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(54) Metallo-porphyrins for use as bleach catalyst.

(57) Metallo-porphyrins having improved stability against oxidation for use as peracid bleach catalyst in the bleaching of fabrics are disclosed. The metallo-porphyrins are Mn(III)- or Fe(III)-porphyrins having Ar-substituents on the meso-positions selected from

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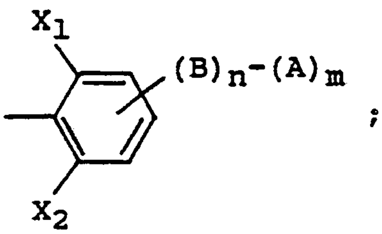

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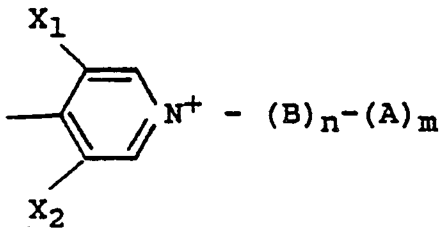
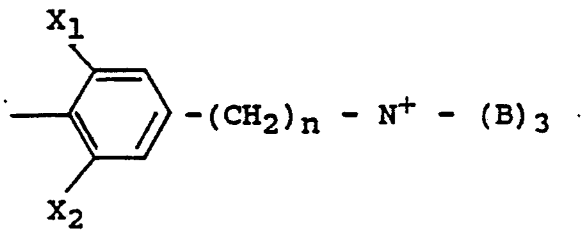


and

(c)



wherein n and m may be 0 or 1; A may be sulphate, sulphonate, phosphate or carboxylate groups; B is C_1-C_{10} alkyl, polyethoxyalkyl or hydroxyalkyl, and X_1 and X_2 are Cl, Br, CH_3, C_2H_5 or CH_3O.

EP 0 384 503 A1

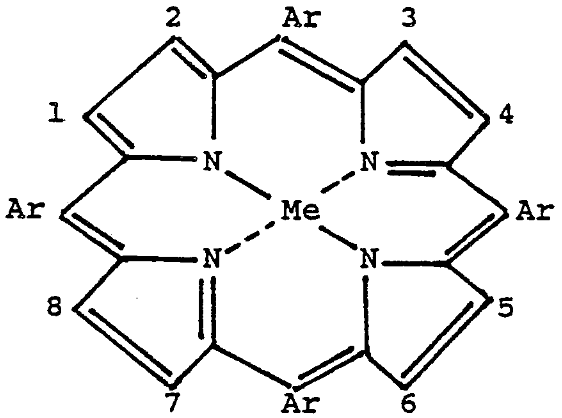
METALLO-PORPHYRINS FOR USE AS BLEACH CATALYST

This invention relates to improved metallo-porphyrins for use as a bleach catalyst in the bleaching of fabrics and to compositions for the cleaning and bleaching of fabrics comprising said metallo-porphyrins.

It is known that metallo-porphyrins can act as an oxidation catalyst. WO 88/07988 describes the use of metallo-porphyrins as catalyst in a variety of oxidative reactions. U.S. Patent N° 4,077,768 describes the use of iron-porphyrins with an oxidising bleach, e.g. hydrogen peroxide and also peracids, in aqueous wash liquors for dye bleaching in solution, i.e. for inhibiting dye-transfer during the washing of fabrics. It is also known from EP-A-0306089 (published 8 March 1989) that metallo-porphyrins under careful conditions can effectively catalyse the fabric stain bleaching action of peroxyacid bleach systems, thereby making the peroxyacid more effective for use in the washing of fabrics at the lower temperature region of between about 10° C and 40° C. A drawback of metallo-porphyrins as bleach catalyst is that they are themselves unstable against oxidation by the oxidising bleach. Although the mode of action of metallo-porphyrin bleach catalysis is not fully understood, it appears that in the presence of an oxidising bleach the metallo-porphyrin catalyst forms an intermediate substance. This can react with substances able to be oxidised and bleached, whereby the catalyst is reformed, and this is the desired reaction. However, the intermediate substance can also react with a second metallo-porphyrin forming a dimeric -oxo bridged species which is ineffective as bleaching agent and quickly degrades under the oxidative conditions. Reaction of the metallo-porphyrin with hydrogen peroxide, in the absence of a substrate, results in degradation via a different pathway in which radicals are believed to play a role. It is thus necessary that careful measures should be taken to avoid the metallo-porphyrins being oxidised. In the bleaching of fabrics with peroxyacids, the art teaches that metallo-porphyrins must be pre-adsorbed on to the fabric to exert their catalytic activity on stain bleaching. Even so, some loss of catalyst due to decomposition, with consequent reduction of catalytic activity cannot be avoided.

