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(54) Title: LIQUID BLEACHING COMPOSITIONS

(57) Abstract

A sodium hypochlorite liquid bleaching composition incorporates a low molecular weight polyacrylate to inhibit limescale deposition when used in a toilet bowl.

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Liquid Bleaching Compositions

The present invention relates to liquid bleaching compositions particularly hypohalite based compositions.

Liquid bleaching compositions have a particular use in cleaning surfaces. Available compositions include those which are suitable for direct application to work surfaces, utensils, cookers, and the like to aid the removal of persistent soiling, as well as having a cleansing effect. Some compositions are proposed for automatic dishwashing, and some are suited to laundry washing applications. The present application is particularly concerned with liquid bleaching compositions which are primarily used for cleaning toilet bowls.

Typically, the surface of a toilet bowl above the waterline, and particularly under the rim of the bowl, is coated with a liquid bleaching composition once a day, or once a week in domestic environments. The composition will remain in place until the toilet is next used, which may be several hours later. Some of the composition will, inevitably, flow down the bowl surface into the water in the bowl. Some liquid bleaching compositions have a tendency to cause limescale deposition (that is deposition of relatively insoluble calcium and magnesium salts), particularly in the region of the rim and also from the water in the toilet bowl. This can impair the shine of the bowl surface which is undesirable as the shine will denote cleanliness to the user, as well as forming a site for enhanced limescale deposition even at other times when the bowl is not treated with the bleaching composition.

There has, therefore, long been a need for a liquid bleaching composition which has a reduced tendency to promote limescale deposition in a toilet bowl.

We have found that limescale deposition in a toilet bowl can be reduced by incorporating a polyacrylate polymer in the bleaching composition.

Thus, a first aspect of the present invention provides the use, in a bleaching composition, of a polyacrylate polymer for the purpose of inhibiting limescale deposition when the bleaching composition is used in a toilet bowl.

A second aspect of the invention provides a process of cleaning a toilet bowl, comprising coating the surface of the bowl with a liquid bleaching composition which incorporates a polyacrylate polymer to inhibit limescale deposition in the bowl in the presence of the composition.

For use in a toilet, the bleaching composition is a thick composition, having a viscosity of at least about 50 cps measured at 20 degrees centigrade with a Brookfield LV viscometer, spindle 2. The viscosity is preferably less than about 5000 cps, and most preferably is in the range from about 300 to about 500 cps.

The present invention also contemplates a thick bleaching composition incorporating a carboxylic type polyacrylate polymer.

The bleaching composition very preferably is a hypohalite based composition, particularly sodium and/or potassium hypochlorite.

The polyacrylate family of polymers has long been recognised as having efficacy in liquid bleaching compositions for various uses and reasons. Higher molecular weight polymers may simply be used as viscosity enhancers, whilst a variety of polymers are proposed as sequestering agents, particularly to stabilise chlorine based bleaching compositions during storage by sequestering metal ions, and also as sequestrants in many laundry formulations.

EP-A-824 147 describes a liquid bleaching compositions for laundry use. The compositions incorporate sodium hypochlorite as the bleaching agent and 0.2 weight % or less of a polyacrylate polymer. These compositions have a reduced tendency to cause fabric damage and yellowing and are suitable for use with natural fabrics as well as synthetics.

US-A-3 663 442 also describes a liquid bleaching composition for whitening fabrics, incorporating a terpolymer. WO97/43395 describes the use of a polycarboxylate sequestrant to reduce the attack of manganese and iron cations on fabrics during laundry washing.

EP-A-442 191 describes a liquid bleaching composition for detergent use, in particular removing milk solids from utensils and work surfaces. The compositions have an active chlorine source, a high alkali metal hydroxide content (10 weight %) and an acrylic co-polymer. The specific copolymers used are thought to be active at the site

of the soil, removing calcium from the protein-calcium-fat complexes to break down the complex.

EP-A-606 707 describes the use of a cross-linked polyacrylate polymer to increase the viscosity and reduce odour of a liquid bleach for hard surface cleaning.

US-A-4 839 077 uses an ethylene and acrylic acid copolymer to thicken a liquid bleach for surface cleaning.

EP-A-373 864 describes a thickened aqueous bleach composition which is particularly suited to toilet bowls.

