Abstract:
Dispersions of fumed silica comprising a silanized, structurally modified silica and a solvent. It is used for producing coating materials.
Fumed silica dispersion

The invention relates to a dispersion of fumed silica and to its use for producing coating materials.

The incorporation of fumed silica into coating materials is known. From the document Schriftenreihe Pigmente No. 18 (April 1980) page 5, the incorporation of hydrophobic fumed silica (Aerosil® 972), together with pigments and fillers, is known. To produce a clearcoat material, for instance, the preparation is recommended of an approximately 10% paste in the respective binder solution, for which it is possible to use the typical dispersing equipment. The paste prepared in this way is used as a grinding medium for the further steps for producing the coating material.

Also known is the incorporation into coating materials of silanized, structurally modified fumed silica, the binder being mixed with solvent, and the silica being mixed into this mixture using a high-speed mixer. The resulting mixture is subsequently dispersed using a bead mill (WO 2004/020532).

The known methods of incorporating fumed silica into the coating system have the disadvantage that the clearcoat materials produced in this way exhibit unwanted haze and/or unwanted frosting.

An object which existed, therefore, was to develop a process with which the fumed silica can be incorporated into coating systems in such a way that it is possible to avoid frosting.

The invention provides a dispersion of fumed silica which is characterized in that it comprises a silanized, structurally modified silica and a solvent.

In one embodiment of the invention the dispersion may
further comprise additives. Examples of possible such additives include curing agents.

The silanized, structurally modified silica may in one preferred embodiment of the invention be a fumed silica. The silica may be present in an amount of 5% to 60% by weight, based on the dispersion. With preference the solids content may amount to 20% to 40% by weight. The silanized, structurally modified, fumed silica is known from WO 2004/020532.

The silanized, structurally modified fumed silica may have dimethylsilyl and/or monomethylsilyl groups, preferably dimethylsilyl groups, on the surface.

The silica useful in accordance with the invention may have the following physicochemical parameters:

BET surface area m²/g: 25 - 400

Average primary particle size nm: 5 - 50

pH: 3 - 10

Carbon content % by weight: 0.1 - 10

DBP value %: < 200

The silanized, structurally modified silica useful in accordance with the invention may be prepared by surface-modifying a fumed silica with dimethyldichlorosilane and/or monomethylsilane and structurally modifying the surface-modified silica.

The silanized, structurally modified, fumed silica used may in one preferred embodiment of the invention be a silica that has been prepared from a fumed silica having a BET surface area of 200 ± 25 m²/g that has
been silanized with dimethyldichlorosilane and then structurally modified in accordance with WO 2004/020532. This fumed silica is known in the form of Aerosil® R9200.

In one preferred embodiment of the invention the dispersion may have the following size distribution of the particles of fumed, silanized, structurally modified silica:

20% to 98% by weight in the range from 0.01 µm to 1.5 µm

2% to 80% by weight in the range from 1.5 µm to 4.0 µm.

In particular the particle size distribution may be as follows:

60% to 95% by weight in the range from 0.2 µm to 1.5 µm

5% to 40% by weight in the range from 1.5 µm to 3.5 µm.

The dispersion of the invention may contain the silica in an amount of 5% to 70% by weight, preferably in an amount of 20% to 40% by weight.

The dispersion of the invention may be prepared by mixing and dispersing the silanized, structurally modified, fumed silica with the solvent.

In one embodiment of the invention the dispersing can be carried out by means of a bead mill.

Solvents which can be employed include organic solvents.

It is possible in particular to use solvents from the group n-hexane, n-heptane, cyclohexane, toluene,
xylene, ethylbenzene, cumene, styrene, dichloromethane, 
1,2-dichloroethane, methanol, ethanol, 1-propanol, 
2-propanol, 1-butanol, isobutanol, 2-ethylhexanol, 
cyclohexanol, diacetone alcohol, acetone, methyl ethyl
ketone, methyl isobutyl ketone, diisobutyl ketone, 
cyclohexanone, mesityl oxide, isophorone, methyl
acetate, ethyl acetate, butyl acetate, isobutyl
acetate, methylglycol acetate, butylglycol acetate, 
ethylidiglycol acetate, butyldiglycol acetate, methoxy-
propyl acetate, ethoxypropyl acetate, ethylene
carbonate, propylene carbonate, diethyl ether, methyl
tert-butyl ether, tetrahydrofuran, dioxane, 
ethylglycol, propylglycol, butylglycol, ethyldiglycol,
butyldiglycol, 1-methoxy-2-propanol, 1-ethoxy-2-
propanol, 1-isopropanoxy-2-propanol, 1-isobutoxy-2-
propanol, methyldipropylene glycol, dimethylformamide, 
dimethylacetamide, dimethyl sulfoxide, carbon
disulphide, 1-nitropentane, 2-nitropentane, nitro-
benzene or N-methyl-2-pyrrolidone, individually or in a
mixture.

The invention further provides a process for preparing
solventborne coating materials, which is characterized
in that the inventive dispersion of a fumed silica is
mixed and dispersed with at least one curing agent
and/or at least one binder.

In one embodiment of the invention the dispersing can
be carried out by means of a bead mill.

Water-soluble coating materials are excluded in
accordance with the invention.

The invention has the advantage that a relatively low
level of frosting is found in the clearcoat material.

Furthermore, owing to the relatively high concentration
of silica in the dispersion, the volume of clearcoat
material produced is substantially higher.

Examples

In Examples 1 to 3 the silanized, structurally modified fumed silica Aerosil® R9200 is incorporated by means of the known methods into a clearcoat system. According to Example 4 the silanized, structurally modified fumed silica is incorporated by means of the dispersion of the invention.

It is found that the inventively prepared clearcoat material has less frosting and also a very good coating-material homogeneity.

Figures 1, 2, 3, 4 and 5 show the particle diameters of the silica particles present in the coating material.

For instance, in accordance with Examples 1, 2 and 3, 77% to 85% by weight of the particles are between 0.4 µm and 1.5 µm, while 15% to 23% by weight are between 1.5 µm and 4 µm.

In accordance with inventive Example 4, the coating material has a substantially lower coarse fraction. Thus 90% by weight of the particles are in the range from 0.4 to 1.5 µm and only 15% by weight of the particles are between 1.5 and 2.9 µm.

This means that the fraction of particles smaller than 2.9 µm, which are responsible for the haze and/or for the frosting, is significantly lower.

<table>
<thead>
<tr>
<th>Example</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grinding medium</td>
<td>x4</td>
<td>x4</td>
<td>x4</td>
<td></td>
</tr>
<tr>
<td>Macrynal SM 565 [g]</td>
<td>244</td>
<td>244</td>
<td>244</td>
<td>0</td>
</tr>
<tr>
<td>Methoxypropyl acetate [g]</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>240</td>
</tr>
<tr>
<td>Butyl acetate [g]</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Solvesso 100 [g]</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>Xylene [g]</td>
<td>10.8</td>
<td>10.8</td>
<td>10.8</td>
<td>0</td>
</tr>
<tr>
<td>LA-D 1045 [g]</td>
<td>0</td>
<td>0</td>
<td>1.5</td>
<td>9</td>
</tr>
<tr>
<td>Dispers 652 [g]</td>
<td>0</td>
<td>3</td>
<td>1.5</td>
<td>9</td>
</tr>
<tr>
<td>AEROSIL R 9200 [g]</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>117</td>
</tr>
<tr>
<td>Total [g]</td>
<td>330.8</td>
<td>333.8</td>
<td>333.8</td>
<td>375</td>
</tr>
</tbody>
</table>

| Dispersing | BM | BM | BM | BM |
| Revolutions per minute | 3000 | 3000 | 3000 | 3000 |
| Dispersing time [minutes] | 60 | 60 | 60 | 60 |
| Power [W] | 220 | 230 | 250 | 160 |
| Temperature [°C] | 42 | 42 | 42 | 25 |

| Viscosity 0.1 l/s [mPa s] | - | - | - | 315 |
| Grindometer [µm] | < 10 |
| Coulter d 50 [µm] | 0.757 |
| Coulter d 95 [µm] | 1.948 |

| Millbase | x2 |
| Macrynal SM 565 [g] | - | - | - | 122 |
| Grinding medium [g] | - | - | - | 32 |
| MPA [g] | 0.5 |
| Butyl acetate [g] | 3 |
| Solvesso 100 [g] | 4 |
| Xylene [g] | 5.4 |
| Total [g] | 166.9 |

| Viscosity 0.1 l/s [mPa s] | 670 | 440 | 300 | 315 |
| Grindometer [µm] | < 10 | < 10 | < 10 | < 10 |
| Coulter d 50 [µm] | 0.821 | 0.911 | 0.938 | 0.736 |
| Coulter d 95 [µm] | 0.911 | 2.749 | 2.631 | 1.844 |

| Letdown |
| Grinding medium/millbase | 82.7 | 83.45 | 83.45 | 83.45 |
| Curing agent | 22.3 | 22.3 | 22.3 | 22.3 |
La-D 1045: Dispersing additive from Tego
Dispers 652: Dispersing additive from Tego
Macrynal SM 565: Acrylic copolymer from Surface Specialties, USB

20° gloss 82.3 83.5 81.6 82.1

Haze 8 8 6 6
Black number M 268 270 270
Hue contribution dM 15 12.5 14 13.6
Flow  good  poor  good  good
Scratch resistance compared to AEROSIL®-free formulation, Elcometer 1720**  good  somewhat  better  good  good
Visual assessment of coating-material homogeneity  good  severe  agglomeration  good  very  good

LA-D 1045: Dispersing additive from Tego
Dispers 652: Dispersing additive from Tego
Macrynal SM 565: Acrylic copolymer from Surface Specialties, USB

Solvenso 100: Aromatics mixture from Imperial Oil
BM: Dispermat SL 5 from Getzmann

*) Grindometer 30 µm means coating material unusable
**) Technical Information No. 1284, Degussa AG
****) The samples were measured by means of laser diffraction in a Coulter LS230 Micro Volume module. This was done by introducing the pure varnish system or the solvent as the measurement medium and adding a few drops of the sample.

The dispersing time and the volume of grinding medium are identical in each of Examples 1, 2, 3 and 4.

In inventive Example 4 the amount of fumed silica is present in more concentrated form, so that for the same dispersing effort a volume of clearcoat material greater by 5.8 times can be produced.
Claims

1. Dispersion of fumed silica, characterized in that it comprises a silanized, structurally modified silica and a solvent.

2. Dispersion of fumed silica according to Claim 1, characterized in that it further comprises additives.

3. Process for producing solventborne coating materials, characterized in that the dispersion according to Claim 1 is mixed with at least one binder.

4. Process according to Claim 3, characterized in that at least one curing agent is added.
Fig. 1: Example 1, Coating material
**Fig. 2:** Example 2, Coating material
**Fig. 3:** Example 3, Coating material
**Fig. 4:** Example 4, Grinding medium
Fig. 5: Example 4, Coating material