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(71) Applicant:  
**Manitoba Italia S.p.A.  
20124 Milano (IT)**

(72) Inventors:  
• **Massarani, Giorgio  
20135 Milano (IT)**  
• **Banzatti, Carlo Arnaldo  
20149 Milano (IT)**

(74) Representative:  
**Sama, Daniele, Dr.  
Sama Patents,  
Via G.B. Morgagni, 2  
20129 Milano (IT)**

(54) **Compositions based on percarboxylic acids as cleaning and hygienizing agents**

(57) Use of an aqueous liquid composition, comprising a percarboxylic acid, as a pre-treating, cleaning and antibacterial additive at room, high and low temperatures, for washing machine or hand washing, both for delicate and/or coloured and resistant textiles, to be directly applied on the stains before washing.

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## Description

The present invention relates to the use of cleaning and antibacterial hygienizing compositions to be preferably applied, as laundry pretreat, or prewash, directly on stains before laundering by-hand or in domestic washing machine. The compositions of the present invention, are particularly suitable for stain removal on wool, silk and other delicate or coloured fabrics.

It is known in the art that the removal of the bleachable stains (for instance tea, coffee, red wine, coloured fruits such as plums or bilberries, grass) and disinfection and hygiene of fabrics, in domestic laundering by-hand or in washing machine, are difficult tasks requiring the use of bleaching additives, either alone or in combination with laundry detergents. The task is particularly difficult in the case of stains on coloured and delicate fabrics because delicates need to be washed at warm temperatures (usually not above 30°C) and in slightly acid to slightly basic solutions, i.e. under very mild conditions to avoid fabric damage and similarly for coloured fabrics lower washing temperature are needed to reduce the colour damage. Unfortunately the milder the conditions, the lower the stain removal and disinfection efficacy. On the contrary, when the fabrics can be washed at high temperatures (at or above 60°C), the use of any bleaching additives gives poor improvements because of the good efficiency given by detergents themselves.

It is well established the use of chlorine based bleaching agents: they are very effective, but can be used only on white or few resistant colours and on alkaline- and chlorine-resistant fabrics, such as cotton and some synthetics, but cannot be used on delicates and most coloured fabrics.

Another bleaching system, widely used in powder heavy duty laundry detergents, is based on solid carriers or precursors of active oxygen, for instance persalts as perborates, percarbonates, and/or on percarboxylic acids, generated in situ in the washing solution by reaction of their precursors, known as activators, with hydrogen peroxide; amongst them the most used activator in Europe is TAED. Even if less alkaline and less aggressive than chlorine base bleach towards colours and fabrics, the above mentioned solid oxygen based bleaching systems cannot be used on delicate fabrics and are not fully satisfactory on coloured ones. Furthermore, they cannot be used directly on stains, but only in solution, i.e. in a more or less diluted, and therefore less active, form.

It is also known the use of liquid additives, containing hydrogen peroxide: they can be either directly applied on stains and soiled fabrics before washing or added into the laundry machine or laundry solution. Examples of such compositions commercialised in Italy are: OMINO BIANCO CANDEGGINA DELICATA®, ACE GENTILE®, in Spain: NEUTREX®, in Greece: KLINEX®, SENSO®, in France: BLANCO®, VANISH®, ACE DESICAT®, in Germany: SIL®, ACE MILDE BLEACH®. The hereabove mentioned bleach products are fully compatible with coloured and delicate fabrics, but they are much less effective than the above mentioned other bleaching systems.

The need was therefore felt to find out cleaning and hygienizing liquid additives to be directly applied on the stains both in resistant articles at high temperatures, and on delicate and coloured articles, at room and/or low temperatures, able to produce an effective bleaching action without halos, with a wide applicability range, overcoming the drawbacks of the products of similar use commercially existing.

The Applicant has surprisingly and unexpectedly found that the liquid compositions of the invention to be directly applied on the stains before washing, lead to improved cleaning and hygienizing results.

It is therefore an object of the present invention the use of aqueous liquid compositions, comprising a percarboxylic acid, as stain removing, a pre-treating, cleaning and antibacterial additives very effective at low temperatures, for by-hand or washing machine laundry, both for delicate and/or coloured fabrics. They can be preferably applied directly on the stains before washing, which allows to obtain, washing at room or at low temperature (20-30°C), either much higher disinfecting and stain removing results, than the ones given by the above-mentioned existing liquid additives under the same conditions or the same results given by the above-mentioned existing liquid additives at higher temperatures, so achieving the important goal of a minor colour and fabric damage.

Specifically the aqueous liquid compositions of the present invention to be directly applied on the stains, comprise:

- percarboxylic acid;
- one or more surfactants;
- hydrogen peroxide;
- one or more optional minor components preferably selected from: dyes, perfumes, viscosity thickeners, solvents, hydrotropic agents, suspending agents, antiredeposition agents, optical brighteners, antifoam, opacifying, sequestering agents, dye transfer inhibitors, pH modifiers.

The percarboxylic acid used to prepare the liquid composition is a crystalline solid, having generally sizes in the range 0.1 ÷ 1000 µm, more preferably in the range 1 ÷ 200 µm, even more preferably in the range 5 ÷ 100 µm, only slightly soluble in acid environment but readily soluble in alkaline or weakly alkaline environment, highly stable as a solid also in aqueous suspension as well as a liquid composition.

In the invention compositions the percarboxylic acid is present in a percentage in the range 0.5÷20.0% by weight,

more preferably 2.0÷10.0% by weight. Preferably the percarboxylic acid is an amido- or imido-percarboxylic acid, more preferably the  $\epsilon$ -N,N-phthaloyl-amino-peroxycaproic acid or  $\epsilon$ -phthalimido-peroxycaproic acid, named PAP.

