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(54) Title: PROCESS OF BLEACHING

(57) Abstract: The present invention concerns bleaching of substrates with an aqueous solution of a water soluble salt of a pre-formed transition metal catalyst together with hydrogen peroxide.

WO 2006/125517 A1

- 1 -

PROCESS OF BLEACHING

FIELD OF INVENTION

The invention concerns the use of bleaching solutions.

5

BACKGROUND OF THE INVENTION

Raw cotton (gin output) is dark brown in colour due to the natural pigment in the plant. The cotton and textile industries recognise a need for bleaching cotton prior to its use in textiles and other areas. The object of bleaching such cotton fibres is to remove natural and adventitious impurities with the concurrent production of substantially whiter material.

15 There have been two major types of bleach used in the cotton industry. One type is a dilute alkali or alkaline earth metal hypochlorite solution. The second type of bleach is a peroxide solution, e.g., hydrogen peroxide solutions. This bleaching process is typically applied at high temperatures, i.e. 80 to 95 °C. Controlling the peroxide decomposition due to trace metals is key to successfully using hydrogen peroxide. Often Mg-silicates or sequestering agents such as EDTA or analogous phosphonates are applied to reduce decomposition. A problem with the above types of treatment
20
25 is that the cotton fibre is susceptible tendering.

Wood pulp produced for paper manufacture either contains most of the originally present lignin and is then called mechanical pulp or it has been chiefly delignified, as in
30 chemical pulp. Mechanical pulp is used for e.g. newsprint and is often more yellow than paper produced from chemical

- 2 -

pulp (such as for copy paper or book-print paper). Further, paper produced from mechanical pulp is prone to yellowing due to light- or temperature-induced oxidation. Whilst for mechanical pulp production mild bleaching processes are applied, to produce chemical pulp having a high whiteness, various bleaching and delignification processes are applied. Widely applied bleaches include elemental chlorine, hydrogen peroxide, chlorine dioxide and ozone.

10 Whilst for both textile bleaching and wood pulp bleaching, chlorine-based bleaches are most effective, there is a need to apply oxygen-based bleaches for environmental reasons. Hydrogen peroxide is a good bleaching agent, however, it needs to be applied at high temperatures and long reaction times. For industry it is desirable to be able to apply hydrogen peroxide at lower temperatures and shorter reaction times than in current processes. Towards this end, the use of highly active bleaching catalysts would be desirable.

20 As a particular class of active catalysts, the azacyclic molecules have been known for several decades, and their complexation chemistry with a large variety of metal ions has been studied thoroughly. The azacyclic molecules often lead to transition-metal complexes with enhanced thermodynamic and kinetic stability with respect to metal ion dissociation, compared to their open-chain analogues.

United States Application 2001/0025695, discloses the use of a manganese transition metal catalyst of 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me₃-TACN); the transition metal catalyst has as a non-coordinating counter ion PF₆⁻. United

- 3 -

States Application 2001/0025695A1 also discloses a manganese transition metal catalyst of 1,2,-bis-(4,7,-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane (Me₄-DTNE); the transition metal catalyst has as a non-coordinating counter ion ClO₄⁻. The
5 solubility, in water at 20 °C, of the Me₄-DTNE complex having non-coordinating counter ion ClO₄⁻ is about 16 gram/Liter. The solubility, in water at 20 °C, of the Me₄-DTNE complex having non-coordinating counter ion PF₆⁻ is about 1 gram/Liter.

10

US 2002/0066542 discloses the use of a manganese transition metal complex of Me₃-TACN in comparative experiments and makes reference to WO 97/44520 with regard to the complex; the non-coordinating counter ion of the manganese transition
15 metal complex of Me₃-TACN is PF₆⁻. The X groups as listed in paragraph [021] of US 2002/0066542 are coordinating.

EP 0458397 discloses the use of a manganese transition metal complex of Me₃-TACN as bleaching and oxidation catalysts and
20 use for paper/pulp bleaching and textile bleaching processes. Me₃-TACN complexes having the non-coordinating counter ion perchlorate, tetraphenyl borate (BPh₄⁻) and PF₆⁻ are disclosed. The solubility, in water at 20 °C, of the Me₃-TACN complex having non-coordinating counter ion ClO₄⁻ is
25 between 9.5 to 10 gram/Liter. The solubility, in water at 20 °C, of the Me₃-TACN complex having non-coordinating counter ion BPh₄⁻ is less then 0.01 gram/Liter.

