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## (54) A sizing composition usable for the neutral sizing of paper or board, and a process for the manufacture of paper or board

(57) The invention relates to a sizing composition usable for the neutral sizing of paper or board, which composition contains a size capable of reacting with cellulose, such as alkyl ketene dimer or alkenyl succinic acid anhydride, and an organic complexing agent. The invention also relates to a process for the manufacture of paper or board.

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## Description

**[0001]** The present invention relates to a sizing composition usable for the neutral sizing of paper or board. The invention additionally relates to a process for the manufacture of paper or board.

**[0002]** At a neutral pH, alkyl ketene dimer (AKD) or alkenyl succinic acid anhydride (ASA) is commonly used as a size in order to enhance the water repellence (hydrophobicity) of paper or board. Both of these molecules are deemed to react with cellulose fiber. The reaction occurs most rapidly in particular in alkaline or slightly basic conditions. In paper making, AKD and ASA are added to an aqueous dispersion which contains fiber and additives (e.g. fillers, retention agents, anti-foaming agents, pH control agents), and from which an effort is made to separate the solids onto the wire as effectively as possible, i.e. the aim is as high a retention as possible. The water used for the dispersion is commonly circulation water and pure raw water added to it, in which case the water used for the dispersing usually contains, for example, approx. 200 ppm of alkaline earth metals: calcium and magnesium ions.

**[0003]** It is commonly known that pulps which contain calcium carbonate, which is used for increasing the brightness of paper, consume more hydrophobification chemicals than do pulps without carbonate.

**[0004]** Carboxyl groups on the surface of cellulose generate a negative charge in the fibers. The magnitude of the charge depends on the surrounding pH. In alkaline conditions the carboxyl group becomes protolyzed, and therefore the quantity of negative charges increases.

**[0005]** In general the sizes used for purposes of hydrophobification are prepared by emulsifying the water-repellent substance in a cationically charged starch. The starch surrounds the water-insoluble hydrophobification agent, whereupon a dispersion evenly distributed in the water is formed. Owing to the starch the dispersion particles are cationic. They tend to adhere to negatively charged surfaces, for example cellulose fibers.

**[0006]** In particular in hard waters, bivalent alkaline earth metal ions, such as $Ca^{2+}$ ions, and also other multivalent ions, neutralize the carboxyl groups of cellulose fibers, and consequently the negative charge of the fibers respectively decreases. Since it has been conceived that a size particle formulated using a cationic starch attaches to the fiber surface by means of charges, the presence of surface charges both in the size particle and the fiber is important in terms of retention. $Ca^{2-}$ ions neutralize the surface charge, and consequently the retention of cationic size particles weakens. Likewise, the adherence of cationic retention agents to fiber also depends on the surface charge of the fiber.

**[0007]** By the use of chelating and sequestering chemicals, by means of which the quantity of free ions in waters can be lowered, it is also possible to decrease the number of $Ca^{2+}$ ions on fiber surfaces and to create free anionic groups to enhance retention. However, if these complexing agents were used directly, for example, in the circulation waters of the paper machine, their use would be relatively high and would cause problems in the rest of the operation of the machine.

**[0008]** It has been observed, surprisingly, that paper hydrophobification by using AKD- and ASA-based chemicals can be improved when small amounts of agents which form complexes with metals are added to their formulations or are dosed together with them. Thus, by means of the agents added to the size, the complexing of the cations in the fiber is brought close to the size particles, whereby the retention of the size is improved, while the concentration of complexing agents in the circulation waters of the paper machine can, nevertheless, be maintained low.

**[0009]** Since, for example, calcium carbonate is a commonly used filler in paper making, the use of complexing agents for chelating all of the calcium is not sensible, since this would lead to the dissolving of the calcium carbonate. What is inventive here is specifically the fact that it has been observed, surprisingly, that a very small dose of complexing agents in the size formulation considerably improves sizing. In terms of the performance of the invention it is required that the complexing agent sufficiently rapidly forms sufficiently stable complexes with the metal cations which are present in the paper machine and possibly have a deleterious effect on AKD sizing. It is essential for the performance of the invention that a suitable quantity of complexing agents is added to the size formulation.

