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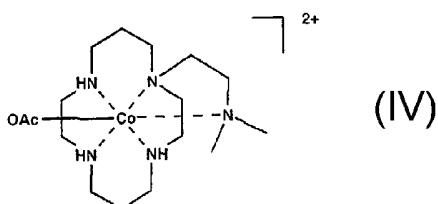
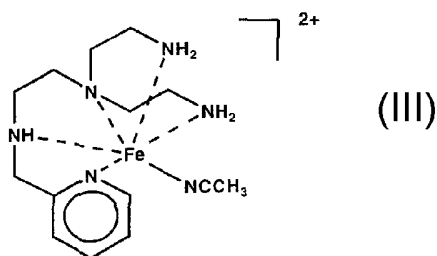
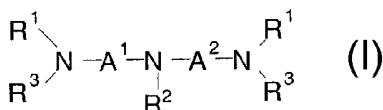
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[Continued on next page]

(54) Title: USE OF TRANSITION METAL COMPLEXES AS A BLEACHING CATALYST



(57) Abstract: Transition metal complexes are used as bleaching catalysts for peroxy compounds. Transition metal complexes to be used according to the invention contain an at least pentadentate ligand, which can be open-chain or cyclic. The ligand contains the structural element wherein in cyclic ligands the two R₁ together form Preferred complexes are .

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USE OF TRANSITION METAL COMPLEXES AS A BLEACHING CATALYST

Description:

5 The invention relates to the use of transition metal complexes with nitrogen-containing polydentate ligands as a bleaching catalyst and to bleaching agent compositions comprising such a bleaching catalyst. The activity of peroxy compounds in washing, bleaching and cleaning
10 processes at low temperature is increased by the transition metal complexes to be used according to the invention.

Inorganic peroxy compounds, in particular hydrogen peroxide and compounds which liberate hydrogen peroxide, such as sodium perborate monohydrate, sodium perborate tetrahydrate
15 and sodium percarbonate, have been employed for a long time as oxidizing agents in bleaching, washing and cleaning processes. Sufficiently rapid bleaching of soiled textiles requires a temperature of at least 80°C.

The oxidizing action of inorganic peroxygen compounds at
20 reduced temperature can be improved by co-using so-called bleaching activators. Bleaching activators are, in particular, N- and O-acyl compounds, for example polyacylated alkylenediamines, such as tetraacetylenehydrazine (TAED), acetylated glycolurils,
25 N-acetylated hydantoins, diketopiperazines, carboxylic acid anhydrides, carboxylic acid esters, such as, in particular, sodium nonanoyloxy-benzenesulfonate (NOBS), and acylated sugar derivatives.

By using a combination of a peroxy compound and an
30 activator, bleaching can be carried out at about 60°C instead of above 80°C without a loss in activity.

In efforts to be able to carry out washing and bleaching below 60°C, the use of transition metal complexes, in particular complexes of manganese, iron, cobalt and copper with at least one polydentate organic ligand, in particular
5 nitrogen-containing ligands, has been described in many documents.

Reference is made by way of example to the complexes described in the following documents: EP 0 544 490, WO 98/54282, WO 00/12808, WO 00/60043, WO 00/52124, EP 0 392
10 592, WO 99/64156 and WO 00/12667.

Although numerous different transition metal complexes are thus known for the use aimed for, they only partly meet some of the expectations imposed on them.

Thus, if the reactivity is too high there is the risk of a
15 change in colour of dyed textiles, and in the extreme case oxidative damage to the fibres. Furthermore, some complexes decompose the peroxygen compound without a bleaching action, are insufficiently stable to hydrolysis or are susceptible to oxidation.