The invention now provides improved metallo-porphyrins as peroxyacid bleach catalysts which are more stable against oxidation by mono oxygen donor type oxydators (like peroxyacids, hypochlorite and tert.butyl hydroperoxide), than the metallo-porphyrins suggested in the art for use in the bleaching of fabrics.

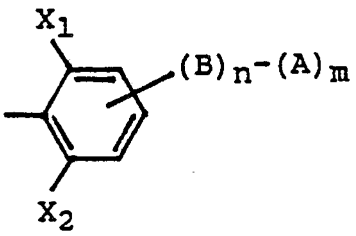
The metallo-porphyrins for use as peroxyacid bleach catalyst in the bleaching of fabrics according to the invention are compounds having the following structural formula:



(I)

wherein Me is a metal ion, selected from Mn(III) and Fe(III); and Ar is a substituent selected from the group consisting of

(a)



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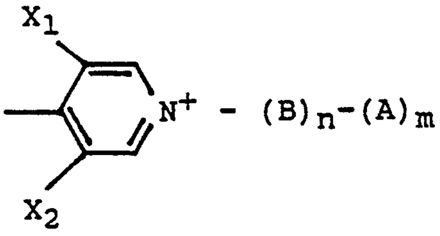

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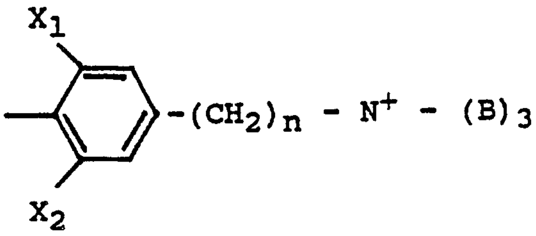
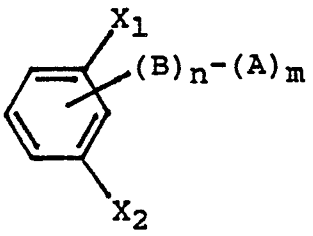


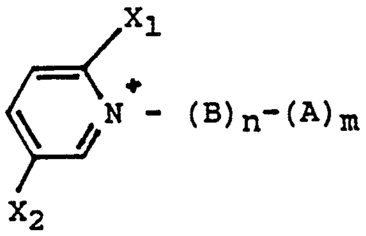
wherein n and m may be 0 or 1; A may be sulphate, sulphonate, phosphate or carboxylate groups; B is C_1-C_{10} alkyl, polyethoxy alkyl or hydroxy alkyl and X_1 and X_2 are Cl, Br, CH_3, C_2H_5 or CH_3O.

Although not essential, the porphyrin core formula (I) may be substituted at one or more of the remaining carbon positions indicated by the numbers 1-8, with e.g. C_1-C_{10} alkyl, hydroxy alkyl or oxyalkyl groups.

The phenyl or pyridyl group (a), (b) or (c) may or may not contain other substituents, but it has been found that improved stability is only achieved if the X_1 and X_2 substituents are attached on the phenyl or pyridyl group at exactly the indicated places near the porphine core. X_1 and X_2 substituents attached on other places of the phenyl or pyridyl group such as:



or



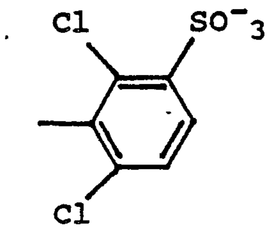
have no effect on stability whatsoever.

