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54 **Bleaching composition.**

57 Solutions of hydrogen peroxide which are alkaline, and which are thickened with a combination of surfactant and electrolyte, can be stabilised with colloidal hydrous stannic oxide.

EP 0 376 706 A1

BLEACHING COMPOSITION

This invention relates to liquid bleach compositions which may be thickened liquids suitable for sale and use as a domestic bleach. The compositions of the invention may be pourable liquids, albeit more viscous than water, or may be even more viscous liquids which cannot be poured easily. Thickening of a pourable domestic bleach helps the user to control dispensing of the composition and retards drainage from surfaces to which it is applied.

A domestic bleach needs to be adequately stable so that a substantial proportion of the bleaching agent survives during storage between manufacture and use. Prior to the present invention, commercial liquid bleach products have frequently utilised hypochlorite as bleaching agent.

It is well known that hydrogen peroxide is unstable unless stabilising agents are present. These counteract decomposition catalysed by transition metal ions. Hydrogen peroxide gives better bleaching action if used under alkaline conditions. However, stabilisation of hydrogen peroxide under alkaline conditions is difficult and in consequence commercial solutions of hydrogen peroxide have generally been acidic for the sake of stability.

EP-B-9839 discloses that the stabilisation of hydrogen peroxide under alkaline conditions can be accomplished using certain specified phosphonate compounds. It also contains comparative results testing the effectiveness of various materials as stabilisers under alkaline conditions. These comparative results show that many materials which are known to stabilise acidic hydrogen peroxide have very little effect under alkaline conditions.

One material which has been disclosed as a stabiliser for hydrogen peroxide in acidic solution is colloidal hydrous stannic oxide. US 3781409 and US 3607053 are examples of disclosures of the use of sodium stannate as a stabilising agent for acidic hydrogen peroxide solution. In these US patents the sodium stannate is dissolved in an alkaline but peroxide-free solution which is then added as a stabiliser to very much larger volumes of acidic hydrogen peroxide solution. The sodium stannate will undergo hydrolysis to colloidal hydrous stannic oxide in the solution. The alkaline solution contains other salts in addition to sodium stannate but these are diluted to a very low electrolyte level when added to the acidic hydrogen peroxide solution.

Pourable domestic liquid bleach is frequently thickened by including one or more surfactants which, in the presence of electrolyte, act to thicken the solution so that it becomes more viscous than water.

The presence of electrolyte tends to cause decomposition of alkaline hydrogen peroxide solution. For instance, we have found that a 4% by weight solution of hydrogen peroxide, made alkaline to pH 10 and containing 0.25% of ethylene diamine tetramethylene phosphonic acid as stabiliser (which is not as effective as phosphonates in accordance with EP-B-9839) was found to retain 95% of its hydrogen peroxide after two weeks storage at 37°C. By contrast, 85% or less of the hydrogen peroxide was retained if the solution also contained 1% by weight of sodium chloride, while only about 50% of the hydrogen peroxide was retained if the solution contained 10% by weight of sodium chloride. Similar results were observed using sodium tripolyphosphate rather than sodium chloride as the added electrolyte. Doubling the quantity of the phosphonate stabiliser had little effect on the rate of decomposition.

Thus, any attempt to make a surfactant-thickened, alkaline domestic liquid bleach product using hydrogen peroxide as the bleaching agent would encounter the potential problem that the thickening of the solution would require the presence of some electrolyte but that this electrolyte would serve to accelerate decomposition of the peroxide.

A further potential problem arises because electrolyte inherently tends to bring about flocculation of colloidal suspensions. Consequently the presence of electrolyte also has the potential to bring about a reduction of the effectiveness of any stabilising agent which is in the form of a colloidal suspension.

It is surprising that - as we have now found - colloidal hydrous stannic oxide can act as a very effective stabilising agent for alkaline hydrogen peroxide solutions. It is also surprising that colloidal hydrous stannic oxide will tolerate the inclusion of surfactant and electrolyte in sufficient quantities to effect thickening.

In a first aspect, therefore, the present invention provides a liquid bleaching composition which is an alkaline aqueous solution containing hydrogen peroxide and also containing colloidal hydrous stannic oxide.

Preferably the composition also contains a viscosity-increasing agent which is one or more surfactants in the presence of electrolyte. Preferably therefore a composition according to the invention also contains an electrolyte other than surfactant, together with at least one surfactant which serves in the presence of electrolyte to increase the viscosity of the solution.

