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# (54) A papermaking process and a cationic chemical

(57) The invention relates to a process for the making of paper or a corresponding fiber product, in which process a cationic chemical is added to the paper or the corresponding fiber product in order to render hydrophobic the paper or the corresponding fiber product, the cationic chemical having the formula

$$R_{4} - N + R_{3}$$

$$R_{2}$$

where  $R_1$ ,  $R_2$  and  $R_3$  are the same or different and are each a saturated or unsaturated acyclic, cyclic or aromatic hydrocarbon containing 1-41 carbon atoms,  $R_4$  is a saturated or unsaturated acyclic, cyclic or aromatic hydrocarbon containing 1-41 carbon atoms and at least one oxygen atom, and X is an anion. The invention also relates to a cationic chemical which has an ability to attach to anionic surfaces.

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## Description

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**[0001]** The invention relates to a process for making paper or a corresponding fiber product, which process comprises rendering hydrophobic the paper or corresponding fiber product. The invention also relates to a cationic chemical which can be used as a hydrophobification chemical, for example as a stock size or a surface size or a fixative or a dispersing agent.

**[0002]** In hydrophobic sizing of paper, the paper is rendered water repellent, i.e. hydrophobic, and thereby the penetration of aqueous liquids into the paper is prevented or decelerated. The hydrophobification can be carried out by hydrophobic stock sizing, in which a hydrophobification chemical is added to the water-containing fiber pulp suspension before web forming, or by hydrophobic surface sizing, in which a hydrophobification chemical is added to a preformed web.

**[0003]** There are known different types of synthetic chemicals usable for papermaking, some examples being the following:

- alkenylsuccinic acid anhydride (ASA), described in US patent publication 3 821 069;
- alkylketene dimer (AKD), described in US patent publication 2 627 477;
- acid chloride, acid anhydride, enol ester, alkyl isocyanate and resin anhydride;
- quaternary organic ammonium salt, described in DE patent publication 36 34 277 A1.

[0004] The two biggest cellulose hydrophobification chemicals within the neutral range, ruling the market at present, are ASA and AKD.

**[0005]** In papermaking it is also possible to add to the fiber pulp suspension auxiliary chemicals, which include a chemical providing wet strength, i.e. a wet strength size, such as formaldehyde urea adduct and dimethylol melamine, and a fixative, such as polyaluminum chloride (PAC), which lowers the anionic quality of the pulp suspension by attaching to anionic surfaces.

[0006] Known hydrophobification chemicals usually have one or more of the following drawbacks:

- they are not water-soluble and require stabilizers when being dispersed in water;
- they are not adsorbed to the fiber surface effectively enough from dilute aqueous solutions;
- in an aqueous solution AKD and ASA become rapidly hydrolyzed to unusable hydrophobification chemicals;
- they do not work effectively in the presence of a filler; and
- their manufacture is difficult.
- An essential ingredient in the mixture described in DE patent publication 36 34 277 A1 is a polymer which contains anionic groups, in which case a quaternary ammonium salt alone, without the said polymer, softens the paper fibers, resulting in the reduction of the paper breaking length.

**[0007]** The object of the present invention is generally to provide a cationic chemical by the use of which as a hydrophobification chemical the drawbacks stated above are avoided and which can also be used, for example, as a surface size, a fixative or a dispersing agent. It is also an object of the invention to provide a process for rendering a fiber product hydrophobic by the use of such a cationic chemical.

**[0008]** These objects have been achieved by the process according to the invention and with the cationic chemical according to the invention, the main characteristics of which are stated in the accompanying claims.

**[0009]** Thus the invention relates to a process for making paper or a corresponding fiber product, the process being characterized in that a cationic chemical is added to paper or a corresponding fiber product in order to render hydrophobic the paper or the corresponding fiber product, the cationic chemical having the formula

$$R_{4} \xrightarrow{\stackrel{R_{1}}{\underset{R}{\longrightarrow}} R_{3}} I$$

where R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are the same or different and are each a saturated or unsaturated acyclic, cyclic or aromatic hydrocarbon containing 1-41 carbon atoms, R<sub>4</sub> is a saturated or unsaturated acyclic, cyclic or aromatic hydrocarbon containing 1-41 carbon atoms and at least one oxygen atom, and X is an anion.