Therefore the invention compositions appear either in the form of either a solution or suspension depending on the solution pH. Preferably the compositions of the invention have acid pH whereby they appears as suspension.

The surfactant is present in the range 1.0%÷25.0% by weight, preferably in the range 3.0%÷15.0% by weight. Preferably the surfactants are selected from the anionic and the nonionic ones. Preferably a mixture of surfactants comprising at least an anionic surfactant and at least a nonionic surfactant is used.

Among the anionic surfactants sodium, potassium, ammonium salts, preferably sodium or potassium salts alkyl-benzenesulphonates acid are preferred, wherein alkyl is preferably a linear or branched aliphatic chain, preferably linear, or also alicyclic having a number of carbon atoms between 6 and 18, preferably between 8 and 15. Other preferred anionic surfactants are of the sodium alkanesulphonate type having a linear or branched chain comprised between C8 and C20, preferably between C10 and C16.

Anionic surfactants are present in a percentage in the range 0.5÷15.0% by weight, preferably 1.5÷10.0% by weight, more preferably 2.0÷8.0% by weight.

Nonionic surfactants are preferably derived from aliphatic alcohols polycondensed with alkyleneoxide, for instance ethyleneoxide or propyleneoxide: the aliphatic alcohols have a linear or branched chain, preferably comprised between C8 and C18 and are condensed with 2-12 units of ethyleneoxide and/or propyleneoxide. The use of 2 or more alcohols polycondensed with ethyleneoxide is particularly preferred.

These are indicated for the sake of brevity with initials indicating the length in carbon atom number of the aliphatic chains of the prevailing alcohols, followed by the average ethoxylation number; for instance the C12-13 • 3EO abbreviation is used to indicate a mixture of ethoxylated alcohols wherein the largely predominant alkyl chains are dodecyl and tridecyl and the average number of condensed ethoxylic groups is 3.

Nonionic surfactants are present in a percentage in the range 0.5÷15.0% by weight, preferably 1.5÷10.0% by weight, more preferably 2.0÷8.0% by weight.

Hydrogen peroxide is present in a percentage in the range 1.0÷10.0% by weight, preferably 2.0÷8.0% by weight.

Auxiliary agents can be used to achieve a stable suspension of the percarboxylic acid. Preferred auxiliary suspending agents are water soluble or dispersible polymers, of ionic type, such as polycarboxylates, of which various kinds of acrylic homopolymers or acrylic-maleic copolymers having a different molecular weight, are commercially available, for instance with the trademark SOKALAN® by BASF, or associative/non associative ones of non ionic type; such as for instance ACUSOL® polymers by ROHM & HAAS. The auxiliary agents can be present in percentages in the range 0.01÷3.0% by weight, preferably 0.1÷1.5% by weight.

In addition or in alternative to the suspending polymers stable suspensions of the compositions can preferably be obtained by the formation of liquid crystal structures of continuous lamellar and/or vesicular types. These liquid crystal structures can be easily obtained by methods well known to the ones skilled in the art, for instance, by the addition of suitable amounts of some electrolytes, organic or inorganic salts, to mixtures of anionic and non ionic surfactants or of hydrophobic organic substances such as for instance long chain alcohols or fatty acids. The electrolytes may be present in amounts in the range 0.5÷15.0% by weight, more preferably 1.0÷8.0% by weight. Without any purpose of any limitation, the electrolytes are preferably selected from: sodium citrate, sodium or potassium hydrogensulphate, sodium or magnesium sulphate, potassium sulphate, sodium or potassium nitrate and mixtures thereof.

Optionally stable suspensions of the percarboxylic acid can be obtained by combining the use of the electrolytes with the above mentioned polymers.

Optional minor components may be present in small amounts (0.05÷ 4.0% by weight), such as: acidifiers, as for instance citric acid, sulphuric acid, sodium hydrogensulphate, sulphamic acid; hydrotropes, such as sodium cumene- or xylene-sulphonate; perfumes, antifoam agents, optical brighteners, heavy or alkaline-earth metal sequestering agents.

The compositions generally appear as a stable suspension which does not give signs of evident sedimentation on the bottom either after centrifugation or after 4 weeks ageing at 30°C, but they can also appear with partial separation of the percarboxylic acid on the bottom and therefore require the container agitation without any influence on the use efficacy.

The compositions of the present invention have viscosity at 20°C in the range 400-5000 mPa • s, more preferably between 600 and 2000 mPa • s.

Preferably the compositions of the invention have a pH in the range 1.0 and 6.0, more preferably 2.0-5.0.

Water is present as the complement to 100% by weight.

The process for preparing the compositions in the form of suspension is hereinafter described.

It has been found that the physical stability of the suspension, obtained during the process for preparing the compositions, is difficult to be obtained using the percarboxylic having the characteristics of the type industrially available. For instance the PAP wet cake appears as aggregate/conglomerate of crystals having sizes in the range 10÷1000  $\mu$ m. A milling system of the percarboxylic acid has been set up which remarkably reduces the crystal sizes in liquid phase

without danger of decomposition. The suspension obtained after milling the percarboxylic acid results physically more stable and appears as a viscous, turbid, opaque, creamy, homogeneous or almost homogeneous liquid, characterised by an easier pourability from the bottle and by a quicker solubilization of the percarboxylic acid in the washing solution.

The crystal sizes of percarboxylic acid after milling are in the range of  $5.0 \div 100 \mu\text{m}$ .

