(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 May 2005 (19.05.2005)

PCT

(10) International Publication Number
WO 2005/045127 A1

(51) International Patent Classification[7]: D21C 9/10, 9/147

(21) International Application Number:
PCT/AU2004/001534

(22) International Filing Date:
8 November 2004 (08.11.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2003906155 7 November 2003 (07.11.2003) AU

(71) Applicant *(for all designated States except US)*: **COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION** [AU/AU]; Limestone Avenue, Campbell, Australian Capital Territory 2612 (AU).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: **CAI, Jackie, Yun,** [CN/AU]; 16 O'Driscol Court, Highton, Victoria 3216 (AU).

(74) Agent: **GRIFFITH HACK**; 509 St Kilda Road, Melbourne, Victoria 3004 (AU).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2005/045127 A1

(54) Title: A METHOD FOR BLEACHING LIGNOCELLULOSIC MATERIALS

(57) Abstract: A method of bleaching a lignocellulosic material comprising contacting the lignocellcellulosic material during a peroxide and/or oxygen bleaching process with a peroxide and/or oxygen bleaching agent, substituted urea-based additive such as an alkyl urea and an inorganic silicate such as sodium silicate. This combination of additives in the bleaching process improves the brightness of the bleached pulp without increasing energy and bleaching agent consumption.

A METHOD FOR BLEACHING LIGNOCELLULOSIC MATERIALS

RELATED APPLICATIONS

The present application claims priority from Australian provisional application 2003906156, the entire disclosure of which is hereby incorporated by reference.

TECHNICAL FIELD

The present invention relates to a method and bleaching medium for bleaching lignocellulosic material. More particularly, the present invention relates to the use of additives that improves the performance of peroxide and/or oxygen bleaching processes.

BACKGROUND OF THE INVENTION

Lignocellulosic materials such as wood pulps can be bleached with many kinds of bleaching agents including peroxides, oxygen, chlorine, chlorine dioxide and hypochlorite, and so on.

Chlorine-containing bleaching agents are inexpensive and effective. They are especially useful for lignin-containing cellulosic materials like wood pulps, due to their selective reactions on lignin. One major problem associated with the use of chlorine-containing bleaches is their great impairment on the environment. Unfortunately, chlorine-containing compounds are still predominantly used in paper pulp industry. This is because the chlorine-free bleaching agents like hydrogen peroxide and oxygen have limited bleaching action and are unable to achieve a satisfactory quality of bleached pulp economically.

To reduce the use of chlorine-containing agents

in pulp industry, an effort has been made to use peroxide and/or oxygen bleaching agents and improve the performance of the chlorine-free bleaching processes.

To date, a number of methods have been proposed for achieving this. Generally these methods involve the use of a bleaching assistant, activator or agent to enhance the bleaching effect of hydrogen peroxide and/or oxygen.

US Patent Nos. 4,392,975 and 5,034,096 describe methods for bleaching textiles and wood pulps using hydrogen peroxide assisted by cyanamide and derivatives thereof for improving the bleaching performance of hydrogen peroxide.

US Patent Nos. 6,248,209 and 6,342,124 describe methods of bleaching paper pulp using hydrogen peroxide or oxygen assisted by polyether compounds of a particular formula.

US Patent Nos. 5,145,558 and 5,013,404 and EP Patent No. 0639666 describe methods of bleaching paper pulp using hydrogen peroxide assisted by quaternary ammonium compounds.

US Patent No. H479 describes a method of bleaching paper pulp using hydrogen peroxide assisted by alkenylsuccinic anhydride.

US Patent Nos. 4,404,061 and 5,698,075 and EP Patent No. 1111033 describe improved methods of pulping and bleaching pulps by using peroxymonosulfuric acid or its salt peroxymonosulfate.

In addition to the above examples, a process is presently available for bleaching substrates containing

cellulose and lignocellulose using a hydrogen peroxide bleaching agent in combination with tetraacetylethylenediamine (TAED). TAED has poor water solubility, which can prevent it from being used in some commercial applications.

All the above methods suffer from various drawbacks, one of them being that they are not sufficiently efficient and effective for industrial bleaching practice.

Accordingly, there is still a need for an alternative method and bleaching medium that is efficient and effective in industrial lignocellulose bleaching operations.

SUMMARY OF THE INVENTION

According to the present invention there is provided a method of bleaching a lignocellulosic material comprising contacting the lignocellcellulosic material during a peroxide and/or oxygen bleaching process with a peroxide and/or oxygen bleaching agent, substituted urea-based additive and an inorganic silicate.

Although a large range of substituted urea-based additives are effective, the more preferred class of substituted urea-based additives are alkyl ureas. These substituted urea-based additives perform especially well in enhancing the performance of peroxide and/or oxygen bleaching agents in lignocellulose bleaching processes with minimum deterioration on fibre strength.

It has been found that a synergistic activation/acceleration bleaching effect can be achieved when an inorganic persulfate or perphosphate compound is used together with a substituted urea-based additive and

an inorganic silicate.

The present applicant has found that the use of a substituted urea-based additive, an inorganic silicate and an inorganic persulfate or perphosphate compound during a peroxide and/or oxygen bleaching process enhances the bleaching action of the peroxide and/or oxygen bleaching agent with reduced chemical and energy consumption.