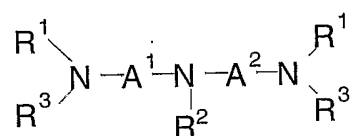
20 Cyclic and open-chain pentadentate aminic ligands are known - see DE 100 51 317 A1, EP 055 519 A2 and WO 00/12808. These catalysts are suitable for increasing the oxidizing and bleaching action of hydrogen peroxide. A further increase is achieved by combination of such a bleaching
25 catalyst with a so-called activator which can form a peroxycarboxylic acid in the presence of a source of hydrogen peroxide. As has been shown in practice, different property profiles of bleaching catalysts which the products known to date do not achieve satisfactorily in all points
30 are required in washing, bleaching and cleaning compositions.

The object of the present invention is accordingly to provide further transition metal complexes with at least

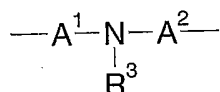
one nitrogen-containing polydentate ligand which are suitable as a bleaching catalyst for activation of a peroxy compound and preferably also oxygen.

It has been found that transition metal complexes with a transition metal from the series consisting of manganese, iron, cobalt or copper are very active and gentle bleaching catalysts if these contain at least one nitrogen-containing polydentate ligand which differs from the ligands of the documents acknowledged above at least in one feature.

The invention thus provides the use of a transition metal complex with at least one nitrogen-containing ligand as a bleaching catalyst for activation of a peroxy compound or of oxygen, wherein the complex is mono- or polynuclear, the transition metal (M) is manganese, iron, cobalt or copper and the nitrogen-containing ligand (L) is at least pentadentate, can be cyclic or open-chain and includes the structural element of the general formula

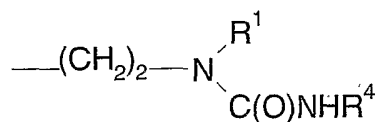


wherein A¹ and A² independently of one another are chosen from the series consisting of ethylene and 1,3-propylene, wherein propylene can have a functional substituent in the 2-position, wherein the two R¹ groups together can represent

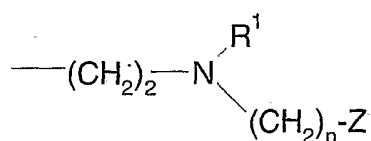


to form a tetraaza ring, R² in cyclic ligands is chosen from the series consisting of H, alkyl and -(CH₂)_n-Z, wherein n is 1 or 2 and Z is a substituent from the series consisting of COOH, CONR⁴₂, NH₂, NHR⁴, NR⁴₂, 2-pyridyl, imidazol-2-yl, 1,3-oxazolin-2-yl and C(O)-NHR⁴,

R^2 in open-chain ligands is chosen from the series consisting of



and



- 5 the radicals R^1 in open-chain ligands independently of one another are chosen from the series consisting of H and alkyl and the radicals R^3 and R^4 in open-chain or cyclic ligands independently of one another are chosen from the series
10 consisting of H and linear, cyclic or branched alkyl and R^3 additionally can be a radical C(O)-NHR^4 .

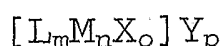
Embodiments of the use according to the invention.

The present invention also provides the bleaching agent composition defined in the claims, which comprises a peroxy
15 compound, in particular a source of hydrogen peroxide, and a transition metal complex to be used according to the invention in an amount effective for activation. The subclaims of the bleaching agent composition relate to preferred embodiments thereof.

20

The transition metal complex to be used according to the invention can be mono- or polynuclear and contains as the transition metal one from the series consisting of manganese in the valency level II to IV, iron in the

valency level II or III, cobalt in the valency level II or III and copper in the valency level I or II. Depending on the number of heteroatoms capable of ligand formation and their steric alignment in the ligand L, the complex can
5 contain one or more transition metal atoms, preferably one or two metal atoms of the same type. In general the complex has the general formula