WO 95/27773 discloses the use of manganese transition metal
30 catalysts of 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me₃-

- 4 -

TACN); the transition metal catalysts have as a non-coordinating counter ion ClO_4^- and PF_6^- .

1,4,7-Trimethyl-1,4,7-triazacyclononane ($\text{Me}_3\text{-TACN}$) has been used in dishwashing for automatic dishwashers, SUN™, and has also been used in a laundry detergent composition, OMO Power™. The ligand ($\text{Me}_3\text{-TACN}$) is used in the form of its manganese transition-metal complex, the complex having a counter ion that prevents deliquescence of the complex. The counter ion for the commercialised products containing manganese $\text{Me}_3\text{-TACN}$ is PF_6^- . The $\text{Me}_3\text{-TACN PF}_6^-$ salt has a water solubility of 10.8 g per litre at 20 °C. Additionally, the perchlorate (ClO_4^-) counter ion is acceptable from this point of view because of its ability to provide a manganese $\text{Me}_3\text{-TACN}$ that does not appreciably absorb water. Reference is made to United States Patent 5,256,779 and EP 458397, both of which are in the name of Unilever. One advantage of the PF_6^- or ClO_4^- counter ions for the manganese $\text{Me}_3\text{-TACN}$ complex is that the complex may be easily purified by crystallisation and recrystallisation from water. In addition, for example, the non-deliquescent PF_6^- salt permits processing, e.g., milling of the crystals, and storage of a product containing the manganese $\text{Me}_3\text{-TACN}$. Further, these anions provide for storage-stable metal complexes. For ease of synthesis of manganese $\text{Me}_3\text{-TACN}$ highly deliquescent water soluble counterions are used, but these counterions are replaced with non-deliquescent, much less water soluble counter ions at the end of the synthesis. During this exchange of counter ion and purification by crystallisation loss of product results. A drawback of using PF_6^- is its

- 5 -

significant higher cost compared to other highly soluble anions.

United States Patents 5,516,738 and 5,329,024 disclose the
5 use of a manganese transition metal catalyst of 1,4,7-
Trimethyl-1,4,7-triazacyclononane (Me₃-TACN) for epoxidizing
olefins; the transition metal catalyst has as a non-
coordinating counter ion ClO₄⁻. United States Patents
5,329,024 also discloses the use of the free Me₃-TACN ligand
10 together with manganese chloride in epoxidizing olefins.

WO 2002/088063, to Lonza AG, discloses a process for the
production of ketones using PF₆⁻ salts of manganese Me₃-TACN.

15 WO 2005/033070, to BASF, discloses the addition of an
aqueous solution of Mn(II)acetate to an aqueous solution of
Me₃-TACN followed by addition of a organic substrate followed
by addition of hydrogen peroxide.

20 Use of a water-soluble salt negates purification and
provides a solution, which may be used directly, and reduces
loss by purification.

SUMMARY OF INVENTION

25 We have found that there is an advantage in using a
preformed transition metal complex of azacyclic molecules
over in situ generation, for example by mixing the
appropriate ligand with the MnCl₂, MnSO₄ or Mn(OAc)₂ salts in
an industrial process. Further, the addition of one product
30 to a reaction vessel reduces errors in operation.

- 6 -

We have found that for certain applications the use of a highly water-soluble salt of the manganese azacyclic complex is preferable. We have found that the dominant factor in the solubility of these transition metal complexes is the non-coordinating counter ion(s). In the solubilities given
5 herein for (Me₃-TACN) the co-ordinating counter ions are three O²⁻ and for Me₄-DTNE the co-ordinating counter ions are two O²⁻ and one acetate.

10 The invention is particularly applicable to industrial bleaching of paper/pulp, cotton-textile fibres, and the removal or degradation of starches. By using a transition metal catalyst that is significantly water soluble the synthesis negates the preparation of significantly water
15 insoluble salts and hence reduces cost. The transition metal catalyst may be shipped in solution or as a solid form of transition metal catalyst which is easily dissolved in water.

