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(12) # EUROPEAN PATENT SPECIFICATION

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(54) **Use of peroxycarboxylic acid-containing suspensions as bleaching compositions, novel bleaching compositions and bleaching compositions in the packaged form.**

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Description

The invention relates to the use as pourable bleaching composition of a suspension in water comprising as a bleaching component a peroxycarboxylic acid derived from a dicarboxylic acid containing 8 to 13 carbon atoms.

Such use is known from British Patent Specification GB 1 535 804. It describes liquid bleach compositions having a viscosity of from 200 to 100 000 mPa.s and containing a peroxide, a thickening agent and water. They are suitable for use in washing machines and automatic clothes dryers.

The advantages to using liquid bleaching compositions over solid bleaching compositions are that in their preparation there is no need for cost-increasing shaping steps, such as drying and granulating, and the fabrics to be treated are rapidly and evenly bleached, so that high concentrations of the bleaching agent in places can be satisfactorily avoided.

To the bleaching compositions of GB—A—1 535 804, at least as far as they are pourable (see below), there is the disadvantage that they are not physically stable, which after prolonged storage results in phase-separated products with a thick bottom layer which is difficult to disperse or homogenize, as a result of which said advantage of even distribution over the fabric to be cleaned may partly be eliminated again.

The present bleaching composition does not show this drawback.

The invention relates to the use of the above type, characterized in that the bleaching composition also comprises an alkali metal salt of an alkyl benzene sulphonic acid having a linear or branched alkyl group containing 9 to 22 carbon atoms in an amount of 0.5 to 15% by weight, calculated on the weight of the composition.

An additional advantage to the present composition is that, provided that the proportions of the constituents to be used are properly chosen, it is protected from hazards due to spilling and drying up, as a result of which solid peroxide particles are formed. Of peroxides in the solid state it is known that they exposed to explosion, shock and abrasion hazards. But in the event of spilling and drying up of properly chosen present suspensions solid peroxide particles will form that are provided with a coating such that they are desensitized. The pourable compositions disclosed in GB—A—1 535 804 are not protected in that way, the amount of thickening agent required for these compositions being so small that in the event of spilling and drying up solid particles are formed that are insufficiently desensitized. From experiments it has moreover been found that this drawback cannot be eliminated by the addition to these suspensions of well-known desensitizing agents such as sodium sulphate, because the properties of these suspensions will be even further deteriorated then.

It should be noted that the present suspensions, containing a peroxycarboxylic acid and an alkali metal salt of an alkyl benzene sulphonic acid, are disclosed in US—A—4 126 573. Said patent specification, however, relates to solid, granular bleaching compositions and the present suspensions are merely applied for the preparations of these solid compositions by drying, which is in the light apparently of what is mentioned in the introductory part of US—A—4 126 573 (column 1, lines 17—20), namely that the liquid bleaching compositions containing peroxyacid materials as the active bleaching agent have the tendency to diminish in bleaching effectiveness over prolonged storage periods.

Therefore, in view of US—A—4 126 573, the use of the present suspensions as bleaching composition is not at all obvious. For, if the peroxycarboxy acid is finely dispersed in the water, the chance of decomposition during storage is great. Moreover, from experiments it has been found that such decomposition occurs in the case of a great many anionic and nonionic emulsifiers. It has been found, however, that the presence of an alkali metal salt of an alkyl benzene sulphonic acid as emulsifier has no or hardly any detrimental effect on the active oxygen content of the composition.

The composition according to the invention is physically stable, i.e. after storage for 6 weeks at 20°C the peroxycarboxylic acid is well dispersed and the suspension does not display any phase-separation. If precipitation takes place at all, the homogeneity of the dispersion can be readily restored by gently shaking it.

Moreover, the composition according to the invention is chemically stable, i.e. after storage for 2 weeks at 40°C it still has the same or practically the same active oxygen content.

The composition according to the invention is pourable, by which is to be understood that at 20°C the composition has a viscosity between 1 and 1200 mPa.s, preferably between 50 and 500 mPa.s (Brookfield rotational viscometer [RV type], 20 rpm).

The invention also relates to those bleaching compositions that are new as such and to the present bleaching compositions in the packaged form.

The bleaching component in the present composition consists of a peroxycarboxylic acid derived from a dicarboxylic acid containing 8 to 13 carbon atoms. Such peroxycarboxylic acids are not, or hardly soluble in water (solubility less than 1% by weight in water at 20°C).