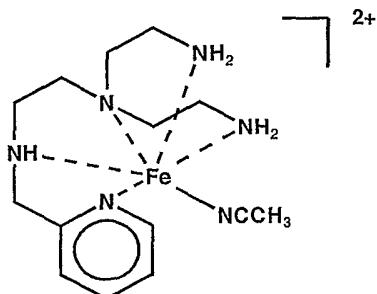


In this formula, L denotes the ligand to be used according
10 to the invention, M denotes a transition metal atom from the abovementioned series, X denotes a coordinating neutral or mono- or polyvalent ligand for saturation of the ligand sphere and Y denotes a non-coordinating counter-ion, which can be anionic or, if the sum of anionic ligands X and
15 ionic substituents in the ligand L exceeds the sum of the valency of the metal atoms M, can also be cationic. The index m represents an integer in the range from 1 to 4, in particular 1 or 2, the index n represents an integer, preferably 1 or 2, the index o represents zero or an
20 integer in the range from 1 to 8 and the index p represents zero or an integer in order to achieve a complete charge compensation. Y can also be a substituent, such as carboxylate or sulfonate, in the ligand.

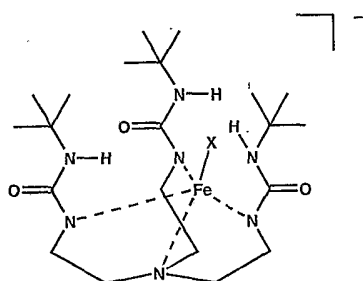
According to a further preferred embodiment, the radicals
25 R^1 to R^4 or the C atoms of the nitrogen-containing ring system directly contain hydrophilic substituents in order to increase the solubility of the complex. Examples of these are salt-forming functional substituents and hydroxyalkoxy groupings, which additionally can also
30 contain one or more ether bridges.

The chemical name for some examples of suitable ligands and formulae of some complexes containing them follow below:

N,N-bis(2-aminoethyl)-N'-(2-pyridylmethyl)-ethane-1,2-diamine (TrenPy)

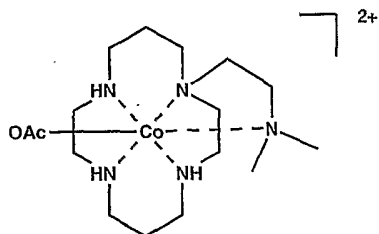


tris[(N'-tert-butylureayl)N-ethyl]amine (Trenta)

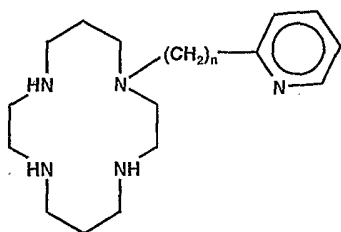


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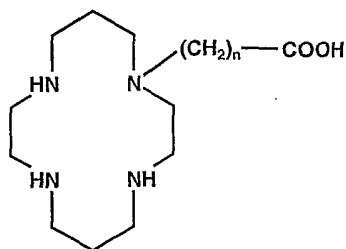
N-(N',N'-dimethylaminoethyl)-1,4,8,11-tetraazacyclotetradecane (MATATD)



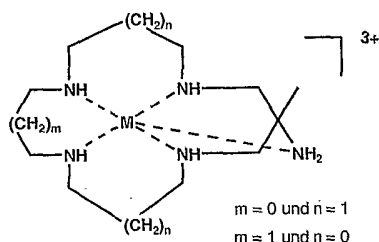
10 1-(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (for n = 1) (PMTATD)



1-(2-carboxyethyl)-1,4,8,11-tetraazacyclotetradecane (for n = 2)



10-methyl-1,4,8,12-tetraazacyclopentadecan-10-amine (for $m = 0$ and $n = 1$) (MATACTD)



5 The Co complex of TrenPy is particularly preferred.

Apart from the ligand L, the catalyst can additionally contain coordinating co-ligands X. X here can be a mono-, di- or trivalent anion or a neutral molecule, which can be coordinated with the transition metal atom in a mono-, bi- or tridentate manner. The co-ligand is preferably the following groupings: OH^- , O^{2-} , NO_3^- , PO_4^{3-} , CN^- , SCN^- , HSO_4^- , SO_4^{2-} , Cl^- , Br^- , F^- , ClO_4^- , OCN^- , HCO_3^- , RS^- , CO_3^{2-} , SO_3^{2-} , RSO_3^- , $\text{S}_2\text{O}_6^{2-}$, RCO_2^- ; H_2O , ROH , CH_3CN , $\text{NRR}'\text{R}''$.

