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(54) Ethylenediaminetriacetic acid and salts thereof as chelating agents in pulp bleaching

Ethylendiamintriessigsäure und ihre Salze als chelatbildende Mittel für das Bleichen von Zellstoff

L'acide éthylène diamine tri-acétique et les sels obtenus à partir de celui-ci comme agents de chélation dans le blanchiment de pâte

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US-A- 4 732 650 **US-A- 5 250 728**

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Description

BACKGROUND OF THE INVENTION

[0001] The invention pertains to a method of inhibiting decomposition of hydrogen peroxide as well as to a method for pre-treating wood pulp prior to bleaching.

[0002] Hydrogen peroxide solutions are commonly used for bleaching cellulosic materials, including paper pulps, cotton, linen, jute, etc. However, the peroxide should be stabilized to prevent premature depletion thereof, in view of the deleterious presence of metal ions such as iron, manganese and copper. Conventionally, sodium silicate has been used as a peroxide bleach stabilizer, but tends to form insoluble silicates which can be deposited onto the fibers being bleached, as well as onto the apparatus.

[0003] Similarly, prior to bleaching of pulps, a pretreatment with a chelating agent is a standard operation in order to control the metal profile of the pulp. Chelant pre-treatment is a key factor in achieving feasible brightness levels and viscosities upon bleaching/delignification with peroxide. Decomposition of peroxide under alkaline conditions is greatly influenced by the presence of certain inorganic compounds which behave as peroxide decomposition catalysts. Transition metal ions, such as manganese, iron and copper are examples of such catalysts, and thus should be removed prior to bleaching. Such deleterious transition metal ions can be sequestered by the chelating agent and are subsequently washed out of the system in a subsequent washing step.

[0004] The bleaching process with peroxide usually takes place between a pH of 10 and 11 and a temperature of 71-77°C. Under these alkaline conditions, the following reaction occurs:

$$H_2O_2 + OH^- \rightarrow OOH^- + H_2O$$

The perhydroxyl ion (OOH^-) created is what performs the bleaching. However, if transition metals are present, the following reaction takes place:

$$M + H_2O_2 \rightarrow M^+ + HO^- + HO^\cdot$$

The radicals created enhance the decomposition process. Manganese is the metal of most concern when peroxide is the bleaching agent used.

[0005] When hydro-sulfite is the preferred bleaching agent, the metal of most concern is iron. Hydro-sulfite bleaches pulp by a reduction reaction with the chromofors in the pulp. If iron is present, however, the hydro-sulfite will reduce the iron before the chromofors, hence a larger amount of bleach is needed.

[0006] Basta et al., "Reducing Levels of AOX - Part 3, Lowering of Kappa No. Prior to ClO_2 Bleaching", pgs. 23-33, discloses that pre-treatment with ethylenediaminetetraacetic acid (EDTA) at a pH of between 5 and 7 substantially improves delignifying and brightening action of hydrogen peroxide on oxygen predelignified softwood kraft pulp. EDTA performed better in this regard than other chelating agents tested, namely, DTPA, TRILON ES9910 and DEQUEST 2060S. Similarly, US-A-No. 4,732,650 discloses the silicate-free bleaching of wood pulp by the combination of a pre-treatment of the pulp with a polyaminocarboxylic acid or salt such as ethylenediaminetetraacetic acid, followed by a bleaching with a peroxide solution together with stabilizing components.

[0007] Ethylenediaminetriacetic acid (ED3A) and its salts (such as $ED3ANa_3$) have applications in the field of chelating chemistry, and may be used as a starting material in the preparation of strong chelating polymers, oil soluble chelants, surfactants and others. Conventional routes for the synthesis of ethylenediaminetriacetic acid were achieved via its N-benzyl derivative, which was subsequently hydrolyzed in alkaline solutions to $ED3ANa_3$, thus avoiding cyclization to its 2-oxo-1,4-piperazinediacetic acid (3KP) derivative. One example of the synthesis of ethylenediamine-N, N,N'-triacetic acid is disclosed in *Chemical Abstracts* 78, Vol. 71, page 451, no. 18369c, 1969. There it is stated that ethylenediamine reacts with ClH_2CCO_2H in a 1:3 molar ratio in basic solution at 10°C for 24 hours to form a mixture from which ethylenediamine-N,N,N'-triacetic acid can be separated by complexing the same with Co(III). The resulting cobalt complexes can be isolated through ion exchange.

[0008] US-A-5,250,728 discloses a simple process for the synthesis of ED3A or its salts in high yield. Specifically, a salt of N,N'-ethylenediaminediacetic acid ($ED2AH_2$) is condensed with stoichiometric amounts, preferably slight molar excesses of, formaldehyde, at temperature between 0° and 110°C, preferably 0° to 65°C and pH's greater than 7.0 to form a stable 5-membered ring intermediate. The addition of a cyanide source, such as gaseous or liquid hydrogen cyanide, aqueous solutions of hydrogen cyanide or alkali metal cyanide, in stoichiometric amounts or in a slight molar excess, across this cyclic material at temperatures between 0° and 110°C, preferably between 0° and 65°C, forms ethylenediamine N,N'-diacetic acid-N'-cyanomethyl or salts thereof (mononitrile-diacid). The nitrile in aqueous solutions may be spontaneously cyclized in the presence of less than 3.0 moles base: mole $ED2AH_2$, the base including alkali metal or alkaline earth metal hydroxides, to form 2-oxo-1,4-piperazinediacetic acid (3KP) or salts thereof, which is the desired cyclic intermediate. In the presence of excess base, salts of ED3A are formed in excellent yield and purity. This patent also discloses an alternative embodiment in which the starting material is $ED2AH_aX_b$, where X is a base cation, e.g., an alkali or alkaline earth metal, a is 1 to 2, and b is 0 to 1 in aqueous solutions. The reaction mixture also can be acidified to ensure complete formation of carboxymethyl-2-oxopiperazine (the lactam) prior to the reaction. Formaldehyde is added, essentially resulting in the hydroxymethyl derivative. Upon the addition of a cyanide source, 1-cyanomethyl-4-carboxymethyl-3-ketopiperazine (mononitrile monoacid) or a salt thereof is formed. In place of CH_2O and a cyanide source, $HOCH_2CN$, which is the reaction product of formaldehyde and cyanide, may also be employed in this method. Upon the addition of any suitable base or acid, this material may be hydrolyzed to 3KP. The addition of a base will open this ring structure to form the salt of ED3A.

