(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 456 032 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **91106496.2**

(51) Int. Cl.[5]: **D21C 9/16**, D21C 9/10

(22) Date of filing: **23.04.91**

(30) Priority: **25.04.90 JP 107397/90**

(43) Date of publication of application:
13.11.91 Bulletin 91/46

(84) Designated Contracting States:
AT CH DE ES FR GB IT LI NL SE

(71) Applicant: **HOECHST JAPAN LIMITED**
10-16, 8-chome, Akasaka, Minato-ku
Tokyo(JP)

Applicant: **MIKI CO., Limited**
20, Nakasu, Nakakirai-aza
Matsushige-cho, Itano-gun, Tokushima(JP)

(72) Inventor: **Endo Hajime,Dr.**
1 A706, Sanraitopasutoraru
3-296 Shinmatsudo, Matsudo-shi, Chiba(JP)
Inventor: **Aoki Toshiyuki**
7-39-2-312, Oojima
Koto-ku, Tokyo(JP)
Inventor: **Hamada Takashi**
206 Hiramatsu-haitsu
506, Nishizawada, Numazu-shi, Shizuoka(JP)

(74) Representative: **Valentin, Joachim et al**
Hoechst AG Zentrale Patentabteilung
Postfach 80 03 20
W-6230 Frankfurt am Main 80(DE)

(54) **Process for bleaching pulps.**

(57) A novel process for bleaching pulps with a bleaching solution, containing peroxide, which comprises use of, as an additional component of the bleaching solution, an activator which liberates nascent oxygen upon reaction with the peroxide, such as, tetraacetylethylenediamine and so on. The inventive method permits economization of the bleaching agent used, reduction of the bleaching time and a lowering of the bleaching temperature.

EP 0 456 032 A1

FIELD OF THE INVENTION

The present invention relates to a process for bleaching pulps, such as wood pulp and regenerated pulp, which can be realized at lower temperatures within a short period of time.

BACKGROUND OF THE INVENTION

For realizing bleaching of wood pulps, namely, mechanical pulps (high efficiency pups), such as ground pulp (GP), refiner ground pulp (RGP), thermo-mechanical pulp (TMP), chemical ground pulp (CGP) and semi-chemical pulp (SCP); chemical pups, such as craft pulp (KP) and sulfite pulp (SP); and deinked waste paper pulp (DIP), namely regenerated pulp, there have been in wide use peroxides, such as hydrogen peroxide, sodium percarbonate and so on.

Peroxidic bleaching liquors conventionally employed have, in general, additives inclusive of sequestering agent, for example, a metal chelating agent, such as sodium diethylenetriaminepentaacetate (DTPA), tetra- and disodium ethylenediaminetetraacetate (EDTA), nitrilotriacetic acid (NTA) and so on, and magnesium sulfate, sodium silicate of commercial grade No. 3 and so on, for preventing useless decomposition of the peroxide under the bleaching condition due to the presence of contaminant trace metals of natural occurrence or delivered from waste paper.

It has been known that sodium silicate of commercial grade No. 3 functions also as a buffer and stabilizes the pH of the bleaching solution, in addition to the function of preventing useless decomposition of the peroxide. It has been confirmed further that sodium silicate of commercial grade No. 3 causes the formation of a protective coating film on the surface of metals, thus preventing corrosion of the metal.

Caustic soda is also employed in general, due to its low price pH regulator, since peroxides exhibit their bleaching action in an alkaline condition.

It is also known that treatment by these chemicals can be imparted to the pulp not only during but also before, the oxidative bleaching takes place.

In terms of the typical parameters of conventional tower bleaching of pulp with a bleaching solution in which hydrogen peroxide is used as the peroxide, the conditions for bleaching include, in general, a longer bleaching duration of 1-4 hours at 40-70 °C and a solution pH of 10-11. For higher temperature bleaching, the conditions include, in general, a bleaching duration of 20-30 minutes at 75-85 °C. For attaining the maximum whiteness, a bleaching duration of 4-3 hours at 40-60 °C is required at each concentration of the peroxide used.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a process for bleaching pulps that is able to be carried out at a lower temperature within a shorter operation duration as compared with the conventional technique.

Thus, the above object is attained according to the present invention by a process for bleaching pulps with a peroxide, which method comprises use of, as an additional component, an activator which liberates active or nascent oxygen upon reaction with the peroxide.

By this method, maximum whiteness at each concentration of the peroxide can be attained within a very short period of time, say, 5-60 minutes at a relatively low temperature of 5-70 °C, referably 20-60 °C.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a graph showing the relationship between the whiteness of the bleached pulp and the bleaching duration based on the experimental results of Example according to the present invention and Comparison Example according to the prior technique.

DETAILED DESCRIPTION OF THE INVENTION

Pulps to be bleached by the method according to the present invention include every sort of pulp, such as those enumerated previously.

For the peroxide to be employed in the method according to the present invention, there may be enumerated, for example, hydrogen peroxide and various inorganic peroxides, such as sodium peroxide, sodium and potassium salts of percarbonate, perborate, persulfate and perphosphate.

The activator to be employed in the method according to the present invention encompasses various known compounds. It includes N-acyl compounds, such as tetraacetylethylenediamine (TAED), tetraacetyl-

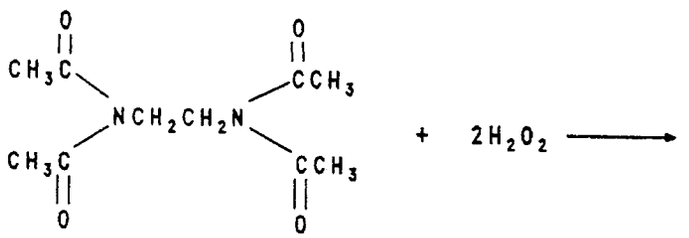
methylmethylenediamine, tetraacetylglycol uril (TAGU) and so on, and activated esters, such as pentaacetylglucose (PAG), sodium acetoxybenzenesulfonate, sodium nonanoyloxybenzenesulfonate (NOBS), sodium benzoyloxybenzenesulfonate (BOBS) and so on. Above all, tetraacetylethylenediamine (TAED) is particularly advantageous.

In the method according to the present invention, additional components other than the peroxide and the activator can be employed, such as for example, conventional additives employed in the prior bleaching technique, i. e., additives for preventing the useless decomposition of the peroxide under the bleaching condition in the presence of contaminant metals of natural occurrence or originated from waste papers to be regenerated including a sequestering agent, such as, a metal chelating agent, for example, sodium diethylenetriaminepentaacetate (DTPA), tetra- and disodium ethylenediaminetetraacetates (EDTA), nitrilotriacetic acid (NTA) and so on, and magnesium sulfate, sodium silicate of commercial grade No. 3 and so on, as well as a pH regulator, corrosion inhibitors for various metals and so on.

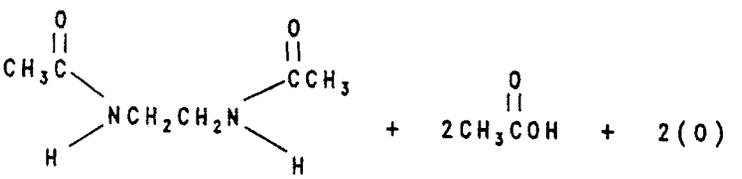
The pH value of the bleaching solution at the start of bleaching by the method according to the present invention may preferably be in the range from 8 to 12, the highest bleaching effect being attained, in particular, in the pH range of 9-10. For the pH regulator, there may be employed various inorganic alkaline compounds, such as caustic soda, sodium silicate of commercial grade No. 3, sodium sulfite and so on.

The activator may be added to the bleaching solution either before the addition of the peroxide and during the step of adding the metal chelating agent, pH regulator and so on, or at the same time with or after the addition of the peroxide.

The reaction scheme of liberating the nascent oxygen upon reaction of the activator with the peroxide employed in the method according to the present invention exemplified for the case of using hydrogen peroxide and TAED is represented as follows:



TAED



Diacetylethylenediamine (DAED)

In the above reaction scheme, (O) represents the active oxygen nascent oxygen, which brings about an efficient bleaching.

Theoretically calculated, one mole of TAED will be required to react with 2 moles of hydrogen peroxide.

Since the molecular weight of hydrogen peroxide is 34 and that of TAED is 228, 3.35 grams of TAED will react with 1 gram, calculated as pure substance, of hydrogen peroxide employed for bleaching the pulp.

In the widely realized conventional practice for bleaching pulps, the amount of hydrogen peroxide, calculated as pure substance, is, in general, in the range from 0.3 to 10 %.

In the method according to the present invention, however, the lower limit of the amount of hydrogen peroxide can be reduced to 0.05%; Therefore, the amount of TAED to be employed in the method

according to the present invention will, theoretically, be in the range from 3.35 times 0.05% to 3.35 times 10 %.

Practically, however, it may be reasonable to employ hydrogen peroxide, which has a lower price than TAED, in an excess amount, in order to further increase the rate of reaction of hydrogen peroxide with TAED and to improve the bleaching effect. In addition, more hydrogen peroxide becomes effectively active in the bleaching of pulps by the addition of TAED, so that the amount of hydrogen peroxide actually employed can be reduced.

While the advantageous effects of the method according to the present invention is explained for the case of using hydrogen peroxide and TAED, corresponding effects will be achieved using other peroxides and activators.

Below, the method according to the present invention is explained for the case of application to a pulp product used for papers for domestic uses.

A pulp used for papers for domestic uses is obtained from waste papers of high quality and medium quality papers and of simili paper. For producing pulp from such waste papers, the so-called globe kettle method may be employed. This method comprises treating the raw stock of waste papers in the kettle by cooking under the condition of high temperature (130-140 °C) and high pressure using a digesting agent and a bleaching agent at a pulp concentration of 15-25% for 4-5 hours.

According to Report No. 36 of the Paper Manufacturing Testing Laboratory of Shizuoka Prefecture Japan, effects of preventing useless decomposition of sodium percarbonate and of deinking of pulp were attained by the concurrent use of sodium percarbonate and sodium silicate of commercial grade No. 3, with a simultaneous improvement in the whiteness, a decrease in the COD load of waste water, a lowering of the digestion temperature and an increase in the paper quality and so on, as compared with the conventional practice of digestion with sodium sulfite. By the concurrent use of TAED with sodium percarbonate or further with sodium silicate of commercial grade No. 3, it becomes possible to lower the bleaching temperature in the globe kettle from the conventionally employed temperature of 130-140 °C to 5-70 °C and to reduce the bleaching time to the range of 5-30 minutes. In the modified globe kettle method in which the pulp is digested beforehand by the solution of another alkaline compound, such as sodium sulfite, before bleaching it with the addition of sodium percarbonate, it is made possible according to the present invention to reduce the bleaching time and to economize energy for effecting the digestion and bleaching, as compared to the conventional technique.

In the method according to the present invention, the activator does not serve for any acceleration of decomposition of the peroxide, but does serve for the generation of active oxygen from the peroxide efficiently for realizing the bleaching and, thus, reducing the bleaching time.

The advantages realized by the present invention exist in that the energy cost can be reduced, the pulp bleaching apparatus can be designed compactly and the bleaching performance per unit operation time can be increased.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Below, the present invention is described in more detail by an Example and a Comparison Example.

Example

Bleaching tests were carried out using a ground pulp in accordance with the following procedures:

1) dispersing the ground pulp (GP), preparing an absolutely dried pulp on a hot plate, collecting a sample of 25 g of this absolutely dried pulp in a bag of polyethylene film and sealing the bag in a gas-tight condition so as to exclude absorption of moisture;

2) dissolving 1 gram of tetraacetylethylenediamine (TAED) in a warm water of 55 °C to prepare a 1% aqueous solution thereof and maintaining it at a temperature of 50-55 °C;

3) formulating a 4% aqueous solution of sodium diethylenetriaminepentaacetate (DTPA) to be used as the chelating agent;

4) preparing a 1% aqueous solution of sodium silicate of commercial grade No. 3;

5) preparing a 1% aqueous solution of sodium hydroxide and

6) preparing an aqueous solution of hydrogen peroxide having an effective component concentration of 3%.

To the polyethylene bag containing 25 g of GP collected as 1) above, there was added an amount of the DTPA solution prepared as 3) above so as to reach a DTPA concentration of 0.4%, based on the dry weight of the pulp, whereto the TAED solution prepared as 2) above was admixed so as to adjust a TAED

concentration of 3.35%, based on the dry weight of the pulp. This dispersion was supplemented with warm water so as to reach a final pulp concentration of 20%, that is, an amount of the warm water was added to the dispersion after the addition of hydrogen peroxide so as to adjust the pulp concentration of 20%. Then, the pulp dispersion was homogeneously mixed by rubbing with hand in order to reach a uniform distribution of GP, DTPA and TAED, whereupon the dispersion was left standing for 30 minutes.

Thereto was then added the aqueous solution of sodium silicate prepared as 4) above so as to reach a sodium silicate concentration of 3%, based on the dry weight of the pulp, whereto was further added the solution of sodium hydroxide prepared as 5) above so as to reach a concentration thereof of 1% and the dispersion was then homogeneously mixed by rubbing with hand in order to reach a uniform distribution of each component among the pulp dispersion. The polyethylene bag containing the GP dispersion with the additives was placed in a hot bath and warmed to a temperature of 55 °C, whereupon the bag was held at this temperature for 15 minutes.

Three bags of the same pulp dispersion were tested (Test lots A, C and E).

To each of these bags of Lots A, C and E, the hydrogen peroxide solution prepared as 6) above was added so as to reach a concentration of hydrogen peroxide of 3.53%, 1.76% and 0.88% respectively, based on the dry weight of the pulp, whereupon each pulp dispersion was supplemented with an amount of warm water so as to reach a pulp concentration of 20%. The so treated bags were again placed in the hot bath and were observed for their whiteness at 55 °C according to Hunter, after 5, 10, 15, 30, 60 and 120 minutes respectively. Results are summarized in the Table given below and are also illustrated graphically in Fig. 1, in which the whiteness values (%) were based on Hunter-Whiteness and the original whiteness of the pulp before bleaching was 41.6%.

Comparison Example

Three samples of pulp dispersion were prepared and tested as in the above Example, except that the employment of TAED was omitted. Results obtained are also recited in the Table below (Test Lots B, D and F) and illustrated in Fig. 1.

As seen from these experimental results, the present invention provides a marked contribution to the industry by the attainment of capability of realizing bleaching of pulps at lower bleaching temperature within a very short bleaching time.

Table

Whiteness of Pulp bleached with or without TAED

Test Lot	Bleaching Liqu. %		Whiteness (Hunter) after						
	TAED %	H_2O_2 %	0 min (Blank)	5 min	10 min	15 min	30 min	60 min	120min
A	3.35	3.53	41.6	52.6	52.5	53.0	53.7	54.0	–
B	0	3.53	41.6	43.9	–	47.4	49.3	51.9	54.6
C	3.35	1.76	41.6	49.7	50.9	51.4	52.4	53.0	–
D	0	1.76	41.6	43.0	–	43.8	46.1	49.1	51.7
E	3.35	0.88	41.6	47.9	49.1	50.0	51.4	51.4	–
F	0	0.88	41.6	42.3	–	43.7	49.6	50.2	50.2

