ABSTRACT

The present invention relates to a process for the sizing of materials containing cellulosic fibers (e.g. paper) by the use of carbamoyl chlorides.

14 Claims, No Drawings
PROCESS FOR SIZING CELLULOSE FIBERS

BACKGROUND

"Sizing" refers to the treatment of either cellulosic pulp fibers or an already formed cellulosic material with chemicals which control the wettability and surface properties of the final cellulosic product.

Paper frequently is sized with resinsates which are fixed to the cellulose fibers by means of aluminum sulphate (alum). Another well known sizing agent which is fixed by means of reacting with the hydroxyl groups of the cellulose is based on alkyl ketene dimers. This agent is usually added to the stock dispersed in a cationic emulsifier. Alkylketene dimers have certain advantages over resinate. One advantage is that the pH of the stock is kept within the range of 7 – 8 compared to a pH range of 4.5 – 6.5 which is used when the resinate is used as sizes – which among other things imparts improved aging properties to the paper and makes it possible to use alkaline fillers, such as calcium carbonate. Furthermore, considerably lesser amounts of ketene dimers are required to obtain a certain degree of hydrophobicity and the sizing thus obtained is permanent. Moreover the paper will have improved resistance to lactic acid, ink, etc.

A disadvantage when employing alkylketene dimers that no complete sizing effect is achieved until curing of the material for example, by storing at room temperature for about 48 hours or by heating to a temperature of 100°C for 20 minutes. Another disadvantage is that the sizing with alkylketene dimers is sensitive to alum present in the stock.

It also has been previously known to employ anhydrides of carboxylic acids as sizing agents, such as anhydrides of stearic acid or alkyl succinic acid. Said anhydrides do not have any of the above mentioned disadvantages that are encountered when employing resinate and ketene dimers, but greater amounts of the anhydride additives are required in order to achieve the same sizing effect as with the ketene dimers. In order to enhance the sizing effect it is common to add catalysts to the anhydrides so these catalysts are called sizing promoters and are used in relatively large amounts in combination with the anhydrides.

THE INVENTION BROADLY

The present invention involves sizing materials containing cellulosic fibers by bringing such cellulosic materials into contact with at least one carbamoyl chloride having the general formula

\[ \text{R}_1 \text{N} = \text{C} \text{R}_2 \]

where \( \text{R}_1 \) is an organic, hydrophobic hydrocarbon group comprising 8 – 40 carbon atoms and \( \text{R}_2 \) is hydrogen, lower alkyl or has the same meaning as \( \text{R}_1 \).

THE MATERIALS CONTAINING CELLULOSE FIBERS

The cellulosic fibers can be present in the form of a water suspension or in a more concentrated form, such as paperboard, fiberboard, or particle board, or they can be included or admixed with other materials such as semi-synthetic paper containing plastics in addition to the cellulosic fibers.

THE CARBAMOYL CHLORIDE

As noted above, the carbamoyl chloride has the general formula

\[ \text{R}_1 \text{N} = \text{C} \text{R}_2 \]

where \( \text{R}_1 \) is an organic, hydrophobic hydrocarbon group comprising 8 – 40 carbon atoms and \( \text{R}_2 \) is hydrogen, lower alkyl or has the same meaning as \( \text{R}_1 \). Examples of suitable hydrophobic groups are (a) a higher alkyl having between 8 and 40 carbon atoms (such as decyl, undecyl, dodecyl, tridecyl, tetradecyl, penta-decyl, hexadecyl, octadecyl, tetracosyl, and pentacosyl although those having about 12 – 30 carbon atoms are generally preferred, (b) the corresponding alkenyl groups having between 8 and 40 carbon atoms (such as decenyl, tridenecyl, heptadecenyl, octadecenyl, eicosenyl, tricosenyl etc.) (c) aralkyl, alkyl, and alkyl substituted cycloalkyl having at least 8 carbon atoms (e.g. 4-tertbutilphenyl, octylphenyl, dinonylphenyl, dodecylphenyl, tridecylphenyl, pentadecylphenyl, octadecylphenyl, hencosylphenyl, nonylcyclopentyl, dodécyclyclobutyl, tridecyclobutyl, tetradecyl-cyclohexyl, pentaethylcyclohexyl, octadecyl cyclohexyl etc.) and (d) any of the aforementioned alkenyl alkenyl alkylaryl and alkylycloalkyl groups containing non-interfering, inert substituents. Of the inert substituents may be mentioned ether, carboalkoxy, alkyloxy, aryl-oxy, aryalkyloxy, keto(carbonyl)-tert. amide groups etc. Examples of radicals which should not be present to any great extent in the hydrophobic group may be mentioned e.g. hydroxyl groups, primary and secondary amino groups, unstable halogens, and carboxyl groups or other acidic groups. In the art it is obvious which groups should be employed if undesired side reactions are to be avoided.