[0010] Furthermore, the invention relates to a cationic chemical for rendering paper or a corresponding fiber product

hydrophobic, the chemical being characterized in that it contains a component derived from a compound having an OH group and a quaternary ammonium salt component, and that it has the formula I presented above, and that it has an ability to attach to anionic surfaces.

**[0011]** When the hydrocarbon groups  $R_1$ - $R_4$  are unsaturated, they may contain one or more double bonds. The hydrocarbon groups  $R_1$ - $R_4$  may be derived from fatty acids. Examples of such suitable fatty acids include stearic acid, palmitic acid, linoleic acid, oleic acid, montanic acid, pinoleic acid, and tallow fatty acid. The hydrocarbon groups  $R_1$ - $R_4$  may also be derived from resin acid or disproportionated resin, which contain fused ring structures.

**[0012]** The oxygen atom in group  $R_4$  may, for example, be part of a chain (e.g. an ether or ester) or part of a cyclic structure (e.g. a cyclic ether) or it may be a hydroxyl substituent.

10 **[0013]** One advantageous compound group is made up of compounds according to Formula I, where R<sub>4</sub> is a glycidyl group.

[0014] Another advantageous compound group is made up of compounds having the formula

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$$B-O-A-N-R_3$$

$$R_2$$
II

where  $R_1$ ,  $R_2$ ,  $R_3$  and  $X^*$  stand for the same as in Formula I, A is a hydrocarbon which contains 1-6 carbon atoms and may contain one or more oxygen atoms, and B is a saturated or unsaturated acyclic, cyclic or aromatic hydrocarbon which contains 1-41 carbon atoms. B may be derived from an alcohol, such as polyol (such as Penta E or starch).

[0015] A third advantageous group of compounds is made up of compounds having the formula

where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, X<sup>-</sup> and A stand for the same as in Formulae I and II, and R is a saturated or unsaturated acyclic, cyclic or aromatic hydrocarbon which contains 1-41 carbon atoms. R may be derived from carboxylic acid.

[0016] X<sup>-</sup> is preferably a halogen, but it may also be some other anionic component.

**[0017]** According to one embodiment of the invention, in Formula I two of groups  $R_1$ - $R_3$  are hydrocarbon groups containing 7-20 carbon atoms and the third is an alkyl group containing 1-6 carbon atoms, such as a methyl group,  $R_4$  is propylene oxide, and X- is a halogen.

**[0018]** According to another embodiment of the invention, in Formula I one of groups  $R_1$ - $R_3$  is a hydrocarbon group containing 7-20 carbon atoms and the other two groups are alkyl groups containing 1-6 carbon atoms, such as methyl groups,  $R_4$  is propylene oxide, and X is a halogen.

**[0019]** According to a third embodiment of the invention, in Formula II groups  $R_3$  and B are hydrocarbon groups containing 7-41 carbon atoms, groups  $R_1$  and  $R_2$  are alkyl groups containing 1-6 carbon atoms, such as methyl groups, A is hydroxypropyl, and X is a halogen.

**[0020]** According to a fourth embodiment of the invention, in Formula III groups  $R_3$  and R are hydrocarbon groups containing 7-41 carbon atoms, groups  $R_1$  and  $R_1$  are alkyl groups containing 1-6 carbon atoms, such as methyl groups, A is hydroxypropyl, and  $X^-$  is a halogen.

[0021] According to one preferred embodiment, the said cationic chemicals are added as a stock size to an aqueous fiber pulp suspension which possibly contains a filler, in which case possibly a retention agent is also added to the fiber pulp suspension. The filler may be, for example, calcium carbonate. The said cationic chemicals may also be used as a surface size, in which case they are applied to the web by means of a size press. In this case the stock size used may be a known stock size, such as ASA or AKD.

[0022] The process according to the invention may additionally comprise a maturation treatment at an elevated temperature, the maturation temperature being preferably approx. 110-140 °C and the maturation period being preferably approx. 1-120 min.

[0023] The said cationic chemicals are added typically approx. 0.01-2 % by weight, preferably approx. 0.3-0.6 % by

weight, calculated from the dry matter of the fiber.

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**[0024]** The cationic chemical according to Formula I may be used together with known auxiliary chemicals which chemically bond the chemical to the fiber. Such auxiliary chemicals include wet strength sizes, such as formaldehyde urea adduct and dimethylol melamine, and other chemicals generally known to persons skilled in the art.