[0009] In view of this relatively new technology, ethylenediaminetriacetic acid (ED3A) and its salts now can be readily produced in bulk and high yield. Use of ED3A and ED3A salts as chelating agents in pulp bleaching would result in a cost-effective process. Surprisingly, the inventors of the present invention have found that ED3A and ED3A salts actually enhance brightness and equal or outperform EDTA in such applications, notwithstanding the presence of only three carboxylate groups in ED3A as compared to four in EDTA.

SUMMARY OF THE INVENTION

[0010] The problems of the prior art have been overcome by the instant invention as described in claims 1 and 5, which provides a method for metal ion chelation in aqueous solution and in wood pulps. Extraction and removal of detrimental metal ions, preferentially manganese, iron and copper, prior to delignification and bleaching is carried out on pulp, preferably kraft pulp, using ethylenediaminetriacetic acid or ethylenediaminetriacetic acid salts as the chelating agent.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011]

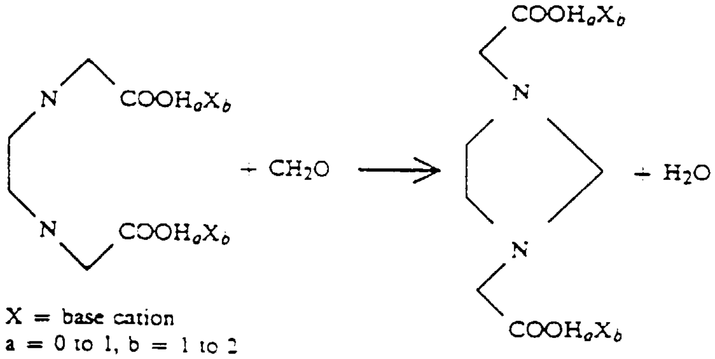
Figure 1 is a graph of brightness gains of various chelating agents;
Figure 2 is a graph of various brightness gains of various chelating agents after peroxide bleaching; and
Figure 3 is a graph of iron and manganese removal by various chelating agents prior to bleaching.

DETAILED DESCRIPTION OF THE INVENTION

[0012] Suitable salts of ethylenediaminediacetic acid that are useful in the present invention include alkali metal and alkaline earth metals, preferably sodium and potassium, and ammonium and amine (such as triethanol amine and monoethanolamine) salts, which can easily be prepared from ED3A acid by conventional means. For purposes of illustration, the sodium salt will be used, although it should be understood that other salts may be employed.

[0013] *Step 1* in the overall reaction scheme for producing ED3A is the alkaline condensation of formaldehyde with N,N'-ethylenediamine disodium acetate to form a 5-membered ring structure, 1,3-bis(carboxymethyl)imidazolidine, and is illustrated as follows:

Step I



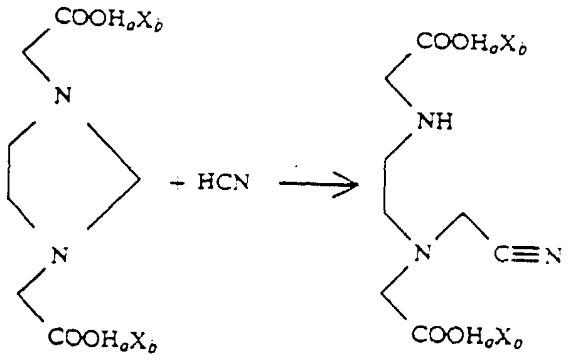
X = base cation
a = 0 to 1, b = 1 to 2
where a + b = 2

(I)

[0014] The above reaction may be carried out in the presence of additional base. Suitable bases include alkali and alkaline earth metal hydroxides, preferably sodium and potassium hydroxide. Compound (1) is the bridged reaction product of EDDANa$_{(1.0\rightarrow 2.0)}$ and formaldehyde, which the is a stable intermediate in the ED3A synthesis. Compound (I) is formed easily between 0° and 110°C. The *Step I* reaction proceeds quickly and forms readily at pH's greater than about 7.0. Preferably the temperature employed is about 0 to 65°C, most preferably 15 to 65°C, although temperatures higher than 65°C are operable. Formaldehyde can be used in stoichiometric amounts, although it is preferred that a slight molar excess be used, preferably 0.5%-2.0%. Preferably the concentration of the formaldehyde is 55% or less in aqueous solution. Paraformaldehyde also can be used.

[0015] The second step in the reaction scheme is illustrated below:

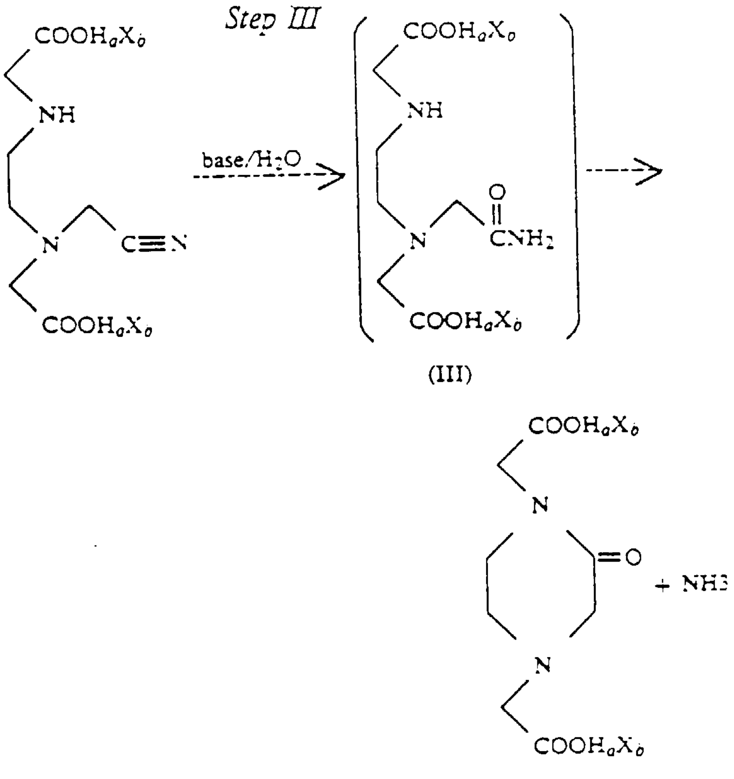
Step II



(II) Mononitrile-diacid

[0016] Compound (II) is readily formed at temperatures between 0° and 110°C. The reaction should be conducted at temperatures at or below the boiling point of the solution. Preferably the reaction is carried out at temperatures from about 0° to about 65°C, most preferably about 15° to 65°C to enhance the reaction rate. Suitable sources of cyanide include gaseous hydrogen cyanide, an aqueous solution of hydrogen cyanide, or alkali metal cyanide such as sodium cyanide or potassium cyanide, etc. The cyanide may be used in stoichiometric amounts, although slight molar excesses may be used, preferably 0.5% - 2.0%.

