

METHOD FOR PRODUCING A COATED QUARTZ GLASS COMPONENT

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Description

The present invention relates to method for producing a coated component of quartz glass in that a base body of quartz glass is provided that has a coating
10 surface onto which a SiO_2 slurry layer is applied by spraying a SiO_2 slurry thereon, drying the slurry layer to obtain a green body layer, and sintering the green body layer to obtain a SiO_2 -containing functional layer.

Prior art

Components of quartz glass are used for many applications, e.g. in lamp
15 manufacture as cladding tubes, bulbs, cover plates, or reflector carriers for lamps and radiators in the ultraviolet, infrared and visible spectral range, in chemical apparatus engineering or in semiconductor production in the form of reactors and apparatus of quartz glass for the treatment of semiconductor components, trays, bell jars, crucibles, protective shields or simple quartz-glass components, such as
20 tubes, rods, plates, flanges, rings or blocks.

For setting special surface properties or for improving the given mechanical, optical or chemical surface properties, the surface of the component is often modified in that the previously produced quartz glass component is provided completely or partially with a functional layer adapted to the specific purpose.
25 Examples thereof are the improvement of the service life by a coating showing a higher softening temperature or better chemical resistance, a reduction of the contamination risk posed by the component by way of a coating consisting of a high-purity material, and a change in the heat insulation or reflectivity by transparent or opaque surfaces layers.

30 A method of the aforementioned type is known from DE 2004 051 846 A1. The publication describes the manufacture of a quartz glass component provided with

a reflector layer. The reflector layer is produced by means of a slurry method in that highly filled, castable, aqueous slurry is produced that contains amorphous SiO_2 particles. The slurry is applied in the form of a slurry layer to the surface of a base body of quartz glass, which surface is to be coated.

- 5 For the application of the slurry layer to the base body, spraying, electrostatically supported spraying, flow coating, spinning, immersion and dispersion coating are suggested. The slurry layer is dried to form a green body layer and is subsequently sintered to form the reflector layer of opaque quartz glass.

- The amorphous SiO_2 particles of the slurry are produced by wet grinding SiO_2 granules and have a mean particle size ranging from 1 μm to 50 μm . The solids content, the particle size and the particle size distribution of the SiO_2 particles of the slurry have impacts on the drying shrinkage of the slurry layer. The use of rather coarse SiO_2 particles can diminish the drying shrinkage and thus the risk of the formation of cracks during drying. With a simultaneously high solid content
- 10 SiO_2 particles in the order of 1 μm to 50 μm show a good sintering behavior and a comparatively small drying shrinkage, so that the slurry layer can be dried and sintered without the formation of cracks.

- However, it has been found that the flow behavior of the known, highly filled slurry for producing thick layers and layers on arched component surfaces or component
- 20 surfaces inclined to the vertical is not suited for all application methods of the slurry layer. To improve the spreadability of the SiO_2 slurry, DE 10 2006 046 619 A1 suggests the addition of SiO_2 nanoparticles, namely with a weight fraction in the range of 0.2% by wt. to 15% by wt., based on the total solids content. Due to the addition of SiO_2 nanoparticles the flow behavior of the SiO_2 rather tends to
- 25 show structural viscous thixotropic characteristics, which improves the spreadability of the slurry and counteracts the flowing off from arched surfaces.

- An even further fixation of the slurry layer is achieved with the help of the process described in DE 10 2005 058 819 A1 in that the slurry is applied together with a textile auxiliary means in the form of a quartz glass nonwoven or a cellulose strip
- 30 to the surface to be coated. For instance, a quartz glass nonwoven impregnated

with the SiO₂ slurry is applied to the surface to be coated and is then dried and sintered.

This procedure permits the manufacture of relatively thick layers on arched surfaces or surfaces inclined to the vertical, but has the drawback that the textile auxiliary means either remains in the coating or must be burnt out in a complicated way, both procedures entailing drawbacks and being not suited for applications where high demands are made on layer homogeneity.