EP-A-018 344 describes the use of sodium polyacrylate to inhibit manganese staining in toilet bowls. The polyacrylate is contained in a separate dispenser to the bleaching compound.

Despite the apparently widespread use of polyacrylates, the selection of an appropriate polyacrylate is not straightforward. Some polymers can have a decomposing effect on sodium hypochlorite as well as affecting the viscosity. These parameters must remain within acceptable limits during the expected storage time of the bleach.

Preferably the polyacrylate is a carboxylic polymer, that is a polymer formulated from unsaturated carboxylic acid monomer units such as acrylic acid. The poly(acrylic acid) polymer is preferred.

The liquid bleaching composition used in this invention preferably incorporates a polyacrylate having *weight average* a molecular weight less than 5,000 and preferably from about 2,000 to about 5,000, more preferably from about 2,000 to about 4,000 and most preferably from about 3,000 to about 4,000.

Very preferably the polyacrylate is a phosphono terminated carboxylic polymer having a *weight average* molecular weight of about 3,500. Such a polymer is marketed by Rohm & Haas under the trade name NORASOL 470 N.

Preferably the polyacrylate is present in an amount of from about 0.001 to about 2 per cent by weight, preferably less than 1.0 per cent and more preferably about 0.1 to about 0.5 per cent. It is particularly preferred if the polacrylate is present in an amount from about 0.2 to about 0.3 per cent, with 0.25 percent being the preferred amount as a balance between cost and performance.

The preferred liquid bleaching composition utilises a hypohalite, preferably a hypochlorite and, preferably in an amount of from about 0.5 to about 10 percent by weight, preferably from about 3 to about 7 per cent, and most preferably about 5 per cent by weight of the composition.

A potassium hypohalite is particularly preferred. A sodium hypohalite may also be used, and may be used in combination with a potassium hypohalite.

A thickening agent other than a polyacrylate is preferred. The thickening agent is used to give the required viscosity of the formulation. Thickening agents are discussed in, for example, EP-A-137 551, EP-A-256 638 and WO 95/02664. A particularly preferred thickening agent is a combination of alkyl ether sulphate and alkoyl sarcosinate. Preferably the thickening agent will be present in an amount of less than about 5% by weight of the composition.

An alkaline sodium or potassium hydroxide is preferably present in an amount less than 5 % by weight, more preferably less than about 2.0 % by weight of the composition, and preferably between about 0.6 and about 1.0 % by weight. Alkaline buffering agents such as sodium or potassium carbonate, silicate or phosphate may also be used.

A bleach stable perfume may also be present, and a colourant such as a phthalocyanine.

Examples

The following control formulation was prepared

	Wt%	
Sodium hypochlorite	5.0	(4.7% as available chlorine)
Sodium lauryl ether sulphate[1]	2.0	
Alkoyl sarcosinate[2]	0.15	
Sodium hydroxide	0.8	
Perfume	0.016	
Sodium metaperiodate[3]	0.004	
Soft Water	balance to 100.	

1. EMPICOL ESB3D
2. HAMPOSYL L30
3. Metal ion sequestrant for bleach stability.

Further formulations were prepared by adding to the control 0.25% and 0.5% by weight (of the control formulation) of a carboxylic polymer as follows.

EXAMPLE	1	2	3	4	5	6	7	8
POLYMER/WT%								
LMW-45N	0.25	0.50						
470 N			0.25	0.50				
440N					0.25	0.50		
420							0.25	0.50

All the polymers were from the NORASOL (trade mark) range of polyacrylate polymers marketed by the NorsoHaas division of Rohm & Haas.

LMW-45N is a polyacrylic acid homopolymer of molecular weight about 4,500.
470 N is a carboxylic polymer having a phosphono end group, MWt. about 3,500.
440 N is a carboxylic polymer having a phosphino end group, MWt. about 3,500.
420 is a carboxylic polymer having a phosphono end group, MWt. about 2000.

The formulations were stored for 3 days at room temperature and then 16.5 ml aliquots of the control solution and of the exemplary formulations were added to respective beakers containing 1 litre of tap water having a hardness of about 300 ppm measured as $CaC0_3$.

