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(54) **A PEROXIDE BLEACHING SOLUTION COMPRISING A BLEACHING ACTIVATOR AND METHOD FOR USING THE ACTIVATOR**

EINE PEROXIDLÖSUNG FÜR DIE BLEICHE ENTHALTEND EINEN BLEICHAKTIVATOR UND VERFAHREN ZU SEINER VERWENDUNG

UNE SOLUTION PEROXIDE POUR LE BLANCHIMENT COMPRENANT UN ACTIVATEUR DE BLANCHIMENT ET SON PROCEDE D'UTILISATION

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(56) References cited:
EP-A1- 0 481 792 WO-A1-94/18299
WO-A1-95/21290

- **DATABASE WPI Derwent Publications Ltd., London, GB; AN 1981-10766D 'Peroxide bleaching of wood pulp - in presence of sodium silicate, sodium carbonate and calcium hydroxide and/or oxide' & JP 55 158 394 A (OJI PAPER CO) 09 December 1980**

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Description

[0001] The invention relates to a peroxide bleaching solution comprising a bleaching activator for improving the opacity of bleached pulps containing lignin, and to a method for bleaching pulp with such a peroxide bleaching solution.

[0002] Opacity is used to describe the nontransparent aspect of paper, which, along with brightness, is an important property of pulp in paper manufacture. Almost invariably, however, the opacity of the pulp decreases when the brightness increases. At present, mechanical pulps are more and more often bleached with hydrogen peroxide. Dithionite bleaching is also used either alone or together with peroxide bleaching, whereupon dithionite is either used as refiner bleaching or after-bleaching. In the peroxide bleaching of pulp, mechanical pulp in particular, the decrease of opacity is clearly detectable, while the dithionite bleaching does not necessarily decrease the opacity. Generally, the lighter the level of bleaching the pulp, the lower the opacity of the pulp. The appended Fig. 1 that shows a variation in the opacity of spruce TMP, when peroxide is used to bleach pulp to various degrees of brightness manifests this. In certain paper grades, opacity is an important property. If we want to advance peroxide bleaching at the expense of dithionite bleaching, it would be important to be able to optimize peroxide bleaching so that the opacity remains as high as possible while the brightness grows.

[0003] Generally, the chemicals used in the peroxide bleaching of mechanical pulps are hydrogen peroxide, lye (alkali), and waterglass. The purpose of the base is to increase the pH to a sufficiently high level, so that the hydrogen peroxide, which works as the actual bleaching agent, is dissociated producing perhydroxyl anions. The purpose of the waterglass is to stabilize the hydrogen peroxide.

[0004] We have observed that peracetic acid treatment, for example, can provide a clearly higher opacity with the same level of brightness than when pulp is bleached with hydrogen peroxide alone.

[0005] Peracetic acid can also be produced in situ, for example, from acetanhydride or TAED (tetra acetyl ethylene diamine) or some other corresponding activator. One disadvantage of TAED is its high price and that it is a solid substance. It would be necessary to disperse the TAED in water before use, which makes it difficult to use. Furthermore, TAED contains nitrogen, which might constitute a problem for environmental protection. Acetanhydride is relatively cheap, but it would cause odour nuisance and be an inconvenient substance from the point of view of industrial safety. In addition, when fed into an alkaline bleaching solution ($\text{NaOH} + \text{H}_2\text{O}_2 + \text{waterglass}$), it would readily cause silicate precipitate and consume the lye.

[0006] Paper manufacture aims at ever-higher brightness levels. The brightness of paper can be affected, for example, by treating the paper with coating agents containing, among other things, pigments, binding agents, and plasticizing agents (JP application 284598). However, the use of several coating agents at the final stage of paper manufacture adds to the manufacturing costs.

[0007] EP-A-0 481 792 discloses a detergent composition in tablet form comprising a persalt and a bleach activator. The persalt is preferably sodium percarbonate, and the bleach activator can for example be glycerol triacetate.