5 Thus a dispersion of the percarboxylic acid, in demineralized acidified water, or in a premixture containing some components of the invention composition, such as the antifoam and/or the anionic and/or non ionic surfactants and/or hydrogen peroxide and/or the inorganic salts of the suspending system (for instance sodium citrate, sodium or magnesium sulphate) and/or acidity regulators (for instance citric or sulphuric acid) and/or heavy metals chelant agents (for instance derivatives or analogues of the ethylenediaminetetracetic acid), is treated in a mixer, preferably a Silverson  
10 type mixer or passed through a gear pump or a colloid mill for a time suitable to obtain the desired milling level of suspended solids, while temperature is monitored and anyway maintained below  $50^{\circ}\text{C}$ , preferably below  $35^{\circ}\text{C}$ .

This milling process can be made directly in the mixer of the composition preparation or in a separate vessel transferring then the milled dispersion in the final mixer.

On the basis of what above reported but without any purpose of any limitation two preferred general methods are  
15 described in detail hereinafter for the preparation of present invention compositions.

#### Preparation method A

A premix composition is prepared under stirring: to an anionic surfactant solution (preferably prepared by neutralization of the anionic surfactant in acid form with a sodium or potassium hydroxide solution under stirring or by solubilization of sodium or potassium salt of the anionic surfactant), antifoam, electrolytes (sodium or potassium or magnesium sulphate; sodium bisulphate; sodium citrate or mixtures thereof) optionally predissolved in demineralized water and hydrogen peroxide are added and the pH is adjusted to the desired value, for instance by sulphuric, or citric or sulphamic acid addition.

25 In a separate vessel, a PAP dispersion in a suitable amount of demineralized water having  $\text{pH} < 4.0$ , is passed through a gear pump or a colloid mill or is treated with Silverson type mixer for about 20 minutes. Temperature is monitored and, if the case, maintained below  $50^{\circ}\text{C}$ , more preferably below  $35^{\circ}\text{C}$  by cooling or regulating mixer (or pump) speed.

The PAP dispersion is then transferred into the main mixer. Nonionic surfactants are added. The dispersion is completed with the optional components and when necessary it is brought to 100% by weight with water. The stirring is continued for about 1 hour.

#### Preparation method B

35 The anionic surfactant solution is prepared under stirring preferably by neutralization of the anionic surfactant in acid form with a sodium or potassium hydroxide solution under stirring or by solubilization of sodium or potassium salt of the anionic surfactant. The pH is adjusted to the required value with sulphuric acid (or with citric or sulphamic acid). Then antifoam, hydrogen peroxide and PAP are added. The dispersion is passed through a gear pump or a colloid mill or is treated with Silverson type mixer for about 20 minutes at a suitable speed to obtain the desired milling level. Temperature is monitored and, if the case, maintained below  $50^{\circ}\text{C}$ , more preferably below  $35^{\circ}\text{C}$  by cooling or regulating mixer (or pump) speed. The electrolytes (sodium or potassium or magnesium sulphate; sodium bisulphate; sodium citrate) optionally predissolved in the minimum necessary amount of demineralized water, ethoxylated alcohols are added under stirring; the dispersion is completed with the optional components. Stirring is continued for about 1 hour.

For illustrative but not limitative purposes some examples of the invention compositions are reported in Tables 1 and 2, wherein all the reported values appearing therein are in per cent weight/weight (% W/W).

45 Some examples of the cleaning and hygienizing performances of the present invention compositions and of some products present on the market, are reported hereinafter for illustrative but not limitative purposes.

50

55

TABLE 1

| Composition                   | 1                | 2                | 3                | 4                | 5                | 6                 |
|-------------------------------|------------------|------------------|------------------|------------------|------------------|-------------------|
| PAP (wet cake 90%)            | 4.0              | 4.0              | 4.0              | 6.0              | 6.0              | 6.0               |
| Hydroxide Na or K             | as suff.         | as suff.         | as suff.         | as suff.         | as suff.         | as suff.          |
| Alkylbenzene sulphononic acid | 4.0              | 4.0              | 4.0              | 4.0              | 6.0              | 6.0               |
| H <sub>2</sub> O <sub>2</sub> | 7.0              | 7.0              | 7.0              | 3.5              | 3.5              | 3.5               |
| Citric or sulphuric acid      | as suff. to pH 4 | as suff. to pH 4 | as suff. to pH 4 | as suff. to pH 3 | as suff. to pH 3 | as suff. to pH 3  |
| Sodium citrate                | 3.0              | 3.0              | -                | -                | -                | 2.0               |
| Sodium sulphate               | -                | -                | 2.0              | -                | 6.0              | -                 |
| Magnesium-sulphate            | -                | -                | 2.0              | 3.0              | -                | -                 |
| C10-C11 • 8,5 EO              | 1.0              | -                | -                | 1.0              | -                | 2.0               |
| C13-C15 • 9 EO                | -                | 1.5              | 1.5              | -                | -                | -                 |
| C10-C11 • 2 EO                | 5.0              | -                | -                | -                | 3.0              | -                 |
| C12-C13 • 3 EO                | -                | 4.5              | 3.5              | 6.0              | -                | 4.0               |
| Sodium cumen sulphonate       | 0.6              | 0.6              | 0.6              | 0.6              | -                | Acusol 882<br>2.0 |
| Minor components§             | 0.2 -0.5         | 0.2 -0.5         | 0.2 -0.5         | 0.2 -0.5         | 0.2 -0.5         | 0.2 -0.5          |
| Demineralized water           | as suff. to 100  | as suff. to 100  | as suff. to 100  | as suff. to 100  | as suff. to 100  | as suff. to 100   |
| Total surfactants#            | 10               | 10               | 9                | 11               | 9                | 12                |
| active O* (%)                 | 3.5              | 3.5              | 3.5              | 1.9              | 1.9              | 1.9               |