The present invention also provides a bleach additive composition for use in bleaching lignocellulosic materials, the bleach additive composition containing one or more substituted urea-based additives and an inorganic silicate. The bleach additive composition may optionally further comprise one or more components selected from the group consisting of stabilisers, buffers and formulating agents.

The bleach additive composition preferably also contains an inorganic persulfate or perphosphate compound.

The bleach additive composition may be in the form of a solution, concentrate or solid. If in the form of a concentrate or solid, it can be diluted with water prior to use in a bleaching process.

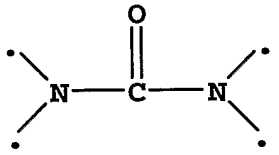
The present invention also provides for the use of a substituted urea-based compound as a bleaching additive in a peroxide and/or oxygen bleaching process conducted in the presence of an inorganic silicate, to improve the bleaching action in the bleaching process. There is also provided the use of a substituted urea-based compound and an inorganic silicate as bleaching additives in a peroxide and/or oxygen bleaching process to improve the bleaching action in the bleaching process.

The present invention also provides for the use of a substituted urea-based compound to increase the selectivity of a peroxide and/or oxygen bleaching agent in reaction with the lignin content of the cellulosic material over the carbohydrate content, in the presence of an inorganic silicate.

DETAILED DESCRIPTION OF THE INVENTION

According to the method of the present invention, a substituted urea-based compound and inorganic silicate are used as additives in a peroxide and/or oxygen bleaching process for bleaching lignocellulosic materials.

The term "substituted urea-based additive" or "substituted urea-based compound", which may be abbreviated to "substituted urea", is used to refer to a compound containing the following group:



Consequently, the term encompasses biureas and derivatives thereof as these compounds contain the group illustrated above. However, where compounds containing a single urea unit only are intended, the term "monoureas" will be used to distinguish from the broader class of ureas of which biurea is a member. In the case of biureas, these are suitably substituted biureas.

The term encompasses salt forms of such compounds, since by definition the salts are substituted urea-based compounds.

Aromatic and aliphatic ureas are encompassed by the term substituted urea-based additive.

It is noted, however, that the term does not include urea itself (H_2N-C(=O)-NH_2), since by definition urea is unsubstituted.

Although a large range of substituted urea-based additives are effective, the preferred substituted urea-based additives are alkyl-, alkenyl-, alkynyl-, aryl-, sulfonyl-, acyl-, alkoxyl-, halo- and imino- ureas, including derivatives and/or salts thereof.

The more preferred class of substituted urea-based additives is the alkyl ureas. The alkyl substituted urea may be monourea or a biurea.

By way of explanation, "alkyl urea" refers to urea substituted with an alkyl group or a derivative thereof. Unless otherwise indicated by the context, an alkyl urea, for example, can also be an acyl urea if the urea compound is also substituted with an acyl group. Such a compound may also be referred to as an alkyl acyl urea. It is also noted that the term "alkyl urea", for instance, encompasses dialkyl, trialkyl and tetraalkyl urea.

The term "alkyl" used either alone or in compound words such as "aralkyl" refers to straight chain, branched chain or cyclic hydrocarbon groups having from 1 to 10 carbon atoms, preferably 1 to 6 carbon atoms. Illustrative of such alkyl groups are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, neopentyl, hexyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and the like.

Of the alkyl ureas, those containing no covalent substituents other than the alkyl substituent are preferred. Of these alkyl ureas, those containing asymmetric substitution pattern (like N-alkyl and 1,1-dialkyl substitution) or tetraalkyl substitution (i.e. alkylureas other than 1,3-dialkyl ureas) produce excellent results.

Preferably, the alkyl group or groups are C1-C6 alkyl. More preferably, each alkyl group in the alkyl ureas include 1 to 4 carbon atoms.

Preferably the alkyl ureas are monoureas.

The most preferred alkyl ureas are 1,1-dimethylurea, 1,1-diethylurea, 1,1-dipropylurea, 1,1-dibutylurea and tetramethylurea.

The term "acyl urea" is used to refer to ureas containing at least one acyl group.

The term "acyl" denotes carbamoyl-, aliphatic-acyl group, acyl group containing an aromatic ring, which is referred to as aromatic acyl or an acyl group containing a heterocyclic ring, which is referred to as heterocyclic acyl. Preferably the acyl group or groups have 1 to 20 carbon atoms. More preferably, each acyl group in the acyl ureas has 1 to 14 carbon atoms. Examples of acyl include carbamoyl, such as $-C(O)-NH_2$, $-C(O)NHCH_3$ and so forth; straight chain or branched alkanoyl, such as acetyl, propanoyl, butanoyl, 2-methylpropanoyl, octanoyl; alkoxycarbonyl, such as ethoxycarbonyl; cycloalkylcarbonyl, such as cyclohexylcarbonyl; aroyl, such as benzoyl, toluoyl or naphthoyl; and aralkanoyl, such as phenylalkanoyl, for example, phenylacetyl.

Typical examples of acyl groups are benzoyl and acetyl.

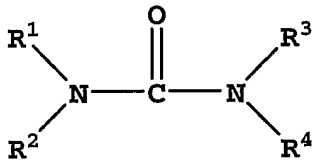
The substituted ureas and their salts, which have good water solubility, are particularly suitable for use in the present invention. Any organic or inorganic salt may be used, although for human health and safety reasons nitrate salts are not preferred. Examples of suitable salts are hydrochloride, sulfate, acetate and sulfonate.