15 The counter-ion Y of the complex to be used can be anionic or cationic, wherein the number p is chosen such that complete charge compensation is achieved. The counter-ion Y can preferably have the following meaning: F^- , Cl^- , Br^- , I^- , NO_3^- , RSO_3^- (R e.g. preferably CF_3), ClO_4^- , RCO_2^- , PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , SO_4^{2-} , HSO_4^- , CO_3^{2-} , HCO_3^- , BF_4^- , PF_6^- , SO_3^{2-} ; Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} .

The bleaching catalysts to be used according to the invention activate elemental oxygen and peroxy compounds. Peroxy compounds are to be understood as meaning, in particular, hydrogen peroxide, compounds which liberate
5 hydrogen peroxide, such as, in particular, sodium perborate monohydrate, sodium perborate tetrahydrate and sodium percarbonate, perphosphates and persulfates, peroxydicarboxylic acids and salts thereof and peroxydicarboxylic acid bleaching precursors, so-called
10 activators, and mixtures of such substances. Suitable peroxydicarboxylic acids can be aliphatic or aromatic in nature and contain one or more peroxydicarboxylic acid groups. Aliphatic peroxydicarboxylic acids usually contain 1 to 20 C atoms, preferably 1 to 12 C atoms, and the
15 particularly preferred peroxydicarboxylic acid is peroxyacetic acid. Among the peroxydicarboxylic acids with 2 peroxydicarboxylic acid groups, those having 4 to 18 C atoms are preferred; examples are diperoxyadipic acid, diperoxyazelaic acid, diperoxydodecanedioic acid, as well as salts of the acids
20 mentioned, for example magnesium salts. Among the aromatic peroxydicarboxylic acids there are, in particular, peroxybenzoic acid, m-chlorobenzoic acid, p-sulfonatoperoxybenzoic acid, diperoxyisophthalic acid, phthalimidopercaproic acid, 4,4'-sulfonyl-diperoxybenzoic
25 acid and magnesium salts of these acids.

The peroxydicarboxylic acids can also be formed in situ under the use conditions, and in particular from so-called
30 activators, which are in general O-acyl compounds and N-acyl compounds. Such compounds form the corresponding peroxydicarboxylic acid under perhydrolysis conditions in the presence of hydrogen peroxide or a source of hydrogen peroxide. Activators which are particularly preferably to
35 be used are: N,N,N',N'-tetraacetylenediamine (TAED), Na

1-methyl-2-benzoyloxybenzene-4-sulfonate, Na nonanoyloxybenzenesulfonate (NOBS), 2-(N,N,N-trimethylammonium)ethyl-sodium 4-sulfophenylcarbonate chloride (SPCC), pentaacetylglucose, phthalic anhydride.

5

For activation of peroxy compounds, the transition metal complexes to be used according to the invention are in general employed in an amount of 0.0001 to 50 wt.%, in particular 0.01 to 20 wt.%, based on the peroxy compounds.

10

Bleaching agent compositions according to the invention comprise at least one peroxy compound and a transition metal complex to be used according to the invention in an active amount. Such compositions expediently comprise 15 0.0001 to 50 wt.%, in particular 0.01 to 20 wt.% and particularly preferably 0.01 to 1 wt.% of a transition metal complex with a ligand according to the invention, based on the content of peroxy compounds or precursor of one.

20

Bleaching agent compositions according to the invention expediently additionally comprise one or more surfactants from the series consisting of anionic, cationic, zwitter-ionic and nonionic surfactants, in particular surfactants 25 such as are used in conventional washing, bleaching and cleaning compositions. Bleaching agent compositions according to the invention can furthermore also comprise organic and/or inorganic builders, such as zeolites. Further constituents can be those such as are used in 30 conventional washing, bleaching and cleaning compositions, including enzymes, pH regulators and conventional alkali metal carriers, such as alkali metal silicate and alkali metal carbonates.