A glass slide was placed at the bottom of each beaker. In the control solution, the glass slide began clouding immediately, indicating deposition of scale. The formulations of the invention, incorporating the polyacrylate, all showed better performance, with the glass slide remaining clear for a substantial period of time.

The higher molecular weight polymer, examples 1 and 2, showed some noticeable clouding in a matter of hours. The examples 3 to 8 using the lower molecular weight polymer showed better performance. The examples incorporating the greater amount of polymer (examples 2, 4, 6 and 8) all showed somewhat better performance

than the respective examples 1, 3, 5 and 7 which incorporated the lower amount of polymer. However, in the commercial formulation the lower amount is to be preferred.

The affect of molecular weight on chlorine stability was measured by adding to the control formulation above 0.5% by weight (of active polymer) as follows

Polymer	Supplier	Molecular Weight	Inclusion Concentration (active Polymer)	% Chlorine Remaining After 62 days at 37°
POC AS2020 (50% Polycarboxylate, sodium salt)	Degussa	8200	0.50	3.40
POC AS5060 (40% polycarboxylate, sodium salt)	Degussa	22500	0.50	11.68
Degapas 1105N (45% polyacrylate, sodium salt)	Degussa	6500	0.50	2.12
Norasol 470N	Norsohaas	3500	0.50	46.92
Norasol lMW45N	Norsohaas	4500	0.50	48.41
Norasol 440N	Norsohaas	3500	0.50	47.77
Control	None	N/A	N/A	49.04

It can be seen that the lower molecular weight polymers have only a marginal affect on chlorine stability, whereas the higher molecular weights resulted in quite poor chlorine stability. (It is anticipated that the polymer end grouping may also have some effect on stability).

CLAIMS:

1. The use, in a bleaching composition, of a polyacrylate polymer for the purpose of inhibiting limescale deposition when the bleaching composition is used in a toilet bowl.

2. A process of cleaning a toilet bowl, comprising coating the surface of the bowl with a liquid bleaching composition which incorporates a polyacrylate polymer to inhibit limescale deposition in the bowl in the presence of the composition.

3. The process or use of claim 1 or 2, wherein the bleaching composition is a hypohalite based composition.

4. The process or use of claim 3, wherein the hypohalite is sodium hypochlorite.

5. The process or use of any one of claims 1 to 4, wherein the polyacrylate is a carboxylic polymer.

6. The process or use of any one of claims 1 to 5, wherein the polyacrylate has a molecular weight of from about 2,000 to about 5,000, more preferably from about 2,000 to about 4,000, and most preferably from about 3,000 to about 4,000.

7. The process or use of claim 6, wherein the polyacrylate is a phosphono terminated carboxylic polymer.

8. The process or use of any one of claims 1 to 7, wherein the polyacrylate is present in an amount of from 0.001 to 2.0 per cent by weight.

9. The process or use of claim 8, wherein the polyacrylate is present in an amount of from 0.2 to 0.3 per cent.

10. The process or use of any one of claims 1 to 9, wherein the bleaching composition has a viscosity of at least 50 cps.

11. The process or use of claim 10, wherein the bleaching composition has a viscosity of from 300 to 500 cps.

12. A liquid bleaching composition having a viscosity of at least 50 cps and incorporating from 0.1 to 5.0 per cent by weight of a carboxylic polymer.

INTERNATIONAL SEARCH REPORT

Internal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/37 C11D3/395 C11D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	WO 98 21308 A (JOHNSON & SON INC S C) 22 May 1998 (1998-05-22) page 1, line 9 - line 13 page 12, line 1 - line 15 claims 1-5	1,3-5,8, 9
X	EP 0 649 898 A (CLOROX CO) 26 April 1995 (1995-04-26) page 4, line 20 -page 5, line 27	12
A	claims 1-9	1-6,8-10

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	claim 1	1-11
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A	page 2, line 10 - line 14 claims 1-13	1-11
A	EP 0 407 187 A (UNILEVER PLC ;UNILEVER NV (NL)) 9 January 1991 (1991-01-09) page 4, line 34 - line 54 page 6, line 44 - line 49	1-5,8,9, 12
A	EP 0 824 146 A (PROCTER & GAMBLE) 18 February 1998 (1998-02-18) page 5, line 2 - line 22 claims 1-15	1,12

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