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54 **Metallo-porphirins as bleach catalyst and process for cleaning fabrics.**

57 A process for cleaning and bleaching fabrics comprising the treatment of the fabric with a metallo-porphyrin compound, leaving the fabric in contact therewith for a predetermined time to effect sufficient adsorption of metallo-porphyrin on to the fabric, and thereafter washing the fabric with a peroxyacid bleach composition. Compositions for use in this cleaning and bleaching process and pretreatment products for local application of metallo-porphyrin catalyst on to fabrics are also disclosed.

EP 0 306 089 A2

METALLO-PORPHYRINS AS BLEACH CATALYST AND PROCESS FOR CLEANING FABRICS

This invention relates to a method for using metallo-porphyrins as bleach catalyst, a process for cleaning fabrics and to products for use in carrying out the process. More particularly, the invention relates to catalytic fabric stain bleaching at low to ambient temperatures, e.g. from 10-30 °C, and to products comprising metallo-porphyrins.

5 Hydrogen peroxide releasing bleaching agents, such as sodium perborate, sodium percarbonate, sodium persulfate and sodium perpyrophosphate, are effective only at high washing temperatures, e.g. from 80 °C up to the boil. They can be made more effective at lower temperatures by adding "activators", which are usually organic acid anhydrides, esters, amides or imides, functioning by a perhydrolysis reaction with the percompound forming organic peroxyacids which, unlike the percompound, are effective at lower
10 temperatures. Indeed organic peroxyacids, i.e. percarboxylic acids, as a class and persulfates, e.g. potassium monopersulfate, are effective bleaches at 40-60 °C and their use as a bleach system in detergent compositions has been proposed in the art. Still, a large number of peroxyacids do not exhibit adequate bleaching performance at and below 40 °C.

With the trend towards lower fabric-washing temperatures, to e.g. 40 °C and below, there is continuous
15 incentive to look for more effective low temperature bleach systems. The present invention seeks to provide a method for improving the bleaching effect of peroxyacid bleach systems comprising a peroxyacid per se or formed in situ.

It is known that iron porphyrins can act as an oxidation catalyst. US Patent N° 4,077,768 describes the application of this catalyst with an oxidising bleach, e.g. hydrogen peroxide and also peroxyacids, in
20 aqueous wash liquors for dye bleaching in solution, i.e. for inhibiting dye-transfer. The method as described in this patent comprises treating the fabrics in a bath containing a dissolved or solubilised iron porphyrin, to which bath is also supplied the oxidising bleach which is added or released slowly and in small amounts at a rate not substantially greater than that at which it is removed from said bath by reaction with the contents thereof.

Said rate of bleach release in or bleach addition to the bleaching bath, according to this reference, is
25 necessary so as to prevent catalyst decomposition. Gradual introduction of hydrogen peroxide over a period of at least 5 minutes to 30 minutes is said to be suitable, and compositions comprising iron porphyrins and an oxidising bleach in a form such that it dissolves in the bath at said controlled rate are also suggested. Indeed, the method and compositions of this US Patent are particularly designed for inhibiting dye-transfer
30 but they are no good in the effective bleaching of stains on fabrics at the lower wash temperature region of e.g. between 10 and 40 °C.

Surprisingly, however, metallo-porphyrins do effectively catalyse the fabric stain bleaching action of peroxyacid bleach systems if certain conditions are fulfilled.

It has now been found that metallo-porphyrins, when adsorbed on to fabrics, can effect a catalysing
35 action on the fabric stain bleaching of peroxyacids, making them effective for use in washing at lower temperatures. The term "peroxyacids" used here includes both the organic peroxyacids, i.e. percarboxylic acids, and the inorganic peroxyacid salts, e.g. persulfates, such as potassium monopersulfate. Pre-adsorption of the metallo-porphyrin catalyst on to the fabric is a prerequisite for catalytic activity on stain bleaching. Direct mixture of catalyst and peroxyacid in solution (either slowly added or in one aliquot) or
40 inadequate adsorption of the metallo-porphyrin on to the fabric upon peroxyacid release in the bath do not give the desired benefit.