**[0010]** According to the invention, there is thus provided for the neutral sizing of paper or board a sizing composition which contains a sizing agent capable of reacting with cellulose and an organic complexing agent.

**[0011]** The size is preferably alkyl ketene dimer (AKD) or alkenyl succinic acid anhydride (ASA).

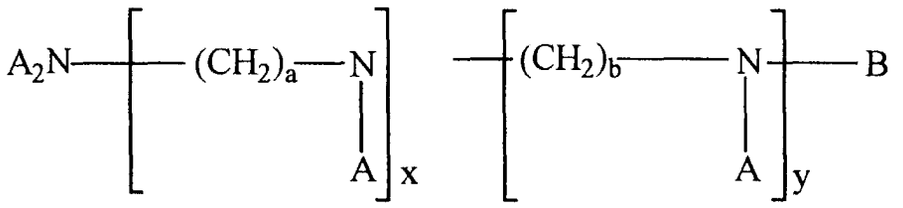
**[0012]** The term chelating agent is also used for complexing agents.

**[0013]** Suitable complexing agents which can be used in accordance with the invention include

a) aminopolycarboxylic acids
b) N-bis- or tris-[(1,2-dicarboxylethoxy)ethyl]amines and
c) phosphonic acids.

**[0014]** The complexing agents cited above may be in the form of an acid or a salt. Suitable salts include alkali metal salts and ammonium salt. Sodium and potassium salts are preferred salts.

**[0015]** Preferred complexing agents of group a) include aminopolycarboxylic acids having the following general Formula I.



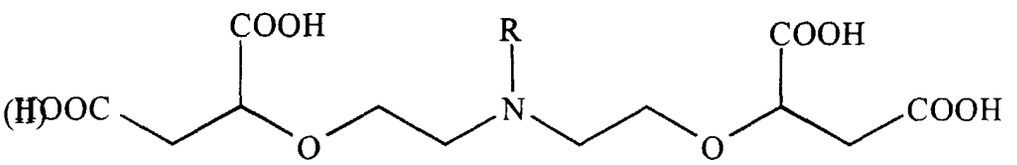
(I)

where

A is $-CH_2COOH$,
B is $-CH_2COOH$ or $-CH_2CH_2OH$,
x is 0-6, preferably 0-3,
y is 0-6, preferably 0-2,
a is 2-10, preferably 2-4, and
b is 2-10, preferably 2-6.

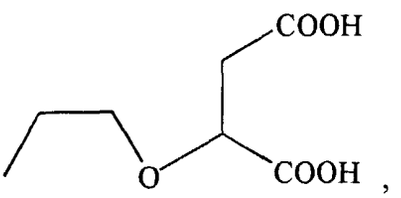
**[0016]** Especially preferable compounds according to Formula I include ethylene diamine tetra-acetic acid, i.e. EDTA (B=A, x=0, b=2 and y=1), diethylene triamine penta-acetic acid, i.e. DTPA (B=A, x=1, a=2, b= 2 and y=1), and nitrilo-triacetic acid, i.e. NTA (B=A, x=0 and y=0).

**[0017]** Preferred complexing agents of group b) include N-bis- or tris-[(l,2-dicarboxylethoxy)ethyl]amines having the general Formula II