\*: % of active oxygen by iodometric titration

§: Perfume/Antifoam in a rate 3:1

#: total amount of anionic and non ionic surfactants

TABLE 2

| Composition                   | 7               | 8                | 9               | 10               | 11               | 12               |
|-------------------------------|-----------------|------------------|-----------------|------------------|------------------|------------------|
| PAP (wet cake 90%)            | 6.0             | 6.0              | 8.0             | 8.0              | 8.0              | 8.0              |
| Hydroxide Na or K             | as suff.        | as suff.         | as suff.        | as suff.         | as suff.         | as suff.         |
| Alkyl benzensulphonic acid    | 4.0             | 4.0              | 6.0             | 6.0              | 8.0              | 8.0              |
| H <sub>2</sub> O <sub>2</sub> | 3.5             | 3.5              | 3.5             | 5.0              | 5.0              | 5.0              |
| Citric or sulphoric acid      | -               | as suff. to pH 3 | -               | as suff. to pH 3 | as suff. to pH 3 | as suff. to pH 3 |
| Sodium bisulphate             | 1.0 (to pH 3)   | -                | 2.0 (to pH 3)   | -                | -                | 5.0              |
| Potassium sulphate            | 2.0             | -                | -               | -                | 1.0              | -                |
| Magnesium sulphate            | -               | 4.0              | 2.0             | 3.0              | -                | -                |
| iso C10 • 6 EO                | -               | 3.0              | -               | 1.0              | -                | 2.0              |
| C13-C15 • 9 EO                | 1.5             | -                | 1.5             | -                | -                | -                |
| C10-C11 • 2 EO                | 5.0             | -                | -               | -                | -                | -                |
| C12-C13 • 3 EO                | -               | -                | 3.5             | 6.0              | 4.0              | 4.0              |
| Sodium cumenesulphonate       | 0.6             | -                | 0.6             | 0.6              | -                | -                |
| Minor components§             | 0.2 -0.5        | 0.2 -0.5         | 0.2 -0.5        | 0.2 -0.5         | 0.2 -0.5         | 0.2 -0.5         |
| Demineralized water           | as suff. to 100 | as suff. to 100  | as suff. to 100 | as suff. to 100  | as suff. to 100  | as suff. to 100  |
| Total surfactants#            | 10.5            | 7                | 11              | 13               | 12               | 14               |
| active O*(%)                  | 1.9             | 1.9              | 2.0             | 2.8              | 2.8              | 2.8              |

\*: % of active oxygen by iodometric titration

§: Perfume/Antifoam in a rate 3:1

#: total amount of anionic and non ionic surfactants

**EXAMPLES OF CLEANING PERFORMANCES (GROUP I)**

The tests on cotton were doubly carried out in domestic washing machine (REX RF 228X) by using a normal washing cycle at the temperature indicated in table without prewashing and with 3 rinsing, cycles with water having an average hardness (ca. 25° French degrees) and with 2 kg of white cotton articles. In each washing two series of articles with standard dirt are introduced. As oxidable stains the following dirt were used: raw cotton (EMPA 222), red wine (EMPA 114), "immediata" black (EMPA 115), tea (Wfk), coffee (Wfk). The removal of the stains is determined by measuring with a Elrepho 2000 reflectometer the increase of the percentage of reflected light before and after the washing.

The washings were carried out at the washing machine temperatures indicated in the tables with:

- High quality detergent (Dash®) for washing machine (160 g in the small basin)
- additive (70 g) on the stains (2 g/dm<sup>2</sup> applied on the stains 5 minutes before the washing) + same detergent (160 g in the small basin).

**NOTES**

The liquid additive containing hydrogen peroxide (indicated with the name "Liquid additive" in tables "liq. add.") is representative of the Italian market (Omino Bianco Candeggina Delicata®, Ace Gentile®) and contains, in weight/weight %:

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- active oxygen about 3.3% (under the form of hydrogen peroxide)
- anionic surfactant about 1.2%
- non ionic surfactant about 1.0% (under the form of ethoxylated alcohol).

5 The results of the washings belong to group I, carried out in the presence of the compositions of the invention and those of the comparative tests are reported in Tables from 3a to 3c.

Table 3a

| COOL WASHINGS§                                                |                                                 |                           |                           |                                                 |
|---------------------------------------------------------------|-------------------------------------------------|---------------------------|---------------------------|-------------------------------------------------|
| Washings                                                      | Detergent<br>(Reference)                        | Det.+ comp. 8<br>on stain | Det.+ comp. 4<br>on stain | Det.+<br>liq. add.*<br>on stain<br>(Comparison) |
| Stains                                                        | Variation as % of reflected light after washing |                           |                           |                                                 |
| EMPA 115                                                      | 2.42                                            | 7.10                      | 8.12                      | 4.54                                            |
| EMPA 222                                                      | 5.59                                            | 14.90                     | 17.69                     | 13.46                                           |
| EMPA 114                                                      | 23.07                                           | 34.91                     | 37.03                     | 33.34                                           |
| Tea (Wfk)                                                     | 14.54                                           | 31.22                     | 29.76                     |                                                 |
| Coffee (Wfk)                                                  | 31.88                                           | 39.58                     | 40.79                     |                                                 |
| Total average<br>of the<br>variation of<br>reflected<br>light | 15.50                                           | 25.54                     | 26.68                     | 17.11                                           |

Detergent: Dash® powder.  
\*: Omio Bianco Candeggina Delicata®.  
§: at temperature of 20°C.

