An additive for paper or board production e.g. for decreasing pitch problems. The additive includes at least a component including fatty acid glycerides, preferably triglycerides, comprising a high percentage of unsaturated, preferably polyunsaturated, fatty acids. Raw or partly polymerized plant oil, such as sunflower oil, may be used.
The present invention relates to an additive, to the use of said additive in paper or board production, to a method of improving paper or board manufacturing and to a method of improving paper or board product according to what is stated in the preambles of appending independent claims.

Pulp suspensions used in paper or board production contain besides cellulose fibers different kinds of extractives, that is a heterogeneous group of lipophilic and/or hydrophilic substances. Particularly pulp suspensions including mechanical pulp may have considerable amounts of lipophilic substances, such as fatty acids, glycerides, sterol esters, sterols and resin acids. Also an addition of high amounts of broke may increase the amount of lipophilic substances in pulp suspensions.

The lipophilic substances are by nature hydrophobic and form insoluble tacky aggregates, called pitch, which easily, particularly at certain temperatures, cause deposits on various surfaces of the paper or board machines. The tacky aggregates typically adhere to cylinders, rolls and fabrics in the drying section of the paper or board machines, but may cause troubles elsewhere in the paper or board machines, as well, e.g., by depositing on feltels and rolls in the press section. The troubles may lead to runability problems, web breaks and the need to thoroughly clean the machine. The insoluble aggregates may further cause quality problems such as holes and spots in the paper or board product.

The deposition of pitch on paper or board machines has seemed to occur in a seemingly irregular way. Various methods to tackle the problem have been suggested. For instance, longer storage of wood seems to decrease the amount of glycerides in mechanical pulp. Longer storage leads, however, to brightness loss of paper or board and, of course, to storage costs. Regular wash outs of the paper or board machine with some chemicals may help to tackle the problems. Also the use of some additives such as anionic dispersants, aluminum sulfate, adsorbents, cationic polymers or enzymes has been suggested. Also the materials and design of paper or board machines are chosen so as to avoid corrosion, for avoiding deposits build up. Still problems occur.

Sometimes paper or board products may be impaired by inexplicable unpleasant odors. The surface sizing component used, e.g., starch, has often been blamed for the odor. Also degradation products from wood originating fatty acids have been found problematic in this sense. No single simple answer to the odor problem has been found. Odor problems tend to arise more often at some paper machines than at other.

In the paper or board making process internal and external hydrophobic sizing of the paper or board is used to provide a good hydrophobicity to the paper or board product. Resin acids (rosin sizes) are commonly used together with various aluminum components as sizing agents at lower pH-levels, i.e. at pH<6. At higher pH-levels synthetic sizes, such as ASA- and AKD-sizes, are commonly used. A possible drawback of these sizes is the formation of hydrolysis products, which may even be tackier than the sizing components themselves.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an improved additive to be used in paper or board production for minimizing the above-mentioned disadvantages.

It is particularly an object of the present invention to provide an additive decreasing the formation of tacky aggregates.

It is also an object of the present invention to provide an additive providing an increase in the hydrophobicity of the paper or board product.

It is still further an object of the present invention to provide an improved method of decreasing pitch problems in paper or board manufacture.

It is furthermore an object of the present invention to provide an improved method of increasing hydrophobicity, for example the so-called short-term hydrophobicity, of paper or board manufactured.

It is also an object of the present invention to provide an improved method of decreasing odor problems in paper or board product manufactured.

In order to fulfil the above objects an additive, a method of improving paper or board manufacturing and a method of improving paper or board product according to the present invention are characterized by what is disclosed in the characterizing portions of the appended independent claims.

A typical adhesive according to the present invention includes at least a component including fatty acid glycerides, typically triglycerides, having a high percentage of unsaturated, particularly polyunsaturated, fatty acids.

It is believed that the unsaturated fatty acids in the component may form cross-links between glycerides present in the added component, as well as, glycerides already present in the pulp suspension, whereby polymerization, so called drying, of the glycerides will take place.

The unsaturated fatty acids in the glycerides are believed to react with air oxygen, particularly at higher temperatures, to form the cross-links between glycerides. Saturated fatty acids or resin acids are not believed to form cross-links in a similar manner, whereby similar polymerization is not believed to take place.

It has surprisingly been noticed that it is possible to influence the behavior of the lipophilic substances present in pulp suspensions by the addition of the new additive comprising glycerides, preferably triglycerides, with a high content of unsaturated, particularly polyunsaturated, fatty acids. The additive makes it possible e.g. to influence the formation and behavior of tacky aggregates in the pulp suspension and paper or board web, to influence the formation of unpleasant odors in the paper or board product and/or to influence the hydrophobicity of the final paper or board product.

