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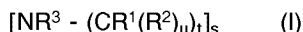
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NL-3130 AC Vlaardingen (NL)(54) **Bleach and detergent compositions.**

(57) There is provided a storage-stable and highly potent, particulate bleach composition for laundry use, comprising sodium percarbonate, optionally a bleach activator, and a bleach catalyst including a source of Mn and/or Fe ions and a ligand which is a macrocyclic organic compound of formula I:



wherein t is an integer from 2 to 3; s is an integer from 3 to 4, u is zero or one; and R¹, R² and R³ are each independently selected from H, alkyl and aryl, both optionally substituted.

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TECHNICAL FIELD

The present invention is concerned with bleach compositions (bleach additives) for use in conjunction with a detergent product (bleaching or non-bleaching) to enhance bleaching performance. The bleach compositions of the invention are especially intended for use as part of a Baukasten (building block) laundry detergent system.

BACKGROUND AND PRIOR ART

Laundry detergent systems of the Baukasten or building block-type are disclosed, for example, in EP 419 036A (Unilever): A main wash powder (or liquid) is supplied together with separately packaged additives, for example, water softener (builder) and bleach, that need only be used when the wash demands them.

EP 427 314A (Unilever) discloses a stable and highly effective particulate bleach additive suitable for use in a Baukasten system. The bleach additive comprises sodium percarbonate, a bleach activator (preferably tetraacetyl ethylene diamine (TAED)), and an alkali metal bicarbonate, sesquicarbonate or dihydrogen orthophosphate.

EP 458 397A, EP 458 398A and EP 509 787A (Unilever) disclose novel bleach catalysts which are transitional metal (manganese or iron) complexes. These catalysts are shown to enhance the bleaching power of sodium perborate monohydrate, both in the presence and absence of bleach activators such as TAED, in various detergent products.

The persalt sodium percarbonate (sodium carbonate perhydrate) is more environmentally acceptable than sodium perborate, but it is substantially less stable. Not only is it unstable to moisture, but if together with a bleach activator in a concentrated environment such as a bleach additive, there is a danger of premature reaction between the two, leading to self-heating.

The present invention is based on the discovery of a storage-stable and highly potent bleach composition comprising a bleach catalyst of the type just described, in conjunction with sodium percarbonate. The sodium percarbonate may be provided with a protective coating, but that is not essential.

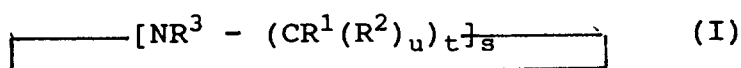
DEFINITION OF THE INVENTION

The present invention accordingly provides a particulate bleach composition for laundry use, comprising

(a) sodium percarbonate,

(b) optionally, a bleach activator,

(c) a bleach catalyst comprising a source of Mn and/or Fe ions and a ligand which is a macrocyclic organic compound of formula I:



wherein t is an integer from 2 to 3; s is an integer from 3 to 4, u is zero or one; and R¹, R² and R³ are each independently selected from H, alkyl and aryl, both optionally substituted.

The invention further provides a laundry detergent system of the Baukasten (building block)-type, comprising as separate components:

(i) a main wash powder comprising one or more organic surfactants and one or more detergency builders;

(ii) optionally a builder additive, and

(iii) a bleach additive which is a composition as defined in the previous paragraph.

DETAILED DESCRIPTION OF THE INVENTIONThe bleach composition

The particulate bleach composition of the invention contains as essential ingredients a peroxy bleach compound (sodium percarbonate), optionally assisted by a bleach activator, and a transition metal bleach catalyst.

The sodium percarbonate

The bleach composition of the invention may suitably contain from 10 to 90 wt.% of sodium percarbonate, preferably from 30 to 85 wt.%

Any grade of sodium percarbonate may be used without any prior treatment being necessary, but a coarse grade is preferable. A highly suitable grade is that of which at least 60 wt.% has a particle diameter larger than 250 micrometres. Other components present will preferably also be of similar coarse grades.

As mentioned previously, it is well known that the stability of sodium percarbonate to moisture is not optimal. The sodium percarbonate may, therefore, be provided with a protective coating. The protective coating preferably comprises one or more salts selected from sodium borates (especially sodium metaborate), sodium silicate, and sodium citrate.

Sodium percarbonate having a protective coating comprising sodium metaborate and sodium silicate is disclosed in GB 2 123 044B (Kao).

Our co-pending unpublished European Patent Application No. 92 311 225.4, filed on 9 December 1992, claims sodium percarbonate having a protective coating comprising sodium citrate.