The colloidal hydrous stannic oxide which is used as a stabilising agent is preferably formed in-situ in the solution as the product of hydrolysis of a soluble tin compound. Consequently in a second aspect this

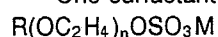
invention provides a method of preparing a liquid bleaching composition which comprises including in the composition, successively or together, hydrogen peroxide, sufficient alkaline material to give the solution an alkaline pH, and a tin compound capable of hydrolysis to stannic oxide, so that the tin compound is hydrolysed in the solution to colloidal hydrous stannic oxide. The hydrolysis may take place in a solution which is already thickened by the presence of surfactant therein, even though the peroxide may not yet have been added to the solution. Various tin compounds can be added to the solution to undergo hydrolysis to form the stannic oxide. Those preferred are tin sulphate and sodium stannate. Other tin compounds can be used, including tin dichloride and tin tetrachloride.

The concentrations of tin compound included in the composition may lie in the range from 10^{-4} molar to 10^{-2} molar, preferably 3×10^{-3} to 6×10^{-4} molar. The quantity of tin compound should not be substantially greater than necessary, since excess of it can itself cause peroxide decomposition. An optimum concentration of the tin compound can be determined by making test solutions with various concentrations of the tin compound and analytically determining the amount of peroxide retained on storage.

The compositions of this invention preferably have a pH in the range from 8.0 to 10.5, better 8.5 to 9.8 or 10.0, yet more preferably 8.7 to 9.3. A buffer may be included to set the pH.

As already mentioned above, it is preferred to include at least one surfactant to increase the viscosity of the composition. It is desirable that this surfactant or surfactants has the ability to thicken a solution in the presence of a fairly low electrolyte concentration. This may make it possible for the electrolyte to be provided by salts which are in the composition for another purpose, without deliberate addition of any salt for the sole purpose of enhancing ionic strength. Since electrolyte is known to be detrimental to hydrogen peroxide stability, it is desirable to keep the electrolyte concentration low. A further benefit of a low electrolyte concentration is a reduced tendency for the composition to leave streaks on a surface which is cleaned with it.

One surfactant which is suitable to effect thickening is alkyl ether sulphate having the formula:



where R is an alkyl group, preferably linear alkyl, containing 8 to 20 carbon atoms, n has an average value in the range from 0.5 to 12 better 1 to 6 and M is a solubilising cation, preferably alkali metal such as sodium.

A pair of surfactants used to effect thickening may be a combination of a nonionic or amphoteric surfactant together with an anionic surfactant. Two specific possibilities are the combinations of:

i) an amine oxide surfactant, preferably a trialkyl amine oxide with one long chain alkyl of 8 to 20 carbon atoms and two alkyl groups of 1 to 4 carbon atoms; and

ii) an anionic surfactant which is either primary alcohol sulphate with 8 to 20 carbon atoms in the alkyl group thereof or alkane sulphonate derived from alkane of 8 to 20 carbon atoms.

Further surfactants may also be present. The total amount of surfactant(s) included may be a small proportion of the composition, for example the thickening surfactant(s) may constitute 0.75 to 3% of the composition. Larger amounts, giving greater viscosity, may be used but are less preferred.

When primary alcohol sulphate is employed, the weight ratio of amine oxide:alcohol sulphate preferably ranges from 82:18 or 80:20 to 65:35, better 80:20 to 70:30.

Alkane sulphonate is preferred over alcohol sulphate, because the viscosity is less sensitive to changes in the composition, so making it easier to produce an end product with repeatable viscosity. The weight ratio of amine oxide to alkane sulphonate is preferably in the range from 80:20 to 50:50 or 65:35, better 70:30 to 65:35.

The electrolyte concentration in a composition of this invention may be such that the total of salts other than surfactant is not more than 7% by weight, better not more than 5% or 3%. The electrolyte level may be such as to give a concentration of electrolyte in the range 0.05 to 0.30 molar, preferably 0.1 to 0.2 molar. Once again higher concentrations may be used but are less preferred.

The concentration of hydrogen peroxide in compositions of this invention, reckoned as pure H_2O_2 , desirably lies in the range from 1 to 15% by weight preferably 2 to 10% by weight.

An appropriate viscosity for a pourable composition having the appearance of a thick liquid is a dynamic viscosity in the range from 50 to 250 centipoise (0.05 to 0.25 Pa.sec), preferably about 100 centipoise (0.1 Pa.sec). More viscous liquids for example with viscosity in the range from 250 to 1000 centipoise or more are also within the scope of the invention.

Since the compositions of this invention are generally aqueous, they will usually have specific gravity close to unity. Consequently values of kinematic viscosities (in stokes) will be numerically approximately the same as values of dynamic viscosity (in poise). Dynamic viscosities expressed in Pascal.sec will be approximately 1000 times kinetic viscosities expressed in $m^2.sec^{-1}$.

Example 1

Formulations were prepared containing the constituents set out in Table 1 below. The compositions were stored in plastic bottles at 37° C. At intervals aliquots were removed and titrated with potassium permanganate to determine the level of hydrogen peroxide remaining. Results are included in Table 1.

The viscosity of these formulations was measured using a Ubbelohde capillary viscometer and found to be approximately 100cS.