It has been noticed that it is possible to increase the speed of polymerization of glycerides by increasing the content of unsaturated, particularly polyunsaturated, fatty acids in the pulp suspension. Thus the concentration of non-polymerized glycerides, i.e. tacky glyceride aggregates, is decreased. Also, the polymerized glycerides are believed to be able to form layers around non-polymerized tacky aggregates present in the pulp suspension and the paper or board
web, thus decreasing the negative influence of these tacky aggregates in the papermaking or boardmaking process.

[0020] It has been noticed that the higher the amount of unsaturated, particularly polysaturated, fatty acids present in a pulp suspension the less runnability problems caused by pitch, i.e. tacky aggregates, arise. A high enough percentage of unsaturated and polysaturated fatty acids are needed to ensure polymerization. An addition of at least 0.5 kg/t (t meaning ton produced paper), typically 0.5-10 kg/t, more typically 2-5 kg/t, glycerides, comprising a high percentage of polysaturated fatty acids, may thereby provide desired results.

[0021] To improve the hydrophobicity of the final paper or board product an addition of at least 1 kg/t, at least 2 kg/t, or at least 3 kg/t, may be sufficient.

[0022] The additive, including a high percentage of unsaturated or polysaturated fatty acids, may be added to the pulp suspension or onto the paper or board web, e.g. by internal or surface sizing. The additive may be added to the pulp suspension by internal sizing before the head box, in the head box or at any other suitable location. The additive may, on the other hand, be added onto the wet or dry web in conjunction with surface sizing or coating.

[0023] A component for decreasing pitch problems, unpleasant odors or increasing hydrophobicity may thereby according to the present invention include

**[0024]** fatty acid glycerides in which more than 10%, typically more than 40%, of the fatty acids have more than 1 double bond,

**[0025]** fatty acid glycerides in which >60%, preferably >65%, typically >70%, of the fatty acids have 2 double bonds, and/or

**[0026]** fatty acid glycerides in which >10%, preferably >30%, typically >45%, of the fatty acids have 3 double bonds.

**[0027]** A component according to the present invention may e.g. be a raw or partly polymerized plant oil, such as sunflower oil, including high amounts of linoleic (C18:2) acid, and/or linseed oil, including high amounts of linoleic (C18:3) acid.

**[0028]** An additive according to the present invention may include in addition to the said component

**[0029]** one or more emulsion stabilizers, such as natural or synthetic polymers or inorganic particles, e.g. starches, starch derivatives, CMC, mannan, polyacrylamides, polyacrylonitriles, bentonites, silicas,

**[0030]** one or more surfactants and/or

**[0031]** at least one conventional sizing component, such as a synthetic sizing agent.

**[0032]** Typically cationic emulsion stabilizers may be used. Thereby cationic starch derivatives, such as

**[0033]** cold water soluble starches with DS (degree of cationic substitution) of >0.1 or

**[0034]** conventional wet end starches with DS 0.01-0.05, may be used. Synthetic sizing agents, such as AKD, ASA, styrene acrylate, styrene maleic anhydride or styrene acrylic acid copolymers, may be used.

**[0035]** Pulp suspensions in the papermaking or boardmaking process normally contain certain amounts of resin acids and fatty acids, the latter as free acids or esterified as glycerides or sterol esters. The resin and fatty acids normally present in pulp suspensions may be divided in two groups:

- [0036] drying acids, i.e. unsaturated fatty acids, such as pinolenic or linolenic acid (C18:3), linoleic acid (C18:2) and oleic acid (C18:1), and
- [0037] non-drying acids, such as resin acids and saturated fatty acids, such as stearic acid (C18:0), ante-iso-heptadecanoic acid (C17:0ai) and palmitic acid (C16:0).

**[0038]** It has now been noticed that the proportion of drying acids, i.e. unsaturated fatty acids, compared to non-drying acids, i.e. resin acids and saturated fatty acids, seems to play an important role in the polymerization and drying of glycerides. The higher the amount of unsaturated, particularly polysaturated, fatty acids compared to the amount of non-drying components the more rapidly will the polymerization take place.

**[0039]** It has now also been noticed that decomposition of some non-drying fatty acids in the pulp suspension or in the paper or board web may form components, such as heptadecyl alcohol or hexadecyl alcohol, causing a very unpleasant odor. It has further surprisingly been noticed that polymerization of fatty acids and/or glycerides in the pulp suspension or in the paper or board web according to the present invention may prevent such odor causing decomposition to take place.

**[0040]** In the following Example 1 results of measurements made on a paper machine show that polymerization of glycerides in the pulp suspension coincides with less tacky agglomerates in the paper product, i.e. with less pitch problems. The example shows that polymerization of glycerides is favored by a high relative concentration of drying acids, i.e. unsaturated fatty acids.

**EXAMPLE 1**

**[0041]** Samples were taken

**[0042]** of the paper product from the wet end of the paper machine and

**[0043]** of the dried paper product.

**[0044]** The concentration of following fatty acids, ante-iso-heptadecanoic acid (C17:0ai), pinolenic and linolenic acid (C18:3), linoleic acid (C18:2) and oleic acid (C18:1), were analyzed in each sample.

**[0045]** An analysis method was used which

**[0046]** measured the concentration of free fatty acids, as well as, fatty acids in non-polymerized glycerides, but which

**[0047]** did not measure the concentration of fatty acids in polymerized glycerides.

**[0048]** The concentration of ante-iso-heptadecanoic acid (C17:0ai) was used as reference = 1.

**[0049]** Following almost constant relation between the different fatty acids was noticed in all samples taken of the paper product at the wet end of the paper machine:

<table>
<thead>
<tr>
<th>C17:0ai</th>
<th>C18:3 pinolenic or linolenic</th>
<th>C18:2 linoleic</th>
<th>C18:1 oleic</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>about 10</td>
<td>about 15</td>
<td>about 8</td>
</tr>
</tbody>
</table>

**[0050]** In samples taken of the dried paper product, however, two distinctly different results were achieved. It could be
proven, by further tests, that the difference corresponded with a difference in resin acid concentration in the pulp suspension.

<table>
<thead>
<tr>
<th>C17:0ai</th>
<th>C18:3</th>
<th>C18:2</th>
<th>C18:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>ante-iso-hepta decanoic acid</td>
<td>pinolenic or ante-iso-hepta decanoic acid</td>
<td>linolenic acid</td>
<td>oleic acid</td>
</tr>
<tr>
<td>IIA</td>
<td>18</td>
<td>about 10</td>
<td>about 15</td>
</tr>
<tr>
<td>IIB</td>
<td>1</td>
<td>about 1</td>
<td>about 1</td>
</tr>
</tbody>
</table>

[0051] It can be seen that in samples IIA the measured relative concentrations of unsaturated fatty acids are the same as in samples taken of the paper product at the wet end. This indicates that no polymerization of unsaturated fatty acids took place in the paper machine.

[0052] In samples IIB the measured relative concentrations of unsaturated fatty acids are significantly lower than in samples IIA. This indicates a polymerization or drying of glycerides, rendering the unsaturated fatty acids not measurable by the analysis method used.

[0053] Samples IIA were taken when the resin acid concentration, i.e. the concentration of a non-drying component, in the pulp suspension was high, generally above 0.6 kg/t (measured in ready paper) and samples IIB were taken when the resin acid concentration was low, generally below 0.6 kg/t (measured in ready paper). Polymerization of glycerides was seen to take place in this particular pulp suspension as long as the resin acid concentration remained below about 0.6 kg/t. As the resin acid concentration increased the speed of polymerization decreased.

[0054] It is therefore believed that in a pulp suspension the relation of drying and non-drying extractives plays an important role in the polymerization of glycerides. Thus the speed of polymerization can be increased, as suggested by the present invention, by increasing the concentration of drying fatty acid components. Unsaturated, preferably polymersaturated, fatty acids can be used for this purpose.

EXAMPLE 2

The same analysis method as in Example 1 was used to determine the concentration of free fatty acids and fatty acids in non-polymerized glycerides in linseed oil and linseed oil varnish. The latter (from this on named varnish) is partly polymerized linseed oil.

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>Linseed oil</th>
<th>Varnish</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>28.5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>29.0</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>54.0</td>
<td>28.2</td>
</tr>
<tr>
<td>8</td>
<td>49.6</td>
<td>28.4</td>
</tr>
<tr>
<td>9</td>
<td>49.2</td>
<td>25.2</td>
</tr>
<tr>
<td>10</td>
<td>49.2</td>
<td>24.4</td>
</tr>
<tr>
<td>11</td>
<td>50.4</td>
<td>24.0</td>
</tr>
</tbody>
</table>

[0055] Unsized paper was produced from a standard furnish containing 30% softwood and 70% hardwood cellulose.

[0056] Hydrophobic sizing properties of linseed oil/varnish were compared using solvent sizing procedure.

EXAMPLE 4

[0057] Hydrophobic sizing properties of varnish emulsion was tested and compared with those of resin and AKD dispersions.

[0058] Cationic starch with DS 0.2 was used as stabilizer with ratio to sizing agent of 2:1.

[0059] The sizing evaluation was carried out using laboratory handsheet former. A standard furnish (30% softwood and 70% hardwood) was used at different addition levels of the sizing agent. Percel 63 was added 300 g/t as retention aid. Alum was used with ratio 2:1 to sizing agent.

[0060] Cobb tests of the prepared handsheet were performed without oven drying and with oven drying at 105°C. for 1 hour, 4 hours, 1 day and 3 days.

[0061] The varnish sizing performance at different addition levels with different heating times was:

<table>
<thead>
<tr>
<th>Addition (kg/t)</th>
<th>Cobb (g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Heating for</td>
</tr>
<tr>
<td>2</td>
<td>106.1</td>
</tr>
<tr>
<td>3</td>
<td>105.2</td>
</tr>
<tr>
<td>4</td>
<td>101.5</td>
</tr>
<tr>
<td>5</td>
<td>101.0</td>
</tr>
<tr>
<td>6</td>
<td>83.4</td>
</tr>
<tr>
<td>7</td>
<td>83.0</td>
</tr>
<tr>
<td>8</td>
<td>83.1</td>
</tr>
<tr>
<td>9</td>
<td>79.9</td>
</tr>
<tr>
<td>10</td>
<td>79.0</td>
</tr>
<tr>
<td>15</td>
<td>72.0</td>
</tr>
<tr>
<td>20</td>
<td>70.8</td>
</tr>
<tr>
<td>30</td>
<td>65.7</td>
</tr>
</tbody>
</table>

[0062] The sizing was poor with natural curing as the Cobb values were more than 60 g/m² at addition level of as high as 30 kg/t. However, with 3 day heating in an oven at 105°C., a 3 kg/t addition level gave a good sizing result (Cobb 20.4 g/m²).
Sizing performance of varnish emulsion was compared to that of rosin and AKD dispersions with 3 day heating time at 105°C. The results are gathered in the table below.

<table>
<thead>
<tr>
<th>Addition (kg/t)</th>
<th>Varnish</th>
<th>Rosin</th>
<th>AKD</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>25.4</td>
<td>23.0</td>
<td>20.4</td>
</tr>
<tr>
<td>3</td>
<td>20.4</td>
<td>19.6</td>
<td>18.9</td>
</tr>
<tr>
<td>4</td>
<td>20.1</td>
<td>20.1</td>
<td>19.4</td>
</tr>
</tbody>
</table>

At addition level of 3 kg/t varnish gave better hydrophobicity than rosin and almost as good as AKD.

1. An additive for paper or board production, the additive includes at least:
   a. a component including fatty acid glycerides, wherein the fatty acid glycerides are characterized by a high percentage of unsaturated fatty acids.
   b. The additive of claim 1, is characterized by the component including fatty acid glycerides in which more than 10 wt. % of the fatty acids have more than 1 double bond.
   c. The additive of claim 1, is characterized by the component including fatty acid glycerides in which >60 wt. % of the fatty acids have 2 double bonds.
   d. The additive of claim 1, the component including fatty acid glycerides in which >10 wt. % of the fatty acids have 3 double bonds.
   e. The additive of claim 1 is characterized by the component being raw or partly polymerized plant oil.
   f. The additive of claim 1 further including one or more emulsion stabilizer selected from the group consisting of natural or synthetic polymers or inorganic particles.
   g. The additive of claim 1 is characterized by further including one or more surfactants.
   h. The additive of claim 1 characterized by further including at least one conventional sizing component.

2. A method for decreasing pitch problems occurring in paper or board production, comprising adding to the paper or board suspension or web an additive including at least a component including fatty acid glycerides, characterized by
   a. a component including fatty acid glycerides comprising a high percentage of unsaturated fatty acids.
   b. The method of claim 9, is characterized by the component including fatty acid glycerides in which more than 10 wt. % of the fatty acids have more than 1 double bond.
   c. The method of claim 9, is characterized by the component including fatty acid glycerides in which >60 wt. % of the fatty acids have 2 double bonds.
   d. The method of claim 9, is characterized by the component including fatty acid glycerides in which >10% of the fatty acids have 3 double bonds.
   e. The method of claim 9, is characterized by the component being raw or partly polymerized plant oil.

3. A method for increasing hydrophobicity of a paper or board product, or for decreasing odor problems in the paper or board product, the method comprises adding to the paper or board suspension or web an additive comprising at least a component including fatty acid glycerides, characterized by
   a. a component including fatty acid glycerides comprising a high percentage of unsaturated fatty acids.
   b. The method of claim 14, is characterized by the component including fatty acid glycerides in which more than 10 wt. % the fatty acids have more than 1 double bond.
   c. The method of claim 14, is characterized by the component including fatty acid glycerides in which >60 wt. % the fatty acids have 2 double bonds.
   d. The method of claim 14, is characterized by the component including fatty acid glycerides in which >10 wt. % the fatty acids have 3 double bonds.
   e. The method of claim 14 is characterized by the component being raw or partly polymerized plant oil.

4. A method of improving runnability in paper or board production by adding the additive according to claim 1 to a fiber suspension including mechanical pulp, and/or a fiber suspension resulting in a paper or board product containing, wherein the additive is added in the amount of at least 0.5 kg/t.

20-21. (canceled)

22. The method according to claim 19 wherein the additive is added in the amount of at least 0.5-10 kg/t.