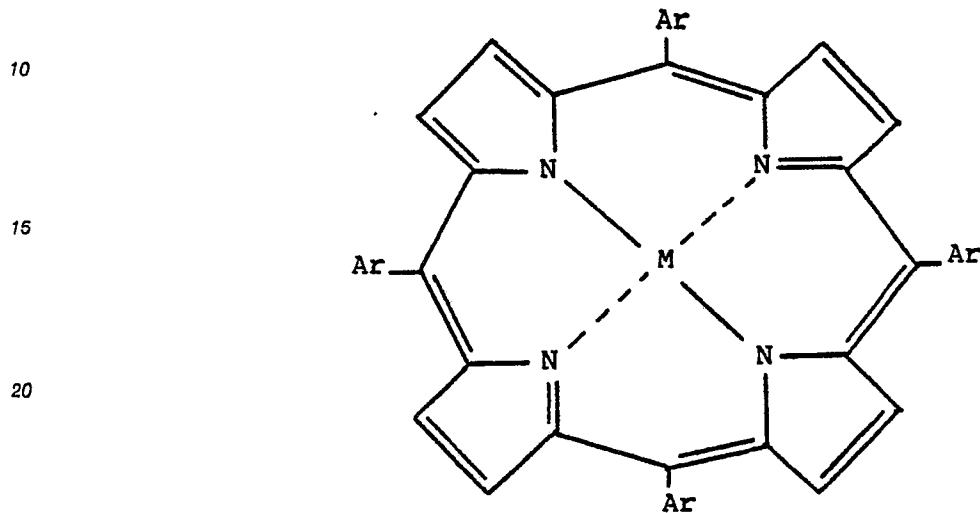
Hence the metallo-porphyrin catalyst must be pre-adsorbed on to the fabric prior to contacting the fabric with the peroxyacid. Pre-adsorption can be effected by applying the metallo-porphyrin manually upon the fabric stains or by treating the fabric in a bath containing a dissolved or solubilised amount of
45 metallo-porphyrin. Sufficient time, however, must be allowed for the catalyst to sufficiently adsorb on to the fabric. Generally at least 2 minutes should be allowed for the fabric to adsorb an effective amount of metallo-porphyrin from solution, preferably 5 to 30 minutes, particularly from 7-15 minutes. When the metallo-porphyrin catalyst is manually applied, via an applicator, upon the fabric stains to effect local stain removal, a shorter residence time in the order of 1 to 5 minutes, preferably 2 to 5 minutes, will normally be
50 sufficient for the catalyst to be effective. It goes without saying that longer residence times will favour the adsorption degree and that in principle there is no upper time limit for the fabric being in contact with the catalyst prior to washing or treating with the peroxyacid solution other than for economic and practical reasons.

Once the metallo-porphyrin is adequately adsorbed on to the fabric, for which the above-stated period of time must be allowed, it is of no benefit, rather it can be detrimental to the bleaching effect if the fabric is

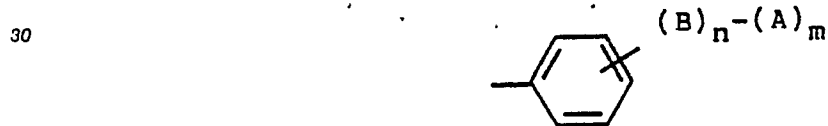
then treated with a bleaching bath wherein the peroxyacid is released at the controlled rate as defined in the art. Treatment of the fabric in a bleaching bath comprising the full amount of peroxyacid is thus advantageous and preferred to obtain the full benefit of the metallo-porphyrin bleaching catalysis action.

Here lies the essential difference between the present invention and the subject matter of the art disclosed in US Patent N° 4,077,768.

The metallo-porphyrins usable as a catalyst in the present invention are compounds having the following structural formula:



wherein M can be Fe (III), Mn (III), Ru (II/III) or Mo (V); Ar is a substituent on the meso-positions and selected from the group consisting of :



35 and



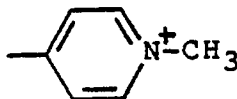
wherein n and m may be 0 or 1, A may be sulphate, sulphonate, phosphate or carboxylate groups; and B is C₁-C₁₀ alkyl, polyethoxyalkyl or hydroxyalkyl. Preferred molecules are those in which the substituents on the phenyl or pyridyl groups are selected from the group consisting of :

-CH₃; -C₂H₅; -CH₂CH₂CH₂SO₃⁻;
-CH₂CH(OH)CH₂SO₃⁻ and SO₃⁻.

