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(54) **Catalytic bleaching of substrates**

(57) The present invention concerns the bleaching of cellulosic substrates with hydrogen peroxide and a transition metal catalyst.

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Description**FIELD OF INVENTION**

5 **[0001]** The present invention concerns the bleaching of cellulosic substrates with hydrogen peroxide and a transition metal catalyst.

BACKGROUND OF INVENTION

10 **[0002]** The bleaching of raw cotton and wood pulp are massive industries.

[0003] Raw cotton originating from cotton seeds contains mainly colourless cellulose, but has a yellow-brownish colour due to the natural pigment in the plant. Many impurities adhere, especially to the surface. They consist mainly of protein, pectin, ash and wax.

15 **[0004]** The cotton and textile industries recognise a need for bleaching cotton prior to its use in textiles and other areas. The cotton fibres are bleached to remove natural and adventitious impurities with the concurrent production of substantially whiter material.

[0005] 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 most common types of such hypochlorite solutions are sodium hypochlorite and calcium hypochlorite. Additionally, chlorine dioxide as bleaching agent has been developed and shows less cotton damage than hypochlorite does. Also mixtures of chlorine dioxide and hypochlorite can be applied. The second type of
20 bleach is a peroxide solution, e.g., hydrogen peroxide solutions. This bleaching process is typically applied at high temperatures, i.e., 90 to 120°C. However, room temperature treatment has been used when the treatment time is extended (cold pad batch process).

[0006] Controlling the peroxide decomposition due to trace metals is key to successfully apply hydrogen peroxide.
25 Often Mg-silicates or sequestering agents such as EDTA or analogous phosphonates can be applied to reduce decomposition.

[0007] EP 0458397 discloses the use manganese 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me₃-TACN) complexes as bleaching and oxidation catalysts and use for paper/pulp bleaching and textile bleaching processes.

30 **[0008]** United States Application 2002/010120 discloses the bleaching of substrates in an aqueous medium, the aqueous medium comprising a transition metal catalyst and hydrogen peroxide.

[0009] Transition metal catalysts having bleaching activity with hydrogen peroxide towards substrates are numerous; the following documents describing wide classes of ligands are indicative of such: WO98/39098, WO00/12667, WO02/077145, WO02/48301, WO03/104379, and EP0909809.

35 **SUMMARY OF THE INVENTION**

[0010] We have found that by applying in a sequentially separate operation a transition metal catalyst (catalyst) in the form of a spray or foam to a cellulosic substrate serves to reduce wastage of expensive reagents, i.e., hydrogen peroxide and transition metal catalyst, in industrial bleaching process.

40 **[0011]** In one aspect the present invention provides a continuous or semi continuous bleaching method for industrial bleaching of a cellulosic substrate, the method comprising the following steps: (a) subjecting the cellulosic substrate to moisture, and hydrogen peroxide to provide a wet peroxide enriched cellulosic substrate; (b) applying to the cellulosic substrate from step (a), in the form of a spray or foam, a 0.1 to 200 micromolar aqueous solution of a preformed transition metal catalyst, wherein the transition metal is selected from Fe(II) and Fe(III), Mn(II), Mn(III), and Mn(IV) and the ligand
45 of the preformed transition metal catalyst is selected from a tridentate, tetradentate, pentadentate or hexadentate nitrogen donor.

DETAILED DESCRIPTION OF THE INVENTION50 **METHOD**

[0012] The method is applied either as a continuous or semi continuous process rather than a batch process. A continuous process is, in essence, a process in which a material to be treated is continuously fed into a processing system, travels through it, undergoes changes and continuously exits the system with the target modified properties. Simultaneously,
55 chemicals and energy are fed in a flow without interruption into a system so that the processing operating conditions are maintained in equilibrium during the operation of the process.

[0013] A semi continuous system is similar to the continuous, but with the difference that the material is stored for a dwell time at a stage between the start and end of the process and then re-fed at that point and allowed to finish the process.

[0014] Most preferably, the method is applied to a cellulosic substrate that is in the form of a moving web. This facilitates movement of the cellulosic substrate by runners and guides from one area of treatment to another; the use of rollers to convey the web is conventional. At the end of the method the web may be easily rolled up in predetermined amounts before shipping or further processing.

CELLULOSIC SUBSTRATE

[0015] The cellulosic substrate may be derived from, for example, wood pulp, cotton hemp, straw, bamboo, flax (linin), jute, kenaf, Abaca, sisal, soy protein fibre. The cellulosic substrate may be a processed product such as viscose.

[0016] The cellulosic substrate is preferably wood pulp or cotton.

[0017] The cellulosic substrate of cotton is most preferably in the form of a web. A web is a long thin and flexible material. A web is generally processed by moving over rollers. Between processing stages, webs are stored and transported as rolls also known as coils, packages and doffs. The end result or use of web manufacturing is usually sheets.

APPLICATION OF MOISTURE AND HYDROGEN PEROXIDE

[0018] The cellulosic substrate is treated with hydrogen peroxide prior to spraying with the aqueous solution of transition metal catalyst. The hydrogen peroxide may be applied by passing the cellulosic substrate through a bath or spraying.

[0019] Hydrogen peroxide is provided as an aqueous solution per se, or as peroxy salts, such as perborate monohydrate, perborate tetrahydrate, percarbonate, perphosphate, etc. However, for cost reasons liquid hydrogen peroxide is preferred. A preferred concentration of hydrogen peroxide applied is: 0.1 to 20 % (w/w), more preferably 1 to 10 %, most preferably 1 to 5%.

[0020] The hydrogen peroxide is preferably provided in an alkali medium, the alkalinity of which is preferably provided by sodium hydroxide.

[0021] Most preferably the cellulosic substrate is run as a web through a bath containing aqueous hydrogen peroxide. However, the cellulosic substrate may be treated with hydrogen peroxide a bath as a roll before spraying with catalyst in the form of a web.

[0022] Satisfactory results are obtained at room temperature, i.e., 20 °C. However, the temperature of the cellulosic substrate after treating with hydrogen peroxide is preferably at least 70 °C, more preferably at least 80 °C, and most preferably at least 90 °C. This temperature may be provided by the temperate of the bath or spray. The temperature of the cellulosic substrate may also be provided for with steam and the use of steam chambers.

[0023] Alternatively, the bleaching of cotton may be obtained at room temperature leaving rolls of cotton, treated with hydrogen peroxide and catalyst, for longer periods of time under ambient conditions. It is understood that at lower temperatures, the duration of the reactions will be longer than in the steaming conditions as described above. Typically the periods of time will be in the range 1h to 48 h, with 2h to 24 h being more preferred and 3 to 12 h being most preferred.