[0008] WO-A-94/18299 relates to the in situ production of peroxygen-based oxidising species from a peroxygen source and an activator followed by the use of the product as an oxidising agent, for instance as a bleach or a biocide. The preferred activator compounds are nonanoyloxy-benzene-sulphonate sodium salt (NOBS), isononanoyloxy-benzenesulphonate sodium salt (ISONOBS) and benzyloxy-benzenesulphonate sodium salt (BOBS).

[0009] WO-A-95/21290 relates to pulp bleaching and teaches the steps of forming an aqueous solution containing hydrogen peroxide or an inorganic persalt and a bleach activator compound which is an acyl donor to form a strong oxidising agent, and contacting the pulp with this oxidising agent. The produced pulp is claimed to have good brightness reversion properties. The preferred activator seems to be tetraacetylene diamine (TAED) which is the only activator used in the examples.

[0010] A technically useful activator should be liquid and stable, and it should preferably have a suitable pH value, so that no silicate precipitate would form in the alkaline peroxide bleaching. Because of environmental matters, a nitrogen-free activator would provide an additional benefit. The additive of the bleaching should also be cost-effective for the paper manufacturers. Consequently, an activator should be found for pulp bleaching, which, to fulfil the conditions mentioned above, is a registered, reasonable, commercial chemical that is easy to get and can be added to the pulp as early as at the peroxide bleaching stage. Furthermore, attention should also be paid to the other effects of the substance, such as applicability in plant conditions.

[0011] The purpose of this invention is to find a useful activator that is used in pulp bleaching and that fulfils the conditions mentioned above.

[0012] The main features of the invention are disclosed by the appended Claims.

[0013] According to the invention, we have surprisingly observed that carboxylic acid esters of glycerol known per se are very suitable to be used as activator agents, said carboxylic esters of glycerol being the monoesters, diesters, and triesters of formic acid, acetic acid, and propionic acid. From the point of view of industrial hygiene, the carboxylic acid esters of glycerol are almost harmless. Especially preferable activator agents to be added to the bleaching process comprise acetic esters of glycerol, such as triacetine and diacetine. Even if these esters as such were not water soluble,

they dissolve completely in an alkaline peroxide solution, because the acetyl groups split off producing percarboxylic acid in situ. Glycerol and carboxylic acid are the residues of the chemical. By default, bleaching produces glycerol and acetic acid.

[0014] Activators to be used in the peroxide bleaching solution according to the invention are mono-, di- and triformic, acetic and propionic esters of glycerol. Mono-, di- and triacetic esters of glycerol are preferable.

[0015] As it is assumed that the generation of peracid in peroxide bleaching is the reaction mechanism of the activator, the excess length of the hydrocarbon chain reduces the effect of the activator. When the hydrocarbon chain increases, a smaller amount of peracid is obtained as the amount of material than with shorter hydrocarbon chains.

[0016] A suitable dose of the activator has been found to be 0.2 - 5 kg/ton of pulp. A preferable dosage is 1 - 3 kg/ton of pulp. The bleaching conditions can be normal; in bleaching mechanical pulps, for example, we have used a temperature of 50 - 90°C, a consistency of 5 - 40%, and a retention of 30 - 240 min. Depending on the level of brightness, the dose of peroxide may vary within 5 - 50 kg/ton of pulp. Correspondingly, the doses of lye and waterglass must be adjusted to be suitable for the dose of peroxide. In addition to lye, waterglass, and hydrogen peroxide, the bleaching solution can contain a chelating agent, such as DTPA or some other stabilizers. The activators are suitable to be used for bleaching mechanical pulps in particular, such as ground wood (SGW, PGW), refiner mechanical pulp (TMP) or chemimechanical pulps (CTMP). Activators can also be used in the peroxide bleaching of chemical pulps, such as sulphate and sulphite pulp. The sort of wood used for the manufacture of pulp has no significance for the functioning of the invention.

[0017] In the following, the invention is described mainly with the aid of examples 1 to 4.

Example 1

[0018] Chemi-mechanical pulp (CTMP) was treated with peroxide in a normal manner. The effect of the bleaching activator is shown in Table 1.

Table 1

CTMP, bleaching solution: 24 kg of NaOH + 20 kg of waterglass + 30 kg/ton of pulp of H ₂ O ₂ t = 70°C, consistency 30%, 120 min, chelated pulp				
Activator	Dosage, kg/ton of pulp	Brightness, % ISO	Yellowness	Opacity
None	-	78.4	17.7	64.9
PAA	2	79.1	17	67.2
Triacetine	5	78	17.9	67.2
Triacetine	2	78.3	17.8	68.6

[0019] The results indicate that by adding the activator to the peroxide bleaching, a distinctly higher opacity with the same brightness level is achieved than by using peroxide bleaching alone. The results also show that the activators had hardly any effect on the ISO brightness.

Example 2

[0020] Refiner mechanical pulp of spruce with a brightness of 60.4% ISO, opacity of 86.5, containing 100 ppm of Mn and 18 ppm of Fe, was brought to peroxide bleaching. The results are in Table 2.

Table 2

TMP (spruce), bleaching stages Chelating treatment: Consistency 10%, pH 5.5, 45 min, t = 55°C, 2 kg/ton of pulp of DTPA Consistency to 15% Peroxide bleaching: 120 min, t = 70°C, consistency 15%, 22 kg of H ₂ O ₂ , 22 kg of NaOH, 17.6 kg/ton of pulp of waterglass				
Activator	Dosage kg/ton of pulp	H ₂ O ₂ residue, kg/ton of pulp	Brightness, % ISO	Opacity, %
None	0	9.2	74.5	81.4
Triacetine	1	9.4	75.8	83.1

Table 2 (continued)

TMP (spruce), bleaching stages Chelating treatment: Consistency 10%, pH 5.5, 45 min, t = 55°C, 2 kg/ton of pulp of DTPA Consistency to 15% Peroxide bleaching: 120 min, t = 70°C, consistency 15%, 22 kg of H ₂ O ₂ , 22 kg of NaOH, 17.6 kg/ton of pulp of waterglass				
Activator	Dosage kg/ton of pulp	H ₂ O ₂ residue, kg/ton of pulp	Brightness, % ISO	Opacity, %
Triacetine	2	9.9	75.5	82.8

[0021] The results show that the activator in peroxide bleaching obviously had a positive effect on the opacity of the pulp, when compared with peroxide bleaching without the added activator.

Example 3

[0022] Pressure groundwood pulp was treated with peroxide in a normal manner. The effect of the bleaching activator is shown in Table 3.

Table 3

PGW (pressure groundwood pulp) Peroxide bleaching: Consistency 28%, 12 0min, t = 70°C, 25 kg of H ₂ O ₂ , 18.8 kg of waterglass, 25 kg of NaOH, chelated at the plant				
Triacetine, kg/ton of pulp	Brightness, % ISO	Opacity, %	Light scattering	Light absorption
0	77.5	86.4	67.4	0.37
1	77.8	87.8	70.3	0.36
2	77.8	88.6	73.9	0.37

Example 4

[0023] Mechanical pulp was treated with peroxide in a normal manner. The effect of the bleaching activator in peroxide bleaching is shown in Table 4.

Table 4

TMP, bleaching solution: 20 kg of NaOH + 18.8 kg of waterglass + 20 kg of H ₂ O ₂ , 2 kg of DTPA			
t = 70°C, consistency 28%, 120 min, plant-chelated pulp			
Activator	Dosage, kg/ton of pulp	Brightness, % ISO	Opacity
None -		77.8	79.4
Triacetine 1		77.9	81.3
Triacetine 2		77.8	81.1
Triacetine 5		77.5	81.7
Diacetine 2		77.8	81.5

[0024] The results show that the activator had a distinct effect on the opacity with the same level of brightness as peroxide bleaching alone. We can also observe that the activators have no effect on the ISO brightness.

Claims

1. A peroxide bleaching solution for bleaching paper pulp containing lignin, **characterized in that** said bleaching activator comprises said bleaching solution comprising a bleaching activator, a mono-, di- or triformic, acetic or

propionic ester of glycerol.