20 In order to avoid the use of costly non-coordinating counter ions required for isolation, formulation and stabilisation, one might form the transition metal catalyst *in situ*. US 5,516,738 discloses the use of free Me₃-TACN ligand with Mn(II)Cl₂ in epoxidizing olefins. However the *in situ*
25 preparation has some drawbacks, for example, it is a more complicated process and uncontrolled side reactions occur which result in less efficient formation of the catalyst and undesirable side products like MnO₂. Fast decomposition of hydrogen peroxide, catalysed by some of the undesirable side
30 products might occur, reducing the efficiency of the bleach process.

- 7 -

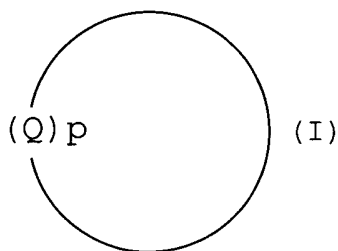
In one embodiment the present invention provides a method of catalytically treating a substrate, the substrate being a cellulose-containing substrate or starch containing substrate, with a preformed transition metal catalyst salt, the preformed transition metal catalyst salt having a non-coordinating counter ion, the method comprising the following steps:

(i) optionally dissolving a concentrate or solid form of a preformed transition metal catalyst salt in an aqueous medium to yield an aqueous solution of the preformed transition metal catalyst salt;

(ii) adding the aqueous solution of the preformed transition metal catalyst salt to a reaction vessel; and,

(iii) adding hydrogen peroxide to the reaction vessel,

wherein the preformed transition metal catalyst salt is a mononuclear or dinuclear complex of a Mn (III) or Mn(IV) transition metal catalyst for catalytically treating the substrate with hydrogen peroxide, the non-coordinating counter ion of said transition metal selected to provide a preformed transition metal catalyst salt that has a water solubility of at least 30 g/l at 20 °C and wherein the ligand of the transition metal catalyst is of formula (I):



- 8 -

wherein: $Q = \begin{array}{c} R \\ | \\ \text{---N---} \end{array} [CR_1R_2CR_3R_4) \text{---} ;$

p is 3;

R is independently selected from: hydrogen, C1-C6-alkyl, CH₂CH₂OH, and CH₂COOH, or one of R is linked to the N of
5 another Q via an ethylene bridge;

R₁, R₂, R₃, and R₄ are independently selected from: H, C1-C4-alkyl, and C1-C4-alkylhydroxy, and the substrate is
brought into contact with a mixture of the aqueous solution
of the preformed transition metal catalyst salt and the
10 hydrogen peroxide. The dinuclear complex may have two
manganese in same or differing oxidation states.

R is preferably C1-C6-alkyl, most preferably Me, and/or one
of R is an ethylene bridge linking the N of Q to the N of
15 another Q.

The reaction vessel may be part of a continuous flow
apparatus or a vessel used in a batch process. Preferably
pulp and cotton are treated in a continuous flow process.
20 Steps (ii) and (iii) provide a mixture of the aqueous
solution of the preformed transition metal catalyst salt and
the hydrogen peroxide; the substrate is brought into contact
with this mixture and hence is treated with such within the
reaction vessel.

25

The preformed transition metal catalyst salt is one which
has been provided by bringing into contact the free ligand
or protonated salt of the free ligand and a manganese salt
in solution followed by oxidation to form a Mn (III) or
30 Mn(IV) transition metal catalyst. Preferred protonated salts

- 9 -

of the ligand are chloride, acetate, sulphate, and nitrate. The protonated salts should not have undesirable counterions such as perchlorate or PF_6^- . The contact and oxidation step is preferably carried out in an aqueous medium, at least 24
5 hours before use, preferably at least 7 days before use.

The rate of formation of the transition metal catalyst depends upon the ligand. The formation of a transition metal catalyst from Me_3 -TACN ligand is typically complete within 5
10 min. The formation of a transition metal catalyst from Me_4 -DTNE ligand requires about 20 to 30 min for optimal complexation. After complex formation an aqueous solution of $\text{H}_2\text{O}_2/\text{NaOH}$ may be slowly added to form a desired $\text{Mn(IV)}/\text{Mn(IV)}$ or $\text{Mn(IV)}/\text{Mn(III)}$ species. This second step, the oxidation
15 step, provides a sufficiently stable complex for storage.

In another aspect the present invention provides the preformed transition metal catalyst salt as defined herein, wherein the preformed transition metal catalyst salt has
20 been formed by a contact and oxidation step that is carried out at least 24 hours previously, preferably 7 days previously, and is stored in a closed, preferably sealed, container.