The optional bleach activator

The sodium percarbonate is advantageously used in conjunction with a bleach activator (bleach precursor). The bleach precursor is suitably present in an amount of from 4 to 40 wt.%, preferably from 5 to 30 wt.%.

Preferred bleach precursors are peroxycarboxylic acid precursors, more especially peracetic acid precursors and peroxybenzoic acid precursors, and peroxycarbonic acid precursors.

Examples of peroxyacid bleach precursors suitable for use in the present invention include:

N,N,N',N'-tetraacetyl ethylene diamine (TAED);

2-(N,N,N-trimethyl ammonium) ethyl sodium-4-sulphophenyl carbonate chloride (SPCC), also known as cholyl-p-sulphophenyl carbonate (CSPC);

sodium nonanoyloxy benzene sulphonate (SNOBS);

sodium 4-benzoyloxy benzene sulphonate (SBOBS);

sodium 3,5,5-trimethyl hexanoyloxy benzene sulphonate (STHOBS);

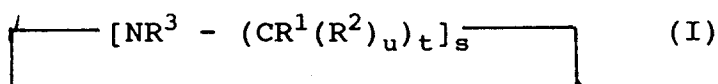
and glucose pentaacetate (GPA).

The bleach activator may be used in normal crystalline form or, preferably, in the form of agglomerates or granulated particles having a particle size of from 0.2 to 2.0 mm. The use of such agglomerates or granules minimises direct contact between the sodium percarbonate and the bleach activator. The technique of agglomeration and granulation is well known in the art, and any of those techniques may be used to prepare the bleach activator granules. For example, bleach activator granules as described in EP 240 057A and EP 241 962A (Unilever) are very suitable for use in the present invention.

The bleach catalyst

The bleach catalyst present in the compositions of the invention is described and claimed in EP 458 397A, EP 458 398A and EP 509 787A (Unilever).

The bleach catalyst is defined as comprising a source of Mn and/or Fe ions and a ligand which is a macrocyclic organic compound of formula I:



wherein t is an integer from 2 to 3; s is an integer from 3 to 4, u is zero or one; and R¹, R² and R³ are each independently selected from H, alkyl and aryl, both optionally substituted.

Examples of preferred ligands are:

1,4,7-triazacyclononane (TACN);

1,4,7-trimethyl-1,4,7-triazacyclononane (1,4,7-Me₃TACN);

2-methyl-1,4,7-triazacyclononane (2-MeTACN);

1,2,4,7-tetramethyl-1,4,7-triazacyclononane (1,2,4,7-Me₄TACN);

1,2,2,4,7-pentamethyl-1,4,7-triazacyclononane (1,2,2,4,7-Me₅TACN);

1,4,7-trimethyl-2-benzyl-1,4,7-triazacyclononane; and
1,4,7-trimethyl-2-decyl-1,4,7-triazacyclononane.

Especially preferred is 1,4,7-trimethyl-1,4,7-triazacyclononane (1,4,7-Me₃TACN).

The aforementioned ligands may be synthesised by the methods described in K. Wieghardt et al.,
5 Inorganic Chemistry 1982, 21, page 3086.

The source of iron and/or manganese ions and ligand may be added separately or in the form of a mono-, di- or tetranuclear manganese or iron complex. When added separately, the ligand may be in the form of an acid salt such as 1,4,7-Me₃TACN hydrochloride. The source of iron and manganese ions may be a water-soluble salt such as iron or manganese nitrate, chloride, sulphate or acetate or a co-ordination
10 complex such as manganese acetylacetonate. The source of iron and/or manganese ions should be such that the ions are not too tightly bound, i.e. all those sources from which the ligand of formula (I), as hereinbefore defined, may extract the Fe and Mn in a wash liquor.

Preferred mononuclear complexes have the formula:



wherein Mn is manganese in the +4 oxidation state;

R is a C₁-C₂₀ radical selected from the group alkyl, cycloalkyl, aryl, benzyl and radical combinations thereof;

20 at least two R radicals may also be connected to one another so as to form a bridging unit between two oxygens that co-ordinate with the manganese;

L is a ligand of formula (I) as hereinbefore defined;

and Y is an oxidatively-stable counter-ion;

or the formula :



wherein Mn can be either in the II, III or IV oxidation state;

each X independently represents a co-ordinating species with the exception of RO⁻, such as Cl⁻, Br⁻,
30 I⁻, F⁻, NCS⁻, N₃⁻, I₃⁻, NH₃, RCOO⁻, RSO₃⁻, RSO₄⁻ in which R is alkyl or aryl, both optionally substituted, OH⁻, O₂²⁻, HOO⁻, H₂O, SH, CN⁻, OCN⁻, S₄²⁻ and mixtures thereof;

p is an integer from 1-3;

z denotes the charge of the complex and is an integer which can be positive, zero or negative;