Also mixtures of these acids may be used.

It is preferred that the present composition should contain diperoxy dicarboxylic acids, such as 1,12-diperoxydodecanedioic acid, 1,13-diperoxytridecanedioic acid or suitable mixtures thereof.

The preparation of these acids is effected in a known manner by reacting the corresponding dicarboxylic acids with hydrogen peroxide in the presence of sulphuric acid.

Generally, the composition according to the invention contains peroxycarboxylic acid in an amount

such that the active oxygen content of the composition is between 0,1 and 4%, preferably between 0,1 and 3%.

The present composition must contain an alkali metal salt of an alkyl benzene sulphonic acid. The alkyl group may be branched or linear and contains 9 to 22 carbon atoms, preferably 9 to 15 carbon atoms, more particularly 11 to 13 carbon atoms. As examples of these alkyl benzene sulphonates may be mentioned sodium undecyl benzene sulphonate, sodium dodecyl benzene sulphonate and sodium tridecyl benzene sulphonate. Also mixtures of these sulphonates may be used.

It is preferred that the composition according to the invention should contain sodium dodecyl benzene sulphonate.

The alkali metal salt of an alkyl benzene sulphonic acid should be used in an amount such that the composition is pourable and physically stable. Therefore, the composition will contain alkali metal salt of an alkyl benzene sulphonic acid in an amount of 0,5 to 15% by weight, and preferably 2 to 10% by weight, calculated on the weight of the composition. Use of amounts less than 0,5% by weight will result in compositions that have insufficient physical stability; use of amounts higher than 15% by weight will result in obtaining viscous compositions that are no longer pourable.

The alkali metal salts of alkyl benzene sulphonic acids commonly used in actual practice as emulsifier are so-called technical products in which as impurity an inorganic salt such as sodium sulphate is contained. Although these technical products can very well be used for preparing the present compositions, a preferred embodiment consists in that also particular inorganic salts are added. It has been found that adding sodium sulphate, potassium sulphate or mixtures thereof has a favourable effect on the physical stability of the compositions, i.e. if there appears to be any precipitation at all upon using a technical emulsifier alone, it can entirely be stopped by the additional use of said inorganic salts. It has also been found that when use is made of said inorganic salts, compositions with the same properties can be prepared that contain less emulsifier than when no use is made of these inorganic salts. This last-mentioned embodiment is preferred in actual practice because of the considerably lower cost price of the inorganic salts as compared with that of the emulsifier to be used. A preferred inorganic salt is sodium sulphate.

The amount of inorganic salt to be used will partly be dependent on the amount of inorganic salt originating from the emulsifier as impurity and should be such that the bleaching composition is pourable and physically stable. Generally, the bleaching composition according to the invention will contain inorganic salt, including the inorganic salt originating from the emulsifier, in an amount of 0,01 to 20% by weight, preferably 2 to 10% by weight, calculated on the weight of the composition.

The composition according to the invention may still contain other additives, as examples of which may be mentioned:

— thickening agents; examples thereof are described in GB—A—1 535 804. Thickeners can be used in maximum amounts such that the composition remains pourable;

— sequestering agents, which serve to bind any metal ions present that may accelerate the decomposition of peroxides. Examples of sequestering agents are ethylene diamine tetra acetate, sodium pyrophosphate, phosphoric acid, dipicolinic acid and hydroxy ethylidene diphosphonic acid. They may be used in amounts of 0,01 to 1% by weight, calculated on the weight of the composition;

— builders, such as polycarboxylates, and finally optical brighteners, perfumes and organic solvents.

The present bleaching compositions may very effectively be used in the pre-bleaching treatment of dirty washing at low temperature (say, about 30°C). In the treatment of dirty washing with the usually applied heavy and light duty detergents they are also very suitable to be separately added to the wash liquor. Their effect is at least equivalent to that of the bleaching compositions disclosed in GB—A—1 535 804.