A large number of substituted urea-based compounds of a range of classes are commercially available. Examples include 1,1-dimethylurea, 1,3-

dimethylurea, 1',1',3',3'-tetramethylurea, 1-ethylurea, 1,1-diethylurea, 1-benzoylurea, 1-benzylurea, guanylurea, N-guanylurea sulfate, hydroxyethylurea, acetylurea, 1,3-diethylurea, tetraethylurea, allylureas, diallylureas and cyclohexylurea.

Either one type or a mixture of substituted urea-based additives can be used.

In one embodiment of the invention, the substituted urea-based additive is of Formula I:



Formula I

wherein

R^1 is selected from the group consisting of alkyl or a derivative thereof, alkenyl or a derivative thereof, alkynyl or a derivative thereof, aryl or a derivative thereof, sulfonyl or a derivative thereof, acyl or a derivative thereof, alkoxyl, halo and imino or their derivatives thereof; and

R^2 to R^4 each are independently selected from the group consisting of H, alkyl or a derivative thereof, alkenyl or a derivative thereof, alkynyl or a derivative thereof, aryl or a derivative thereof, aminocarbonyl or a derivative thereof, acyl, sulfonyl, alkoxyl, halo and imino or their derivatives thereof.

According to one embodiment of the invention, at least one of R^2 to R^4 is H.

Compounds containing aminocarbamoyl as one of the substituents R^2 to R^4 are commonly referred to as biureas.

In the foregoing, the term "derivative" refers

to replacement of one or more hydrogen atoms in the said compound or substituent by one or more functional groups selected from alkyl, alkenyl, alkynyl, aryl, acyl, sulfonyl, hydroxyl, alkoxyl, halo and amine. Where aryl groups are mentioned, the aryl group is preferably carbocyclic, such as phenyl, napthyl and so forth. The most preferred substituted urea-based compounds are not further derivatised.

The term "inorganic silicate" is used broadly to encompass alkali metal silicates and alkali metal metasilicates. One specific example is sodium silicate or sodium metasilicate.

Although inorganic silicate is sometimes used as a stabilizer in bleaching operations, in the method of this invention, the function of the silicate is far beyond a stabilizing role. Replacement of the inorganic silicate with another organic or inorganic stabiliser in the bleaching system containing peroxide (and/or oxygen) and a substituted urea, does not produce the same results as produced with the inorganic silicate, i.e. diminishes the activated bleaching effect. Test work conducted using the substituted urea, inorganic silicate and bleaching agent on non-lignocellulosic material such as cotton also did not produce bleaching enhancement (i.e. no more than using peroxide alone). Therefore, without wishing to be bound by theory, it is believed that the inorganic silicate is involved in the production of an active complex formed in situ with the substituted urea-based additive, the bleaching agent, and possibly another component present in the lignocellulosic material.

Peroxide and/or oxygen can be used as the bleaching agent, however, it is preferred for the bleaching agent to include a peroxide. The term "peroxide" is used herein in the broadest sense to refer to all peroxide-containing or peroxide-generating/releasing

compounds, such as hydrogen peroxide, sodium peroxide, sodium perborate, sodium percarbonate, peroxymonosulfate, peroxymonosulfuric acid, potassium peroxydisulfate, sodium peroxydisulfate (often called persulfate), ammonium persulfate, potassium peroxydiphosphate, ammonium peroxydiphosphate and peroxy acids. Hydrogen peroxide is the most commonly used peroxide bleaching agent, and therefore in one embodiment of the invention, the bleaching agent is hydrogen peroxide.

Any other additives known in the art can also be present during the peroxide and/or oxygen bleaching process. Possible additives include peroxide activators, stabilisers, buffers, chelating agents, alkali sources and formulating agents. These are well known in the art of the invention. The additives used may have more than one function. Further, for the avoidance of any doubt, it is noted that the singular forms "a" "an" and "the" should be read as encompassing plural forms, and less the context clearly indicates otherwise. Consequently, for example, the reference to "a substituted urea-based additive" should be read as encompassing one, two or more such substituted urea-based additives.

It has been found that an inorganic persulfate or perphosphate can be used in conjunction with the peroxide, sodium silicate and the substituted urea-based additive to achieve a further improved bleaching effect or a synergistic activation/acceleration effect.

It is contemplated that a substituted urea-based additive or combination of the substituted urea-based additive with the inorganic silicate, and/or the inorganic peroxide compound could be supplied in a pre-packaged form with other components. Such components may help to maintain the substituted urea-based additive or the additive combination in a solution, mixture or suspension

form, or in a state resistant chemical change. Examples of these additional components include stabilisers, buffers and formulating agents. The composition may be supplied in a suitable ratio, so that the composition can be simply diluted to the required extent to be used directly in the bleaching operation.

The term "stabiliser" refers to an agent that controls the decomposition rate of the peroxide bleaching agent, and combines with metal impurities that may catalyse decomposition of peroxide and induce fiber damage. Stabilisers are well known in the art of the invention. Examples of bleaching stabilisers are the inorganic stabilisers, such as sodium silicate and polyphosphates, and the organic stabilisers such as aminocarboxylates (diethylenetriaminepentaacetic acid), hydroxycarboxylates (glucoheptonic acid) and organophosphonates [ethylenediaminetetra (methylenephosphonic acid) and diethylenetriaminepenta (methylenephosphonic acid)]. These are sometimes referred to as sequestering or chelating agents.

The term "buffer" refers to an agent that minimises the change in the pH of a solution when an acid or base is added to the solution. Examples of suitable buffers are sodium acetate/acetic acid, citric acid/sodium citrate, potassium hydrogen phthalate/HCl and citric acid/disodium hydrogen phosphate.

The term "formulating agents" generally refers to additives such as surfactants, solvents, binders and encapsulating materials.

The invention can be implemented in most existing bleaching plants and processes that utilise peroxide and/or oxygen bleaching agents with little or no alterations to the equipment of the plant.

The method of the present invention can be carried out over a broad range of operating conditions. The optimal operating conditions for the method will depend, amongst other things, on the precise nature of the substrate being bleached and the required properties of the final product.

Preferably, the lignocellulosic material contacts the peroxide and/or oxygen bleaching agent and the additives (substituted urea and silicate) at the peroxide and/or oxygen bleaching stage of the bleaching process.

The substituted urea-based additives may, in fact, be contacted with the lignocellulosic material before, at the same time as, or following contact of the cellulosic material with the peroxide and/or oxygen bleaching agent. Consequently, it will be understood that the reference to the bleaching process broadly encompasses the period preceding and following contacting of the lignocellulosic material with the bleach. However, it is preferred that the peroxide and/or oxygen bleaching agent be contacted with lignocellulosic material in the presence of the substituted urea-based additive and the inorganic silicate. The additives may additionally be used in multiple stages.

Preferably, the substituted urea-based additive is used in an amount of 0.1-5.0% (more preferably 0.1-3.0%) by weight based on the amount of oven-dried lignocellulosic material (such as pulp).

Preferably, the inorganic silicate is used in an amount of 0.5% - 5.0%, more preferably from 1 to 2%, on weight of oven dried lignocellulosic material (such as pulp).

In the situation where the bleaching agent is hydrogen peroxide, preferably the peroxide is used in an amount of 0.1-5.0% (more preferably 0.1-2.5%) by weight based on the amount of oven-dried lignocellulosic material (such as pulp).

In the situation where an inorganic persulfate or perphosphate compound is used, a preferred ratio of the substituted urea-based compound to the inorganic peroxide compound in the additive composition ranges from 1:1 to 10:1.

The peroxide bleaching process is preferably conducted at a temperature between 20°C and 100°C, preferably 50°C and 100°C, and more preferably between 55°C and 90°C. When oxygen bleaching is conducted, the temperature is preferably between 80ºC and 115ºC.

The bleaching process is suitably conducted in an alkaline environment. This can be achieved by the addition of an alkaline medium. Any suitable alkaline medium can be used. The amount of alkaline medium to be added, based on the amount of oven-dried pulp, is preferably from 0.1% to 3.0% in terms of sodium oxide (Na_2O), more preferably 0.2 to 3.0%, or a comparative amount for other alkaline mediums. When an inorganic peroxide compound is incorporated, the bleaching process is more preferably carried out at relatively mild conditions in order to minimise cellulose degradation.

The term "lignocellulosic material" refers to lignin-containing cellulosic materials. The term encompasses wood fibres, non-wood natural fibres, secondary or recycled fibres, and pulps originating from any of the above mentioned fibres.

In the context of wood fibres, it is noted that trees are classified botanically as softwoods and hardwoods. Softwoods generally contain a higher percentage of lignin and lower percentage of hemicellulose than the hardwoods.

The non-wood lignosic fibres include bast fibres such as hemp, jute, flax and kenaf; stalk or core fibres from cereal grains, grasses, and other straw.

Pulps can be classified as mechanical pulps, chemi-mechanical pulps, semi-mechanical pulps and chemical pulps, according to the pulping processes used. More than 70% of pulps produced industrially are chemical pulps. Chemical pulps are most often sulfite pulps or kraft pulps. Sulfite pulps constitute 5% of chemical pulping operations, and utilise bisulfite or sulfite in the pulping process. Kraft pulps constitute 95% of all industrial chemical pulping operations, and typically utilise a mixture of sodium hydroxide and sodium sulfide in the pulping process.

The methods of the present invention are suitable for use on both softwood and hardwood fibres, and non-wood lignosic fibres; and pulps derived from these fibres by various pulping processes.

The methods of the present invention are preferably for use on chemical pulps derived from the lignocellulosic fibres, and most preferably for use on kraft pulp derived from these fibres.

The method is also effective for bleaching both unbleached pulp and the pulp that have been pre-bleached by various pulp bleaching sequences, such as, O(EO), O(EOP), OZ(EOP), D(EO), OD(EOP) and (EOP)(D/C)(EOP).

In the above sequences mentioned, the standard abbreviations known in the art are used as short-hand reference for the following stages:
C=chlorination; reaction with elemental chlorine in acidic medium.
D=chlorine dioxide; reaction with ClO_2 in acidic medium.
H=hypochlorite; reaction with hypochlorite in alkaline medium.
Z=ozone; reaction with ozone in acidic medium.
E=alkaline extraction; dissolution of reaction products with NaOH;
O=oxygen; reaction with oxygen at high pressure.
P=peroxide; reaction with peroxide in alkaline medium.

The invention allows bleaching of substrates containing lignocellulose to be carried out at relatively milder operating conditions, which reduces energy and bleaching agent consumption and preserves desirable qualities of the substrate being bleached.