\( \text{R}_1 \) preferably is an alkyl group comprising 12 – 30 carbon atoms and \( \text{R}_2 \) is hydrogen, lower alkyl or has the same meaning as \( \text{R}_1 \).

The carbamoyl chlorides can be prepared according to known methods for instance by phosgenisation of the corresponding amines.

The advantages of the present invention are not dependent on what method is chosen to bring the carbamoyl chloride into contact with the cellulosic fibers. According to one method an aqueous suspension of cellulosic fibers can be brought into contact with the carbamoyl chloride, which optionally can be dispersed in a suitable way. A solution or dispersion of the carbamoyl chloride chlorofomate also can be brought into contact with a material containing cellulosic fibers, such as paper.

The carbamoyl chlorides which are employed in the process of the present invention show a certain cationic activity and consequently retention to the cellulosic fibers. Thus for certain purposes some additional retention agent may be omitted, e.g. for surface sizing of dipping concentrated cellulosic fibers such as paper board,
special type of emulsion agent showing a good retention to the fibers are quertones or aminohydrochlorides containing at least one alkyl group having 8 – 22 carbon atoms, such as dimethyldeicarlaylmethanol or dimethylstearyl aminohydrochloride. The amount of the emulsifier should exceed 0.05% by weight based on the dry fibers, and preferably 0.1 – 10% by weight based on the dry fibers.

The carbamoyl chlorides according to the invention are employed in an amount exceeding 0.001 percent by weight based on the dry fibers by addition to the stock of fibers or by surface sizing of paper. The upper limit is not critical and is only limited by economical considerations. Preferably the amount of the carbamoyl chloride should fall within the range of from 0.001 to 5 percent by weight, most preferably 0.005 to 0.5 percent by weight based on the dry fibers. The fiber suspension or the concentrated fibers may also contain other additives commonly used in the manufacturing of paper, cardboard, fiberboard, particle board, etc. such as alum, fillers, pigments, retention agents, foam quenching agents, etc.

The present invention will now be described more in detail in the following examples which are given for illustration but are not intended to restrict the invention. Percentages and parts are by weight, unless otherwise specified.

EXAMPLE 1

Unsized paper sheets having a surface weight of about 70 g/m² were formed from a bleached sulphate pulp beaten to about 30° SR at a pH of 8.0 in a laboratory sheet machine. The sheets were dried and conditioned (at 20°C and 65% relative humidity). The sheets then were impregnated by submersing them in a solution of 0.1% of substituted carbamoyl chloride in benzene for a few seconds and the excess of the solution was adsorbed. The impregnated sheets were dried at a temperature of 60°C for 40 minutes and cured at 105°C for 30 minutes. After conditioning the Cobb-number was determined according to the norm SCAN-P 12:64, which is a measure of the water absorbivity of the sheets. (The Cobb number for unsized paper is 100).

<table>
<thead>
<tr>
<th>Type of substituent</th>
<th>melting point °C</th>
<th>% sizing agent based on weight of dry fibers</th>
<th>Cobb 100 g/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₁ = CH₃</td>
<td>67-69</td>
<td>0.015</td>
<td>20</td>
</tr>
<tr>
<td>R₂ = C₆H₄</td>
<td>56-58</td>
<td>0.015</td>
<td>18</td>
</tr>
<tr>
<td>R₁ = CH₃</td>
<td>54-56</td>
<td>0.015</td>
<td>22</td>
</tr>
<tr>
<td>R₁ = phenyl</td>
<td>101-103</td>
<td>0.015</td>
<td>22</td>
</tr>
<tr>
<td>R₁ = CH₃</td>
<td>39-42</td>
<td>0.020</td>
<td>24</td>
</tr>
<tr>
<td>R₁ = CH₃</td>
<td>39.42</td>
<td>0.020</td>
<td>21</td>
</tr>
<tr>
<td>R₁ = CH₃</td>
<td>&lt;20</td>
<td>0.10</td>
<td>20.5</td>
</tr>
<tr>
<td>R₁ = C₆H₄</td>
<td>&lt;20</td>
<td>0.05</td>
<td>22.5</td>
</tr>
</tbody>
</table>

EXAMPLE 2

10 g of a carbamoyl chloride R₁ = R₂ = C₆H₄CH₂, were melted at 60°C and then 90 g distilled water (60°C) were added during homogenization for 5 minutes. The emulsion was thereupon rapidly cooled to 25°C to give a stable dispersion.

