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(54) Title: A METHOD OF BLEACHING CELLULOSIC FIBRE MATERIAL WITH OZONE

(57) Abstract

A method of improving the selectivity when bleaching cellulosic fibre material with ozone while using at least one organic compound selected from the group consisting of alcohols, aldehydes and carboxylic acids. According to the invention the organic compound is added to the ozone-containing gas so that it is mixed homogeneously therewith before the ozone-containing gas is brought into contact with the cellulosic fibre material.
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A method of bleaching cellulosic fibre material with ozone

The present invention relates to a method of improving the selectivity when bleaching cellulosic fibre material with ozone while using at least one organic compound selected from the group consisting of alcohols, aldehydes and carboxylic acids.

Ozone reacts with water to form free radicals. Free radicals are also formed at the autogenic decomposition of the ozone. The free radicals constitute extremely strong oxidants which react with the cellulose thereby breaking down it, which may considerably lower the viscosity of the pulp.

It is known to pre-treat the pulp with a carboxylic acid such as acetic acid and oxalic acid which, upon subsequent addition of ozone, reduces the content of present damaging radicals, see for instance Mbachu, R.A.D. and Manley, R.S.J., Tappi J. 94(1):67 (1981); Lachenal, D. and Bokström, M., J. Pulp Paper Sci. 12(2):J50 (1986); Lindholm, C.-A., Cellulose Chem. Technol. 23(3):307 (1989); Allison, R.W., 1985 International Pulp Bleaching Conference, CPPA, Quebec City, page 47; H. Kamishima, T. Fujii, I. Akamatsu and S. Nakayama, Mokuza Gakkaishi, Vol.28, No.6, pages 370-375 (1982). Thus the acetic acid and oxalic acid act as inhibitors, eliminating the free radicals and thus preventing decomposition of the cellulose by these radicals. In other words, pre-treating with acetic acid or oxalic acid enables improved selectivity to be achieved when treating pulp with ozone. Selectivity can be expressed as reduction of kappa (lignin) obtained and improved lightness in comparison with a specific, unavoidable decomposition of the cellulose during the bleaching process, i.e. as compared with a specific viscosity value. Relatively large quantities of acetic and
oxalic acid must be added to the pulp during said pre-
treatment in order to reduce the free radicals which
exist in the ozone gas when this is added to the pulp,
and which are formed during the bleaching process as long
as ozone remains. Not negligible quantities of fresh
chemicals must thus be handled in the factory. These
chemicals and their reaction products are recovered after
the ozone treatment. Alternatively the chemicals and the
reaction products are allowed to leave with the waste
water from the factory. This result in not negligible
increase of discharge of chemically oxygen-consuming sub-
stances (COD). However, the selectivity improvement is
limited since there are harmful free radicals in the
ozone gas when this is mixed into the pulp, these free
radicals having time to break down the cellulose before
the acetic acid or oxalic acid captures them.

The object of the present invention is to further improve
the selectivity, to reduce the quantity of radical-
capturing chemicals and to eliminate the need for re-
covery or reduce the discharge to negligible values.

The novelty of the invention consists in that the organic
compound is added to the ozone-containing gas so that it
is mixed homogeneously therewith before the ozone-
-containing gas is brought into contact with the
cellulosic fibre material.

The organic compound is suitably added to the ozone-
-containing gas immediately after the ozone has been
produced.

The organic compound preferably has a vapour pressure
which stoichiometrically at least corresponds to the
total amount of free radicals formed in the ozone-
-containing gas before it is mixed with the cellulosic
fibre material.
Furthermore, it may be advantageous to add the organic compound initially to the ozone-containing gas in a small excess, so that a radical-capturing effect is obtained even during the bleaching process. The method according to the invention entails at an early stage, or more specifically when the ozone is in gaseous form, breaking the chain reaction which starts with the autogenic decomposition of the ozone immediately after the ozone has been produced. During this initial stage before the ozone is mixed into the pulp, the content of free radicals is probably at most 1% of the ozone content. The amount of aliphatic hydrocarbon compound, expressed as COD, necessary to remove these radicals is at most 1.0 kg and preferably at most 0.1 kg per ton pulp and this amount and any correspondingly small excess of the organic compound, is negligible from the discharge aspect.

The organic compound can be added to the ozone-containing gas in any suitable manner. According to one embodiment the ozone-containing gas produced is brought to pass through a bell-bottomed column supplied with acetic acid, for instance, of suitable concentration, which corresponds to the requisite partial pressure of the acetic acid to eliminate the free radicals. The gas can also be dispersed in the acetic acid via spargers (gas distributors). According to another embodiment the acetic acid is added in spray form by ejector action or through spray nozzles. According to yet another embodiment the acetic acid is added to the cooling or sealing water brought into contact with the ozone-containing gas mixture produced before or after it is compressed.

Any suitable alcohol, aldehyde or carboxylic acid, or mixtures of these, may be used, methanol, formaldehyde and acetic acid being the preferred substances from respective classes. The effluent obtained from the bleach-
ing process, which is sufficiently rich in various carboxylic acids such as oxalic acid, acetic acid, formic acid, etc., may advantageously be utilized as source of carboxylic acids.
CLAIMS

1. A method of improving the selectivity when bleaching cellulosic fibre material with ozone while using at least
one organic compound selected from the group consisting of alcohols, aldehydes and carboxylic acids, charac-
terized in that the organic compound is added to the ozone-containing gas so that it is mixed homogeneously
therewith before the ozone-containing gas is brought into contact with the cellulosic fibre material.

2. A method as claimed in claim 1, characterized in that the organic compound is added to the ozone-
containing gas immediately after the ozone has been produced.

3. A method as claimed in claim 1, characterized in that the organic compound utilized is one from said group
that has a vapour pressure which stoichiometrically at least corresponds to the total amount of free radicals
formed in the ozone-containing gas before it is mixed with the cellulosic fibre material.

4. A method as claimed in claim 3, characterized in that the amount of organic compound, expressed as chemi-
cally oxygen-consuming substances, added to the ozone-
containing gas in order to remove the free radicals formed in the ozone-containing gas before it is added to the cellulosic fibre material, is at most 1.0 kg, preferably at most 0.1 kg per ton cellulosic fibre material.

5. A method as claimed in claim 3 or 4, characterized in that the organic compound is added in an excess over said stoichiometric amount so that it is also active in capturing the free radicals formed after the ozone-
containing gas has been mixed with the cellulosic fibre material.
6. A method as claimed in any of claims 1-5, characterized in that the organic compound is methanol.

7. A method as claimed in any of claims 1-5, characterized in that the organic compound is formaldehyde.

8. A method as claimed in any of claims 1-5, characterized in that the organic compound is acetic acid.
1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 93/00400

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: D21C 9/153
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)

IPC5: D21C

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

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>US, A, 4229252 (MICHAEL D. MEREDITH), 21 October 1980 (21.10.80), claim 1</td>
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 Further documents are listed in the continuation of Box C.

X See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search 23 August, 1993

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Form PCT/ISA/210 (second sheet) (July 1992)
**INTERNATIONAL SEARCH REPORT**

Information on patent family members

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