2. A peroxide bleaching solution according to Claim 1, wherein the activator is glycerol triacetate.
- 5 3. A peroxide bleaching solution according to Claim 1, wherein the activator is glycerol diacetate.
4. A peroxide bleaching solution according to Claim 1, wherein the bleaching solution additionally comprises a chelating agent, a stabilizer, lye, and waterglass.
- 10 5. A peroxide bleaching solution according to Claim 1, wherein the bleaching solution comprises peracetic acid.
6. Use of mono-, di- or triformic, acetic or propionic ester of glycerol as a bleaching activator in peroxide bleaching of paper pulp containing lignin to improve the opacity.
- 15 7. A method for bleaching pulp containing lignin with a bleaching solution containing hydrogen peroxide and a bleaching activator, **characterized in that** said bleaching activator comprising a mono-, di- or triformic, acetic or propionic ester of glycerol is added to the bleaching to improve the opacity.
8. A method according to claim 7, wherein the pulp to be bleached comprises a mechanical pulp.
- 20 9. A method according to Claim 7, wherein the activator is added in an amount of 0.2 - 5 kg/ton of pulp.
10. A method according to Claim 7, wherein the activator is added in an amount of 1 - 3 kg/ton of pulp.

Patentansprüche

1. Peroxid-Bleichlösung zum Bleichen von ligninhaltigem Papier-Faserstoff, die einen Bleichaktivator aufweist, **dadurch gekennzeichnet, dass** der Bleichaktivator einen Mono-, Di- oder Triameisensäureester, -essigsäureester oder -propionsäureester von Glycerin aufweist.
- 30 2. Peroxid-Bleichlösung nach Anspruch 1, in der der Aktivator Glycerintriacetat ist.
3. Peroxid-Bleichlösung nach Anspruch 1, in der der Aktivator Glycerindiacetat ist.
- 35 4. Peroxid-Bleichlösung nach Anspruch 1, in der die Bleichlösung zusätzlich einen Komplexbildner, einen Stabilisator, Lauge und Wasserglas aufweist.
5. Peroxid-Bleichlösung nach Anspruch 1, in der die Bleichlösung Peressigsäure aufweist.
- 40 6. Verwendung von Mono-, Di- oder Triameisensäureester, -essigsäureester oder -propionsäureester von Glycerin als Bleichaktivator beim Peroxidbleichen von ligninhaltigem Papier-Faserstoff, um die Opazität zu verbessern.
7. Verfahren zum Bleichen von ligninhaltigem Faserstoff mit einer Bleichlösung, die Wasserstoffperoxid und einen Bleichaktivator enthält, **dadurch gekennzeichnet, dass** der Bleichaktivator, der einen Mono-, Di- oder Triameisensäureester, -essigsäureester oder -propionsäureester von Glycerin aufweist, der Bleiche zugegeben wird, um die Opazität zu verbessern.
- 45 8. Verfahren nach Anspruch 7, bei dem der zu bleichende Faserstoff einen Holzstoff aufweist.
- 50 9. Verfahren nach Anspruch 7, bei dem der Aktivator in einer Menge von 0,2 - 5 kg/Tonne Faserstoff zugegeben wird.
10. Verfahren nach Anspruch 7, bei dem der Aktivator in einer Menge von 1 - 3 kg/Tonne Faserstoff zugegeben wird.

Revendications

1. Solution de blanchiment au peroxyde, pour le blanchiment de pâte à papier contenant de la lignine, ladite solution

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de blanchiment contenant un activateur de blanchiment, **caractérisée en ce que** ledit activateur de blanchiment comprend un mono-, un di- ou un triester de glycérol et d'acide formique, acétique ou propionique.

2. Solution de blanchiment au peroxyde selon la revendication 1, dans laquelle l'activateur est le triacétate de glycérol.

3. Solution de blanchiment au peroxyde selon la revendication 1, dans laquelle l'activateur est le diacétate de glycérol.

4. Solution de blanchiment au peroxyde selon la revendication 1, contenant en outre un agent chélatant, un stabilisant, de la soude caustique et du silicate de soude.