The compositions according to the invention may be prepared by adding the peroxycarboxylic acid, with stirring, to an acidified mixture (preferably pH 3,5—4,5) of water, alkyl benzene sulphonate and any other additives. The peroxycarboxylic acid may be used in the form of powder (primary particle size 1—100 micrometers) or in the form of wet filter cake, as obtained after the peroxycarboxylic acid preparation from the corresponding dicarboxylic acid and hydrogen peroxide. If necessary, the pH of the composition is finally set to a particularly desired value, which should be in the acid range, use being made of, for instance, aqueous sodium hydroxide or hydrochloric acid. It is preferred that the pH should not be higher than 5. Higher values would have a detrimental effect on the chemical stability of the composition. A pH lower than 2, however, should also be avoided. For, due to dilution with water of such composition the resulting insufficiently high final pH would cause the metal parts of the washing machine in which it is used to be subject to corrosion. Particularly preferred are compositions having a pH of 3,5—4,5, more particularly 3,9—4,1.

The invention will be further described in the following examples. All percentages are by weight.

Example 1

Compositions as mentioned in Table 1 were prepared. Compositions 1—6 are according to the invention. The pH values of these compositions were in the range of 3,5 to 4,5. Composition 7 is according to GB—A—1 535 804.

Table 1

Composition	1	2	3	4	5	6	7
diperoxydodecane-dioic acid wet filter cake (g) content 5,1% active oxygen	23,3	31,8	31,8				31,8
content 4,8% active oxygen				62,5	62,5	67,5	
sodium dodecyl benzene sulphonate content 85% (g)	6,44	6,44	6,44	5,8	5,8		
sodium tridecyl benzene sulphonate content 30% (g)						18,7	
methyl hydroxybutyl cellulose Methocel HB® (g)							0,8
sodium sulphate [anh] (g)	12	12		1,7	5,8	3,7	
hydroxyethylidene diphosphonic acid Dequest 2010® (g)	0,5	0,5	0,5	0,4	0,4	0,4	
water (g)	58	49,3	61,3	30	26	10	68
active oxygen content (%)	1,19	1,61	1,61	3,02	3,08	3,24	1,62
viscosity (mPa.s)	223	460	26	300	890	470	465

Of each composition a sample was stored for the purpose of evaluating the chemical stability. After 2 weeks at 40°C all samples had retained their active oxygen content.

Moreover, of each composition a sample was stored for the purpose of assessing the physical stability. After 6 weeks at 20°C samples of the compositions 1, 2, 4, 5, and 6 did not display any phase-separation or precipitation phenomena. Although the sample of composition 3 had precipitated, no thick bottom layer had formed and the original homogeneity of the dispersion could be restored by gentle shaking. But the sample of composition 7 had precipitated and a thick bottom layer had formed (phase-separated) which could not very well be re-dispersed.

For the purpose of assessing the differences in safeguarding against the hazards resulting from spilling and drying up between the compositions according to the invention on the one hand and a composition according to GB—A—1 535 804 on the other, samples of compositions 2, 3 and 7 were evaporated to dryness by means of an air stream at 25°—30°C, after which the material thus obtained was subjected to a Pressure Vessel Test. This test is described in Vervoer Gevaarlijke stoffen, 23 December 1980, Aanhangsel AI bij bijlage A, pp. 907, 908, 915: Staatsuitgeverij. In this test 10 grammes of the material to be tested are heated by a standardized gas flame in a pressure vessel fitted with a bursting disk set to 6 bar. In the side wall of the pressure vessel is a blow-off opening with variable diameter.

The test procedure implies that such a blow-off opening is found that after decomposition (explosion, combustion) of the peroxide, the bursting disk is still just intact. The smaller the admissible opening, the safer the formulation. The admissible opening (in mm) is given as PVT value.

The PVT values found for the material from composition 2 were less than 1 mm, from composition 3 less than 1 mm, and from composition 7 they were 6 mm. (The PVT value for pure diperoxydodecanedioic acid is 7 mm).

Example 2

In this example the effect is given of different anionic and nonionic emulsifiers on the chemical stability of peroxycarboxylic acid suspensions.

Suspensions were prepared from diperoxydodecanedioic acid (11,65 g of wet filter cake with an active oxygen content of 5,1%), hydroxyethylidene diphosphonic acid (Dequest 2010®; 0,25 g), emulsifier and water; the pH of the suspensions was 3,9—4,1.

The nature of the emulsifiers and the amounts thereof as well as the amounts of water are given in the table below. The data on the chemical stability of the suspensions, i.e. the active oxygen content of the suspensions after storage at 40°C, are mentioned in the lower part of the table.

