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

(11) EP 0 951 599 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
28.05.2003 Bulletin 2003/22

(21) Application number: **97912616.6**

(22) Date of filing: **06.11.1997**

(51) Int Cl.[7]: **D21C 9/10**, D21C 9/16

(86) International application number:
PCT/SE97/01853

(87) International publication number:
WO 98/029597 (09.07.1998 Gazette 1998/27)

(54) **TREATMENT OF PULP WITH A CHELATING AGENT WITHOUT USING A BLEACHING TOWER**

ZELLSTOFFBEHANDLUNG MIT EINEM KOMPLEXBILDNER OHNE VERWENDUNG EINES BLEICHTURMS

TRAITEMENT DE PATE AVEC UN CHELATEUR SANS UTILISER DE TOUR DE BLANCHIMENT

(84) Designated Contracting States:
AT DE ES FI FR PT SE

(30) Priority: **03.01.1997 SE 9700030**

(43) Date of publication of application:
27.10.1999 Bulletin 1999/43

(73) Proprietor: **Valmet Fibertech AB**
851 94 Sundsvall (SE)

(72) Inventors:
- **GERMGARD, Ulf**
  S-865 31 Alnö (SE)
- **LINDQUIST, Jonas**
  S-952 42 Kalix (SE)

(74) Representative: **Sundqvist, Hans et al**
Valmet Fibertech AB
Patents Department
851 94 Sundsvall (SE)

(56) References cited:
WO-A-93/23607
WO-A-94/29514
WO-A-95/08666
WO-A-97/08380

EP 0 951 599 B1

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] This invention relates to the bleaching of chemical pulp with chlorine-free chemicals. The invention, more precisely, refers to a method of pretreating the pulp with chelating agents in combination with the bleaching.

[0002] Totally chlorine-free bleaching (TCP) of chemical papermaking pulp has become a success, and the world production of chlorine-free pulp will soon have got up to five million year-tons, which is an exceptional development considering that the bleaching method was introduced less than six years ago. There exist, besides, variants of this theme, where the prebleaching is chlorine-free and the final bleaching is either of ECF (elementary chlorine-free) or TCF (totally chlorine-free) type.

[0003] Bleaching is carried out in most cases by treating the papermaking pulp to be bleached with chlorine-free chemicals first with a chelating agent of the type EDTA or DTPA. The chelating agent has the object to remove from the pulp certain metal ions, particularly manganese, copper, iron a.o., which affect the bleaching result negatively, if they remain in the pulp. The chelating agent usually is designated by the letter Q.

[0004] The pulp is washed after the Q-step, so that the exposed metal ions are eliminated from the pulp as completely as possible. Thereafter the bleaching takes place, which normally is carried out with hydrogen peroxide, at times in combination with oxygen. Hydrogen peroxide steps are designated with the letter P, and P-steps reinforced with oxygen are designated with OP or PO where the dominating chemical is mentioned first. The thumb rule is that the greater the number of harmful metal ions eliminated from the pulp is, the more effective the subsequent bleaching will be.

[0005] A method, at which the pulp is treated in a Q-stage and thereafter bleached in a P-stage, usually is called the "Lignox"-method, which is disclosed, for example, in EP-A-402 335.

[0006] The original pulp normally is oxygen delignified to a relatively low kappa number prior to the QP-bleaching. A low kappa number before the bleaching implies that the obtainable maximum bleaching result increases in the subsequent step, and that the bleaching chemical demand is reduced.

[0007] In mills, the QP-bleaching most often is carried out in such a way, that the pulp first is passed through a pump, which pumps the pulp suspension through the treatment steps. Thereafter follows a mixer where the chelating agent is added to the pulp. The next step is a bleaching tower, where the pulp without additional agitation slowly passes through and where all remaining reaction takes place. The pulp finally passes to a washing step where the exposed and complexed metal ions are washed out. The freed liquid enriched on metal ions most often is discharged.