TABLE 1

Constituent	% by weight		
	A	B	C
Hydrogen peroxide (reckoned as anhydrous)	5	5	5
Tallow dimethylamine oxide	1.0	1.0	1.0
Sodium alkane sulphonate	0.5	0.5	0.5
Perfume	1.0	1.0	1.0
Tetrasodium pyrophosphate (reckoned as anhydrous)	1.8	-	-
Phosphonate stabiliser according to EP 9839	0.15	-	-
Borax (reckoned as anhydrous)	-	1.6	1.6
Sodium stannate trihydrate	-	0.5	0.1
Sodium hydroxide to give:	pH 9.6	pH 9.6	pH 9.0
Water	----- balance to 100% -----		
H ₂ O ₂ remaining after 50 days:	85%	79%	
H ₂ O ₂ remaining after 100 days:			96%

The stabiliser in accordance with EP 9839 was diethylene triamine penta (methylene phosphonic acid).

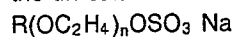
Example 2

The procedure of Example 1 was repeated, using formulations with the same amounts of hydrogen peroxide, surfactant, perfume and dye. Various tin compounds were used at a concentration of 6×10^{-3} molar, both with and without 3.0% borax decahydrate. Glass bottles were used, which are somewhat detrimental to stability. In every case pH was 9.6 initially. Proportions of hydrogen peroxide remaining after 28 days were:-

SnCl ₂ with borax	68%
Na ₂ SnO ₃ with borax	47%
SnSO ₄ with borax	45%
Na ₂ SnO ₃ without borax	96%
SnSO ₄ without borax	95%

Example 3

The procedure of Example 1 was repeated using a different surfactant and with stannous chloride as the tin salt. The surfactant used was a linear alkyl ether sulphate of general formula:



where the alkyl group R was C₁₁ and C₁₃ linear alkyl groups, and n had an average value of 3. A comparative experiment replaced the stannous chloride with the same phosphonate stabiliser according to EP 9839 as used in Example 1. The formulations and results are set out in the following Table. Viscosities

were determined using a Haake roto-viscometer and were approximately 100cP at a shear rate of 21 sec⁻¹.

TABLE 2

Constituent	% by weight	
	A	B
Hydrogen peroxide (reckoned as anhydrous)	5	5
Alkyl ether sulphate	1.25	1.25
Sodium chloride	6.5	6.5
Perfume	0.08	0.08
Stannous chloride dihydrate	0.14	-
Phosphonate stabiliser according to EP 9839	-	0.15
Sodium hydroxide to give:	pH 9.6	pH 9.6
Water	-- balance to 100% --	
H ₂ O ₂ remaining after 5 weeks at 37 ° C	80%	79%

Example 4

An alkaline solution of hydrogen peroxide was prepared containing 4% by weight hydrogen peroxide (reckoned as anhydrous) sodium hydroxide to give a pH of 10 and a 5.7×10^{-3} molar quantity of stannic chloride which hydrolysed to colloidal hydrous stannic oxide.

The composition was stored at 40 ° C and the amount of hydrogen peroxide remaining was determined analytically at intervals. It was found that 75% of the hydrogen peroxide remained after 3 weeks.

Although this test was made without surfactant or much electrolyte present, it confirms the effectiveness of colloidal stannic oxide as a stabiliser in alkaline solution.

Example 5

Alkaline solutions of hydrogen peroxide were prepared containing surfactant, sodium chloride and stannic chloride which hydrolysed to colloidal hydrous stannic oxide. Two surfactant combinations were used.

The quantities of surfactant and sodium chloride were such as to give viscosities well in excess of that preferred for a pourable type of bleach product. Smaller quantities could be used to give a "thick liquid" type of bleach product.

In each case the initial concentration of hydrogen peroxide, reckoned as anhydrous, was 4% by weight. The solutions were made alkaline to pH 10 with sodium hydroxide.

Stannic chloride was used at a concentration of 2.3×10^{-3} molar.

One surfactant system consisted of 4.5% by weight of C₁₂-C₁₄ alkyl dimethyl amine oxide and 4.5% by weight sodium lauryl sulphate. This was used with a sodium chloride concentration of 9% by weight.

The second surfactant system consisted of 5% by weight of C₁₁-C₁₅ secondary alcohol ethoxylated with average 3 ethylene oxide residues, and 5% by weight of sodium lauryl sulphate. This combination was used with 3.37% by weight sodium chloride.

The solutions were stored at 40 ° C and the amount of hydrogen peroxide remaining was determined at intervals. It was found that the amounts of hydrogen peroxide remaining were between 80 and 85% with either of the surfactant combinations.

Example 6

A base solution was prepared containing tallow dimethylamine oxide, sodium alkane sulphonate and borax. This was used to make up solutions containing hydrogen peroxide and colloidal stannic oxide, but

two procedures were used.

In one procedure stannous chloride dihydrate was added to the base solution and stirred until it was completely dissolved or dispersed, after which hydrogen peroxide solution was added. The solution pH at this stage was 6.5. It was adjusted to pH 9.9 by adding 20% w/v sodium hydroxide solution and some distilled water.

The quantities used were such that the composition contained:

Hydrogen peroxide (reckoned as anhydrous)	4.98g
Tallow dimethylamine oxide	0.98g
Sodium alkane sulphonate	0.48g
Borax (reckoned as anhydrous)	1.6 g
SnCl ₂ .2H ₂ O	0.14g
Sodium hydroxide to give:	pH 9.9
Water	balance to 100g total

In the alternative procedure a suspension of stannic oxide was prepared by dissolving 5g of stannous chloride dihydrate in approximately 115g distilled water, and then adding sodium hydroxide solution to give a pH of 9.7. The resulting suspension of stannic oxide was stored overnight.

Hydrogen peroxide was added to the base solution, followed by sodium hydroxide solution and some distilled water to give a pH of 9.9. A small quantity of suspension was then added. This was calculated to be the quantity of suspension produced from 0.14g of SnCl₂.2H₂O. Other quantities were as for the first procedure.

The solutions were both stored at 37° C (to accelerate aging) and the concentration of hydrogen peroxide remaining was determined by analysis after 48 and 120 hours. The results were as follows:

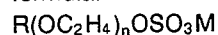
	H ₂ O ₂ concentrations		
	Initially	After 48 hours	After 120 hours
Stannic oxide formed in presence of H ₂ O ₂ and surfactant	4.98	4.95	4.88
Stannic oxide formed separately and aged	4.98	4.81	4.82

Claims

1. A liquid bleaching composition comprising an aqueous alkaline solution containing hydrogen peroxide, electrolyte other than surfactant, at least one surfactant serving, in the presence of the electrolyte, to increase the viscosity of the solution, and also containing colloidal hydrous stannic oxide.

2. A composition according to claim 1 or claim 2 wherein the amount of electrolyte in solution is such that the total quantity of inorganic salts in the composition does not exceed 5% by weight based on the whole composition.

3. A composition according to claim 1 or claim 2 wherein the surfactant is an alkyl ether sulphate of the formula:



where R is an alkyl group containing 8 to 20 carbon atoms, n has an average value in the range from 0.5 to 12 and M is a solubilising cation.

4. A composition according to claim 1 or claim 2 wherein the surfactant is a combination of a nonionic or amphoteric surfactant and an anionic surfactant.

5. A composition according to claim 4 wherein the surfactant is a combination of (i) a trialkyl amine oxide having one C₈ to C₂₀ alkyl group and two C₁ to C₄ alkyl groups and (ii) either a C₈ to C₂₀ alkane sulphonate or a C₈ to C₂₀ alcohol sulphate.

6. A composition according to any one of the preceding claims wherein the amount of surfactant present is in the range from 0.75 to 3% by weight based on the whole composition.

7. A composition according to any one of the preceding claims wherein the concentration of hydrogen peroxide, reckoned as pure H_2O_2 , lies in the range from 1 to 15% by weight of the composition.

8. A composition according to any one of the preceding claims wherein the concentration of tin compound lies in the range from 10^{-4} to 10^{-2} molar.

5 9. A composition according to any one of the preceding claims wherein the pH is in the range from 8.5 to 9.3.

10. A method of preparing a liquid bleaching composition which method comprises including in the composition, successively or together, hydrogen peroxide, sufficient alkaline material to give the solution an alkaline pH, preferably in the range 8.5 to 10, and a tin compound capable of hydrolysis to stannic oxide, so
10 that the tin compound is hydrolysed in the solution to colloidal hydrous stannic oxide.

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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)
Y	EP-A-0 097 305 (FMC CORP.) * abstract; page 3, lines 25-32; page 4, lines 13-21; claims * ---	1,7	C 11 D 3/39 C 11 D 1/29 C 11 D 1/75
Y	CHEMICAL ABSTRACTS vol. 99, no. 22, 28 November 1983, page 113, column 2, abstract no. 177871e, Columbus, Ohio, USA; & JP - A - 83 38 800 (MITSUBISHI GAS CHEMICAL CO.) 07.03.1983 * abstract * ---	1,7	C 11 D 1/83 C 01 B 15/037
Y	CH-A- 356 235 (UNILEVER N.V.) * whole document * ---	1,7	
A	GB-A- 855 679 (UNILEVER LTD.) * whole document * ---	1-7	
A	US-A-3 701 825 (K.J. RADIMER et al.) * abstract; column 3, lines 56-74; claims * -----	1,7-9	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 11 D C 01 B
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 16-03-1990	Examiner 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	