Table 2

suspension	water (g)	emulsifier
1	20,7	17,65 g sodium dodecyl benzene sulphonate (85%)
2	23,35	15 g sodium lauryl sulphate
3	23,35	15 g sodium C_{15}-alkyl.3 EO sulphate (Tergitol 15 S3A®)
4	23,35	15 g ethoxylated (9 EO) nonyl phenol
5	23,35	15 g ethyleneoxide/propyleneoxide copolymer (Genapol PF 20®)
6	13,35	25 g sodium sec.alkyl sulphate (60%) Hostapur SAS®

	active oxygen content (%)					
suspension	1	2	3	4	5	6
start	1,15	1,15	1,15	1,15	1,18	1,18
1 day		1,02	1,12			
3 days				1,00		
4 days		0,82	0,97	0,93		
5 days		0,75	0,91	0,87		
1 week	1,15				1,17	1,03
2 weeks	1,12				<0,86	1,00

The results in the table show that emulsifiers other than alkyl benzene sulphonate have a detrimental effect on the chemical stability of peroxycarboxylic acid-containing suspensions.

It should be added that suspension 1 is not a composition according to the invention; it contains about 30% of emulsifier and has a viscosity of 1975 mPa.s. It has been found that the effect of emulsifiers on the chemical stability of peroxycarboxylic acid compositions can very well be established when they are used in relatively high concentrations.

Claims

1. Use as pourable bleaching composition of a suspension in water comprising as a bleaching component a peroxycarboxylic acid derived from a dicarboxylic acid containing 8 to 13 carbon atoms, characterized in that the bleaching composition also comprises an alkali metal salt of an alkyl benzene sulphonic acid having a linear or branched alkyl group containing 9 to 22 carbon atoms in an amount of 0,5 to 15% by weight, calculated on the weight of the composition.

2. Use according to claim 1, characterized in that the alkyl group of the alkali metal salt of an alkyl benzene sulphonic acid contains 9 to 15 carbon atoms.

3. Use according to claim 1, characterized in that the alkali metal salt of an alkyl benzene sulphonic acid is sodium dodecyl benzene sulphonate.

4. Use according to claim 1, characterized in that the bleaching composition also comprises sodium sulphate, potassium sulphate or a mixture thereof.

5. Use according to claim 4, characterized in that the sodium sulphate, potassium sulphate or mixture thereof is used in an amount of 0,01 to 20% by weight, calculated on the weight of the bleaching composition.

6. A pourable, aqueous bleaching composition comprising as a bleaching component a suspended peroxycarboxylic acid derived from a dicarboxylic acid containing 8 to 13 carbon atoms, characterized in that the bleaching composition also comprises an alkali metal salt of an alkyl benzene sulphonic acid having a linear or branched alkyl group containing 9 to 22 carbon atoms in an amount of 0,5 to 15% by weight and sodium sulphate, potassium sulphate or a mixture thereof in an amount of 0,01 to 20% by weight, said amounts being calculated on the weight of the composition.

7. A pourable, aqueous bleaching composition according to claim 6, characterized in that the peroxycarboxylic acid is 1,12-diperoxydodecanedioic acid and the alkyl group of the alkali metal salt of an alkyl benzene sulphonic acid contains 9 to 15 carbon atoms.

8. A packaged bleaching composition, the bleaching composition being of the type described in any one of the preceding claims.

Patentansprüche

1. Verwendung eines giessbaren Bleichmittels aus einer Suspension in Wasser, enthaltend als Bleichkomponente eine Peroxycarbonsäure, die von eine Dicarbonsäure mit 8 bis 13 Kohlenstoffatomen abgeleitet ist, dadurch gekennzeichnet, dass das Bleichmittel ausserdem ein Alkalimetallsalz einer Alkylbenzolsulfonsäure, die eine lineare oder verzweigte Alkylgruppe mit 9 bis 22 Kohlenstoffatomen aufweist, in einem Anteil von 0,5 bis 15 Gew.%, bezogen auf das Gewicht des Mittels, enthält.

2. Verwendung nach Anspruch 1, dadurch gekennzeichnet, dass die Alkylgruppe der Alkylbenzolsulfonsäure, von der das Alkalimetallsalz abgeleitet ist, 9 bis 15 Kohlenstoffatome enthält.