The process is suitably incorporated in one or several stages of a multiple step bleaching sequence. Any combination of suitable stages known or developed in the art may be used in combination with the bleaching process of the present invention.

The invention allows lignocellulosic materials to be bleached to ISO brightness of 90% with a Total Chlorine-Free process (TCF process). Examples of TCF processes include a bleaching process involving oxygen bleaching/delignification stage followed by a peroxide bleaching stage, an oxygen bleaching/delignification stage followed by an ozone treatment and peroxide bleaching stage, and multi-peroxide bleaching processes. The stages outlined above are all chlorine-free procedures.

Where there are multiple bleaching stages, the

additives may be used in one, some or all of the bleaching stages. For example, the substituted urea-based additive may be contacted with the lignocellulosic material prior to a peroxide bleaching stage or in an extraction stage following an oxygen bleaching/delignifying stage. These applications are also included in the present invention.

The use of a substituted urea-based additive increases the selectivity of a peroxide and/or oxygen bleaching agent in reaction with the lignin content of the cellulosic material over the carbohydrate content. As a result, the lignin content of the cellulosic material is reduced with minimal degradation on cellulose thereby maintaining the viscosity and/or strength of the cellulosic material.

The term "bleaching medium" is used broadly to refer to a bleaching liquid, concentrate or solution. The bleaching medium of the present invention contains at least a bleaching agent containing peroxide and/or oxygen and a substituted urea-based additive. These are described above in full with respect to the method of the invention.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features.

ILLUSTRATIVE EXAMPLES

The present invention will now be described with reference to the following non-limiting Examples.

Each example consisted of a set of trials that involved bleaching a lignocellulosic material with the control bleaching solution, and a bleaching solution of the present invention. The bleaching solutions of the present invention were made by adding a substituted urea-based additive to the control solution (sodium silicate was added in the control solution, if not specified).

A control bleaching solution used in the trials conducted by the applicant consisted of the following:

Chemicals	% on weight of oven dried pulp (on o.d.pulp)
Sodium Silicate	1.2-1.8
H_2O_2	0.5-2.0
NaOH	0.1-0.8

The substituted urea-based additives used in the following examples included:

1,3-dimethylurea (1,3-DMU)
1,1-dimethylurea (1,1-DMU)
1',1',3',3'-tetramethylurea (TMU)
1,1-diethylurea (1,1-DEU)
1',1',3',3'-tetraethylurea (TEU)
N-allylurea
benzoylurea
benzylurea
N-guanylurea sulfate
(2-hydroxyethyl)urea

Procedure

Pulp samples were first de-watered in a mechanical press to about 27% to 34% consistency and crumbed. Samples of 50g each (o.d. basis) were then placed in a plastic bag and make up liquor and chemicals added to give a pulp consistency of 20 to 24%, if not specified.

The treated pulp was held in a waterbath or an oven at a set temperature for certain hours.

After bleaching, the bleached samples were washed and neutralised with diluted sulfuric acid.

The ISO brightness (%) and CIE whiteness (%) of bleached pulp samples were measured on a GretagMacbeth Color-Eye 7000A Spectrophotometer.

Examples 1 to 9 involved the bleaching of a hardwood eucalypt kraft pulp.

The following trials were carried out using unbleached native forest eucalypt Kraft pulp from a commercial mill (with Kappa number 9.2). The Kappa numbers of the pulps were determined according to Australian Standard method AS 1301.201m-86.

Example 1. Bleaching of unbleached eucalypt kraft pulp with 2% H_2O_2 at 70°C for 4 hours.

Trial No.	Additive in the control solution (% on o.d. pulp)	CIE Whiteness	ISO Brightness
1	Control	10.52	60.47
2	0.65% 1,1-DEU	21.81	65.47
3	1.0% TMU	19.72	64.37

Trial No. 1 was carried out using the control solution. Trial Nos. 2 and 3 were carried out using a bleaching solution of the present invention, i.e. containing a substituted urea-based additive in the presence of sodium silicate. As can be seen, a greater degree of whiteness and brightness was achieved in Trial Nos. 2 and 3.

Example 2. Bleaching of unbleached eucalypt kraft pulp with 2% H_2O_2 at 90°C for 2.5 hours.

Trial No.	Additive in the control solution (% on o.d. pulp)	CIE Whiteness	ISO Brightness
4	Control	18.43	63.76
5	0.65% 1,1-DEU	30.29	68.81
6	0.65% benzoylurea	21.38	64.96

Trial No. 4 was carried out using the control solution. Trial Nos. 5 and 6 were carried out using a bleaching solution of the present invention. Again, using a bleaching solution of the present invention achieved a greater degree of whiteness and brightness.

Example 3. Bleaching of unbleached eucalypt kraft pulp with 2% H_2O_2 at 55°C for 28 hours.

Trial No.	Additive in the control solution (% on o.d. pulp)	CIE Whiteness	ISO Brightness
7	Control	23.01	66.42
8	0.25% 1,1-DEU	30.20	69.34
9	0.5% 1,1-DEU	34.12	70.94
10	1.0% 1,1-DEU	39.71	73.57

As can be seen, a greater degree of whiteness and brightness was achieved at 55ºC when the control solution contained a substituted urea-based additive.