SPRAY/FOAM

[0024] The application of an aqueous medium in the form of a spray should be evident to one skilled in the art. The may be formed from a single spray head or a plurality of spray heads. The spray heads include spinners, rotary, and jets. The spray provides an aqueous solution in a mass or jet of droplets.

[0025] The application of an aqueous medium in preferably applied to the cellulosic substrate in the form of a spray.

[0026] The spray may be provided by a pneumatic atomizing nozzle, a hollow cone nozzle of the single pore type, a hollow cone nozzle of the multi pore type, whirl spray nozzle, an oval spray nozzle, square spray nozzle, rectangular spray nozzle, full cone nozzle, flat pattern nozzle etc. These nozzles may be provides as an array of individual nozzles. There are many established firms that supply spray nozzles and arrays thereof, for example, Kyoritsu Gokin Co.,Ltd, and Spraying Systems Co., P.O. Box 7900, Wheaton, IL, 60189-7900, USA.

[0027] The selection of the nozzle is such that the aqueous medium is applied without damaging the integrity of cellulosic substrate by hydrodynamic pressure whilst ensuring optimum application.

[0028] Foam application is discussed in Textile Research Journal, Vol. 52, No. 6, 395-403 (1982). The foam is preferably generated by the integrated use of a suitable surfactant which imparts bubble stability. This may be pumped at a specific rate to slot dispenser positioned against the cellulosic substrate, most preferably on both sides of the material.

[0029] Foam application provides a rapidly-breaking low-density foam or froth as the delivery medium for finishing chemicals. Foam application permits precise metering and flow control for delivery of foam to the substrate and pressure-driven impregnation of the foam into the substrate. Foam application permits uniform high-speed application and collapse of the foam in a single step. The pick-up can be as low as 10%, which also results in lower energy consumption (less water needs to be evaporated). The semi-stable foam is necessary to get spontaneous foam collapse and spreading though the substrate, and is in contrast to stable foams specified in various foam coating processes normally requiring

a separate step to break and distribute the foam through the textile material. A particularly suitable system has been developed by Gaston County Dyeing Machine Company.

PREFORMED TRANSITION METAL CATALYST

[0030] The preformed transition metal catalyst is formed from a tridentate, tetradentate, pentadentate or hexadentate nitrogen donor ligand.

[0031] The tridentate, tetradentate, pentadentate or hexadentate nitrogen donor ligand may be built up within any organic structure which will support coordinating nitrogen atoms. For example one can take a basic tridentate ligand such as 1,4,7-triazacyclononane and have further nitrogen coordination groups, e.g., -CH₂-CH₂-NH₂, -CH₂-Py, covalently bound to one or more of the cyclic nitrogens or aliphatic groups.

[0032] Preferably the iron ion is selected from Fe(II) and Fe(III) and the manganese ion is selected from Mn(II), Mn(III), and Mn(IV).

[0033] Preferably the ligand is present in one or more of the forms [MnLCl₂]; [FeLCl₂]; [FeLCl]Cl; [FeL(H₂O)](PF₆)₂; [FeL]Cl₂, [FeLCl]PF₆ and [FeL(H₂O)] (BF₄)₂. However water soluble counter ions conferring increasing solubility, say over PF₆, are also preferred.

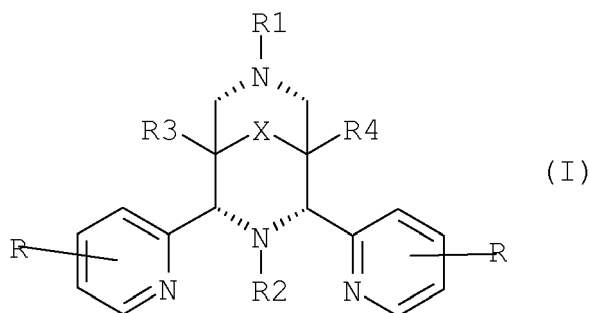
[0034] The following are preferred classes of catalyst that are iron or manganese complexes of tetradentate, pentadentate or hexadentate nitrogen donor ligands.

[0035] If unspecified the length of any alkyl chain is preferably C1 to C8-alkyl chain and preferably linear. If unspecified the aryl group is a phenyl group.

BISPIDON

[0036] The bispidon class are preferably in the form of an iron transition metal catalyst.

[0037] The bispidon ligand is preferably of the form:



wherein each R is independently selected from: hydrogen, F, C1, Br, hydroxyl, C1-C4-alkylo-, -NH-CO-H, -NH-CO-C1-C4-alkyl, -NH₂, -NH-C1-C4-alkyl, and C1-C4-alkyl;

R1 and R2 are independently selected from:

C1-C24-alkyl,

C6-C10-aryl, and,

a group containing a heteroatom capable of coordinating to a transition metal;

R3 and R4 are independently selected from hydrogen, C1-C8 alkyl, C1-C8-alkyl-O-C1-C8-alkyl, C1-C8-alkyl-O-C6-C10-aryl, C6-C10-aryl, C1-C8-hydroxyalkyl, and -(CH₂)_nC(O)OR₅

wherein R₅ is independently selected from: hydrogen, C1-C4-alkyl, n is from 0 to 4, and mixtures thereof; and,

X is selected from C=O, -[C(R₆)₂]_Y- wherein Y is from 0 to 3 each R₆ is independently selected from hydrogen, hydroxyl, C1-C4-alkoxy and C1-C4-alkyl.

[0038] Preferably R3 = R4 and selected from -C(O)-O-CH₃, -C(O)-O-CH₂CH₃, -C(O)-O-CH₂C₆H₅ and CH₂OH.

[0039] Preferably the heteroatom capable of coordinating to a transition metal is pyridin-2-ylmethyl optionally substituted by -CO-C4-alkyl.

[0040] Preferably X is C=O or C(OH)₂.

[0041] Preferred groups for R1 and R2 are CH₃, -C₂H₅, -C₃H₇, benzyl, -C₄H₉, -C₆H₁₃, -C₈H₁₇, -C₁₂H₂₅, and

-C18H37 and pyridin-2-yl. A preferred class of bispidon is one in which at least one of R1 or R2 is pyridin-2-ylmethyl or benzyl, preferably pyridin-2-ylmethyl.

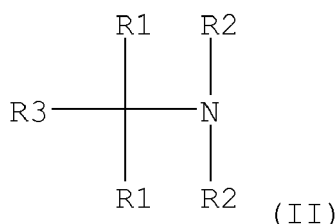
[0042] A preferred bispidon is dimethyl 2,4-di-(2-pyridyl) -3-methyl-7-(pyridin-2-ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate (N2py3o-C1) and the iron complex thereof FeN2py3o-C1 which was prepared as described in WO02/48301. Other preferred bispidons are one in which instead of having a methyl group (C1) at the 3 position have longer alkyl chains, namely isobutyl, (n-hexyl) C6, (n-octyl) C8, (n-dodecyl) C12, (n-tetradecyl) C14, (n-octadecyl) C18, which were prepared in an analogous manner.

[0043] Preferred tetradentate bispidons are also illustrated in WO00/60045 and preferred pentadentate bispidons are illustrated in WO02/48301 and WO03/104379.

N4py type

[0044] The N4py are preferably in the form of an iron transition metal catalyst.

[0045] The N4py type ligands are preferably of the form:



wherein

each R¹, R² independently represents -R⁴-R⁵,

R³ represents hydrogen, optionally substituted alkyl, aryl or arylalkyl, or -R⁴-R⁵,

each R⁴ independently represents a single bond or optionally substituted alkylene, alkenylene, oxyalkylene, aminoalkylene, alkylene ether, carboxylic ester or carboxylic amide, and

each R⁵ independently represents an optionally N-substituted aminoalkyl group or an optionally substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, pyrrolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl.

[0046] Preferably R¹ represents pyridin-2-yl or R² represents pyridin-2-yl-methyl. Preferably R² or R¹ represents 2-aminoethyl, 2-(N-(m)ethyl)amino-ethyl or 2-(N,N-di(m)ethyl)aminoethyl. If substituted, R⁵ preferably represents 3-methyl pyridin-2-yl. R³ preferably represents hydrogen, benzyl or methyl.

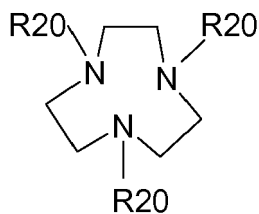
[0047] The preferred ligands are N4Py (i.e. N, N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine) which is disclosed in WO95/34628 and MeN4py (i.e. N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, as disclosed in EP0909809.

TACN-Nx

[0048] The TACN-Nx are preferably in the form of an iron transition metal catalyst.

[0049] The ligands possess the basic 1,4,7-triazacyclononane structure but have one or more pendent nitrogen groups that complex with the transition metal to provide a tetradentate, pentadentate or hexadentate ligand. Preferably, the basic 1,4,7-triazacyclononane structure has two pendent nitrogen groups that complex with the transition metal (TACN-N2).

[0050] The TACN-Nx is preferably of the form:



(III)

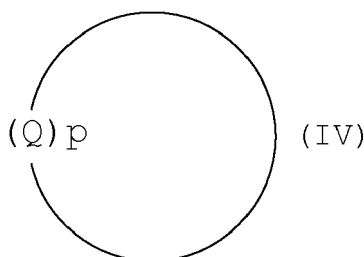
wherein each R₂₀ is selected from: an alkyl, cycloalkyl, heterocycloalkyl, heteroaryl, aryl and arylalkyl groups optionally substituted with a substituent selected from hydroxy, alkoxy, phenoxy, carboxylate, carboxamide, carboxylic ester, sulphate, amine, alkylamine and N⁺(R₂₁)₃, wherein R₂₁ is selected from hydrogen, alkanyl, alkenyl, arylalkanyl, arylalkenyl, oxyalkanyl, oxyalkenyl, aminoalkanyl, aminoalkenyl, alkanyl ether, alkenyl ether, and -CY₂-R₂₂, in which Y is independently selected from H, CH₃, C₂H₅, C₃H₇ and R₂₂ is independently selected from an optionally substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, pyrrolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl; and wherein at least one of R₂₀ is a -CY₂-R₂₂.

[0051] Preferably R₂₂ is selected from optionally substituted pyridin-2-yl, imidazol-4-yl, pyrazol-1-yl, quinolin-2-yl groups. Most preferably R₂₂ is either a pyridin-2-yl or a quinolin-2-yl.

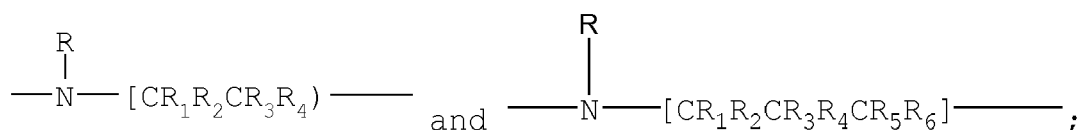
CYCLAM AND CROSS BRIDGED LIGANDS

[0052] The cyclam and cross bridged ligands are preferably in the form of a manganese transition metal catalyst.

[0053] The cyclam ligand is preferably of the form:



wherein: Q is independently selected from:



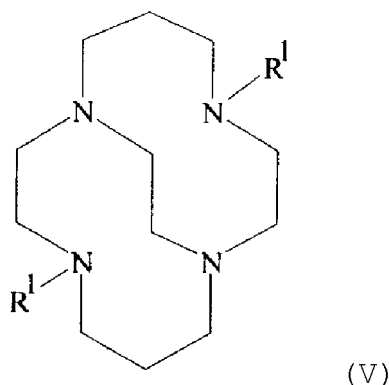
p is 4;

R is independently selected from: hydrogen, C1-C6-alkyl, CH₂CH₂OH, pyridin-2-ylmethyl, and CH₂COOH, or one of R is linked to the N of another Q via an ethylene bridge;

R₁, R₂, R₃, R₄, R₅ and R₆ are independently selected from: H, C1-C4-alkyl, and C1-C4-alkylhydroxy.

[0054] Preferred non-cross-bridged ligands are 1,4,8,11-tetraazacyclotetradecane (cyclam), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me₄cyclam), 1,4,7,10-tetraazacyclododecane (cyclen), 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane (Me₄cyclen), and 1,4,7,10-tetrakis(pyridine-2ylmethyl)-1,4,7,10-tetraazacyclododecane (Py₄cyclen). With Py₄cyclen the iron complex is preferred.

[0055] A preferred cross-bridged ligand is of the form:



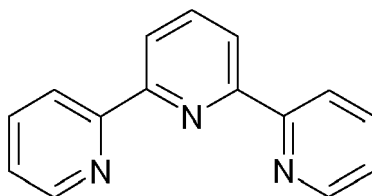
wherein "R¹" is independently selected from H, and linear or branched, substituted or unsubstituted C1 to C20 alkyl, alkylaryl, alkenyl or alkynyl; and all nitrogen atoms in the macropolycyclic rings are coordinated with the transition metal.

[0056] Preferably R¹ = Me, which is the ligand 5,12-dimethyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane of which the complex [Mn(Bcyclam)Cl₂] may be synthesised according to WO98/39098.

[0057] Other suitable crossed bridged ligands are also found in WO98/39098.

TRIDENTATE LIGANDS WITH MANGANESE

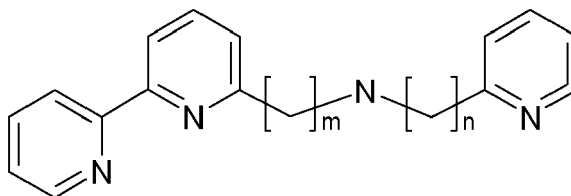
[0058] A suitable class of tridentate ligands is based on terpyridine-type ligands, depicted below.



[0059] Also terpyridine derivatives could be employed, such as bispyridylpyrimidine or bispyridyltriazine. Preferred classes include the ones disclosed in WO2002088289; WO2004007657; WO2004039933; WO2004039934; WO2005068075; and WO2005068074; WO2005105303.

TETRADENTATE LIGANDS WITH MANGANESE AND IRON

[0060] Another suitable class of molecules contains a substituted bipyridine-alkylamine-alkylpyridine unit, depicted below with m, n = 1 or 2 as disclosed in WO2007090461.



TRISPICEN-type

[0061] The trispicens are preferably in the form of an iron transition metal catalyst.

[0062] The trispicen type ligands are preferably of the form:

R17R17N-X-NR17R17

(VI),

wherein:

X is selected from $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{C}(\text{OH})\text{HCH}_2-$; and,

R17 independently represents a group selected from: R17 and alkyl, cycloalkyl, heterocycloalkyl, heteroaryl, aryl and arylalkyl groups optionally substituted with a substituent selected from hydroxy, alkoxy, phenoxy, carboxylate, carboxamide, carboxylic ester, sulphonate, amine, alkylamine and $\text{N}^+(\text{R}19)_3$, wherein R19 is selected from hydrogen, alkanyl, alkenyl, arylalkanyl, arylalkenyl, oxyalkanyl, oxyalkenyl, aminoalkanyl, aminoalkenyl, alkanyl ether, alkenyl ether, and $-\text{CY}_2\text{-R}18$, in which Y is independently selected from H, CH₃, C₂H₅, C₃H₇ and R18 is independently selected from an optionally substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, pyrrolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl; and wherein at least two of R17 are $-\text{CY}_2\text{-R}18$.

[0063] The heteroatom donor group is preferably pyridinyl optionally substituted by $-\text{C}0\text{-C}4\text{-alkyl}$.

[0064] Other preferred heteroatom donor groups are imidazol-2-yl, 1-methyl-imidazol-2-yl, 4-methyl-imidazol-2-yl, imidazol-4-yl, 2-methyl-imidazol-4-yl, 1-methyl-imidazol-4-yl, benzimidazol-2-yl and 1-methyl-benzimidazol-2-yl.

[0065] Preferably three of R17 are $\text{CY}_2\text{-R}18$.

[0066] The ligand Tpen (i.e. N, N, N', N'-tetra(pyridin-2-yl-methyl)ethylenediamine) is disclosed in WO97/48787.

[0067] The following are preferred trispicens: N-methyl-tris(pyridin-2-ylmethyl)ethylene-1,2-diamine; N-octyl-tris(pyridin-2-ylmethyl)ethylene-1,2-diamine; N-octadecyl-tris(pyridin-2-ylmethyl)ethylene-1,2-diamine; N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; N-methyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; N-ethyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; N-benzyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

[0068] N-butyl-N,N',N'-tris(pyridin-2-ylmethyl)ethylene-1,2-diamine; N-octyl-N,N',N'-tris(pyridin-2-ylmethyl)ethylene-1,2-diamine; N-dodecyl-N,N',N'-tris(pyridin-2-ylmethyl)ethylene-1,2-diamine; N-octadecyl-N,N',N'-tris(pyridin-2-ylmethyl)ethylene-1,2-diamine; N-Methyl-N,N',N'-Tris(imidazol-2-ylmethyl)-ethylenediamine; N-ethyl-N,N',N'-Tris(imidazol-2-ylmethyl)-ethylenediamine; N,N'-dimethyl-N,N'-bis(imidazol-2-ylmethyl)-ethylenediamine; N-(1-propan-2-ol)-N,N',N'-Tris(imidazol-2-ylmethyl)-ethylenediamine; N-(1-propan-2-ol)-N,N',N'-Tris(1-methyl-imidazol-2-ylmethyl)-ethylenediamine; N,N-diethyl-N,N',N'-Tris(5-methyl-imidazol-4-ylmethyl)-diethylenetriamine; N-(3-propan-1-ol)-N,N',N'-Tris(1-methyl-imidazol-2-ylmethyl)-ethylenediamine; N-hexyl-N,N',N'-Tris(imidazol-2-ylmethyl)-ethylenediamine; N-methyl-N,N',N'-tris(benzimidazol-2-ylmethyl)-ethylenediamine; and, N-(3-propan-1-ol)methyl-N,N',N'-tris(benzimidazol-2-ylmethyl)-ethylenediamine.

[0069] Other suitable trispicens are found in WO02/077145.

[0070] Of the non-bispidon type catalysts the following are most preferred:

5,12-dimethyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane,

5,12-dibenzyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane,

1,4,8,11-tetraazacyclotetradecane, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, 1,4,7,10-tetraazacyclododecane, 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane, and 1,4,7,10-tetrakis(pyridine-2-ylmethyl)-1,4,7,10-tetraazacyclododecane, N,N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, N,N-bis(pyridin-2-yl-methyl-1,1-bis(pyridin-2-yl)-1-aminoethane, N,N,N',N'-tetra(pyridin-2-yl-methyl)ethylenediamine, N-methyl-tris(pyridin-2-ylmethyl)ethylene-1,2-diamine; N-butyl-N,N',N'-tris(pyridin-2-ylmethyl)ethylene-1,2-diamine; N-octyl-N,N',N'-tris(pyridin-2-ylmethyl)ethylene-1,2-diamine; N-dodecyl-N,N',N'-tris(pyridin-2-ylmethyl)ethylene-1,2-diamine; N-octadecyl-N,N',N'-tris(pyridin-2-ylmethyl)ethylene-1,2-diamine; N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; N-methyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; N-ethyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; N-benzyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; N-methyl-N,N',N'-tris(imidazol-2-ylmethyl)-ethylenediamine; N-ethyl-N,N',N'-tris(imidazol-2-ylmethyl)-ethylenediamine; N,N'-dimethyl-N,N'-bis(imidazol-2-ylmethyl)-ethylenediamine; N-(1-propan-2-ol)-N,N',N'-tris(imidazol-2-ylmethyl)-ethylenediamine; N-(1-propan-2-ol)-N,N',N'-tris(1-methyl-imidazol-2-ylmethyl)-ethylenediamine; N,N-diethyl-N,N',N'-tris(5-methyl-imidazol-4-ylmethyl)-diethylenetriamine; N-(3-propan-1-ol)-N,N',N'-tris(1-methyl-imidazol-2-ylmethyl)-ethylenediamine; N-hexyl-N,N',N'-tris(imidazol-2-ylmethyl)-ethylenediamine; N-methyl-N,N',N'-tris(benzimidazol-2-ylmethyl)-ethylenediamine; and, N-(3-propan-1-ol)methyl-N,N',N'-tris(benzimidazol-2-ylmethyl)-ethylenediamine; 1,4-bis(quinolin-2-ylmethyl)-7-octyl-1,4,7-triazacyclononane; 1,4-bis(quinolin-2-ylmethyl)-7-ethyl-1,4,7-triazacyclononane; 1,4-bis(quinolin-2-ylmethyl)-7-methyl-1,4,7-