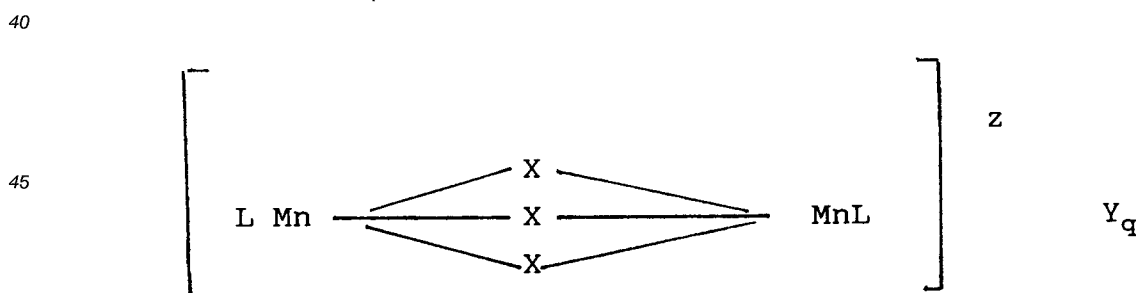
Y is a counter-ion, the type of which is dependent upon the charge z of the complex;

35 q = z/[charge Y];

and L is a ligand as hereinbefore defined.

Such mononuclear complexes are further described in our co-pending European Patent Application No
93 211580.2.

Preferred dinuclear complexes have the formula:



50 wherein

Mn is manganese which can independently be in the III or IV oxidation state;

X is independently a co-ordinating or bridging species selected from the group consisting of H₂O, O₂²⁻,
-OH, HO₂⁻, SH⁻, S²⁻, >SO, Cl⁻, SCN⁻, N₃⁻, RSO₃⁻, RCOO⁻, NH₂⁻ and NR₃, with R being H, alkyl, aryl,
55 both optionally substituted, and R¹COO, where R¹ is an alkyl or aryl radical, both optionally substituted;

L is a ligand of formula (I) as hereinbefore defined;

z denotes the charge of the complex and is an integer which can be positive or negative;

Y is a monovalent or multivalent counter-ion, leading to charge neutrality, which is dependent upon the

charge z of the complex; and

$$q = z / [\text{charge } Y].$$

The amount of bleach catalyst present in the compositions of the invention may suitably range from 0.01 to 1.0 wt.%, depending on the amount of sodium percarbonate present.

5 The bleach catalyst is preferably in the form of granules as described and claimed in our co-pending unpublished European Patent Application No. 92 310 504.3, filed on 18 November 1992.

These granules comprise:

- (i) from 0.5 to 8 wt.% of the catalyst itself,
- (ii) optionally from 0 to 90 wt.% of an inert salt selected from chlorides, carbonates and mixtures thereof,
- 10 and
- (iii) from 5 to 91 wt.% of a binding agent selected from water-soluble non-oxidisable polymers, alkali metal silicates, saturated fatty acid soap mixtures, and combinations of these.

A preferred binding agent is sodium silicate, and a preferred inert salt is sodium carbonate.

15 Preferred granules include catalyst/sodium stearate/lauric acid granules, and catalyst/sodium carbonate/sodium silicate/zeolite granules.

Other ingredients

20 The bleach compositions of the invention may also contain any carrier material, diluent, binder or other adjuvant necessary or beneficial in order to obtain a stable, free-flowing granule.

It is also within the scope of the invention for the bleach composition to contain other active ingredients useful in the laundry process, provided, of course, that any such ingredients are compatible with the bleach ingredients. Such ingredients are preferably present only in minor amounts, for example, up to 10 wt.% and preferably not exceeding 5 wt.%.

25 The bleach compositions of the invention preferably contain, as a carrier or diluent, a salt selected from alkali metal bicarbonates, alkali metal sesquicarbonates, and alkali metal dihydrogen phosphates. The salt is suitably present in an amount of from 5 to 85 wt.%, preferably from 10 to 70 wt.%.

The preferred salt is sodium bicarbonate.