[0025] The process according to the invention is suitable for rendering hydrophobic not only paper but also other corresponding fiber products, such as board.

**[0026]** Compounds according to Formula I in which  $R_4$  is a glycidyl group may be prepared, for example, by reacting a glycidyl halide with an amine  $R_1R_3NR_2$ , whereupon the desired product is obtained with a high yield. This reaction can be carried out in NTP conditions. The compound according Formula I may also be prepared by any other method commonly known by persons skilled in the art.

[0027] The compounds according to Formula II can be prepared by reacting an alcohol having the formula

where B stands for the same as above, with a 2,3-epoxypropyl ammonium halide having the formula

$$CH_{2}-CH-CH_{2}-N_{-R_{3}}^{R_{1}}$$

where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and X<sup>-</sup> stand for the same as above.

[0028] The compounds according to Formula III may be prepared by reacting a carboxylic acid having the formula

where R stands for the same as above, with a 2,3-epoxypropyl ammonium halide according to Formula V.

**[0029]** The compound according to Formula V, used as the initial substance, may be prepared by reacting a glycidyl halide with an amine  $R_2R_3NR_1$ , whereupon the desired product is obtained with a high yield. This reaction can be carried out in NTP conditions. The compound according to Formula V may also be prepared by any other method commonly known by persons skilled in the art.

- [0030] The advantageous and surprising characteristics of the invention include the following:
  - the compounds according to the invention are water-soluble or readily dispersible in water;
  - the compounds according to the invention attach to fiber surface from dilute agueous solutions (cf. Table 5 below);
  - a complete sizing is achieved by maturing a fiber material to which compounds according to the invention have adhered: Cobb 60 number <20 (cf. Table 1 below);
  - works both in neutral and in acid conditions:
  - it is possible to use different types of pulps and mixtures thereof (e.g. pine, spruce, groundwood; cf. Table 1 below);
  - works also in the presence of a filler (CaCO<sub>3</sub> 2-20 %; cf. Table 1 below);
  - by regulating the length of the hydrocarbon chains B/R and R<sub>1</sub>-R<sub>3</sub> it is possible to reduce the maturation period of the chemical used with respect to dosing/temperature (cf. Table 1 below);
  - serves also as, for example, a fixative, in which case it is 2-3 times as effective as PAC (cf. Tables 3 and 4 below);
  - can be bonded chemically by means of the epoxy group or the remaining OH group (cf. Table 7 below);
  - the chemical bonding improves hydrophobification (cf. Table 6 below).

[0031] By the Cobb number, i.e. the water absorbency of paper, is meant the amount of water that is absorbed by the paper surface within a predetermined period from a 1 cm water head. The lower the Cobb number, the better the sizing result. The Cobb method is described in greater detail in standard SCAN-P12:64.

[0032] The invention is described below in greater detail with the help of examples and experiments.

## Example 1

(Formula I;  $R_1$  = dodecyl,  $R_2$  and  $R_3$  = methyl,  $R_4$  = 2,3-epoxypropyl)

[0033] A cationization reagent which contains one long hydrocarbon chain is prepared. The initial substances used are epibromohydrin and dodecyldimethylamine. The reaction is carried out, for example, according to the method stated in BE patent 671 687. The epoxide content obtained for the product is approx. 90 %.

## Example 2

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(Formula I; R<sub>1</sub> = hydrocarbon derived from tallow fat, R<sub>2</sub> and R<sub>3</sub> = methyl, R<sub>4</sub> = 2,3-epoxypropyl)

**[0034]** The reaction is carried out in accordance with Example 1 by using dimethyl tallow amine as the amine. The epoxide content obtained for the product is approx. 80 %.

#### Example 3

(Formula I;  $R_1$  = hydrocarbon derived from tallow fat,  $R_2$  and  $R_3$  = methyl,  $R_4$ = 2,3-epoxypropyl)

[0035] The reaction is carried out in accordance with Example 2 by using epichlorohydrin as the source of epoxide. The epoxide content obtained for the product is approx. 80 %.