5. Solution de blanchiment au peroxyde selon la revendication 1, comprenant en outre de l'acide peracétique.

6. Utilisation d'un mono-, d'un di- ou d'un triester de glycérol et d'acide formique, acétique ou propionique comme activateur de blanchiment lors du blanchiment au peroxyde de pâte à papier contenant de la lignine, pour améliorer l'opacité.

7. Procédé pour le blanchiment de pâte à papier contenant de la lignine à l'aide d'une solution de blanchiment contenant du peroxyde d'hydrogène et un activateur de blanchiment, **caractérisé en ce que** ledit activateur de blanchiment comprend un mono-, un di- ou un triester de glycérol et d'acide formique, acétique ou propionique, pour améliorer l'opacité.

8. Procédé selon la revendication 7, dans lequel la pâte à blanchir comprend de la pâte mécanique.

9. Procédé selon la revendication 7, dans lequel l'activateur est ajouté en une quantité de 0,2 à 5 kg/tonne de pâte.

10. Procédé selon la revendication 7, dans lequel l'activateur est ajouté en une quantité de 1 à 3 kg/tonne de pâte.

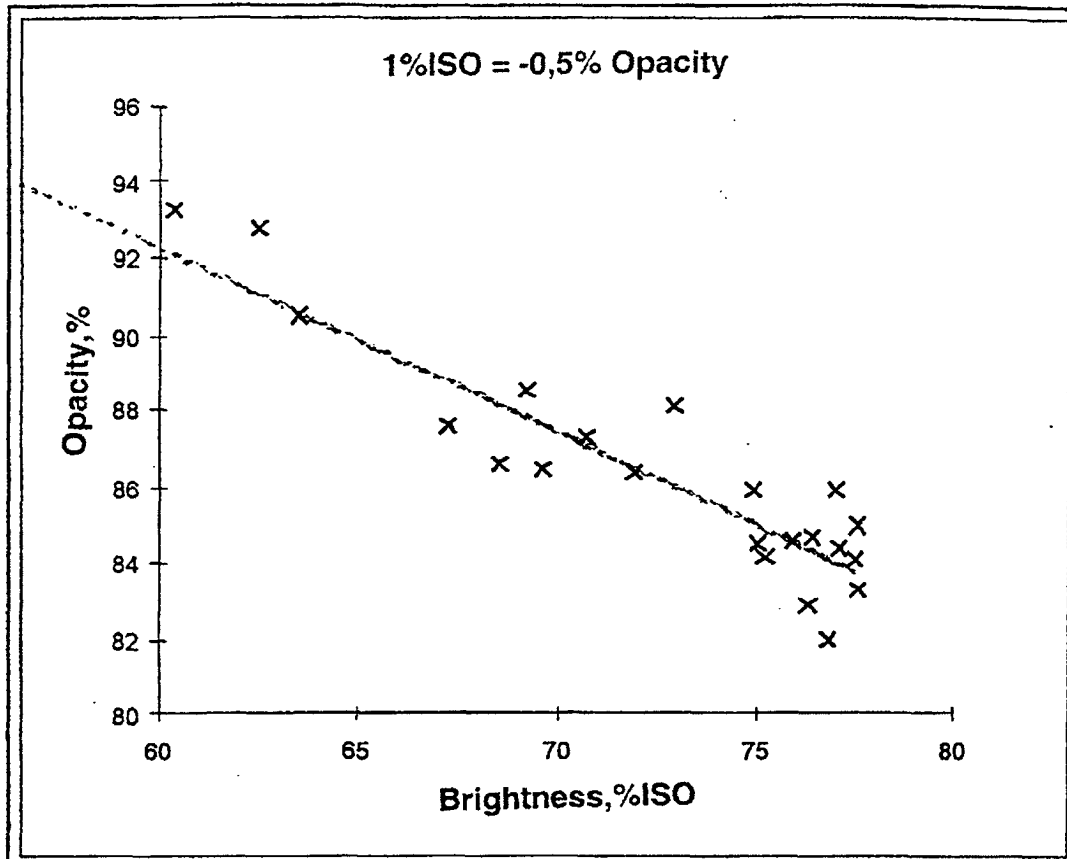


Fig. 1