[0008] The conditions normally applied in a Q-step are a temperature of 70-90°C, a retention time of 1-2 hours, a pulp consistency of 10-14%, a pH of 5-7 and a charge of chelating agent of 1-3 kg per ton pulp. By these conditions a very good metal separation can be achieved, which is necessary if subsequent bleaching is carried out on pulp with low lignin content (the kappa number is below about 5) and if a large amount of hydrogen peroxide is used in the stage (more than 15 kg/t). If, however, the pulp still contains a considerable amount of lignin (kappa number above about 5), and the hydrogen peroxide charge in the subsequent step is limited to about 5-10 kg/t, the demand for a complete metal elimination is less critical. Another case when it is sufficient that less metal is eliminated in the stage, i.e. less than 60% reduction, is for example the case when the metal content before the Q-step is so low in relation to the metal content required after the Q-step. In such positions a somewhat simplified Q-process should, therefore, be possible.

[0009] From a strict bleaching point of view, the Q-step per se is an unnecessary treatment step, because no proper bleaching takes place there. The Q-treatment, however, is necessary for a following successful P- or PO-bleaching, as appears from the aforesaid. If the Q-step could be simplified without reducing the effectiveness in the elimination of metals, great savings could be made, because a complete bleaching stage is expensive.

[0010] The present invention is directed to a simplification of the Q-step, especially for pulps with kappa number above about 5, and for chelating agent treatments which require less than 60% metal reduction. The simplification implies, that the investment cost decreases in relation to a conventional Q-step.

[0011] The invention is based on the surprising observation, that the effectiveness of the Q-step is considerably less affected by increased reaction temperature than by increased retention time. This indicates, according to classical chemical cinetics, that the Q-step is diffusion controlled and not reaction controlled. This means, that the Q-step should be carried out so that the diffusion is facilitated, and if this is made effectively, the total retention time can thereby be reduced substantially.

[0012] The characterizing features of the invention are apparent from the attached claims.

[0013] The best method to reduce the diffusion resistance is to decrease the diffusion distance for active reactants and released reaction products. On a technical scale this is made by effective mixing, for example in a mixer with long retention time. Thus, by effective mixing, the retention time in the Q-step can be shortened. The number of mixing steps is not critical, but the total mixing time must be above a certain critical level, alternatively at least two mixing apparatuses shall be used. For economic reasons, however, the number of mixing steps must be held on a reasonable level. For a pulp with kappa number above about 5, which shall be bleached further with at maximum about 5-10 kg hydrogen peroxide exclusive possible oxygen, a suitable number of mixing steps is 1-2. The same applies, if the metal reduction to be achieved in the chelating agent step is limited and need not be above 60%.

[0014] When two mixing steps are used, a certain retention time between the mixing steps is favourable, but this time need not be long, because the diffusion rate without mixing yet is much slower than what can be achieved by mixing, for example in a mixer. The stay-time between the mixing steps, thus, shall be short, less than 10 minutes and preferably less than 5 minutes. The mixing steps then shall be carried out one after the other without intermediate washing. The washing required for removing the metals from the pulp suspension shall be carried out less than 15 minutes after the last mixing step.

[0015] When more than one mixing step is used, the entire charge of chelating agent shall be added in the first mixing step, and subsequent mixing steps bring about only a renewed mixing. To divide the charge in such a way that at maximum one third of the chelating agent charge is added in the last step, however, is not detrimental, if the subsequent mixing is sufficiently effective.

[0016] The chelating agent preferably is of the type EDTA (ethylene diamine tetraacetic acid) or DTPA (diethylene triamine pentaacetic acid), but also other types of chelating agent can be used, for example NTA (nitrilotriacetic acid) or DTPMP (diethylene triamine pentamythylene phosphoric acid). The total amount of added chelating agent should be 0.5-3 kg per ton pulp (calculated as pure chelating agent), preferably 1-2 kg per ton pulp.

[0017] The temperature in the Q-step should be above 75°C, suitably over 80°C and more preferably over 85°C. A preferred temperature interval is 85-110°C. The desired pH interval is pH 5 to pH 11. The pulp consistency should be between 2 and 16%.

[0018] An especially effective mixing can be achieved by using high-intensity mixers or with another type of mixer, where the mixing is effective and the retention time is sufficient, so that a homogenous mixture of fibres and chelating agent is obtained.

[0019] In the Table below some results from a one-stage Q-treatment are shown, which was carried out with a high-intensity mixer for 3 seconds and with a subsequent retention time without mixing for 40 seconds before the pulp washing, and where the treatment was carried out at 95°C. For comparison, data are also shown from a conventional Q-treatment with conventional lab mixing of chelating agent with the pulp and a subsequent retention time of 60 minutes, where the step was carried out at 90°C.

Experiment:

[0020] The starting pulp was oxygen bleached and of coniferous sulphate type with kappa number 10.1, viscosity 975 dm^3/t and brightness 43.0% ISO. The bleaching was carried out according to Q(OP) with 10 kg H_2O_2/t.

PH 8.6 in the Q-stage	Q acc. to invention	Q acc. to conv. technique
Kappa number	5.7	5.7
Viscosity dm^3/kg	771	807
Brightness % ISO	63.4	64.9

pH 10.6 in the Q-stage	Q acc. to invention	Without Q-step before (OP)-step
Kappa number	5.7	6.1
Viscosity dm^3/kg	771	790
Brightness % ISO	62.2	59.1

[0021] The invention, of course, is not restricted to the embodiments described above, but can be varied within the scope of the patent claims.

Claims

1. A method at chlorine-free bleaching of pulp where metals are eliminated by means of a chelating agent, the kappa number of the pulp before the chelating stage being above 5 and the desired metal reduction in the chelating stage being less than 60%, wherein the chelating agent is mixed with the pulp, without using a bleaching tower, in at least one effective mixing stage using high-intensity mixers at a pH between 5 and 11, that the pulp is washed less than 15 minutes after the last mixing stage, and that the pulp thereafter is bleached in a chlorine-free bleaching stage.

2. A method as defined in the preceding claim, **characterized in that** the kappa number of the pulp before the chelating agent stage is above 5, or that the desired metal reduction in the chelating agent stage is less than 60%.

3. A method as defined in any one of the preceding claims, **characterized in that** the entire addition of chelating agent amounts to 0.5-3 kg per ton pulp, preferably 1-2 kg per ton pulp.

4. A method as defined in any one of the preceding claims, **characterized in that** the temperature in the chelating agent stage is above 75°C and at maximum 110°C.

5. A method as defined in any one of the preceding claims, **characterized in that** the pulp consistency in the chelating agent stage is 2-16%.

6. A method as defined in any one of the preceding claims, where at least two mixing stages are used, **characterized in that** the entire addition of chelating agent is made in the first mixing stage, and that subsequent mixing stages only bring about renewed mixing.

7. A method as defined in claim 6, **characterized in that** the chelating agent is added in several mixing stages.

8. A method as defined in any one of the preceding claims, **characterized in that** the chelating agent is of the type EDTA or DTPA.

9. A method as defined in any one of the preceding claims, **characterized in that** the chelating agent is of the type NTA or DTPMP.

10. A method as defined in any one of the preceding claims, **characterized in that** the high-intensity mixers break up the fibre network in the pulp and bring about close contact between fibres and the chelating agent.

Patentansprüche

1. Verfahren zum chlorfreien Bleichen von Pulpe, in der Metalle mittels eines chelatbildenden Mittels eliminiert werden, die Kappa-Zahl der Pulpe vor dem Chelationsschritt über 5 und die erwünschte Metallreduktion in der Chelationsstufe weniger als 60% ist, wobei das chelatbildende Mittel mit der Pulpe ohne Verwendung eines Bleichturms in wenigstens einer effektiven Mischstufe unter Verwendung eines hochintensiven Mischers bei einem pH-Wert zwischen 5 und 11 gemischt wird, die Pulpe weniger als 15 Minuten nach der letzten Mischstufe gewaschen wird und die Pulpe danach in einer chlorfreien Bleichstufe gebleicht wird.

2. Verfahren nach dem vorhergehenden Anspruch,
dadurch gekennzeichent, dass die Kappa-Zahl der Pulpe vor der Chelationsstufe über 5 ist oder dass die gewünschte Metallreduktion in der Chelationsstufe weniger als 60% ist.

3. Verfahren nach einem der vorhergehenden Ansprüche,
dadurch gekennzeichnet, dass die gesamte Zugabe des chelatbildenden Mittels bis 0,5 - 3kg pro Tonne Pulpe, vorzugsweise 1-2 kg pro Tonne Pulpe beträgt.

4. Verfahren nach einem der vorhergehenden Ansprüche,
dadurch gekennzeichnet, dass die Temperatur in der Chelationsstufe über 75° C und maximal 110°C beträgt.

5. Verfahren nach einem der vorhergehenden Ansprüche,

dadurch gekennzeichnet, dass die Pulpenkonsistenz in der Chelationsstufe 2-16% ist.

6. Verfahren nach einem der vorhergehenden Ansprüche,
wobei wenigstens zwei Mischstufen verwendet werden,
dadurch gekennzeichnet, dass die gesamte Zugabe des chelatbildenden Mittels in der ersten Mischstufe ausgeführt wird und dass die nachfolgenden Mischstufen nur ein erneutes Mischen ergeben.

7. Verfahren nach Anspruch 6,
dadurch gekennzeichnet, dass das chelatbildende Mittel in verschiedenen Mischstufen zugegeben wird.

8. Verfahren nach einem der vorhergehenden Ansprüche,
dadurch gekennzeichnet, dass das chelatbildende Mittel vom Typ EDTA oder DTPA ist.

9. Verfahren nach einem der vorhergehenden Ansprüche,
dadurch gekennzeichnet, dass das chelatbildende Mittel vom Typ NTA oder DTPMP ist.

10. Verfahren nach einem der vorhergehenden Ansprüche,
dadurch gekennzeichnet, dass die hochintensiven Mischer die Faservernetzung in der Pulpe aufbrechen und einen engen Kontakt zwischen den Fasern und dem chelatbildenden Mittel ergeben.

Revendications

1. Procédé de blanchiment de pâte à papier exempt de chlore où des métaux sont éliminés au moyen d'un agent chélatant, l'indice kappa de la pâte à papier avant l'étape de chélation étant supérieur à 5 et la réduction métallique souhaitée dans l'étape de chélation étant inférieure à 60%, dans lequel l'agent chélatant est mélangé avec la pâte à papier, sans utiliser do tour do blanchiment, dans au moins une étape de blanchiment efficace en utilisant des mélangeurs à intensité élevée à un pH compris entre 5 et 11, la pâte à papier est lavée moins de 15 minutes après la dernière étape de mélange, et la pâte à papier est ensuite blanchie dans une étape de blanchiment exempte de chlore.

2. Procédé selon la revendication précédente, **caractérisé en ce que** l'indice kappa de la pâte à papier avant l'étape de l'agent chélatant est supérieur à 5, ou **en ce que** la réduction du métal souhaitée dans l'étape de l'agent chélatant est inférieure à 60%.

3. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'addition complète des quantités d'agent chélatant s'élève entre 0,5 et 3 kg par tonne de pâte à papier, de préférence entre 1 et 2 kg par tonne de pâte à papier.

4. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la température dans l'étape mettant en oeuvre l'agent chélatant est supérieure à 75°C et est au maximum de 110°C.

5. Procédé selon l'une quelconque des revexidications précédentes, **caractérisé en ce que** la consistance de la pâte à papier dans l'étape mettant en oeuvre l'agent chélatant est comprise entre 2 et 16%.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel au moins deux étapes de mélange sont utilisées, **caractérisé en ce que** l'addition complète de l'agent chélatant est réalisée dans la première étape de mélange, et **en ce que** les étapes de mélange ultérieures n'entraînent qu'un mélange renouvelé.

7. Procédé selon la revendication 6, **caractérisé en ce que** l'agent chélatant est ajouté en plusieurs étapes de mélange.

8. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'agent chélatant est du type EDTA ou DTPA.

9. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'agent chélatant est du type NTA ou DTPMP.

10. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** les mélangeurs à intensité élevée rompent le réseau fibreux dans la pâte à papier et provoquent un contact étroit entre les fibres et l'agent chélatant.