## Example 4

25 (Formula I;  $R_1$  = methyl,  $R_2$  and  $R_3$  = tallow fat,  $R_4$  = 2,3-epoxypropyl)

**[0036]** A cationization reagent which contains two long hydrocarbon chains is prepared. The initial substances used are epibromohydrin and di-tallow fat methylamine. The reaction is carried out, for example, according to the method stated in BE patent 671 687. The epoxide content obtained for the product is approx. 80 %.

## Example 5

(Formula I;  $R_1$  = methyl,  $R_2$  and  $R_3$  = tallow fat,  $R_4$  = 2,3-epoxypropyl)

[0037] The reaction is carried out in accordance with Example 4 by using epichlorohydrin as the source of epoxide. The epoxide content obtained for the product is approx. 80 %.

#### Example 6

(Formula III; R =saturated acyclic hydrocarbon, A =hydroxypropyl,  $R_1 = R_2 = R_3 =$ methyl)

[0038] 50 g is weighed of a mixture of stearic acid and palmitic acid, which is a commercial product (palmitic acid approx. 60 % and stearic acid approx. 40 %).

[0039] This is dissolved in 2-propanol and is poured into a reaction vessel. The solution is heated in a 100 °C oil bath, while stirring.

**[0040]** 100 g of 2,3-epoxypropyltrimethylammonium chloride is added. Stirring is continued at the same temperature, whereafter the mixture is poured into a separation funnel and is allowed to cool to room temperature. Two phases are obtained. The lower phase contains the excess of the cationization reagent. The upper phase contains the product and 2-propanol. The upper phase is washed with water and the 2-propanol is removed by evaporation. The analysis of the reaction product was carried out by, for example, FT-IR, which yielded 1708.9/1737.3 as the numeric value of the acid/ester signal peaks.

#### Example 7

(Formula III; R = unsaturated acyclic hydrocarbon having one or more double bonds/saturated acyclic hydrocarbon, A = hydroxypropyl,  $R_1 = R_2 = R_3 = \text{methyl}$ )

[0041] The reaction is carried out in accordance with Example 6 by using as the acid a fatty acid which is typically

made up of oleic acid, linoleic acid, pinoleic acid, palmitic acid and stearic acid. The analysis of the reaction product was carried out by using, for example, FT-IR, which yielded 1695.0/1720.6 as the numeric value of the acid/ester signal peaks.

## 5 Example 8

(Formula III; R = unsaturated cyclic hydrocarbon having one or more double bonds/saturated or aromatic hydrocarbon, A = hydroxypropyl,  $R_1 = R_2 = R_3 = methyl$ )

[0042] The reaction is carried out in accordance with Example 6 by using as the acid a resin acid or a disproportion-ated resin, which is typically made up of abietic acid, levopimaric acid, palustric acid, dehydroabietic acid, dihydroabietic acid, tetrahydroabietic acid, pimaric acid and isopimaric acid. The analysis of the reaction product was carried out by using, for example, FT-IR, which yielded 1707.3/1738.3 as the numeric value of the acid/ester signal peaks.

## 15 Example 9

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(Formula III; R = saturated acyclic hydrocarbon, A = hydroxypropyl,  $R_1 = \text{dodecyl}$ ,  $R_2 = R_3 = \text{methyl}$ )

**[0043]** In the first step, a cationization reagent which contains one long hydrocarbon chain is prepared. The initial substances used are epibromohydrin and dodecyldimethylamine. The reaction is carried out, for example, according to the method stated in BE patent 671 687. The epoxide content obtained for the product is approx. 90 %.

**[0044]** In the second step, a water-soluble chemical which contains two long hydrocarbon chains is prepared in accordance with Example 6. The analysis of the reaction product was carried out by using, for example, FT-IR, which yielded 1708.9/1736.6 as the numeric value of the acid/ester signal peaks.

## Example 10

(Formula III; R =saturated acyclic hydrocarbon, A =hydroxypropyl,  $R_1 = R_2 = R_3 =$ methyl)

[0045] The reaction is carried out in accordance with Example 6, by using montan wax as the acid. The analysis of the reaction product was carried out by using, for example, FT-IR, which yielded 1708.9/1737.3 as the numeric value of the acid/ester signal peaks.

