

(12) **EUROPEAN PATENT SPECIFICATION**

- (45) Date of publication and mention of the grant of the patent:
09.04.2003 Bulletin 2003/15
- (21) Application number: **99957058.3**
- (22) Date of filing: **10.06.1999**
- (51) Int Cl.7: **C07D 471/18**, C11D 3/39
// (C07D471/18, 257:00, 221:00), C07D221:00
- (86) International application number:
PCT/GB99/01850
- (87) International publication number:
WO 99/065905 (23.12.1999 Gazette 1999/51)

(54) **BLEACH CATALYSTS AND FORMULATIONS CONTAINING THEM**

BLEICHKATALYSATOREN UND SIE ENTHALTENDE FORMULIERUNGEN

CATALYSEURS DE BLANCHIMENT ET FORMULATIONS LES CONTENANT

- (84) Designated Contracting States:
BE DE ES FR GB IT
- (30) Priority: **15.06.1998 GB 9812916**
01.09.1998 GB 9819046
19.03.1999 GB 9906474
- (43) Date of publication of application:
04.04.2001 Bulletin 2001/14
- (73) Proprietors:
- **UNILEVER PLC**
London EC4P 4BQ (GB)
Designated Contracting States:
GB
 - **UNILEVER N.V.**
3013 AL Rotterdam (NL)
Designated Contracting States:
BE DE ES FR IT
- (72) Inventors:
- **BANSE, Frédéric, Lab. de Chimie Inorganique**
91405 Orsay (FR)
 - **CARINA, Riccardo,**
Unilever Research Port Sunlight
Bebington, Wirral, Merseyside L63 3JW (GB)
- **DELROISSE, Michel, Unilever Res. Port Sunlight**
Bebington, Wirral, Merseyside L63 3JW (GB)
 - **GIRERD, Jean-Jacques,**
Lab. de Chimie Inorganique
91405 Orsay (FR)
 - **HAGE, Ronald, Unilever Research Vlaardingen**
3133 AT Vlaardingen (NL)
 - **SIMAAN, Jalila Ariane,**
Lab. de Chimie Inorganique
91405 Orsay (FR)
 - **TETARD, David,**
Unilever Research Port Sunlight
Bebington, Wirral, Merseyside L63 3JW (GB)
- (74) Representative: **Elliott, Peter William et al**
Unilever plc
Patent Division
Colworth House
Sharnbrook
Bedford MK44 1LQ (GB)
- (56) References cited:
WO-A-94/26276 **WO-A-96/06154**
WO-A-98/10286

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] The present invention relates to new macrocyclic bleach catalysts, to formulations comprising these catalysts, as well as bleaching processes which employ these catalysts.

Background of the Invention:

[0002] Metal ion catalysis of oxygen bleaches, particularly in fabric washing processes, is well known. In these systems, a metal such as manganese, generally attached to a suitable ligand is exposed to the fabric together with an oxygen bleach such as hydrogen peroxide. A known disadvantage of such systems is that the metal species can be abstracted from the ligand and oxidised to form an insoluble oxide precipitate which deposits at the fabric surface.

[0003] Two mechanisms have been proposed for catalysed bleaching, in one the oxygen bleach is decomposed in the presence of the catalyst to a short-lived but highly active species such as the hydroxyl radical. In the other proposed mechanism, the oxygen bleach reacts with the catalyst to form an intermediate species which either transfers oxygen or abstracts hydrogen atoms or electrons to the substrate. As will be appreciated, the first type of reaction is relatively non-specific as regards the substrate while the second is likely to be influenced strongly by the nature of the substrate and its reactivity with the intermediate.

[0004] While the non-specific reaction is likely to attack most materials which are susceptible to bleaching, it is not suitable for many applications. There is a need for electron or oxygen transfer systems which are capable of reacting with structures such as catechols, and curcumin etc., which are found in the components of, for example, wine and tea stains (catechol) or curry stains (curcumin). It is important that the components of such electron or oxygen transfer systems are hydrolytically stable so as avoid the disadvantages mentioned above.

[0005] Bottino et al (*J. Org. Chem.* **1988**, 53, 3521-3529) disclose the synthesis of symmetrical N-tosyl aza macrocycles. Kruger (*Chem. Ber.* **1995**, 128, 531-539) discloses the N, N - Dimethyl-2,11-diazo[3.3] (2,6)pyridinophane (NND-DP) complexes of copper, nickel and cobalt. The corresponding vanadium complex is disclosed in *Inorg. Chem.* (**1996**), 35, 3533.

NNDDP is a macrocyclic ligand. Other manganese macrocyclic ligand complexes are known as mimics of superoxide dismutase form Riley et. al. (*J. Am. Chem. Soc.*, **1994**, 116, 387-388). However, these are not aryl ligands.

[0006] WO 94 26276 and WO 97 31005 disclose pyridinophanes as contrast agents for diagnostic purposes.

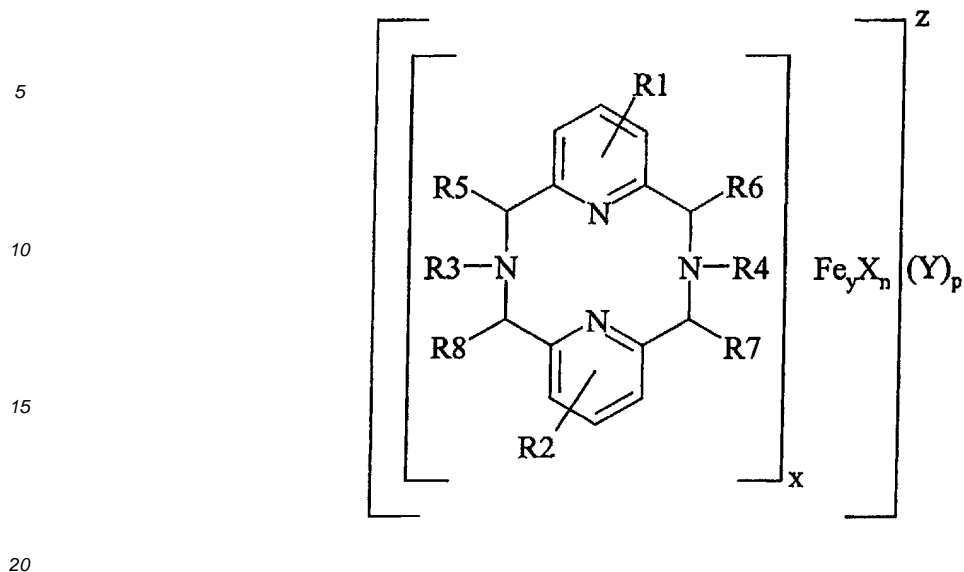
[0007] Koch et. al. (*Angew. Chem. Int. Ed. Engl.*, **1995**, 34, No 23/24 p 2671-2674) (hereinafter called the "First Koch Reference") disclose that certain Iron III complexes of NNDDP are capable of mimicking the biological activity of intradiol-cleaving catechol dioxygenases and converting catechols, in the presence of oxygen to the corresponding muconic acid. The synthesis of certain eight-co-ordinate iron II and iron III complexes of bis(2,11-diaza [3.3] (2,6) pyridinophane, i.e. certain non-methylated analogues of NNDDP is described by Koch et. al. in *Angew. Chem., Int. Ed. Engl.*, (**1996**), 35(4), 422-4 (hereinafter called the "Second Koch Reference"). However, there is no disclosure of the suitability of such materials as bleach catalysts for detergent products, nor any description of corresponding iron complexes having a lower co-ordination number.

Brief Description of the Invention:

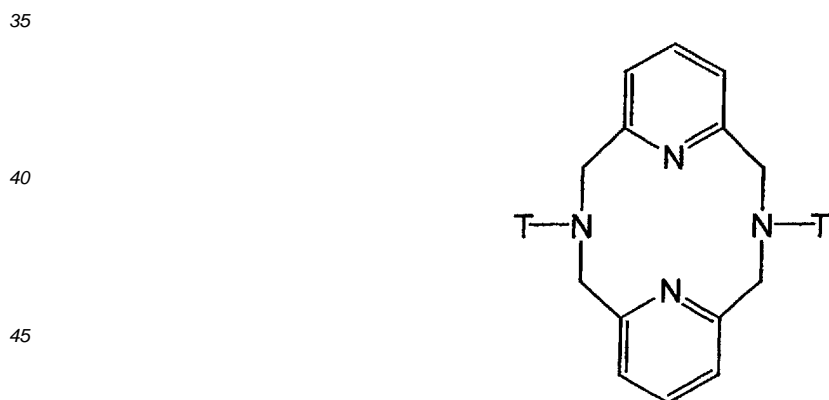
[0008] It has now been discovered that certain novel ligands which are NNDDP analogues have novel activities in themselves and furthermore in complex with various metals, also have better activity than known iron III NNDDP complexes. They exhibit unexpected hydrolytic stability, as well as stability against metal abstraction by metal abstracting agents. Furthermore, these new materials show unexpected activity with air, or molecular oxygen or other oxygenated bleaching materials such as peroxides, persalts or peracids, against catechol and catechol-like materials which form a significant component of several common laundry stains.

They could also find application in a wide range of other uses where a bleaching effect is desired.

[0009] The present invention provides a bleach catalyst of formula (IV) :

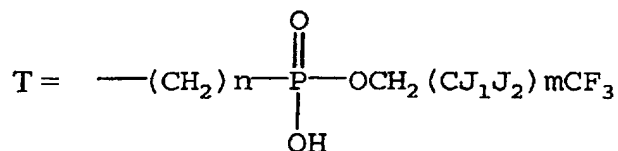


wherein Fe represents an iron atom in oxidation state II or III, X is a group which is either a bridge or is not a bridge between iron atoms, Y is a counter-ion, x and y being ≥ 1 , $0 \leq n \leq 3$, and z being the charge of the metal complex, and $p = z / \text{charge of Y}$; R₁ and R₂ being independently one or more ring substituents selected from hydrogen and electron donating and withdrawing groups selected from: halo, C₁₋₆ alkoxy, hydroxy, hydroxyalkyl, (optionally mono- or di-substituted) amine groups, (optionally mono- or di-substituted) thiol groups, carboxyl, ester, amide, substituted carbonyl groups in general, nitrile, nitro, (optionally substituted) sulphonyl, alkenyl, aryl, quaternary ammonium (+) and sulphonium (+); R₃ - R₈ being independently hydrogen, alkyl, hydroxyalkyl, alkenyl or variants of any of these when substituted by one or more electron donating or withdrawing groups selected from: halo, C₁₋₆ alkoxy, hydroxy, hydroxyalkyl, (optionally mono- or di-substituted) amine groups, (optionally mono- or di-substituted) thiol groups, carboxyl, ester, amide, substituted carbonyl groups in general, nitrile, nitro (optionally substituted) sulphonyl, alkenyl, aryl, quaternary ammonium (+) and sulphonium (+) with the proviso that in the bleach catalyst of formula (IV) the following ligand is excluded:



50 wherein in case 1, both T = CH₃,
wherein in case 2, T = H or

55



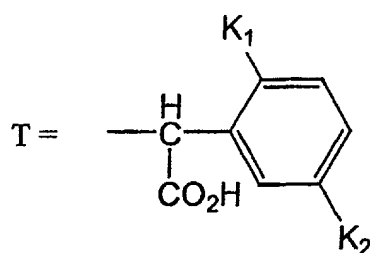
where m is 0 or an integer of 1, 2, 3 or 4;

n is an integer of 1, 2 or 3;

J₁ and J₂ = H or F,

wherein in case 3, T = -CH₂COOH, -CH₂P(O)OHW

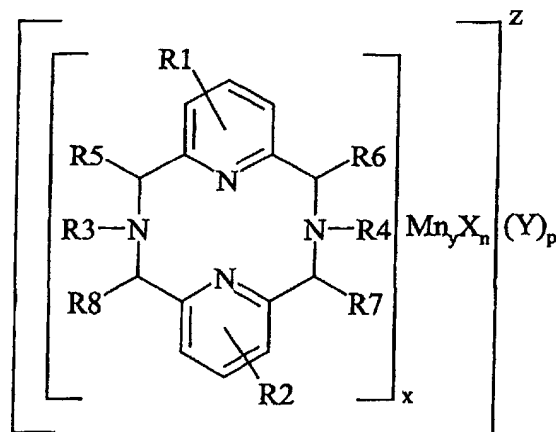
where W is OH or, C1-C5-alkyl or -O-(C1-C5)-alkyl, or



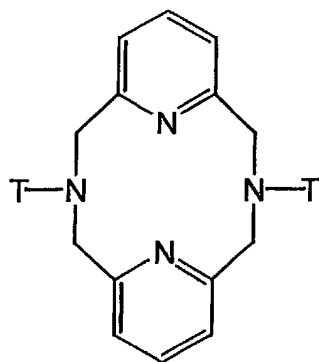
where K₁ = -OH or -OCH₃

K₂ is -NO₂, -NH₂, isothiocyanato, semicarbazido, thiosemicarbazido, maleimido, bromoacetamido or carboxyl.

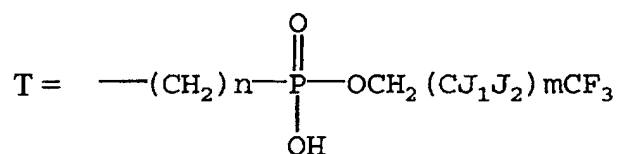
[0010] The present invention also provides a bleach catalyst of formula (V):



wherein Mn represents a manganese atom in oxidation state II, III, IV, or V, X is a group which is either a bridge or is not a bridge between manganese atoms, Y is a counter-ion, x and y being ≥ 1 , $0 \leq n < 3$, and z being the charge of the metal complex, and $p = z / \text{charge of Y}$; R₁ and R₂ being independently one or more ring substituents selected from hydrogen and electron donating and withdrawing groups selected from: halo, C₁₋₆alkoxy, hydroxy, hydroxyalkyl, (optionally mono- or di-substituted) amine groups, (optionally mono- or di-substituted) thiol groups, carboxyl, ester, amide, substituted carbonyl groups in general, nitrile, nitro, (optionally substituted) sulphonyl, alkenyl, aryl, quaternary ammonium (+) and sulphonium (+), R₃, R₄, R₅, R₆, R₇ and R₈ being independently hydrogen, alkyl, hydroxyalkyl, alkenyl or variants of any of these when substituted by one or more electron donating or withdrawing groups with the proviso that in the bleach catalyst of formula (IV) the following ligand is excluded:



15 wherein in case 1, T = H or



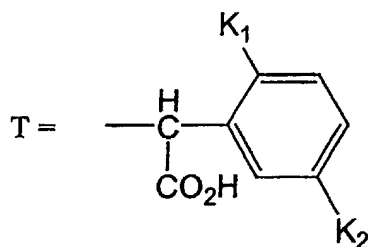
25 where m is 0 or an integer of 1, 2, 3 or 4;

n is an integer of 1, 2 or 3;

J₁ and J₂ = H or F,

wherein in case 2, T = -CH₂COOH, -CH₂P(O)OHW

30 where W is OH or, C1-C5-alkyl or -O-(C1-C5)-alkyl, or



where K₁ = -OH or -OCH₃

K₂ is -NO₂, -NH₂, isothiocyanato, semicarbazido, thiosemicarbazido, maleimido, bromoacetamido or carboxyl.

45 The present invention comprises a bleaching composition comprising a ligand of formula (IV) and/or an ion pair of formula (V). Particularly preferred are such compositions further comprising a surfactant. In the case of compositions according to this aspect of the invention, no further bleach component need be included of catalytic free oxygen bleaching is the mode of bleaching.

In other cases, a bleach or bleach system, especially a peroxygen bleach or bleach system will be included.

50 **[0011]** The invention further extends to use of compositions according to the said aspect of the invention for laundry cleaning, hard surface cleaning (including cleaning of lavatories, kitchen work surfaces, floors, mechanical ware washing etc.), as well as other uses where a bleach is needed, for example waste water treatment or pulp bleaching during manufacture of paper, dye transfer inhibition, starch bleaching, sterilisation and/or whitening in oral hygiene preparation, contact lens disinfection.

55 **[0012]** Throughout this specification, unless specifically stated to the contrary, all alkyl, hydroxyalkyl alkoxy, and alkenyl groups preferably have from 1 to 6, more preferably from 1 to 4 carbon atoms.

[0013] Moreover, throughout this specification, preferred electron donating groups include alkyl (e.g. methyl), alkoxy (e.g. methoxy) and unsubstituted-, monosubstituted and disubstituted amine groups. Preferred electron withdrawing groups include nitro, carboxy, sulphonyl and halo groups.

[0014] Thus, according to the values of x and y, the aforementioned preferred iron or manganese catalysts may be in the form of a monomer, dimer or oligomer. Without being bound by any theory, it has been conjectured that in the raw material or detergent composition state, the catalyst exists mainly or solely in monomer form but could be converted to dimer, or even oligomeric form, in the wash solution.

[0015] The catalysts of formula (IV) and (V) have been found to be capable of a catalysing bleaching by both free oxygen and oxygen bleach compounds/systems. Therefore, even without the presence of a chemical bleach/bleach system, catalysts according to the present invention can catalyse bleaching by atmospheric oxygen. Thus, compositions according to the present invention do not have to contain a bleach *per se*. However, they may also contain an oxygen bleach.

[0016] Another aspect of the present invention provides a bleaching process which comprises the step of treating a substrate with a source of free oxygen and/or an oxygen bleach, and a bleach catalyst as defined herein.

Detailed Description of the Invention:

Bleach Catalyst:

[0017] In formula (IV) or formula (V) preferably, R₁ and R₂ are both hydrogen. R₃ and R₄ are preferably C₁₋₄ alkyl, especially methyl. R₅-R₈ are each preferably hydrogen.

[0018] Preferably the oxidation state n is III.

[0019] X is preferably independently selected from H₂O, OH⁻, O₂²⁻, O²⁻, -HO₂⁻, SH⁻, S²⁻, -SO⁻, NR₉R₁₀⁻, RCOO⁻, NR₉R₁₀R₁₁, Cl⁻, Br⁻, F⁻, N₃⁻, SCN⁻, N³⁻, or combinations thereof, wherein R₉, R₁₀ and R₁₁ are independently selected from H, C₁₋₄ alkyl and or aryl optionally substituted by one or more electron donating or withdrawing groups, X is preferably a halogen, especially a fluoride ion.

[0020] The cationic counter-ion equivalent Z is preferably absent.

[0021] The anionic counter-ion equivalent Y is preferably selected from Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₄⁻, SCN⁻, PF₆⁻, RSO₃⁻, RSO₄⁻, CF₃SO₃⁻, BF₄⁻, BPh₄⁻, and OAc⁻.

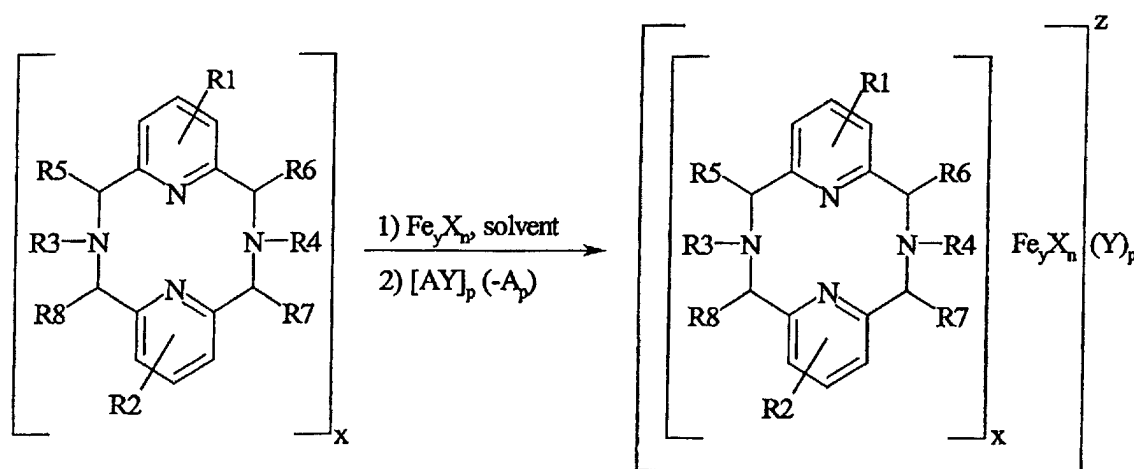
[0022] Especially preferred examples of the catalyst of formula (IV) comprise salts of an iron dihalo-2,11-diazo[3.3](2,6)pyridinophane and dihalo-4-methoxy-2,11-diazo [3.3] (2,6) pyridinophane and mixtures thereof, especially in the form of their chloride salts.

[0023] An especially preferred example of the catalyst of formula (V) comprises a salt of a manganese dihalo, N, N' -dimethyl-2,11-diazo[3.3](2,6)pyridinophane, especially in the form of its monohexafluorophosphate salt.

[0024] In typical washing compositions the level of [1] is such that the in-use level is from 1µM to 50mM, with preferred in-use levels falling in the range 10-100 µM.

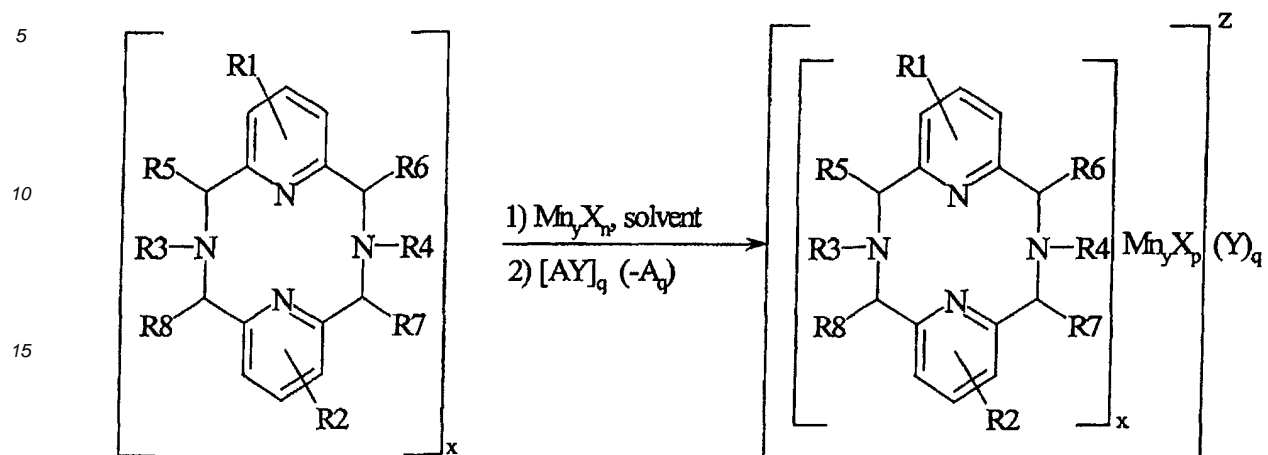
Preparation

[0025] The bleach catalysts of formula (IV) wherein may for example be prepared by the following generalised reaction:-



[0026] The bleach catalysts of formula (V) wherein may for example be prepared by the following generalised reac-

tion:-



[0027] The ligands in the aforementioned generalised reaction schemes may for example be prepared by:-

25

30

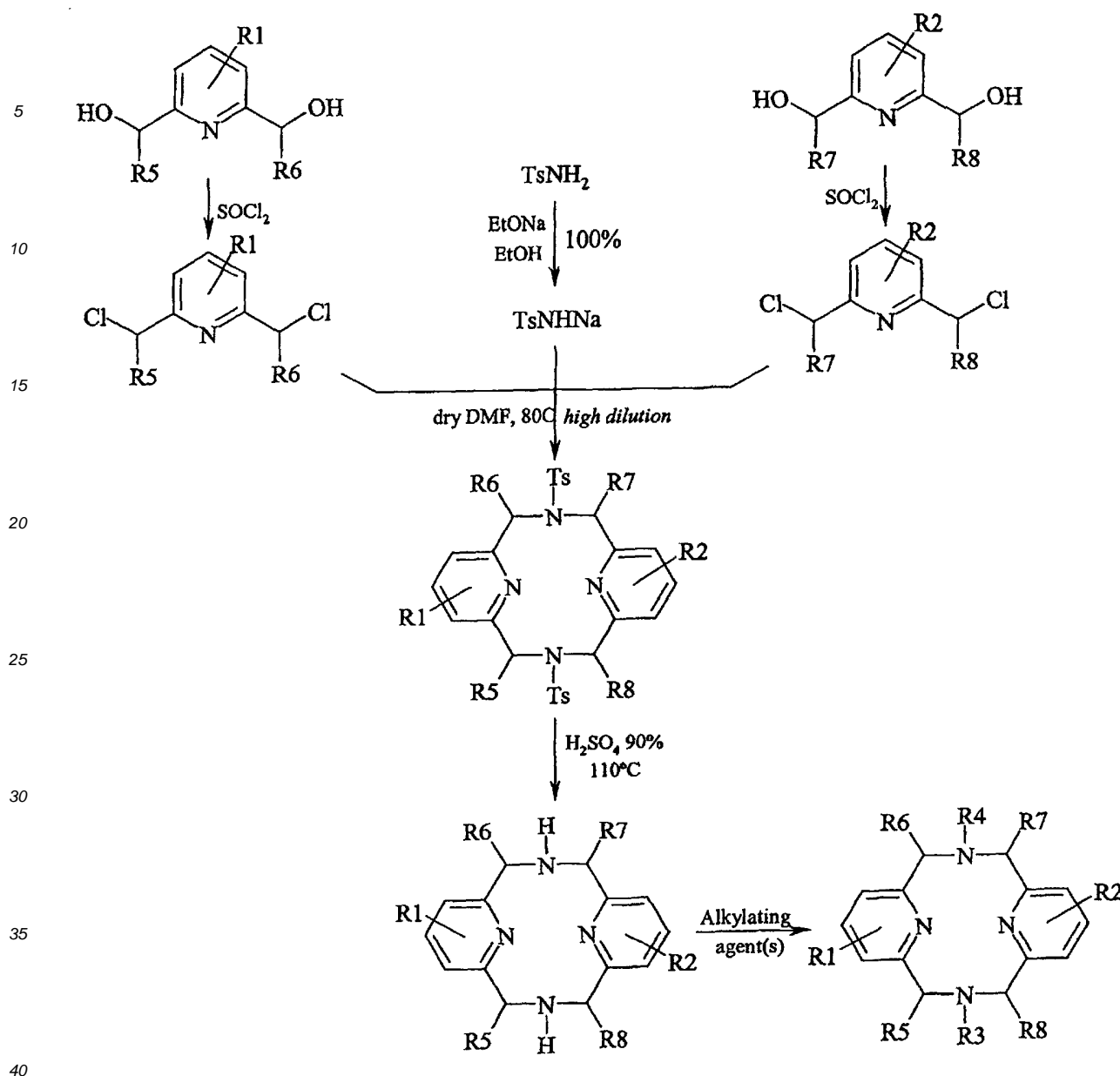
35

40

45

50

55



[0028] Persons skilled in the art will readily be capable of extrapolating these synthetic routes to all ligands of formula (I), ion pairs of formula (II) and complexes of formula (III).

45 Detergent and/or bleach compositions

[0029] The present invention has particular application in formulations to form a new and improved detergent and/or bleach compositions, comprising an oxygen bleach and/or surfactant. In the absence of a separate bleach, many materials within the scope of the invention are capable of catalysing bleaching by atmospheric oxygen.

50

Oxygen Bleach

[0030] Preferably the oxygen bleach comprises a peroxygen compound. Generally speaking the peroxygen compound is selected from compounds of the general formula R_{11}OOH wherein R_{11} representing H or optionally substituted alkyl, the source of peroxygen is another inorganic or organic peroxy salt. Most preferably the R is H and the source of peroxygen is hydrogen peroxide.

55

[0031] More specifically, the peroxy bleaching compound may be a compound which is capable of yielding hydrogen peroxide in aqueous solution. Hydrogen peroxide sources are well known in the art. They include the alkali metal

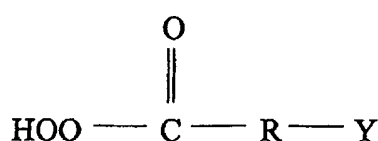
peroxides, organic peroxides such as urea peroxide, and inorganic persalts, such as the alkali metal perborates, percarbonates, perphosphates persulfates and persulphates. Mixtures of two or more such compounds may also be suitable.

[0032] Particularly preferred are sodium perborate tetrahydrate and, especially, sodium perborate monohydrate. Sodium perborate monohydrate is preferred because of its high active oxygen content. Sodium percarbonate may also be preferred for environmental reasons. The amount thereof in the composition of the invention usually will be within the range of about 5-35% by weight, preferably from 10-25% by weight.

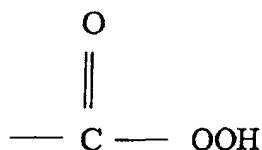
[0033] Another suitable hydrogen peroxide generating system is a combination of a C₁-C₄ alkanol oxidase and a C₁-C₄ alkanol, especially a combination of methanol oxidase (MOX) and ethanol. Such combinations are disclosed in International Application PCT/EP 94/03003 (Unilever).

[0034] Alkylhydroxy peroxides are another class of peroxy bleaching compounds. Examples of these materials include cumene hydroperoxide and t-butyl hydroperoxide.

[0035] Organic peroxyacids may also be suitable as the peroxy bleaching compound. Such materials normally have the general formula:



wherein R is an alkylene or substituted alkylene group containing from 1 to about 20 carbon atoms, optionally having an internal amide linkage; or a phenylene or substituted phenylene group; and Y is hydrogen, halogen, alkyl, aryl, an imido-aromatic or non-aromatic group, a COOH or



group or a quaternary ammonium group.

[0036] Typical monoperoxy acids useful herein include, for example:

- (i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy-a-naphthoic acid;
- (ii) aliphatic, substituted aliphatic and arylalkyl monoperoxyacids, e.g. peroxy lauric acid, peroxy stearic acid and N, N-phthaloylaminoperoxy caproic acid (PAP); and
- (iii) 6-octylamino-6-oxo-peroxyhexanoic acid.

Typical diperoxyacids useful herein include, for example:

- (iv) 1,12-diperoxydodecanedioic acid (DPDA);
- (v) 1,9-diperoxyazelaic acid;
- (vi) diperoxybrassicic acid; diperoxysebacic acid and diperoxyisophthalic acid;
- (vii) 2-decyldiperoxybutane-1,4-dioic acid; and
- (viii) 4,4'-sulphonylbisperoxybenzoic acid.

[0037] Also inorganic peroxyacid compounds are suitable, such as for example potassium monopersulphate (MPS). If organic or inorganic peroxyacids are used as the peroxygen compound, the amount thereof will normally be within the range of about 2-10% by weight, preferably from 4-8% by weight.

[0038] All these peroxy compounds may be utilised alone or in conjunction with a peroxyacid bleach precursor and/or an organic bleach catalyst not containing a transition metal. Generally, the bleaching composition of the invention can be suitably formulated to contain from 2 to 35%, preferably from 5 to 25% by weight, of the peroxy bleaching agent.

[0039] Peroxyacid bleach precursors are known and amply described in literature, such as in the British Patents 836988; 864,798; 907,356; 1,003,310 and 1,519,351; German Patent 3,337,921; EP-A-0185522; EP-A-0174132; EP-A-0120591; and US Patents 1,246,339; 3,332,882; 4,128,494; 4,412,934 and 4,675,393.

[0040] Another useful class of peroxyacid bleach precursors is that of the cationic i.e. quaternary ammonium substituted peroxyacid precursors as disclosed in US Patent 4,751,015 and 4,397,757, in EP-A-0284292 and EP-A-331,229. Examples of peroxyacid bleach precursors of this class are:

- 5 2-(N,N,N-trimethyl ammonium) ethyl sodium-4-sulphonphenyl carbonate chloride - (SPCC) ;
 N-octyl,N,N-dimehyl-N10-carbophenoxy decyl ammonium chloride - (ODC) ;
 3-(N,N,N-trimethyl ammonium) propyl sodium-4-sulphophenyl carboxylate; and
 N,N,N-trimethyl ammonium toluoyloxy benzene sulphonate.

10 **[0041]** A further special class of bleach precursors is formed by the cationic nitriles as disclosed in EP-A-303,520 and in European Patent Specification No.s 458,396 and 464,880.

[0042] Any one of these peroxyacid bleach precursors can be used in the present invention, though some may be more preferred than others.

15 **[0043]** Of the above classes of bleach precursors, the preferred classes are the esters, including acyl phenol sulphonates and acyl alkyl phenol sulphonates; the acyl-amides; and the quaternary ammonium substituted peroxyacid precursors including the cationic nitriles.