Preferred molecules are those in which the $-(B)_n-(A)_m$ substituents on the phenyl or pyridyl groups are selected from:

$-CH_3$; $-C_2H_5$; $-CH_2-CH_2-CH_2.SO_3^-$; $-CH_2CH(OH)CH_2SO_3^-$ and $-SO_3^-$.

Preferably X_1 and X_2 are Cl, Br or CH_3, particularly Cl or CH_3.

Typical examples of preferred Fe(III) and Mn(III) porphyrins are thus compounds wherein the Ar-substituents are: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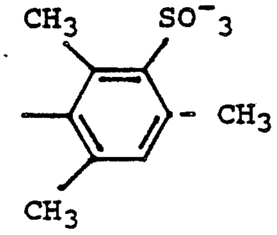

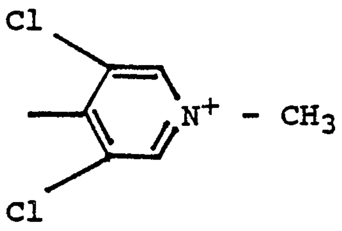
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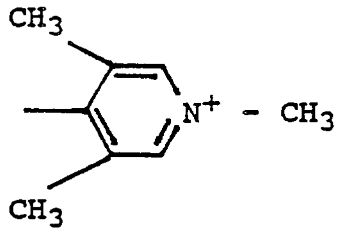

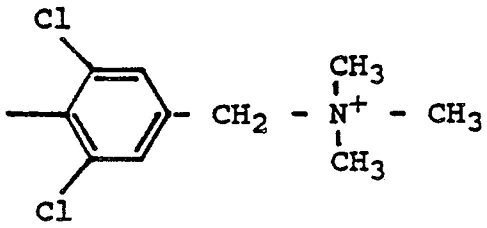
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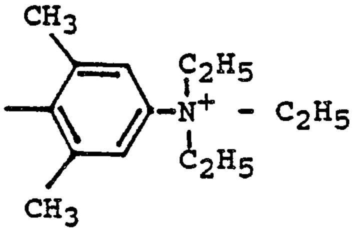


The metallo-porphyrins of the invention can be used as a catalyst for peroxyacids or peroxyacid salts for the bleaching of fabrics in the same manner as applied with the known metallo-porphyrins of the art, but it can easily be appreciated that the improved stability thereof will result in a more effective and efficient use of the catalyst.

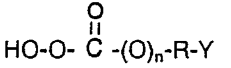
A common process of using metallo-porphyrins as catalyst in the bleaching and cleaning of fabrics with peroxy acid or a peroxyacid salt is by treating the fabrics with the metallo-porphyrin compound, leaving the fabric in contact therewith for a predetermined time to effect sufficient adsorption of said compound on to the fabric, and thereafter washing the fabric with a peroxyacid bleach composition. The fabrics may be treated in a bath comprising an effective amount of a dissolved or solubilised metallo-porphyrin (normally in the range of 2 to 25 ppm) for several minutes, to which bath is then added a peroxyacid bleaching agent in an amount sufficient to effect the required bleaching effect (normally at a level of about 20-1000 ppm). The amount of solubilised or dissolved metallo-porphyrin in the bath and also the amount of peroxyacid bleach added thereto will depend upon the fabric wash load and the rate of staining, the adjustment thereof being within the ability of the skilled artisan.

An alternative way of pretreating the fabrics is by manual application on to the fabric on places with stubborn and persistent stains, and leaving the fabric treated therewith for a couple of minutes, whereafter the fabric is 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.

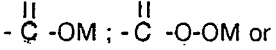
The peroxyacids, the activity of which can be catalysed by the metallo-porphyrins of the invention, include any organic peroxyacids and inorganic peroxyacid salts.

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

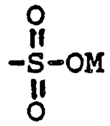


$$HO\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(O)_n\text{-}R\text{-}Y$$

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:



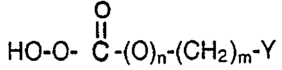
$$-\overset{\overset{O}{\|}}{C}\text{-}OM\ ;\ -\overset{\overset{O}{\|}}{C}\text{-}O\text{-}OM\ \text{or}$$



$$-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OM$$

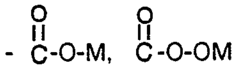
wherein M is H or a water-soluble, salt-forming cation.

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:

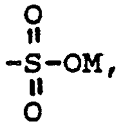


$HO\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}(O)_n\text{-}(CH_2)_m\text{-}Y$

wherein Y can be H, $-CH_3$, $-CH_2Cl$,



$-\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}M$, $\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}OM$ or

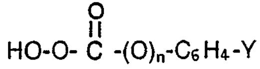


$$-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OM,$$

and m can be an integer from 1 to 20.

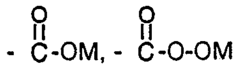
Specific examples of compounds of this type are peracetic acid, perlauric acid and diperoxydodecanedioic acid.

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

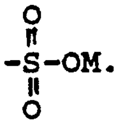


$HO\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}(O)_n\text{-}C_6H_4\text{-}Y$

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



$-\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OM$, $-\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}OM$ or



$$-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OM.$$

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 acids m-chloroperoxybenzoic acid, p-nitro-peroxybenzoic acid, p-sulphonato-peroxybenzoic acid, diperoxyisophthalic acid and peroxy-alpha-napthoic acid.

A specific example of inorganic peroxyacid salts is potassium monopersulphate. A product comprising this compound is the triple salt, $K_2SO_4.KHSO_4.2KHSO_5$, available commercially under the trade-name Oxone ^{R} from E.I. Dupont de Nemours and Company.

Accordingly, the invention provides the use of a metallo-porphyrin of structural formula (I), as defined herein above, as a bleach catalyst for the bleaching of fabrics with a peroxyacid bleach system.

The invention also provides a fabric washing product comprising a detergent active-material, a peroxyacid bleach and said metallo-porphyrin as catalyst therefor.

Fabric washing products according to the invention may be presented in any form, including that of a packages washing powder comprising the metallo-porphyrin catalyst, together with a separate pack of one-wash peroxyacid containing sachets.

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 a 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 for example that of a washing powder comprising a peroxyacid and the 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.

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 as defined herein in a suitable liquid or semi-liquid carrier, presented in a suitable dispenser for manual application of any known form of applicators, such as an aerosol pressure container, pump-spray bottle, roller-ball capped bottle, pad applicators and the like.

In such applicators 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 absorb. An example of a suitable carrier is a mixture of a nonionic surfactant and a lower alcohol, e.g. methanol.

Compositions comprising the metallo-porphyrins of the invention 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 detergent-active materials of the anionic, nonionic, zwitterionic and cationic types and mixtures thereof can be present, in an amount from about 3 to about 40% by weight.

Suitable detergent-actives 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 copolymers); 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.

Fabric washing compositions usable in the present invention may contain from about 3 to about 40% by weight of organic detergent active material, 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.

The invention will now be illustrated by way of the following non-limiting examples.

Example I

Preparation of metallo-porphyrins according to the invention.

(i) Tetrakis-(2,4,6-trimethyl-3-sulphonatophenyl)-porphyrinato-Mn(III)OH^{4-} $(Na^{+})_4$

To 2.14 g pyrrole (0.02 mol) and 2.96 g 2,4,6-trimethylbenzaldehyde solved in 3 l dichloromethane (dry) is added 0.5 ml of boron trifluoride-etherate. After 24 h stirring under argon in the dark, the mixture is refluxed for 30 minutes in the presence of 15 g chloranil (0.06 mol). The mixture is concentrated and chromatographed on alumina with chloroform as eluent. The porphyrin-containing fractions are pooled and evaporated. From the residue the tetrakis-(2,4,6-trimethyl phenyl) porphyrin is obtained by crystallisation from hexane. Treatment of this porphyrin with concentrated sulphuric acid yields the tetrakis-(2,4,6-trimethyl-3-sulphonato)-porphyrin as its four atropisomers. Stirring the latter in aqueous Mn-acetate (1M), subsequent treatment with ion exchanger (Dowex 50 W-H^{+}-form) and final neutralisation yields the compound (i) which is further purified by chromatography on a Sephadex L H-20 column in methanol and obtained in a yield of 0.8 gram (20%).

The system is characterised by its UV/VIS, IR and FAB-mass-spectrometry.

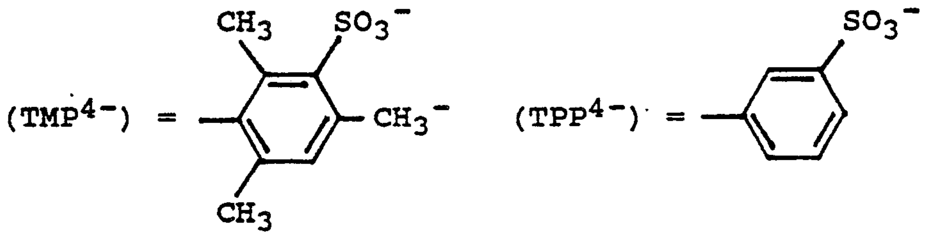
(ii) Tetrakis-(2,4,6-trimethyl-3-sulphonatophenyl)-porphyrinato-Fe(III)OH^{4-} (Na^{+})$_4$

This system was prepared in a manner similar to that as described for (i) above, except that now metalation was performed using $FeSO_4$, giving the compound (ii) in a 0.3 gram (7%) yield, similary characterised as described for the manganese porphyrin.

Example II

The oxidation stability of the substituted mangano-porphyrin of Example I (i) (TMP^{4-}) against potassium monopersulphate (HSO_5^-) and peracetic acid (per-Ac) was determined and compared with a non-substituted mangano-porphyrin (TPP^{4-}).

Ar-substituents:



Stabilities were measured by means of a UV/VIS spectroscopic method in the absence of a substrate at catalyst concentration of 10-6 mol/l.

The results are tabulated below.

Table 1

Stability values from tests with HSO_5^-(3.8 x 10^{-3} mol/l)							
Time (min.)	0	4	8	15	30	60	T ½
TMP^{4-}	100	96	92	89	83	75	120.0 minutes
TPP^{4-}	100	63	33	18	-	-	5.5 minutes

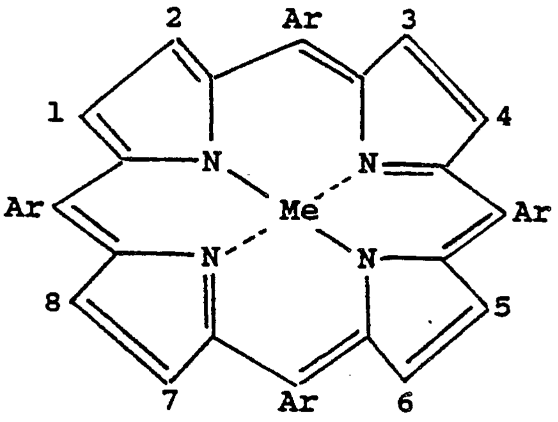
Table 2

Stability values from tests with Per-Ac (2.4 x 10^{-3} mol/l)					
Time (min.)	0	5	10	30	T ½
TMP^{4-}	100	96	94	91	150.0 minutes
TPP^{4-}	100	30	15	-	2.0 minutes

From the above tables it is clearly seen that TMP^{4-} of the invention is more stable than TPP^{4-} of the art against peracetic acid and potassium monopersulphate. In terms of half-life time, TMP^{4-} is about 20 times more stable against HSO_5^- and about 75 times more stable against peracetic acid than TPP^{4-}.