EXAMPLE 3

10 g of a carbamoyl chloride R₁ = R₂ = C₆H₄CH₂ and 0.5 g of a stearylamine hydrochloride were melted together at 60°C, then 89.5 g of distilled water (60°C) were added during homogenization for 5 minutes. The emulsion was rapidly cooled to 25°C to give a stable dispersion.

EXAMPLE 4

10 g of carbamoyl chloride R₁ = R₂ = C₆H₄CH₂ and 0.5 g of diestearylimethyl ammonium chloride were melted together and then 89.5 g distilled water (60°C) were added during the homogenization for 5 minutes. The emulsion was then rapidly cooled to 25°C to give a stable dispersion.

EXAMPLE 5

10 g of carbamoyl chloride R₁ = R₂ = C₆H₄CH₂ were melted and then 90.0 g of distilled water (60°C) containing 0.5 g of a water-soluble cationic polycrylamide were added during the homogenization for 5 minutes. The emulsion then was rapidly cooled to 25°C to give a stable dispersion. The obtained dispersions thereafter were used as sizing agents for paper in the same manner as described in Example 1. The results are shown in the
A dispersion as defined in example 2 was added to a suspension of cellulose fibers in water together with a cationic polyacrylamide having a molecular weight of more than one million.

EXAMPLE 7

A dispersion as defined in example 2 was added to a suspension of cellulose fibers in water together with an anionic polyacrylamide having a molecular weight of more than one million.

EXAMPLE 8

A dispersion as defined in example 2 was added together with a cationic polyacrylamide having a high molecular weight to a suspension of cellulose fibers in water pre-treated with an anionic polyacrylamide having a molecular weight of more than one million. The cellulose fiber suspension according to examples 6–8 were then drained and sheets were produced in a laboratory sheet machine. The sheets were dried for 40 minutes at 60°C and were cured for 30 minutes at 105°C. After conditioning, the Cobb-number according to the norm SCAN-P 12:64 was determined. The results are shown in the following table:

<table>
<thead>
<tr>
<th>Sizing system according to example</th>
<th>Amount of cationic polymer based on dry fiber wt</th>
<th>Amount of anionic polymer based on dry fiber wt</th>
<th>Amount of sizing agent based on dry fiber wt</th>
<th>Cobb&lt;sub&gt;5&lt;/sub&gt; g/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.02</td>
<td>0.30</td>
<td>0.25</td>
<td>24</td>
</tr>
<tr>
<td>7</td>
<td>0.02</td>
<td>0.25</td>
<td>0.30</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>0.02</td>
<td>0.25</td>
<td>0.30</td>
<td>24</td>
</tr>
</tbody>
</table>

The tests show that no substantial improvement in sizing was obtained by adding a retardation agent. (The Cobb number for unsized paper is 100).

EXAMPLE 9

In manufacturing of a porous fiberboard 0.20% of methylesterly carbamoyl chloride were added to the stock based on the dry fiber weight. The board panels were dried for 2 hours at 20°C – 160°C at a continuously elevating temperature.

The water absorption of the board panels was determined according to the norm SIS–235105 whereby test specimens having the dimensions of 100 × 100 × 10 mm were submerged in water for 2 hours. The standard rate of absorption during large scale production of boards varied from 155 to 300% depending on the curing condition. The following results were obtained:

Wherein R₁ is an organic, hydrophobic hydrocarbon group containing 8–40 carbon atoms and R₂ is selected from the group consisting of hydrogen, lower alkyl and organic, hydrophobic hydrocarbon group containing 8–40 carbon atoms.

What we claim is:

1. A process for sizing cellulose fibers or material containing cellulose fibers wherein the cellulose fibers are brought into contact with at least 0.001% by weight based upon the weight of the dry cellulose fibers of a carbamoyl chloride having a general formula

\[ R_1 - N - C - O - R_2 \]

wherein R₁ is an organic, hydrophobic hydrocarbon group containing 8–40 carbon atoms and R₂ is selected from the group consisting of hydrogen, lower alkyl and organic, hydrophobic hydrocarbon group containing 8–40 carbon atoms, and wherein the amount of said
carbamoyl chloride is at least 0.001% by weight based upon the weight of dry cellulose fibers.

11. The cellulose fibers or material containing cellulose fibers of claim 10 wherein the amount of said carbamoyl chloride is within the range of from 0.001 to 5% by weight based upon the weight of dry cellulose fibers.

12. The cellulose fibers or material containing cellulose fibers of claim 10 wherein the amount of said carbamoyl chloride is within the range of from 0.005 to 0.5% by weight based upon the weight of dry cellulose fibers.

13. The cellulose fiber or material containing cellulose fibers of claim 10 which further includes an emulsifier.

14. The cellulose fiber or material containing cellulose fibers of claim 13 wherein said emulsifier is a cationic emulsifier.

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