Examples:

Example 1:

Preparation of the ligand N,N-bis(2-aminoethyl)-N'-(2-pyridylmethyl)-ethane-1,2-diamine (TrenPy)

Pyridine-2-carboxaldehyde and tris(2-aminoethyl)amine were reacted in a ratio of 1:5 in accordance with the instructions of *Inorg. Chem.* **1994**, 33(21), 4664 to give TRENPy. Purification was carried out by means of flash chromatography (silica gel, chloroform/methanol/ammonia = 10:4:2). (Yield: 74%)

Fe complex:

500 mg (2.10 mmol) TRENPy were initially introduced into 25 ml of a 1:1 mixture of acetonitrile/methanol, and 762 mg (2.10 mmol) iron(II) perchlorate hexahydrate were added. The solution was stirred for 2 hours at room temperature and then concentrated to approx. half, carefully covered with a layer of ethyl acetate and stored overnight in a refrigerator at -20°C. The violet solid which had precipitated out was filtered off and dried at 50°C in vacuo. (Yield: 54%)

Co complex

The Co complex was also prepared in a similar manner:

25

200 mg (0.84 mmol) of ligand (TRENPy), which was dissolved in 5 ml methanol beforehand, were added to a solution of 200 mg (0.84 mmol) cobalt(II) chloride hexahydrate and 236 mg (1.68 mmol) sodium perchlorate in 2 ml water. A dark red solution was formed. After stirring for 10 min at room temperature, air was passed moderately through the solution

30

in the course of 2 hours. The solution was left to stand overnight at room temperature and then concentrated completely and the residue was dried in air. (Yield: 98%, red-brown solid)

5

Example 2:

Preparation of the ligand N-(N',N'-dimethylaminoethyl)-1,4,8,11-tetraazacyclotetradecane (MATATD)

10 A solution of 270 mg (1.87 mmol) 1-chloro-2-dimethylaminoethane hydrochloride in 2.0 ml dimethylformamide was slowly added to 1.48 g (7.40 mmol) 1,4,8,11-tetraazacyclotetradecane (Cyclam) in 40 ml dimethylformamide at 110-120°C, the mixture was stirred for
15 2 hours at 110-120°C and for a further 12 hours at 5°C and the excess Cyclam was then filtered off. The filtrate was largely evaporated in vacuo. The oily residue was taken up in 10 ml water and the solution was brought to pH = 12 with 30 per cent aqueous sodium hydroxide solution and then
20 extracted with 4 x 50 ml chloroform. The combined organic phases were dried over anhydrous magnesium sulfate and the solvent was distilled off in vacuo. 50 ml methyl *tert*-butyl ether were added to the residue and the mixture was filtered again. After distillation of the solvent, the
25 residue was taken up in a little ethanol and the product was precipitated as the tetrahydrochloride with concentrated hydrochloric acid. Yield: 98% (colourless, crystalline solid).

30 **Co complex:** 676 mg (1.62 mmol) of the tetrahydrochloride in 5.0 ml methanol were brought to pH = 13 with 30 per cent aqueous sodium hydroxide solution and the solution was stirred for 2 hours at room temperature. 910 mg (6.48 mmol)

- sodium perchlorate and 403 mg (1.62 mmol) cobalt(II) acetate tetrahydrate, which was dissolved in a little water beforehand, were then added in succession. Atmospheric oxygen was then passed through the solution at room temperature in the course of 45 minutes, a fine beige-brown precipitate being formed. This was filtered off and dried in vacuo at 50°C.

Examples 3 to 7

- 10 The complexes of examples 1 and 2 and complexes prepared in an analogous manner or a manner known from the literature were investigated for their catalytic action by means of the Morin test and in some cases by means of a washing test.

- 15 Morin test: A sodium perborate monohydrate solution, a methanolic solution of tetraacetythylenediamine and a dilute solution of the combination to be investigated are added to an aqueous Morin solution.