Claims

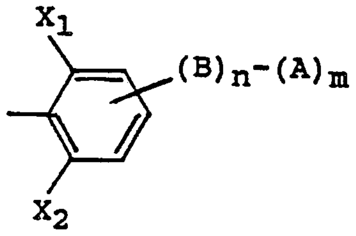
1. Use as a peroxyacid bleach catalyst in the bleaching of fabrics of a metallo-porphyrin having the following structural formula:



(I)

wherein Me is a metal ion, selected from Mn(III) and Fe (III); Ar is a substituent selected from the groups consisting of

(a)



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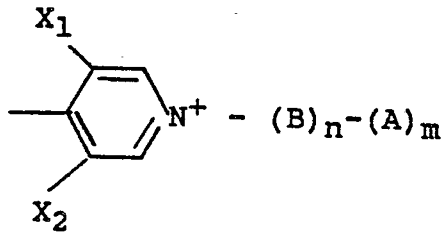

and

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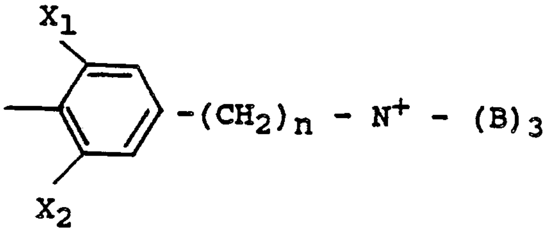

wherein n and m may be 0 or 1; A may be sulphate, sulphonate, phosphate or carboxylate groups; B is C_1-C_{10} alkyl, polyethoxy alkyl or hydroxy alkyl and X_1 and X_2 are Cl, Br, CH_3, C_2H_5 or CH_3O.

2. Use according to claim 1, characterized in that the $-(B)_m-(A)_m$ substituent is selected form $-CH_3$; $-C_2H_5$; $-CH_2-CH_2-CH_2-SO_3^-$; $CH_2-CH(OH)-CH_2-SO_3^-$ and SO_3^-.

3. Use according to claim 1 or 2, characterized in that X_1 and X_2 are Cl, Br or CH_3.

4. A fabric washing composition comprising a detergent active material, a peroxyacid bleach and a metallo-porphyrin having the structural formula (I) of claim 1.

5. A fabric washing according to claim 4; characterized in that the $-(B)_n-(A)_m$ substituent is selected from $-CH_3$; $-C_2H_5$; $CH_2-CH_2-CH_2-SO_3^-$; $CH_2-CH(OH)-CH_2-SO_3^-$; and SO_3^-.

6. A fabric washing composition according to claim 4 or 5, characterized in that X_1 and X_2 are Cl, Br of CH_3.

7. 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 having structural formula (I) of claim 1, in a suitable liquid or semi-liquid carrier, presented in a suitable dispenser for manual application.

8. A pretreatment product according to claim 7, characterized in that the $-(B)_n-(A)_m$ substituent is

selected form $-CH_3$; $-C_2H_5$; $CH_2\text{-}CH_2\text{-}CH_2\text{-}SO_3^-$; $CH_2\text{-}CH(OH)\text{-}CH_2\text{-}SO_3^-$ and SO_3^-.

9. A pretreatment product according to claim 7 or 8, characterized in that X_1 and X_2 are Cl, Br or CH_3.

European Patent
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EUROPEAN SEARCH REPORT

Application number
EP 90200228.6

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl^5)
D,P,X	<u>EP - A2 - 0 306 089</u> (UNILEVER NV) * Claims * --	1,2,4,5,7,8	C 11 D 3/395 D 06 L 3/04 C 09 B 47/32
D,X	<u>US - A - 4 077 768</u> (JOHNSTON) * Claims * --	1-9	
D,Y	<u>WO - A1 - 88/07 988</u> (DOLPHIN) * Claims * ----	1-3	

TECHNICAL FIELDS SEARCHED (Int Cl^5)

C 11 D
D 06 L
C 09 B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	08-05-1990	SCHÄFER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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