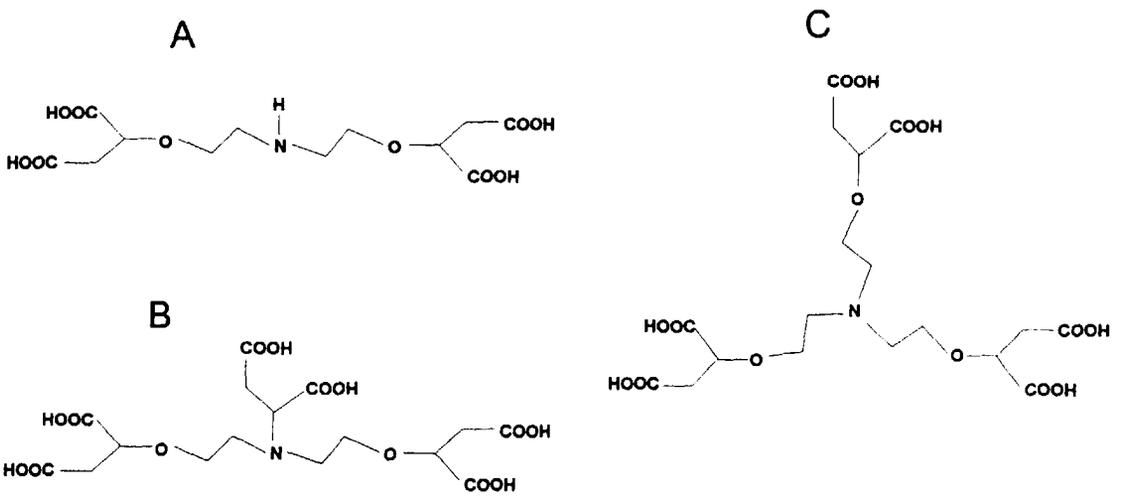
where

R is hydrogen,



an alkyl group having 1-30 carbon atoms,
an alkyl group having 1-30 carbon atoms and additionally 1-10 carboxylic acid groups,
an alkyl group having 1-30 carbon atoms and additionally 1-10 carboxylic acid ester groups,
a (poly)ethoxylated hydrocarbon group having 1-20 ethoxyl groups, or
a carboxylic acid amide group having 1-30 carbon atoms, in which case the N-R bond is an amide bond.

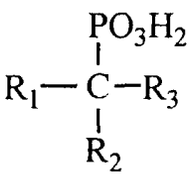
**[0018]** Especially preferable complexing agents in Formula II include the following compounds according to Formulae A, B and C:




A= N-bis[(1,2-dicarboxylethoxy)ethyl]amine (hereinafter the acronym BCEEA will be used)
B= N-bis[(1,2-dicarboxylethoxy)ethyl]aspartic acid (hereinafter the acronym BCEEAA will be used)
C= N-tris[(1,2-dicarboxylethoxy)ethyl]amine (hereinafter the acronym TCEEA will be used)

**[0019]** These complexing agents A, B and C and their preparation have been described in patent application FI-962261. It is also possible to use mixtures of compounds A and B.

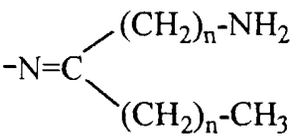
**[0020]** Preferred complexing agents of group c include phosphonic acids having the general Formula III



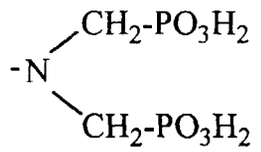

(III)

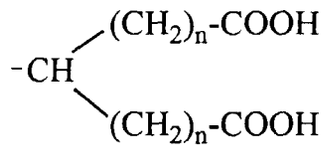
where

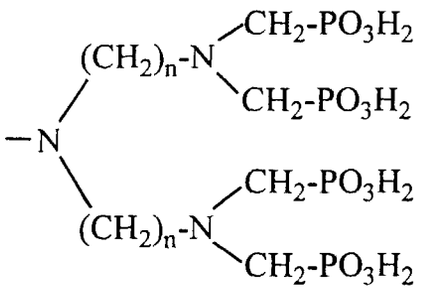
$R_1$ is hydrogen, a lower alkyl such as $-CH_3$ or $-(CH_2)_n-CH_3$, an amino group $-NH_2$, hydroxy methyl $-CH_2OH$, a lower carboxylic acid group $-(CH_2)_n-COOH$, a lower alkyl phosphonic acid group $-(CH_2)_n-PO_3H_2$, or a group having the formula