- 20 After intensive mixing, the extinction/transmission is measured at 400 nm after 30 minutes at 30°C. The blank value is measured in the absence of the combination to be investigated.

- Washing test: Laboratory washing apparatus type ATLAS
25 LAUNDER-O-METER
Temperature: 30 °C
Washing time: 30 minutes
Water hardness: 14°d
Staining: tea, in some cases also grass on cotton

Detergent recipe:

- 12.2% anionic surfactant
- 7.7% nonionic surfactant
- 5 2.0% soap
- 34.8% zeolite A
- 4.2% polycarboxylate
- 0.5% phosphonic acid
- 4.1% corrosion inhibitor
- 10 1.1% magnesium silicate
- 1.1% greying inhibitor (CMC)
- 2.2% sodium sulfate
- 4.1% sodium citrate

Bleaching component:

- 15 17% sodium percarbonate
- 5% activator TAED
- Metal complex: 2,400 ppm
- Detergent concentration: 5 g/l

As a comparison, the base recipe plus percarbonate/TAED,
20 but without a metal complex (= catalyst) was always run
(CE1). This change in reflection compared with the starting
fabrics is subtracted from the change in reflection
achieved with percarbonate/TAED/bleaching catalyst.

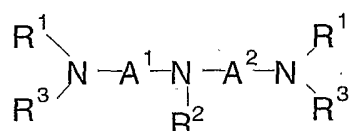
The results follow from the table:

Table:

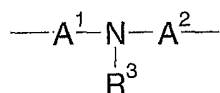
No.	Complex			Morin test transmission %	Washing test (ΔR) %
	M	L	X		
3	Fe	TrenPy	CH ₃ CN	5.4	n.d.
4	Co	TrenPy	(μ O ₂)	92.2	3.1
5	Fe	Trenta	(Cl) ₂	18.6	0.4
6	Fe	Trenta	OH ²	10	0.3
7	Mn	MATATD	CH ₃ O ⁻	6.2	n.d.

Patent claims

1. Use of a transition metal complex with a nitrogen-containing ligand as a bleaching catalyst for activation of a peroxy compound or of oxygen, wherein
 5 the complex is mono- or polynuclear, the transition metal (M) is manganese, iron, cobalt or copper and the nitrogen-containing ligand (L) is at least pentadentate, can be cyclic or open-chain and includes the structural element of the general formula



- 10 wherein A¹ and A² independently of one another are chosen from the series consisting of ethylene and 1,3-propylene, wherein propylene can have a functional substituent in the 2-position, wherein the two R¹ groups together can represent



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to form a tetraaza ring,

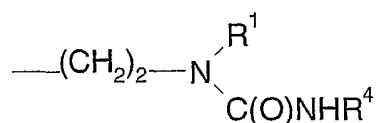
R² in cyclic ligands is chosen from the series

consisting of H, alkyl and -(CH₂)_n-Z, wherein n is 1 or 2

and Z is a substituent from the series consisting of

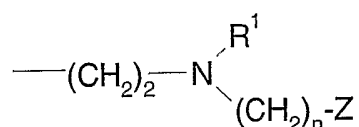
- 20 COOH, CONR⁴₂, NH₂, NHR⁴, NR⁴₂, 2-pyridyl, imidazol-2-yl, 1,3-oxazolin-2-yl and C(O)-NHR⁴,

R² in open-chain ligands is chosen from the series consisting of



and

25

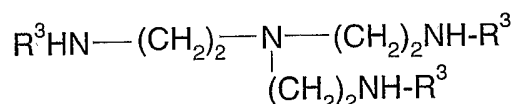


the radicals R^1 in open-chain ligands independently of one another are chosen from the series consisting of H and alkyl

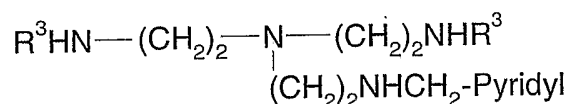
- 5 and the radicals R^3 and R^4 in open-chain or cyclic ligands independently of one another are chosen from the series consisting of H and linear, cyclic or branched alkyl and R^3 additionally can be a radical $\text{C}(\text{O})\text{---NHR}^4$.