Technical object

It is the object of the present invention to provide a method which allows the
 10 reproducible manufacture of a surface layer of quartz glass on a base body by simply spraying thereon a slurry layer also in the case of arched surfaces or surfaces inclined to the vertical with large layer thicknesses, and which satisfies the high demands made on layer homogeneity.

Starting from the aforementioned method, this object is achieved according to the
 15 invention in that the slurry contains the following components in a dispersion liquid:

- (a) splintery amorphous SiO₂ granules with a grain size distribution having a D₅₀ value in the range between 3 µm and 30 µm, with a weight fraction of at least 10% by wt., based on the total solids content,
- 20 (b) spherical amorphous SiO₂ particles with a particle size distribution with a D₅₀ value in the range between 1 µm and 50 µm, with a weight fraction of at least 30% by wt., based on the total solids content,
- (c) SiO₂ nanoparticles with particle sizes of less than 100 nm with a weight fraction between 0.2% by wt. and 10% by wt., based on the total solids content,
- 25 (d) a nonionic surfactant with a fraction in the range of from 0.005% to 0.5%, based on the volume of the dispersion liquid.

A spray slurry must fulfill requirements that are opposite to and exclude one another. On the one hand, the viscosity during spraying should be low to enable the spraying operation itself as well as a uniform distribution of the slurry layer, which is promoted by a low solids content. On the other hand, such a flow-off of the slurry layer from the surface as well as the formation of cracks during drying of the slurry layer should be avoided, which is promoted by a high solids content that is normally also accompanied by high viscosity. It has been found that the above-mentioned four components supplement one another as regards sprayability and adhesion of the SiO_2 slurry, which permits the manufacture also of thick homogeneous slurry layers by spraying a SiO_2 slurry without any auxiliary means onto surfaces of the base body that are arched, curved or inclined to the vertical.

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- The splintery SiO_2 granules contribute to the integrity of the sprayed-on slurry layer and to denticulation with the surface, thereby facilitating the production of relatively thick layers and improving the adhesion thereof to arched surfaces. Moreover, an addition of splintery granules changes the rheology of the slurry towards a more dilatant flow behavior. Dilatancy manifests itself in an increase in viscosity at increased shear forces independently of time. It has been found that the desired effect on denticulation and adhesion improvement presupposes a specific grain size distribution with a D_{50} value between $3\text{ }\mu\text{m}$ and $30\text{ }\mu\text{m}$ and a content of at least 10% by wt. Splintery granules with a D_{50} value of less than $5\text{ }\mu\text{m}$ increase the drying shrinkage of the slurry layer, and granules with a D_{50} value of more than $30\text{ }\mu\text{m}$ counteract a high solids density in the slurry, which also contributes to an increased drying shrinkage. At a weight fraction of less than 10% by wt. the contribution to denticulation and adhesion improvement of the slurry layer is small. The splintery granules are produced in the easiest way by grinding, preferably by wet grinding.
 - The spray slurry is a composite slurry which, apart from the splintery SiO_2 granules, also contains a proportion of amorphous spherical SiO_2 particles. The higher the proportion of spherical particles is, the higher can the solids density be set in the slurry layer after the spraying operation; this counteracts the formation of stresses during drying and sintering. The spherical SiO_2 particles have a particle size distribution with D_{50} values between $1\text{ }\mu\text{m}$ and 50

μm . Spherical particles with a D_{50} value of less than $1\ \mu\text{m}$ increase the drying shrinkage of the slurry layer, and particles with a D_{50} value of more than $50\ \mu\text{m}$ rather counteract a high solids density in the slurry. At a low weight fraction of less than 30% by wt., the contribution to the desired high solid density in the
5 spayed-on slurry layer is negligible. The spherical SiO_2 particles are produced in the easiest way by synthesis according to the CVD method and are commercially available.