## Example 11

(Formula III; R = saturated acyclic hydrocarbon, A = hydroxypropyl,  $R_1 = \text{a hydrocarbon derived from tallow fat}$ ,  $R_2 = \text{R}_3 = \text{methyl}$ )

[0046] The first step of the reaction is carried out in accordance with Example 9, by using dimethyl tallow amine as the amine. The epoxide content obtained for the product is ~80 %. The second step of the reaction is carried out in accordance with Example 6. The analysis of the reaction product was carried out by using, for example, FT-IR, which yielded 1708.9/1736.6 as the numeric value of the acid/ester signal peaks.

#### Example 12

(Formula II; B = starch, A = hydroxypropyl,  $R_1 = methyl$ ,  $R_2$  and  $R_3 = hydrocarbons derived from tallow fat.$ 

**[0047]** The first step of the reaction is carried out in accordance with Example 7 by using di-tallow fat methylamine as the amine. The epoxide content obtained for the product is  $\sim$ 80 %.

[0048] The second step is carried out, for example, in accordance with the method stated in US patent 2 516 633, by using barley starch as the starch. The analysis of the reaction product was carried out, for example, by a total nitrogen determination, which yielded 0.1 as the DS (degree of substitution) value.

# Experiment 1

[0049] Use of a compound according to the invention as a stock size

[0050] The results of the experiment are shown in following Table 1.

Table 1

5	Chemical of Example No.	Pulp	Maturation temperature	Maturation period	Dose	Retention	Cobb 60
<i>3</i>   		(Туре)	(°C)	(min)	(% of pulp)	(% of dose)	Before/after maturation
10	4	100 % brown chem. pulp, 4 % CaCO <sub>3</sub>	125	5	0.15		42/28.9
į	6	100 % pine	130	60	1.75	20	111/25
; ;	7	100 % pine	130	60	15	i - i	125/105
15 ¦	8	100 % pine	130	60	15	-	119/100
	8	100 % pine	-	! -	20	-	120/93.5
i	9	100 % pine	130	60	0.4	50	110/20
20	9	70 % groundwood 30 % pine	130	60	0.3	-	142/20
i !	10	2 % CaCO <sub>3</sub> 100 % pine	130	2.5	0.2	-     -   	104/48
25	11	100 % pine 10 % CaCO <sub>3</sub>	130	5	0.4	-	112/18
 	PILOT run						
30 i	11	100 <b>%</b> pine 20 % PCC	110-115	2.5	0.4	-    -	-/21
	11	70 % groundwood 30 % broke 2 % CaCO <sub>3</sub>	110-115	15	0.5	-	-/20
35	PCC stands for precipitated calcium carbonate.					l J	

# **Experiment 2**

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Use of one compound according to the invention as a surface size

**[0051]** A 2.5 per cent aqueous solution of the product according to Example 4 was tested as a surface size in paper which contained pine pulp 30 % and birch pulp 70 % and to which there had been added PCC (precipitated calcium carbonate) 20 %. Both ASA and AKD were used as stock size.

[0052] When ASA was used as the stock size, the Cobb 60 instant number obtained was 71.7 and the Cobb 60 oven (125 °C/5 min) number obtained was 15.6.

When AKD was used as the stock size, the Cobb 60 instant number obtained was 20.7 and the Cobb 60 oven (125 °C/5 min) number obtained was 17.5.

# **Experiment 3**

Use of another compound according to the invention as a surface size

**[0053]** A 2.5 per cent aqueous dispersion of the product according to Example 12 was tested as a surface size in paper which had been made from 100 % chemical pine pulp. The reference used was a commercial SMA (styreic maleic anhydride) surface size. The results are shown in Table 2.

Table 2

Chemical used	Maturation period (min)	Maturation temperature (°C)	Cobb 60 number
SMA	2.5	115	22
Chemical of Example 12	2.5	115	22

## **Experiment 4**

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Use of one compound according to the invention as a fixative

[0054] A 1 per cent aqueous solution of the product according to Example 2 was tested as a fixative in coated broke having a consistency of 2.53 %. The change in the turbidity of the filtrate was measured as a function of the chemical dose and the obtained values were compared with respective values obtained with PAC (polyamine chloride). The results are shown in Table 3.