Example 4. Bleaching of unbleached eucalypt kraft pulp with 2% H_2O_2 at 55°C for 19 hours.

Trial No.	Additives in the control solution (% on o.d. pulp)	CIE Whiteness	ISO Brightness
11	Control	13.63	61.52
12	1.0% 1,1-dimethylurea	20.03	65.02
13	1.0% 1,1-diethylurea	27.62	68.39
14	1.0% TMU	23.13	66.27
15	1.0% TEU	16.52	63.59
16	1.0% N-allylurea	16.40	63.32
17	0.6% 1,3-DMU	14.70	62.18
18	0.6% N-guanylurea sulfate	17.12	63.45
19	0.6% benzylurea	19.95	64.48
20	0.6% (2-hydroxyethyl)urea	14.52	61.96

The results in Example 4 demonstrate the effectiveness of variously substituted ureas.

Example 5. Bleaching of eucalypt kraft pulp (unbleached) with triple P (peroxide) Stages

The unbleached Kraft pulp was bleached sequentially or successively with triple peroxide bleaching processes. The first stage of the bleaching process was carried out at a temperature of 55ºC for 38 hours with 2% H_2O_2 and pulp consistency of 21.4%. Both the second and third stages of the bleaching process were carried out at a temperature of 55ºC for 23 hours with 1% H_2O_2 and pulp consistency of 30%.

Trial No.	Additive in the control solution (% on o.d. pulp)	CIE Whiteness	ISO Brightness	Pulp Viscosity (mPa.s)
21	Control	57.689	80.529	7.50
22	1.0% 1,1-DEU	74.738	88.857	7.29
23	2.0% 1,1-DEU	77.631	89.660	7.14

Trial No. 21 was carried out using the control solution at each of the bleaching stages. Trial Nos. 22 and 23 were carried out using a bleaching solution of the present invention, i.e. containing a substituted urea-based additive in the presence of sodium silicate, in each of the bleaching stages.

These results clearly demonstrate the effectiveness and selectiveness of the substituted urea-based additive, i.e. substantially improved pulp whiteness and brightness with minor change in pulp viscosity. The results also demonstrate that by employing a substituted urea-based additive, a high level of pulp whiteness and brightness (fully bleached pulp) can be achieved with a Totally Chlorine-Free (TCF) process.

* The pulp viscosity was measured according to a Standard Method TAPPI T230.

Example 6. Comparative bleaching trials

A substituted urea-based additive of the present invention was compared with the prior art additives such as N,N,N',N'-tetraacetylethylenediamine (TAED), nonanoylbenzene sulfonate (NOBS) and cyanamide (nitrilamine).

Bleaching was carried out at a temperature of 55ºC for 20 hours with 2% H_2O_2.

Trial No.	Additives in the control solution (% on o.d. pulp)	CIE Whiteness	ISO Brightness
24	Control	15.72	62.81
25	0.7% cyanamide	20.11	64.01
26	0.7% TAED	22.01	64.90
27	0.7% NOBS	17.67	63.81
28	0.7% 1,1-DEU	25.65	66.99

Results of these comparative trials show that under the conditions examined, 1,1-DEU is significantly superior to the prior art additives in Kraft pulp bleaching.

Example 7. Bleaching of unbleached eucalypt kraft pulp with 2% H_2O_2 at 70°C for 2 hours.

Trial No.	Additives in the control solution (% on o.d. pulp)	CIE Whiteness	ISO Brightness
29	Control	13.17	60.93
30	0.6% persulfate	18.08	63.16
31	0.6% 1,1-DEU	21.09	65.02
32	0.3% potassium persulfate + 0.3% 1,1-DEU	23.92	66.96

The results of Trial No. 32 highlight the synergistic effect of a substituted urea-based additive with an inorganic peroxide compound.

Example 8. Bleaching of D(EO) pre-bleached eucalypt kraft pulp with 2% H_2O_2 at 55°C for 24 hours.

The Kraft pulp samples used for Example 8 were pre-bleached with a standard sequence, i.e. chlorine dioxide was used to treat the pulp first (followed by a wash stage), and then an alkali extraction boosted with oxygen (again followed by a wash stage). In standard notation this sequence is abbreviated as D(EO), where D = chlorine dioxide, E = alkali extraction and O = oxygen. Bracketing the letters (EO) together indicates that the two chemicals were added concurrently, i.e. without a wash stage between the chemical treatments. After this pre-bleaching sequence, the Kappa number was 2.4.

Trial No.	Additives in the control solution (% on o.d. pulp)	CIE Whiteness	ISO Brightness
33	Control	64.36	83.56
34	1% 1,1-DEU	68.88	86.18
35	2% 1,1-DEU	72.84	88.01

The results show that the substituted urea-based additive can also be used in a conventional bleaching sequence to provide a substantial increase in brightness and whiteness of the D(EO) pulp.

Example 9. Bleaching of O(EOP) pre-bleached eucalypt kraft pulp.

The Kraft pulp samples used in Example 9 were pre-bleached with O(EOP) sequence. After this pre-bleaching sequence, the Kappa number was 4.1.

In Example 9, the O(EOP) pulp was sequentially bleached with double peroxide bleaching stages. The first stage of the bleaching process was carried out at a temperature of 55ºC for 40 hours with 2% H_2O_2. The second stage of the bleaching process was carried out at a temperature of 55ºC for 12 hours with 0.5% H_2O_2.

Trial No.	Additives in the control solution (% on o.d. pulp)	CIE Whiteness	ISO Brightness
36	Control	66.50	84.33
37	1% 1,1-DEU +0.2% potassium persulfate	75.09	88.96

The results of these trials demonstrate that by employing a combination of the substituted urea-based additive with persulfate in the presence of sodium silicate, a high level of pulp whiteness and brightness can be achieved with a Totally Chlorine-Free (TCF) process.

Examples 10 to 12 involved the bleaching of a softwood pine kraft pulp. The pine kraft pulp used for the trials in Examples 10 to 12 was pre-bleached with OZ(EOP)bleaching sequence. After this pre-bleaching sequence, the pulp brightness was 77%.

Example 10. Bleaching of the OZ(EOP) pine kraft pulp with 2% H_2O_2 at 55ºC for 21 hours

Trial No.	Additive in the control solution (% on o.d. pulp)	CIE Whiteness	ISO Brightness
38	Control	77.36	88.83
39	1.5% 1,1-DEU	83.78	92.22

Trial No. 38 was carried out using the control solution. Trial No. 39 was carried out using a bleaching solution of the present invention. As can be seen, a greater degree of whiteness and brightness was achieved in

Trial No. 39.

Example 11. Bleaching of the OZ(EOP) pine kraft pulp with 2% H_2O_2 at 70ºC for 3.5 hours

Trial No.	Additive in the control solution (% on o.d. pulp)	CIE Whiteness	ISO Brightness
40	Control	70.50	86.54
41	1.5% 1,1-DMU	73.15	88.02
42	1.5% 1,1-DEU	76.96	89.80

The results in Examples 10 and 11 demonstrate that by employing the bleaching conditions of the present invention, a pulp brightness of 90% ISO can be achieved with a Totally Chlorine-Free (TCF) bleaching process.

Example 12. Bleaching of the OZ(EOP) pine kraft pulp with 2% H_2O_2 at 70ºC for 3.5 hours in the absence of sodium silicate

Example 12 was designed to test the impact of the sodium silicate on the bleaching performance.

In Example 12, the same OZ(EOP) pine kraft pulp was subjected to bleaching under the same conditions as those used in Example 11, except that sodium silicate was replaced by a suitable amount of Stabilisator 9188 (Böhme), a commercial organic stabiliser.

Trial No.	Additive in the control* solution (% on o.d. pulp)	CIE Whiteness	ISO Brightness
43	Control* (no silicate)	70.93	86.81
44	1.5% 1,1-DMU	70.35	86.42
45	1.5% 1,1-DEU	70.69	86.77

Similar results were obtained with other stabilisers such as DTMPA = diethylenetriamine-penta(methylenephosphonic) acid.

By comparing the results of Trials 43 to 45 with

those of Trials 40 to 42 respectively, it can be seen that the inorganic silicate has a significant impact on the bleaching operation, beyond its role as a stabilizer in this invention. The alkylurea compounds could not provide any improvement in pulp brightness in the absence of sodium silicate.

Overall, the trials show that the addition of a substituted urea-based additive and an inorganic silicate to a peroxide bleaching solution greatly enhances the performance of the bleaching process, particularly in terms of whiteness and brightness. The trials also show that the additives of the present invention work well at different temperatures and over varying time periods, making it suitable for use in industrial bleaching processes. The process may be incorporated with other bleaching and/or delignifying steps in a paper pulp treatment or production operation.

While the present application has been illustrated by bleaching paper pulps, it is to be understood that other lignocellulosic materials may be bleached in an identical or similar fashion. Accordingly, the bleaching of all such materials using a substituted urea-based additive and inorganic silicate or combinations of these additives with other additives and/or activators known in the art is expressly within the scope of the present invention.

It will be understood to persons skilled in the art of the invention that many modifications may be made without departing from the spirit and scope of the invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of bleaching a lignocellulosic material comprising contacting the lignocellcellulosic material during a peroxide and/or oxygen bleaching process with a peroxide and/or oxygen bleaching agent, substituted urea-based additive and an inorganic silicate.

2. The method of claim 1, wherein the substituted urea-based additive is selected from alkyl-, alkenyl-, alkynyl-, aryl-, sulfonyl- and acyl- ureas, or a derivative and/or salt thereof.

3. The method of claim 1, wherein the substituted urea-based additives is an alkyl urea or a derivative and/or salt thereof.

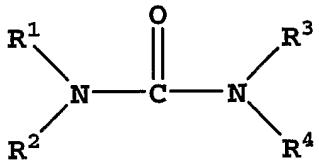
4. The method of claim 3, wherein the alkyl urea contains an asymmetric substitution pattern or tetraalkyl substitution.

5. The method of claim 3 or claim 4, wherein the alkyl group or groups of the alkyl urea are C1-C6 alkyl.

6. The method of any one of claims 3 to 5, wherein the alkyl urea is a monourea.

7. The method of claim 3, wherein the alkyl urea is 1,1-diethylurea, tetramethylurea, 1,1-dimethylurea, 1,1-dipropylurea and 1,1-dibutylurea or a salt thereof.

8. The method of claim 1, wherein the substituted urea-based additive is of Formula I:



Formula I

wherein

R^1 is selected from the group consisting of alkyl or a derivative thereof, alkenyl or a derivative thereof, alkynyl or a derivative thereof, aryl or a derivative thereof, sulfonyl or a derivative thereof, and acyl or a derivative thereof; and

R^2 to R^4 each are independently selected from the group consisting of H, alkyl or a derivative thereof, alkenyl or a derivative thereof, alkynyl or a derivative thereof, aryl or a derivative thereof, aminocarbonyl or a derivative thereof, acyl or a derivative thereof, sulfonyl or a derivative thereof, alkoxyl or a derivative thereof, halo and imino or a derivative thereof,

or a salt thereof.

9. The method of any one of claims 1 to 8, wherein the inorganic silicate is selected from alkali metal silicates and alkali metal metasilicates.

10. The method of any one of claims 1 to 9, wherein the peroxide is hydrogen peroxide.

11. The method of any one of claims 1 to 10, wherein the lignocellulosic material is contacted with any one or more compounds selected from additional peroxide activators, stabilisers, buffers, chelating agents, alkali sources and formulating agents, during the peroxide and/or oxygen bleaching process.

12. The method of any one of claims 1 to 11, wherein the lignocellulosic material is contacted with an inorganic peroxide activator selected from inorganic persulfate or inorganic perphosphate or salts thereof during the peroxide and/or oxygen bleaching process.

13. The method of claim 12, wherein the ratio of substituted urea-based compound to the inorganic peroxide activator selected from persulfate or perphosphate contacted with the lignocellulosic material is in within the range of 1:1 to 10:1.

14. The method of any one of claims 1 to 13, wherein the substituted urea-based additive is used in an amount of 0.1-5.0% by weight based on the amount of oven-dried lignocellulosic material.

15. The method of any one of claims 1 to 14, wherein the inorganic silicate is used in an amount of 0.5% - 5.0% by weight of oven dried lignocellulosic material.

16. The method of any one of claims 1 to 15, wherein the bleaching agent is hydrogen peroxide, and the hydrogen peroxide is contacted with the lignocellulosic material in an amount of 0.1-5.0% by weight based on the amount of oven-dried lignocellulosic material.

17. The method of any one of claims 1 to 16, wherein peroxide is used as the bleaching agent, and the bleaching process is conducted at a temperature of between 20°C and 100°C.

18. The method of any one of claims 1 to 16, wherein the oxygen is used as the bleaching agent, and the bleaching process is conducted at a temperature of between 85ºC and 115ºC.

19. The method of any one of claims 1 to 18, wherein the process is conducted in an alkaline environment.

20. A process for the treatment of a lignocellulosic material, comprising the method of any one of claims 1 to 19.

21. A process for the production of paper, comprising the method of any one of claims 1 to 19.

22. A product produced by the method of any one of claims 1 to 19, or produced by the process of any one of claims 20 and 21.

23. A bleach additive composition for use in bleaching lignocellulosic materials, the bleach activator composition comprising one or more substituted urea-based additives and an inorganic silicate.

24. The bleach additive composition of claim 23, further comprising one or more components selected from the group consisting of stabilisers, activators, chelating agents, buffers, alkali sources and formulating agents.

25. The bleach activator composition of claim 23 or claim 24, further comprising an inorganic persulfate or perphosphate compound.

26. The bleach activator composition of claim 25, wherein the ratio of substituted urea-based compound to inorganic persulfate or perphosphate compound is in within the range of 1:1 to 10:1.

27. Use of a substituted urea-based compound as a bleaching additive in a peroxide and/or oxygen bleaching process conducted in the presence of an inorganic silicate, to improve the bleaching action in the bleaching

process.

28. Use of a substituted urea-based compound and an inorganic silicate as bleaching additives in a peroxide and/or oxygen bleaching process to improve the bleaching action in the bleaching process.

29. Use of a substituted urea-based compound to increase the selectivity of a peroxide and/or oxygen bleaching agent in reaction with the lignin content of the cellulosic material over the carbohydrate content, in the presence of an inorganic silicate.

30. Use of a substituted urea-based compound and an inorganic silicate as bleaching additives in a total chlorine free or an elemental chlorine free bleaching sequence to improve final pulp brightness.

31. Use of a substituted urea-based compound and an inorganic silicate as bleaching additives to bleach pulp to at least 90% ISO brightness in a total chlorine free process.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2004/001534

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. [7]: D21C 9/10, 9/147

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(7): D21C 9/10, 9/147

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DWPI + D21C 9/10, 9/147 + (urea or silicate)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5246543 A (Meier et al.), 21 September 1993 Whole document (Especially Column 6, lines 15-28 and claims 1, 3 and 21).	1-31
Y	US 6380142 B (Vogt et al.), 30 April 2002 Whole document	1-31
Y	Derwent Abstract Accession No. 95-273938/36, Class F09 SE 9303971 A (SUNDS DEFIBRATOR IND AB), 31 May 1995	1-31
Y	Derwent Abstract Accession No. 2001-560486/63, Class F09 JP 2001192991 A (TSUKUBA LIAISON KENKYUSHO KK), 17 July 2001	1-31

☐ Further documents are listed in the continuation of Box C ☒ See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 December 2004	21 DEC 2004
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized officer **ADRIAN GILLMORE** Telephone No : (02) 6283 2125

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/AU2004/001534

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
US	6380142	DE	19948989	EP	1092762		
US	5246543	CA	2023429	EP	0415149	US	5091054
JP	2001192991	NIL					
SE	9303971	NIL					

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX