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PATT et al.

(43) **Pub. Date:****Oct. 4, 2001**(54) **METHOD FOR THE DELIGNIFICATION OF FIBROUS MATERIAL AND USE OF CATALYST**(76) Inventors: **RUDOLF PATT, REINBEK (DE); HANS-JURGEN MIELISCH, HAMBURG (DE); JURGEN ODERMATT, REINBEK (DE); KARL WIEGHARDT, MULHEIM/RUHR (DE); THOMAS WEYERMULLER, MULHEIM/RUHR (DE)**

Correspondence Address:

**THE FIRM OF KARL F ROSS  
5676 RIVERDALE AVENUE BOX 900  
RIVERDALE BRONX, NY 104710900**

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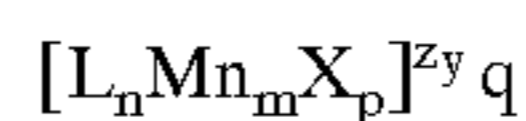
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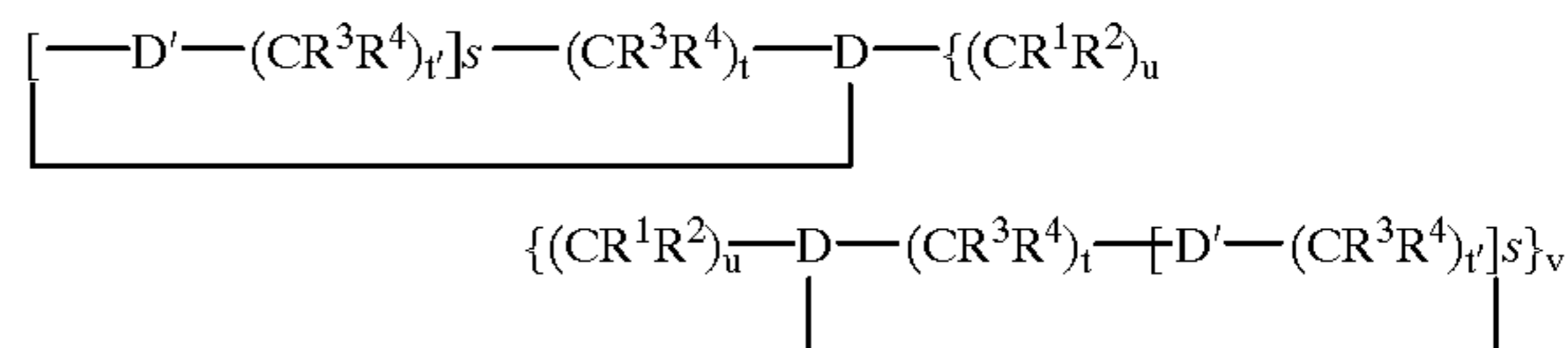
**Publication Classification**(51) **Int. Cl.<sup>7</sup>** ..... **D21C 9/10; D21C 9/16**(52) **U.S. Cl.** ..... **162/72; 162/78; 8/111; 252/186.39; 252/186.41**(57) **ABSTRACT**

The invention refers to a method to delignify fibrous material comprising an aqueous suspension of fibers which has a

consistency between 5%-40%, with a peroxy compound that is used in amounts between 0.5%-10% based on bone dry fibrous material, and with a metal complex of this general formula



wherein Mn stands for manganese or iron, which can be present in the oxidation state II, III, IV or V or in mixtures of these states; n and m are the integers 1-4, X is a coordinating ligand; p is an integer from 0 to 12; z is the charge of the complex and can be positive, neutral or negative; Y is a counter-ion or -molecule which depends on the charge of the complex; q is equal to z divided by the charge of Y; and L is a ligand and is represented by a macrocyclic organic molecule with the following general formula:



wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> can be either zero, H, alkyl, aryl or otherwise optionally substituted; D and D' are either N, NR, PR, O, or S, wherein R can be substituted by H or alkyl or aryl or otherwise optionally substituted; t and t' are whole integers from 2 to 3, s is an integer between 2 and 4, u is an integer from 1 to 20, and v is 0 or 1; this metal complex is used at an amount of 0.0001%-0.1% based on bone dry fibrous material, wherein the fibers are delignified at an initial pH-level between 7.5 and 13.5, at a reaction temperature between 20° C. and 130° C., and with a reaction time between 15 and 360 minutes. Further, the invention relates to the use of a metal complex.

## METHOD FOR THE DELIGNIFICATION OF FIBROUS MATERIAL AND USE OF CATALYST

### DESCRIPTION

[0001] This invention relates to a method for the delignification of fibrous material and the use of a catalyst for application of this method.

[0002] Hereinafter, the term fibrous materials comprises fibers, containing lignin, which have either been pre-treated mechanically or chemically e.g. by the method of ground wood production or pulp production, or which, as chemically or mechanically untreated natural fibers, shall be used in this method. The fibers also could have already been processed in several chemical and/or mechanical process steps, for example in a pulping step and then in an initial delignification step after pulping.

[0003] Fibers containing lignin from wood or annual plants should be, for most purposes, free of lignin. In addition, the fibers should possess a high degree of brightness, preferably 90% ISO. It is only possible to attain these high degrees of brightness after having removed almost all of the lignin from the fiber or its surface. By using elemental chlorine and other chlorine bleaching chemicals, the fibers containing lignin could be efficiently and selectively delignified.

[0004] Since the use of chlorine and chlorine-based chemicals is avoided nowadays, oxygen and oxygen-based chemicals are used to delignify these fibers. The reaction mechanism of these chemicals is however much less selective, causing thereby greater cellulose degradation during delignification. This effect is obviously unwanted. There is, therefore, a large demand for a method and chemicals which can selectively remove the residual lignin.

[0005] After as much of the residual lignin has been removed as possible, bleaching chemicals in pulp production are used to brighten the fibers to the highest possible degree. During these bleaching steps, residual chromophore groups, or chromophore groups formed during previous process steps, should be removed by oxidation. The decomposition of fibrous material should be avoided, e.g. to reduce the load of organic material in the waste water of the bleaching steps. Hydrogen peroxide is one of the bleaching agents used in the pulping industry for this purpose. Hydrogen peroxide is used for reasons of environmental protection. It is more expensive than chlorine-based bleaching agents and is much less selective.

[0006] Peroxide is used, therefore, only under mild reaction conditions for brightening of fibers but not for delignification steps. Under more severe reaction conditions, such as higher temperature above 100° C.), greater amounts of chemicals, and/or extended reaction times, residual lignin is still removed to a certain extent but at the cost of fiber damage and yield loss. The most unwanted side effect to be avoided is cellulose degradation, caused by the non-selective reaction of hydrogen peroxide, which results in poorer fiber strengths.

[0007] Hydrogen peroxide has hardly been used as a delignifying agent because due to its reacting mechanisms it is not able to remove the highly condensed phenol components of the residual lignin under sufficiently mild reaction conditions. Some methods, in which the use of hydrogen

peroxide is proposed also for delignification of pulp, achieve a delignification rate of the residual lignin of approximately 30%.

[0008] Some known methods, as for example the one described in WO 94/00234, use a catalyst to accelerate the reactions of the oxidizing agent. These methods recommend the joint or separate addition of metal and ligand and the treatment of the pulp fibers at reaction temperatures between 60° C.-98° C. and at a pH level of 3.7. This acid treatment method results however in considerable cellulose degradation.

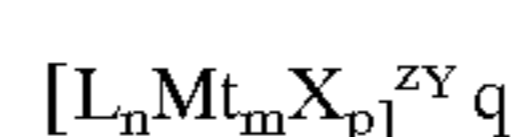
[0009] In order to utilize the brightening effect of hydrogen peroxide more effectively, the search for catalysts, which can repress the many undesired side effects of its reaction and thereby free more hydrogen peroxide for an increased removal of chromophore groups, has been conducted for several years. Different agents, used for example to bleach and brighten textiles, have been tested for their effectiveness to this end. The results of these tests were, however, unsatisfactory, as not only the fibers to be bleached but also many other chemicals are contained in the process water during industrial pulp production. In addition, the textile fibers do not contain any lignin. Until now none of the numerous tests have proven that the addition of catalysts to the hydrogen peroxide bleaching step can improve bleaching results.

[0010] Because of the widespread use of oxygen-based delignifying agents instead of chlorine-based agents, process technology has greatly changed in the pulp industry. Thus, there is a great need for chemicals or methods, which allow to largely reduce the amount of residual lignin present after pulping or an initial oxygen bleaching step and thereby yield a chlorine-free bleached pulp with high degrees of brightness and good strength properties.

[0011] It is the object of this invention, therefore, to provide a method which allows an improved and highly selective delignification of fibers using chlorine-free chemicals.

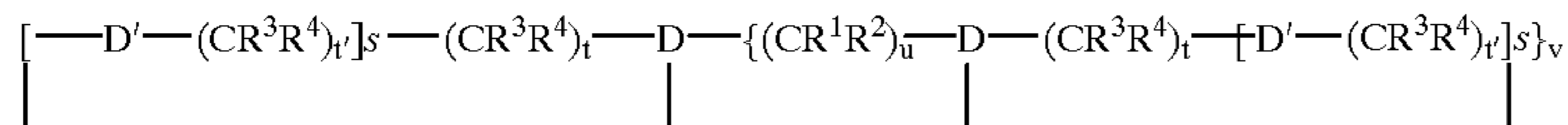
[0012] It is noteworthy that catalysts, which contain transition metals improve the bleaching and brightening effects of peroxides in washing agents, also enable a greatly improved delignification of fibers by a very selective removal of lignin.

[0013] For the method according to the invention, catalysts are applied that have been described in the European patent applications EP 0 458 397 A2, EP 0 458 398 A2, EP 0 544 490 A1, as well as in WO 95/30681 and its priority document DE OS 44 16 438, and that are herewith expressly incorporated into the description of this invention at least as far as the detailed description of metal complexes is concerned. These catalysts are single or multiple nuclea metal complexes with the following general formula:



[0014] wherein Mt stands for manganese or iron, which can be present in the oxidation state II, III, IV or V or in mixtures of these state; n and m are an integer of 1-4, X is a coordinating ligand; p is an integer of 0 to 12; Y is a counter ion or—molecule which depends on the charge of z of the complex and can be positive, neutral or negative; q is equal to z divided by the charge of Y; and L is a ligand and

is represented by a macrocyclic organic molecule with the following general formula:



[0015] wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  can be either zero, H, alkyl, aryl or otherwise optionally substituted; D and D' are either N, NR, PR, O, or S, wherein R can be substituted by H or alkyl or aryl or otherwise optionally substituted; t and t' are whole integers from 2 to 3, s is an integer between 2 and 4, u is an integer of 1 to 20, and v is 0 or 1.

[0016] The complexes with the following ligands, used as described in the invention, have been found to be especially suitable for delignification:

[0017] Bis-azamacrocycles, in which two molecules of the general formula I to V are connected between both nitrogen atoms by one of the residuals  $R^1$  to  $R^4$  or  $R^5$  through a connecting part of the  $\text{---T---}$  or  $\text{---A---(O---A)}_h$  structure, wherein h stands for a whole integer between 1 and 19 and the residual  $R^5$  herein can also be  $R^1$  to  $R^4$ ;

[0018] T is a  $C_2$  to  $C_8$ -alkylene group and

[0019] A is a  $C_2$  to  $C_4$  alkylene group;

[0020]  $R^1$  and  $R^4$  stand for hydrogen,  $C_1$  to  $C_{60}$ -alkyl, which can be interrupted by up to 19 disconnected oxygen atoms and can contain up to 5 additional hydroxyl groups,  $C_1$ - $C_{30}$ -alkyl-, phenyl- or benzyl-groups, wherein the aromatic ring can be substituted by up to 3  $C_1$  to  $C_4$  alkyl groups,  $C_1$  to  $C_4$  alkoxy groups, halogen atoms, hydroxyl groups, sulfo groups or carboxyl groups, or groups of the formula  $\text{---(CH}_2\text{)}_I\text{---COOH}$ ,  $\text{---(CH}_2\text{)}_I\text{---SO}_3\text{H}$ ,  $\text{---(CH}_2\text{)}_I\text{---PO}_3\text{H}_2$  or  $\text{---(CH}_2\text{)}_I\text{---OH}$ , wherein I means a whole integer from 1 to 4, respectively and the named acid groups can also be present in the form of salt;

[0021]  $R^5$  stands for the groups of the formula  $\text{---(CH}_2\text{)}_I\text{---COOH}$ ,  $\text{---(CH}_2\text{)}_I\text{---SO}_3\text{H}$ ,  $\text{---(CH}_2\text{)}_I\text{---PO}_3\text{H}_2$  or  $\text{---(CH}_2\text{)}_I\text{---OH}$ , or for a  $C_2$ - $C_{60}$  alkyl, which is either interrupted by 1 to 19 disconnected oxygen atoms and/or contains 1 to 5 hydroxyl groups, wherein I is a whole integer from 1-4, respectively and the named acid groups can also be present in the form of salt;

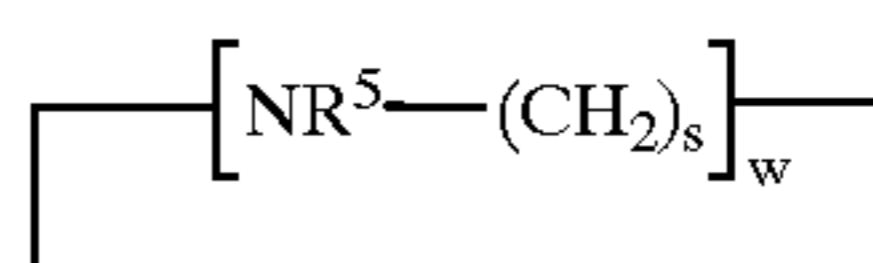
[0022]  $R^6$  stands for hydrogen,  $C_1$  to  $C_{60}$  alkyl, which can be interrupted by up to 19 disconnected oxygen atoms and can contain up to 5 additional hydroxyl-, phenyl- or benzyl-groups, wherein the aromatic ring can be substituted by up to 3  $C_1$  to  $C_4$  alkyl groups,  $C_1$  to  $C_4$  alkoxy groups, halogen atoms, hydroxyl groups, sulfo groups or carboxyl groups, or groups of the formula  $\text{---(CH}_2\text{)}_r\text{---COOH}$ ,  $\text{---(CH}_2\text{)}_r\text{---SO}_3\text{H}$ ,  $\text{---(CH}_2\text{)}_r\text{---PO}_3\text{H}_2$  or  $\text{---(CH}_2\text{)}_r\text{---OH}$ , wherein r is a whole integer from 0 to 4, respectively and the named acid groups can also be present in the form of salt;

[0023] Q is a group comprising 1 to 3 C-atoms with 1 or 2 carbonyl groups and methylene groups as residual elements.