30 As previously indicated, bleach compositions comprising sodium percarbonate, a bleach activator and a salt as defined above are described and claimed in EP 427 314A (Unilever). The presence of sodium bicarbonate or one of the other proposed salts is highly effective in preventing premature reaction between sodium percarbonate and the bleach activator, and renders the use of coated or treated percarbonate unnecessary.

35 If desired, the sodium bicarbonate may be partially replaced by sodium carbonate, up to a level of equality with the sodium bicarbonate, without loss of stability.

A preferred embodiment which is a fairly concentrated bleaching composition essentially comprises:

- (a) from 30 to 85 wt.% of sodium percarbonate,
- (b) from 5 to 30 wt.% of bleach activator,
- (c) from 0.01 to 1.0 wt.% of bleach catalyst (in granular form),
- 40 (d) from 10 to 70 wt.% of sodium bicarbonate, and
- (e) from 0 to 35 wt.% of sodium carbonate.

To this composition, for example, about 1 wt.% of coloured speckles may be added for the purpose of product identification. Preferred speckles are, for example, blue- or green-coloured sodium carbonate speckles.

45 Specifically preferred are those compositions which combine optimal stability with optimal performance when used as a bleach additive, comprising essentially:

- (a) from 40 to 60 wt.% of sodium percarbonate,
- (b) from 12 to 25 wt.% of bleach activator,
- (c) from 0.01 to 1.0 wt.% of bleach catalyst (in granular form),
- 50 (d) from 20 to 50 wt.% of sodium bicarbonate, and
- (e) from 0 to 15 wt.% of sodium carbonate.

Preparation of the bleach composition

55 The bleach compositions of the invention may be prepared by simple mixing of the dry ingredients in any suitable mixing equipment.

The Baukasten detergent system

In its second aspect, the invention is concerned with a laundry detergent system of the Baukasten (building block)-type which provides, in separate packs, a main wash powder, adequate in itself for lightly soiled loads, and a bleach additive to supplement the main wash powder when the load is heavily soiled. The Baukasten system has the environmental benefit of reducing the unnecessary usage of chemicals.

In some Baukasten systems the main wash powder may be underbuilt, and thus suitable for soft water usage, and a separately packaged builder additive may be available to supplement its performance under hard water conditions.

A preferred Baukasten system is described in detail in EP 419 036A (Unilever).

The invention will now be illustrated by the following non-limiting Examples, in which parts and percentages are by weight unless otherwise stated.

Examples 1 and 2, Comparative Example A

The following bleach compositions (in parts by weight) were prepared by dry-mixing sodium percarbonate, sodium bicarbonate, TAED granules (83 wt.% active), and catalyst granules (1.2 wt.% active):

	1	2	A
Sodium percarbonate	51.0	51.0	51.0
Sodium bicarbonate	27.0	27.0	27.0
TAED (as 100 wt.% active)	18.3	18.3	18.3
Mn catalyst (as 100% active)	0.02	0.03	-

The composition of the TAED granules was as follows:

TAED	83.0
Sodium sulphate	9.2
Acrylic/maleic copolymer	2.3
Bentonite clay	2.3
Water and minor salts	3.2

	100.0

The composition of the catalyst granules was as follows:

Mn catalyst	1.2
Light soda ash	52.8
Sodium silicate	18.5
Zeolite 4A (as anhydrous)	14.0
Water	13.5

	100.0

Examples 1 and 2 were in accordance with the invention, while Example A was a control containing no bleach catalyst.

The use of these bleach additives in a Baukasten detergent product consisting of a main wash powder, a builder additive, and a bleach additive was studied. The main wash powder and builder additive had the following compositions:

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Main wash powder (spray-dried with some post-dosed ingredients)	
	%
Anionic surfactant (primary alcohol sulphate)	6.22
Nonionic surfactants	14.12
Soap	2.29
Zeolite 4A (as anhydrous)	38.78
Sodium carbonate	16.55
Sodium carboxymethyl cellulose	0.60
Moisture	11.48
Antifoam granules	2.50
Sodium disilicate granules	5.00
Enzymes	1.95
Perfume	0.50

	100.00

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Builder additive	
Granular zeolite	77.00
Sodium citrate dihydrate	5.00
Sodium carbonate	18.00

	100.00

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Wash appraisals were carried out in a Siemens Siwamat machine using the 40 °C and 60 °C wash cycles (main wash only), 3.5 kg naturally soiled cotton wash loads including test cloth monitors, and 26 ° French hard water.