[0017] *Step III* in the reaction sequence is the hydrolysis of compound (II) to the monoamide-diacid compound (III) (partially hydrolyzed mononitrile diacid) and its spontaneous cyclization to 3KP. Compound (IV) forms readily in the presence of a base such as alkali metal or alkaline earth metal hydroxides. Preferably the base is NaOH. Mole ratios of < 3.0M base : 1M $ED2AH_2$ but preferably < 2.0 M base : 1M $ED2AH_2$ are employed. Higher concentrations of base (i.e. > 3.0 M base : M $ED2AH_2$) cause some disproportionation of the diacid mononitrile and some ED4A (ethylenediaminetetraacetic acid) is formed, especially at temperatures > 65°C. In particular, the concentration of ED4A is found to be in direct proportion to the amount of excess caustic employed, when high temperature reactions are conducted and high molar ratios of base are employed (> 2.0M base : 1M $ED2AH_2$), which may be attributed to the simultaneous hydrolysis of 3KP and disproportionation of the mononitrile-diacid. When the mole ratio of base to ED2A is < 2.0, higher temperatures may be used. Also, in *Step III* ammonia is eliminated between an amide group and an imino group on the same molecule. However, at lower temperatures (< 65°C) higher amounts of base may be employed (> 2.0M) and hydrolysis of compound (II) can proceed directly to ED3A without cyclization.

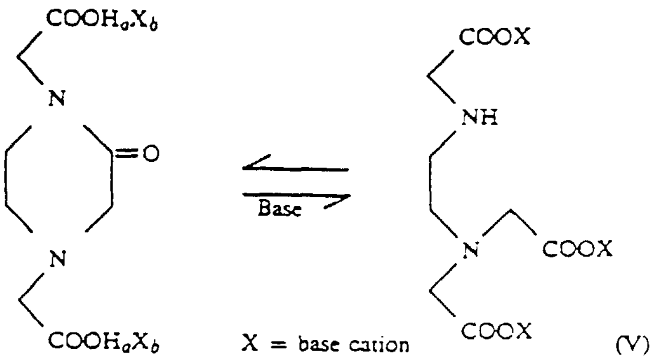


(III)

(IV)

[0018] *Step IV* is the hydrolysis of $3KPNa_2$ by at least the addition of 1 equivalent of caustic, preferably a 1 molar excess of caustic. This amounts to approximately 5% weight excess (free) caustic in solution on a 40% $ED3ANa_3$ solution. The solution is boiled under atmospheric pressure to the desired concentration. Preferably the reaction is carried out by raising the temperature from the temperature in *Step III* to the boil over a period from about 30 minutes to about 6 hours.

Step IV



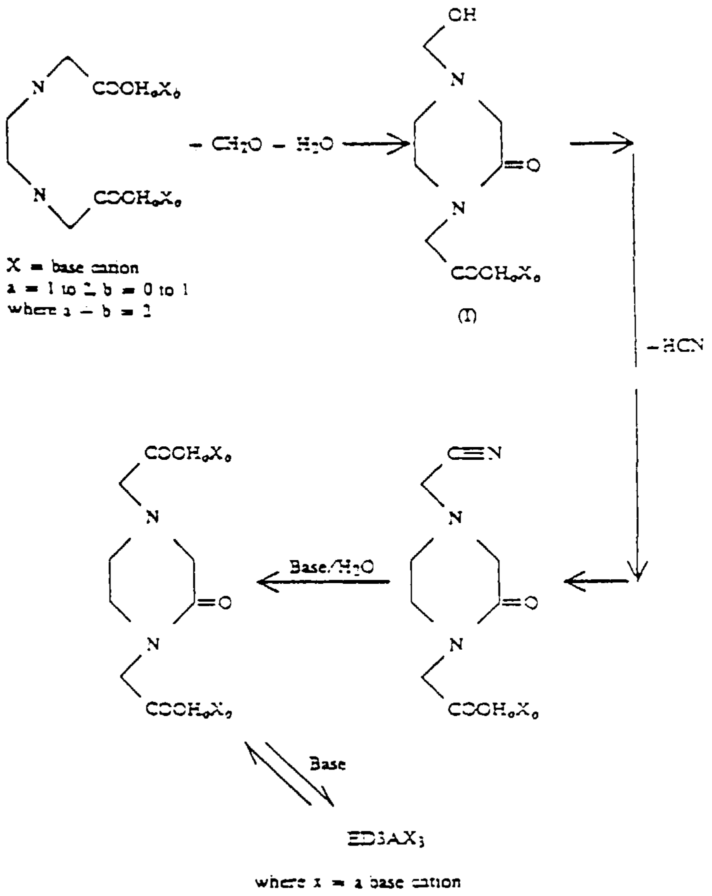
(V)

[0019] The resulting solutions typically give approximately 35-40% $ED3ANa_3$, with approximately 2% $3KPNa_2$ remaining as an unopened ringed structure. This corresponds to about a 94% conversion to $ED3ANa_3$, with the remaining 6% of mass existing as $3KPNa_2$. Acidification of this mass to pH's < 6.0 to produce $ED3AH_3$ is not possible, as cyclization to $3KPH_2$ will eventually occur.

[0020] The foregoing synthetic scheme results in conversions to $ED3ANa_3$ in excess of 90%, with the residual proportion being $3KPNa_2$ to give a total mass balance of virtually 100%. The reactions are tolerant to a wide pH range.