Table 3b

| WASHINGS AT 40°C                                        |                                                 |                           |                                                |
|---------------------------------------------------------|-------------------------------------------------|---------------------------|------------------------------------------------|
| Washings                                                | Detergent<br>(Reference)                        | Det.+ comp. 4<br>on stain | Det.+<br>liq.add.*<br>on stain<br>(Comparison) |
| Stains                                                  | Variation as % of reflected light after washing |                           |                                                |
| EMPA 115                                                | 5.66                                            | 14.97                     | 7.12                                           |
| EMPA 222                                                | 16.59                                           | 21.66                     | 20.68                                          |
| EMPA 114                                                | 42.49                                           | 46.66                     | 47.21                                          |
| Tea (Wfk)                                               | 34.08                                           | 42.55                     | 41.13                                          |
| Coffee (Wfk)                                            | 45.33                                           | 50.87                     | 50.34                                          |
| Total average of<br>the variation of<br>reflected light | 28.83                                           | 35.34                     | 33.30                                          |

Detergent: Dash® powder.

\*: Omino Bianco Candeggina Delicata®.

Table 3c

| WASHINGS AT 60°C                                           |                                                 |                           |                            |                                                |
|------------------------------------------------------------|-------------------------------------------------|---------------------------|----------------------------|------------------------------------------------|
| Washings                                                   | Detergent<br>(Reference)                        | Det.+ comp. 9<br>on stain | Det.+ comp. 12<br>on stain | Det.+<br>liq.add.*<br>on stain<br>(Comparison) |
| Stains                                                     | Variation as % of reflected light after washing |                           |                            |                                                |
| EMPA 222                                                   | 54.50                                           | 57.00                     | 58.10                      | 56.50                                          |
| EMPA 114                                                   | 96.70                                           | 101.70                    | 102.60                     | 103.30                                         |
| Tea (Wfk)                                                  | 54.60                                           | 59.40                     | 63.40                      | 57.40                                          |
| Total average of<br>the variation of<br>reflected<br>light | 68.60                                           | 72.70                     | 74.20                      | 72.40                                          |

Detergent: Dash® powder.

\*: Omino Bianco Candeggina Delicata®.

## EXAMPLES OF STAIN REMOVING AND CLEANING PERFORMANCES (GROUP II)

The results of the washings belong to group (II) carried out in the presence of the compositions of the invention and those of the comparative tests, are reported in Tables 4a, 4b, 4c, 4d, 4e and 4f.

Bleach performances have been evaluated on artificially soiled testfabrics over three washing cycles without pre-washing in domestic washer in the washing condition indicated below.

In each wash cycle two series of testfabrics are washed. As bleachable stains the following soiled testfabrics were used: crude cotton (EMPA 222), red wine (EMPA 114), apple (CFT-CS 13), black-currant (CFT-CS 12), tea (CTTN), coffee (CTTN) in the case of cotton and tea soiled wool (CTTN), red wine soiled wool (CTTN), red wine soiled silk (CTTN) in the case of delicate fabric tests.

Reflectance value are determined without optical brightening effect by ELREPHO 3300 (DATACOLOR) reflectometer. Four tristimulus measures are determined for each sample. The average measured values are then expressed in Tables 4a, 4b, 4c, 4e and 4f as follows:

**s.r.** = Stain removal of each stain kind. It is calculated as follows:

$$s.r. (\%) = (C-B) / (A-B) \times 100$$

wherein:

**A** = reflectance value of white (unsoiled and unwashed) testfabric;

**B** = reflectance value of stained testfabric before washing;

**C** = reflectance value of stained testfabric after washing.

**average s.r.** = stain removal calculated as the average of s.r. of bleachable stain series

**s.r. difference** = is the difference between s.r. of additive (+ detergent) in question and s.r. of reference detergent alone, i.e. is the stain removal improvement given by the additive.

**% increase** = is the percent ratio between s.r. difference of the additive in question and s.r. of reference detergent.

#### Composition used:

Composition 4 and composition 4' equal to composition 4 but the amount of PAP is 9.0 % by weight instead of 6.0 %.

| WASHING CONDITIONS (EXAMPLES GROUP II) |                                                                                                                                                                                                                                                       |
|----------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| washing temperatures                   | 20 and 40°C in the case of cotton (representative of coloured fabrics)<br>20 and 30°C in the case of wool and silk (representative of delicate fabrics)                                                                                               |
| reference detergent                    | suitable market leading laundry detergent (Dash <sup>®</sup> , Perlana <sup>®</sup> ) in washing machine detergent dispenser is used at a proper dose.                                                                                                |
| test additive                          | either a composition of present invention or MARKET LIQ. ADDITIVE (see below), is applied (3g/dm <sup>2</sup> ) directly on the above listed soiled testfabrics. After 5 minutes washing programme is started in presence of the reference detergent. |
| Washing machine                        | CANDY C 577 T                                                                                                                                                                                                                                         |
| washing programme                      | without prewash cycle<br>heating time: 5-10 min. (depending on washing temperature)<br>washing time: 24 min.<br>rinses: 4 (11 min. in total)<br>overall time: 70-80 min. (depending on washing temperature)                                           |
| Water                                  | 19 litres in washing cycle<br>63 litres in rinses cycle                                                                                                                                                                                               |

(continued)

| WASHING CONDITIONS (EXAMPLES GROUP II)                                                                                                                                                                                                                                               |                                                                                                       |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|
| Water Hardness                                                                                                                                                                                                                                                                       | 22°Hf                                                                                                 |
| Load Ballast                                                                                                                                                                                                                                                                         | in the case of cotton: 3.5 Kg of white cotton in the case of delicates: 1.0 Kg of knitted PES patches |
| wherein "MARKET LIQ. ADDITIVE" is a liquid laundry additive, representative Italian and European markets (Ace Gentile®, Omino Bianco Candeggina Delicata®, containing (w/w %):<br>- active oxygen (as hydrogen peroxide): about 3.3%<br>- anionic and nonionic surfactants: about 2% |                                                                                                       |