- The surfactant reduces the surface tension of the SiO_2 slurry, thereby increasing the viscosity thereof at low shear stresses. The addition of the
10 surfactant thereby also changes the rheology of the slurry. It has been found that the SiO_2 slurry in the quiescent state and upon impact of small shear forces gets relatively solid, which counteracts a slipping off of the slurry layer on arched surfaces and also facilitates the manufacture of relatively thick layers. Surfactants, however, often contain impurities, particularly alkali-
15 containing compounds. When quartz glass is heated, already small concentrations of such alkali compounds effect a crystallization while forming cristobalite. A cristobalite formation during sintering of the slurry layer may, however, lead to cracks and spalling of the layer because the thermal expansion coefficients of cristobalite and quartz glass are different. Therefore,
20 according to the invention a nonionic, alkali-free surfactant is used, and the amount of surfactant in the slurry is kept as small as possible, namely in the range of 0.005-0.5 vol. % (based on the volume of the dispersion liquid). Suitable nonionic surfactants are e.g. fatty alcohol ethoxylates, fatty alcohol propoxylates, alkyl glucosides, alkyl polyglucosides, octylphenol ethoxylates or
25 nonylphenol ethoxylates.

- An addition of surfactant that is as small as possible is enabled according to the invention by the additional use of SiO_2 nanoparticles. Due to the addition of the SiO_2 nanoparticles the surface of the solid contained in the slurry is increased to a relatively great extent, which improves the action of the
30 surfactant. In this respect the SiO_2 nanoparticles act for the surfactant as "activator", so that relatively small amounts of surfactant are needed. Nanoparticles consist typically of a bond of a few thousands of SiO_2 molecules

and usually have a BET specific surface area in the range of from 50-400 m²/g. At a content of less than 0.2% by wt. of said particles in the slurry the nanoparticles have no significant impact on the increase in the solid surface in the slurry, whereas contents of more than 10% by wt. lead to an enhanced shrinkage of the slurry layer during drying, which shrinkage may aggravate a defect-free drying and sintering. The nanoparticles seal the outer surface of the green body and bring about an increase in the green strength of the dried slurry and in the sintering activity.

Splintery SiO₂ granules, spherical SiO₂ particles and SiO₂ nanoparticles add up, apart from possible dopants and impurities, to 100% by wt. of the SiO₂ solids content.

The base body consists of synthetically produced quartz glass or of quartz glass produced from naturally occurring raw materials. The quartz glass may be transparent or opaque (translucent).

After the slurry layer has been dried, the vitreous SiO₂ functional layer is obtained without any tools by sintering (melting) the green body layer. Sintering or sintering of the dried green body layer is carried out by heating in a furnace, or by means of a combustion flame, by means of plasma or arc or by means of a laser having a predetermined working wavelength. The green body layer may here contain a component that absorbs the working wavelength of the laser or plasma radiation, so that the heat impact during densification is short in time and is locally restricted, and plastic deformations or the introduction of thermal stresses can be predominantly avoided. The component which preferably absorbs the plasma or laser radiation is an additive in the form of particles of a chemical composition differing from SiO₂, or doped amorphous SiO₂ particles, or boundaries on which the plasma or laser radiation shows diffuse reflection and is thereby absorbed.

Depending on the application, the sintered functional layer is transparent or is completely or partly opaque and is distinguished at any rate by the absence of cracks and by high adhesion on the quartz glass of the base body. In its properties it can be modified by simple method modifications, e.g. the sintering temperature

or the addition of dopants for a multitude of concrete applications, e.g. for the use in semiconductor manufacture or in lamp and reactor manufacture.

The SiO₂ functional layer is normally configured in the form of a flat layer, but it may also have a geometry which forms a functional part of the component, e.g. as
5 a thickening or a bead.

It has turned out to be advantageous when the splintery amorphous SiO₂ granules are present at a weight fraction in the range of 20-60% by wt., based on the total solids content, and when the splintery amorphous SiO₂ granules have a grain size distribution with a D₅₀ value in the range between 5 µm and 20 µm.

10 The amount and the grain size distribution of the splintery granules constitute an appropriate compromise between improvement of the adhesion and integrity of the slurry layer on the one hand and a solid density as high as possible as well as a small tendency to cracking of the slurry layer or the green body layer on the other hand.

15 In this respect a procedure has also turned out to be advantageous where the spherical amorphous SiO₂ granules are present at a weight fraction in the range of 40-80% by wt., based on the total solids content, and the spherical amorphous SiO₂ granules have a grain size distribution with a D₅₀ value in the range between 5 µm and 40 µm.

20 As for a drying shrinkage that is as small as possible, and a contribution to the „activation“ of the surfactant that is as great as possible, it has turned out to be advantageous when the SiO₂ nanoparticles are present at a weight fraction in the range of 3-8% by wt., based on the total solids content.

A method variant is preferred in which the surfactant is present with a fraction in
25 the range of 0.005-0.04%, based on the volume of the dispersion liquid.

Owing to the relatively small amount of surfactant in the dispersion liquid, a contamination of the SiO₂ slurry layer with impurities is prevented. In connection with the additional addition of SiO₂ nanoparticles the relatively small surfactant concentration effects a fast solidification of the slurry layer after spray application

also in the case of a sprayable slurry of low viscosity, thereby permitting the application of a uniform and firmly adhering slurry layer, which is to be dried without any cracks, to the base body surface by means of spraying methods.

A mixture of water and an organic solvent with a lower boiling temperature,
5 preferably an alcohol, is preferably used as the dispersion liquid.

Part of the dispersing agent/water is here replaced by an organic solvent having a lower boiling temperature than water. Due to the lower boiling temperature the slurry is dried at the same liquid amount more quickly than in the case of a purely aqueous dispersing agent; especially also already when the slurry layer is sprayed
10 on. This leads to a faster fixation of the slurry layer to the surface, which counteracts a flowing off of the slurry layer. Hence, a sufficiently high liquid amount guarantees the sprayability of the slurry and, on the other hand, a comparatively high solids content is achieved in the slurry layer. The complete replacement of the water by an organic solvent may lead to a rapid drying off of
15 the slurry layer and to cracks. The organic solvent with a lower boiling temperature than water is preferably a low-boiling alcohol, such as ethanol or propanol. Suitable mixing ratios have to be determined empirically. In the case of ethanol suitable proportions are in the range of 10-75 vol. % of the total volume of the dispersion liquid, particularly preferably in the range between 23 vol. % and 40 vol.
20 %.

It has also turned out to be advantageous when the solids content of the SiO_2 slurry is in the range between 70-80% by wt., preferably between 74-78% by wt.

A solids content that is as high as possible contributes to a uniform and small shrinkage of the slurry layer, so that drying and sintering cracks are avoided. At
25 solids contents of less than about 10% by wt., drying cracks may easily occur. On the other hand, the sprayability of the slurry requires a low viscosity and thus a low solids content. At solids contents of more than 78% by wt. the sprayability of the slurry is restricted. It has been found that at a solids content within the said ranges the sprayed-on slurry layer can be dried without the formation of cracks.

The SiO₂ content of the amorphous SiO₂ particles is preferably at least 99.99% by wt. This is true for both the splintery SiO₂ granules and the spherical SiO₂ particles. The solids content of the slurry produced by using such SiO₂ particles consists of at least 99.99% by wt. of SiO₂. Binders or similar additives are not intended. The content of metallic impurities is preferably less than 1 wt. ppm. This starting material does not pose any contamination or crystallization risk. The cristobalite amount in the dried SiO₂ slurry layer (= green body layer) should not be more than 0.1% by wt. because, otherwise, crystallization may occur during sintering, which may lead to component rejects.

- 10 In a particularly preferred method variant it is intended that a plurality of successive layers of the SiO₂ slurry layer are applied for producing the functional layer.
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Particularly thick functional layers and functional layers with specifically adapted properties can in particular be produced in this way.

- 15 In the light of this, preference is given to a procedure in which neighboring layers have different compositions.

Depending on the composition of the respective slurry layers and the treatment parameters, such as the temperature during sintering, one can produce functional layer portions of different porosity or with different property gradients over the thickness of the functional layer. For instance, it is possible to produce an inner layer of high porosity that has reflecting properties and an outer layer that is transparent and leads to the sealing of the coating surface. Neighboring layers can particularly differ from one another in the amounts of splintery granules, amorphous particles and nanoparticles and their size distributions.

- 25 The simple spraying of the SiO₂ slurry modified according to the invention particularly also facilitates the production of relatively thick functional layers, so that the method is preferably used for producing a functional layer having a layer thickness in the range between 0.1 mm and 4 mm.

The coating surface of the base body can be heated during spraying of the slurry layer, for instance to a temperature in the range of 100°C to 1000°C, preferably to

a temperature in the range of 300°C to 800°C. The slurry layer is here applied to a hot coating surface, e.g. to a base body which is heated in a furnace, or to a strand-shaped base body which is drawn in a drawing process from a crucible or a preform. Due to the high temperature of the base body the dispersion liquid
 5 evaporates relatively quickly, which counteracts a flowing off of the slurry mass. The application of the slurry layer and the drying operation for obtaining the green body layer are carried out substantially simultaneously. The temperature of the coating surface can even be so high that a certain thermal solidification of the slurry layer or the green body layer occurs immediately.

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Embodiment

The invention will now be explained with reference to embodiments.

1. Preparation of a SiO₂ basic slurry with splintery SiO₂ granules

For a batch of 10 kg basic slurry (dispersion liquid consisting of 70 vol. % of deionized water and 30 vol. % of ethanol + SiO₂ granules), 7.5 kg amorphous
 15 quartz glass granules of natural raw material with grain sizes in the range between 250 µm and 650 µm are mixed with 2.5 kg deionized water of a conductivity of less than 3 µS in a drum type mill which is lined with quartz glass and has a volume of about 20 liters. The quartz glass granules were cleaned in a hot chlorination process before; attention is paid that the cristobalite content is below
 20 1% by wt.

This mixture is ground by means of grinding balls of quartz glass on a roller support at 23 rpm for a period of three days to such a degree that a homogeneous basic slurry with a solids content of 75% is formed. In the course of the grinding process, the pH is lowered to about 4 due to the dissolving SiO₂.

25 The SiO₂ granule particles obtained after the grinding of the quartz glass granules are of a splintery type and have a particle size distribution that is distinguished by a D₅₀ value of about 8 µm and by a D₉₀ value of about 40 µm. The basic slurry produced in this way shows a rather dilatant flow behavior.

2. Preparation of a SiO₂ basic slurry with spherical SiO₂ granules

SiO₂ nanoparticles with diameters of about 40 nm (also called "pyrogenic silica" hereinafter) and commercial, spherical, amorphous SiO₂ particles are mixed into a dispersion liquid consisting of 70 vol. % of deionized water and 30 vol. % of ethanol, and are homogenized to obtain a further basic slurry.

The spherical amorphous SiO₂ particles are produced synthetically and are present in standardized particle size distributions with D₅₀ values of 5 µm, 15 µm, 30 µm and 40 µm. The particle size distribution is each time distinguished by a relatively narrow maximum of the size distribution in the range of the respective D₅₀ value and by a secondary maximum in the range of about 2 µm.

The particles are first of all cleaned in a hot chlorination process. The contamination content of the purified raw-material components is small and is all in all less than 1 wt. ppm. Especially the content of Li₂O is less than 10 wt. ppb.

These raw material components are used in the following formulation, each raw material component being designated with the letter R and its respective D₅₀ value as appendix:

Formulation:

R ₃₀	250 g
R ₁₅	500 g
20 R ₅	200 g

Pyrogenic silica: 50 g with BET surface area of 60 m²/g

These raw material components are dispersed in deionized water having a conductivity of less than 3 µS, resulting in a solids content of 75% by wt. The basic slurry produced in this way shows a thixotropic flow behavior.

25 3. Preparation of a spray slurry

A spray slurry is produced by mixing and homogenizing proportions of the first, rather dilatant, basic slurry with splintery granules of naturally occurring raw material and of the second, rather thixotropic, basic slurry with amorphous particles of synthetically produced SiO₂. The mixing ratio depends primarily on the

desired thickness of the functional layer to be produced and on the degree of curvature or inclination of the coating surface. The greater the desired thickness, the more inclined is the coating surface and the greater is the proportion of the first basic slurry.

- 5 In the embodiment a functional layer is produced with a desired thickness of 2 mm on the outside of a dome-shaped quartz glass reactor, as is used for etching or CVD processes in semiconductor production. The quartz glass reactor has an outer diameter of 420 mm, a height of 800 mm, and a wall thickness of 4 mm.

For this intended use, 1 proportion of the first basic slurry is mixed with 2
10 proportions of the second basic slurry. 0.015 vol. % (based on the volume of the water) of a nonionic surfactant is added to this mixture. After homogenization one obtains a spray slurry which is distinguished by the following properties:

- component K1: weight fraction (based on the total solids content) of splintery, amorphous SiO₂ granules consisting of natural quartz glass with a grain size
15 distribution with a D₅₀ value of 80 µm: 33%
- component K2: weight fraction (based on the total solids content) of spherical, synthetically produced amorphous SiO₂ particles with a grain size distribution with a D₅₀ value of about 15 µm: 63.5%
- component K3: weight fraction (based on the total solids content) of SiO₂
20 nanoparticles with particle sizes of about 40 nm: 3.5%
- component K4: surfactant: 0.015 vol.% (based on the liquid volume of the spray slurry)
- component K5: dispersing agent: 70 vol. % H₂O / 30 vol. % ethanol
- solids content: 75% by wt.

25 Coating of a dome-shaped quartz-glass reactor

The quartz-glass reactor is introduced into a spray chamber. Subsequently, the outer wall is completely provided, except for a flange arranged on the underside of the reactor, with a SiO₂ slurry layer of a thickness of about 4 mm in successive

order by spraying of the spray slurry. A spray gun which is continuously fed with the spray slurry is used for this operation.

The slurry layer applied in this way is slowly dried by allowing it to stand in air for several hours. Complete drying is carried out by using an IR radiator in air. The dried green-body layer is subsequently sintered in a known manner in a sintering furnace at a temperature of about 1200°C to obtain a crack-free, homogeneous SiO₂ reflector layer of opaque quartz glass with a density of about 1.6 g/cm³.

The homogeneity of the layer manifests itself as a substantially uniform layer thickness without the formation of "noses" that are created by the slurry flowing off from the curved surface. Opacity manifests itself in that the direct spectral transmission in the wavelength-range between 200 nm and 2500 nm is below 5%. When the green body layer is sintered, the constituents of the surfactant will disappear almost completely.

The slurry described above by way of example and the results of the coating test obtained by using this slurry and of further coating tests with other slurry compositions are listed in Table 1.

Embodiment

Table 1

No.	K1	K2	K3	K4	K5	„R“	„H“
1	33/8	63.5/15	3.5/0.04	0.015	25/(70/30)	++	++
2	20/8	63.5/15	3.5/0.04	0.015	25/(70/30)	+	0
3	15/8	63.5/15	3.5/0.04	0.015	25/(70/30)	0	-
4	33/8	40/15	3.5/0.04	0.015	25/(70/30)	0	+
5	33/8	35/15	3.5/0.04	0.015	25/(70/30)	-	0
6	33/8	63.5/15	0	0.015	25/(70/30)	+	-
7	33/8	63.5/15	10/0.04	0.015	25/(70/30)	-	+
8	33/8	63.5/15	3.5/0.04	0	25/(70/30)	0	-
9	33/8	63.5/15	3.5/0.04	0.015	33/(70/30)	-	-
10	33/8	63.5/15	3.5/0.04	0.015	20/(70/30)	+	0
11	33/20	63.5/15	3.5/0.04	0.015	25/(70/30)	0	++

12	33/8	63.5/40	3.5/0.04	0.015	25/(70/30)	0	++
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Explanations regarding Table 1:

- Components K1, K2, K3: concentration data given in wt. % (based on the solids content of the slurry) / mean particle size in μm (D_{50} value)
- Component K4: concentration of „Triton X-100“ in vol. % (based on the liquid volume of the spray slurry)
- Component K5: weight fraction of the dispersion liquid in wt. % / fractions of water and alcohol (in vol. % based on the total volume of the dispersion liquid)
- „R“ is a qualitative measure of the visually detected crack formation of the dried slurry layer.
- 10 - „H“ is a qualitative measure of the visually detected homogeneity of the dried slurry layer.
- Samples nos. 3 and 5 to 9 are comparative examples.
- Symbols of the qualitative assessment: ++ very good
 - + good
 - 0 acceptable
 - poor

The qualitative results of Table 1 demonstrate that when using a slurry layer with the composition according to sample 1, one will obtain a quartz-glass component with a particularly homogeneous and low-crack SiO_2 surface layer.

CLAIMS

1. A method for producing a coated component of quartz glass,
said method comprising:
providing a base body of quartz glass that has a coating surface;
applying onto said coating surface a SiO₂ slurry layer by spraying a SiO₂ slurry thereon;
drying the slurry layer so as to obtain a green body layer, and
sintering the green body layer so as to obtain a SiO₂ containing functional layer,
wherein the slurry contains the following components in a dispersion liquid:
(a) splintery amorphous SiO₂ granules with a grain size distribution having a D₅₀ value in a range between 3 μm and 30 μm,
wherein the splintery amorphous SiO₂ granules are present with a weight fraction in a range of 20% by wt. to 60% by wt., based on the total solids content,
(b) spherical amorphous SiO₂ particles with a particle size distribution with a D₅₀ value in a range between 1 μm and 50 μm, with a weight fraction of at least 30% by wt., based on the total solids content,
(c) SiO₂ nanoparticles with particle sizes of less than 100 nm with a weight fraction between 0.2% by wt. and 10% by wt., based on the total solids content,
(d) a non-ionic, alkali-free surfactant with a fraction in a range from 0.005% to 0.5%, based on the volume of the dispersion liquid.
2. The method according to claim 1, wherein the spherical amorphous SiO₂ granules are present with a weight fraction in a range of 40% by wt. to 80% by wt., based on the total solids content.
3. The method according to claim 1, wherein the spherical amorphous SiO₂ granules have a grain size distribution with a D₅₀ value in a range between 5 μm and 40 μm.
4. The method according to claim 1, wherein the SiO₂ nanoparticles are present with a weight fraction in a range of 3% by wt. to 8% by wt., based on the total solids content.
5. The method according to claim 1, wherein the surfactant is present with a fraction in a range of 0.005% to 0.05%, based on the volume of the dispersion liquid.
6. The method according to claim 1, wherein the dispersion liquid is a mixture of water and an organic solvent with a boiling temperature lower than that of water.
7. The method according to claim 1, wherein the solids content of the SiO₂ slurry is in a range between 70-80% by wt.
8. The method according to claim 1, wherein a plurality of successive layers of the SiO₂ slurry layer are applied so as to produce the functional layer.
9. The method according to claim 8, wherein neighboring layers have different compositions.

10. The method according to claim 1, wherein the functional layer is produced with a layer thickness in the range between 0.1 mm and 4 mm.
 11. The method according to claim 1, wherein the dispersion liquid is a mixture of water and an alcohol with a boiling temperature lower than that of water.
 12. The method according to claim 1, wherein the solids content of the SiO₂ slurry is in a range between 74-78% by wt.
 13. The method according to claim 1, wherein the splintery amorphous SiO₂ granules have a grain size distribution with a D₅₀ value in a range between 5 μm and 20 μm.
 14. The method according to claim 13, wherein the spherical amorphous SiO₂ granules are present with a weight fraction in a range of 40% by wt. to 80% by wt., based on the total solids content.
 15. The method according to claim 14, wherein the spherical SiO₂ amorphous SiO₂ granules have a grain size distribution with a D₅₀ value in a range between 5 μm and 40 μm.
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16. The method according to claim 15, wherein the SiO₂ nanoparticles are present with a weight fraction in a range of 3% by wt. to 8% by wt., based on the total solids content.
 17. The method according to claim 16, wherein the surfactant is present with a fraction in a range of 0.005% to 0.05%, based on the volume of the dispersion liquid.
 18. The method according to claim 17, wherein a plurality of successive layers of the SiO₂ slurry layer are applied so as to produce the functional layer.