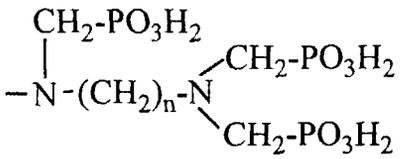


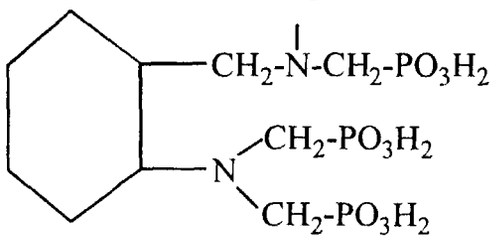

$R_2$ is hydrogen, hydroxyl -OH, a phosphonic acid group $-PO_3H_2$, a lower carboxylic acid group $-(CH_2)_n-COOH$ or a group having the formula











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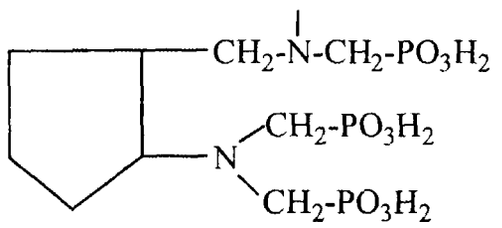
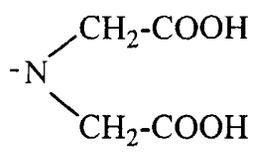


$R_3$ is hydrogen, hydroxyl -OH, an amino group $-NH_2$, a lower alkyl such as $-CH_3$ or $-(CH_2)_n-CH_3$, a lower carboxylic acid group $-(CH_2)_n-COOH$ or a group having the formula -NH-(CH$_2$)n-$PO_3H_2$ -NH-$CH_2$-COOH or



n is 0-6, preferably 0-3.

**[0021]** In a sizing composition according to the invention, the amount of the organic complexing agent may be 0.1-50

% by weight, preferably 0.1-20 % by weight, and especially preferably 0.2-3 % by weight, of the amount of the size.

**[0022]** The sizing composition according to the invention is preferably in the form of a dispersion, in which case it additionally contains a dispersion stabilizing agent.

**[0023]** The stabilizing agents of AKD dispersions include starch, cationic starch and other polymers, such as polyethylene imine, polyepiamine, a polydiethyl diallyl or dicyandiamide compound, polyacrylamide or polyacrylic acid, or salts of these.

**[0024]** For the stabilization of ASA dispersions it is possible to use, for example, starch or other polymers, such as water-soluble cellulose derivatives, e.g. hydroxyethyl or hydroxypropyl, methyl hydroxypropyl ethyl hydroxyethyl cellulose, carboxymethyl cellulose, gelatin, guar gum, xanthan gum or polyvinyl alcohol.

**[0025]** In a sizing composition according to the invention the amount of complexing agent may be 0.2-20 % by weight, preferably 0.2-10 % by weight, and especially preferably 1-5 % by weight, of the amount of the stabilizing agent.

**[0026]** According to the invention there is also provided a process for the manufacture of paper or board by neutral sizing by using a size capable of reacting with cellulose, the process being characterized in that an organic complexing agent defined above is used together with the size.

**[0027]** The complexing agent may be incorporated into the size or it may be dosed at the same location in the paper or board machine as the size.

**[0028]** The invention additionally relates to the use of the sizing composition defined above for the neutral sizing of paper or board.