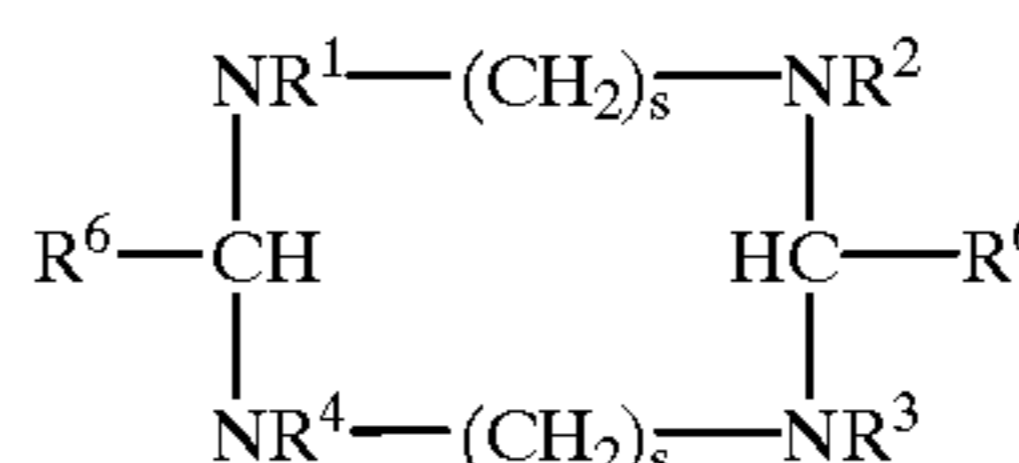
[0024] s designates the integer 2 or 3

[0025] w designates the integer 3 or 4

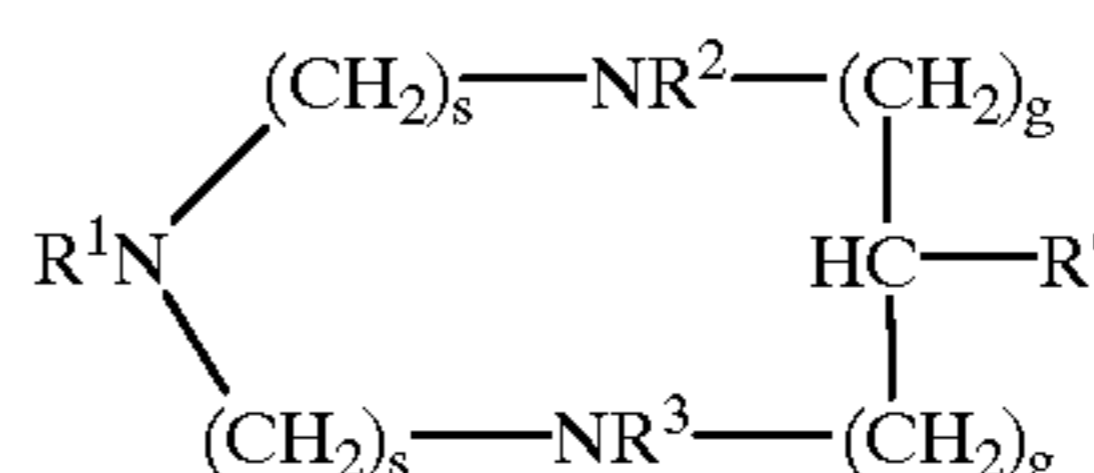
[0026] g stands either for 0 or 1



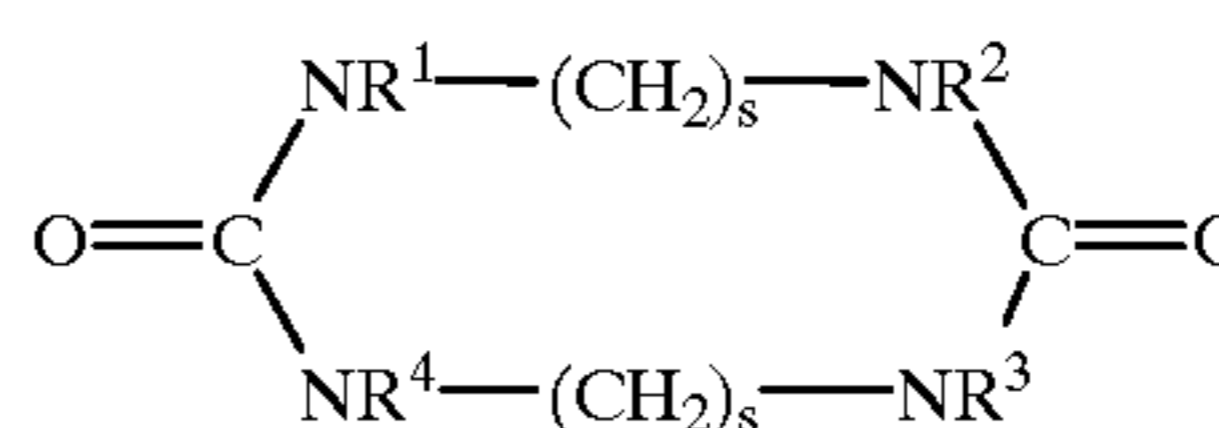
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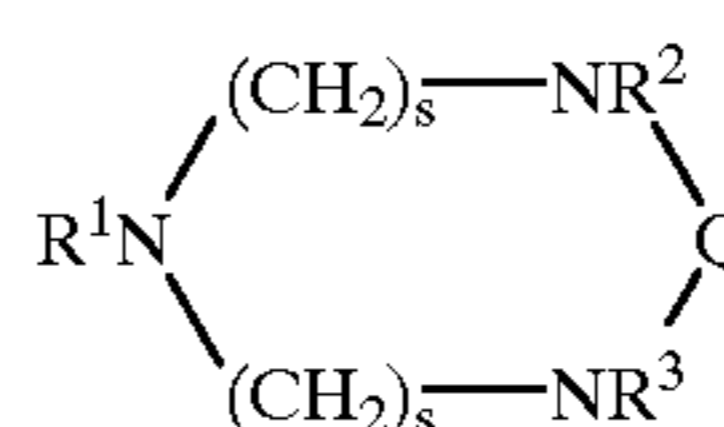
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III



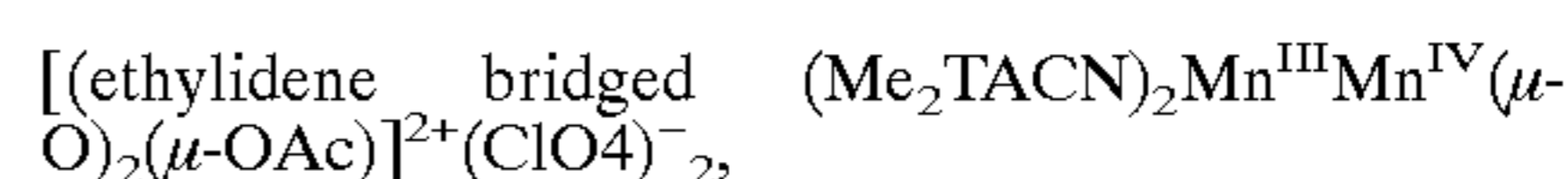
IV



V

[0027] A further, well-suited ligand is 1,2-bis-(4,7-dimethyl-1,4,7-triaza-1,8-cyclononyl)ethane.

[0028] An example of a particularly well-suited manganese complex is



[0029] wherein Me stands for methyl group and TACN stands for triazacyclononane.

[0030] Surprisingly, with these metal complexes, which are used in concentrations of 0.0001 to 0.1% based on the

amount of bone dry fibers, it is possible to increase the delignification of the fibers by up to approximately 220% with only small amounts of cellulose being removed as compared to the known P-step, which only brightens the fibers. It is also remarkable that this increase was achieved at rather low amounts of residual lignin, especially as this lignin is normally present in a highly condensed and poorly reactive form.

[0031] This extensive delignification is attained when the method parameters described in claim 1 are fulfilled. The method according to the invention can be used for all types of fibers, including mechanically and/or chemically pre-treated fibers, recycled paper fibers, and untreated natural fibers.

[0032] Hydrogen peroxide, compounds which release hydrogen peroxide, organic or inorganic peroxy acids or their salts, i.e. per-acetic acid, per-monosulfuric-acid, or per-carbonic acid and their salts can all be used as a peroxy compound. Mixtures of different peroxy compounds can also be used in a delignification step. This allows an exact adjustment to any special process requirements.

[0033] The method according to the invention can be used within a broad spectrum of consistency (consistency refers to the quantity of bone dry fiber mass based on the total weight). Consistency may range from 3 to 40%, but a consistency between 10% and 15% is preferred.

[0034] A peroxy compound to bone dry fiber mass ratio of 0.5% to 10%, or more preferably 1% to 6% based on bone dry fiber mass, respectively, should be used in order to attain an optimal delignification.

[0035] The method according to the invention yields excellent delignification results when a metal complex to bone dry fiber mass ratio of 0.0001% to 0.06% based on bone dry fiber mass is used.

[0036] The removal of the residual lignin proceeds very efficiently when the pH-level at the beginning of the reaction is higher than 10 or more preferably higher than 11.

[0037] The reaction temperature may be varied greatly, depending on the type of fibrous raw material. Most fibers will be delignified between 20° C. to 130° C. or more preferably between 40° C. to 1100° C. A temperature range between 50° C. to 98° C. is especially preferred, because a very selective delignification is induced under mild conditions and with relatively short reaction times.

[0038] The reaction time, in coordination with the reaction temperature, can also be varied within the range of 15 to 360 minutes. A reaction time of 30 to 240 minutes is, however, preferred. Choosing a reaction time of 45 to 150 minutes will show a favourable result. A very extensive delignification is attained during a reaction time of 60 to 120 minutes. Often, the reaction time is shorter than in conventional P-stages.

[0039] The metal complexes used for delignification, in accordance with this invention, improve not only the effectiveness of a simple peroxide stage but also increase the delignification rate of an oxygen stage conducted with the addition of peroxide. When bleaching with the addition of oxygen, very good results can be attained by using pressures between 0.15 to 1.5 MPa. A reaction pressure of 0.2 to 0.9 MPa is especially preferred.

[0040] Chelating of the heavy metal ions has a positive effect. DPTA, DTPMPA or poly-a-hydroxyacrylic acid, which is also stable at higher pH-levels, are preferably used

as chelating agents. Additionally or alternatively sodium silicate and/or magnesium sulfate may be used.

[0041] The method according to this invention will be described by the following examples:

[0042] For the experiments of the catalyzed delignification steps with application of chemicals containing peroxy and/or oxygen compounds as described in Examples 1-3, spruce kraft pulp with the following technological data was used:

[0043] Kappa number: 19.3

[0044] Brightness: 29.3% ISO

[0045] Viscosity: 1020 mg/l

[0046] In the Examples 4 to 7 the same spruce kraft pulp was used after conducting an oxygen stage:

[0047] Kappa number: 10.1

[0048] Brightness: 34.1 % ISO

[0049] Viscosity: 901 mg/l

[0050] For Example 8, ASAM softwood pulp with the following properties was used:

[0051] Kappa number: 26.7

[0052] Brightness: 45.4% ISO

[0053] Viscosity: 1237 mg/l

[0054] The method according to the invention was conducted in a water bath adjusted to reaction temperature with charges of 10 g bone dry pulp in polyethylene bags. Pulp, water and chemicals were mixed as described in the following procedure. The chemicals were added in three steps, first by mixing an aqueous solution of the additives and catalyst into the pulp. NaOH was then added to adjust the pH-level of the reaction. Finally, the amount of hydrogen peroxide required for delignification was added. After measuring the pH-level of each sample, the samples were sealed into the plastic bags and placed into the water bath which was adjusted to temperature.

[0055] All of the tests were conducted, unless noted otherwise, at 10% consistency. Figures marked with “%” refer, unless noted otherwise, to the amount of bone dry fibers. The analyses were conducted according to the following regulations:

[0056] The Kappa number was determined according to the Zellcheming regulation number IV/37/80, and the micro kappa number according to TAPPI regulation number UM 246. The pulp viscosity was determined in a copper-ethylene-diamine solution according to Zellcheming regulation number IV/36/61. Brightness was measured with an Elrepho 2000 (Datacolor) according to the SCAN-C regulation 11:75.

[0057] Every example includes a table of the same number which lists the corresponding reaction conditions, especially the catalyst used in each case, and the corresponding results.

#### EXAMPLE 1

[0058] The data for this example is listed in Table 1. The catalyst used is recorded as a footnote. Experiments were conducted with and without catalysts at different temperatures (50° C. and 90° C.). No other additives were used for these tests.

[0059] The use of the catalyst resulted in an increase of the delignification rate by 70% at 50° C. and by 52% at 90° C. reaction temperature. The amount of hydrogen peroxide used in the experiment was very efficiently and completely used. It must be noted that the catalyzed P-stage (experiment P2) yielded not only an improved delignification but also the same viscosity as compared to experiment P3, which was not catalyzed. The improved selectivity (same viscosity at lower amounts of residual lignin) which results thereof indicates less degradation and improved strength properties of the fibers after a P-stage because of the correlation between viscosity and strength properties. For more information on the relationship between viscosity loss (reduction of degree of polymerisation) and impaired strength properties please refer to: GURNAGUL et al.: "The effect of cellulose degradation on the strength of wood pulp fibres" (Nordic Pulp and Paper Research Journal 7, (3), 1992, p. 152-154).

#### EXAMPLE 2

[0060] An acid wash of the pulp before the P-stage was conducted prior to the experiments P5-P8. The conditions were: consistency 3.0%, pH-level 2.0, reaction temperature: 70° C., reaction time: 30 minutes. The results are listed in Table 2. The acid pre-treatment (A) effectively removes heavy metal ions, most of which were in the pulp as it entered the system. This one additional step (all of the other conditions remained constant) yielded distinctly improved delignification results compared to the tests in Example 1.

[0061] It must be noted that the use of the catalyst in experiments P6 and P7 effected distinctly improved viscosity results at approximately the same kappa number (kappa number: 12.7 and 12.8, respectively). Therefore, improved pulp strength properties can be expected.

[0062] It also became apparent during the experiments P1-P8 that the use of the catalyst caused only approximately the same increase in brightness as the use of hydrogen peroxide without a catalyst. In most cases the brightness was however poorer.

[0063] Apart from the fact that chemicals, which improve the bleaching or brightening effect of peroxy chemicals, normally do not positively influence the removal of lignin, the catalysts, which were tested during these experiments, would normally not have been considered after standard experiments concerning the use of hydrogen peroxide in the pulp and paper industry which only analyze brightness development.

#### EXAMPLE 3

[0064] Table 3 shows the influence of increasing amounts of catalysts on delignification. Kraft pulp is again being used here after acid washing. An increase of the delignification rate can be determined at amounts of the catalyst of up to 0.006% of bone dry pulp. No further increase in delignification was observed with amounts of the catalyst greater than 0.006%. The catalyst that was used is noted in Table 3.

[0065] At increasing amounts of the catalyst, the amount of residual peroxide decreases but does not cause any improvements in delignification or any increases in brightness. To attain a maximal removal of the residual lignin, the amount of the catalyst for the following experiments will be 0.006%.

#### EXAMPLE 4

[0066] During experiments P15-P18 the effect of the chelating agent DTPMPA (Diethylene-triaminepentameth-

ylene phosphonic acid) will be tested on pulp pretreated in oxygen and acid washing stages. Unrelated to the use of the chelating agent, the delignification rate can be increased with a double amount of peroxide despite initially low kappa numbers. The kappa number when using the catalyst is 83% lower compared to the delignification rate of the non-catalyzed P-stage. Despite this considerable removal of lignin, the test results of P15 demonstrate a much higher viscosity than those of P16. The higher brightness of the catalyzed P-stage can be explained by the lower residual lignin content, because a further reduction of kappa numbers below 10 is always correlated with a high increase in brightness.

[0067] The addition of the chelating agent causes higher residual peroxide levels in the filtrates. It must be noted, however, that in presence of the catalyst the hydrogen peroxide is much more effectively utilized than in the conventional P-stage.

#### EXAMPLE 5

[0068] Table 5 shows that the same pulp was used as in the previous Example. Two different catalysts, K1 and K2, were tested. The catalysts and the corresponding ligands are described in Table 5. The use of DTPA (Diethylene-triamine-pentaacetic acid) and DTPMPA, each applied together with 0.5% magnesium sulfate on bone dry pulp, is also tested.

[0069] Both catalysts cause distinctly higher delignification rates as compared to the conventional P-stage (experiments P21 and P24). Because catalyst K1 effects 100% greater delignification rates than the conventional P-stage, it is particularly suitable. In addition, K1 exhibits higher and therefore better viscosities of the pulp fibers than K2. Finally, K1 also caused higher brightness increase than K2. Principally, both catalysts are, however suitable for the projected purpose.

#### EXAMPLE 6

[0070] This series of experiments shows the delignification in relation to reaction times. Most of the residual lignin is removed during the initial 15 minutes. By the end of the maximum reaction time of 60 minutes, the residual lignin is removed at a delignification rate which is 120% greater than during a conventional P-stage.

[0071] In the tests conducted without the catalyst, a high percentage of the hydrogen peroxide remains unused in the bleaching liquor, whereas, in the presence of the catalyst, more than 80% of the chemicals are used up within the first 15 minutes.

[0072] Reaction development of the delignification differs thereby greatly from that of the bleaching. Whereas the delignification finishes after approx. 45 minutes with or without a catalyst, the brightness increases slowly but continually.

#### EXAMPLE 7

[0073] Table 7 shows the influence of the use of alkali and the initial pH-level on the delignification rate, the brightness development, and the viscosity. With or without the catalyst, the removal of the residual lignin increases with increasing amounts of NaOH. This increase is, however, extremely low in the conventional P-stages (Experiments P37 to P40), whereas the delignification rate increases in the presence of the catalyst from 42,6% to 64,4%. A distinct improvement of

the delignification rate can be determined already at an initial pH-level of 10.4 (Experiment P33) as compared to the standard experiment without the catalyst. An initial pH-level above 11 is especially efficient. At an initial pH-level of 11.8 (P36), the removal of residual lignin at extremely low temperatures is increased by 217% compared to standard experiment (P40).

[0074] Correspondingly, the increase in brightness is more pronounced. Considering the low kappa numbers, the viscosities during experiments P33-P36 are surprisingly stable and are, at the end, somewhat higher than those of the conventional P-stage. It can be expected, therefore, that strength properties of the pulps delignified with the use of the catalyst are better than those of the pulps delignified without catalyst.

#### EXAMPLE 8

[0075] In these experiments, an unbleached ASAM softwood pulp is delignified after a conventional chelating treatment. EDTA (0.4% ethylene-diamine-tetraacetic acid based on bone dry pulp) was used at a pH-level of 4.5 at 70° C. and 3.0% consistency for 30 minutes.

[0076] The following delignification was conducted with both oxygen and hydrogen peroxide (OP-stage) with 0.8 MPa oxygen pressure. Reaction conditions were chosen as given in Table 8: 5.0% NaOH, 0.5% MgSO<sub>4</sub>, 90° C., 80 min reaction time (including time for heating of the digester), 10% consistency, 800 g bone dry pulp per trial. The trials were conducted in an electrically heated tumbling digester. The additives used are also listed in Table 8.

[0077] A kappa number of 12 was attained without a catalyst in the OP-stage. A kappa number of approx. 7 and a brightness above 85% ISO was attained by adding the catalyst and 0.1% DTPMPA on bone dry pulp. The use of DTPA or sodium silicate resulted in similar delignification rates, but also in a lower increase in brightness. The pulp delignified with the use of the catalyst possesses higher viscosities between 1033 and 1074.

[0078] Until now, such an extremely high rate of delignification in the OP-stage (Experiment OP 50: 73% based on pulp parameters prior to OP-stage) could be attained only by applying especially pronounced reaction conditions, i.e. not without high losses of viscosity. It was thus technically not applicable because fiber damages were too high and therefore not acceptable for further processing.

[0079] Surprisingly, it was not previously known that the delignifying effect of peroxide is more than doubled when the catalysts described above are used. The careful removal of the residual lignin, when using the method described in this invention, will presumably yield high final brightnesses (90% ISO). In addition, the pulps that have been delignified

and bleached with the mild and selective method possess higher viscosities and are thus stronger than fibers treated with known chlorine-free methods.

#### EXAMPLE 9

[0080] An oxygen bleached softwood kraft pulp from industrial production was first subjected to an acid chelating treatment (Q-stage). Then an oxygen-peroxide-delignification stage was conducted with the addition of a catalyst. For final bleaching, a peroxide bleaching stage followed.

[0081] Bleaching was conducted at 10% consistency, the other reaction conditions are given in table 9.

[0082] The properties of the finally bleached pulp of Example 9 as well as of the pulp after conducting the Q-stage are given in table 10. Further, table 10 comprises data of a reference pulp sample after a bleaching sequence which is identical to O Q (OP)<sub>cat</sub> P, only that no "cat" i.e. catalyst was applied.

[0083] Residual lignin content was reduced from 11.9 to 3.8 in the catalysed bleaching sequence. The reference shows a residual lignin content of 4.7. Viscosity of the finally bleached pulp is almost identical for both sequences, 833/839 vs. 983 of the unbleached pulp. Due to the difference in residual lignin content, the final brightness after bleaching has risen from 32.2 to 81.7 for the reference sample whereas catalysed bleaching has yielded a final brightness of 87.8.

[0084] As outlined above, viscosity of the pulp is an indicator of fiber strength. Here, at a standard beating degree of 25° SR, strength testing reveals that the strength properties of the fibers after final bleaching are not in the least impaired. Catalysed bleaching does not affect the fiber structure as might be expected because of the enhanced delignification. Instead, burst index and tensile index are even higher than for the reference sample and the development of the tear index is as high as after reference bleaching.

[0085] Thus, the catalyst improves delignification of lignocellulosic material with peroxy compounds without affecting strength properties of the fibers. This highly selective reaction allows extensive delignification of fibers with chlorine free bleaching compounds and as a consequence of extensive delignification, high final brightness of the pulp. Example 9 shows further that the catalyst proves to be beneficial in delignification stages. The final P-stage in both, the catalysed and the reference bleaching sequence was conducted without catalyst. The catalyst application was limited to the (OP) delignification stage.

#### EXAMPLE 1

[0086]

TABLE 1

pretreatment	trial	catalyst [%]	H <sub>2</sub> O <sub>2</sub> [%]	NaOH [%]	temperature [° C.]	reaction time (incl. heating) [min]	residual peroxide [% of charge]	kappa number [-]	brightness [% ISO]	viscosity [ml/g]	delignification [%]
untreated pulp								19.3	29.3	1020	
—	P1	—	1.0	1.5	50	210	—	16.0	33.4	977	17.1
—	P2	0.0071	1.0	1.5	50	210	—	13.7	32.7	950	29.0

TABLE 1-continued

pretreatment	trial	catalyst [%]	H <sub>2</sub> O <sub>2</sub> [%]	NaOH [%]	temperature [° C.]	reaction time (incl. heating) [min]	residual peroxide [% of charge]	kappa number [-]	brightness [% ISO]	viscosity [ml/g]	delignification [%]
—	P3	—	1.0	1.5	90	210	—	14.4	34.3	940	25.4
—	P4	0.0071	1.0	1.5	90	210	—	12.0	34.5	923	37.8

catalyst = [LMn<sup>IV</sup>(μ-O)<sub>2</sub>(μ-OAc)Mn<sup>III</sup>]<sup>2+</sup>(ClO<sub>4</sub><sup>-</sup>)<sub>2</sub>  
 L = 1,2-bis-(4,7,-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane

## EXAMPLE 2

[0087]

TABLE 2

pretreatment	trial	catalyst [%]	H <sub>2</sub> O <sub>2</sub> [%]	NaOH [%]	temperature [° C.]	reaction time (incl. heating) [min]	residual peroxide [% of charge]	kappa number [-]	brightness [% ISO]	viscosity [ml/g]	delignification [%]
untreated pulp								19.3	29.3	1020	
A	P5	—	1.0	1.5	50	210	16.3	15.3	42.0	965	17.7
A	P6	0.0071	1.0	1.5	50	210	—	12.7	40.8	923	31.7
A	P7	—	1.0	1.5	90	210	—	12.8	43.8	885	31.2
A	P8	0.0071	1.0	1.5	90	210	—	11.1	42.7	916	40.3

catalyst = [LMn<sup>IV</sup>(μ-O)<sub>2</sub>(μ-OAc)Mn<sup>III</sup>]<sup>2+</sup>(ClO<sub>4</sub><sup>-</sup>)<sub>2</sub>  
 L = 1,2-bis-(4,7,-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane

## EXAMPLE 3

[0088]

TABLE 3

pretreatment	trial	catalyst [%]	H <sub>2</sub> O <sub>2</sub> [%]	NaOH [%]	temperature [° C.]	reaction time [min]	residual peroxide [% of charge]	kappa number [-]	brightness [% ISO]	viscosity [ml/g]	delignification [%]
untreated pulp								19.3	29.3	1020	
A	P9	—	1.0	1.5	50	120	45.6	16.2	40.6	963	14.7
A	P10	0.00067	1.0	1.5	50	120	31.0	14.8	39.5	951	22.1
A	P11	0.00200	1.0	1.5	50	120	19.2	14.9	39.7	950	21.6
A	P12	0.00400	1.0	1.5	50	120	6.1	13.3	40.0	961	30.0
A	P13	0.00600	1.0	1.5	50	120	2.7	12.6	39.0	947	33.7
A	P14	0.00730	1.0	1.5	50	120	0.5	13.4	40.9	949	29.5

catalyst = [LMn<sup>IV</sup>(μ-O)<sub>2</sub>(μ-OAc)Mn<sup>III</sup>]<sup>2+</sup>(ClO<sub>4</sub><sup>-</sup>)<sub>2</sub>  
 L = 1,2-bis-(4,7,-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane

## EXAMPLE 4

[0089]

TABLE 4

pre-treatment	trial	catalyst [%]	H <sub>2</sub> O <sub>2</sub> [%]	NaOH [%]	DTPMPA [%]	temperature [° C.]	reaction time [min]	residual peroxide [% of charge]	kappa number [-]	brightness [% ISO]	viscosity [ml/g]	delignification [%]
O pretreated									10.1	34.1	901	
O A	P15	0.006	2.0	2.0	—	50	120	—	4.8	65.5	778	52.5
O A	P16	—	2.0	2.0	—	50	120	22.8	7.2	54.1	689	28.7
O A	P17	0.006	2.0	2.0	0.2	50	120	25.8	4.8	68.5	845	52.5
O A	P18	—	2.0	2.0	0.2	50	120	88.4	7.2	55.7	904	28.7

catalyst = [LMn<sup>IV</sup>(μ-O)<sub>2</sub>(μ-OAc)Mn<sup>III</sup>]<sup>2+</sup>(ClO<sub>4</sub><sup>-</sup>)<sub>2</sub>  
 L = 1,2-bis-(4,7,-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane

## EXAMPLE 5

[0090]

TABLE 5

pre-treatment	trial	catalyst K1 [%]	catalyst K2 [%]	H <sub>2</sub> O <sub>2</sub> [%]	NaOH [%]	DTPA [%]	DTPMPA [%]	MgSO <sub>4</sub> [%]	temperature [° C.]	reaction time [min]	residual peroxide [% of charge]	kappa number [-]	brightness [% ISO]	viscosity [ml/g]	delignification [%]
O pretreated												10.1	34.1	901	
O A	P19	0.006	—	2.0	2.0	0.2	—	0.5	50	120	9.5	3.7	69.2	836	63.4
O A	P20	—	0.006	2.0	1.0	0.2	—	0.5	50	120	5.6	3.8	66.7	657	62.4
O A	P21	—	—	2.0	2.0	0.2	0.2	0.5	50	120	83.0	6.7	53.1	884	33.7
O A	P22	0.006	—	2.0	2.0	—	0.2	0.5	50	120	12.9	3.5	69.0	840	65.3
O A	P23	—	0.006	2.0	1.0	—	0.2	0.5	50	120	2.6	3.9	65.2	669	61.4
O A	P24	—	—	2.0	2.0	—	0.2	0.5	50	120	90.8	6.8	54.4	889	32.7

catalyst K1 = [LMn<sup>IV</sup>(μ-O)<sub>2</sub>(μ-OAc)Mn<sup>III</sup>]<sup>2+</sup>(ClO<sub>4</sub><sup>-</sup>)<sub>2</sub>  
L = 1,2-bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)-ethane  
catalyst K2 = [LMn<sup>IV</sup>(μ-O)<sub>3</sub>Mn<sup>IV</sup>L]<sup>2+</sup>(PF<sub>6</sub><sup>-</sup>)<sub>2</sub>  
L = 1,4,7-trimethyl-1,4,7-triazacyclononane

## EXAMPLE 6

[0091]

TABLE 6

pretreatment	trial	catalyst [%]	H <sub>2</sub> O <sub>2</sub> [%]	NaOH [%]	temperature [° C.]	reaction time [min]	residual peroxide [% of charge]	kappa number [-]	brightness [% ISO]	viscosity [ml/g]	delignification [%]
O pretreated								10.1	34.1	901	
O A	P25	0.006	2.0	2.0	50	15	15.6	5.1	58.7	826	49.5
O A	P26	0.006	2.0	2.0	50	30	5.7	4.7	64.5	803	53.5
O A	P27	0.006	2.0	2.0	50	45	0.6	4.4	65.4	775	56.4
O A	P28	0.006	2.0	2.0	50	60	—	4.4	66.9	775	56.4
O A	P29	—	2.0	2.0	50	15	85.7	7.9	46.8	904	21.8
O A	P30	—	2.0	2.0	50	30	78.7	7.9	48.4	878	21.8
O A	P31	—	2.0	2.0	50	45	69.0	7.4	50.6	843	26.7
O A	P32	—	2.0	2.0	50	60	63.5	7.5	50.9	834	25.7

catalyst = [LMn<sup>IV</sup>(μ-O)<sub>2</sub>(μ-OAc)Mn<sup>III</sup>]<sup>2+</sup>(ClO<sub>4</sub><sup>-</sup>)<sub>2</sub>  
L = 1,2-bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)-ethane

## EXAMPLE 7

[0092]

TABLE 7

pre-treatment	trial	catalyst [%]	H <sub>2</sub> O <sub>2</sub> [%]	NaOH [%]	temperature [° C.]	reaction time [min]	residual peroxide [% of charge]	initial pH	kappa number [-]	brightness [% ISO]	viscosity [ml/g]	delignification [%]
O									10.1	34.1	901	
O A	P33	0.006	2.0	0.5	50	120	73.5	10.4	5.8	51.4	893	42.6
O A	P34	0.006	2.0	1.0	50	120	6.9	11.2	4.8	57.6	837	52.5
O A	P35	0.006	2.0	1.5	50	120	1.8	11.4	4.2	63.4	789	58.4
O A	P36	0.006	2.0	2.0	50	120	0.4	11.8	3.6	66.9	778	64.4
O A	P37	—	2.0	0.5	50	120	95.8	10.5	7.8	48.4	906	22.8
O A	P38	—	2.0	1.0	50	120	70.0	11.2	7.6	54.5	878	24.8
O A	P39	—	2.0	1.5	50	120	51.7	11.5	7.3	55.9	832	27.7
O A	P40	—	2.0	2.0	50	120	49.3	11.8	7.1	56.4	773	29.7

catalyst = [LMn<sup>IV</sup>(μ-O)<sub>2</sub>(μ-OAc)Mn<sup>III</sup>]<sup>2+</sup>(ClO<sub>4</sub><sup>-</sup>)<sub>2</sub>  
L = 1,2-bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)-ethane



## EXAMPLE 8

[0093]

TABLE 8

pre-treatment	trial	catalyst [%]	H <sub>2</sub> O <sub>2</sub> [%]	NaOH [%]	MgSO <sub>4</sub> [%]	DTPMPA [%]	DTPA [%]	sodium silicate [%]	temperature [° C.]	reaction time [min]	residual peroxide [% of charge]	kappa number [-]	brightness [% ISO]	viscosity [ml/g]	delignification [%]
untreated pulp												26.7	45.4	1237	
O	OP49	—	4.0	5.0	0.5	0.1	—	—	90	80	32.4	12.1	75.8	1137	54.7
O	OP50	0.006	4.0	5.0	0.5	0.1	—	—	90	80	10.0	7.2	85.3	1074	73.0
O	OP51	0.006	4.0	5.0	0.5	—	0.3	—	90	80	0.7	7.3	80.7	1067	72.7
O	OP52	0.006	4.0	5.0	0.5	—	—	30	90	80	1.8	6.9	81.3	1033	74.2

catalyst = [LMn<sup>IV</sup>(μ-O)<sub>2</sub>(μ-OAc)Mn<sup>III</sup>]<sup>2+</sup>(ClO<sub>4</sub><sup>-</sup>)<sub>2</sub>  
 L = 1,2-bis-(4,7,-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane

## EXAMPLE 9

[0094]

an aqueous suspension of fibers which has a consistency between 5%-40%, with

TABLE 9

REACTION CONDITIONS OF THE (OP) AND P BLEACHING STAGES OQ(OP) <sub>cat</sub> P												
trial	pre-treatment	catalyst [ppm]	temperature [° C.]	reaction time (incl. heating)* [min]	pressure O <sub>2</sub> [MPa]	NaOH [%]	H <sub>2</sub> O <sub>2</sub> [%]	MgSO <sub>4</sub> [%]	DTPMPA [%]	EDTA [%]	H <sub>2</sub> SO <sub>4</sub> [%]	
Q	O	—	60	30	—	—	—	—	—	0.4	0.3	
(OP) <sub>cat</sub>	OQ	20	90	80*	0.6	2.0	2.0	0.25	0.05	—	—	
P	OQ(OP) <sub>cat</sub>	—	85	240*	—	1.75	3.0	—	0.05	—	—	

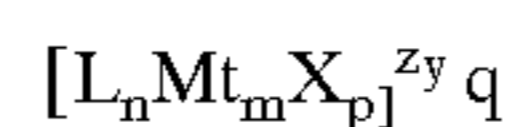
catalyst = [LMn<sup>IV</sup>(μ-O)<sub>2</sub>(μ-OAc)Mn<sup>III</sup>]<sup>2+</sup>(ClO<sub>4</sub><sup>-</sup>)<sub>2</sub>  
 L = 1,2-bis-(4,7,-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane

## EXAMPLE 9

[0095]

a peroxy compound that is used in amounts between 0.50%-10% based on bone dry fibrous material, and with

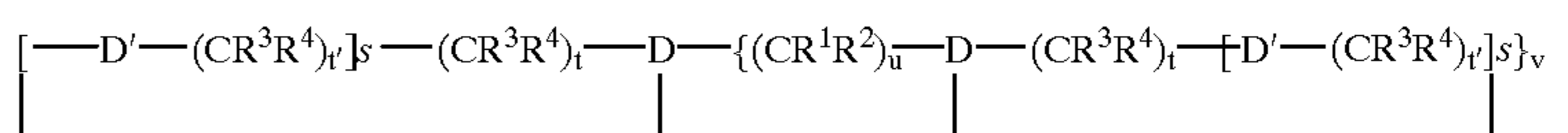
a metal complex of this general formula



wherein Mt stands for manganese or iron, which can be present in the oxidation state II, III, IV or V or in mixtures of these states; n and m are the integers 1-4; X is a coordinating ligand; p is an integer from 0 to 12; z is the charge of the complex and can be positive, neutral or negative; Y is a counter-ion or -molecule which depends on the charge of the complex; q is equal to z divided by the charge of Y; and L is a ligand and is represented by a macrocyclic organic molecule with the following general formula:

What is claimed is:

1. Method to delignify fibrous material comprising



wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  can be either zero, H, alkyl, aryl or otherwise optionally substituted; D and D' are either N, NR, PR O, or S, wherein R can be substituted by H or alkyl or aryl or otherwise optionally substituted; t and t' are whole integers from 2 to 3, s is an integer between 2 and 4, u is an integer from 1 to 20, and v is 0 or 1; this metal complex is used at an amount of 0.0001%-0.1% based on bone dry fibrous material, wherein the fibers are delignified at an initial pH-level between 7.5 and 13.5, at a reaction temperature between 20° C. and 130° C., and with a reaction time between 15 and 360 minutes thereby reducing the residual lignin content of the fibrous material by at least 20% compared to the residual lignin content of the fibrous material prior to catalyst treatment.

2. Method according to claim 1, characterized in that the fibrous materials are pulp or natural fibers.

3. Method according to claim 1, characterized in that hydrogen peroxide or compounds which release hydrogen peroxide are used as peroxy compound.

4. Method according to claim 1, characterized in that anorganic or organic peroxy acids or their salts are used as peroxy compounds.

5. Method according to one of the claims described above, characterized in that a mixture of different peroxy compounds is used.

6. Method according to claim 1, characterized in that the delignification is conducted at a consistency between 3% and 40%.

7. Method according to claim 6, characterized in that the delignification is conducted at a consistency between 10% and 15%.

8. Method according to claim 1, characterized in that 0.5% to 10% of a peroxy compound is used for delignification.

9. Method according to claim 8, characterized in that 1% to 6% of a peroxy compound is used for delignification.

10. Method according to claim 1, characterized in that 0.001% to 0.06% of the metal complex based on bone dry fiber is used for delignification.

11. Method according to claim 1, characterized in that the pH-level at the beginning of the delignification is above 10.

12. Method according to claim 1, characterized in that the pH-level at the beginning of the delignification is above 11.

13. Method according to claim 1, characterized in that the reaction temperature is 40° C. to 110° C.

14. Method according to claim 13, characterized in that the reaction temperature is 50° C. to 98° C.

15. Method according to claim 1, characterized in that the ID reaction time is between 30 minutes to 240 minutes.

16. Method according to claim 15, characterized in that the reaction time is between 45 minutes to 150 minutes.

17. Method according to claim 1, characterized in that the delignification is conducted at a pressure between 0.15 and 1.5 MPa.

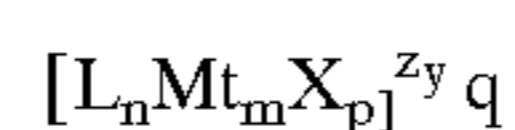
18. Method according to claim 18, characterized in that the delignification is conducted at a pressure between 0.2 and 0.9 MPa.

19. Method according to claims 1, 17 or 18, characterized in that the delignification is conducted in the presence of oxygen.

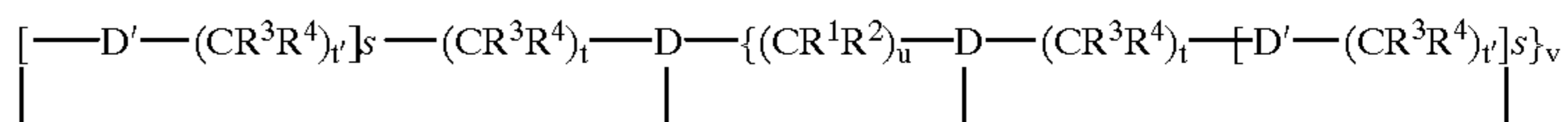
20. Method according to one of the claims described above, characterized in that chelating agents, sodium silicate and/or magnesium sulfate are added before delignification.

21. Method according to claim 20, characterized in that DTPA and/or DTPMPA are added as chelating agent before delignification.

22. Use of a manganese complex with the general formula



wherein Mt stands for manganese or iron, which can be present in the oxidation state II, III, IV or V or in mixtures of these states; n and m are an integer of 1-4, respectively; X is a coordinating ligand; p is an integer of 0 to 12; z is the charge of the complex and can be positive, neutral or negative; Y is a counter-ion or -molecule which depends on the charge of the complex; q is equal to z divided by the charge of Y; and L is a ligand and is represented by a macrocyclic organic molecule with the following general formula:



wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  can be either zero, H, alkyl, aryl or otherwise optionally substituted; D and D' are either N, NR, PR O, or S, wherein R can be substituted by H or alkyl or aryl or otherwise optionally substituted; t and t' are whole integers from 2 to 3, respectively; s is an integer between 2 and 4, u is an integer of 1 to 20, and v is 0 or 1;

wherein this metal complex is used with 0.00010%-0.1% based on bone dry fiber material, for application of a method according to one or more of the patent claims 1-21 for the delignification of fibrous material thereby reducing the residual lignin content of the fibrous material by at least 20% compared to the residual lignin content of the fibrous material prior to catalyst treatment.

\* \* \* \* \*