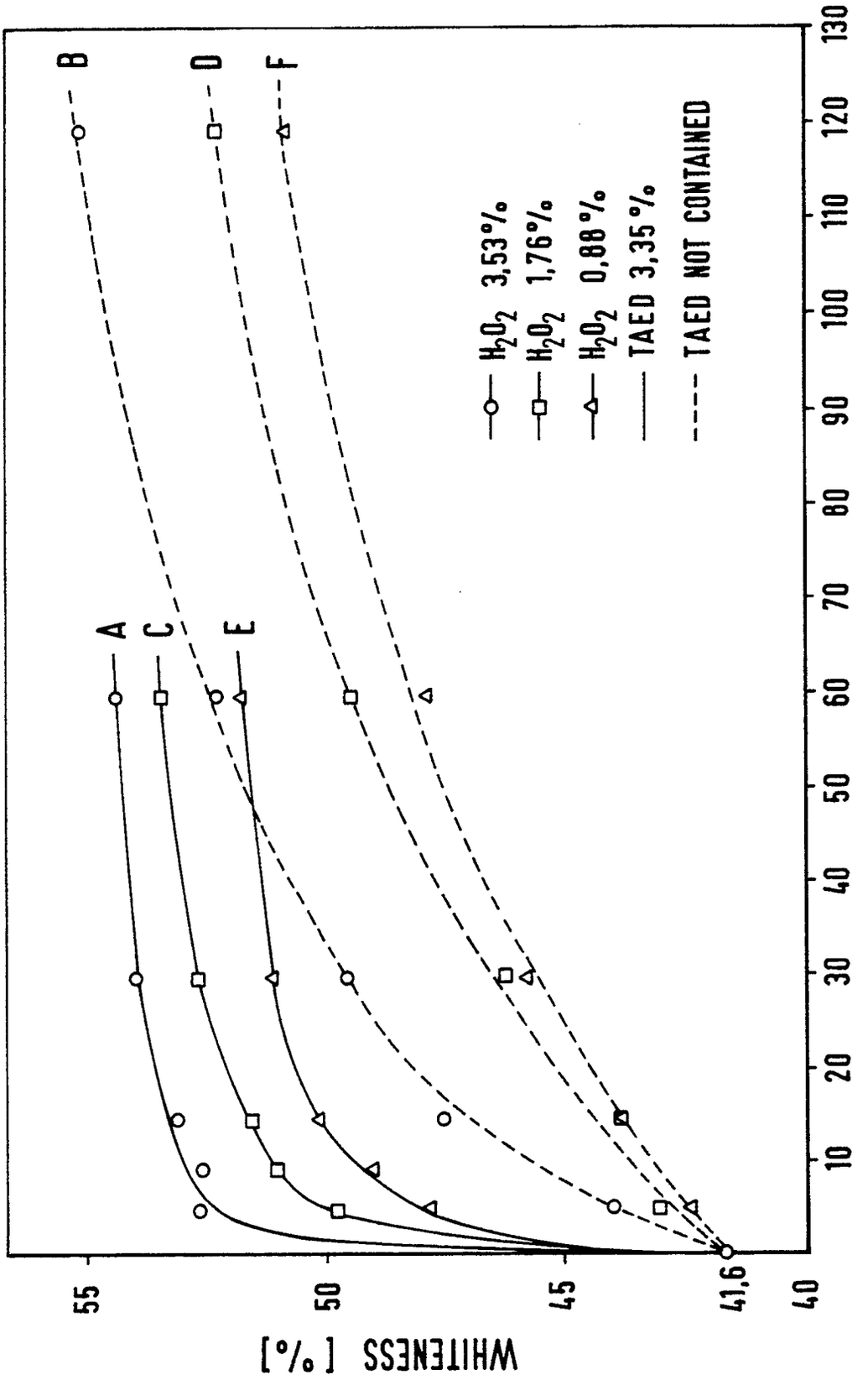
Claims

1. A process for bleaching pulps with a peroxide comprising use of, as an additional component, an activator compound which liberates nascent oxygen upon reaction with the peroxide.

2. The process of claim 1, wherein hydrogen peroxide, sodium peroxide or a sodium or potassium percarbonate, perborate, persulfate or perphosphate is used as peroxide.

3. The process according to claim 1 or 2, wherein as activator compound tetraacetylethylenediamine, tetraacetyl methylmethylenediamine, tetraacetyl glycol uril, pentaacetylglucose, sodium acetoxybenzenesulfonate, sodium nonanoyloxybenzenesulfonate or sodium benzoyloxybenzesulfonate are used.

4. The process according to claim 1 or 2, wherein as activator compound tetraacetylethylenediamine is used.


WHITENESS [%]
55
50
45
41,6
40
10
20
30
40
50
60
70
80
90
100
110
120
130
BLEACHING TIME [min]
A
B
C
D
E
F
H_2O_2 3,53%
H_2O_2 1,76%
H_2O_2 0,88%
TAED 3,35%
TAED NOT CONTAINED

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 6496

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-3 687 803 (AMERICAN CYANAMID CO.) * column 2, lines 38 - 45 * * column 3, line 34 - column 4, line 3 *	1,2	D 21 C 9/16 D 21 C 9/10
A	GB-A-1 383 741 (CIBA-GEIGY AG) * page 2, lines 84 - 95 * * page 3, lines 23 - 44 *	1-4	
A	Journal f. prakt. Chemie vol. 332, no. 2, 1990, Leipzig, Germany pages 176 - 180; Hofmann,J. et al.: "Bleaching activators as acylating agents. Kinetics of the acetylation of piperidine by some bleaching activators." * pages 176,177 *	1-4	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

D 21 C
D 06 L

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	23 August 91	BERNARDO NORIEGA F.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention

E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document