The invention relates to aqueous dispersions for paper sizing containing a sizing agent and one or more emulsifiers, the sizing agent having a molecular weight of < 2000 g/mol and being predominantly in the form of particles with a particle diameter of less than 1 μm, characterised in that 50% of the sizing agent particles have a particle diameter (D₅₀) of less than 600 nm and 90% of the sizing agent particles have a particle diameter (D₉₀) of less than 800 nm, the difference between D₅₀ and D₉₀ ranging from 50 nm to 500 nm. The invention also relates to a method for producing the dispersions.
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**Aqueous dispersions for sizing paper**

The invention relates to aqueous dispersions for sizing paper. The invention relates in particular to aqueous dispersions in which the paper sizing agent is in the form of particles, the majority of these particles having a particle size diameter of less than 1 µm, which are also known as nano dispersions.

The use of sizing agents is common practice in paper manufacturing. The main purpose of sizing agents is to waterproof the paper to prevent liquids (for example water or printing ink) penetrating the paper and to prevent the printing ink from running into the paper. The Cobb value is used to measure the penetration of water / printing ink. This is determined in accordance with DIN 53 132. This gives Cobb<sub>60</sub> values. Low Cobb values are preferred in order to ensure good printability of the paper.

The Cobb value is usually dependent on the quantity of sizing agent: with small amounts of sizing agent, high Cobb values are obtained and the paper will have poor printability. If the quantity of sizing agent is increased, the Cobb value improves along with printability. Above a certain quantity of sizing agent, only a slight further reduction, or no reduction at all, in Cobb values is achieved. In papermaking, attempts are thus made to establish the point at which the quantity, i.e. the consumption, of sizing agent can be minimised, whilst still achieving the desirable required Cobb value.

There are currently two different processes available for paper sizing: internal sizing, in which the sizing agent is added directly to the paper pulp, and surface sizing in which the paper web is coated with sizing agent after the paper itself has been made. In both cases the sizing agents are usually used in a starch or polymer solution, optionally with additional additives.

Common standard paper sizing agents at present are sizing agents based on fatty acid anhydrides (FAA), alkenyl ketene dimer (AKD), alkyl succinic anhydride (ASA) or polymers.

Sizing agents are usually applied without solvents in the form of aqueous emulsions or dispersions. In order to produce such emulsions or dispersions, an oily phase (the liquid or molten sizing agent) is usually emulsified/dispersed in the form of fine droplets in an aqueous polymer solution (for example, starch) using high shear forces. These droplets
usually have a D90 particle diameter of 0.7 to 3 µη. The methods used in this process to produce such emulsions are prior art and are used to emulsify the known sizing agents, it being necessary for emulsification to take place directly before using the sizing agent in papermaking in the case of ASA sizing agents which are susceptible to hydrolysis, for example.

Despite the sizing agents and the methods used for emulsification / dispersion of these sizing agents having been implemented for a long time, there is still interest in improving surface sizing with a view to achieving a more even distribution of the sizing agent on the surface and thus achieving improved sizing and a more efficient use of the sizing agents.

Dispersions of various paper sizing agents with a particle size of, inter alia, less than 1 µm are known in the prior art. Thus, DE 1 122 200 describes a method for producing finely dispersed resin dispersions, and in particular rosin dispersions, which are particularly stable and should have an increased sizing ability. This document explains that the sizing effect of a dispersion increases as the particle size reduces. The examples given in the examined and published application should have particle sizes of around 0.5 µm, for example.

DE 197 35 636 describes resin dispersions for internal or surface sizing based on non-strengthened or strengthened rosin which is esterified with polyvalent alcohols. The particle sizes should be between 0.5 and 1 µm. Particle sizes of 0.1 to 1 µm are given for the sole embodiment.

W098/33979 relates to cellulose-reactive sizing agents such as alkenyl ketene dimer (AKD) and alkyl succinic anhydride (ASA). Emulsions are produced with the sizing agents in which the droplets of sizing agent measure 0.1 to 3.5 µm in diameter.

None of the above-mentioned documents contain references to particle size distribution or to the measurement method which was used to establish the particle size.

Finally, CA 2 175 863 relates to means and methods for manufacturing paper coating systems based on ASA. In the ASA emulsions obtained, at least 33 % of the ASA particles should have a particle size in the range between 0.25 and 2 µm; other ASA emulsions should have a particle size between 0.25 and 2 µm, in particular 0.25 to 1.0 µm.
Despite the dispersions known from the above-mentioned documents, dispersions of paper sizing agents are still used in practice which have D90 particle sizes which are generally not less than 1 \( \mu m \). This is due, inter alia, to the fact that a considerable application of shear forces is usually required when producing the dispersion in order to achieve small particle sizes. These shear forces require special technical equipment which is not widely available.

There is therefore still a need for emulsions or dispersions for paper sizing which contain paper sizing agents in the form of particles with small particle sizes and which can be obtained using low shear forces. In the context of the present invention, it has been found that this object can be achieved by a method using low shear forces in which the dispersions of paper sizing agents not only have a small particle size, but also have a narrow particle size distribution.