[0021] Alternatively, ED3A can be prepared using $ED2AH_aX_b$ as the starting material, where x is a base, e.g., an alkali or alkaline earth metal, a is 1 to 2, and b is 0 to 1 in aqueous solutions. The reaction mixture also can be acidified with acids having pK_a's less than or equal to 3, prior to during or after the addition of a cyanide source, to ensure complete formation of carboxymethyl-2-oxopiperazine (the lactam). Formaldehyde is added, essentially resulting in the hydroxymethyl derivative. Upon the addition of a cyanide source, 1-cyanomethyl-4-carboxymethyl-2-ketopiperazine or a salt thereof is formed, and can be isolated in good yield in crystalline form by conventional means after cooling the reaction mixture. Conversions are quantitative. In place of CH_2O and a cyanide source, $HOCH_2CN$, which is the reaction product of formaldehyde and cyanide, may also be employed in this method. Upon the addition of any suitable base or acid, this material may be hydrolyzed to 3KP. The addition of a base (> 2.0 equivalents but preferably greater than or equal to 3.0 equivalents will open this ring structure to form the salt of ED3A. Heating the reaction mixture will enhance the rate of reaction.

[0022] The overall reaction scheme is shown below:



[0023] EDDA can also be allowed to form the lactam (carboxymethyl-2-oxo-piperazine) by acidification, and the lactam is reacted with chloro or bromo acetic acid to form ED3A or 3KP.

[0024] The chelate pretreatment extraction in accordance with the present invention can be carried out in a pH range of from about 4 to about 11, preferably 4.5-5. Operable temperatures are from about room temperature to no higher than 100°C at atmospheric pressure, preferably about 50°C to about 90°C. Temperatures as high as 90°C actually improve the complexation of metals with the chelating agent.

[0025] Levels of chelating agent from about 1 to 10 kg per tonne (2 to about 20 pounds per ton) of pulp are typical in the pulp and paper industry for enhancing peroxide bleaching systems. The actual amount used will depend upon the level of metals present; the amount of chelating agent being that amount effective for chelating sufficient metals in order to achieve desired brightness and avoid undesirable peroxide decomposition. The metal content of the pulp is typically determined by sampling the pulp and determining its metal content by atomic adsorption. Chelates complex metals on a one-to-one molar basis.

[0026] Preferably the pulp is pretreated with ED3A and then washed so that the complexed metals are washed out of the system. A residence time of at least thirty minutes is needed at this stage to allow the chelates to complex the metals present and subsequently be washed. However, the chelate can be added to the pulp prior to bleaching (generally at pH's of 7-9) but without subsequent washing, or can be added directly to the bleaching process (generally pH's of 10-11), although these methods are generally less effective.

[0027] The efficiency of ethylenediaminetriacetic acid was compared along with $EDTANa_4$ and $DTPANa_5$ and no chelate in extraction of metals from two types of pulp, namely, sulfite, magnesium base 2nd stage unbleached supplied by Wausau Paper, and a mechanical pulp, Aspen Stone Ground Wood (SGW). The second part of the experiment was carried out to ascertain whether there was any enhancement on brightness in peroxide bleaching on the pulp in using chelate extraction.

Method Used for Chelate Extraction

[0028] Five grams of oven dried (OD) pulp is weighed up into a 600 ml beaker with a stirring bar and chelate is added at the rate of 1:1 or 2:1 mole ratio of chelate to total metal content defined as iron, manganese and copper (Fe, Mn, Cu).

[0029] Distilled water is added to the 500 ml mark, (1% consistency pulp). The pH of the extraction slurry was 4.5 to 5.0. The sample was stirred for 1/2 hour at room temperature and then was filtered through a Buchner funnel lined with a #4 Whatman filter paper.

[0030] The wet weight of the pulp pad was recorded to be used later in reconstituting to 10% consistency. This procedure was repeated for all the chelates that where evaluated.

Method Used for Hydrogen Peroxide Bleaching

[0031] Bleaching was carried out in zip lock bags in a water bath set at 70° C. for two hours. A bleach liquor was made up of 2.2% NaOH as 100% based on 5 gm OD pulp, 3% sodium silicate as 100% on 5 g OD pulp, 1% hydrogen peroxide as 100% on 5 gm OD pulp, and water was added to make the pulp 10% consistency. The pH before bleaching was 10.5. The air was squeezed out of the bag and inserted in a water bath for 2 hours. After the two hours in the water bath, the bleached pulp was transferred to a 600 ml beaker and the pulp was diluted to 1% consistency, the sample was mixed and the pH was recorded. The pH was then adjusted with sulfuric acid mixed and filtered, using a Buchner funnel with a #4 Whatman paper. The filtrate was saved for residual peroxide titration with sodium thiosulfate and starch indicator. The pulp pad was pressed between four absorbent pads at 6,89 · 10^6 N/m^2 (1000 psi) for one minute, then oven dried at 100°C for 1/2 hour. The pad was cooled to room temperature and five brightness readings were taken from both sides and then averaged.

Initial pulp analysis		
	2nd stage unbleached	**Aspen stone ground wood**
Consistency	36.8%	3.6%
Iron, ppm	12.5	26.1
Manganese, ppm	4.3	62.4
Copper, ppm	0.4	1.3

Stock solutions used:

[0032]

EDTA Na_4:	1.1292g @ 39.5% activity, diluted to 100 mls (primary solution) then 5 mls of primary solution diluted to 100 mls, to be used as the working solution for the experiments. (0.565 mg EDTANa_4 per ml)
DTPA Na_5:	1.1865g @ 41.4% activity, diluted to 100 mls (primary solution) then 5 mls of primary solution diluted to 100 mls, to be used as the working solution for the experiments. (0.593 mg DTPANa_5 per ml)
ED_3A:	1.0874g @ 35% activity, diluted to 100 mls (primary solution) then 5 mls of primary solution diluted to 100 mls, to be used as the working solution for the experiments. (0.544 mg ED_3A per ml)
NaOH 2% :	8 gm of 50% diluted to 200 mls. (20.0 mg of NaOH (as 100%) per ml.)
Hydrogen Peroxide 3%:	10 mls of 50% peroxide diluted to 200 mls. (30.9 mg peroxide as 100% per ml.)
Sodium Silicate 4.51%:	9.02 gm of sodium silicate (41 baume) diluted to 200 mls. (45.1 mg sodium silicate per ml.)

EXAMPLE 1

EDTANa_4 (1:1) mole ratio to total Fe, Mn, Cu

Extraction:

[0033]

pulp:	2nd stage (13.6 g as is) 5.0g OD
chelate:	2.65 mls of working solution

water: to 500 mls

Bleaching:

[0034]

NaOH: 5.5 mls of working solution

Silicate: 3.33 mls of working solution

Peroxide: 1.62 mls of working solution

Results:

[0035]

brightness: 73.5

residual: 0.5% as 100%

gain: 8.0 points over no chelate extraction, with bleaching

EXAMPLE 2

EDTANa$_4$ (2:1) mole ratio to total Fe, Mn, Cu

Extraction:

[0036]

pulp: 2nd stage (13.6 g as is) 5.0g OD

chelate: 5.30 mls of working solution

water: to 500 mls

Bleaching:

[0037]

NaOH: 5.5 mls of working solution
Silicate: 3.33 mls of working solution
Peroxide: 1.62 mls of working solution

Results:

[0038]

brightness: 73.0
residual: 0.6% as 100%
gain: 7.6 points over no chelate extraction, with bleaching

EXAMPLE 3

DTPANa$_5$ (1:1) mole ratio to total Fe, Mn, Cu

Extraction:

[0039]

pulp:	2nd stage (13.6 g as is) 5.0g OD
chelate:	3.2 mls of working solution
water:	to 500 mls

Bleaching:

[0040]

NaOH:	5.5 mls of working solution
Silicate:	3.33 mls of working solution
Peroxide:	1.62 mls of working solution

Results:

[0041]

brightness:	74.4
residual:	0.6% as 100%
gain:	8.9 points over no chelate extraction, with bleaching

EXAMPLE 4

DTPANa$_5$ (2:1) mole ratio to total Fe, Mn, Cu

Extraction:

[0042]

pulp:	2nd stage (13.6 g as is) 5.0g OD
chelate:	6.4 mls of working solution
water:	to 500 mls

Bleaching:

[0043]

NaOH:	5.5 mls of working solution
Silicate:	3.33 mls of working solution
Peroxide:	1.62 mls of working solution

Results:

[0044]

brightness:	73.7
residual:	0.6% as 100%
gain:	8.3 points over no chelate extraction, with bleaching

EXAMPLE 5

ED_3A (1:1) mole ratio to total Fe, Mn, Cu

Extraction:

[0045]

pulp: 2nd stage (13.6 g as is) 5.0g OD
chelate: 2.39 mls of working solution
water: to 500 mls

Bleaching:

[0046]

NaOH: 5.5 mls of working solution
Silicate: 3.33 mls of working solution
Peroxide: 1.62 mls of working solution

Results:

[0047]

brightness: 75.4
residual: 0.6% as 100%
gain: 9.9 points over no chelate extraction, with bleaching

EXAMPLE 6

ED_3A (2:1) mole ratio to total Fe, Mn, Cu

Extraction:

[0048]

pulp: 2nd stage (13.6 g as is) 5.0g OD
chelate: 4.78 mls of working solution
water: to 500 mls

Bleaching:

[0049]

NaOH: 5.5 mls of working solution
Silicate: 3.33 mls of working solution
Peroxide: 1.62 mls of working solution

Results:

[0050]

brightness: 74.3
residual: 0.6% as 100%
gain: 8.9 points over no chelate extraction, with bleaching

EXAMPLE 7

Blank, no chelate

Extraction:

[0051]

pulp: 2nd stage (13.6 g as is) 5.0g OD
chelate: none
water: to 500 mls

Bleaching:

[0052]

NaOH: 5.5 mls of working solution
Silicate: 3.33 mls of working solution
Peroxide: 1.62 mls of working solution

Results:

[0053]

brightness: 65.4
residual: 0.6% as 100%
gain: 0

[0054] The brightness readings are graphed on Figure 1. The use of 2:1 mole ratio of chelate to total metal (Fe, Mn, Cu) had no significant gains in brightness, compared to the use of a 1:1 mole ratio. ED$_3$A brightness gain was 9.9 points over a no chelate treatment extraction of pulp, and also showed an increase of 1.9 points over EDTANa$_4$ and 1.0 point increase in brightness over DTPANa$_5$.

[0055] The next set of experiments utilized a higher manganese pulp, aspen stone ground wood. The same conditions used in the previous examples were used, except that the % NaOH was increased to 2.6% instead of 2.2%, in order to achieve a higher initial pH for bleaching.

EXAMPLE 8

EDTA Na$_4$ (1:1) mole ratio to total Fe, Mn, Cu

Extraction:

[0056]

pulp: Aspen SGW (137.4 g as is) 5.0g OD
chelate: 14.3 mls of working solution
water: to 500 mls

Bleaching:

[0057]

NaOH: 6.5 mls of working solution
Silicate: 3.33 mls of working solution
Peroxide: 1.62 mls of working solution

Results:

[0058]

brightness: 67.8
residual: 0.2% as 100%
gain: 15 points over no chelate extraction, without bleaching

EXAMPLE 9

DTPA Na_5 (1:1) mole ratio to total Fe, Mn, Cu

Extraction:

[0059]

pulp: Aspen SGW (137.4 g as is) 5.0g OD
chelate: 17.2 mls of working solution
water: to 500 mls

Bleaching:

[0060]

NaOH: 6.5 mls of working solution
Silicate: 3.33 mls of working solution
Peroxide: 1.62 mls of working solution

Results:

[0061]

brightness: 69.2
residual: 0.1% as 100%
gain: 16.8 points over no chelate extraction, without bleaching

EXAMPLE 10

ED_3A (1:1) mole ratio to total Fe, Mn, Cu

Extraction:

[0062]

pulp: Aspen SGW (137.4 g as is) 5.0g OD
chelate: 12.9 mls of working solution
water: to 500 mls

Bleaching:

[0063]

NaOH: 6.5 mls of working solution
Silicate: 3.33 mls of working solution
Peroxide: 1.62 mls of working solution

Results:

[0064]

brightness:	68.9
residual:	0.1% as 100%
gain:	16 points over no chelate extraction, without bleaching

EXAMPLE 11

ED$_3$A (1.25:1) mole ratio to total Fe, Mn, Cu

Extraction:

[0065]

pulp:	Aspen SGW (137.4 g as is) 5.0g OD
chelate:	16.1 mls of working solution
water:	to 500 mls

Bleaching:

[0066]

NaOH:	6.5 mls of working solution
Silicate:	3.33 mls of working solution
Peroxide:	1.62 mls of working solution

Results:

[0067]

brightness:	69.0
residual:	0.1% as 100% %
gain:	16.5 points over no chelate extraction, without bleaching

EXAMPLE 12

Blank, no chelate extraction

Extraction:

[0068]

pulp:	Aspen SGW (137.4 g as is) 5.0g OD
chelate:	0
water:	to 500 mls

Bleaching:

[0069]

NaOH:	6.5 mls of working solution
Silicate:	3.33 mls of working solution
Peroxide:	1.62 mls of working solution

Results:

[0070]

brightness:	66.5
residual:	0.1% as 100%
gain:	13.4 points over no chelate extraction, without bleaching

[0071] The brightness gains are plotted in Figure 2, and the % iron and manganese removal is plotted in Figure 3. ED_3A used at 1:1 mole ratio to metals had a greater brightness gain than $EDTANa_4$ (15 points versus 16), and when used at 25% excess, was comparable to $DTPANa_5$. Manganese extraction with ED_3A was greater than 91%, which was fairly comparable to $EDTANa_4$ and $DTPANa_5$ at 97+%.