[0044] Examples of said preferred peroxyacid bleach precursors or activators are sodium-4-benzoyloxy benzene sulphonate (SBOBS); N,N,N,N'-tetraacetyl ethylene diamine (TAED) ; sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoyloxy benzoate; SPCC; trimethyl ammonium toluoyloxy-benzene sulphonate; sodium nonanoyloxybenzene sulphonate (SNOBS); sodium 3,5,5-trimethyl hexanoyl-oxybenzene sulphonate (STHOBS); and the substituted cationic nitriles.

[0045] The precursors may be used in an amount of up to 12%, preferably from 2-10% by weight, of the composition.

[0046] As an alternative to the above described peroxide generating systems, molecular oxygen may be used as the oxidant.

25 **[0047]** Normally, the amount of peroxygen compound will be in an amount relative to the catalyst of formula (I) such that the catalyst represent from 0.1% to 10% by weight of the peroxygen compound. Preferred molar ratios of peroxygen compound to catalyst are 10000:1 to 1000:1.

Surface-active material

30 **[0048]** Detergent compositions according to the present invention generally contain surface-active material in an amount of from 10 to 50% by weight. Said surface-active material may be naturally derived, such as soap, or a synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof. Many suitable actives are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

35 **[0049]** Typical synthetic anionic surface-actives are usually watersoluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher aryl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and ammonium alkyl sulphates, especially those obtained by sulphating higher (C₈-C₁₈) alcohols produced, for example, from tallow or coconut oil; sodium and ammonium alkyl (C₉-C₁₀) benzene sulphonates, particularly sodium linear secondary alkyl (C₁₀-C₁₅) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ester of the higher alcohols derived from tallow or coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and ammonium salts of sulphuric acid esters of higher (C₉-C₁₈) fatty alcohol alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane mono-sulphonates such as those derived by reacting alpha-olefins (C₈-C₂₀) with sodium bisulphite and those derived by reaction paraffins with SO₂ and C₁₂ and then hydrolysing with a base to produce a random sulphonate; sodium and ammonium C₇-C₁₂ dialkyl sulphoscينات; and olefin sulphonates which term is used to describe material made by reacting olefins, particularly C₁₀-C₂₀ alpha-olefins, with SO₃ and then neutralising and hydroysing the reaction product.

45 The preferred anionic detergent compounds are sodium (C₁₀-C₁₅) alkylbenzene sulphonates, sodium (C₁₆-C₁₈) alkyl ether sulphates.

[0050] Examples of suitable nonionic surface-active compounds which may be used, preferably together with the anionic surface-active compounds, include, in particular, the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C₆-C₂₂) phenols, generally 5-25 EO, i.e. 5-25 units of ethylene oxides per molecule; and the condensation products of aliphatic (C₈-C₁₈) primary or secondary linear or branched alcohols with ethylene oxide, generally 2-30 EO. Other so-called nonionic surface-actives include alkyl polyglycosides, sugar esters, long-chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.

55 **[0051]** Amphoteric or zwitterionic surface-active compounds can also be used in the compositions of the invention

but this is not normally desired owing to their relatively high cost. If any amphoteric or zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and nonionic actives.

[0052] As disclosed by EP-A-544,490, the performance of the hereinbefore described bleach catalyst, may be dependent upon the active detergent system and the builder system present in the detergent bleach composition of the invention.

[0053] The detergent bleach composition of the invention will preferably comprise from 1-15% wt of anionic surfactant and from 10-40% by weight of nonionic surfactant. In a further preferred embodiment the detergent active system is free from C₁₆-C₁₂ fatty acids soaps.

Detergency builder

[0054] The composition of the invention may also contain a detergency builder in an amount of from about 5-80% by weight, preferably from about 10-60% by weight.

[0055] Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

[0056] Examples of calcium sequestrate builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate; nitrilotriacetic acid and its water-soluble salts; the alkali metal salts of carboxymethyloxy succinic acid, ethylene diamine tetraacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, citric acid; and poly-acetal carboxylates as disclosed in US Patents 4,144,226 and 4,146,495.

[0057] Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

[0058] Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P type as described in EP-A-0384070.

[0059] In particular, the compositions of the invention may contain any one of the organic and inorganic builder materials, though, for environmental reasons, phosphate builders are preferably omitted or only used in very small amounts.

[0060] Typical builders usable in the present invention are, of example, sodium carbonate, calcite/carbonate, the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethyloxy malonate, carboxymethyloxy succinate and the water-insoluble crystalline or amorphous aluminosilicate builder material, each of which can be used as the main builder, either alone or in admixture with minor amounts of other builders or polymers as co-builder.

[0061] It is preferred that the composition contains not more than 5% by weight of a carbonate builder, expressed as sodium carbonate, more preferable not more than 2.5% by weight to substantially nil, if the composition pH lies in the lower alkaline region of up to 10.

Other ingredients

[0062] Apart from the components already mentioned, the detergent bleach composition of the invention can contain any of the conventional additives in amounts of which such materials are normally employed in fabric washing detergent compositions. Examples of these additives include buffers such as carbonates, lather boosters, such as alkanolamides, particularly the monoethanol amides derived from palmkernel fatty acids and coconut fatty acids; lather depressants, such as alkyl phosphates and silicones; anti-redeposition agents, such as sodium carboxymethyl cellulose and alkyl or substituted alkyl cellulose ethers; stabilisers, such as phosphonic acid derivatives (i.e. Dequest® types); fabric softening agents; inorganic salts and alkaline buffering agents, such as sodium sulphate, sodium silicate etc.; and usually in very small amounts, fluorescent agents; perfumes; enzymes, such as proteases, cellulases, lipases, amylases and oxidases; germicides and colorants.

[0063] When using a hydrogenperoxide source, such as sodium perborate or sodium percarbonate, as the bleaching compound, it is preferred that the composition contains not more than 5% by weight of a carbonate buffer, expressed as sodium carbonate, more preferable not more than 2.5% by weight to substantially nil, if the composition pH lies in the lower alkaline region of up to 10.

[0064] Of the additives, transition metal sequestrants, such as EDTA and the phosphonic acid derivatives, e.g. ethylene diamine tetra-(methylene phosphonate) -EDTMP- are of special importance, as not only do they improve the stability of the catalyst/H₂O₂ system and sensitive ingredients, such as enzymes, fluorescent agents, perfumes and the like, but also improve the bleach performance, especially at the higher pH region of above 10, particularly at pH 10.5 and above.

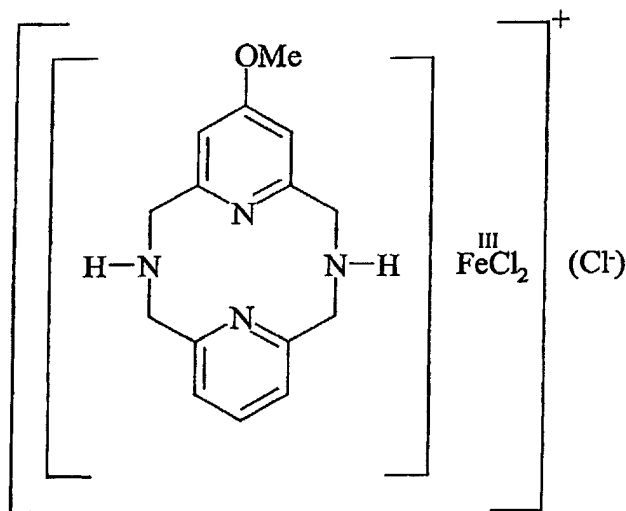
Product Form

[0065] Compositions according to the present invention (whether or not detergent bleach compositions) may be formulated in any form, e.g. as granulates (which may be prepared by spray drying or non-spray drying granulation), as powder additives for dosing into a granulation process or post-dosing to a granulated product, as pills or tablets or as aqueous or non-aqueous liquids.

[0066] The invention will now be further illustrated by way of the following non-limiting Examples.

Example 1: [Fe((4OMe) LN₄H₂)Cl₂]⁺Cl⁻

[0067] The Example is a catalyst of formula (I) wherein:-



R₂-R₈=H; R₁=4-MeO; x=1; y=1; z=1; X=C1, n=2; Y=C1; p=1.

[0068] The (unmethoxylated) basic ligand will be referred to by the abbreviation LN₄.

(i) Syntheses of the ligand: ((4OMe)LN₄H₂) 2,11-diaza[3.3]-(4-methoxy)(2,6)pyridinophane:

[0069] 4-chloro-2,6-pyridyl dimethyl ester (2). A mixture of 4-hydroxy-2,6-pyridine dicarboxylic acid (12.2 g, 60 mmoles) and PCl₅ (41.8g, 200 mmoles) in 100 ml of CCl₄ was refluxed until the evolution of HCl ceased. Absolute methanol (50ml) was slowly added. After cooling, all the volatile material was removed. The mixture was then poured into 200 ml of water and ice. The diester crystallised immediately and was collected by filtration (70%). ¹H NMR (200MHz, H₂O) □ 7.60 (2H, s), 4.05 (6H, s).

[0070] 4-methoxy-2,6-pyridine dimethanol (4). Metallic sodium (1g, 44 mmoles) was dissolved into 200 ml of dry methanol. 4-chloro-2,6-pyridyl dimethyl ester (9.2g, 40 mmoles) was then added and the mixture was refluxed for 3 hours to obtain pure 4-methoxy-2,6-pyridyl dimethyl ester. To this solution, at RT, NaBH₄ (9.1 g, 240 mmoles) was added in small portions and the mixture was refluxed for 16 hours. Acetone (30 ml) was then added and the solution refluxed for an additional 1 hour. After all the volatile material was removed, the residue was heated with 60 ml of a saturated NaHCO₃/Na₂CO₃ solution. After dilution with 80 ml of water, the product was continuously extracted with CHCl₃ for 2-3 days. Evaporation of the CHCl₃ yielded 83 % of 4-methoxy-2,6-pyridine dimethanol. ¹H NMR (200MHz, H₂O) □ 6.83 (2H,s), 5.30 (2H,s), 4.43 (4H,s), 3.82 (3H, s).

[0071] 4-methoxy-2,6-dichloromethylpyridine (5). This synthesis is carried out according to the methods of Baker W. et al, J. Chem. Soc. (1958) 3594 and Lee G., J.Org. Chem., (1996), 61, 8304.

[0072] N,N'-ditosyl-2,11-diaza[3.3]-(4-methoxy)(2,6)pyridinophane. the procedure is similar to that described in the literature. The crude product obtained is practically pure (yield=95%).

[0073] ¹H-NMR (CDCl₃, 250 MHz) : 7.72 (4H, d, J= 7Hz), 7.4 (1H, t, J= 6Hz), 7.35 (4H, d, J= 7Hz), 7.1 (1H, d, J= 6Hz), 6.57 (2H, s), 4.45 (4H, s), 4.35 (4H, s), 3.65 (3H, s), 2.4 (6H, s).

[0074] 2,11-diaza[3.3]-(4-methoxy)(2,6)pyridinophane. The procedure is similar to the one described previously. The crude product obtained is purified by chromatography (alumina, CH₂Cl₂/MeOH 95:5), yield = 65%.

[0075] $^1\text{H-NMR}$ (CDCl_3 , 250 MHz) : 7.15 (1H, t, J= 6Hz), 6.55 (1H, d, J= 6Hz), 6.05 (2H, s), 3.95 (4H, s), 3.87 (4H, s), 3.65 (3H, s).