**[0029]** When the sizing composition or sizing formulation according to the invention contains starch, the complexing agent binds to the starch layer, from which it detaches in dilution and forms a complex with $Ca^{2+}$ ions. When the complexing ion detaches from a fiber, the fiber becomes more anionic and the size particle adheres to the fiber. It is known that the equilibrium constant of cellulose fiber with respect to the complexing of $Ca^{2+}$ ions is approx. 3. On the one hand, this shows that cellulose binds ions out of the circulation water and, on the other hand, this requires that the equilibrium constant of the additive which complexes $Ca^{2+}$ ions must be higher than that of cellulose, as for example the constants of the substances mentioned above are approx. 10.

**[0030]** The sizing composition works in particular in pulps which are made in hard waters and in machines the retention of which is otherwise poor.

**[0031]** It is a common view that the hydrophobicity of paper produced by AKD sizing develops slowly. Rapid sizing is required in particular in the manufacture of base paper for coating. A considerable improvement can be achieved by using the composition according to the present invention.

**[0032]** The performance of the invention is not affected by the other chemicals, such as starch and calcium carbonate, used in the making of the paper, or by the quality of the pulp. Also, the order in which the chemicals are added in the paper machine or the other running parameters of the paper machine do not affect the performance of the invention.

**[0033]** The amount of complexing agent used in the sizing formulation may be 0.1-50 % by weight of the amount of AKD or ASA and 0.2-20 % by weight of the total amount of starch or other polymer stabilizing the formulation. These compounds can be used as such in acid form or in the form of their alkali or ammonium salts. If the agent is used in the form of a salt thereof, the cation of the said salt does not have a substantial effect on the performance of the invention.

**[0034]** Present-day AKD emulsions are physically stable and usable for several weeks. The concentration of AKD in the products may be 0.5-30 % by weight. Various starches are commonly used for the formulation of AKD. They are generally cationated either with quaternary amines, in which case the starch retains its cationic charge also in alkaline conditions, or with primary, secondary or tertiary amines, the charge of which is dependent on the pH. The amount of starch may be 0.1-10 times the proportion AKD. For the dispersing of AKD wax there are generally used various anionic chemicals, such as lignosulfonates, aliphatic or aromatic sulfonates, nonionic surfactants such as fatty acid or fatty alcohol ethoxylates, or cationic surfactants such as fatty acid amines or imidazolines. For the stabilizing of an AKD dispersion it is also possible to use polymers, such as polyethylene imine, polyepiamine, polydimethyl diallyl or dicyandiamide compounds, polyacrylamide or polyacrylic acid and its salts. It is commonly known that the amount of stabilizing chemicals is 1-200 % by weight of the amount of AKD. By the use of polymers it is possible not only to improve the stability of the product but also to affect the performance of the product in paper or board. The adding of stabilizing chemicals is prior art commonly used in the formulation of AKD products.

**[0035]** ASA is dispersed at the paper or board mill by using apparatus installed for this purpose. The prepared dispersion is run immediately to the paper or board machine. To facilitate the preparation of an ASA dispersion, there is usually added to the product a surfactant, such as dioctyl sulfosuccinate, octyl phenoxy polyethoxy ethanol, and polyethylene oxy dinonyl phenyl phosphate, polyethylene oxy sorbitane trioleate.

**[0036]** In general, at the preparation stage it is possible to use as stabilizing agents for liquid ASA dispersions starch or other polymers, such as water-soluble cellulose derivatives, e.g. hydroxy ethyl and hydroxy propyl, methyl hydroxy propyl and ethyl hydroxy ethyl cellulose, carboxy methyl cellulose, or gelatin, guar gum. xanthan gum, polyvinyl alcohol, etc. The drop size of the dispersion is in general on average 0.2-3 μm. The complexing agents can be added to ASA-

based commonly known compositions.

**[0037]** The sizing composition according to the invention is suitable for use for chemical pulps, mechanical pulps, chemimechanical pulps, and mixtures of these.

**[0038]** The performance of the compositions which are the object of the present invention is illustrated with the following examples. The percentages are percentages by weight, unless otherwise indicated.