50 Preferred metallo-porphyrins are those wherein M is Fe(III) or Mn(III), the iron porphyrins and manganese porphyrins.

A particularly preferred iron or manganese porphyrin is one in which the Ar substituent is 4-N-methylpyridyl:

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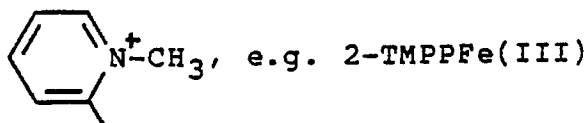
Typical examples of these preferred compounds are 4-4-TMPPFe(III) and 4-TMPPMn(III), known as: [tetra-(N-methylpyridyl)-porphyrinato-iron(III)]Cl₅ and

10 [tetra-(N-methylpyridyl)-porphyrinato-manganese(III)]Cl₅, respectively.

Other specific examples of suitable metallo-porphyrins are :

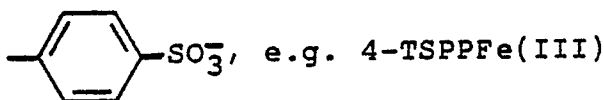
i) Iron or manganese porphyrin in which the Ar substituent is 2-N-methylpyridyl:

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ii) Iron or manganese porphyrin in which the Ar substituent is 4-sulphonatophenyl:



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[tetra-(sulphonatophenyl)-porphyrinato-iron(III)]Cl₅.

The major determinant of catalytic activity appears to be the cationic or anionic nature of the catalyst. Since the catalyst must interact with both the oxidant and substrate, both of which are normally anionic, the advantage of a cationic catalyst is easily understood in terms of favourable electrostatic interactions. With 4-TSPPF(III) the interaction with the substrate is electrostatically disfavoured and electron transfer to the substrate will be less able to compete with catalyst decomposition. Since most substrates in stains are likely to be anionic, a cationic metallo-porphyrin catalyst such as 4-TMPPFe(III); 4-TMPPMn(III); 2-TMPPFe(III) and 2-TMPPMn(III), would be the best choice for practical purposes.

Accordingly, the invention provides a process for cleaning and bleaching fabrics, which process comprises treating the fabric with a metallo-porphyrin compound selected from Fe(III)-, Mn(III)-, Ru(II/III)- and Mo(V)-porphyrins, leaving the fabric in contact therewith for a predetermined time of not less than 1 minute, preferably 2 minutes, to effect sufficient adsorption of said compound on to the fabric, and thereafter washing the fabric with a peroxyacid bleach composition.

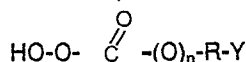
In one aspect of the invention the fabrics are treated in a bath comprising 2 to 25 ppm of a dissolved or solubilised metallo-porphyrin for not less than 2 minutes, normally 5-30 minutes, preferably 7-15 minutes, to which bath a peroxyacid bleaching agent is then added at a level of about 20 to 1000 ppm. The amount of solubilised or dissolved metallo-porphyrin in the bath will depend upon the fabric wash load and the rate of staining, and adjusting the amount is within the ability of the skilled artisan.

In another aspect of the invention an effective amount of metallo-porphyrin is manually applied from an applicator on to the fabric on places with stubborn or persistent stains, leaving the fabric treated therewith for at least 1 minute, preferably 2 minutes, normally 2-5 minutes, which fabric is then washed in a conventional manner with a peroxyacid bleach composition.

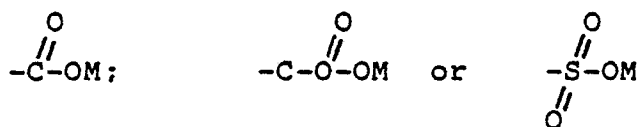
It should be appreciated that the fabrics which are treated in a bath comprising a dissolved or solubilised metallo-porphyrin may, or may not, have been manually pretreated with metallo-porphyrin as is deemed necessary and processes involving this combined treatment are also within the purview of the invention.