Table 3

Chemical dose (%)	Turbidity, NTU *10 <sup>3</sup>	PAC dose (%)	Turbidity, NTU *10 <sup>3</sup>
0.1	0.204	0.4	0.274
0.3	0.147	0.8	0.260
1.0	0.075	1.0	0.240

## 25 Experiment 5

Use of another compound according to the invention as a fixative

[0055] A 1.5 per cent aqueous solution of a product according to Example 10 was tested as a fixative in peroxidebleached TMP having a consistency of 3.8 %. Measurements were carried out in accordance with Experiment 3. The results are shown in Table 4.

Table 4

Chemical dose (%)	Turbidity, NTU *10 <sup>3</sup>	PAC dose (%)	Turbidity, NTU *10 <sup>3</sup>					
0.05	0.196	0.3	0.200					
0.1	0.177	0.6	0.141					
0.3	0.172	1.0	0.073					
1.0	0.036	1.5	0.048					

# **Experiment 6**

Adsorption of a chemical according to the invention

**[0056]** The chemicals according to the invention, shown in the following Table 5, were prepared in a manner corresponding to that in Example 6, by using stearic acid, abietic acid, oleic acid and resin acid.

[0057] The results obtained from the adsorption measurements are shown in Table 5.

Table 5

155575 - 5					
Chemical	Dose (%) of dry matter of fiber	Adsorbed amount (%) of dry matter of fiber			
Stearic acid derivative	1.75	0.55			
	2.75	0.90			
Abietic acid derivative	1.75	0.16			
Oleic acid derivative	1.00	0.15			

Table 5 (continued)

Chemical	Dose (%) of dry matter of fiber	Adsorbed amount (%) of dry matter of fiber		
	1.75	0.37		
Resin acid derivative	1.75	0.14		

## **Experiment 7**

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[0058] Cobb 60 s, g/m² means, before and after maturation (1 h, 125-128 °C), when a chemical according to the invention is used alone or together with a known wet strength size, or when a known wet strength size is used alone as a reference chemical.

**[0059]** The chemical according to the invention shown in the following Table 6 was prepared in a manner corresponding to that of Example 6, by using stearic acid.

[0060] The test results are shown in following Table 6.

Table 6

Chemical 1.75 per cent sizing	Cobb 60 s, g/m <sup>2</sup> mean before maturation	Cobb 60 s, g/m <sup>2</sup> mean after maturation 94.8		
Formaldehyde urea adduct (reference)	112			
Dimethylol melamine (reference)	110	94.5		
Stearic acid derivative	111.5	26		
Stearic acid der.+ formaldehyde urea adduct	97.3	20.6		
Stearic acid der.+ dimethylol melamine	93.6	21.6		

# **Experiment 8**

[0061] In order to determine the amount bonded chemically to the fiber of a size according to the invention, sizing of a certain percentage was performed on a suitable number of sheets. The sheets were weighed while dry, whereafter they were leached overnight with boiling methanol. After this treatment, the amount of size remaining chemically bonded to the sheets was calculated according to the following equation: weight of sheets before the leach - mass of matter detached in the leach - amount of chemically bonded size. The material detached from unsized sheets has been taken into account in the calculations. The test results are shown in following Table 7.

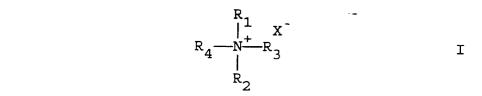
[0062] The chemical according to the invention shown in Table 7 was prepared in a manner corresponding to that in Example 6, by using stearic acid.

Table 7

Chemical 1.75 per cent sizing	Cobb 60 s, g/m <sup>2</sup> mean before maturation	Chemically bonded chemical (%)		
Stearic acid derivative	106	0		
Stearic acid der. + formaldehyde urea adduct	85.6	6.7		
Stearic acid der. + dimethylol melamine	80	8.2		

## Claims

1. A process for the making of paper or a corresponding fiber product, **characterized** in that a cationic chemical is added to paper or a corresponding fiber product in order to render hydrophobic the paper or the corresponding fiber product, the cationic chemical having the formula



where R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are the same or different and are each a saturated or unsaturated acyclic, cyclic or aromatic hydrocarbon containing 1-41 carbon atoms, R<sub>4</sub> is a saturated or unsaturated acyclic, cyclic or aromatic hydrocarbon containing 1-41 carbon atoms and at least one oxygen atom, and X is an anion.