Claims

1. A method of inhibiting decomposition of hydrogen peroxide in aqueous solution containing transition metal ions, comprising contacting said solution with an effective amount of ethylenediaminetriacetic acid or a salt thereof for chelating said transition metal ions.

2. The method of claim 1, wherein said transition metal ions comprise iron, manganese and copper.

3. The method of claim 1, wherein said salt of ethylenediaminetriacetic acid is selected from the group consisting of alkali metal salts, alkaline earth metals salts, ammonium salt, and amine salts.

4. The method of claim 1, wherein said salt of ethylenediaminetriacetic acid is the sodium salt.

5. A method for pre-treating wood pulp prior to bleaching with a bleaching agent susceptible to decomposition by transition metal ions in aqueous solution, comprising preparing an aqueous solution comprising said wood pulp dispersed therein and at least one transition metal ion, and adding to said aqueous dispersion an effective amount of ethylenediaminetriacetic acid or a salt thereof to chelate said at least one transition metal ion.

6. The method of claim 5, wherein said at least one transition metal ion is selected from the group consisting of iron, manganese, copper and a mixture thereof.

7. The method of claim 5, wherein said salt of ethylenediaminetriacetic acid is selected from the group consisting of alkali metal salts, alkaline earth metals salts, ammonium salt, and amine salts.

8. The method of claim 8, wherein said salt of ethylenediaminetriacetic acid is the sodium salt.

Patentansprüche

1. Verfahren zum Inhibieren der Zersetzung von Wasserstoffperoxid in einer wässerigen Lösung, die Übergangsmetallionen enthält, umfassend das In-Kontakt-bringen der Lösung mit einer wirksamen Menge Ethylendiamintriessigsäure oder eines Salzes davon, um mit den Übergangsmetallionen ein Chelat zu bilden.

2. Verfahren nach Anspruch 1, wobei die Übergangsmetallionen Eisen, Mangan und Kupfer umfassen.

3. Verfahren nach Anspruch 1, wobei das Ethylendiamintriessigsäuresalz ausgewählt ist aus der Gruppe bestehend aus Alkalimetallsalzen, Erdalkalimetallsalzen, Ammoniumsalz und Aminsalzen.

4. Verfahren nach Anspruch 1, wobei das Salz der Ethylendiamintriessigsäure das Natriumsalz ist.

5. Verfahren zur Vorbehandlung von Holzpulpe vor dem Bleichen mit einem Bleichmittel, das durch Übergangsmetallionen in wässeriger Lösung zur Zersetzung neigt, umfassend das Herstellen einer wässerigen Lösung, die die Holzpulpe darin dispergiert und mindestens ein Übergangsmetallion umfasst, und Zugeben einer wirksamen Menge Ethylendiamintriessigsäure oder eines Salzes davon zu der wässerigen Dispersion, um mit dem mindestens

einen Übergangsmetallion ein Chelat zu bilden.

6. Verfahren nach Anspruch 5, wobei das mindestens eine Übergangsmetallion ausgewählt ist aus der Gruppe bestehend aus Eisen, Mangan, Kupfer und einem Gemisch davon.

7. Verfahren nach Anspruch 5, wobei das Salz der Ethylendiamintriessigsäure ausgewählt ist aus der Gruppe bestehend aus Alkalimetallsalzen, Erdalkalimetallsalzen, Ammoniumsalz und Aminsalzen.

8. Verfahren nach Anspruch 5, wobei das Salz der Ethylendiamintriessigsäure das Natriumsalz ist.

Revendications

1. Méthode d'inhibition de la décomposition du peroxyde d'hydrogène dans une solution aqueuse contenant des ions de métaux de transition, comprenant la mise en contact de ladite solution avec une quantité efficace d'acide éthylènediaminetriacétique ou son sel pour chelater lesdits ions de métaux de transition.

2. Méthode de la revendication 1, où lesdits ions de métaux de transition comprennent du fer, du manganèse et du cuivre.

3. Méthode de la revendication 1, où ledit sel de l'acide éthylènediaminetriacétique est sélectionné dans le groupe consistant en sels de métaux alcalins, sels de métaux alcalinoterreux, sel d'ammonium et sels d'amine.

4. Méthode de la revendication 1, où ledit sel de l'acide éthylènediaminetriacétique et le sel de sodium.

5. Méthode pour le prétraitement de pâte de bois avant blanchiment avec un agent de blanchiment susceptible d'une décomposition par des ions de métaux de transition en solution aqueuse, consistant à préparer une solution aqueuse comprenant ladite pâte de bois qui est dispersée et au moins un ion d'un métal de transition est ajouté à ladite dispersion aqueuse, une quantité efficace d'acide éthylènediaminetriacétique ou son sel pour chélater ledit au moins un ion d'un métal de transition.

6. Méthode de la revendication 5, où ledit au moins un ion d'un métal de transition est sélectionné dans le groupe consistant en fer, manganèse, cuivre et un mélange de ceux-ci.

7. Méthode de la revendication 5, où ledit sel de l'acide éthylènediaminetriacétique est sélectionné dans le groupe consistant en sels de métaux alcalins, sels de métaux alcalinoterreux, sels d'ammonium et sels d'amine.

8. Méthode de la revendication 8, où ledit sel de l'acide éthylènediaminetriacétique est le sel de sodium.

Fig. 1

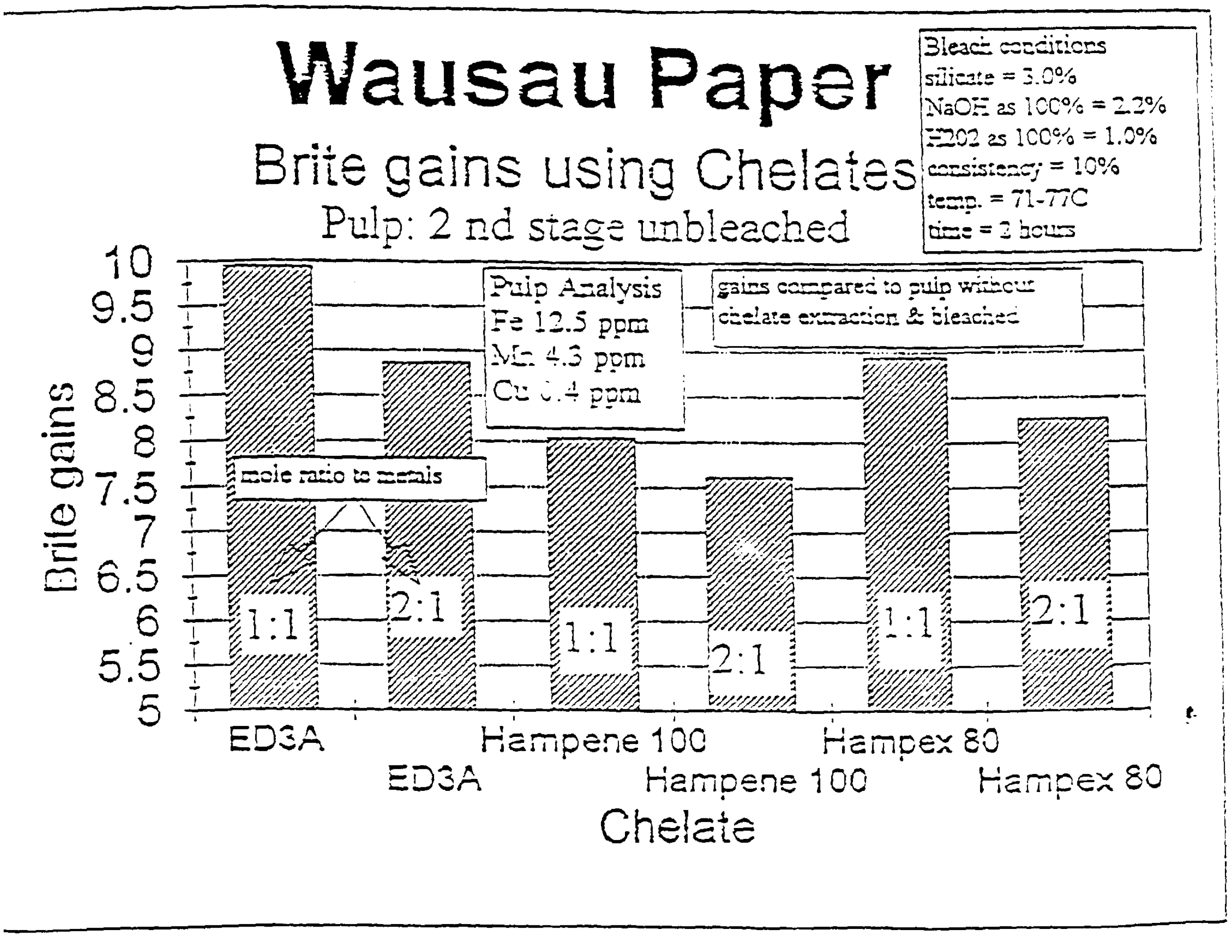

Wausau Paper
Brite gains using Chelates
Pulp: 2 nd stage unbleached
Bleach conditions
silicate = 3.0%
NaOH as 100% = 2.2%
H202 as 100% = 1.0%
consistency = 10%
temp. = 71-77C
time = 3 hours
Pulp Analysis
Fe 12.5 ppm
Mn 4.3 ppm
Cu 0.4 ppm
gains compared to pulp without chelate extraction & bleached
mole ratio to metals
1:1
2:1
1:1
2:1
1:1
2:1
Brite gains
10
9.5
9
8.5
8
7.5
7
6.5
6
5.5
5
ED3A
ED3A
Hampene 100
Hampene 100
Hampex 80
Hampex 80
Chelate