The peroxyacid, the activity of which can be catalysed by metallo-porphyrins, particularly iron and manganese porphyrins, includes any organic peroxyacid and inorganic peroxyacid salt.

55 Examples of such organic peroxyacids can be represented by compounds of the general formula :

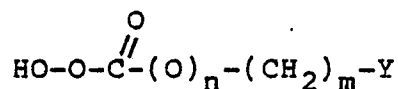


wherein R is an alkylene or substituted alkylene group containing 1 to 20 carbon atoms or an arylene group containing from 6 to 8 carbon atoms, n is 0 or 1, and Y is hydrogen, halogen, alkyl, aryl or any group which provides an anionic moiety in aqueous solution. Such groups can include, for example

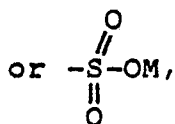


wherein M is H or a water-soluble, salt-forming cation.

The organic peroxyacids and salts thereof can contain either one, two or more peroxy groups and can be either aliphatic or aromatic. When the organic peroxyacid is aliphatic, the unsubstituted acid may have the general formula :



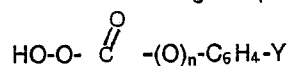
wherein Y can be H, $-\text{CH}_3$, $-\text{CH}_2\text{Cl}$, $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{M}$, $\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{OM}$



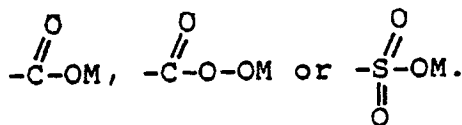
and m can be an integer from 1 to 20.

Specific examples of compounds of this type are peracetic acid, perlauric acid and diperoxydodecanedioic acid.

When the organic peroxyacid is aromatic, the unsubstituted acid may have the general formula :



wherein Y is, for example, hydrogen, halogen, alkyl,



The percarboxy or percarbonic and Y groupings can be in any relative position around the aromatic ring. The ring and/or Y group (if alkyl) can contain any non-interfering substituents, such as halogen or sulphonate groups.

Specific examples of such aromatic peroxyacids and salts thereof include peroxybenzoic acid, m-chloroperoxybenzoic acid, p-nitro-peroxybenzoic acid, p-sulphonato-peroxybenzoic acid, diperoxyisophthalic acid and peroxy-alpha-naphthoic acid.

A specific example of inorganic peroxyacid salts is potassium monopersulphate. A product comprising this compound is the triple salt, $\text{K}_2\text{SO}_4 \cdot \text{KHSO}_4 \cdot 2\text{KHSO}_5$, available commercially under the trade-name Oxone® from E.I. DuPont de Nemours and Company.

The process of the invention may be carried out by simply preparing an aqueous bath comprising a dissolved or solubilised metallo-porphyrin, immersing in said bath the fabric with agitation for a predetermined period of not less than 2 minutes, and thereafter adding to said bath an oxidising bleaching agent in one aliquot, comprising a peroxyacid whilst further agitating the system during a normal washing/soaking time of about 10-60 minutes.

An essential element in the fabric bleaching (cleaning and stain removal) of the invention is that the metallo-porphyrin catalyst has already been present on the cloth upon addition of the oxidising peroxyacid. Without wishing to be bound by any theory, it is believed that this is because the catalyst is stable only in the presence of the substrate which it can oxidise; otherwise it is itself oxidised to a less active form. This can be a drawback for a potential fabric washing product where convenience is all-important. One way around this problem would be to delay the release of the oxidant peroxyacid for 5 to 15 minutes, thereby allowing time for the majority of the catalyst to adsorb on to the fabric.

Accordingly, in one of its product or composition aspects the invention provides a washing product comprising a peroxyacid bleach and, as catalyst therefor, a metallo-porphyrin compound, the peroxyacid being in a form such that it is released into the wash solution only 5 to 15 minutes, preferably 7 to 10 minutes, after the product has been dissolved or dispersed in water. A product that will meet this requirement may be presented in the form of a packaged washing powder comprising a metallo-porphyrin, e.g. [tetra-(N-methylpyridyl)-porphyrinato Fe(III)]Cl₅, together with a separate pack of one-wash peroxyacid-containing sachets which release their contents only 5-15 minutes after contact with the wash liquor.

Alternatively, the product can be in the form of a sachet within a sachet, the inner sachet containing a peroxyacid and being provided by means of delaying release of the contents, and the outer sachet containing a washing composition comprising the metallo-porphyrin catalyst and releasing its contents fairly rapidly upon immersion in water.

Another product form is that of a washing powder comprising a peroxyacid and a metallo-porphyrin catalyst in which the peroxyacid is provided in the form of coherently coated particles. Still other product forms are feasible and those skilled in the art will have no difficulty in selecting product forms by means of existing technology.

Sachets comprising the peroxyacid made of a material consisting of paper coated (at 200 g/m) with a mixture of tallow alcohol (80%) and stearic acid (20%) has proved effective in that they give a delay of release of approximately 7-10 minutes. The same mixture of tallow alcohol and stearic acid can be used as the coating material for peroxyacid particles.

Delayed release as meant here should avoid slow and gradual leaching of the peroxyacid in the wash solution; the contents as a whole should preferably be isolated from the wash solution before the time of release.

In another embodiment, the invention provides a pretreatment product for local application on to fabrics, textiles and clothes, consisting essentially of a liquid or paste-like composition comprising a dispersion or solution of a metallo-porphyrin catalyst in a suitable liquid or semi-liquid carrier, presented in a suitable dispenser for manual application. This composition may be dispensed from any known form of applicator, e.g. aerosol pressure bottles, pump-spray bottles, roller-ball capped bottles, pad applicators etc.

Usually the liquid carrier will also contain a volatile solvent which evaporates upon application, leaving the metallo-porphyrin firmly attached on to the fabric surface to adsorb. An example of a suitable carrier is a mixture of a nonionic surfactant and a lower alcohol, e.g. methanol.

Compositions comprising metallo-porphyrins, e.g. 4-TMPPFe(III), dispersed in a carrier of this type are typical for roller ball capped bottle and pad applicators. Liquid or paste-like compositions for use in a pretreatment product may contain from about 0.1-1.0 g/l metallo-porphyrin, usually from about 0.2-0.5 g/l.

The treating bath as well as the washing composition comprising the metallo-porphyrin catalyst can contain any of the usual components of detergent compositions in the usual amounts. Thus organic detergents of the anionic, nonionic, zwitterionic and cationic types and mixtures thereof may be present, the amount of which generally will be from about 3 to about 40% by weight.

Suitable detergents are well known in the art and examples of such suitable compounds commonly used in the art are given in "Surface Active Agents", Vol. I, by Schwartz and Perry (Interscience 1949) and "Surface Active Agents", Vol. II, by Schwartz, Perry and Berch (Interscience 1958).

Detergency builders, whether inorganic or organic, phosphate or non-phosphate, water-soluble or insoluble, and other water-soluble salts and buffering agents may preferably also be present. In addition thereto the washing composition may contain any other non-interfering ingredients normally used in detergent compositions in minor amounts, which serve to improve the bleaching and laundering characteristics of the composition or which add aesthetic appeal to the composition. Such minor ingredients can include sequestering agents and co-builders (e.g. homo- and co-polymers); suds control agents; soil suspending agents and anti-redeposition agents; enzymes, particularly proteolytic and lipolytic enzymes; corrosion inhibitors, optical brightening agents, colouring agents, perfumes, clays and fillers.

Detergent compositions usable in the present invention may contain from about 3 to about 40% by weight of organic detergent, 0 to 60%, preferably from 5 to about 40% by weight of detergency builder, from about 1 to 10% by weight of peroxyacid, and from about 0.05 to 1.0% by weight of metallo-porphyrin.

They are usable normally at a dosage of 2-10 g/l for washing fabrics at wash loads of about 4-5 kg.

EXAMPLE I

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The catalytic activity of 4-TMPPFe(III) upon the stain removing capacity of various peroxyacids was demonstrated.

The experiments were carried out with tea-stained test cloths immersed in a bath containing 9 ppm 4-TMPPFe (III) and 0.1 M borax (pH 9.2 and T = 30 °C) for 10 minutes. To each bath was then added peroxyacid at a concentration of 1 mM and the reflectance at 460 nm of the test cloths was measured after 25 minutes' wash. These reflectances were compared against control washing with peracid only under the same conditions.

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Bleaching enhancement $\Delta\Delta R_{460}^*$ observed.

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Peracid	$\Delta\Delta R_{460}^*$
Perbenzoic acid	5.3
p-nitroperbenzoic acid	3.0
p-sulphonato perbenzoic acid	5.5
Peracetic acid	7.2
Potassium monopersulphate	3.0

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These bleaching experiments were repeated at 10 °C over a slightly longer time, as any change in temperature will not affect the outcome of the composition reaction, but will affect only the rate at which the reactions take place.

Because of this slow rate, the concentration of the peroxyacid was increased from 1 mM to about 2-3 mM to obtain the full benefit of catalysis within an hour.

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Similar benefits were observed for perbenzoic acid, p-nitroperbenzoic acid, p-sulphonatoperbenzoic acid and potassium permonosulphate. No repeated experiments were made with peracetic acid.

EXAMPLE II

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In this Example bleaching experiments were carried out at 30 °C on tea-stained test cloths using sachets (2.5 x 2.5 cm) made of paper coated (at 200 g/m) with a mixture of tallow alcohol (80%) and stearic acid (20%), which gave a delayed release of approximately 7-10 minutes. Each sachet contained sufficient potassium monopersulphate to give a final concentration of 1.95 mM (0.6 g/l).

These sachets were used in treating baths of pH 9.2 comprising 0.1 M borax with and without 4-TMPPFe(III) at a concentration of 10 ppm.

The results are shown in Fig. 1.

45

In the experiment involving the 4-TMPPFe(III) catalyst a rapid and intensive darkening of the cloth was seen as the intensely coloured porphyrin complex was adsorbed (see run A). With a sufficient monopersulphate level bleaching began after 5 minutes and gave 2 units more bleaching than the monopersulphate only control after approximately 40 minutes (run A vs. B).

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EXAMPLE III

The following liquid pretreatment product was prepared:

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4-TMPPFe(III) 0.2 g/l

*C₁₃ -C₁₅ alcohol/7 ethoxylate.

nonionic surfactant
 (Synperonic®A7) * 50% v/v
 methanol 50% v/v

5 The product dispensed from a roller-ball capped bottle was applied directly to the stain and the solvent, methanol, allowed to evaporate (abt. 4 minutes) leaving a high level of catalyst and nonionic adsorbed on to the stained area. Washing the pretreated cloth with a peracid (monopersulphate) containing product resulted in improved bleaching of the treated area.

10 A striking demonstration of the potential of the product is obtained by the use of Direct Red 80 dyed cotton as monitor. This dye is a particularly good substrate for catalyst bleaching and the cloth is heavily dyed. The bleaching of the pretreated cloths was performed in the absence of a detergent base using only borax as buffer to adjust the pH at 9.4 with potassium monopersulphate (1 g/l) as the bleach. The results are presented below, where the bleaching was assessed using K/S values from reflectance measurements at the dye maximum of 540 nm.

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Temp. (°C)	Wash time (min.)	% removal	
		treated	untreated
20	15	37	3
35	3	65	3

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25 When a percompound/precursor system was used, sufficient time must be allowed for the precursor to generate the peracid. With 5 g/l of a detergent formulation comprising 10% sodium perborate/2.3% tetraacetyl ethylenediamine at 30°C, a generation time of 10 minutes, followed by a wash of 15 minutes, resulted in an additional benefit of 3.9 units on tea-stained test cloth. This represented an increase of 24% to 40% removal of the stain.

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EXAMPLE IV

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Stain bleaching with manganese porphyrin

40 A sample of 4-TMPPMn(III) was prepared as a penta(hexafluorophosphate) salt with a molecular weight of 1,300.

Bleaching was performed on test pieces that had been soaked in a 10 ppm solution of 4-TMPPMn(III) for 30 minutes. This level was sufficient to saturate the cloths present, although the adsorption appeared to be about 2.5 times slower than for 4-TMPPFe(III).

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Potassium monopersulphate was used as the oxidant and the catalyst was tested on three different bleach-sensitive cloths, viz tea, EMPA 114 (= red wine) and Direct Red 80.