2. Process according to claim 1,
characterized in that
10 a catalyst with a cyclic ligand based on 1,4,8,11-tetraazacyclotetradecane with a radical, bonded to an N atom, from the series consisting of 2-pyridylmethyl, $\text{---}(\text{CH}_2)_n\text{---COOH}$ and $\text{---}(\text{CH}_2)_2\text{---CON(alkyl)}_2$ is used.

3. Use according to claim 1,
15 characterized in that a catalyst with an open-chain ligand of the general formula



wherein R^3 represents $\text{---C}(\text{O})\text{NH}^+\text{butyl}$, or of the general formula



- 20 wherein R^3 is H or C_1 to C_4 -alkyl is used.

4. Use according to one of claims 1 to 3
characterized in that
the complex has the general formula $[\text{L}_m\text{M}_n\text{X}_o]\text{Y}_p$,
wherein L denotes a ligand according to one of claims 1
25 to 3,
M denotes a transition metal from the series consisting

- of Mn(II) to Mn(IV), Fe(II), Fe(III), Co(II), Co(III),
Cu(I) and Cu(II), in particular Co(II) or Co(III),
X denotes a coordinating neutral or charged mono- or
polyvalent ligand for saturation of the ligand sphere
5 and
Y denotes a non-coordinating counter-ion which can be
anionic or, if the sum of anionic substituents in the
ligand L exceeds the sum of the valency of the metal
atoms M, can also be cationic,
10 m denotes an integer in the range from 1 to 4, in
particular 1 or 2,
n denotes the number 1 or 2,
o denotes zero or an integer in the range from 1 to 8
and
15 p denotes zero or an integer in the range from 1 to 8,
in order to achieve complete charge compensation.
5. Use according to one of claims 1 to 4,
characterized in that
hydrogen peroxide or a peroxycarboxylic acid having 2 to
20 18 C atoms, which can also have been formed in situ from
a source of hydrogen peroxide and an activator from the
series consisting of O-acyl or N-acyl compounds, is
activated.
6. Use according to one of claims 1 to 5
25 characterized in that
the transition metal complex is employed in an amount of
0.0001 to 50 wt.%, based on the peroxy compound.
7. Bleaching agent composition comprising a peroxy compound
and a transition metal complex in an amount effective
30 for activation of the peroxy compound,
characterized in that
it comprises a transition metal complex according to one
of claims 1 to 5.

8. Bleaching agent composition according to claim 7,
characterized in that
the peroxy compound is chosen from the series consisting
of hydrogen peroxide, a source of hydrogen peroxide, in
5 particular an alkali metal perborate monohydrate
tetrahydrate or alkali metal percarbonate, a
peroxycarboxylic acid having 2 to 18 C atoms or a
combination of a source of hydrogen peroxide and a
peroxycarboxylic acid precursor, in particular an O-acyl
10 or N-acyl compound, or from mixtures thereof.
9. Bleaching agent composition according to claim 8,
characterized in that
it additionally comprises one or more surfactants, in
particular wash-active surfactants.
- 15 10. Bleaching agent composition according to one of claims 8
to 9,
characterized in that
it additionally comprises builders, in particular
zeolites.
- 20 11. Bleaching agent composition according to claim 10,
characterized in that
it is a constituent of a washing, bleaching or cleaning
composition comprising one or more surfactants and one
or more builders.
- 25 12. Bleaching agent composition according to one of claims 8
to 11,
characterized in that
it comprises 0,0001 to 50 wt.%, in particular 0.01 to
20 wt.% of a transition metal complex according to one
30 of claims 1 to 7, based on the content of peroxy
compound or precursor thereof.

INTERNATIONAL SEARCH REPORT

Internal Application No

PCT/EP 03/05673

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/39

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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