the various bleach compositions as well as details of their composition.

In all cases, the sample tested contained 80 parts of ground DPDA-granules, containing 20% by weight of DPDA and 80% by weight of sodium sulphate.

Where an agent was added, this was added in an amount of 20 parts the addition being effected by dry-blending.

Agent	AT (in °C)
none	129
WS-24	none
WS-24, acidified	120
A-1 N	none
A-1 (unneutralized)	127
Sodium laurate	none
Lauric acid	132
Sodium stearate	none
Stearic acid	116
Sokalan CP ₇ (neutralized)	none
Sokalan CP ₇ (acidified)	108

Example II

DPDA granules, containing 22% DPDA, 77% sodium sulphate and 1% polyacrylic acid as binder, the granules having a mean particle size of 630 microns, were charged into a fluidized bed in an amount of 1 kilogram. When the product temperature reached the temperature for proper drying, i.e. 30-60°C, 1 kilogram of the Rohm and Haas copolymer WS-24, (36% solids) identified heretofore, was sprayed onto the granules at a rate of 10 ml/min. The granules, coated with 21% of the fully neutralized copolymer, were then subjected to the autoignition test. They did not autoignite.

Claims

1. A granular bleach composition comprising a granular organic peroxycarboxylic acid containing 5 - 45% by weight of the peroxycarboxylic acid, in intimate contact with a fully neutralized carboxylated polymer or fully neutralized fatty acid, the weight ratio of the organic peroxycarboxylic acid, to the fully neutralized polymer or the fully neutralized fatty acid being from 5:1 to 1:5.

2. A composition according to claim 1, wherein the weight ratio is from 2:1 to 1:2.

3. A composition according to claim 1 or 2, wherein the fully neutralized carboxylated polymer is selected from the group consisting of the alkalimetal, alkaline earth metal and aluminium salts of polyacrylic acid, polymethacrylic acid, copolymers of acrylic acid with maleic anhydride, copolymers of methacrylic acid with maleic anhydride, copolymers of acrylic acid with styrenic monomers, copolymers of methacrylic acid with styrenic monomers, copolymers of acrylic acid with alkylacrylates, copolymers of methacrylic acid with alkylacrylates, copolymers of acrylic acid with mixtures of styrenic monomers and alkylacrylates, copolymers of methacrylic acid with mixtures of styrenic monomers and alkylacrylates, and mixtures thereof.

4. A composition according to claim 3, wherein the fully neutralized carboxylated polymer is selected from the group consisting of sodium polyacrylate, the sodium salt of the copolymer of n-butylacrylate with styrenic monomer and sodium methacrylate, the sodium salt of the copolymer of styrene, n-butyl acrylate and methacrylic acid, the sodium salt of the copolymer of maleic acid and acrylic acid, and mixtures thereof.

5. A composition according to claim 1, wherein the fully neutralized fatty acid is the alkalimetal, alkaline earth metal or aluminium salt of saturated or unsaturated, natural or synthetic fatty acids having an alkyl group with 10 - 32 carbon atoms.

6. A composition according to claim 5, wherein the fully neutralized fatty acid is the sodium salt of saturated fatty acids having an alkyl group with 12 - 18 carbon atoms.

7. A composition according to claim 1, wherein the granular organic peroxycarboxylic acid is in intimate contact with the fully neutralized carboxylated polymer or the fully neutralized fatty acid in the form of a coating of the latter materials on the granular organic peroxycarboxylic acid.

8. A composition according to claim 7, wherein the granular organic peroxycarboxylic acid is in admixture with an alkaline, hydrated inorganic salt, said mixture being in intimate contact with the fully neutralized carboxylated polymer or the fully neutralized fatty acid in the form of a coating of the latter materials on the granular mixture of the organic peroxycarboxylic acid and alkaline hydrated inorganic salt.

9. A particulate detergent and bleaching composition comprising one or more detergent-active compounds, one or more builders and a bleaching agent, wherein the bleaching agent is a granular organic peroxycarboxylic acid bleach composition as claimed in any of the above claims 1-8.