The product dosage was as follows:

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Main wash powder	63.75 g
Builder additive	12.40 g
Bleach additive (1, 2 or A)	18.00 g

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The measure of bleaching efficiency used was the reflectance increase at 460 nm of test cloth monitors carrying various bleach-sensitive stains, for example, tea, red wine, shoe polish, lipstick, cocoa, grass, and blood. Some representative results at 40 °C were as follows:

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Stain	Reflectance increase at 460 nm	
	2	A
Tea (baked)	16.8	7.0
Tea (fresh)	20.7	12.5
Wine (fresh)	15.7	5.4
Shoe polish	45.8	44.4
Lipstick	9.0	4.2
Wine (baked)	20.4	17.8

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In general, the compositions containing bleach additives 1 and 2 showed very similar results, which were always significantly better than those obtained using the composition containing the control bleach additive A at both 40 °C and 60 °C. This was true over a wide range of different stains.

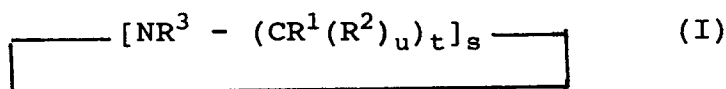
The results obtained from the compositions containing bleach additives 1 and 2 also compared favourably with corresponding results obtained using the recommended dosages of two commercially available fully formulated bleaching detergent compositions. The difference was particularly marked on tea

stains at both wash temperatures.

Claims

- 5 1. A particulate bleach composition for laundry use, comprising :
 (a) sodium percarbonate,
 (b) optionally, a bleach activator;
 (c) a bleach catalyst comprising a source of Mn and/or Fe ions and a ligand which is a macrocyclic organic compound of formula I:

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wherein t is an integer from 2 to 3; s is an integer from 3 to 4, u is zero or one; and R¹, R² and R³ are each independently selected from H, alkyl and aryl, both optionally substituted.

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2. A bleach composition as claimed in Claim 1, wherein the ligand of the bleach catalyst (c) is 1,4,7-trimethyl-1,4,7-triazacyclononane (1,4,7-Me₃TACN).

3. A bleach composition as claimed in Claim 1 or Claim 2, wherein the sodium percarbonate has a protective coating.

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4. A bleach composition as claimed in Claim 3, wherein the protective coating of the sodium percarbonate comprises one or more salts selected from sodium metaborate, sodium silicate and sodium citrate.

5. A bleach composition as claimed in any preceding Claim, wherein the bleach catalyst (c) is in the form of a granular material comprising from 0.5 to 8 wt.% of catalyst.

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6. A bleach composition as claimed in Claim 5, wherein the bleach catalyst granules also comprise from 0 to 90 wt.% of an inert salt selected from chlorides, carbonates and mixtures thereof, and from 5 to 91 wt.% of a binding agent selected from water-soluble non-oxidisable polymers, alkali metal silicates, saturated fatty acid soap mixtures, and combinations of these.

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7. A bleach composition as claimed in any preceding Claim, which further comprises an adjuvant selected from carriers, diluents, fillers and binders.

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8. A bleach composition as claimed in Claim 7, which further comprises a salt selected from alkali metal bicarbonates, alkali metal sesquicarbonates, and alkali metal dihydrogen orthophosphates.

9. A bleach composition as claimed in any preceding Claim, which comprises as bleach activator tetraacetyl ethylene diamine.

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10. A bleach composition as claimed in any preceding Claim, which comprises:

- (a) from 10 to 90 wt.% of sodium percarbonate,
 (b) from 4 to 40 wt.% of bleach activator,
 (c) from 0.01-1.0 wt.% of bleach catalyst in granular form, and
 (d) from 5 to 85 wt.% of sodium bicarbonate.

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11. A bleach composition substantially as described in Example 1 or Example 2 herein.

12. A detergent system of the Baukasten (building block)-type for washing soiled laundry, comprising as separate components:

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- (i) a main wash powder comprising one or more organic surfactants and one or more detergency builders;
 (ii) optionally a builder additive, and
 (iii) a bleach additive which is a composition as claimed in any preceding claim.



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EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 94200634.7
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X, D	<u>EP - A - 0 458 397</u> (UNILEVER) * Claims; page 2, line 58 - page 5, line 53; page 11, lines 37-39; page 12, lines 2-6; page 13, lines 5-8; examples VI, VIII *	1, 2, 5, 7-9, 12	C 11 D 3/39
Y, D	--	1, 3, 4, 6	
Y, D	<u>GB - A - 2 122 044</u> (KAO) * Claims; examples *	1, 3, 4, 6	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 11 D
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 27-04-1994	Examiner SEIRAFI
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			