- 2. A process according to Claim 1, **characterized** in that the cationic chemical added to paper or a corresponding fiber product has the Formula I, where R<sub>4</sub> is a glycidyl group.
- 3. A process according to Claim 1, **characterized** in that the cationic chemical added to paper or a corresponding fiber product has the Formula I, where  $R_4$  is a group

or

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where A is a hydrocarbon which contains 1-6 carbon atoms and may contain one or more oxygen atoms, and B and R are the same or different and are each a saturated or unsaturated acyclic, cyclic or aromatic hydrocarbon containing 1-41 carbon atoms.

- **4.** A process according to any of the above claims, **characterized** in that the said cationic chemical is water-soluble or readily dispersible in water.
- 5. A process according to any of the above claims, **characterized** in that the said cationic chemical is added to an aqueous fiber pulp suspension which possibly contains a filler, and that a retention agent is possibly added to the fiber pulp suspension.
- **6.** A process according to any of the above claims, **characterized** in that it additionally comprises a maturation treatment at an elevated temperature, the maturation temperature being preferably approx. 110-140 °C and the maturation period being preferably approx. 1-120 min.
- 7. A process according to any of the above claims, **characterized** in that the said cationic chemical is added in an amount of approx. 0.01-2 % by weight, preferably approx. 0.3-0.6 % by weight, calculated from the dry matter of the fiber.
- 8. A cationic chemical for rendering hydrophobific paper or a corresponding fiber product, **characterized** in that it contains a component obtained from a compound having an OH group and a quaternary ammonium salt component, and that it has the formula

where  $R_1$ ,  $R_2$  and  $R_3$  are the same or different and are each a saturated or unsaturated acyclic, cyclic or aromatic hydrocarbon containing 1-41 carbon atoms,  $R_4$  is a saturated or unsaturated acyclic, cyclic or aromatic hydrocarbon containing 1-41 carbon atoms and at least one oxygen atom, and  $X^-$  is an anion, and that it has an ability to attach to anionic surfaces.

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9. A chemical according to Claim 8, characterized in that in Formula I  $R_4$  is a glycidyl group or group

B-O-A-

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or

dispersion.

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where A is a hydrocarbon with contains 1-6 carbon atoms and may contain one or more oxygen atoms, B and R are the same or different and are each a saturated or unsaturated acyclic, cyclic or aromatic hydrocarbon containing 1-41 carbon atoms.

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11. A chemical according to any Claims 8-10, **characterized** in that it is used as a stock size or a surface size or a

fixative or a dispersing agent in the making of paper or a corresponding fiber product.

10. A chemical according to Claim 8 or 9, characterized in that it is in the form of an aqueous solution or an aqueous

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# **EUROPEAN SEARCH REPORT**

Application Number EP 98 66 0107

Category	Citation of document with in of relevant passa	dication, where appropriate,	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DATABASE WPI Section Ch, Week 900 Derwent Publications Class A82, AN 90-064 XP002094837 & JP 02 019600 A (DA) , 23 January 1990 *formulae at pages 1	09 s Ltd., London, GB; 4785 AISO CO LTD)		D21H21/16 D21H17/07
Х	US 3 872 138 A (OGA 18 March 1975 * the whole document		1,3,4,8,	
X	DATABASE WPI Section Ch, Week 89: Derwent Publications Class All, AN 89-104 XP002094838 & JP 01 052877 A (S/ , 28 February 1989	s Ltd., London, GB; 1959	8-11	TECHNICAL FIELDS
А	* abstract *		1,3-7	SEARCHED (Int.Cl.6)
	The present search report has b	een drawn up for all claims		
	Place of search THE HAGUE	Date of completion of the sear 26 February 19		Examiner nardo Noriega, F
X : part Y : part docr A : tech O : non	ATEGORY OF CITED DOCUMENTS icularly relevant if taken alone icularly relevant if combined with anothument of the same category innological backgroundwritten disclosure rmediate document	T : theory or pr E : earlier pate after the filli er D : document c L : document c	rinciple underlying the introduction of the interest of the in	invention shed on, or

EPO FORM 1503 03.82 (P04C01)

# ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 98 66 0107

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

26-02-1999

cite	Patent document cited in search report		Publication date	date		Patent family member(s)	
US 	3872138	A 	18-03-1975	JP GB	48052716 1390534	A A	24-07-1973 16-04-1975
			Official Journal of the Europ				

13