**Example 1**

**[0039]** The change in the surface charge of fiber under the effect of a complexing agent was studies as follows.

**[0040]** A mixture of pine and birch sulfate pulps at a ratio of 50:50 was dispersed in ion exchange water and was ground to a Schopper number of 20°. The pulp was filtered and redispersed to a consistency of 1 % a) in ion exchange water and b) in ion exchange water which contained 0.1 % DTPA as an Na salt. The pulps were stirred for approx. 1 hour. The pulps were washed with ion exchange water at pH 7. The charge of the fiber was determined using polydiallyl dimethyl ammonium chloride and its back titration with a Na salt of polyethylene sulfonate by a Mütek apparatus.

**[0041]** a. Charge of pulp after wash anionic 3.8 μequiv/g of pulp

**[0042]** b. Charge of pulp after DTPA anionic 5.6 μequiv/g of pulp and wash

**Example 2**

**[0043]** The effect of a complexing agent on the charge of an AKD size formulation was studied using a Mütek apparatus. To an AKD dispersion stabilized with cationic starch there was added the active ingredient of Complexing Agent 1 and Complexing Agent 2 in an amount of 6 % calculated from the amount of starch. The cationic charge was determined by titration with an Na salt of polyethylene sulfonate at pH 3.5. In this example and the examples presented hereinafter, Complexing Agent 1 contains BCEEA and BCEEAA at a molar ratio of 2:3 and Complexing Agent 2 is TCEEA.

| Test | Charge (μequiv/g of product) pH 3.5 | Charge (μequiv/g) pH 8 |
|---|---|---|
| No complexing agent | cationic 3.3 | anionic 2.8 |
| Complexing Agent 1 | cationic 2.7 | anionic 3.3 |
| Complexing Agent 2 | cationic 2.2 | |

**Example 3**

**[0044]** In this example there was used a pulp the composition of which was 40 % chemical birch pulp, 40 % chemical pine pulp and as the filler 20 % calcium carbonate and pulp starch 5 kg/t. A dispersion of AKD was prepared in a 2% starch, the concentrations of Complexing Agents 1 and 2 in the dispersion being 0.6 % of the amount of AKD. The AKD dose used was 1 kg/t, in which case the amount of active ingredient forming the complex was 6 g/t. Test sheets having a grammage of 80 g/m$^2$ were prepared from the pulp according to the instructions by Scan-C 26:76. Cobb 60 min was determined from the sheets immediately and after 10 min of curing at 105 °C. The Cobb 60 values lowered even if the total retentions in the sheets were almost 100 %. Cobb values describe the water absorption of the paper, and they mean the amount of water which the paper absorbs within a certain time (g/m$^2$). The lower the Cobb value, the better the sizing result.

Table 1

| Laboratory test | | | |
|---|---|---|---|
| | Normal | Compl. agent 1 | Compl. agent 2 |
| Cobb 60 unmatured | 34.2 | 28 | 27.9 |
| Cobb 60 matured | 27.6 | 25.3 | 25.8 |

**Example 4**

**[0045]** The pulp used in the pilot machine was 35 % chemical pine pulp and 65 % chemical birch pulp. The filler used was calcium carbonate 23 % of the dry pulp. At a speed of 80 m/min of the pilot machine a paper was run the grammage of which was 70 g/m$^2$. The rate of AKD used was 1 kg/t. The AKD size contained Complexing Agent 1 in an amount of 0.3 % of the amount of AKD. Although the total retentions of the pilot machine were good, in the product containing

the complexing agent the uncured immediate Cobb 60 ($g/m^2$) was clearly lower than in the corresponding product without a complexing agent.

Table 2

| **Pilot machine** | | |
|---|---|---|
| | **Normal** | **Complexing agent 1** |
| Total retention (%) | 95.2 | 95.0 |
| Cobb 60 ($g/m^2$) immediately, uncured | 20.5 | 16.9 |

**Claims**

1. A sizing composition usable for the neutral sizing of paper or board, the composition containing a size capable of reacting with cellulose and an organic complexing agent.