Table 4a

Cotton fabrics washings at 20 °C

| Washings                       | $\alpha$<br>(Reference) | $\alpha$ +<br>composition 4<br>(on stain) | $\alpha$ +<br>composition<br>4'<br>(on stain) | $\alpha$ + MARKET<br>LIQ.<br>ADDITIVE.*<br>(on stain)<br>(Comparison) |
|--------------------------------|-------------------------|-------------------------------------------|-----------------------------------------------|-----------------------------------------------------------------------|
| Stains                         | Stain removal (s.r., %) |                                           |                                               |                                                                       |
| Tea<br>(CTTN)                  | 0.7                     | 25.7                                      | 33.4                                          | 11.3                                                                  |
| Crude cotton<br>(EMPA 222)     | 4.5                     | 18.4                                      | 21.1                                          | 10.8                                                                  |
| Red wine<br>(EMPA 114)         | 32.1                    | 66.5                                      | 67.4                                          | 59.7                                                                  |
| Apple<br>(CFT/CS13)            | 55.9                    | 75.2                                      | 80.5                                          | 70.2                                                                  |
| Black<br>currant<br>(CFT/CS12) | 37.5                    | 41.6                                      | 46.0                                          | 38.9                                                                  |
| Coffee<br>(CTTN)               | 15.4                    | 30.2                                      | 34.7                                          | 20.1                                                                  |
| average<br>s.r.                | 24.3                    | 42.9                                      | 47.2                                          | 35.2                                                                  |
| s.r.<br>difference             | -                       | + 18.6                                    | + 22.9                                        | + 10.9                                                                |
| %<br>increase                  | -                       | + 76.5 %                                  | + 94.2 %                                      | + 44.8 %                                                              |

 $\alpha$ : 150 g of powder detergent Dash®.

\*: Ace Gentile®

Table 4b

Cotton fabrics washings at 40 °C

| Washings                     | $\alpha$<br>(Reference) | $\alpha$ + composition 4'<br>(on stain) | $\alpha$ + MARKET<br>LIQ. ADDITIVE.*<br>(on stain)<br>(Comparison) |
|------------------------------|-------------------------|-----------------------------------------|--------------------------------------------------------------------|
| Stains                       | Stain removal (s.r., %) |                                         |                                                                    |
| Tea<br>(CTTN)                | 29.3                    | 57.1                                    | 38.6                                                               |
| Crude cotton<br>(EMPA 222)   | 13.8                    | 31.8                                    | 21.3                                                               |
| Red wine<br>(EMPA 114)       | 62.5                    | 83.4                                    | 83.7                                                               |
| Apple<br>(CFT/CS 13)         | 77.1                    | 91.2                                    | 83.9                                                               |
| Black currant<br>(CFT/CS 12) | 48.1                    | 57.6                                    | 50.0                                                               |
| Coffee<br>(CTTN)             | 30.5                    | 58.3                                    | 34.7                                                               |
| average<br>s.r.              | 43.5                    | 63.2                                    | 52.1                                                               |
| s.r.<br>difference           | -                       | + 19.7                                  | + 8.6                                                              |
| %<br>increase                | -                       | + 45.3 %                                | + 19.7 %                                                           |

 $\alpha$ : 150 g of powder detergent Dash®.

\*: Omio Bianco Candeggina Delicata®.

Table 4c

Cotton fabrics washings at 20 °C

| Washings                   | $\beta$<br>(Reference)  | $\beta$ + composition 4'<br>(on stain) | $\beta$ + MARKET<br>LIQ. ADDITIVE.*<br>(on stain)<br>(Comparison) |
|----------------------------|-------------------------|----------------------------------------|-------------------------------------------------------------------|
| Stains                     | Stain removal (s.r., %) |                                        |                                                                   |
| Tea<br>(CTTN)              | 0.1                     | 22.8                                   | 5.5                                                               |
| Crude cotton<br>(EMPA 222) | 0.1                     | 15.2                                   | 7.4                                                               |
| Red wine<br>(EMPA 114)     | 36.6                    | 67.2                                   | 56.7                                                              |
| average<br>s.r.            | 12.2                    | 35.1                                   | 23.2                                                              |
| s.r.<br>difference         | -                       | + 22.9                                 | + 11.0                                                            |
| %<br>increase              | -                       | + 187.7 %                              | + 90.1 %                                                          |

 $\beta$ : 150 ml of detergent Dash® liquido.

\*: Ace Gentile®.

Table 4d

Cotton fabrics washings at 40 °C

| Washings                   | $\beta$<br>(Reference)  | $\beta$ +<br>composition 4<br>(on stain) | $\beta$<br>+<br>composition<br>4'<br>(on stain) | $\beta$ + MARKET<br>LIQ. ADDITIVE.*<br>(on stain)<br>(Comparison) |
|----------------------------|-------------------------|------------------------------------------|-------------------------------------------------|-------------------------------------------------------------------|
| Stains                     | Stain removal (s.r., %) |                                          |                                                 |                                                                   |
| Tea<br>(CTTN)              | 1.9                     | 25.2                                     | 31.1                                            | 9.6                                                               |
| Crude cotton<br>(EMPA 222) | 0.6                     | 18.3                                     | 20.6                                            | 10.0                                                              |
| Red wine<br>(EMPA 114)     | 38.0                    | 67.8                                     | 62.9                                            | 57.9                                                              |
| average<br>s.r.            | 13.5                    | 37.1                                     | 38.2                                            | 25.8                                                              |
| s.r.<br>difference         | -                       | + 23.6                                   | + 24.7                                          | + 12.3                                                            |
| %<br>increase              | -                       | + 174.8 %                                | + 183.0 %                                       | + 91.1 %                                                          |

 $\beta$ : 150 ml of detergent Dash® liquido.

\*: Ace Gentile®.

Table 4e

Wool and silk fabrics washings at 20 °C

| Washings                    | $\gamma$<br>(Reference) | $\gamma$ +<br>composition 4<br>(on stain) | $\gamma$ +<br>composition<br>4'<br>(on stain) | $\gamma$ + MARKET<br>LIQ.<br>ADDITIVE.*<br>(on stain)<br>(Comparison) |
|-----------------------------|-------------------------|-------------------------------------------|-----------------------------------------------|-----------------------------------------------------------------------|
| Stains                      | Stain removal (s.r., %) |                                           |                                               |                                                                       |
| Tea/wool<br>(CTTN)          | 5.2                     | 10.1                                      | 11.4                                          | 6.4                                                                   |
| Red wine/<br>wool<br>(CTTN) | 64.0                    | 103.4                                     | 104.5                                         | 89.3                                                                  |
| Red wine/<br>silk<br>(CTTN) | 5.6                     | 33.5                                      | 42.6                                          | 33.7                                                                  |
| average<br>s.r.             | 24.9                    | 49.0                                      | 52.8                                          | 43.1                                                                  |
| s.r.<br>difference          | -                       | + 24.1                                    | + 27.9                                        | + 18.2                                                                |
| %<br>increase               | -                       | + 96.7 %                                  | + 112.0 %                                     | + 73.1 %                                                              |

 $\gamma$ : 90 ml of liquid detergent Perlana® effetto balsamo.

\*: Ace Gentile®.

Table 4f

Wool and silk fabrics washings at 30 °C

| Washings                    | $\gamma$<br>(Reference) | $\gamma$ +<br>composition 4<br>(on stain) | $\gamma$ +<br>composition<br>4'<br>(on stain) | $\gamma$ + MARKET<br>LIQ.<br>ADDITIVE.*<br>(on stain)<br>(Comparison) |
|-----------------------------|-------------------------|-------------------------------------------|-----------------------------------------------|-----------------------------------------------------------------------|
| Stains                      | Stain removal (s.r., %) |                                           |                                               |                                                                       |
| Tea/wool<br>(CTTN)          | 6.6                     | 11.6                                      | 8.8                                           | 7.3                                                                   |
| Red wine/<br>wool<br>(CTTN) | 66.6                    | 108.2                                     | 107.6                                         | 94.2                                                                  |
| Red wine/<br>silk<br>(CTTN) | 24.5                    | 37.2                                      | 52.0                                          | 46.3                                                                  |
| average<br>s.r.             | 32.6                    | 52.3                                      | 56.1                                          | 49.3                                                                  |
| s.r.<br>difference          | -                       | + 19.7                                    | + 23.5                                        | + 16.7                                                                |
| %<br>increase               | -                       | + 60.4 %                                  | + 72.1 %                                      | + 51.2 %                                                              |

$\gamma$ : 90 ml of liquid detergent Perlana® effetto balsamo.

\*: Ace Gentile®.

#### EXAMPLES OF DISINFECTANT PERFORMANCES

The bactericide action of the present invention compositions is very effective at low temperatures. The following results are given as an example.

Indeed according to the primary bactericide action test PhEN 1040 September 1996, it is necessary that the examined product at the use concentration causes a decrease of at least  $10^5$  colonies/millilitre (col/ml) wherein colonies means unit forming colonies, in a solution having in suspension pathogenic bacteria (PSEUDO MONAS AERUGINOSA and STAPHYLOCOCCUS AUREUS) with an initial Total Bacteric Charge (TBC) of  $10^8$ - $10^9$  colonies/ml. By carrying out the above test on solutions having a pH 8.0 of the exemplified compositions, the following results are obtained:

**at 30°C:** after 5 minutes with a concentration of 4.0 g/l of the composition 4 or of 2.5 g/l of the composition 12 (corresponding to the addition respectively of 80 g and 50 g in a machine washing machine) a decrease higher than  $10^5$  col/ml is obtained.

For comparison with a powder disinfectant additive (containing as active starting materials for an hygienizing effect about: 3% by weight of active oxygen as perborate or percarbonate and 1-6% by weight of the activator TAED) at a concentration of 5.0 g/l, the reduction of  $10^5$  col/ml is obtained only after 15 minutes.

**at 20°C:** after 10 minutes with a concentration of 4.0 g/l of the composition 8 of the EXAMPLES or of 2.5 g/l of the composition 12 (corresponding to the addition respectively of 80 g and 50 g in a washing machine) a reduction of  $10^5$  col/ml is obtained. The application of the compositions directly on the cloth allows to obtain the same action using a much less use of product since locally it has a concentration even higher than that above described.

For comparison a powder disinfectant additive, of the above indicated composition, after 60 minutes, with a concentration of 5.0 g/l, causes a reduction of  $10^5$  col/ml.

For comparison a liquid additive selected from those indicated in the art for instance OMINO BIANCO® added in the washing is effective after 60 min at a concentration of 3.5 g/l equal to 70 ml in washing machine.

The above test was carried out also on solutions of the exemplified compositions without any pH modification, and the following results have been obtained:

**at 30°C:** the composition 4' causes a TBC decrease higher than  $10^5$  u.f.c./ml after 15 minutes at a 5 g/l concentration.

For comparison a powder disinfectant additive (containing as active starting materials for an hygienizing effect about: 3% by weight of active oxygen as perborate or percarbonate and 1-6% by weight of TAED as activator) produce the above description action only at a concentration of 14.0 g/l after 15 minutes.

**at 20°C:** the composition 4' causes a TBC decrease higher than  $10^5$  u.f.c./ml within 30 minutes at a 7 g/l concentration obtained. The direct application of the compositions on the cloth allows to obtain the same action using a much less amount of product since in the application area the concentration is higher than that above described.

For comparison a powder disinfectant additive, of the above indicated composition, after 120 minutes, with a concentration of 5.0 g/l, causes a reduction of  $10^5$  u.f.c./ml.

## Claims

1. Use of aqueous liquid compositions, comprising a percarboxylic acid, as stain removing, a pre-treating, cleaning and antibacterial additives very effective at low temperatures (20-30°C), for by-hand or washing machine laundry, both for delicate and/or coloured fabrics, preferably applied directly on the stains before washing.
2. Use of compositions according to claim 1 having an acid pH in the range 1.0-6.0, more preferably 2.0-5.0, and comprising:
  - percarboxylic acid;
  - one or more surfactants;
  - hydrogen peroxide;
  - optional components: dyes, perfumes, viscosity thickeners, solvents, hydrotropic agents, suspending agents, antiredeposition agents, optical brighteners, antifoam, opacifying, sequestering agents, dye transfer inhibitors, pH modifiers.
3. Use of a composition according to claims 1 and 2 wherein the percarboxylic acid is a crystalline solid with sizes in the range 0.1÷1000  $\mu$ m, more preferably 1÷200  $\mu$ m, even more preferably 5÷100  $\mu$ m.
4. Use of a composition according to claims 1-3 wherein the percarboxylic acid is an amido- or imido-percarboxylic acid.
5. Use of a composition according to claim 4, wherein the percarboxylic acid is the  $\epsilon$ -N,N-phthaloyl-amino-peroxycaproic acid.
6. Use of a composition according to claims 1-5, wherein the percarboxylic acid is present in a percentage by weight in the range 0.5÷20.0%, more preferably 2.0÷10.0%.
7. Use of a composition according to claims 2-6 wherein the surfactants is in the range 1.0%÷25.0% by weight, preferably in the range 3.0%÷15.0% by weight and the optional components are in the range 0.05÷4.0% by weight.
8. Use of a composition according to claim 7 wherein the surfactants are anionic selected from sodium, potassium or ammonium salts of alkylbenzenesulphonates.
9. Use of a composition according to claims 7-8 wherein the anionic surfactant amount ranges from 0.5 ÷ 15% by weight, more preferably 1.5 ÷ 10.0% by weight.
10. Use of a composition according to claims 7-9 wherein the surfactant is a mixture of anionic and non ionic surfactants, the non ionic surfactants are selected from an aliphatic greasy alcohol having a C8-C18 chain and/or one or more aliphatic greasy alcohols having a C8-C18 chain polycondensed with ethyleneoxide and/or propyleneoxide.
11. Use of a composition according to claim 10 wherein the non ionic surfactants are preferably two or more aliphatic greasy alcohols having a C8-C18 chain polycondensed with ethyleneoxide.
12. Use of a composition according to claims 10-11 wherein the content of non ionic surfactants is in the range 0.5 ÷15.0% by weight, preferably 1.5÷10.0% by weight, more preferably 2.0÷8.0% by weight.

13. Use of a composition according to claims 2-12 wherein the content of hydrogen peroxide is preferably is in the range 1.0÷10.0% by weight, more preferably 2.0÷8.0% by weight.
14. Use of a composition according to claims 2-13 wherein the suspending agents is formed by: polymers, soluble or dispersible in water, of ionic type, selected from polycarboxylates, or associative/non associative non ionic, whose content is in the range 0.01%÷3.0% by weight, preferably 0.1÷1.5% by weight, and/or one or more electrolytes, organic or inorganic salts, preferably selected from: sodium citrate, sodium bisulphate, sodium sulphate, magnesium sulphate, potassium sulphate, used separately or combined with each other, the content of which is preferably in the range 0.5÷15.0% by weight, more preferably 1.0÷8.0% by weight.
15. Aqueous liquid composition according to claims 2-14.
16. Process for preparing the composition according to claim 15, wherein a dispersion of the percarboxylic acid in demineralized acidified water, or in a premixture containing antifoam and/or the anionic and/or non ionic surfactants and/or hydrogen peroxide and/or the inorganic salts of the suspending system and/or acidity regulators and/or heavy metals chelant agents; the pH ranging from 1 to 6, is treated in a mixer or passed through a gear pump or a colloid mill for a time suitable to obtain the desired milling level of suspended solids, while temperature is monitored and anyway maintained below 50°C, preferably below 35°C; the PAP dispersion is completed by stirring for about 1 hour, in case by adding the optional components, and bringing to 100% by weight with water.
17. Process according to claim 16 wherein in a main mixer a premix composition is prepared under stirring and obtained by adding to an anionic surfactant solution, antifoam, electrolytes, optionally predissolved in demineralized water and hydrogen peroxide, the pH is adjusted to the value of claim 16; in a separate vessel a PAP dispersion in a suitable amount of demineralized water having pH < 4.0, is passed through a gear pump or a colloid mill or is treated with a mixer, preferably Silverson type, for about 20 minutes; temperature is monitored and maintained below 50°C, preferably below 35°C by cooling or regulating mixer (or pump) speed; the PAP dispersion is then transferred into the main mixer, then nonionic surfactants are added, the dispersion is completed with the optional components and brought to 100% by weight with water, the stirring being continued for about 1 hour.
18. Process according to claim 16 wherein the anionic surfactant solution is prepared under stirring, preferably by neutralisation of the anionic surfactant in acid form with a sodium or potassium hydroxide solution under stirring or by solubilization of sodium or potassium salt of the anionic surfactant, the pH is adjusted to the indicated value, then antifoam, hydrogen peroxide and PAP are added; The dispersion is passed through a gear pump or a colloid mill or treated in a mixer for about 20 minutes at a speed capable to give the desired milling level, the temperature is monitored and maintained below 50°C, preferably below 35°C, then it is added under stirring the electrolytes, optionally predissolved in the minimum necessary amount of demineralized water, ethoxylated alcohols, the dispersion is completed with the optional components, stirring is continued for about 1 hour.