3. Verwendung nach Anspruch 1, dadurch gekennzeichnet, dass das Alkalimetallsalz der Alkylbenzolsulfonsäure das Natriumdodecylbenzolsulfonat ist.

4. Verwendung nach Anspruch 1, dadurch gekennzeichnet, dass das Bleichmittel ausserdem Natriumsulfat, Kaliumsulfat oder eine Mischung hiervon enthält.

5. Verwendung nach Anspruch 4, dadurch gekennzeichnet, dass das Natriumsulfat, das Kaliumsulfat oder die Mischung hiervon in einem Anteil von 0,01 bis 20 Gew.%, bezogen auf das Gewicht des Bleichmittels, verwendet wird.

6. Giessbares, wässriges Bleichmittel, enthaltend als Bleichkomponente eine suspendierte Peroxycarbonsäure, die abgeleitet ist von einer Dicarbonsäure, welche 8 bis 13 Kohlenstoffatome enthält, dadurch gekennzeichnet, dass das Bleichmittel ausserdem ein Alkalimetallsalz einer Alkylbenzolsulfonsäure, die eine lineare oder verzweigte Alkylgruppe mit 9 bis 22 Kohlenstoffatomen aufweist, in einem Anteil von 0,5 bis 15 Gew.% und Natriumsulfat, Kaliumsulfat oder eine Mischung hiervon in einem Anteil von 0,01 bis 20 Gew.% enthält, wobei die Anteile auf das Gewicht des Mittels bezogen sind.

7. Giessbares, wässriges Bleichmittel nach Anspruch 6, dadurch gekennzeichnet, dass die Peroxycarbonsäure die 1,12-Diperoxydodecandisäure ist und die Alkylgruppe der das Alkalimetallsalz bildenden Alkylbenzolsulfonsäure 9 bis 15 Kohlenstoffatome enthält.

8. Verpacktes Bleichmittel, wobei das Bleichmittel der in einem der vorangehenden Ansprüche beschriebenen Art ist.

Revendications

1. Utilisation en tant que composition de blanchiment capable de s'écouler d'une suspension aqueuse contenant en tant qu'agent de blanchiment un acide peroxycarboxylique dérivant d'un acide dicarboxylique en C_8—C_{13}, caractérisée en ce que la composition de blanchiment contient également un sel de métal alcalin d'un acide alkylbenzène-sulfonique portant un groupe alkyle linéaire ou ramifié en C_9—C_{22}, en proportion de 0,5 à 15% en poids par rapport au poids de la composition.

2. Utilisation selon la revendication 1, caractérisée en ce que le groupe alkyle du sel de métal alcalin d'acide alkylbenzène-sulfonique contient 9 ax 15 atomes de carbone.

3. Utilisation selon la revendication 1, caractérisée en ce que le sel de métal alcalin d'acide alkylbenzène-sulfonique est un dodécylbenzène-sulfonate de sodium.

4. Utilisation selon la revendication 1, caractérisée en ce que la composition de blanchiment contient également du sulfate de sodium, du sulfate de potassium ou un mélange de ces sels.

5. Utilisation selon la revendication 4, caractérisée en ce que le sulfate de sodium, le sulfate de potassium ou leur mélange est utilisé en proportions de 0,01 à 20% du poids de la composition de blanchiment.

6. Une composition de blanchiment aqueuse capable de s'écouler, contenant en tant qu'agent de blanchiment un acide peroxycarboxylique en suspension dérivant d'un acide dicarboxylique en C_8—C_{13}, caractérisée en ce qu'elle contient également un sel de métal alcalin d'un acide alkylbenzène-sulfonique portant un groupe alkyle linéaire ou ramifié en C_9—C_{22}, en proportions de 0,5 à 15% en poids, et du sulfate de sodium, du sulfate de potassium ou un mélange de ces sels en proportions de 0,01 à 20% en poids, ces proportions étant calculées par rapport au poids de la composition.

7. Une composition de blanchiment aqueuse capable de s'écouler selon la revendication 6, caractérisée en ce que l'acide peroxycarboxylique est l'acide 1,12-diperoxydodécane-dioïque et en ce que le groupe alkyle du sel de métal alcalin d'acide alkylbenzène-sulfonique contient 9 à 15 atomes de carbone.

8. Une composition de blanchiment en emballages, la composition de blanchiment étant du type décrit dans l'une quelconque des revendications qui précèdent.