25 The present invention also extends to the substrate treated with preformed transition metal catalyst and hydrogen peroxide.

DETAILED DESCRIPTION OF THE INVENTION

30 The solubility, in water at 20 °C, of the Me_3 -TACN complex having non-coordinating counter ion acetate is more than 70

- 10 -

gram/Liter. The solubility, in water at 20 °C, of the Me₃-TACN complex having non-coordinating counter ion sulphate is more than 50 gram/Liter. The solubility, in water at 20 °C, of the Me₃-TACN complex having non-coordinating counter ion chloride is 43 gram/Liter. It is most preferred the preformed transition metal catalyst salt is a dinuclear Mn(III) or Mn(IV) complex with at least two O²⁻ bridges.

The method of treating paper/pulp, cotton-textile fibres, or starch containing substrate is most applicable to industrial processes. Other examples of such processes are laundry or mechanical dish washing applications, fine chemical synthesis. Most preferably the method is applied to wood pulp, raw cotton, or industrial laundering. In this regard, the wood pulp is bleached which has not been processes into a refined product such as paper. The raw cotton is in most cases treated/bleached after preparation of the raw cotton cloths or bundled fibres. Preferably the method of treatment is employed in an aqueous environment such that the liquid phase of the aqueous environment is at least 80 wt% water, more preferably at least 90 wt% water and even more preferably at least 95 wt% water. After treatment of the substrate the reactants may be recycled back into the reaction vessel.

25

In addition, poly-cotton may also advantageously be treated in the form of a thread or a woven garment. Another preferred utility is in the industrial bleaching market of laundry, for example, the bleaching of large amounts of soiled white bed linen as generated by hospitals and gaoles.

30

- 11 -

Preferably R is independently selected from: hydrogen, CH₃, C₂H₅, CH₂CH₂OH and CH₂COOH; least preferred of this group is hydrogen. Most preferably R is Me and/or one of R is an ethylene bridge linking the N of Q to the N of another Q.

5 Preferably R₁, R₂, R₃, and R₄ are independently selected from: H and Me. Preferred ligands are 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me₃-TACN) and 1,2,-bis-(4,7-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane (Me₄-DTNE) of which Me₃-TACN is most preferred. The manganese ion is most preferably
10 Mn(III) or Mn(IV), most preferably Mn(IV).

The water solubility of the preformed transition metal catalyst salt is at least 30 g/l at 20 °C, more preferably at least 50 g/l at 20 °C. Even more preferably the water
15 solubility of the preformed transition metal catalyst salt is at least 70 g/l at 20 °C and most preferably the salt is deliquescent. The high solubility provides for concentrates whilst avoiding precipitation or crystallisation of the preformed transition metal catalyst salt. The preformed
20 transition metal catalyst salt (cationic) used in the method is most preferably a single species. In this regard, the aqueous solution used comprises at least 90 % of a single species. The non-coordinating counter ions may, for example, be a mixture of acetate and chloride.

25

The non-coordinating anion of the transition metal catalyst salt is preferably selected from the group consisting of chloride, acetate, sulphate, and nitrate. Most preferably the salt is acetate. The salt is other than the
30 perchlorate.

- 12 -

Co-ordinating counter ions for the transition metal complexes are O^{2-} and/or carboxylate (preferably acetate). It is preferred that the transition metal complexes have at least one O^{2-} co-ordinating counter ion. In particular, for
5 Me_3 -TACN three O^{2-} co-ordinating counter ions are preferred or one O^{2-} co-ordinating counter ion and two carboxylate co-ordinating counter ions are preferred, with two acetate moieties as co-ordinating counter ions being most preferred. For Me_4 -DTNE two O^{2-} co-ordinating counter ions and one
10 acetate co-ordinating counter ion are preferred.

It is preferred that the transition metal catalyst salt is present in a buffer system that maintains the solution in the pH range 2 to 7, and preferably in the pH range 4 to 6.
15 The buffer systems is preferably phosphate or carboxylate containing buffers, e.g., acetate, benzoate, citrate. The buffer system most preferably keeps the transition metal catalyst salt in the range pH 4.5 to 5.5.

20 The catalyst solution may also be provided in a reduced volume form such that it is in a concentrate, solid or slurry which is then dispatched to its place of use. Removal of solvent is preferably done by reduced pressure rather than the elevation of temperature. Preferably the solution,
25 solid or slurry is stored over an inert atmosphere, e.g., nitrogen or argon, with little or no headspace at 4 °C. For storage purposes a preformed transition metal catalyst salt concentration range of 0.1 to 10% is desirable, more desirable is between 0.5 and 8%, and most desirable is
30 between 0.5 and 2%. The concentrate or solid or solid most

- 13 -

preferably has the pH means as described above before reduction of water volume.

In the bleaching process it is preferred that the substrate
5 is contacted with between from 0.1 to 100 micromolar of the preformed transition metal catalyst and from 5 to 1500 mM of hydrogen peroxide.

Preferably the preformed transition metal catalyst salt and
10 hydrogen peroxide are mixed just before introduction to the substrate.

Experimental

Examples on the syntheses of $Mn_2O_3(Me_3-TACN)_2$ complexes with
15 different anions are provided. Synthesis of the $Mn_2O_3(Me_3-TACN)_2 PF_6$ salt is disclosed in US5153161, US5256779, and US5274147. The solubility of the $Mn_2O_3(Me_3-TACN)_2 PF_6$ salt in water at 20 °C is 1.08% (w/w).

20 Preparation of aqueous solution of $[Mn_2O_3(Me_3-TACN)_2].(Cl)_2$
To 10 mmol (1.71 gram Me3-TACN in 10 ml water was added
10 mmol (1.98 gram) solid $MnCl_2.4H_2O$ while stirring under
nitrogen flow. The mixture turned white/bluish. After 5
minutes stirring a freshly prepared mixture of 10 ml 1 M
25 hydrogen peroxide and 2 ml of 5 M (20%) NaOH was added drop-
wise over 5 minutes. The mixture turned immediately dark
brown/red. At the end of the addition some gas evolution was
observed. After completion of the addition the nitrogen flow
was stopped and the stirring was continued for 5 minutes and
30 pH was set with to neutral/acidic (pH 5 paper) with 1 M
hydrochloric acid. The mixture was filtered through G4 glass

- 14 -

frit, washed with water and the collected red filtrate and wash diluted to 50.00 ml in a graduated flask. From this solution a 1000x dilution was made and from the absorption in the UV/Vis spectrum at 244, 278, 313, 389 and 483 nm the concentration in the stock was calculated and the yield

(based on extinction of the PF_6 analogue in water)

Extinction of 1000x diluted sample gave

244 nm 1.692

278 nm 1.619

10 313 nm 1.058

389 nm 0.108

485 nm 0.044

Calculated yield 91%, solution contains 5.2% (on weight basis) of the catalyst.

15

Preparation of aqueous solution of [of $[\text{Mn}_2\text{O}_3(\text{Me}_3\text{-TACN})_2].(\text{OAc})_2$

To 10 mmol (1.71 gram $\text{Me}_3\text{-TACN}$ in 10 ml water was added 10 mmol (2.47 gram) solid $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ while stirring under

20 nitrogen flow. The mixture turned to a bluish solution.

After 5 minutes stirring a freshly prepared mixture of 10 ml 1 M hydrogen peroxide and 2 ml of 5 M (20%) NaOH was added drop-wise over 5 minutes. The mixture turned immediately dark brown/red. At the end of the addition some gas

25 evolution was observed. After completion of the addition the nitrogen flow was stopped and the stirring was continued for 5 minutes and pH was set with to neutral/acidic (pH 5 paper) with 1 M acetic acid. The mixture was filtered through a G4 glass frit, washed with water and the collected red filtrate and wash diluted to 50.00 ml in a graduated flask. From this

30 solution a 1000x dilution was made and from the absorption

- 15 -

in the UV/Vis spectrum at 244, 278, 313, 389 and 483 nm the concentration in the stock was calculated and the yield (based on extinction of the PF₆ analogue in water)

244 nm 1.689

5 278 nm 1.626

313 nm 1.074

389 nm 0.124

485 nm 0.051

10 Calculated yield 88%; solution contains 5.2% (on weight basis) of the catalyst.

Preparation of aqueous solution of [Mn₂O₃(Me₃-TACN)₂].SO₄

To 10 mmol (1.7 gram Me₃-TACN in 10 ml water was added 10 mmol (1.98 gram) solid MnCl₂.4H₂O while stirring under
15 nitrogen flow. The mixture turned to a white suspension. After 5 minutes stirring a freshly prepared mixture of 10 ml 1 M hydrogen peroxide and 2 ml of 5 M (20%) NaOH was added drop-wise over 5 minutes. The mixture turned immediately dark brown/red. At the end of the addition some gas
20 evolution was observed. After completion of the addition the nitrogen flow was stopped and the stirring was continued for 5 minutes and pH was set with to neutral/acidic (pH 5 paper) with 1 M sulphuric acid. The mixture was filtered through a G4 glass frit, washed with water and the collected red
25 filtrate and wash diluted to 50.00 ml in a graduated flask. From this solution a 1000x dilution was made and from the absorption in the UV/Vis spectrum at 244, 278, 313, 389 and 483 nm the concentration in the stock was calculated and the yield (based on extinction of PF₆ analogue in water)

- 16 -

	244 nm	1.648
	278 nm	1.572
	313 nm	1.022
	389 nm	0.103
5	485 nm	0.042

Calculated yield 98%; solution contains 5.2% (on weight basis) of the catalyst.

Stability Experiments

10 Stability of aqueous solutions of chloride, sulphate and acetate salts are provided. Solutions of the bleach catalyst with chloride, sulphate and acetate anion were brought to pH 2, 3, 4 and 5 by hydrochloric acid, sulphuric acid and acetic acid respectively. For the acetate this could only
15 give pH 5. For the lower pH values sulphuric acid was used in the case of acetate. The solutions were kept at 37 °C and after 2 weeks the stability was monitored from the absorptions in the UV/Vis spectra of 1000x diluted solutions.

20

2 week results at 37 °C

Chloride	pH 2	pH 3	pH 4	pH 5
%(UV/Vis)	100	100	97	94

(Precipitate is formed at all pH's)

25

Acetate	pH 2	pH 3	pH 4	pH 5
%(UV/Vis)	87	91	93	95

(No precipitate is formed)

30

Sulphate	pH 2	pH 3	pH 4	pH 5
%(UV/Vis)	78	96	94	98

- 17 -

(Precipitate only at pH = 5)

For the two weeks results it is clear within experimental error (ca 5%) at pH 3 and higher no instability issue
5 occurs.

Softwood chemical mill pulp obtained after the D0 bleaching stage (abbreviated as softwood D0 pulp) was used. The
10 bleaching experiments were conducted on small scale in 100 ml vessels using the pulps at 5% consistency (i.e., 5% oven dry wood pulp; 95% aqueous bleaching liquor). The mixture contained 2.5 microM of the catalyst (as chloride, sulfate, acetate and PF₆ salts - see Table), 1 kg/t of MgSO₄, 8 kg/t
15 of NaOH and 10 kg/t of H₂O₂ (kg/t: kg chemicals per ton oven dry pulp). The mixture was manually stirred to ensure good distribution of the bleaching chemicals. Then the vessel was placed in a water bath and stirred regularly at 50 °C for 1 h. All experiments were carried out at least 6 times. As a
20 reference the experiment was conducted without catalyst. The dosages and exact reaction conditions are given in the sections below. After the allocated bleaching times the pulp batches were removed from the vessels, filtered using a Buchner funnel, and washed with 100 ml of water. From the
25 resultant samples of bleached pulp 4x4cm discs were made having a flat surface on one side. The softwood D0 pulp samples were dried using a L&W Rapid Dryer (Lorentzen and Wetter) at 90 °C for 20 minutes. Whiteness of the bleached pulps was determined using L, a*, b* values as defined by
30 CIE (Commission Internationale de l'Eclairage) of the dried pad was measured using a Minolta spectrophotometer.

- 18 -

Results (all whiteness values show a standard deviation of 0.3 points).

Complex	Whiteness
$[\text{Mn}_2\text{O}_3(\text{Me}_3\text{-TACN})_2] \cdot (\text{PF}_6)_2$ comparative example	84.4
$[\text{Mn}_2\text{O}_3(\text{Me}_3\text{-TACN})_2] \cdot \text{Cl}_2$	84.3
$[\text{Mn}_2\text{O}_3(\text{Me}_3\text{-TACN})_2] \cdot (\text{OAc})_2$	84.0
$[\text{Mn}_2\text{O}_3(\text{Me}_3\text{-TACN})_2] \cdot \text{SO}_4$	84.1
Blank (only H_2O_2)	77.0

- 5 The data presented in the table show clearly that the bleaching effect is the same for all different catalyst-salt complexes.

We Claim:

1. A method of catalytically treating a substrate, the substrate being a cellulose-containing substrate or starch containing substrate, with a preformed transition metal catalyst salt, the preformed transition metal catalyst salt having a non-coordinating counter ion, the method comprising the following steps:

5

10

(i) optionally dissolving a concentrate or solid form of a preformed transition metal catalyst salt in an aqueous medium to yield an aqueous solution of the preformed transition metal catalyst salt;

15

(ii) adding the aqueous solution of the preformed transition metal catalyst salt to a reaction vessel; and,

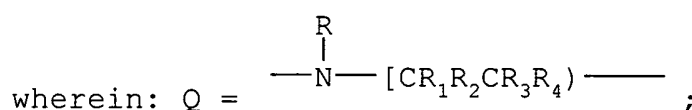
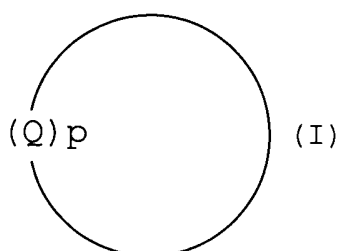
20

(iii) adding hydrogen peroxide to the reaction vessel,

25

wherein the preformed transition metal catalyst salt is a mononuclear or dinuclear complex of a Mn(III) or Mn(IV) transition metal catalyst for catalytically treating the substrate with hydrogen peroxide, the non-coordinating counter ion of said transition metal selected to provide a preformed transition metal catalyst salt that has a water solubility of at least 30 g/l at 20 °C and wherein the ligand of the transition metal catalyst is of formula (I):

- 20 -



p is 3;

R is independently selected from: hydrogen, C1-C6-alkyl, CH₂CH₂OH, and CH₂COOH, or one of R is linked to the N of another Q via an ethylene bridge;

R₁, R₂, R₃, and R₄ are independently selected from: H, C1-C4-alkyl, and C1-C4-alkylhydroxy, and the substrate

is brought into contact with a mixture of the aqueous

solution of the preformed transition metal catalyst salt and the hydrogen peroxide.

2. A method according to claim 1, wherein R is independently selected from: CH₃, C₂H₅, CH₂CH₂OH and CH₂COOH.
3. A method according to claim 1 or 2, wherein R₁, R₂, R₃, and R₄ are independently selected from: H and Me.
4. A method according to claim 1, wherein the catalyst is derived from a ligand selected from the group consisting 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me₃-TACN) and 1,2,-bis-(4,7,-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane (Me₄-DTNE).

- 21 -

5. A method according to claim any preceding claim, wherein the preformed transition metal catalyst salt is a dinuclear Mn(III) or Mn(IV) complex with at least one O²⁻ bridge.
- 5
6. A method according to any preceding claim, wherein the preformed transition metal catalyst salt has a water solubility of at least 50 g/l at 20 °C.
- 10 7. A method according to claim 6, wherein the salt is that selected from the group consisting of chloride, acetate, sulphate, and nitrate.
8. A method according to claim 7, wherein the salt is acetate.
- 15
9. A method according to any preceding claim, wherein the aqueous solution of the preformed transition metal catalyst salt is in a buffer system that maintains the solution in the pH range 2 to 7.
- 20
10. A method according to any preceding claim, wherein the preformed transition metal catalyst salt is present at a concentration in the range from 0.1 to 10 wt % in the aqueous solution in step (ii).
- 25
11. A method according to claim 9, wherein the concentration is in the range from 0.5 to 8 wt %.

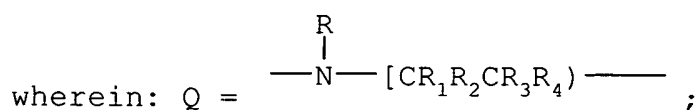
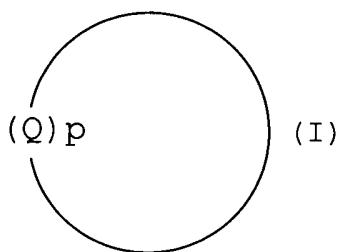
- 22 -

12. A method according to any preceding claim, wherein during treatment of the substrate the aqueous solution comprises at least 80 wt % water.
- 5 13. A method according to claim 12, the aqueous solution comprises at least 90 wt % water.
14. A method according to claim 13, wherein the aqueous solution comprises at least 95 wt % water.
- 10 15. A method according to any preceding claim, wherein the pH of the aqueous solution of the preformed transition metal catalyst salt aqueous solution in step (ii) in the range from 2 to 7.
- 15 16. A method according to claim 15, wherein the pH is in the range from 4 to 6.
17. A method according to claim 16, wherein the pH is in the range from 4.5 to 5.5.
- 20 18. A method according to any preceding claim, wherein the substrate is selected from the group consisting of woven or knitted cotton cloths, industrial laundering and wood pulp.
- 25 19. A method according to any preceding claim, wherein the substrate is wood pulp.
- 30 20. A method according to any preceding claim, wherein the preformed transition metal catalyst salt has been formed

- 23 -

by a contact and oxidation step that is carried out at least 24 hours before use.

21. Use of a preformed transition metal catalyst salt in an aqueous medium to bleach a substrate, the substrate being a cellulose-containing substrate or starch containing substrate, with hydrogen peroxide, wherein the preformed transition metal catalyst salt is a dinuclear Mn(III) or Mn(IV) complex with at least two O²⁻ bridges for catalytically treating the substrate with hydrogen peroxide, said transition metal catalyst a salt, wherein the preformed transition metal catalyst salt has a water solubility of at least 30 g/l at 20 °C and wherein the ligand of the transition metal catalyst is of formula (I):



p is 3;

R is independently selected from: hydrogen, C1-C6-alkyl, CH₂CH₂OH, and CH₂COOH, or one of R is linked to the N of another Q via an ethylene bridge;

R₁, R₂, R₃, and R₄ are independently selected from: H, C1-C4-alkyl, and C1-C4-alkylhydroxy.

- 24 -

22. Use according to claim 21, wherein R is independently selected from: CH₃, C₂H₅, CH₂CH₂OH and CH₂COOH.
23. Use according to claim 21 or 22, wherein R₁, R₂, R₃, and
5 R₄ are independently selected from: H and Me.
24. Use according to claim 23, wherein the catalyst is derived from a ligand selected from the group consisting
1,4,7-Trimethyl-1,4,7-triazacyclononane (Me₃-TACN) and
10 1,2,-bis-(4,7,-dimethyl-1,4,7,-triazacyclonon-1-yl)-
ethane (Me₄-DTNE).

AMENDED CLAIMS
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22. Use according to claim 21, wherein R is independently selected from: CH₃, C₂H₅, CH₂CH₂OH and CH₂COOH.
- 5 23. Use according to claim 21 or 22, wherein R₁, R₂, R₃, and R₄ are independently selected from: H and Me.
24. Use according to claim 23, wherein the catalyst is derived from a ligand selected from the group consisting
10 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me₃-TACN) and 1,2,-bis-(4,7,-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane (Me₄-DTNE).
25. A cellulose-containing substrate or a starch containing
15 substrate, wherein the cellulose-containing substrate or the starch containing substrate has been treated by the method as defined in any one of claims 1 to 5.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/004260

A. CLASSIFICATION OF SUBJECT MATTER
INV. D06L3/02 D21C9/10

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)
D06L D21C 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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2001/025695 A1 (PATT RUDOLF ET AL) 4 October 2001 (2001-10-04) cited in the application examples; tables -----	1-24
A	US 2002/066542 A1 (JAKOB HARALD ET AL) 6 June 2002 (2002-06-06) cited in the application paragraph [0011] - paragraph [0025] paragraph [0052] - paragraph [0058] * comparative examples E-G *	1-24
A	EP 0 458 397 A (UNILEVER N.V; UNILEVER PLC; UNILEVER NV) 27 November 1991 (1991-11-27) cited in the application page 2, line 39 - line 42 examples -----	1-24
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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- *O* document referring to an oral disclosure, use, exhibition or other means
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Date of the actual completion of the international search

Date of mailing of the international search report

21 July 2006

28/07/2006

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/004260

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95/27773 A (THE PROCTER & GAMBLE COMPANY) 19 October 1995 (1995-10-19) cited in the application examples claims 1,3 -----	1-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2006/004260

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