Mass spectrum (EI) : M^+ = 270 (100%)

5 **(ii) Syntheses of the Complex: $[\text{Fe}(\text{4OMeLN}_4\text{H}_2)\text{Cl}_2]\text{Cl}$**

[0076] 270 mg of 2,11-diaza[3.3]-(4-methoxy)(2,6)pyridinophane (1 mmole) were dissolved in 15 ml of dry THF. To this solution was added a solution of 270 mg of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1 mmoles) in 5 ml of MeOH. The resulting mixture is evaporated to dryness and the solid product is dissolved in 10 ml of AcN with a minimum of MeOH. Slow diffusion of THF give 300 mg of brown crystals, yield = 70%. Elemental analysis for $\text{C}_{15}\text{H}_{18}\text{N}_4\text{Cl}_3\text{OFe} \cdot 0.5\text{MeOH}$ (found/theoretical) : C=41.5/41.61 H=4.46/4.52 N=12.5/12.08

[0077] IR (KBr pellets, cm^{-1}) : 3545, 3414, 3235, 3075, 2883, 1615, 1477, 1437, 1340, 1157, 1049, 883, 628, 338.

Example 2:

difluoro[N,N'dimethyl-2,11-diaza[3.3](2,6)pyridinophane]manganese(III) hexafluorophosphate

[0078] The Example is a catalyst of formula (I) wherein:-

25 $\text{R}_1=\text{R}_2=\text{R}_{5-8}=\text{H}$

$\text{R}_3=\text{R}_4=\text{Me}$

$x=1$

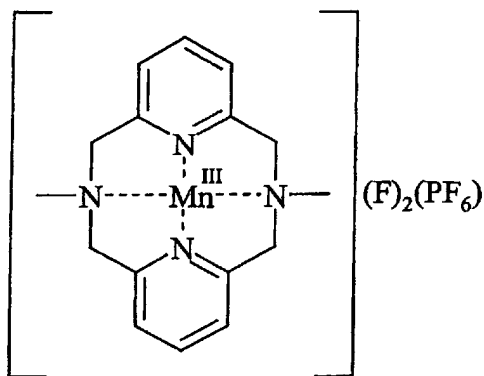
30 $y=1$

$n=2$

$z=1$

35 $\text{X}=\text{F}^-$, $m=2$

$\text{Y}=\text{PF}_6^-$, $p=1$



40 **(i) Synthesis of the ligand: N,N'dimethyl-2,11-diaza[3.3](2,6)pyridinophane**

[0079] 2,6-dichloromethylpyridine. A mixture of 2,6-dimethanolpyridine (5g, 36 mmoles) and 75 ml of SOCl_2 was refluxed for 4 hours. The mixture was concentrated (half volume). Toluene was added (50 ml). The solid formed after cooling was then filtered and dissolved in water and the solution neutralised with NaHCO_3 . The solid obtained is filtered and dried (65%). $^1\text{H NMR}$ (200MHz, CDCl_3) \square 7.8 (1H,t, J=7Hz), 7.45 (2H,d, J=7 Hz), 4.7 (4H, s).

[0080] Sodium p-toluenesulfonamidure. To a mixture of Na^+ in dry EtOH (0.7 g, 29 mmoles) was added p-toluenesulfonamide (5 g, 29 mmoles) and the solution was refluxed for 2 hours. After cooling, the solid obtained was filtered, washed with EtOH and dried (quantitative yield).

50 **[0081]** N,N'-ditosyl-2,11-diaza[3.3](2,6)pyridinophane. To a solution of sodium p-toluenesulfonamidure (1.93 g, 10 mmoles) in 200 ml of dry DMF at 80°C was slowly added 2,6-dichloromethylpyridine (1.76 g, 10 mmoles). After 1 hour a new portion of sodium p-toluenesulfonamidure was added (1.93 g) and the final mixture stirred at 80°C for an addition 4 hours. The solution was then evaporated to dryness. The solid obtained was washed with water and then with EtOH and finally crystallised in an $\text{CHCl}_3/\text{MeOH}$ mixture. The solid obtained is filtered and dried. The yield of (15) was 55

55 **[0082]** 2,11-diaza[3.3](2,6)pyridinophane. A mixture of N,N'-itosyl-2,11-diaza[3.3](2,6)pyridinophane (1.53 g, 2.8 mmoles) and 14 ml of H_2SO_4 90 % was heated at 110°C for 2 hours. The solution, cooled and diluted with 14 ml of water, was then carefully poured into a saturated NaOH solution. The solid formed is extracted with chloroform. The

organic layer is evaporated to dryness to yield 85 % of 2,11-diaza [3.3] (2,6)pyridinophane. ¹H NMR (200MHz, CDCl₃) □ 7.1 (2H,t, J=7Hz), 6.5 (4H,d, J=7 Hz), 3.9 (8H, s).

[0083] *N,N'-dimethyl-2,11-diaza[3.3](2,6)pyridinophane*. A mixture of 2,11-diaza[3.3] (2,6)pyridinophane (0.57 g, 2.4 mmoles), 120 ml of formic acid and 32 ml of formaldehyde (32% in water) was refluxed for 24 hours. Concentrated HCl (10 ml) were added and the solution evaporated to dryness. The solid was dissolved in water and basified with NaOH 5M, and the resulting solution was extracted with CHCl₃. The solid obtained was purified by chromatography on alox (CH₂Cl₂+1% MeOH) to yield 51 % of N,N'-dimethyl-2,11-diaza[3.3](2,6)pyridinophane. ¹H NMR (200MHz, CDCl₃) □ 7.15 (2H,t, J=7Hz), 6.8 (4H,d, J=7 Hz), 3.9 (8H, s), 2.73 (6H,s).

(ii) Synthesis of the Complex:

[0084] MnF₃ (41.8 mg, 373 mmoles) was dissolved in 5 ml of MeOH, and *N,N'-dimethyl-2,11-diaza[3.3](2,6)pyridinophane* (0.1 g, 373 mmoles) was added with 5 ml of THF. After 30 minutes of stirring at RT, 4 ml of THF saturated in NBu₄PF₆ were added, and the solution left without stirring until the crystallisation was finished. The product was collected by filtration to yield 80% of complex. Elemental analysis (found, theoretical): %C (38.35, 37.94), %N (11.32, 11.1), %H (3.75, 3.95). IR (KBr pellet, cm⁻¹) : 3086, 2965, 2930, 2821, 1607, 1478, 1444, 1425, 1174, 1034, 1019, 844, 796, 603, 574, 555. UV-Vis (CH₃CN, □ in nm, □): 500, 110; 850, 30; (CH₃CN/H₂O:1/1, □ in nm, □): 465, 168; 850, 30.

Example 3

(i) Synthesis of bis(4OMe)LN₄Ts₂:

[0085] The procedure is similar to that described in the literature. (B.Alfa, E. Anklam, R. Deschenaux, J.M. Lehn, M. Pitraskiwicz; *Helv. Chim. Acta*, **1988**, 71, 1042.)

[0086] The starting pyridine ring is the 2,6-dichloromethyl-4-OMe-pyridine. (D.J. Markees, G. W. Kidder; *J. Am. Chem. Soc.*, **1956**, 78,4130, Lee G., *J. Org. Chem.*, (**1996**), 61, 8304 and W.Baker, K. M. Buggle, B.A.M. Watkins; *J. Chem. Soc.*, **1958**, 3594.)

[0087] The crude product obtained is purified by a column chromatography (silica, Ethyl Acetate+5% NEt₃), yield=85%.

[0088] ¹H-NMR (CDCl₃, 250MHz): 7.75 (4H,d,J³ = 7Hz), 7.4 (4H,d,J³ = 7Hz), 6.75 (4H,s), 4.45 (8H,s), 3.75 (6H,s), 2.5 (6H,s).

(ii) Synthesis of bis(4OMe)LN₄H₂:

[0089] The product is deprotected as described in the literature. (B.Alfa, E. Anklam, R. Deschenaux, J.M. Lehn, M. Pitraskiwicz; *Helv. Chim. Acta*, **1988**, 71 1042.)

[0090] The starting material is the bis(4OMe)LN₄Ts₂; yield=90%.

[0091] ¹H-NMR (CDCl₃, 250 MHz): 5.95 (4H, s), 3.8 (2H, s), 3.75 (8H, s), 3.65 (6H,s).

(iii) Synthesis of [Fe(bis(4OMe)LN₄H₂)Cl₂]Cl:

[0092] 150mg of ligand (0.5 mmole) were dissolved in 15ml of dry CH₃CN and 3ml of CH₂Cl₂. To this solution is added a solution of 135mg of FeCl₃·6H₂O (0.5mmoles) in 5 ml of CH₃CN. The resulting mixture filtered and devaporated to dryness.

The crude product is dissolved in a minimum of CH₃CN and slow diffusion of THF give 300mg of brown crystals, yield=70%. Elemental analysis for C₁₆H₂₀N₄Cl₃O₂Fe·1MeOH (found/theoretical): C=41.4/41.3 H=4.7/4.86 N=11.4/11.33 IR (KBr pellets, cm⁻¹): 3425, 3072, 2880, 1614, 1477, 1437, 1339, 1043, 880, 335.

Abbreviations

[0093]

cat = catechol(ate)
DTBcat = diterbutylcatechol(ate)
Ts = tosyl

Claims

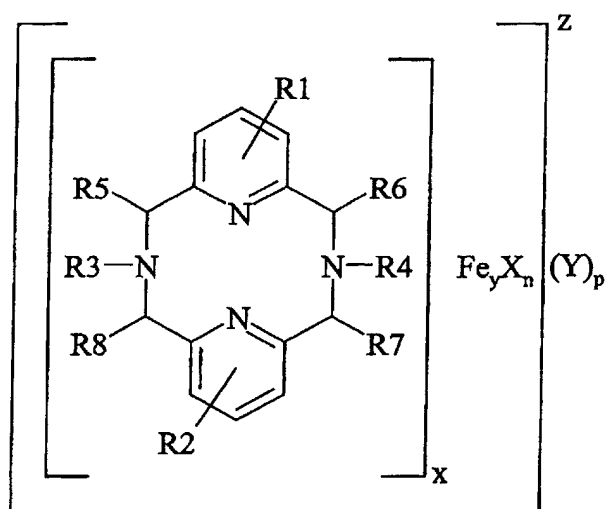
1. A bleach catalyst of formula (IV) :

5

10

15

20



25

wherein Fe represents an iron atom in oxidation state II or III, X is a group which is either a bridge or is not a bridge between iron atoms, Y is a counter-ion, x and y being ≥ 1 , $0 < n < 3$, and z being the charge of the metal complex, and $p = z / \text{charge of Y}$; R_1 and R_2 being independently one or more ring substituents selected from hydrogen and electron donating and withdrawing groups selected from: halo, C_{1-6} alkoxy, hydroxy, hydroxyalkyl, (optionally mono- or di-substituted) amine groups, (optionally mono- or di-substituted) thiol groups, carboxyl, ester, amide, substituted carbonyl groups in general, nitrile, nitro, (optionally substituted) sulphonyl, alkenyl, aryl, quaternary ammonium (+) and sulphonium (+); $R_3 - R_8$ being independently hydrogen, alkyl, hydroxyalkyl, alkenyl or variants of any of these when substituted by one or more electron donating or withdrawing groups selected from: halo, C_{1-6} alkoxy, hydroxy, hydroxyalkyl, (optionally mono- or di-substituted) amine groups, (optionally mono- or di-substituted) thiol groups, carboxyl, ester, amide, substituted carbonyl groups in general, nitrile, nitro (optionally substituted) sulphonyl, alkenyl, aryl, quaternary ammonium (+) and sulphonium (+)

30

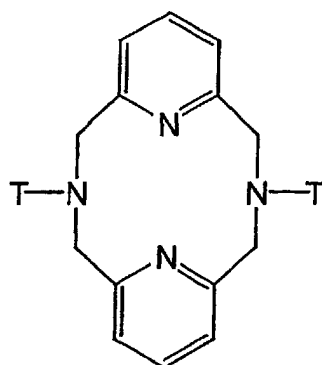
35

with the proviso that in the bleach catalyst of formula (IV) the following ligand is excluded:

40

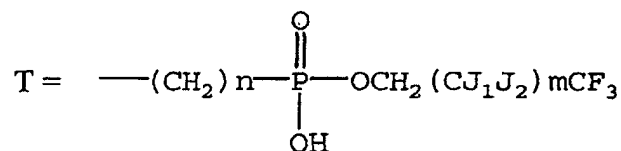
45

50

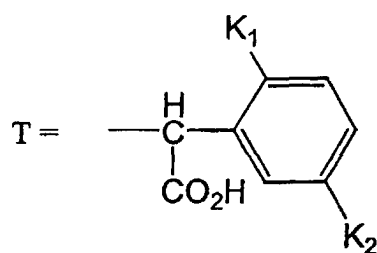


wherein in case 1, both $T = CH_3$,
wherein in case 2, $T = H$ or

55



where m is 0 or an integer of 1, 2, 3 or 4;
 n is an integer of 1, 2 or 3;
 J₁ and J₂ = H or F,
 wherein in case 3, T = -CH₂COOH, -CH₂P(O)OHW
 where W is OH or, C1-C5-alkyl or -O-(C1-C5)-alkyl, or



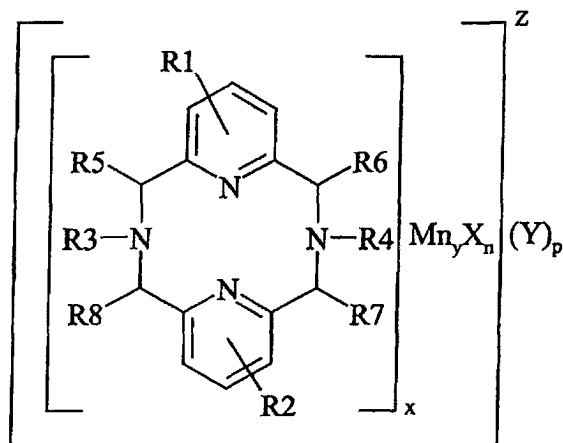
where K₁ = -OH or -OCH₃
 K₂ is -NO₂, -NH₂, isothiocyanato, semicarbazido, thiosemicarbazido, maleimido, bromoacetamido or carboxyl.

2. A bleach catalyst of formula (IV) as defined in claim 1, with the proviso that:

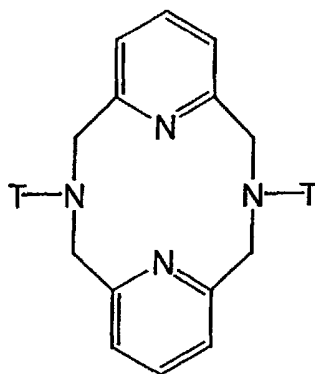
(i) if R₁, R₂ and R₅ - R₈ are all hydrogen, R₃ and R₄ are both methyl;
 x=1, y=1, z= +1, n=1 and p=1; and
 Y is -BPh₄⁻;
 then X is not C1, catecholate or 3,5-di-tertbutyl-1,2-catecholate; and

(ii) if R₁ - R₈ are all hydrogen; and
 x=2, y=1, and n=0;
 then when z= +3 and p=3, Y is not ClO₄⁻ and when z=+2 and p=2, Y is not -BPh₄⁻.

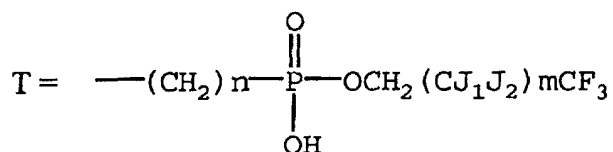
3. A bleach catalyst of formula (V):



wherein Mn represents a manganese atom in oxidation state II, III, IV, or V, X is a group which is either a bridge or is not a bridge between manganese atoms, Y is a counter-ion, x and y being ≥ 1 , $0 \leq n \leq 3$, and z being the charge of the metal complex, and $p = z / \text{charge of Y}$; R_1 and R_2 being independently one or more ring substituents selected from hydrogen and electron donating and withdrawing groups selected from: halo, C_{1-6} alkoxy, hydroxy, hydroxyalkyl, (optionally mono- or di-substituted) amine groups, (optionally mono- or di-substituted) thiol groups, carboxyl, ester, amide, substituted carbonyl groups in general, nitrile, nitro, (optionally substituted) sulphonyl, alkenyl, aryl, quaternary ammonium (+) and sulphonium (+), R_3, R_4, R_5, R_6, R_7 and R_8 being independently hydrogen, alkyl, hydroxyalkyl, alkenyl or variants of any of these when substituted by one or more electron donating or withdrawing groups with the proviso that in the bleach catalyst of formula (IV) the following ligand is excluded:



wherein in case 1, T = H or



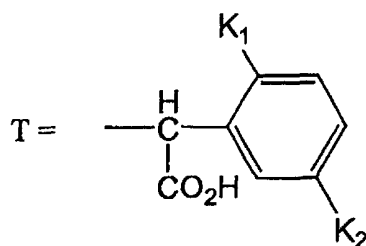
where m is 0 or an integer of 1, 2, 3 or 4;

n is an integer of 1, 2 or 3;

J_1 and $J_2 = \text{H or F}$,

wherein in case 2, T = $-\text{CH}_2\text{COOH}$, $-\text{CH}_2\text{P}(\text{O})\text{OH}$

where W is OH or, C1-C5-alkyl or $-\text{O}-(\text{C1-C5})\text{-alkyl}$, or



where $K_1 = -\text{OH}$ or $-\text{OCH}_3$

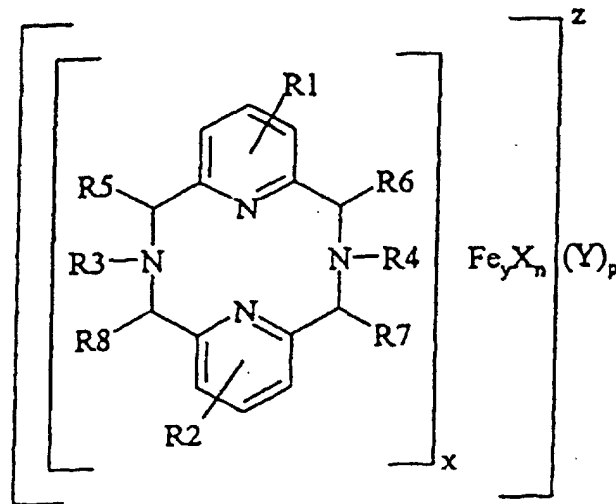
K_2 is $-\text{NO}_2$, $-\text{NH}_2$, isothiocyanato, semicarbazido, thiosemicarbazido, maleimido, bromoacetamido or carboxyl.

4. A bleach catalyst according to any one of claims 1, 2 and 3, wherein R_1 and R_2 are both hydrogen, R_3 and R_4 are independently C_{1-4} alkyl and R_5 - R_8 are each hydrogen.
5. A bleach catalyst according to any one of claims 1 to 3, wherein the metal is in the III oxidation state.

6. A bleach catalyst according to any one of claims 1 to 5, wherein X is selected from H₂O, OH⁻, O₂²⁻, O²⁻, HO₂⁻, SH⁻, S²⁻, -SO-, NR₉R₁₀⁻, carboxylate, NR₉R₁₀R₁₁, C₁⁻, Br⁻, F⁻, N₃⁻ and combinations thereof, wherein R₉, R₁₀ and R₁₁ are independently selected from H, C₁₋₄ alkyl and aryl optionally substituted by one or more electron withdrawing and/or donating groups.
7. A bleach catalyst according to any one of claims 1 to 6, wherein Z is absent.
8. A bleaching composition comprising a catalyst according to any one of claims 1 to 7, wherein Y is selected from ClO₄⁻, SCN⁻, PF₆⁻, sulphonate, sulphate, CF₃SO₃⁻, BF₄⁻, BPh₄⁻, and OAc⁻.
9. A bleach catalyst selected from the the group consisting of dihalo-2,11-diazo[3.3](2,6)pyridinophane, and dihalo-4-methoxy-2,11-diazo[3.3] (2,6) pyridinophane and mixtures thereof, wherein the catalyst is in the form of a manganese salt, said manganese present in an oxidised state.
10. A bleach catalyst, wherein the catalyst is N, N' -dimethyl-2,11-diazo[3.3] (2,6)pyridinophane in the form of a salt of a manganese (in oxidised state).
11. A bleaching composition comprising a bleach catalyst according to any one of claims 1 to 10 and comprising at least one other component selected from surfactants and oxygen bleaches.
12. A process of bleaching and/or cleaning a substrate, the process comprising treating the substrate with a bleach catalyst according to any one of claims 1 to 7, 9 and 10.

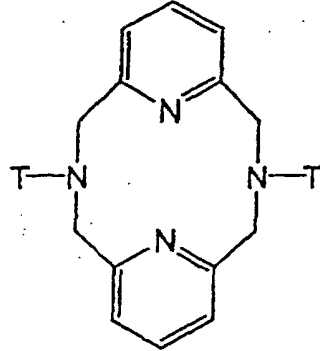
Patentansprüche

1. Bleichkatalysator der Formel (IV):

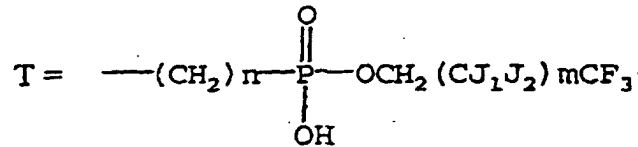


worin Fe ein Eisenatom im Oxidationszustand II oder III bedeutet, X eine Gruppe ist, die entweder eine Brücke oder keine Brücke zwischen den Eisenatomen ist, Y ein Gegenion ist, x und y ≥ 1, 0 ≤ n ≤ 3 und z die Ladung des Metallkomplexes ist und p = z/Ladung von Y; R₁ und R₂ jeweils unabhängig ein oder mehrere Ringsubstituenten sind ausgewählt aus Wasserstoff und elektronschiebenden und -ziehenden Gruppen ausgewählt aus Halogen, C₁-C₆-Alkoxy-, Hydroxy-, Hydroxyalkyl-, (gegebenenfalls mono- oder disubstituierten) Amingruppen, (gegebenenfalls mono- oder disubstituierten) Thiolgruppen, Carboxyl-, Ester-, Amid-, allgemein substituierten Carbonylgruppen, Nitril-, Nitro-, (gegebenenfalls substituierten) Sulfonyl-, Alkenyl-, Aryl-, quaternären Ammonium(+)- und Sulfonium(+)-Gruppen; R₃ bis R₈ unabhängig Wasserstoff, Alkyl-, Hydroxyalkyl-, Alkenylreste oder Varianten von jedem dieser Reste sind, wenn sie mit einer oder mehreren elektronschiebenden oder -ziehenden Gruppen

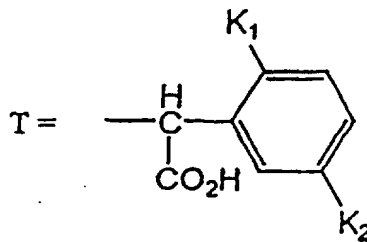
substituiert sind ausgewählt aus Halogen, C₁-C₆-Alkoxy-, Hydroxy-, Hydroxyalkyl-, (gegebenenfalls mono- oder disubstituierten) Amingruppen, (gegebenenfalls mono- oder disubstituierten) Thiolgruppen, Carboxyl-, Ester-, Amid-, allgemein substituierten Carbonylgruppen, Nitril-, Nitro-, (gegebenenfalls substituierten) Sulfonyl-, Alkenyl-, Aryl-, quaternären Ammonium(+)- und Sulfonium(+)-Gruppen, mit dem Vorbehalt, dass in dem Bleichkatalysator der Formel IV der folgende Ligand ausgeschlossen ist:



wobei im Fall 1 beide T = CH₃,
wobei im Fall 2 T = H oder



worin m 0 oder eine ganze Zahl von 1, 2, 3 oder 4 ist;
n eine ganze Zahl von 1, 2 oder 3 ist;
J₁ und J₂ = H oder F sind,
wobei im Fall 3 T = -CH₂COOH, -CH₂P(O)OH ist,
wobei W OH oder ein C₁-C₅-Alkyl- oder -O-(C₁-C₅)-Alkylrest ist oder



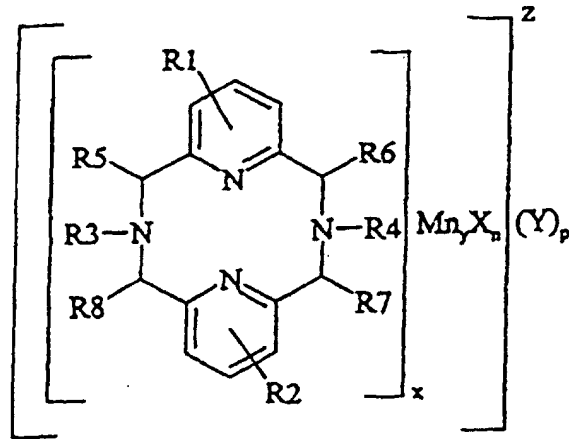
ist, worin K₁ = -OH oder -OCH₃ ist,
K₂ = -NO₂, -NH₂, Isothiocyanato, Semicarbazido, Thiosemicarbazido, Maleimido, Bromacetamido oder Carboxyl ist.

2. Bleichkatalysator der Formel (IV), wie in Anspruch 1 definiert, mit dem Vorbehalt, dass:

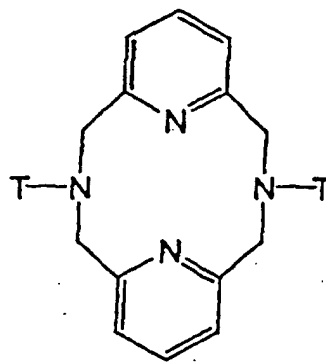
- (i) wenn R₁, R₂ und R₅ bis R₈ alle Wasserstoff sind,
R₃ und R₄ beide Methylreste sind;
x = 1, y = 1, z = +1, n = 1 und p = 1 und
Y = BPh₄⁻ ist;

dass dann X nicht Cl, Katecholol oder 3,5-Ditert.-butyl-1,2-katecholol ist und
 (ii) wenn R₁ bis R₈ alle Wasserstoff sind und
 x = 2, y = 1 und n = 0 ist,
 dann wenn z = +3 und p = 3 ist, Y nicht ClO₄⁻ ist und wenn
 z = +2 und p = 2 ist, Y nicht -BPh₄⁻ ist.

3. Bleichkatalysator der Formel (V):

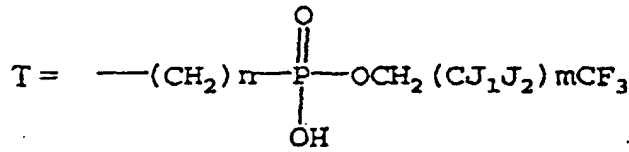


worin Mn ein Manganatom im Oxidationszustand II, III, IV oder V bedeutet, X eine Gruppe ist, die entweder eine Brücke oder keine Brücke zwischen den Manganatomen ist, Y ein Gegenion ist, x und y ≥ 1 sind, 0 ≤ n ≤ 3, und z die Ladung des Metallkomplexes ist und p = z/Ladung von Y; R₁ und R₂ jeweils unabhängig ein oder mehrere Ringsubstituenten sind, ausgewählt aus Wasserstoff und elektronenschiebenden und -ziehenden Gruppen ausgewählt aus Halogen, C₁-C₆-Alkoxy-, Hydroxy-, Hydroxyalkyl-, (gegebenenfalls mono- oder disubstituierten) Amingruppen, (gegebenenfalls mono- oder disubstituierten) Thiolgruppen, Carboxyl-, Ester-, Amid-, allgemein substituierten Carbonylgruppen, Nitril-, Nitro-, (gegebenenfalls substituierten) Sulfonyl-, Alkenyl-, Aryl-, quaternären Ammonium(+)- und Sulfonium(+)-Gruppen; R₃, R₄, R₅, R₆, R₇ und R₈ jeweils unabhängig Wasserstoff, Alkyl-, Hydroxyalkyl-, Alkenylreste oder Varianten von jedem dieser Reste sind, wenn sie mit einer oder mehreren elektronenschiebenden oder -ziehenden Gruppen substituiert sind, mit dem Vorbehalt, dass in dem Bleichkatalysator der Formel IV der folgende Ligand ausgeschlossen ist:



wobei im Fall 1 T = H oder

5

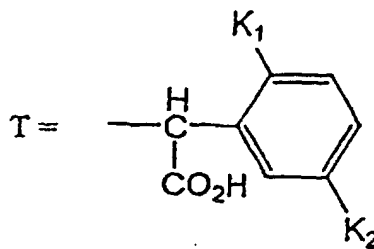


10

ist, worin
 m 0 oder eine ganze Zahl von 1, 2, 3 oder 4 ist;
 n eine ganze Zahl von 1, 2 oder 3 ist;
 J₁ und J₂ = H oder F,
 wobei im Fall 2 T = -CH₂COOH, -CH₂P(O)OHW ist,
 worin W OH oder ein C₁-C₅-Alkyl- oder -O-(C₁-C₅)-Alkylrest ist oder

15

20



25

ist, worin K₁ = -OH oder -OCH₃ ist,
 K₂ -NO₂, -NH₂, Isothiocyanato, Semicarbazido, Thiosemicarbazido, Maleimido, Bromacetamido oder Carboxyl ist.

30

4. Bleichkatalysator nach einem der Ansprüche 1, 2 und 3, worin R₁ und R₂ beide Wasserstoff sind, R₃ und R₄ unabhängig C₁-C₄-Alkylreste sind und R₅ bis R₈ jeweils Wasserstoff sind.
5. Bleichkatalysator nach einem der Ansprüche 1 bis 3, wobei das Metall im Oxidationszustand III ist.
6. Bleichkatalysator nach einem der Ansprüche 1 bis 5, worin X ausgewählt ist aus H₂O, OH⁻, O₂²⁻, O²⁻, HO₂⁻, SH⁻, S²⁻, -SO-, NR₉R₁₀⁻, Carboxylat, NR₉R₁₀R₁₁, Cl⁻, Br⁻, F⁻, N₃⁻ und Kombinationen davon, wobei R₉, R₁₀ und R₁₁ unabhängig ausgewählt sind aus H, C₁-C₄-Alkylresten und Arylresten, die gegebenenfalls mit einer oder mehreren elektronenziehenden und/oder -schiebenden Gruppen substituiert sind.
7. Bleichkatalysator nach einem der Ansprüche 1 bis 6, wobei Z nicht vorhanden ist.
8. Bleichzusammensetzung enthaltend einen Katalysator nach einem der Ansprüche 1 bis 7, wobei Y ausgewählt ist aus ClO₄⁻, SCN⁻, PF₆⁻, Sulfonat, Sulfat, CF₃SO₃⁻, BF₄⁻, BPh₄⁻ und OAc⁻.
9. Bleichkatalysator ausgewählt aus der Gruppe bestehend aus Dihalogen-2,11-diazo[3.3]-(2,6)-pyridinophan und Dihalogen-4-methoxy-2,11-diazo[3.3]-(2,6)-pyridinophan und Mischungen davon, wobei der Katalysator in Form eines Mangansalzes ist, wobei Mangan in einem oxidierten Zustand vorhanden ist.
10. Bleichkatalysator, wobei der Katalysator N,N'-Dimethyl-2,11-diazo[3.3]-(2,6)-pyridinophan in Form eines Salzes eines Mangans (in oxidiertem Zustand) ist.
11. Bleichzusammensetzung enthaltend einen Bleichkatalysator nach einem der Ansprüche 1 bis 10 und enthaltend mindestens eine weitere Komponente ausgewählt aus Tensiden und Sauerstoffbleichmitteln.
12. Verfahren zum Bleichen und/oder Reinigen eines Substrats, wobei das Verfahren umfasst, dass das Substrat mit einem Bleichkatalysator nach einem der Ansprüche 1 bis 7, 9 und 10 behandelt wird.

55

Revendications

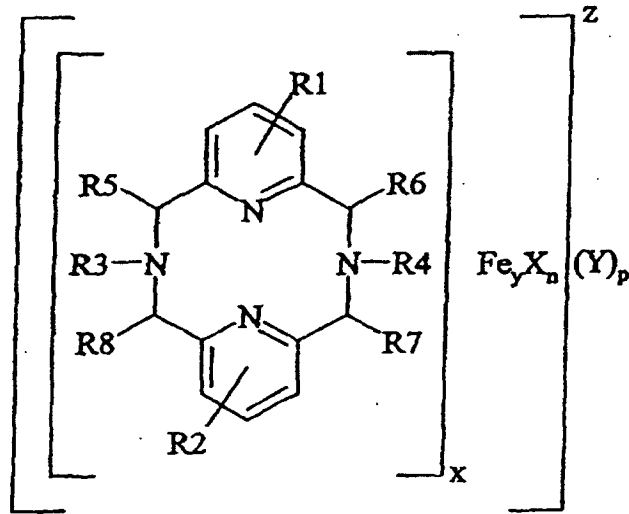
1. Catalyseur de blanchiment de formule (IV) :

5

10

15

20



25

dans laquelle Fe représente un atome de fer à l'état d'oxydation II ou III, X étant un groupe qui est soit pontant, soit non pontant entre les atomes de fer, Y est un ion antagoniste, x et y étant > 1 , $0 < n < 3$, et z étant la charge du complexe métallique et $p = z/$ étant la charge de Y ; R_1 et R_2 étant indépendamment un ou plusieurs anneaux substituants sélectionnés à partir de l'hydrogène et des groupe donnant et retirant des électrons sélectionnés à partir de : groupes thiols halo, C_{1-6} alkoxy, hydroxy, hydroxyalkyl (optionnellement mono- ou di-substitué), en général de groupes carboxyle, ester, amide, substitués carbonyles, nitriles, nitro, sulphonyle (optionnellement substitués), alkényle, aryle, ammonium quaternaire (+) et sulfonium (+) ; $R_3 - R_8$ étant indépendamment hydrogène, alkyle, hydroxyalkyle, alkényle ou des variantes de n'importe lesquels de ceux-ci lorsqu'ils sont substitués par un ou plusieurs groupes donnant ou retirant un électron, sélectionnés à partir de groupes amines halo, C_{1-6} alkoxy, hydroxy, hydroxyalkyl (optionnellement mono- ou di-substitué), des groupes thiols (optionnellement mono- ou di-substitué), des groupes carboxyles, esters, amides, substitués carbonyles en général, nitrile, nitro (optionnellement substitués) sulphonyle, alkényle, aryle, ammonium quaternaire (+) et sulfonium (+), à condition que dans le catalyseur de blanchiment de formule (IV), le ligand suivant soit exclu :

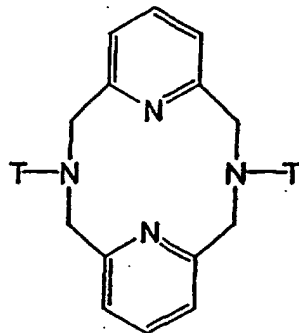
30

35

40

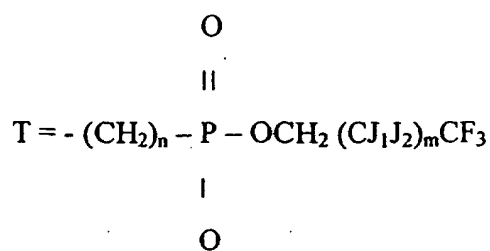
45

50



55

dans lequel, dans le cas 1, les deux T sont CH_3
dans lequel, dans le cas 2, $T = H$ ou



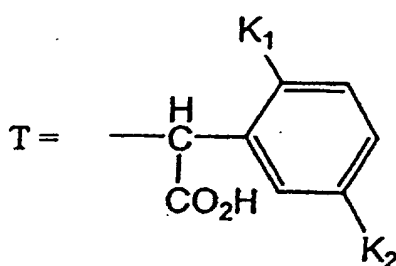
dans laquelle m est 0 ou un nombre entier de 1, 2, 3 ou 4

n est un nombre entier de 1, 2 ou 3

J₁ et J₂ = H ou F

dans laquelle dans le cas 3, T = - CH₂ COOH, - CH₂P(O) OHW

dans laquelle W est OH ou C₁ - C₅ - alkyle ou - O - (C₁ - C₅) - alkyle, ou



dans laquelle K₁ = - OH ou - OCH₃

K₂ est - NO₂, -NH₂, isothiocyanato, semicarbazido, thiosemicarbazido, maleimido, bromoacétamido ou carboxyle.

2. Catalyseur de blanchiment de formule (IV) selon la revendication 1, à la condition que :

(i) si R₁, R₂, et R₅ - R₈ sont tous hydrogène, R₃ et R₄ sont tous les deux méthyle ;

x = 1, y = 1, z = +1, n = 1 et p = 1 ; et

Y est - BPh₄⁻ ;

alors X n'est pas Cl, cathécolate ou 3,5 - di - terbutyl - 1,2 - cathéclate ; et

(ii) si R₁ - R₈ sont tous hydrogène ; et

x = 2, y = 1 et n = 0

alors lorsque z = +3 et p = 3, Y n'est pas ClO₄⁻, et lorsque

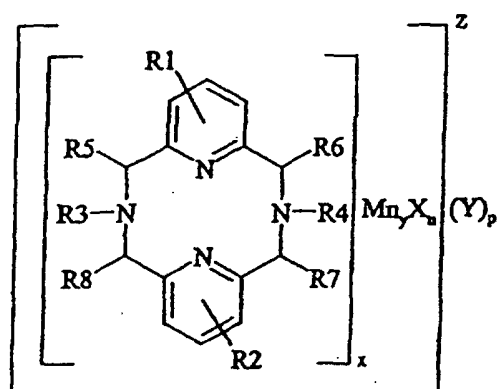
z = + 2 et p = 2, Y n'est pas - BPh₄⁻

3. Catalyseur de blanchiment de formule (V) :

5

10

15



20

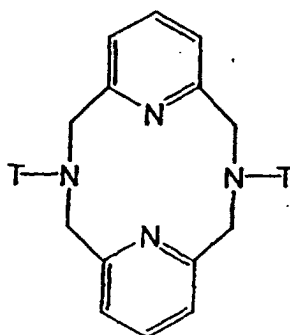
25

30

dans laquelle Mn représente un atome de manganèse à l'état d'oxydation II, III, IV ou V ; X est un groupe qui est soit pontant soit non pontant entre les atomes de manganèse, Y est un ion antagoniste, x et y étant ≥ 1 , $0 < n < 3$, et z étant la charge du complexe métallique, et $p = z / \text{charge de Y}$; R₁ et R₂ sont indépendamment un ou plusieurs anneaux substituants sélectionnés à partir de l'hydrogène est des groupes donnant ou retirant un atome, sélectionnés à partir de : groupes amines halo, C₁₋₆ alkoxy, hydroxy, hydroxyalkyle (optionnellement mono- ou di-substitués), les groupes thiols (optionnellement mono- ou di-substitués), les groupes carboxyles, ester, amide, carbonyles substitués en général nitrile, nitro, sulfonyles (optionnellement substitués) alkényles, aryles, ammonium quaternaire (+) et sulfonium (+) ; R₃, R₄, R₅, R₆, R₇, R₈ étant indépendamment hydrogène, alkyle, hydroxyalkyle, alkényle ou des variantes de n'importe lesquels de ceux-ci lorsqu'ils sont substitués par un ou plusieurs groupes donnant ou retirant un électron, à la conditions que dans le catalyseur de blanchiment de formule (IV) le ligand suivant soit exclu :

35

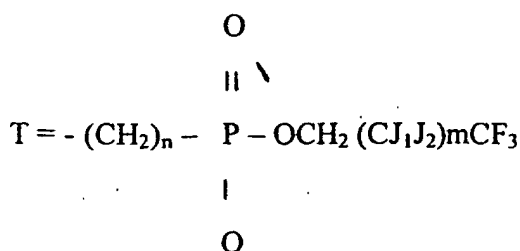
40



45

dans lequel dans le cas 1, T = H ou

50



55

dans laquelle m est 0 ou un nombre entier de 1, 2, 3 ou 4

n est un nombre entier de 1, 2 ou 3

J_1 et $J_2 = H$ ou F

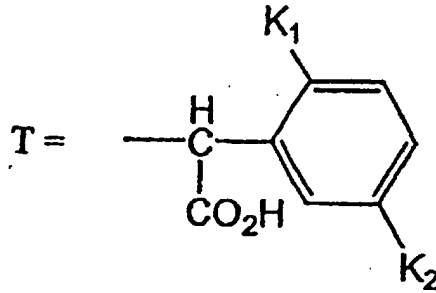
dans laquelle dans le cas 3, $T = -CH_2COOH$, $-CH_2P(O)OH$

dans laquelle W est OH ou $C_1 - C_5$ - alkyle ou $-O - (C_1 - C_5)$ - alkyle, ou

5

10

15



dans laquelle $K_1 = -OH$ ou $-OCH_3$

20

K_2 est $-NO_2$, $-NH_2$, isothiocyanato, semicarbazido, thiosemicarbazido, maleimido, bromoacétamido ou carboxyle.

4. Catalyseur de blanchiment selon l'une quelconque des revendications 1, 2 et 3, dans lequel R_1 et R_2 sont tous les deux hydrogène, R_3 et R_4 sont indépendamment alkyle en $C_1 - C_4$, et $R_5 - R_8$ sont chacun hydrogène.

25

5. Catalyseur de blanchiment selon l'une quelconque des revendications 1 à 3, dans lequel le métal est à l'état d'oxydation III.

6. Catalyseur de blanchiment selon l'une quelconque des revendications 1 à 5, dans lequel X est sélectionné à partir de H_2O , OH^- , O_2^{2-} , O_2^- , HO^2- , SH^- , S^{2-} , $-SO-$, $NR_9R_{10}^-$, carboxylate, $NR_9R_{10}R_{11}$, Cl^- , Br^- , F^- , N_3^- et des combinaisons de ceux-ci, dans lesquels R_9 , R_{10} et R_{11} sont indépendamment sélectionnés à partir de H , es groupes aryles et alkyle en $C_1 - C_4$, optionnellement substitués avec un ou plusieurs groupes donnant ou retirant les électrons.

30

7. Catalyseur de blanchiment selon l'une quelconque des revendications 1 à 6, dans lequel Z est absent.

35

8. Composition de blanchiment comprenant un catalyseur de blanchiment selon l'une quelconque des revendications 1 à 7, dans laquelle Y est sélectionnée à partir de ClO_4^- , SCN^- , PF_6^- , sulfonate, sulfate, $CF_3SO_3^-$, BF_4^- , BPh_4^- et OAc^- .

9. Catalyseur de blanchiment sélectionné à partir du groupe constitué du dihalo - 2,11 - diazo [3.3] (2,6) pyridinophane et du dihalo - 4 - méthoxy - 2,11 - diazo [3.3] (2,6) pyridinophane et des mélanges de ceux-ci, dans lesquels le catalyseur est sous la forme d'un sel de manganèse, ledit manganèse étant présent dans un état oxydé.

40

10. Catalyseur de blanchiment dans lequel le catalyseur est du N,N' - diméthyl - 2,11 - diazo [3.3] (2,6) pyridinophane sous la forme d'un sel de manganèse (à l'état oxydé).

45

11. Composition de blanchiment comprenant un catalyseur de blanchiment selon l'une quelconque des revendications 1 à 10 et comprenant au moins un autre composant sélectionné à partir des tensioactifs et des blanchissants oxygène.

50

12. Procédé de blanchiment et/ou de nettoyage d'un substrat, ledit procédé comprenant le fait de traiter le substrat avec un catalyseur de blanchiment selon l'une quelconque des revendications 1 à 7, 9 et 10.

55