2. A sizing composition according to Claim 1, **characterized** in that the size is alkyl ketene dimer (AKD) or alkenyl succinic acid anhydride (ASA).

3. A sizing composition according to Claim 1 or 2, **characterized** in that the organic complexing agent is a) aminopolycarboxylic acid, b) N-bis- or tris-[(1,2-dicarboxylethoxy)ethyl]amine or c) phosphonic acid.

4. A sizing composition according to Claim 3, **characterized** in that the organic complexing agent of group a) is diethylene triamine penta-acetic acid (DTPA), ethylene diamine tetra-acetic acid (EDTA) or nitrilotriacetic acid (NTA), or a salt thereof or a mixture thereof, and the organic complexing agent of group b) is N-bis[(1,2-dicarboxylethoxy)ethyl]amine (BCEEA), N-bis[(1,2-dicarboxylethoxy)-ethyl]aspartic acid (BCEEAA) or N-tris[(l,2-dicarboxylethoxy)ethyl]amine (TCEEA), or a salt thereof or a mixture thereof.

5. A sizing composition according to any of the above claims, **characterized** in that the amount of the organic complexing agent is 0.1-50 % by weight, preferably 0.1-20 % by weight and especially preferably 0.2-3 % by weight of the amount of the size.

6. A sizing composition according to any of the above claims, **characterized** in that it is in the form of a dispersion and additionally contains a dispersion stabilizing agent.

7. A sizing composition according to Claim 6, **characterized** in that the stabilizing agent is a starch or some other polymer.

8. A sizing composition according to Claim 6 or 7, **characterized** in that the amount of the organic complexing agent is 0.2-20 % by weight, preferably 0.2-10 % by weight and especially preferably 1-5 % by weight of the amount of stabilizing agent.

9. **Use** of a sizing composition defined in any of Claims 1-8 for the neutral sizing of paper or board.

10. A process for the manufacture of paper or board by neutral sizing by using a size capable of reacting with cellulose, **characterized** in that an organic complexing agent is used together with the size.

11. A process according to Claim 10, **characterized** in that the organic complexing agent is incorporated into the size or is dosed at the same location in the paper or board machine as the size.

12. A process according to Claim 10 or 11, **characterized** in that a sizing composition defined in any of Claims 1-8 is used for the sizing.

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number EP 99660129.0

## 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. 6) |
|---|---|---|---|
| A | WO 94/13883 A (RAISIO CHEM. OY.) 23 June 1994, claims. -- | 1 | D21H17/18 |
| A | EP 0073872 A (BILLERUD UDDEHOLM AB) 16 March 1983, claims, page 4, lines 2-9. ---- | 1 | |

TECHNICAL FIELDS SEARCHED (Int. Cl. 6)

D21H

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| VIENNA | 17-11-1999 | PAMMINGER |

CATEGORY OF CITED DOCUMENTS

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ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO. EP 99660129.0

This annex lists the patent family members relating to the patent documents cited in the above-mentioned search report.
The members are as contained in the EPIDOS INPADOC file on 2.12.1999.
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| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| WO A1 9413883 | 23-06-1994 | AT E 148752 | 15-02-1997 |
| | | AU A1 54668/94 | 04-07-1994 |
| | | CN A 1089776 | 13-07-1994 |
| | | DE D0 69308035 | 20-03-1997 |
| | | DE T2 69308035 | 28-08-1997 |
| | | EP A1 672213 | 20-09-1995 |
| | | EP B1 672213 | 05-02-1997 |
| | | FI A0 925535 | 04-12-1992 |
| | | FI A 925535 | 05-06-1994 |
| | | FI B 94535 | 15-06-1995 |
| | | FI C 94535 | 08-04-1997 |
| | | ZA A 9308796 | 30-06-1994 |
| EP A1 73872 | 16-03-1983 | none | |

For more details about this annex see Official Journal of the European Patent Office, No. 12/82.