The DR 80 cloth was dyed with a red Azo-dye that resembles the substrate used for solution bleaching studies and as such represented a good comparison of homo- and heterogeneous bleaching response.

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The EMPA 114 was prewashed before use to remove the detergent fraction. Cloths were removed at different times during the bleaching reaction and resultant reflectance measurements were corrected for contributions from uncatalysed bleaching.

The results showed an additional benefit due to catalysis after some 10-15 minutes, and the results for both 4-TMPPMn(III) and 4-TMPPFe(III) were collected and shown in the following Table:

55

TABLE

Test cloth	$\Delta\Delta R -$ Mn(III)	$\Delta\Delta R -$ Fe(III)
Tea-stained	0	3
EMPA 114	5	3
DR 80-Dye	10.4	7
Test conditions:		
Temperature 30 ° C		
Wash pH = 9.4 (0.1 M Borax)		
Catalyst level 10 ppm		
0.7 mM K-monopersulphate with Fe(III)		
0.65 mM K-monopersulphate with Mn(III)		

20 Two points emerge from this Table:

- 1) the effect of 4-TMPPMn(III) on EMPA 114 and DR 80 was greater than that of the Fe(III) analogue.
- 2) the results for 4-TMPPMn(III) display a particularly interesting selectivity: EMPA 114 and DR 80 underwent catalysed bleaching whereas tea did not.

25 These results could possibly be used as a guidance to use mixtures of metallo-porphyrins for obtaining the best peracid bleaching results at lower temperatures.

Claims

- 30 1. A process for cleaning and bleaching fabrics, which process comprises treating the fabrics with an effective amount of a metallo-porphyrin compound selected from Fe(III)-, Mn(III)-, Ru(II/III)- and Mo(V)-porphyrins, leaving the fabrics in contact therewith for a predetermined time of not less than 1 minute, preferably not less than 2 minutes, to effect sufficient adsorption of said metallo-porphyrin compound on to the fabric, and thereafter washing the fabric with a peroxyacid bleach composition.
- 35 2. A process according to claim 1, wherein the fabrics are treated in a bath comprising 2 to 25 ppm of said dissolved or solubilised metallo-porphyrin for not less than 2 minutes, to which bath is then added a peroxyacid bleaching agent at a level of about 20 to 1000 ppm.
3. A process according to claim 1, wherein said metallo-porphyrin is manually applied from an applicator on to the fabric on places with stubborn or persistent stains.
- 40 4. A process according to claim 1, 2 or 3, wherein said metallo-porphyrin is Fe(III)- or Mn(III)-porphyrin.
5. A process according to any of the claims 1-4, wherein said porphyrin is cationic in nature.
6. A process according to claim 5, wherein the substituent Ar on the meso-positions of the porphyrin structure is 4-N-methylpyridyl or 2-N-methylpyridyl.
7. A washing composition comprising a peroxyacid bleach and, as catalyst therefor, a metallo-porphyrin compound, selected from Fe(III)-, Mn(III)-, Ru(II/III)- and Mo(V)-porphyrins, the peroxyacid being in a form such that it is released into the wash solution only 5 to 15 minutes after the composition has been dissolved or dispersed in water.
8. A washing composition according to claim 7, wherein said metallo-porphyrin is Fe(III)- or Mn(III)-porphyrin.
- 50 9. A washing composition according to claim 7 or 8, wherein said porphyrin is cationic in nature.
10. A washing composition according to claim 9, wherein the substituent Ar on the meso-positions of the porphyrin structure is 4-N-methylpyridyl or 2-N-methylpyridyl.
11. A pretreatment product for local application on to fabrics, textiles and clothes, consisting essentially of a liquid or paste-like composition comprising a dispersion or solution of a metallo-porphyrin catalyst in a suitable liquid or semi-liquid carrier, presented in a suitable dispenser for manual application.
- 55 12. A pretreatment product according to claim 11, wherein said metallo-porphyrin is Fe(III)- or Mn(III)-porphyrin.
13. A pretreatment product according to claim 11 or 12, wherein said porphyrin is cationic in nature.

14. A pretreatment product according to claim 13, wherein the substituent Ar on the meso-positions of the porphyrin structure is 4-N-methylpyridyl or 2-N-methylpyridyl.

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Fig.1.

