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(54) **SILICON DIOXIDE DISPERSION
COMPRISING POLYOL**

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(57) **ABSTRACT**

Stable, pourable silicon dioxide dispersion, in which the average, number-related aggregate diameter of the silicon dioxide particles in dispersion is less than 200 nm, and which comprises at least 35 wt. % of a silicon dioxide powder, 3 to 35 wt. % of at least one polyol, 20 to 60 wt. % of water, 0 to 10 wt. % of an additive and a substance having an alkaline action in an amount such that a pH of $10 < \text{pH} \leq 12$ is established.

It can be prepared by a procedure in which silicon dioxide powder is introduced into water and a polyol in a rotor/stator machine, the pH being less than 5, and the mixture is dispersed until the current uptake of the rotor/stator machine is largely constant, and a substance having an alkaline action is subsequently added in an amount such that a pH of the dispersion of $10 < \text{pH} \leq 12$ results, the substance having an alkaline reaction being added so rapidly that no gel formation takes place.

It can be used as a component of a flame-retardant filling of hollow spaces between building components, in particular for insulating glass arrangements.

SILICON DIOXIDE DISPERSION COMPRISING POLYOL

[0001] The invention relates to a stable silicon dioxide dispersion of high filler content which comprises a polyol, and to the preparation and use thereof.

[0002] It is known to employ silicon dioxide dispersions of high filler content for thermal insulations, in particular for insulating glasses.

[0003] DE-A-19943103 describes a dispersion having a content of amorphous silicon dioxide of more than 80 wt. %. In this context, amorphous is to be understood as meaning a silicon dioxide of very low surface area, preferably having a BET surface area of 0.001 to 0.5 m²/g. Although it is described as being very readily pourable, the dispersion claimed nevertheless retains this property for only a short time, of not more than 2 hours. This means that such a dispersion must be processed immediately after its preparation, that is to say can be neither stored nor transported.

[0004] DE-A-19720269 describes a dispersion having a content of nanoscale particles, for example silicon dioxide, of at least 35 wt. %. This dispersion furthermore comprises 1 to 40% of water or an organic solvent, and furthermore 10 to 60 wt. % of a compound having at least two functional groups, preferably a polyol. This dispersion also has only a very low stability and must be processed rapidly. It has been found that even with higher-energy dispersing conditions, nothing changes in this behaviour.

[0005] The object of the invention is to provide a dispersion of high filler content which comprises silicon dioxide, is stable over a relatively long period of time and has a low viscosity. In particular, it should show advantages over dispersions according to the prior art in the production of insulating glasses.

[0006] The invention provides a stable, pourable silicon dioxide dispersion in which

[0007] the average, number-related aggregate diameter of the silicon dioxide particles in dispersion is less than 200 nm, and which comprises

[0008] at least 35 wt. % of silicon dioxide powder,

[0009] 3 to 35 wt. % of at least one polyol,

[0010] 20 to 60 wt. % of water,

[0011] 0 to 10 wt. % of an additive, in each case based on the total amount of the dispersion,

[0012] and which comprises a substance having an alkaline action in an amount such that a pH of 10 < pH ≤ 12 is established.

[0013] In the context of the invention, stable is to be understood here as meaning that the silicon dioxide dispersion shows no noticeable sedimentation within a period of time of at least one month, as a rule at least 3 months. That is to say, the dispersion can be employed during the period of time without further filtration steps. Furthermore, no or only a minimal increase in the viscosity is to be observed within this period of time. This means that within this period of time the silicon dioxide dispersion retains its property of being pourable at room temperature.

[0014] The silicon dioxide dispersion according to the invention can comprise additives in the form of biocides or dispersing auxiliaries. For many uses, however, these additives may prove to be a disadvantage, so that it may be advantageous if the dispersion according to the invention comprises no such additives.

[0015] The origin of the silicon dioxide powder employed is not decisive. Thus, for example, silicon dioxide powder prepared by precipitation or by pyrogenic processes can be present in the dispersion. However, it has been found that pyrogenically prepared metal oxide powders can advantageously be employed.

[0016] Pyrogenically prepared metal oxide powders are generally understood as meaning those which are obtained from a metal oxide precursor by a flame hydrolysis or flame oxidation in an oxyhydrogen flame. In this process, approximately spherical primary particles are initially formed, these sintering together to aggregates during the reaction. The aggregates can then accumulate into agglomerates. In contrast to the agglomerates, which as a rule can be separated into the aggregates relatively easily by introduction of energy, the aggregates are broken down further, if at all, only by intensive introduction of energy.

[0017] Silicon dioxide is as a rule prepared by flame hydrolysis of silicon tetrachloride. In the case of pyrogenic processes, silicon-metal mixed oxides or silicon dioxides doped with metal oxide can also be obtained by joint flame hydrolysis or flame oxidation. In addition to pyrogenically prepared silicon dioxide powder, the silicon dioxide dispersion according to the invention can advantageously also comprise potassium-doped silicon dioxide powder, the preparation of which is described, for example, in DE-A-10065028.

[0018] The pyrogenically prepared silicon dioxide powder has a specific surface area of preferably 5 to 500 m²/g, and particularly preferably 30 to 60 m²/g.

[0019] The choice of polyol is not limited, as long as it remains miscible with water. Suitable polyols can be glycerol, ethylene glycol, trimethylolpropane, pentaerythritol, sorbitol, polyvinyl alcohol, polyethylene glycol or a mixture thereof. Glycerol is particularly preferred in this context.

[0020] The choice of the substance having an alkaline action likewise is not limited, as long as it is soluble in the liquid phase of water and polyol. It has been found that alkali metal hydroxides, amines, (alkyl)ammonium hydroxides and/or amino alcohols are preferred. Potassium hydroxide is particularly preferred.

[0021] A silicon dioxide dispersion according to the invention which is particularly preferred can be one which comprises

[0022] 38 to 60 wt. % of pyrogenically prepared silicon dioxide powder having a BET surface area of 30 to 60 m²/g,

[0023] 5 to 25 wt. % of glycerol

[0024] 25 to 50 wt. % of water and

[0025] 0.3 to 0.7 wt. % of KOH.

[0026] Any impurities of the starting substances and substances formed during the preparation of the dispersion are included in this. In particular, dispersions of pyrogenically prepared silicon dioxide powder have an acidic pH as a result of the preparation, due to adhering residues of hydrochloric acid. These hydrochloric acid residues are neutralized to potassium chloride by the KOH present in the dispersion.

[0027] The invention also provides a process for the preparation of the silicon dioxide dispersion according to the invention, in which

[0028] from a reservoir, water, at least one polyol and optionally an additive are circulated via a rotor/stator machine in an amount corresponding to the composition desired later, and

- [0029] the amount of silicon dioxide powder desired for the dispersion is introduced via a filling device, continuously or discontinuously and with the rotor/stator machine running, into the shearing zone between the slits of the rotor teeth and the stator slits, the pH being less than 5 and optionally being adjusted by metering in of an acid,
- [0030] the filling device is closed and dispersing is carried out further until the current uptake of the rotor/stator machine is largely constant, and
- [0031] an amount of a substance having an alkaline action such that a pH of the dispersion of $10 < \text{pH} \leq 12$ results is then added, the substance having an alkaline action being added so rapidly that no gel formation takes place.
- [0032] The silicon dioxide dispersion according to the invention can furthermore be obtained by a process in which
- [0033] a mixture of water, at least one polyol, optionally an additive and silicon dioxide powder is initially introduced into the dispersing vessel in an amount corresponding to the composition desired later,
- [0034] dispersing is carried out by means of a planetary kneader at a pH of less than 7, and
- [0035] a substance having an alkaline action is then added in an amount such that a pH of the dispersion of $10 < \text{pH} \leq 12$ results.
- [0036] In both processes it is advantageous to employ an aqueous solution having the highest possible concentration as the substance having an alkaline action, in order not to dilute the dispersion too much. Substances having an alkaline action with a concentration of 20 to 50 wt. % can preferably be employed, potassium hydroxide solution being particularly preferred.
- [0037] The processes can also be carried out by a procedure in which the addition of the polyol takes place only after the dispersing of the silicon dioxide powder and before the addition of the substance having an alkaline action.
- [0038] The dispersion according to the invention can furthermore be obtained by a procedure in which at least two part streams of the dispersion prepared as described above with a rotor/stator or planetary kneader are placed under a pressure of up to 3,500 kg/cm² and let down via a nozzle and the part streams are allowed to collide with one another.
- [0039] The invention also provides the use of the silicon dioxide dispersion according to the invention as a component of a flame-retardant filling of hollow spaces between structural components, in particular between insulating glass arrangements.
- [0040] In addition, the silicon dioxide dispersion according to the invention can also be used as a component of a filling of hollow spaces between structural components of plastic, metal, wood, plaster board, fermacel, pressboard, ceramic and natural or artificial stone, as well as in electric cables, for fireproofing purposes.
- [0041] It can also be employed as a coating composition for structural components, and is suitable for the production of thermally and mechanically stable foams in the form of, for example, bulk goods or mouldings.
- [0042] The dispersion according to the invention can also be used in a mixture with pigments or (organic or inorganic, for example fibrous, pulverulent or lamellar) coarser, non-

nanoscale additives, such as, for example, mica pigments, iron oxides, wood flour, glass fibres, metal fibres, carbon fibres, sands, clays and bentonite, if the transparency of the material which can thereby be produced is not important.

EXAMPLES

Example 1

[0043] 42.5 kg of completely demineralized water and 2.25 kg glycerol are initially introduced into a high-grade steel mixing container. 60 kg AEROSIL® OX50 are then sucked in under shearing conditions with the aid of the suction pipe of a rotor/stator machine (Ystral Conti-TDS 3, stator slits: 4 mm ring and 1 mm ring, rotor/stator distance approx. 1 mm, speed of rotation 3,000 rpm). The pH is lowered to 3.7 during this procedure. Thereafter, 9 kg water, 3.75 kg glycerol and, under the same dispersing conditions, swiftly 2.02 kg 30 per cent strength by weight potassium hydroxide solution are added in succession.

[0044] Examples 2 to 9 are carried out analogously, and in Example 10 no potassium hydroxide solution is added. The amounts employed for the preparation of the dispersions can be seen from Table 1.

[0045] The composition of the dispersions and the physico-chemical values thereof are reproduced in Table 2. Example 3a shows the values of a dispersion from Example 3 subsequently ground under 2,500 bar with a high-energy mill.

[0046] Examples 1 to 8 are dispersions according to the invention, Examples 9 and 10 are comparison examples.

[0047] In Example 11, the silicon dioxide dispersion is first dispersed at a higher silicon dioxide concentration and diluted to the desired concentration before the addition of potassium hydroxide solution.

Example 11

[0048] 36.1 kg of completely demineralized water and 9.0 kg glycerol are initially introduced into a high-grade steel mixing container. 60 kg AEROSIL® OX50 are then sucked in under shearing conditions with the aid of the suction pipe of a rotor/stator machine (Ystral Conti-TDS 3, stator slits: 4 mm ring and 1 mm ring, rotor/stator distance approx. 1 mm, speed of rotation 3,000 rpm) and sheared for 15 minutes. The SiO₂ concentration is 57 wt. %. The pH is lowered to 3.5 during this procedure by the "acidic" AEROSIL®. Thereafter, 15.2 kg glycerol are added and, after some minutes of homogenization, a pH of 10.9 is swiftly established with 2.2 kg 30 per cent strength by weight potassium hydroxide solution under the same dispersing conditions. Finally, a further 1.0 kg water is added in order to establish an SiO₂ concentration of 48.6 and a glycerol concentration of 19.6. The pH is changed only insignificantly by this small amount of water.

[0049] The dispersions according to the invention of Examples 1 to 8 and 11 all have a very low viscosity. The average aggregate diameter (number-related) of the silicon dioxide particles in the dispersion is less than 150 nm.

[0050] The dispersion from Example 11, which is obtained by dispersing at a high silicon dioxide content and subsequent dilution to the desired concentration, shows advantages over the process in which the dispersing is carried out directly with

the desired concentration. The grinding is more intense and the viscosity of the dispersion is lower.

[0051] The dispersion according to the invention from Example 3a, prepared by high-energy grinding, shows a further reduction in the viscosity and particle size.

[0052] Example 7a gives the values of dispersion 7 after storage in a climatically controlled chamber for three months. In this, the temperatures are varied daily between 10° C. and 50° C. Even after three months, the silicon dioxide dispersion according to the invention still shows excellent viscosity values.

[0053] Dispersion 8, with a pH of 11.8, shows a very low viscosity. A further increase in the pH indeed lowers the viscosity further, but initial dissolving of the silicon dioxide particles is already to be observed. Potash silicates are increasingly formed, depending on the temperature and time, due to the initial dissolving of the silicon dioxide. As the reaction progresses, a potash water-glass with an increasing SiO₂/K₂O ratio is increasingly formed from the dilute low-viscosity potassium hydroxide solution as a homogeneous phase. Since potassium hydroxide solution is consumed in this reaction, KOH would have to be added again to maintain

a high pH, but as a result of this the potash water-glass reaction is also accelerated again. However, potash water-glasses show a marked increase in viscosity as the SiO₂/K₂O ratio and concentration increase. In order to suppress such time- and temperature-dependent reactions, a pH of below 12 is essential.

[0054] At alkaline pH values of less than 10, a significant increase in the viscosity is likewise to be observed (Example 9). A dispersion without the addition of KOH shows a significantly higher viscosity and gels within days (Example 10).

[0055] It is surprising that the polyol-containing silicon dioxide dispersion according to the invention has low viscosities only at a pH of more than 10. It is known that in purely aqueous dispersions which comprise no polyol, the lowering in viscosity already starts from a pH of approx. 9.

[0056] In the preparation of the silicon dioxide dispersion according to the invention, it is essential that the silicon dioxide powder is first dispersed in the acidic range at a pH of 5 or less and the substance having an alkaline action is added rapidly under the same dispersing conditions. If the substance having an alkaline action is added slowly, rapid gel formation takes place.

TABLE 1

Starting substances and starting substance amounts (in kg) for the preparation of the dispersions											
Example	1	2	3	4	5	6	7	8	9 ^(e)	10 ^(e)	11
SiO ₂ ^(a)	60.00	95.00	57.84	57.84	57.84	45.79	45.79	45.79	45.79	45.79	60.00
Glycerol	6.00	19.00	6.00	12.00	18.00	18.62	18.62	18.62	18.62	18.62	24.20
Water	51.50	72.00	54.33	48.34	42.01	29.00	28.46	27.71	29.54	30.59	37.10
KOH ^(b)	2.02	3.70	1.63	1.59	1.54	1.60	2.10	2.90	1.10	0	2.20

^(a) Aerosil® OX50;

^(b) 30 wt. % strength KOH in water;

^(e) comparison example;

TABLE 2

Composition and physico-chemical values of the dispersions														
Example		1	2	3	3a ^(e)	4	5	6	7	7a ^(d)	8	9 ^(e)	10 ^(e)	11
SiO ₂	wt. %	50.2	50.1	48.3	48.3	48.3	48.4	48.2	48.2	48.2	48.2	48.2	48.2	48.6
Glycerol	wt. %	5.0	10.0	5.0	5.0	10.0	15.1	19.6	19.6	19.6	19.6	19.6	19.6	19.6
Water	wt. %	44.3	39.4	46.4	46.4	41.3	36.1	31.7	31.5	31.5	31.3	31.9	32.2	30.0
KOH	wt. %	0.5	0.6	0.4	0.4	0.4	0.4	0.5	0.7	0.7	0.9	0.3	0	0.5
pH		10.9	10.9	10.9	10.9	10.9	10.9	10.5	10.9	10.9	11.8	10.0	4.0	10.9
Visc. ^(f)														
10 s ⁻¹ ^(g)	mPas	240	262	119	106	166	236	374	213	320	101	1290	1530	189
1,000 s ⁻¹	mPas	45	58	33	29	37	51	76	64	77	55	115	470	69
Diameter ^(h)	nm	121	121	114	98	113	114	130	132	128	126	133	132	110

^(e) grinding with a high-energy mill;

^(d) after storage for three months;

^(e) comparison example

^(f) viscosity at 23° C.;

^(g) shear rate;

^(h) aggregate diameter (median)

1-13. (canceled)

14. A stable, pourable silicon dioxide dispersion, wherein the average, number-related aggregate diameter of the silicon dioxide particles in dispersion is less than 200 nm, said dispersion comprising:

at least 35 wt. % of silicon dioxide powder,
3 to 35 wt. % of at least one polyol,
20 to 60 wt. % of water,

0 to 10 wt. % of an additive, in each case based on the total amount of the dispersion, and
a substance having an alkaline action in an amount so that a pH of $10 \leq \text{pH} \leq 12$ is established.

15. The stable, pourable silicon dioxide dispersion according to claim **14**, wherein it comprises no additives.

16. The stable, pourable silicon dioxide dispersion according to claim **14**, wherein said silicon dioxide powder is prepared pyrogenically.

17. The stable, pourable silicon dioxide dispersion according to claim **16**, wherein the pyrogenically prepared silicon dioxide powder has a specific surface area of 5 to 500 m²/g.

18. The stable, pourable silicon dioxide dispersion according to claim **14**, wherein said polyol is selected from the group

consisting of glycerol, ethylene glycol, trimethylolpropane, pentaerythritol, sorbitol, polyvinyl alcohol, polyethylene glycol and mixtures thereof.

19. The stable, pourable silicon dioxide dispersion according to claim **14**, wherein said substance having an alkaline action is selected from the group consisting of alkali metal hydroxides, amines, (alkyl)ammonium hydroxides and/or amino alcohols.

20. The stable, pourable silicon dioxide dispersion according to claim **14**, wherein it comprises

38 to 60 wt. % of pyrogenically prepared silicon dioxide powder having a BET surface area of 30 to 60 m²/g,
5 to 25 wt. % of glycerol
25 to 50 wt. % of water and
0.3 to 0.7 wt. % of KOH.

21. A method of using the silicon dioxide dispersion according to claim **14** as a component of a flame-retardant filling of hollow spaces between structural components and for transparent insulating glass arrangements.

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