The aqueous dispersions for paper sizing prepared according to the invention containing sizing agent and one or more emulsifiers, in which the sizing agent has a molecular weight of < 2000 g/mol and is in the form of particles with a particle diameter of less than 1 \( \mu m \), are characterised by the fact that 50 % of the sizing agent particles have a particle diameter (D50) of less than 600 nm and 90 % of the sizing agent particles have a particle diameter (D90) of less than 800 nm, the difference between the D90 value and the D50 value ranging from 50 nm to 500 nm.

In a preferred embodiment of the invention, 50 % of the sizing agent particles have a particle diameter of less than 400 nm and 90 % of the sizing agent particles have a particle diameter of less than 600 nm: in an even more preferable embodiment of the invention, 50 % of the sizing agent particles have a particle diameter of less than 250 nm and 90 % of the sizing agent particles have a particle diameter of less than 400 nm.

In another preferred embodiment of the invention, the difference between D90 and D50 ranges from 50 nm to 350 nm, preferably 50 nm to 250 nm.

The sizing agents according to the invention are in particular characterised by a narrow particle size distribution, the difference between the D90 value and the D50 value ranging from 50 nm to 500 nm. In contrast, standard sizing agent dispersions which are obtained using high shear forces display a difference between the D90 value and the D50 value of up to 3300 nm for example.
Smaller particles, particularly with a narrow particle size distribution, guarantee an even distribution of particles on the surface of the paper web, for example, and thus further improved surface sizing. It is also possible to avoid the effect whereby larger particles in a dispersion form agglomerates with smaller particles, which can lead to a deterioration in the quality of the dispersion when storing dispersions and to problems during use of these dispersions.

A dispersion is in this case understood to mean a mixture of substances which consists of two or more phases, in which one substance forms the so-called disperse phase and is distributed in another substance, the dispersion agent. The disperse phase and the dispersion agent can in principle be solid, liquid or gaseous. In the context of the present invention, the term dispersion therefore comprises both emulsions, in which the disperse phase and the dispersion agent are liquid, and suspensions, in which insoluble solid particles are distributed in a liquid.

The aqueous dispersions according to the invention are characterised by their narrower particle size distribution - compared to traditional dispersions obtained using high shear forces - which in addition cannot be deduced from prior art documents. The particle size distribution in this case is characterised by the D50 and D90 values: here, a D50 value of 600 nm, for example, means that 50 % of the particles have a particle diameter of less than 600 nm; a D90 value of 800 nm, for example, means that 90 % of the particles have a particle diameter of less than 800 nm.

In the method used to establish the particle sizes and the particle size distribution, which is described in greater detail below, it is assumed, as in most methods, that the particles are spherical, which means that the particle size is determined solely by specifying the diameter. This is a measure known to persons skilled in the art.

As sizing agents, the aqueous dispersions according to the invention may contain traditional sizing agents such as cellulose-reactive sizing agents, including alkyl succinic anhydride (ASA) and alkenyl ketene dimer (AKD), the latter in both liquid and solid form, fatty acid anhydrides, preferably tall oil fatty acid anhydride, or tall and balsam resins, preferably fully or partially strengthened and/or esterified. Strengthened tall and balsam resins are in this case understood to mean resins which have been fully or partially reacted with fumaric acid and/or maleic anhydride.
Mixtures of cellulose-reactive sizing agents may also be used as sizing agents according to the invention, provided that these can be mixed together.

Dispersions according to the invention may have higher dry contents than traditional dispersions, namely up to 70 % by weight. For example, dispersions of sizing agents according to the invention which contain ASA as a sizing agent have dry contents of up to 25 % by weight or more, whilst traditional ASA dispersions have dry contents of a maximum of 15 % by weight. Dispersions of sizing agents according to the invention produced using AKD may have sample dry contents of 30 to 70 % by weight, preferably 40 to 60 % by weight, whilst traditional dispersions have a maximum of 25 % by weight. In this case, dry content is understood to mean the total dry substances comprising sizing agent, starches and additives.

Due to the higher dry contents of the dispersions according to the invention, the user may be provided with more concentrated dispersions than are currently used, with smaller amounts of water being required in the production of such dispersions, which leads, inter alia, to reduced manufacturing, transport and storage costs for the dispersions according to the invention.

Natural or synthetic products may be used as emulsifiers. The use of surfactant mixtures is also possible. The emulsifiers may also be selected from among ionic emulsifiers, such as surfactants, which are present in cationic form in aqueous solutions, for example quaternary ammonium salts (cetyltrimethylammonium bromide, benzyl dimethyl tetradecyl ammonium chloride and others), and surfactants which are in anionic form in aqueous solutions, such as alkylcarboxylates, alkylbenzene sulfonates, fatty alcohol sulphates, phosphoric acid esters and others. Amphoteric surfactants can also be used, such as, for example, surfactants from the betaine and sultaine groups. Emulsifiers from the non-ionic emulsifier class can also be used, such as fatty alcohol ethoxylates, for example lauryl alcohol ethoxylate. Silicon-based emulsifiers, polymers and hydrofluorocarbons can also be used as emulsifiers.

The methods for producing the aqueous dispersions according to the invention may be batch-type or continuous methods.

The aqueous dispersions according to the invention may for example be produced using low shear force as described below:
Production method for dispersions containing solid sizing agents such as AKD wax

A 40 to 45 % by weight emulsifier solution in demineralised water is produced in order to produce the dispersion according to the invention. An emulsifier mixture with one part ionic emulsifier (for example, aerosol OT-B) and four parts non-ionic emulsifier (for example, Marlipal 24/50 and Marlipal 24/70 in a 1:1 ratio, or Brij 35P and Marlipal 24/70 in a 1:9 ratio) is used as an emulsifier.

1 g of the emulsifier solution is heated for 0.5 - 2 min in a glass beaker with a suitable volume and in an oil bath adjusted to a temperature of approximately 75°C. The AKD wax melted in the oil bath at a temperature of approximately 75°C is then added dropwise whilst agitating under laminar flow conditions. The amount of AKD can be varied according to the desired emulsifier-wax ratio. Thus, for example, an adequate quantity of AKD can be added to achieve an emulsifier to AKD ratio of approximately 1:9.

The resulting highly concentrated lyotropic, liquid crystalline phase is diluted to the required concentration with demineralised water adjusted to a temperature of 75°C. When adding water, the agitator speed can be kept variable as long as laminar flow conditions prevail and are maintained. The desired dry content of 30 % by weight, for example, can then be adjusted by adding demineralised water. Finally, the dispersion is cooled to approximately 25°C in an ice bath. It is stored at room temperature.

Production method for dispersions containing sizing agents which are liquid at room temperature such as ASA or tall oil fatty acid anhydride

These can be produced in substantially the same way as described above for dispersions containing solid sizing agents, although the sizing agents used and the demineralised water used for dilution purposes do not need to be heated. Final cooling with iced water can also be omitted.

The invention and further advantages are shown in greater detail by way of the following embodiments of the invention and figures.
In the following embodiments of the invention, all percentages are based on weight.

The static light scattering method was used to determine the particle size of the dispersions using an LA300 measurement apparatus supplied by Horiba, Japan. The measurement was performed in a measurement range from 100 nm to 600 μm in very dilute aqueous media (a few drops of measurement solution are diluted in ~250 ml deionised water). The relative refractive index of the sizing agent is used as the refractive index in each case. This is calculated from the ratio of the absolute refractive index and the refractive index of water (1.33). All particle size distributions were evaluated over volume. Compared with evaluating on the basis of quantity, evaluating over volume also allows smaller particles to be recorded.

A laboratory-size press supplied by Einlehner Prufmaschinen was used for surface sizing tests. A speed of 20 m/min and a pressure of approximately 5 kg/cm were selected as standard settings. Sheet drying was carried out at 120°C using a steam drum dryer manufactured by Mathis in Switzerland, Type No. FKD-0583. Water repellence of the resulting paper was determined using the Cobb test (DIN 53132).

Example 1

Particle size distributions in standard dispersions and dispersions of standard sizing agents according to the invention

In order to test the particle size distribution, dispersions of sizing agents according to the invention were produced using low shear forces and compared with standard dispersions which were produced on an industrial scale or in the laboratory using traditional methods with high shear forces. In detail, the following dispersions were used:

Dispersions with AKD wax

An industrially produced AKD dispersion (not according to the invention), produced by dispersing an aqueous starch solution, emulsifier and molten AKD wax at high pressure (~16 % AKD wax in starch solution). This dispersion has a symmetrical particle size distribution, as shown in Figure 1a, with the following characteristics:
- Monomodal distribution
- 50% of the particles are smaller than 819 nm
- 90% of the particles are smaller than 1.751 µm

An AKD wax dispersion (20% AKD wax) produced according to the invention in a laboratory at approximately 60°C. This dispersion has a symmetrical particle size distribution, as shown in Figure 1b, with the following characteristics:
- Monomodal distribution
- 50% of the particles are smaller than 290 nm
- 90% of the particles are smaller than 401 nm

**Dispersions with liquid AKD**

A dispersion containing liquid AKD produced in a laboratory with high shear forces, not according to the invention. To this end, a starch solution is mixed with 1% liquid AKD and dispersed for 2 min using a device known as Ultra-Turrax T50 (IKA - Labortechnik). The dispersion has a bimodal particle size distribution, as shown in Figure 2a, with the following characteristics:
- 1st maximum -500 nm
- 2nd maximum - 1.1 µm
- 50% of the particles are smaller than 854 nm
- 90% of the particles are smaller than 4.086 µm

A dispersion containing liquid AKD (40% AKD) produced in a laboratory with low shear forces according to the invention. This dispersion has a substantially symmetrical particle size distribution, as shown in Figure 2b, with the following characteristics:
- Monomodal distribution
- 50% of the particles are smaller than 224 nm
- 90% of the particles are smaller than 314 nm

The particle size distribution was measured with a relative refractive index of 1.12 for both dispersions.
Dispersions with ASA

An ASA dispersion was produced in a laboratory with high shear forces, not according to the invention. To this end, a starch solution is mixed with 1 % ASA and dispersed for 2 min using a device known as Ultra-Turrax T50 (IKA - Labortechnik). The dispersion has a bimodal particle size distribution, as shown in Figure 3a, with the following characteristics:
- 1st maximum -700 nm
- 2nd maximum - 1.1 μm
- 50 % of the particles are smaller than 932 nm
- 90 % of the particles are smaller than 3.175 μm

An ASA dispersion (20 % ASA) produced in a laboratory with low shear forces according to the invention. This dispersion has a symmetrical particle size distribution, as shown in Figure 3b, with the following characteristics:
- Monomodal distribution
- 50 % of the particles are smaller than 210 nm
- 90 % of the particles are smaller than 293 nm

The particle size distribution was measured with a relative refractive index of 1.10 for both dispersions.

Dispersions with fatty acid anhydride (FAA)

An FAA dispersion produced in a laboratory with high shear forces, not according to the invention. To this end, a starch solution is mixed with 1 % FAA and dispersed for 2 min using a device of make Ultra-Turrax T50 (IKA - Labortechnik). The dispersion has an almost symmetrical monomodal particle size distribution, as shown in Figure 4a, with the following characteristics:
- 50 % of the particles are smaller than 1.354 μm
- 90 % of the particles are smaller than 2.960 μm

An FAA dispersion (20 % FAA) produced in a laboratory with low shear forces according to the invention. This dispersion has a symmetrical particle size distribution, as shown in Figure 4b, with the following characteristics:
- Monomodal distribution
- 50% of the particles are smaller than 289 nm
- 90% of the particles are smaller than 395 nm

The particle size distribution was measured with a relative refractive index of 1.10 for both dispersions.

The aforementioned examples show that dispersions according to the invention which are characterised by a small particle size and a narrow particle size distribution are obtained with a method using low shear forces as described in general terms above. As illustrated in the examples below, such dispersions ensure particular advantages compared with the known dispersions when surface sizing paper, such as improved sizing efficiency inter alia.

Example 2
ASA dispersion (according to the invention)

An aqueous emulsifier mixture is produced first. 1.5 g aerosol OT-B (dioctyl sulfosuccinate, Cytec), 0.6 g Brij 35P Pharma (Laureth-23), 5.4 g Marlipal 24/70 (Laureth-7, Sasol) and 10 g demineralised water are used for this purpose. All components are dissolved in water to create a clear solution by heating to a maximum of 80°C for a short time.

1 g of the solution which has been cooled to room temperature is placed in a 50 ml glass beaker and agitated using the method described in Patent WO2004/082666. The required amount of ASA is then added. A whitish, highly viscous gel is thus formed which is then diluted with water to the required emulsion concentration. The dispersions produced in this manner are summarised in Table 2.
Table 2

ASA dispersions (according to the invention)

<table>
<thead>
<tr>
<th>Emulsifier concentration, based on ASA [ %]</th>
<th>4</th>
<th>6</th>
<th>10</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsifier solution [g]</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>ASA mass [g]</td>
<td>10.3</td>
<td>6.721</td>
<td>3.861</td>
<td>2.43</td>
</tr>
<tr>
<td>Water [g]</td>
<td>31.6</td>
<td>20.88</td>
<td>12.3</td>
<td>8.01</td>
</tr>
<tr>
<td>Dry substance [ %]</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Final ASA concentration [%]</td>
<td>24</td>
<td>23.5</td>
<td>22.5</td>
<td>21.2</td>
</tr>
<tr>
<td>Particle size D50 [nm]</td>
<td>509</td>
<td>301</td>
<td>194</td>
<td>164</td>
</tr>
<tr>
<td>Particle size D90 [nm]</td>
<td>757</td>
<td>411</td>
<td>271</td>
<td>234</td>
</tr>
</tbody>
</table>

Table 2 also shows that the particle size of the ASA dispersions can be adjusted by the selected emulsifier concentration. The advantageous narrow particle size distribution of the dispersions according to the invention is retained in this process.

Example 3

Standard ASA emulsion (not according to the invention)

A 5 % starch solution is boiled. A standard ASA emulsion is produced using a standard method with high shear forces in which the ASA is emulsified directly in starch.

Example 4

Surface sizing using ASA dispersions

Varying quantities of the ASA dispersions produced in Examples 2 and 3 are placed at room temperature and topped up to 500 g with starch solution. They are then agitated well so that the emulsion is distributed homogeneously in the starch solution. These homogenised mixtures are applied to unsized fine paper (135 g/m²) using the laboratory size press. The sheets of paper are then dried at 120°C.
Table 3 shows the Cobb_{60} values obtained in surface sizing tests with selected ASA dispersions from Examples 2 and 3. As shown in the table, the required low Cobb_{60} values are achieved with the dispersion according to the invention, even with low ASA concentrations in the sizing liquor.

<table>
<thead>
<tr>
<th>ASA concentration in the sizing liquor [%]</th>
<th>0.06</th>
<th>0.09</th>
<th>0.1</th>
<th>0.12</th>
<th>0.125</th>
<th>0.15</th>
<th>0.18</th>
<th>0.23</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobb_{60} [g/m²] – ASA dispersion with 4 % emulsifier (according to the invention)</td>
<td>143</td>
<td>48</td>
<td>-</td>
<td>27.5</td>
<td>-</td>
<td>22.5</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>Cobb_{60} [g/m²] Standard ASA emulsion (not according to the invention)</td>
<td>-</td>
<td>-</td>
<td>119</td>
<td>-</td>
<td>38</td>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Example 5
AKD dispersion (according to the invention)

An aqueous emulsifier mixture is produced first. 1 g aerosol OT-B (dioctyl sulfosuccinate, Cytec), 2 g Marlipal 24/50 (Laureth-5, Sasol), 2 g Marlipal 24/70 (Laureth-7, Sasol) and 7 g demineralised water are used for this purpose. All components are dissolved in water to create a clear solution by heating to a maximum of 80°C for a short time.

1 g of the emulsifier solution cooled to room temperature is placed in a 50 ml glass beaker, heated to ~70°C and agitated using the method described in general terms above. The required amount of molten AKD is then added. A whitish, highly viscous gel is thus formed which is then diluted with water at a temperature of ~70°C to the required dispersion concentration.
Table 4
AKD dispersion (according to the invention)

<table>
<thead>
<tr>
<th>Emulsifier concentration based on AKD [%]</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsifier solution [g]</td>
<td>1</td>
</tr>
<tr>
<td>AKD [g]</td>
<td>3.74</td>
</tr>
<tr>
<td>Water [g]</td>
<td>11.9</td>
</tr>
<tr>
<td>Dry substance [%]</td>
<td>25</td>
</tr>
<tr>
<td>Final AKD concentration [%]</td>
<td>22.5</td>
</tr>
<tr>
<td>Particle size D50 [nm]</td>
<td>250</td>
</tr>
</tbody>
</table>

Example 6
Surface sizing using AKD dispersions

A 5% starch solution is prepared. Varying quantities of the AKD dispersion from Example 4 are then placed at room temperature and topped up to 500 g with starch solution. These are then agitated well so that the dispersion is homogeneously distributed in the starch solution. These homogenised mixtures are applied to unsized fine paper (135 g/m²) using the laboratory size press. The sheets of paper are then dried at 120°C.

A commercially available standard AKD dispersion is used for comparison purposes (D50 - 650 nm).

Table 5 shows the Cobb60 values for surface sizing tests with selected AKD dispersions. As shown in the table, the required low Cobb60 values are achieved with the dispersion according to the invention, even with low AKD concentrations in the sizing liquor.
Table 5

<table>
<thead>
<tr>
<th>AKD concentration in the sizing liquor [%]</th>
<th>0.05</th>
<th>0.06</th>
<th>0.07</th>
<th>0.08</th>
<th>0.09</th>
<th>0.10</th>
<th>0.12</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{50}) [g/m²] - AKD dispersion with 10 % emulsifier (according to the invention)</td>
<td>160</td>
<td>149</td>
<td>140</td>
<td>56</td>
<td>25</td>
<td>27</td>
<td>24</td>
</tr>
<tr>
<td>(C_{50}) [g/m²] - standard AKD dispersion (not according to the invention)</td>
<td>206</td>
<td>192</td>
<td>180</td>
<td>72</td>
<td>45</td>
<td>35</td>
<td>31</td>
</tr>
</tbody>
</table>

5

**Example 7**

AKD dispersions with a high active ingredient content (according to the invention)

An aqueous emulsifier mixture is produced first. 1.5 g aerosol OT-B (dioctyl sulfo succinate, Cytec), 0.6 g Brij 35P Pharma (Laureth-23), 5.4 g Marlipal 24/70 (Laureth-7, Sasol) and 10 g demineralised water are used for this purpose. All components are dissolved in water to create a clear solution by heating to a maximum of 80°C for a short time.

1 g of the solution which has been cooled to room temperature is placed in a 50 ml glass beaker, heated to ~70°C and agitated using the method described in Patent WO2004/082666. 3.861 g molten AKD is then added. A whitish, highly viscous gel is thus formed which is then diluted with 5.864 g or 3.72 water to give an emulsion concentration with 40 or 50 % dry content.
Table 6
AKD dispersions with a high active ingredient content (according to the invention)

<table>
<thead>
<tr>
<th>Emulsifier concentration based on AKD [%]</th>
<th>10</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsifier solution [g]</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>AKD [g]</td>
<td>3.86</td>
<td>3.86</td>
</tr>
<tr>
<td>Water [g]</td>
<td>5.86</td>
<td>3.72</td>
</tr>
<tr>
<td>Dry substance [%]</td>
<td>~ 40</td>
<td>~ 50</td>
</tr>
<tr>
<td>Final AKD concentration [%]</td>
<td>~ 36</td>
<td>~ 45</td>
</tr>
<tr>
<td>Particle size D90 [nm]</td>
<td>367</td>
<td>369</td>
</tr>
</tbody>
</table>

Example 8
Dispersions with liquid AKD

10 An aqueous emulsifier mixture is produced first. 1 g aerosol OT-B (dioctyl sulfosuccinate, Cytec), 2 g Marlipal 24/50, 2 g Marlipal 24/70 (Laureth-7, Sasol) and 7 g demineralised water are used for this purpose. All components are dissolved in water to create a clear solution by heating to a maximum of 80°C for a short time.

15 1 g of the solution cooled to room temperature is placed in a 50 ml glass beaker and agitated using the method described in general terms above. The required amount of liquid AKD is then added. A whitish, highly viscous gel is thus formed which is then diluted with water to the required emulsion concentration.

20 Examples of dispersions according to the invention containing liquid AKD are summarised in Table 7 below, which also shows a commercial AKD dispersion produced using high shear forces for comparison purposes.
Example 9
Surface sizing using dispersions with liquid AKD

A 5% starch solution is prepared. A standard liquid AKD dispersion is produced using a standard method with high shear forces in which the liquid AKD is emulsified directly in the starch solution.

Varying quantities of the liquid AKD dispersions according to the invention are placed at room temperature and topped up to 500 g with starch solution. These are then agitated well so that the dispersion is homogeneously distributed in the starch solution. These homogenised mixtures are applied to unsized fine paper (135 g/m²) using the laboratory size press. The sheets of paper are then dried at 120°C.

Table 8 shows the Cobb₀ values for surface sizing tests with selected liquid AKD dispersions. As shown in the table, the required low Cobb₀ values are achieved with the dispersion according to the invention, even with low liquid AKD concentrations in the sizing liquor.
Table 8
Surface sizing using dispersions
with liquid AKD

<table>
<thead>
<tr>
<th>Concentration of liquid AKD in the sizing liquor [%]</th>
<th>0.1</th>
<th>0.11</th>
<th>0.12</th>
<th>0.13</th>
<th>0.14</th>
<th>0.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobβ[60] [g/m²] - standard dispersion</td>
<td>155</td>
<td>100</td>
<td>72</td>
<td>50</td>
<td>36</td>
<td>28</td>
</tr>
<tr>
<td>Cobβ[90] [g/m²] dispersion according to the invention (4 %)</td>
<td>-</td>
<td>71</td>
<td>40</td>
<td>31</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Example 10
Dispersion with tall oil fatty acid anhydride (according to the invention)

An aqueous emulsifier mixture is produced first. 1 g aerosol OT-B (dioctyl sulfosuccinate, Cytec), 2 g Marlipal 24/50, 2 g Marlipal 24/70 (Laureth-7, Sasol) and 7 g demineralised water are used in this case. All components are dissolved in water to create a clear solution by heating to a maximum of 80°C for a short time.

1 g of the solution which has been cooled to room temperature is placed in a 50 ml glass beaker and agitated using the method described in the patent. 6.5 g tall oil fatty acid anhydride (FSA) is then added. A whitish, highly viscous gel is formed which is then diluted with water to the required emulsion concentration. The D90 value is 440 nm.

Example 11
Surface sizing using dispersions
with tall oil fatty acid anhydride

A 5 % starch solution is prepared. 1 % PAX 18 (polyaluminium chloride solution) is added to this solution.
A standard FSA emulsion is produced using a standard method with high shear forces in which the FSA is emulsified directly in the starch solution. The D90 value is < 2800 nm.

Varying quantities of the FSA dispersions according to the invention are placed at room temperature and topped up to 500 g with starch solution. These are then agitated well so that the dispersion is homogeneously distributed in the starch solution. These homogenised mixtures are applied to unsized fine paper (135 g/m²) using a laboratory size press. The sheets of paper are then dried at 120°C.

Table 9 shows the Cobb₆₀ values for surface sizing tests with selected dispersions containing tall oil fatty acid anhydride. As shown in the table, the required low Cobb₆₀ values are achieved with the dispersion according to the invention, even with low tall oil fatty acid anhydride concentrations in the sizing liquor.

<table>
<thead>
<tr>
<th>Concentration of tall oil fatty acid anhydride in the sizing liquor [ %]</th>
<th>0.05</th>
<th>0.075</th>
<th>0.085</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobb₆₀ [g/m²] - standard dispersion</td>
<td>133</td>
<td>131</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cobb₆₀ [g/m²] dispersion according to the invention (6 % emulsifier)</td>
<td>138</td>
<td>41</td>
<td>32</td>
<td>29</td>
</tr>
</tbody>
</table>

The examples show the narrow particle size distribution of the dispersions according to the invention and the improved sizing efficiency which can be achieved with the dispersions according to the invention. In comparison with traditional dispersions produced using high shear forces, adequate Cobb values as required for satisfactory paper printability are achieved even with lower concentrations of sizing agents in the liquor.
Example 12
Internal sizing using AKD dispersions

Laboratory sheets are produced with a standard pulp solution composed of a mixture of 30% short fibres and 70% long fibres with a freeness value of 30°SR for the purpose of testing the sizing effect of AKD dispersions. The 1% pulp solution used also contains 0.25% calcium carbonate. The sheets are produced at a temperature of 45°C and have an average weight of approximately 80 g/m². 0.2 kg/t paper Fennopol K 3400R (Kemira Oyj, Finland) is used as a retention agent.

Various AKD dispersions are diluted to an AKD content of 0.1%. An amount of these diluted solutions corresponding to 1.2 kg/t paper is used in the sheet forming process.

The laboratory sheets are dried twice in the photo dryer (Meteor, Germany, Standard H type) at 115°C and at a speed of approximately 1 revolution per 40 seconds. The Cobb₆₀ values of the sheets are then determined in accordance with DIN 53132.

When using 1.2 kg/t AKD, a traditional AKD dispersion gave a Cobb₆₀ value of 23 g/m² and a particle size distribution of $D_{50} \approx 675$ nm and $D_{90} \approx 1.1$ µm, as shown in Figure 5a.

1.2 kg/t AKD of an AKD dispersion according to the invention was also used and the Cobb₆₀ value was determined. This was also 23 g/m². The particle size distribution of the initial emulsion is characterised by a $D_{50}$ value of 300 nm and $D_{90}$ value of 390 nm, as shown in Figure 5b.

The particle size distributions were once again determined with a relative refractive index of 1.14 using the Horiba LA 300 apparatus.

This example shows that Cobb₆₀ values which at least correspond to the Cobb₆₀ values achieved with traditional AKD dispersions can be achieved when using AKD dispersions according to the invention for internal sizing purposes. However, unlike the traditional AKD dispersions, the AKD dispersions according to the invention advantageously have a higher dry substance content.
Claims

1. Aqueous dispersions for paper sizing containing sizing agent and one or more emulsifiers, in which the sizing agent has a molecular weight of < 2000 g/mol and is predominantly in the form of particles with a particle diameter of less than 1 μm, characterised in that 50 % of the sizing agent particles have a particle diameter (D₅₀) of less than 600 nm and 90 % of the sizing agent particles have a particle diameter (D₉₀) of less than 800 nm, the difference between D₉₀ and D₅₀ ranging from 50 nm to 500 nm.

2. Aqueous dispersion according to Claim 1, characterised in that 50 % of the sizing agent particles have a particle diameter of less than 400 nm and 90 % of the sizing agent particles have a particle diameter of less than 600 nm.

3. Aqueous emulsion or dispersion according to Claim 1, characterised in that 50 % of the sizing agent particles have a particle diameter of less than 250 nm and 90 % of the sizing agent particles have a particle diameter of less than 400 nm.

4. Aqueous dispersion according to Claims 1 to 3, characterised in that the difference between D₉₀ and D₅₀ ranges from 50 nm to 350 nm, preferably from 50 nm to 250 nm.

5. Aqueous dispersion according to Claims 1 to 4, characterised in that the sizing agent is a cellulose-reactive sizing agent or a mixture of cellulose-reactive sizing agents.

6. Aqueous dispersion according to Claim 5, characterised in that the sizing agent is alkyl succinic anhydride (ASA) or liquid or solid alkenyl ketene dimer (AKD).

7. Aqueous dispersion according to Claim 5, characterised in that the paper sizing agent is a fatty acid anhydride, preferably tall oil fatty acid anhydride, or tall resin or balsam resin, preferably fully or partially strengthened and/or esterified.
8. Method for producing an aqueous dispersion according to Claim 1, characterised in that an aqueous phase containing at least one emulsifier is formed in an initial stage, the required quantity of sizing agent then being added to this aqueous phase in a second stage, forming a lyotropic, liquid crystalline mixed phase, and the resulting mixed phase being diluted with water to the required final concentration of the dispersion in a third stage, with the lyotropic, liquid crystalline mixed phase and the aqueous dispersion being formed whilst agitating under laminar flow conditions.
Fig 1a:

D50 Diameter, %

: 0.8190 (µm)

(1) 5.000 (% - 0.3173 (µm)
(2) 10.00 (% - 0.3927 (µm)
(3) 20.00 (% - 0.5081 (µm)
(4) 30.00 (% - 0.6087 (µm)
(5) 40.00 (% - 0.7104 (µm)
(6) 60.00 (% - 0.9460 (µm)
(7) 70.00 (% - 1.1093 (µm)
(8) 80.00 (% - 1.3410 (µm)
(9) 90.00 (% - 1.7513 (µm)
(10) 95.00 (% - 2.1986 (µm)

Fig 1b:

D50 Diameter, %

: 0.2903 (µm)