Fig. 2

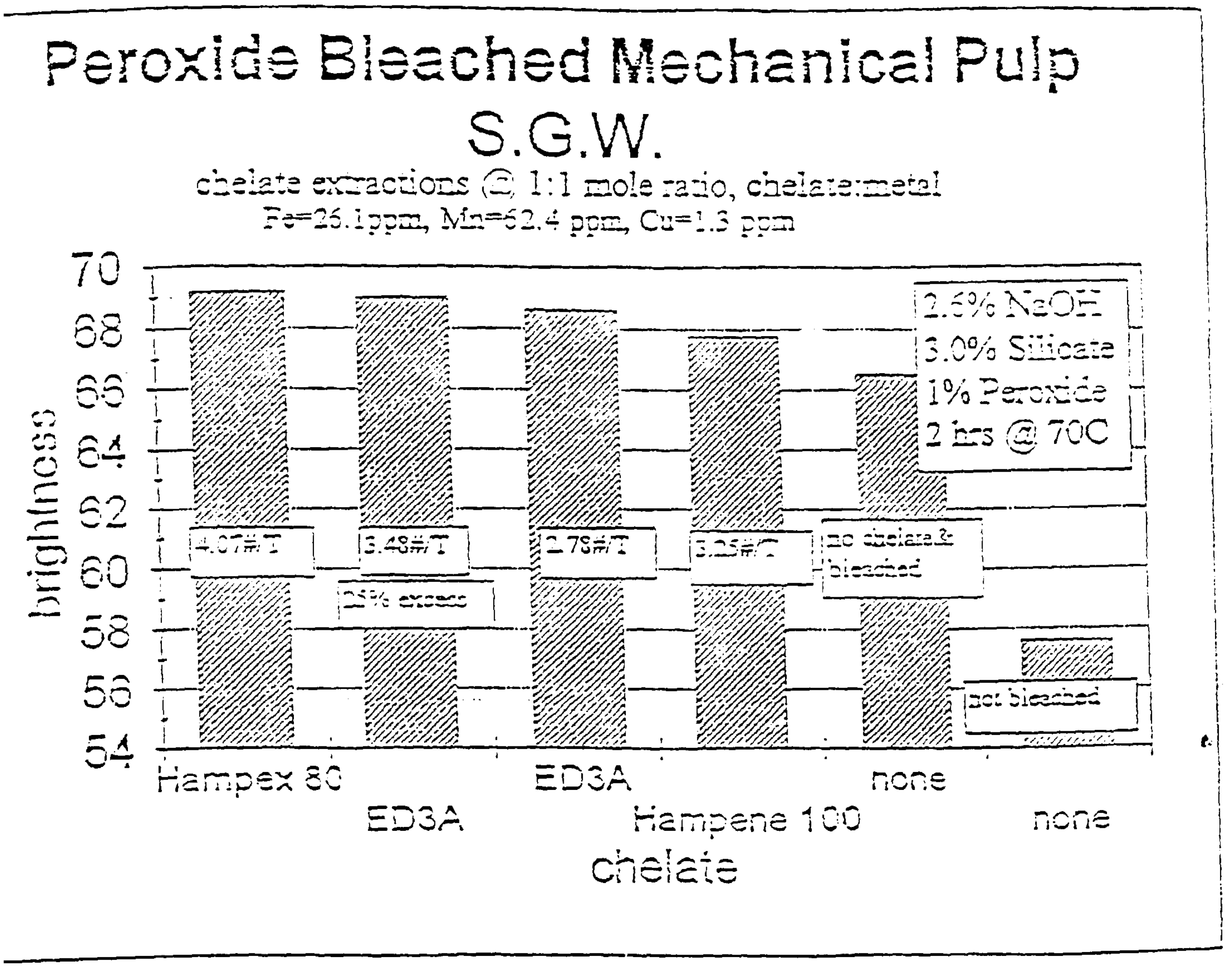
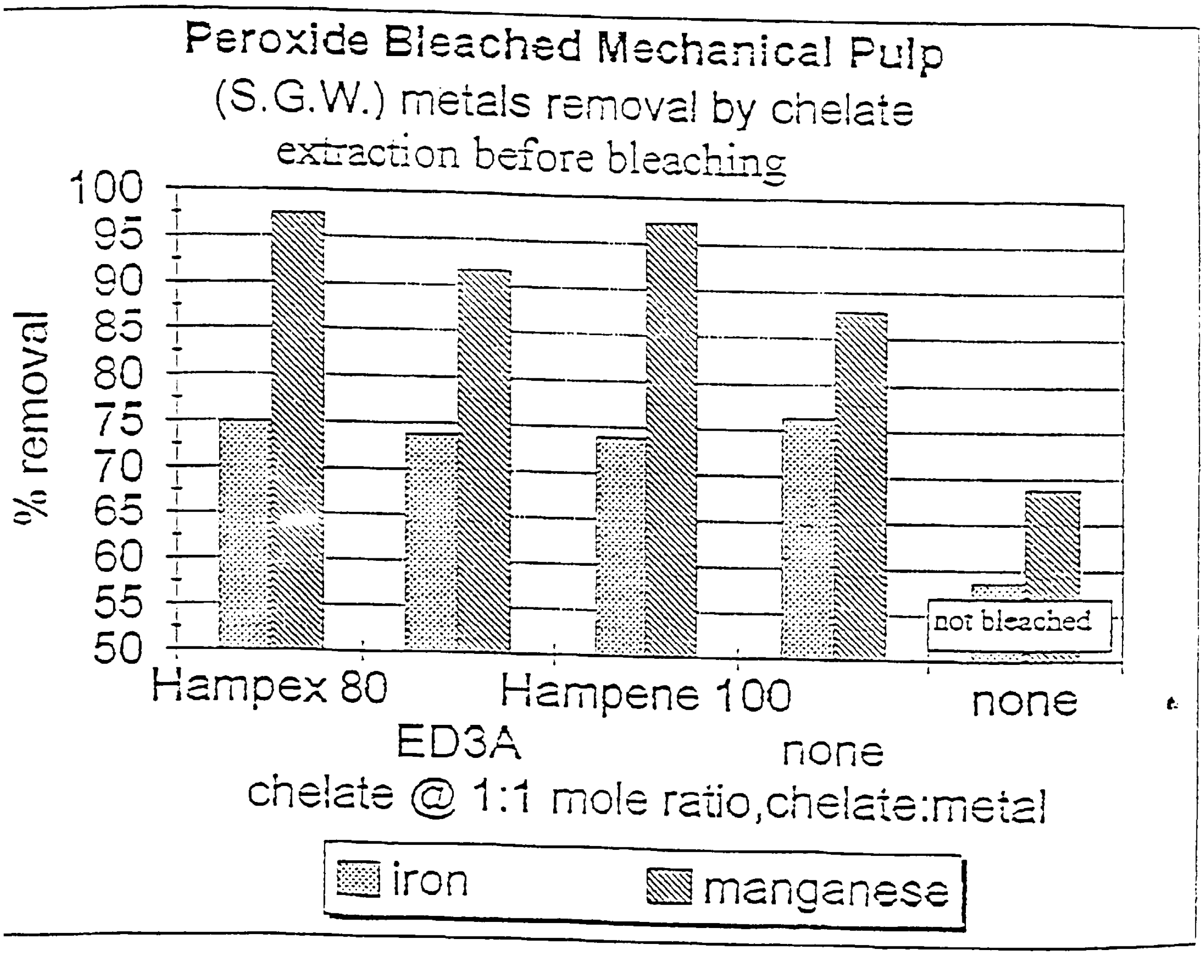

Peroxide Bleached Mechanical Pulp
S.G.W.
chelate extractions @ 1:1 mole ratio, chelate:metal
Fe=26.1ppm, Mn=62.4 ppm, Cu=1.3 ppm
70
68
66
64
62
60
58
56
54
brightness
2.6% NaOH
3.0% Silicate
1% Peroxide
2 hrs @ 70C
4.07#/T
3.48#/T
25% excess
2.78#/T
3.25#/T
no chelate &
bleached
not bleached
Hampex 80
ED3A
ED3A
Hampene 100
none
none
chelate

Fig. 3


Peroxide Bleached Mechanical Pulp
(S.G.W.) metals removal by chelate
extraction before bleaching
% removal
100
95
90
85
80
75
70
65
60
55
50
not bleached
Hampex 80
ED3A
Hampene 100
none
none
chelate @ 1:1 mole ratio,chelate:metal
iron
manganese