triazacyclononane; 1,4-bis(pyridyl-2-methyl)-7-octyl-1,4,7-triazacyclononane; 1,4-bis(pyridyl-2-methyl)-7-ethyl-1,4,7-triazacyclononane; 1,4-bis(pyridyl-2-methyl)-7-methyl-1,4,7-triazacyclononane; 1,4-bis(pyrazol-1-ylmethyl)-7-octyl-1,4,7-triazacyclononane; 1,4-bis(pyrazol-1-ylmethyl)-7-ethyl-1,4,7-triazacyclononane; 1,4-bis(pyrazol-1-ylmethyl)-7-methyl-1,4,7-triazacyclononane; 3,5-dimethylpyrazol-1-ylmethyl)-7-octyl-1,4,7-triazacyclononane; 3,5-dimethylpyrazol-1-ylmethyl)-7-ethyl-1,4,7-triazacyclononane; 3,5-dimethylpyrazol-1-ylmethyl)-7-methyl-1,4,7-triazacyclononane; 1,4-bis(1-methylimidazol-2-ylmethyl)-7-octyl-1,4,7-triazacyclononane; 1,4-bis(1-methylimidazol-2-ylmethyl)-7-ethyl-1,4,7-triazacyclononane; 1,4-bis(1-methylimidazol-2-ylmethyl)-7-methyl-1,4,7-triazacyclononane; and, 1,4,7-tris(quinolin-2-ylmethyl)-1,4,7-triazacyclononane; 1,4,7-tris(pyridin-2-ylmethyl)-1,4,7-triazacyclononane.

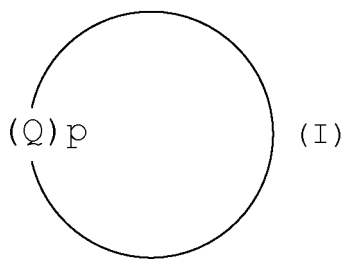
COLLIN'S CATALYST

[0071] A class of oxidatively stable iron(III) complexes with dianionic tetradentate nitrogen donor ligands have been disclosed by Collins and co-workers. References are made to WO1999058634; WO A 9803625 1996; Acc. Chem. Res. 2002, 35, 782; J. Am. Chem. Soc. 1990, 112, 5637; J. Am. Chem. Soc. 1989, 111, 4511; J. Am. Chem. Soc. 1990, 112, 899; Inorg Chem. 1992, 31, 1550; J. Am. Chem. Soc. 1998, 120, 11540; J. Am. Chem. Soc. 1998, 120, 4867; J. Am. Chem. Soc. 2003, 125, 12379; J. Am. Chem. Soc. 2005, 127, 2505.

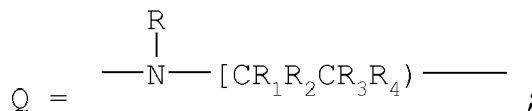
ME3-TACN AND RELATED COMPOUNDS

[0072] A more preferred transition metal catalyst for the method is as described in EP 0458397 and WO06/125517; both of these patents disclose the use of manganese 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me3-TACN) as related compounds as complexes. The PF_6^- ligand of Me3-TACN has been commercialised in laundry detergent powders and dish wash tablets. It is preferred that the preformed transition metal of Me3-TACN and related compounds is in the form of a salt such that it has a water solubility of at least 50 g/l at 20 °C. Preferred salts are those of chloride, acetate, sulphate, and nitrate. Most preferred are the acetate and sulphate salts.

[0073] The catalyst is most preferably a mononuclear or dinuclear complex of a Mn II-V transition metal catalyst, the ligand of the transition metal catalyst of formula (I):



wherein:



p is 3;

R is independently selected from: hydrogen, C1-C6-alkyl, C2OH, C1COOH, and pyridin-2-ylmethyl 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.

R is preferably independently selected from: hydrogen, CH3, C2H5, CH2CH2OH and CH2COOH.

R, R1, R2, R3, and R4 are preferably independently selected from: H and Me.

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) are most preferred.

SURFACTANT

[0074] The surfactant aids the wettability of the cellulosic substrate and aids action of the bleaching chemicals on the substrate.

[0075] The surfactant may be applied in step (a) and/or in step (b).

[0076] The cellulosic substrate is preferably treated with a surfactant prior to or during step (b). Most preferred is the application of most (between 90 and 99%) of the surfactant in step (a) and the remainder is added during step (b) (between 1 and 10%).

[0077] The cellulosic substrate is preferably treated with a surfactant prior to or during step (b) and in this regard, it is preferred that surfactant is present in step (a).

[0078] The surfactant is preferably non-ionic or anionic or a mixture thereof. More preferably mostly nonionic based surfactant mixtures are applied. A non-limiting example includes Sandoclean PCJ™ (ex Clariant).

[0079] The concentration of surfactant is preferably between 1 g/l and 15 g/l and more preferably between 2 and 10 g/l, as applied in the bleaching solution or in conjunction with the spraying solution containing the catalyst or in a combination thereof.

SEQUESTRANT

[0080] Many sequestrants are suitable for use with the present invention. Suitable sequestrants include ethylenediamine tetra-acetate (EDTA), the polyphosphonates such as Dequest™ and non-phosphate stabilisers such as EDDS (ethylene diamine di-succinic acid).

[0081] The sequesterant used in the bleaching step is preferably an aminocarboxylate sequesterant or mixtures thereof. The following are preferred examples of aminocarboxylate sequesterants: ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylenediaminetetraacetic acid (HEDTA), nitrilotriacetic acid (NTA), N-hydroxyethylaminodiacetic acid, diethylenetriaminepentaacetic acid (DTPA), methylglycinediacetic acid (MGDA), and alanine-N,N-diacetic acid. A most preferred aminocarboxylate sequesterant is diethylenetriaminepentaacetic acid (DTPA).

[0082] Phosphonate sequesterants may also be used; a preferred phosphonate sequesterant is Dequest 2066.

[0083] The most preferred concentration of the sequesterant used in the method is 0.05 to 5 g/l in the bleaching solution, most preferably 0.1 to 2 g/l.

EXAMPLES

Example 1

Effect of spraying the manganese bleach catalyst dissolved in water on bleaching of raw cotton in a steamer

[0084] First raw cotton cloths were pretreated using a solution containing 1 g/L Na₅DTPA and 0.5 g/L Sandoclean PCJ (Clariant) at pH 11. Raw cotton is inserted in a flask with the solution described above (liquid:cloth ratio is equal to 10) and is then left at 65°C for 10 minutes. The textile was then washed twice at 80°C, once at 40°C and once at room temperature before being spin dried and in the end dried under ambient conditions.

[0085] Pre-treated textiles (6 g each) were immersed for 30 seconds in an aqueous solution containing 7.5 g/l Sandoclean PCJ (ex Clariant), 3.125 g/l Na₂CO₃, 0.25 g/l Na₅DTPA (diethylenetriamine-N,N,N',N'',N''-penta-acetate), 85 ml hydrogen peroxide (35%) that was adjusted to pH 9.0 by using HCl or NaOH solution (1M). After that, the wet cloths were taken out of the solution and put through a padder, yielding a pick-up of 80% (i.e. 100 gram cotton contains 80 grams of liquid). Subsequently, a solution of 20 μM of [Mn₂O₃(Me₃tacn)₂](CH₃COO)₂ was made in demineralised water. [Mn₂O₃(Me₃tacn)₂](CH₃COO)₂ was obtained as disclosed elsewhere (WO 2006/125517). This solution was brought into a container that was connected to a spraying gun. By using a compressor (JUN-AIR, model OF302) adjusted at 3 bar and a full cone (air atomizing) nozzle, the solution containing the catalyst was sprayed onto the cotton cloth. The amount of solution added was adjusted to generate a pick-up of 100% (i.e. 100 gram cotton contains 80 grams of the bleaching liquid + 20 g of the sprayed catalyst liquid). In the blank (no catalyst), the spraying was done with pure water.

[0086] Then the cloths were put in a steamer (99°C) and left for 3 min in the steamer. After that the cloths were washed twice in a beaker glass using water of 80 °C, then once at 40 °C (in water containing 1g/L acetic acid glacial for allowing the neutralization) and then once using water at room temperature. The cloths were spin dried and then dried under ambient conditions.

[0087] The optical properties of the cloths were then measured using a Minolta spectrophotometer CM-3700d, using

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L, a, b values which are converted to Berger Whiteness values. The values of whiteness are expressed in Berger units. The formula of Berger whiteness is given below:

$$W_{\text{berger}} = Y + a \cdot Z - b \cdot X, \text{ where } a = 3.448 \text{ and } b = 3.904. \text{ The values } X, Y, Z \text{ are the coordinates of the achromatic point.}$$

[0088] The whiteness obtained was 65.9 Berger units in the case when the manganese catalyst was present, whilst the blank furnished a whiteness of 60.2 Berger units.

Example 2

Comparative experiment to show that spraying the manganese bleach catalyst dissolved in water on bleaching of raw cotton in a steamer gives the same result as immersing the raw cotton cloth in a fresh aqueous solution of hydrogen peroxide and the manganese bleach catalyst

[0089] The same experiment was conducted as described above, except that in the bleaching liquid the following composition was used: Sodium Carbonate buffer 3.125 g/L, Na₅DTPA 0.25 g/L, Sandoclean PCJ 7.5 g/L, H₂O₂ (35%) 85 mL/L, pH 10 (pick-up 80% as explained above in example 1). In the spraying solution 20 µM of [Mn₂O₃(Me₃tacn)₂](CH₃COO)₂ was added, giving a total pick up of 100% as explained above. The sprayed cotton cloths were put in a steamer for 3 minutes.

[0090] As a reference, in the bleaching liquid the following composition was used: Sodium Carbonate buffer 2.5 g/L, Na₅DTPA 0.20 g/L, Sandoclean PCJ 6 g/L, H₂O₂ (35%) 68 mL/L, 3.33 µM of [Mn₂O₃(Me₃tacn)₂](CH₃COO)₂ was added. The pH was adjusted to 10.0. Note that now the chemical levels are different as mentioned above. This is due to the fact that the cloths are immersed in the bleaching bath instead of first immersing the bleaching chemicals (without catalyst), then putting the cloths through the padder (to yield 80% pick-up) and then spray the (more concentrated) catalyst solution on the cloths (to yield 100% pick-up). When the chemicals are all added (without spraying), more of the catalyst can be adsorbed, hence a lower concentration in the bath is used. Also the other bleaching chemicals are now added at lower level as one has to obtain 100% instead of 80% pick-up).

[0091] The whiteness obtained was 68.6 Berger units in the case when the manganese catalyst was sprayed, whilst for the comparative test (manganese catalyst present in bleaching solution), whilst the result showed 69.0 Berger units, which is within the error margin of the experiment (+/- 1 Berger unit).

[0092] Therefore, it is shown that spraying the catalyst onto the cotton can lead to a similar bleaching result as bringing all bleaching chemicals in the bleaching bath onto the cotton, without entering the risk of undesired mutual decomposition of hydrogen peroxide and manganese catalyst upon leaving these chemicals mixed in the bleaching liquor for longer periods of time.

Example 3

Effect of spraying the manganese catalyst in combination with a commercial surfactant mixture

[0093] The same experiment was conducted as described above, except that untreated raw cotton was used and in the bleaching liquid the following composition was used: Sodium Carbonate buffer 3.125 g/L, Na₅DTPA 0.25 g/L, Sandoclean PCJ 7.125 g/L, H₂O₂ (35%) 85 mL/L, pH 10 (pick-up 80% as explained above in example 1). In the spraying solution 20 µM of [Mn₂O₃(Me₃tacn)₂](CH₃COO)₂ and 1.5 g/l of Sandoclean PCJ was added, giving a total pick up of 100% as explained above. The sprayed cotton cloths were put in a steamer for 6 minutes. As a reference, no surfactant was added to the spraying solution, but instead all of the surfactant was added in the bleaching liquor (i.e. 7.5 g/l).

[0094] The results were as follows: Spraying Sandoclean with the manganese complex yielded 76.4 Berger whiteness, whilst the reference experiment (spraying the manganese catalyst only) gave 73.0 Berger whiteness.

Example 4

Effect of spraying the manganese catalyst after the cloth was brought into the steamer

[0095] The cotton cloths were first treated with Sandoclean PCJ, Na₅DTPA at pH 11 as described in example 1. The cloths were then brought into a bleaching bath containing Sandoclean PCJ 5 g/l, H₂O₂ (35%) 85 g/l at pH 11 (no buffer applied), Na₅DTPA 0.25 g/l. Subsequently, the cloths were brought into a padder and excess of liquor was squeezed out to get a pick up of 80 %. Then the cloths were brought into a steamer for 6 min at 99 °C.

[0096] Subsequently, the cloths were sprayed with the solution containing the manganese catalyst, [Mn₂O₃(Me₃tacn)₂](CH₃COO)₂ (5 µM in the spraying solution). Subsequently, the impregnated cloths were left in a hot towel (90 °C) for 2

min. Subsequently the cloths were washed and dried as described for experiment 1. A whiteness of 78 Berger units was thus obtained, whilst a comparative experiment (exactly the same protocol, except no catalyst solution was sprayed on the cotton), furnished 73 Berger whiteness points.

5 Example 5

Effect of stability

10 **[0097]** Add to a beaker glass 9.61 ml H₂O, 2.5 ml Carbonate buffer (2.5 g/l), 6 ml Sandoclean PCJ (6 g/l) - ex Clariant; 1.36 ml/l H₂O₂ (68 ml/l, 35%); 0.5 ml 1 M NaOH (25 ml/l) to get pH 10. The solution was warmed up to 40 °C or 60 °C. Add [Mn₂O₃(Me₃tacn)₂](PF₆)₂·H₂O to get a final concentration of 3.33 micromol/l (this is a typical level as would be used when applying the manganese catalyst in conjunction with hydrogen peroxide for a continuous bleaching process). Reference experiments were done using no manganese catalyst in the solution to exemplify the enhanced hydrogen peroxide decomposition in the presence of the manganese Me₃TACN catalyst.

15 **[0098]** The level of hydrogen peroxide was determined using the so-called FOX method, as exemplified in open literature (Gülgün Yildiz, et al., J. Am. Oil Chem. Soc., 80, 103 (2003)) .

[0099] After 45 minutes at 40 °C the hydrogen peroxide level was determined to be about 100 % (wrt to original level) when there was no catalyst present. In the presence of the manganese Me₃tacn catalyst the level of hydrogen peroxide was reduced to 70%. This is a highly undesired situation as for the continuous bleaching process it is very important to have a stable level of bleaching chemicals to get an even bleaching/cleaning process.

20 **[0100]** The same experiment was done at 60 °C. After already 10 minutes, the level of hydrogen peroxide in the presence of the Mn(Me₃tacn) catalyst was reduced to 72%, whilst in the absence of catalyst, the level of hydrogen peroxide was 92%.

25 **[0101]** A further stabilization of the hydrogen peroxide solution (with and without catalyst) can be obtained using 1 g/l DTPA in the solution. After 30 minutes at 60 °C, the level of hydrogen peroxide was 95% in the absence and 76% in the presence of the Mn(Me₃tacn) catalyst.

[0102] All the above examples show that the presence of the Mn-Me₃tacn catalyst will impede the hydrogen peroxide stability in the bleaching bath.

30 Example 6

Bleaching effect of [Mn(III)Mn(IV)(Me₄-DTNE)(μ-O)₂(μ-CH₃COO)](PF₆)₂

35 **[0103]** The same experiments were conducted similarly to what has been shown in example 1, except that untreated raw cotton was used. This compound was prepared as disclosed elsewhere (K. Schaefer et al., J. Am. Chem. Soc., 120, 13104 (1998). [Mn^{III}Mn^{IV}(Me₄-DTNE) (μ-O)₂ (μ-CH₃COO)](PF₆)₂ was sprayed at a level of 10 μmol/l in demineralised water that was sprayed onto the cotton. The level of Sandoclean PCJ was 7.5 g/l, the level of Na₅DTPA was 1.25 g/l and the level of 35% hydrogen peroxide was 85 ml/l in the impregnating solution. The pH of the solution was 11.5 (adjusted using 4 M NaOH). As a reference water without catalyst was sprayed. All experiments were done in four-fold.

40 **[0104]** The results are: 71.0 +/- 1.3 for the blank and 72.7 +/- 0.6 for the solution with the catalyst, showing that the benefit is significant.

Example 7

Bleaching effect of [Mn(Bcyclam)Cl₂]

45 **[0105]** This compound was synthesised according to prior art (WO98/39098).

[0106] The same experiments were conducted similarly to what has been shown in example 6, except that now 50 μmol/l [Mn(Bcyclam)Cl₂] was used in demineralised water that was sprayed onto the cotton (Bcyclam stands for 5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane).

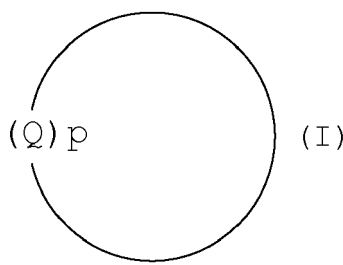
50 **[0107]** The pH of the solution was 9 using 3.125 g/l sodium carbonate buffer (adjusted to the right pH using 0.1 M NaOH or 0.1 M HCl).

[0108] The results are: 60.0 +/- 0.7 for the blank (no catalyst sprayed) and 62.3 +/- 0.5 for the solution with the catalyst, showing that the benefit is significant.

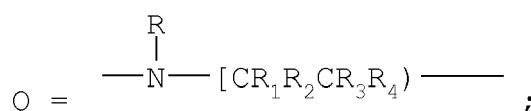
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Claims

1. A continuous or semi continuous bleaching method for industrial bleaching of a cellulosic substrate, the method comprising the following steps: (a) subjecting the cellulosic substrate to moisture, and hydrogen peroxide to provide a wet peroxide enriched cellulosic substrate; (b) applying to the cellulosic substrate from step (a), in the form of a spray or foam, a 0.1 to 200 micromolar aqueous solution of a preformed transition metal catalyst, wherein the transition metal is selected from Fe(II) and Fe(III), Mn(II), Mn(III), and Mn(IV) and the ligand of the preformed transition metal catalyst is selected from a tridentate, tetradentate, pentadentate or hexadentate nitrogen donor.
2. A method according to claim 1, wherein the preformed transition metal catalyst salt is a mononuclear or dinuclear complex of a Mn II-V transition metal catalyst, the ligand of the transition metal catalyst of formula (I):



wherein:



p is 3;

R is independently selected from: hydrogen, C1-C6-alkyl, C2OH, C1COOH, and pyridin-2-ylmethyl 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.

3. A method according to claim 2, wherein R is independently selected from: hydrogen, CH3, C2H5, CH2CH2OH and CH2COOH.
4. A method according to claim 2 or 3, wherein R, R1, R2, R3, and R4 are independently selected from: H and Me.
5. 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), 1,2-bis-(4,7,-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane (Me4-DTNE), and 5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane.
6. A method according to any preceding claim, wherein the cellulosic substrate is treated as a moving web.
7. A method according to claim 6, wherein the aqueous solution of a preformed transition metal catalyst is applied as a spray.
8. A method according to any preceding claim, wherein in step (a) the hydrogen peroxide is applied as an aqueous solution having a pH in the range between 8 and 12 and in step (b) the aqueous solution has a pH between 8 and 12.
9. A method according to any preceding claim, wherein step (b) is applied at least 1 minute after step (a) and a maximum of 30 minutes after step (a).
10. A method according to any preceding claim, wherein the wet peroxide enriched cellulosic substrate is at a temperature of at least 70 °C when the preformed transition metal catalyst is applied as a spray.

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11. A method according to any preceding claim, wherein the wet peroxide enriched cellulosic substrate is treated with surfactant.
12. A method according to claim 11, wherein the wet peroxide enriched cellulosic substrate is treated with a surfactant prior or during (b).
13. A method according to any preceding claim, wherein from between 0.1 to 20 minutes after step (b) the cellulosic substrate is subjected to an aqueous washing step for removing salts from the cellulosic substrate.

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EUROPEAN SEARCH REPORT

Application Number
EP 08 15 2872

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y,D	EP 0 458 398 A (UNILEVER NV [NL]; UNILEVER PLC [GB]) 27 November 1991 (1991-11-27) * claims 1-28 *	1	INV. D21C9/10
Y	EP 0 237 111 A (UNILEVER NV [NL]; UNILEVER PLC [GB]) 16 September 1987 (1987-09-16) * claims 1-24 *	1	
Y	WO 92/13129 A (AMERICAN LAUNDRY MACH [US]) 6 August 1992 (1992-08-06) * claims 1-38 *	1	
A	US 5 965 506 A (BACHER JEAN-PIERRE [FR] ET AL) 12 October 1999 (1999-10-12) * the whole document *	1-13	
A	EP 0 909 809 A (UNILEVER PLC [GB]; UNILEVER NV [NL]) 21 April 1999 (1999-04-21) * the whole document *	1-13	
A	EP 1 225 215 A (CLARIANT GMBH [DE]) 24 July 2002 (2002-07-24) * the whole document *	1-13	TECHNICAL FIELDS SEARCHED (IPC) D21C
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 21 January 2009	Examiner Karlsson, Lennart
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 08 15 2872

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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21-01-2009

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 0458398	A	27-11-1991	AU	622362 B2	02-04-1992
			AU	7712691 A	21-11-1991
			AU	622363 B2	02-04-1992
			AU	7712791 A	21-11-1991
			BR	9102085 A	24-12-1991
			BR	9102086 A	24-12-1991
			CA	2042736 A1	22-11-1991
			CA	2042738 A1	22-11-1991
			DE	69125309 D1	30-04-1997
			DE	69125309 T2	03-07-1997
			DE	69125310 D1	30-04-1997
			DE	69125310 T2	03-07-1997
			EP	0458397 A2	27-11-1991
			ES	2100924 T3	01-07-1997
			ES	2100925 T3	01-07-1997
			IN	173875 A1	30-07-1994
			IN	172881 A1	25-12-1993
			JP	2613707 B2	28-05-1997
			JP	6269676 A	27-09-1994
			JP	2042652 C	09-04-1996
			JP	4270798 A	28-09-1992
			JP	7065074 B	12-07-1995
			NO	911942 A	22-11-1991
			NO	911943 A	22-11-1991
			US	5246621 A	21-09-1993
			US	5244594 A	14-09-1993

EP 0237111	A	16-09-1987	AU	595586 B2	05-04-1990
			AU	6963787 A	10-09-1987
			BR	8701075 A	29-12-1987
			CA	1281024 C	05-03-1991
			DE	3783626 D1	04-03-1993
			DE	3783626 T2	19-05-1993
			ES	2053519 T3	01-08-1994
			JP	6033431 B	02-05-1994
			JP	62225598 A	03-10-1987
			JP	1934613 C	26-05-1995
			JP	6070240 B	07-09-1994
			JP	6088099 A	29-03-1994
			NO	870951 A	08-09-1987
			PH	23697 A	27-09-1989
			TR	24548 A	21-11-1991
			US	4728455 A	01-03-1988
			ZA	8701642 A	30-11-1988

W0 9213129	A	06-08-1992	AU	1189992 A	27-08-1992

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 08 15 2872

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

21-01-2009

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9213129	A	CA 2101050 A1	24-07-1992
		DE 69211982 D1	08-08-1996
		EP 0568595 A1	10-11-1993
		JP 1967818 C	18-09-1995
		JP 4352868 A	07-12-1992
		JP 6102865 B	14-12-1994
		US 5600975 A	11-02-1997
		US 5376144 A	27-12-1994

US 5965506	A	12-10-1999	NONE

EP 0909809	A	21-04-1999	NONE

EP 1225215	A	24-07-2002	DE 10102248 A1
		DE 50204137 D1	25-07-2002
		ES 2249498 T3	13-10-2005
		JP 2002302698 A	01-04-2006
		US 2002165110 A1	18-10-2002
			07-11-2002

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 0458397 A [0007] [0072]
- US 2002010120 A [0008]
- WO 9839098 A [0009] [0056] [0057] [0105]
- WO 0012667 A [0009]
- WO 02077145 A [0009] [0069]
- WO 0248301 A [0009] [0042] [0043]
- WO 03104379 A [0009] [0043]
- EP 0909809 A [0009] [0047]
- WO 0060045 A [0043]
- WO 9534628 A [0047]
- WO 2002088289 A [0059]
- WO 2004007657 A [0059]
- WO 2004039933 A [0059]
- WO 2004039934 A [0059]
- WO 2005068075 A [0059]
- WO 2005068074 A [0059]
- WO 2005105303 A [0059]
- WO 2007090461 A [0060]
- WO 9748787 A [0066]
- WO 1999058634 A [0071]
- WO 9803625 A [0071]
- WO 1996 A [0071]
- WO 06125517 A [0072]
- WO 2006125517 A [0085]

Non-patent literature cited in the description

- *Textile Research Journal*, 1982, vol. 52 (6), 395-403 [0028]
- *Acc. Chem. Res.*, 2002, vol. 35, 782 [0071]
- *J. Am. Chem. Soc.*, 1990, vol. 112, 5637 [0071]
- *J. Am. Chem. Soc.*, 1989, vol. 111, 4511 [0071]
- *J. Am. Chem. Soc.*, 1990, vol. 112, 899 [0071]
- *Inorg Chem.*, 1992, vol. 31, 1550 [0071]
- *J. Am. Chem. Soc.*, 1998, vol. 120, 11540 [0071]
- *J. Am. Chem. Soc.*, 1998, vol. 120, 4867 [0071]
- *J. Am. Chem. Soc.*, 2003, vol. 125, 12379 [0071]
- *J. Am. Chem. Soc.*, 2005, vol. 127, 2505 [0071]
- **Gülgün Yıldız et al.** *J. Am. Oil Chem. Soc.*, 2003, vol. 80, 103 [0098]
- **K. Schaefer et al.** *J. Am. Chem. Soc.*, 1998, vol. 120, 13104 [0103]