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(54) **Granular laundry bleaching composition.**

(57) A granular bleaching composition is disclosed which comprises an alkali metal salt of percarbonate and a crystalline layered silicate or mixtures thereof. Preferred compositions further comprise an anhydrous acidifiant agent. The compositions provide effective bleaching and are as stable as perborate based bleaching compositions.

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Technical field

The present invention relates to bleaching compositions for laundry. Granular laundry bleaching compositions are described which comprise percarbonate as the bleaching specie, said compositions being stable upon storage.

Background of the invention

The inorganic perhydrate bleach most widely used in the context of laundry bleaching is sodium perborate in the form of either the monohydrate or tetrahydrate. However, concerns about the impact of boron salts on the environment have led to an increasing interest in other perhydrate salts, of which sodium percarbonate is the most readily available.

Detergent compositions containing sodium percarbonate are known in the art. Percarbonate salts, particularly sodium percarbonate, are attractive perhydrates for use in detergent compositions because they dissolve readily in water, are weight efficient and, after giving up their available oxygen, provide a useful source of carbonate ions for detergency purposes.

However, the inclusion of percarbonate salts in detergent compositions has been restricted hitherto by the relative instability of the bleach both as is and in use. Sodium percarbonate loses its available oxygen at a significant rate in the presence of ions of heavy metals such as iron, copper and manganese and also in the presence of moisture, these effects being accelerated at temperatures in excess of about 30 °C.

Moisture and heavy metal ions are unavoidable components of conventional granular laundry treatment compositions. Also percarbonate decomposition due to moisture becomes more of an issue during storage as laundry treatment products are often stored in humid environments when the product picks up moisture. This has resulted in marginally acceptable percarbonate bleach stability under Northern European summer conditions, where the average maximum temperature over the hottest months is from 21 °C to 25 °C, and unacceptable stability under temperatures higher than this. Such conditions are found in the Middle East and Southern Asia and also in Southern Europe where average maximum temperatures are in the 27 °C to 33 °C range for the hottest summer month.

There has therefore been much activity by workers in the field to increase percarbonate stability so as to make it a viable component of detergent formulations. This activity has tended to concentrate on the protection of the percarbonate by coating the crystalline product or by inclusion of stabilising agents during its manufacture, or both. Thus, while it has proved possible to incorporate percarbonate salts in conventional detergent compositions so as to have acceptable percarbonate stability over periods reflecting normal product shelf life, the percarbonate salts have proved complex and expensive to manufacture. This has restricted their broadscale utilisation, as evidenced by the relatively small number of commercially available products containing percarbonate.

It is therefore an object of the present invention to provide a granular laundry bleaching composition incorporating an alkali metal percarbonate bleach, said bleach displaying improved stability.

It is a further object of the present invention to provide a granular laundry bleaching composition incorporating an alkali metal percarbonate bleach displaying improved stability, in which the percarbonate bleach does not require complex protection techniques.

It has now been found that these objects could be met by formulating a composition comprising an alkali metal salt of percarbonate together with a crystalline layered silicate or mixtures thereof.

Granular bleaching compositions comprising percarbonate have been described for instance in FR 2,385,837, US 4,428,914 and GB 1,553,505. Crystalline layered silicate and their methods of preparation have been described for instance in EP-A-164 514, DE-A-34 17 649 and DE-A-37 42 043 and their application to the field of laundry treatment has been described in applicant's copending British applications GB 90 21 761.3, GB 90 18157.9 and GB 91 08639.7.

The compositions according to the present invention also allow adequate control of the pH in the bleaching liquor, giving appropriate balance between bleaching performance and fabric safety.

Summary of the invention

Compositions according to the present invention are granular bleaching compositions comprising more than 20% and up to 80% by weight of the total composition of an alkali metal salt of percarbonate bleach and from 5% to 80% by weight of the total composition of a crystalline layered silicate of formula $NaMSi_xO_{2x+1}.yH_2O$ wherein M is sodium or hydrogen, x is a number of from 1.9 to 4 and y is a number of from 0 to 20, or mixtures thereof. Preferred compositions herein further comprise an anhydrous acidifying

agent, preferably citric acid.

Detailed description of the invention

As a first essential component, the compositions according to the present invention comprise an alkali metal salt of percarbonate, preferably sodium percarbonate. Sodium percarbonate is available commercially as a crystalline solid. Most commercially available material includes a low level of a heavy metal sequestrant such as EDTA, 1-hydroxyethylidene 1, 1-diphosphonic acid (HEDP) or an amino-phosphonate, that is incorporated during the manufacturing process. For the purposes of the present invention, the percarbonate can be incorporated into detergent compositions without additional protection.

Whilst heavy metals present in the sodium carbonate used to manufacture the percarbonate can be controlled by the inclusion of sequestrants in the reaction mixture, it is preferred that the percarbonate be protected from heavy metals present as impurities in other ingredients of the product. It has been found that the total level of Iron, Copper and Manganese ions in the product should not exceed 25 ppm and preferably should be less than 20 ppm in order to avoid an unacceptably adverse effect on percarbonate stability.

The compositions according to the present invention comprise more than 20% by weight of the total composition of percarbonate, up to 80% by weight of the total composition, preferably from 40% to 50%.

The second essential component of the invention is a crystalline layered silicate. The crystalline layered silicates suitable for use herein are of the granular formula

$$NaMSi_xO_{2x+1}.yH_2O$$

wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20, or mixtures thereof. Crystalline layered sodium silicates of this type are disclosed in EP-A-164 514 and methods for their preparation are disclosed in DE-A-34 17 649 and DE-A-37 42 043. For the purposes of the present invention, x in the general formula above has a value of 2, 3 or 4 and is preferably 2. More preferably M is sodium and y is 0 and preferred examples of this formula comprise the α, β, γ and δ forms of $Na_2Si_2O_5$ These materials are available from Hoechst AG FRG as respectively NaSKS-5, NaSKS-7, NaSKS-11 and NaSKS-6. The most preferred material is δ - $Na_2Si_2O_5$, NaSKS-6. Crystalline layered silicates are incorporated either as dry mixed solids, or as solid components of agglomerates with other components.

The compositions according to the present invention comprise from 5% to 80% by weight of the total composition of said crystalline layered silicates or mixtures thereof, preferably from 15% to 25%.

As an optional but highly preferred component, the compositions according to the present invention further comprise an anhydrous acidifying agent or mixtures thereof. The purpose of said acidifying agent is to control the alkalinity generated by the percarbonate in the bleaching liquor. Said agent need to be incorporated in the product in an anhydrous form, and to have a good stability in oxidizing environment. Suitable anhydrous acidifying agents for use herein are carboxylic acids such as citric acid, succinic acid, adipic acid, glutaric acid, 3 chetoglutaric acid, citramalic acid, tartaric acid and maleic acid. Other suitable acidifying agents include sodium bicarbonate, sodium sesquicarbonate and silicic acid. Highly preferred for use herein is citric acid. Indeed, citric acid is commercially available in anhydrous form, it additionally acts as a builder and a chelant, and it is biodegradable. The compositions according to the present invention comprise from up to 15% by weight of the total composition of anhydrous citric acid, preferably from 2% to 8%, most preferably about 5%.

Compositions in accordance with the invention can also comprise optional ingredients such as optical brighteners, anti dusting agents such as olefines and waxes, enzymes, chelants, dispersants, surfactants, soil release agents, photoactivated bleaches such as Zn phthalocyanine sulphonate, dyes, pigments and perfumes are examples of such optional ingredients and can be added in varying amounts as desired.

Optional but highly preferred ingredients are peroxy carboxylic acids bleach or precursors thereof, commonly referred to as bleach activators, which are preferably added in a prilled or agglomerated form. Examples of suitable compounds of this type are disclosed in British Patent GB 1 586 769 and GB 2 143 231 and a method for their formation into a prilled form is described in European Published Patent Application EP-A-62 523. Preferred examples of such compounds are tetracetyl ethylene diamine (TAED), sodium 3, 5, 5 trimethyl hexanoylorybenzene sulphonate, diperoxy dodecanoic acid as described for instance in US 4 818 425 and nonylamide of peroxyadipic acid as described for instance in US 4 259 201 and n-nonanoyloxybenzenesulphonate (NOBS), and acetyl triethyl citrate (ATC) such as described in European Patent application 91870207.7.

The compositions according to the present invention naturally comprise inorganic filler salts such as alkali metal carbonates bicarbonates and sulphates. Such fillers, for instance sodium bicarbonate, may also

act as acidifying agent as described herein above. Accordingly, sodium percarbonate is a preferred filler material for use herein.

The compositions according to the present invention can be made by a variety of methods well known in the art, including dry-mixing, spray drying, agglomeration and granulation and combinations thereof.

The compositions according to the present invention can be prepared with different bulk densities, from conventional granular products to so-called "concentrated" products (i.e. with a bulk density above 600g/l).

Examples

1) Part A

The following examples will illustrate the present invention. The following granular compositions are made by dry-mixing the listed ingredients in the listed proportions.:

Compositions	1	2	3	4	5	6
Sodium percarbonate	40.0	35.0	54.0	55.0	46.0	47.0
TAED	8.7	7.6	11.7	-	9.5	-
Silicate layered SKS-6	25.0	30.0	20.0	10.0	18.0	20.0
Anhydrous citric acid	10.0	12.0	12.0	5.0	5.0	5.0
Sodium sulphate	15.3	14.3	1.0	20.0	0.5	15.0
Sodium bicarbonate	-	-	-	5.0	18.0	-
NOBS	-	-	-	-	-	10.3
minors	up to 100%					

2) Part B

The following compositions were made by mixing the listed ingredients in the listed proportions. The self heating rates of the products were monitored as follows. The product is made and put in a bottle. The bottle is then put in an oven which is heated up to 70 °c. A probe in the product allows to monitor the temperature of the product. As soon as the product reaches 70 °c, the bottle is covered and the system is isolated in an adiabatic/thermo bell which maintains the temperature of the oven constant at 70 °c as above. This places the product in adiabatic conditions and from thereon, the temperature of the product is monitored. The temperature increase thus measured is due to the self-heating of the product (runaway reaction). The results below list three self heating rates, all in °c/hour: SHR1 is the average temperature increase measured during the first two hours of adiabatic conditions; SHR2 is the average temperature increase measured during the three following hours, and SHR3 is the average temperature increase measured beyond 5 hours. The table below lists the results obtained for various compositions, with and without crystalline layered silicate. In some cases the runaway reaction was out of control and experiments had to be interrupted for safety reasons. Such experiments are marked "ooc" (out of control).

Compositions	7	7a	8	8a	9	9a
Sodium percarbonate	47.0	47.0	47.0	47.0	47.0	47.0
TAED	10.2	10.2	10.2	10.2	10.2	10.2
Silicate SKS-6	20.0	--	20.0	--	20.0	--
Citric acid	10.0	10.0	8.0	8.0	8.0	8.0
Sodium Sulphate	11.7	31.7	13.7	33.7	9.2	29.2
Sodium bicarbonate	---	---	---	---	4.5	4.5
SHR1*	2.3	4.5	2.2	4.0	2.5	3.9
SHR2**	0.6	8.9	0.6	8.0	0.5	7.7
SHR3***	0	ooc	0	ooc	0	ooc

Compositions	10	10a	11	11a	12	12a
Sodium percarbonate	47.0	47.0	47.0	47.0	47.0	47.0
TAED	10.2	10.2	10.2	10.2	10.2	10.2
Silicate SKS-6	18.0	--	20.0	--	42.8	---
Citric acid	7.0	7.0	5.0	5.0	---	---
Sodium Sulphate	16.7	34.7	16.7	36.7	---	42.8
Sodium bicarbonate	---	---	---	---	---	---
SHR1*	2.7	4.1	2.2	4.1	2.2	4.0
SHR2**	0.6	8.3	0.4	8.2	0.3	10.8
SHR3***	0	ooc	0	ooc	0	ooc

Comments:

Compositions 7-12 show good thermal stability, and no temperature increase is reported after 5 hours storage and beyond. In the absence of crystalline layered silicate i.e. in compositions 7a-12a, self-heating rates measured were so high that experiments had to be stopped for safety purposes.

Claims

1. A granular bleaching composition comprising more than 20% and up to 80% by weight of the total composition of an alkali metal salt of percarbonate bleach and from 5% to 80% by weight of the total composition of a crystalline layered silicate of formula $NaMSi_xO_{2x+1}.yH_2O$ wherein M is sodium or hydrogen, x is a number of from 1.9 to 4 and y is a number of from 0 to 20, or mixtures thereof.

2. A granular bleaching composition according to claim 1 which comprises from 40% to 50% by weight of the total composition of a percarbonate bleach.

3. A granular bleaching composition according to any of the preceding claims, characterized in that it comprises from 15% to 25% by weight of the total composition of said crystalline layered silicate or mixtures thereof.

4. A granular bleaching composition according to any of the preceding claims, characterized in that the crystalline layered silicate is of the formula $NaMSi_xO_{2x+1}.yH_2O$, wherein x is 2, M is sodium and y is 0.

5. A granular bleaching composition according to any of the preceding claims, characterized in that it further comprises an anhydrous acififying agent.

6. A granular bleaching composition according to claim 5 wherein said anhydrous acidifying agent is anhydrous citric acid.

7. A granular bleaching composition according to claim 6 which comprises up to 15%, preferably from 2% to 12%, most preferably 5% by weight of the total composition of anhydrous citric acid.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 20 0005

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 337 219 (HOECHST AKTIENGESELLSCHAFT) * abstract; page 2, lines 24-33,40,41; claims * * page 2, line 42 *	1,3,4 5-7	C 11 D 3/12 C 11 D 3/39 C 11 D 3/20
X	SOFW: Seifen, Ole, Fette, Wachse vol. 116, no. 20, 13 December 1990, pages 805-808, Ausburg, DE; F.J. DANY et al.: "Kristallines Schichtsilikat - ein neuer Builder" * page 807, figure 8; right column, first paragraph and last paragraph; page 808 * idem	1,3,4 5-7	
Y	EP-A-0 416 366 (HOECHST) * claims; page 2, lines 38-47 *	1-7	
Y	FR-A-2 247 533 (E.I. DU PONT DE NEMOURS AND CO) * claims 1-4,9,10 *	1-7	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C 11 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	28-07-1992	PELLI-WABLAT B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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