(1) 5.000 (% - 0.1799 (µm)
(2) 10.00 (% - 0.2010 (µm)
(3) 20.00 (% - 0.2296 (µm)
(4) 30.00 (% - 0.2512 (µm)
(5) 40.00 (% - 0.2709 (µm)
(6) 60.00 (% - 0.3108 (µm)
(7) 70.00 (% - 0.3328 (µm)
(8) 80.00 (% - 0.3613 (µm)
(9) 90.00 (% - 0.4009 (µm)
(10) 95.00 (% - 0.4395 (µm)
Fig 2a:

D50 : 0.8540 \( \mu \text{m} \)

Diameter, %

(1) 5.000 (%) - 0.2671 \( \mu \text{m} \)
(2) 10.00 (%) - 0.3233 \( \mu \text{m} \)
(3) 20.00 (%) - 0.4174 \( \mu \text{m} \)
(4) 30.00 (%) - 0.5206 \( \mu \text{m} \)
(5) 40.00 (%) - 0.6533 \( \mu \text{m} \)
(6) 60.00 (%) - 1.1947 \( \mu \text{m} \)
(7) 70.00 (%) - 1.7029 \( \mu \text{m} \)
(8) 80.00 (%) - 2.4556 \( \mu \text{m} \)
(9) 90.00 (%) - 4.0857 \( \mu \text{m} \)
(10) 95.00 (%) - 7.1218 \( \mu \text{m} \)

Fig 2b:

D50 : 0.2243 \( \mu \text{m} \)

Diameter, %

(1) 5.000 (%) - 0.1458 \( \mu \text{m} \)
(2) 10.00 (%) - 0.1602 \( \mu \text{m} \)
(3) 20.00 (%) - 0.1806 \( \mu \text{m} \)
(4) 30.00 (%) - 0.1977 \( \mu \text{m} \)
(5) 40.00 (%) - 0.2106 \( \mu \text{m} \)
(6) 60.00 (%) - 0.2396 \( \mu \text{m} \)
(7) 70.00 (%) - 0.2561 \( \mu \text{m} \)
(8) 80.00 (%) - 0.2797 \( \mu \text{m} \)
(9) 90.00 (%) - 0.3135 \( \mu \text{m} \)
(10) 95.00 (%) - 0.3381 \( \mu \text{m} \)
**Fig. 3a:**

- **Diameter, %**
  - D50: 0.9322 (μm)
  - (1) 5.00% (μm) 0.2499 (μm)
  - (2) 10.00% (μm) 0.3183 (μm)
  - (3) 20.00% (μm) 0.4376 (μm)
  - (4) 30.00% (μm) 0.5669 (μm)
  - (5) 40.00% (μm) 0.7244 (μm)
  - (6) 60.00% (μm) 1.2230 (μm)
  - (7) 70.00% (μm) 1.6071 (μm)
  - (8) 80.00% (μm) 2.1464 (μm)
  - (9) 90.00% (μm) 3.1750 (μm)
  - (10) 95.00% (μm) 4.6805 (μm)

**Fig. 3b:**

- **Diameter, %**
  - D50: 0.2095 (μm)
  - (1) 5.00% (μm) 0.1374 (μm)
  - (2) 10.00% (μm) 0.1524 (μm)
  - (3) 20.00% (μm) 0.1695 (μm)
  - (4) 30.00% (μm) 0.1834 (μm)
  - (5) 40.00% (μm) 0.1975 (μm)
  - (6) 60.00% (μm) 0.2223 (μm)
  - (7) 70.00% (μm) 0.2391 (μm)
  - (8) 80.00% (μm) 0.2585 (μm)
  - (9) 90.00% (μm) 0.2930 (μm)
  - (10) 95.00% (μm) 0.3258 (μm)
Fig. 4a:

D50 : 1.3542 (μm)

Diameter, %

1. (5.000 (%) - 0.3660 (μm)
2. (10.00 (%) - 0.5007 (μm)
3. (20.00 (%) - 0.7178 (μm)
4. (30.00 (%) - 0.9200 (μm)
5. (40.00 (%) - 1.1319 (μm)
6. (50.00 (%) - 1.5996 (μm)
7. (70.00 (%) - 1.8910 (μm)
8. (80.00 (%) - 2.2797 (μm)
9. (90.00 (%) - 2.9602 (μm)
10. (95.00 (%) - 3.7534 (μm)

Fig. 4b:

D50 : 0.2885 (μm)

Diameter, %

1. (5.000 (%) - 0.1790 (μm)
2. (10.00 (%) - 0.2008 (μm)
3. (20.00 (%) - 0.2287 (μm)
4. (30.00 (%) - 0.2492 (μm)
5. (40.00 (%) - 0.2691 (μm)
6. (50.00 (%) - 0.3091 (μm)
7. (70.00 (%) - 0.3309 (μm)
8. (80.00 (%) - 0.3589 (μm)
9. (90.00 (%) - 0.3952 (μm)
10. (95.00 (%) - 0.4289 (μm)
Fig. 5a:

Fig. 5b: