



(86) Date de dépôt PCT/PCT Filing Date: 2000/05/03
(87) Date publication PCT/PCT Publication Date: 2000/11/16
(85) Entrée phase nationale/National Entry: 2001/11/06
(86) N° demande PCT/PCT Application No.: EP 2000/003950
(87) N° publication PCT/PCT Publication No.: 2000/068163
(30) Priorité/Priority: 1999/05/07 (99109016.8) EP

(51) Cl.Int.⁷/Int.Cl.⁷ C04B 28/24, C04B 41/68, C04B 24/42,
C04B 14/04, C04B 12/04
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(54) Title: SILICATE MATERIAL

(57) **Abrégé/Abstract:**

The invention relates to a silicate material which contains an amorphous binding matrix, consisting of at least an alkali oxide and a silicon dioxide, whereby the alkali oxide is lithium, sodium and/or potassium oxide. In order to produce a weather-resistant, acid-resistant and temperature-resistant silicate material, both for shaped bodies and for coatings that can be produced from a silicate mixture whose characteristics remain stable and are not adversely affected during a storage period of at least three months in a sealed container, the following is recommended: The amorphous binding matrix should contain more than 25 mol silicon dioxide per mol of alkali oxide, in addition to between 10 g and 150 g of a bound, water-repelling additive which contains silicon per 1000 g silicon oxide with a uniform dispersion and between 400 g and 7000 g of a filler, whose particle thickness is less than 200 µm. Hydroxy functional alkylpolysiloxane with a high proportion of linear siloxane chains and a low to medium degree of branching is recommended as the water-repelling additive.





PCT
WELTORGANISATION FÜR GEISTIGES EIGENTUM
Internationales Büro
INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE
INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

(51) Internationale Patentklassifikation ⁷ : C04B 28/24, 12/04, 41/68 // (C04B 28/24, 14:04, 24:42), 111:21	A1	(11) Internationale Veröffentlichungsnummer: WO 00/68163 (43) Internationales Veröffentlichungsdatum: 16. November 2000 (16.11.00)
(21) Internationales Aktenzeichen: PCT/EP00/03950 (22) Internationales Anmeldedatum: 3. Mai 2000 (03.05.00) (30) Prioritätsdaten: 99109016.8 7. Mai 1999 (07.05.99) EP (71) Anmelder (für alle Bestimmungsstaaten ausser US): LA-FARGE BRAAS TECHNICAL CENTERS GMBH [DE/DE]; Frankfurter Landstrasse 2 - 4, D-61437 Oberursel (DE). BAYER AG LEVERKUSEN [DE/DE]; D-51368 Leverkusen (DE). (72) Erfinder; und (75) Erfinder/Anmelder (nur für US): DRECHSLER, Andreas [DE/DE]; Friedrich-Ebert-Strasse 22, D-63500 Seligenstadt (DE). KLEIN, Jürgen [DE/DE]; Langestrasse 107, D-63110 Rodgau (DE). MERKLEIN, Stephan [DE/DE]; Friedrich-Ebert-Strasse 4a, D-63500 Seligenstadt (DE). NEUPERT, Daniel [DE/DE]; Rannenbergring 47, D-63755 Alzenau (DE). REISSER, Andrea [DE/DE]; Beethoven Strasse 11, D-63179 Obertshausen (DE). KÄSLER, Karl-Heinz [DE/DE]; Gezelinallee 45, D-51375 Leverkusen (DE). SCHOBER, Peter [DE/DE]; Mühlheimer Strasse 93, D-51375 Leverkusen (DE). WAGNER, Gebhard [DE/DE]; Ackerstrasse 31, D-51519 Odenthal (DE).		(74) Anwalt: BRÜNING, Rolf; Lafarge Braas GmbH, Intellectual Property Dept., Rembrücker Strasse 50, D-63147 Heusenstamm (DE). (81) Bestimmungsstaaten: AU, BR, CA, CN, CZ, HU, JP, PL, RU, UA, US, ZA. Veröffentlicht <i>Mit internationalem Recherchenbericht.</i>
(54) Title: SILICATE MATERIAL (54) Bezeichnung: SILIKATMASSE (57) Abstract The invention relates to a silicate material which contains an amorphous binding matrix, consisting of at least an alkali oxide and a silicon dioxide, whereby the alkali oxide is lithium, sodium and/or potassium oxide. In order to produce a weather-resistant, acid-resistant and temperature-resistant silicate material, both for shaped bodies and for coatings that can be produced from a silicate mixture whose characteristics remain stable and are not adversely affected during a storage period of at least three months in a sealed container, the following is recommended: The amorphous binding matrix should contain more than 25 mol silicon dioxide per mol of alkali oxide, in addition to between 10 g and 150 g of a bound, water-repelling additive which contains silicon per 1000 g silicon oxide with a uniform dispersion and between 400 g and 7000 g of a filler, whose particle thickness is less than 200 µm. Hydroxy functional alkylpolysiloxane with a high proportion of linear siloxane chains and a low to medium degree of branching is recommended as the water-repelling additive. (57) Zusammenfassung Die Erfindung betrifft eine Silikatmasse, die zumindest eine Alkalioxid und Siliziumdioxid enthaltende amorphe Bindermatrix aufweist, wobei das Alkalioxid Lithium-, Natrium- und/oder Kaliumoxid ist. Um eine witterungs-, säure- und temperaturbeständige Silikatmasse sowohl für Formkörper als auch für Beschichtungen zu schaffen, die aus einer in einem geschlossenen Gefäß mindestens drei Monate ohne Beeinträchtigung ihrer Eigenschaften lagerstabilen Silikatmischung herstellbar ist, wird empfohlen, daß die amorphe Bindermatrix pro Mol Alkalioxid mehr als 25 Mol Siliziumdioxid, außerdem pro 1000 g Siliziumdioxid in gleichmäßiger Verteilung 10 g bis 150 g eines eingebundenen siliconhaltigen hydrophobierenden Additivs und 400 g bis 7000 g Füllstoff enthält, dessen Partikel eine Dicke von weniger als 200 µm besitzen. Als hydrophobierendes Additiv wird hydroxyfunktionelles Alkylpolysiloxan mit hohem Anteil an linearen Siloxanketten und einem niedrigen bis mittleren Verzweigungsgrad empfohlen.		

Specification

Silicate Composition

The invention relates to a silicate composition which comprises at least one amorphous binder matrix including alkali oxide and silicon dioxide, wherein the alkali oxide is lithium, sodium and/or potassium oxide, and a preferred method for the production of this silicate composition.

Such a silicate composition can be employed, for example, for coating structural bodies, in particular roofing pantiles. Concrete roofing tiles, which are pantiles comprising concrete, are coated on their surface in order to avoid efflorescence and to attain an esthetic appearance. In the course of time the coating of a pantile is exposed to strong corrosion through atmospheric conditions. While with strong sun exposure during the summer the temperature on the surface can increase up to approximately 80° C, with frost the temperature can decrease to minus 30° in winter. Critical is the attack by cycles of freezing and thawing as well as by acid rain.

DE 25 39 718 B2 discloses a method for coating preformed structural parts based on inorganic binding means customarily comprising additive substances with glaze-like silicate- and/or phosphate-containing coverings, wherein from the inorganic binding agent and water and conventional additive substances a moldable composition is produced, structural parts are formed therefrom, and onto the preformed structural parts a waterglass- and/or phosphate- and metal oxide-containing, aqueous paste comprising, if appropriate, pigments and fillers, is applied in a thin layer and subsequently hardened, wherein into the composition soluble inorganic salts in minimum quantities of 0.5 percent by weight, relative to the inorganic binding agents or, in the case of lime sand brick, relative to the binding agent plus additive substance is mixed in, which converts the aqueous paste, of which 190 to 400 g/m² are applied onto the preformed structural part, into a gel-like, nonflowable state, whereupon the preformed structural part as well as also the coating are hardened. For coating aqueous alkali-containing pastes are applied with 42 to 63 mole% SiO₂, 11 to 27 mole% alkali oxide and between 19 and 42 mole% metal oxide relative to the total weight of these components. As the metal oxides are added to the paste, for example ZnO, MgO, PbO, CaO, B₂O₃ and/or Al₂O₃.

The molar ratio of silicon dioxide to alkali oxide is between 1.56 and 3.82. In order to convert such a

paste into a gel-like, nonflowable state, the addition of soluble inorganic salts is required. According to the method described here, the paste is applied onto the preformed structural part and, together with it, either hardened in the autoclave under pressure and increased temperatures or through purely thermal treatment at normal pressure.

From EP 0 247 910 is known an inorganic silicate coating, in which the binder matrix comprises, relative to the solids, approximately 100 parts by weight of potassium silicate, approximately 10 to approximately 40 parts by weight fine particles of silicon dioxide and approximately 15 to approximately 100 parts by weight of a pearly luster pigment. When using waterglass in a molar ratio of silicon dioxide to alkali oxide of 3.95, the molar ratio of silicon dioxide to alkali oxide in the coating can be up to 6.15. As the method for the production of a coated object is described that the coating composition is applied onto the substrate and subsequently for the purpose of hardening must be brought, together with it, to a temperature of approximately 200°C to approximately 400°C.

US 2 956 958 discloses aqueous mixtures of colloidal SiO_2 particles, in particular silica sols, wherein the mixture comprises 1 part by weight of particles having a diameter of more than 50 nm and a mean diameter D in the range of 50 nm to 150 nm, x parts by weight, with $x = 0$ to 0.07, of particles having a diameter of $0.25 D$ to $0.4 D$ and 0.04 to $0.4 - x$ parts by weight of particles having a diameter of 4 nm to $0.25 D$. The particles are spherical amorphous SiO_2 particles and from the mixture are produced dried formed bodies or preferably coatings. Due to the use of silica sols with particles of defined different diameters, an especially high density of the dried compositions is attained. Drying takes place at temperatures between 110°C and 400°C.

From WO 95/29 139-A1 is known a silicate composition, which comprises an amorphous binder matrix containing at least alkali oxide and silicon dioxide, and, in addition, comprises oxides from the group of aluminum oxide, calcium oxide, titanium dioxide, magnesium oxide, zirconium dioxide and/or boric oxide. The amorphous binder matrix comprises 4 to 25 moles of silicon dioxide for each mole of alkali oxide, wherein the alkali oxide is lithium, sodium and/or potassium oxide and the amorphous binder matrix comprises, additionally, in uniform distribution for each 100 moles of silicon dioxide up to 80 moles of aluminum oxide and/or up to 45 moles calcium oxide, titanium dioxide, magnesium oxide, zirconium dioxide and/or boric oxide. This silicate composition is formed by hardening an aqueous silicate mixture produced of a strongly alkaline silica sol with a solids content of 30 to 70 percent by weight. After its preparation this silicate mixture hardens very rapidly to form the silicate composition, and thus is not stable in storage.

From EP 0 687 657 B is known a polysiloxane composition, its production and its use for coatings.

The production takes place by drying a mixture comprising water as a dispersing agent and

- A) 10 to 60 percent by weight of at least one polysiloxane resin,
- B) 5 to 65 percent by weight of at least one colloidal silicic acid in the form of a silica sol,
- ~~C) 5 to 80 percent by weight of at least one inorganic pigment and/or inorganic filler substance,~~
- and
- D) 0 to 30 percent by weight of a further additive or a mixture of several additives, wherein the sum of components A), B), C), and D), relative to the active agent, is 100 percent by weight.

Due to the high content of polysiloxane resin, it forms in the dried mixture the continuous phase in which the other components are bound.

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The present invention addresses the problem of providing a silicate composition forming a formed body as well as also a coating of a substrate, which is resistant to attacks by atmospheric conditions, in particular during cycles of freezing and thawing, as well as to attacks by acids. It should be possible to apply the coating by simple methods and it should harden at temperatures below 100°C. The silicate mixture employed for the production of the silicate composition should be stable in storage in a closed vessel for at least three months without degradation of its properties.

The problem is solved according to the invention thereby that the amorphous binder matrix comprises for each mole of alkali oxide more than 25 moles of silicon dioxide, that the amorphous binder matrix, in addition, comprises for every 1000 g of silicon dioxide in uniform distribution 10 g to 150 g of an integrated silicon-containing hydrophobing additive, and that the silicate composition, in addition, comprises for every 1000 g silicon dioxide 400 g to 7000 g of a filler substance, whose particles have a thickness of less than 200 µm.

Alkali oxide is here understood to correspond to the specification, customary in silicate analysis, of the metal content as oxide, even if the metal is, in fact, present in the form of a chemical compound such as silicate or the like.

The binder matrix comprises a very large fraction of silicon dioxide, namely more than 25 moles ~~silicon dioxide for each mole of alkali oxide, preferably 50 to 500 moles silicon dioxide for each mole~~ of alkali oxide. The silicate composition according to the invention is therefore extremely resistant to the attacks listed in the formulation of the object of the invention and yet can be applied in the form of an aqueous silicate mixture onto a substrate. Due to the low alkali content, the silicate mixture

- C) 5 to 80 percent by weight of at least one inorganic pigment and/or inorganic filler substance, and
- D) 0 to 30 percent by weight of a further additive or a mixture of several additives, wherein the sum of components A), B), C), and D), relative to the active agents, is 100 percent by weight.

Due to the high content of polysiloxane resin, it forms in the dried mixture the continuous phase in which the other components are bound.

From US 3 895 956 A an inorganic coating composition with decreased permeability to water is known, wherein the coating composition comprises:

5 to 700 parts by weight of in inorganic filler substance,
0.1 to 30 parts by weight of magnesium silicate or bentonite swellable in water,
0.1 to 50 parts by weight of a water-soluble water-repellent substance,
0.01 to 10 parts by weight of an organic viscosity enhancing agent, and
100 parts by weight of a silica sol having a silicate content of 3 to 50 percent by weight and at least one alkali component, wherein the molar ratio of SiO_2 to M_2O is greater than 4, and wherein M_2O represents an alkali metal oxide, ammonium hemihydrate, amine hemihydrate, quaternary amine hemihydrate, guanidine hemihydrate or hydrazine hemihydrate.

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The binder matrix comprises a very large fraction of silicon dioxide, namely more than 25 moles silicon dioxide for each mole of alkali oxide, preferably 50 to 500 moles silicon dioxide for each mole

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used for the production of the silicate composition is stable in storage in a closed vessel for six months and longer without degradation of its properties. Upon the removal of water, the silicate mixture cures already at ambient temperature to form a water-insoluble solidified silicate composition without chemical curing agents being required. However, these can be added if very rapid curing is desired.

The addition of the hydrophobing additive in small quantities causes already strong reduction of the water absorption of the cured silicate composition, improvement of the weathering resistance, and very good integration of the filler substances and pigments possibly added into the cured silicate composition. After the chalking test, customary in dye technology, namely rubbing the surface with a cloth, no traces of pigment and/or filler substance can be detected on the cloth even after exposure to weathering. Due to the small fraction of hydrophobing additive, SiO_2 always forms the continuous phase in the binder matrix.

The silicon-containing hydrophobing additive advantageously comprises reactive groups, which permit integration into the binder matrix. It is recommended to use preferably a polysiloxane.

Polysiloxanes are very firmly and permanently integrated into the binder matrix, if they contain reactive groups. Especially advantageous are alkyl polysiloxanes with alkoxy- and/or hydroxy-functional groups.

The above described advantageous effects are best attained if the polysiloxane comprises predominantly linear siloxane chains with a low to medium degree of branching. While purely linear polysiloxanes have an oily consistency and highly branched siloxanes a hard, resin-like and brittle consistency, especially suitable polysiloxanes are distinguished by high flexibility.

The silicate composition can be optimally adapted to the intended application purpose by the addition of various filler substances. Due to the use of fine-particle filler substances, only very small voids remain between the particles of the filler substance, which are filled by the binder. The silicate composition is therefore free of cracks. The thickness of the filler substance particles is preferably less than 40 μm . The specification of the thickness of the filler substance particles in the case of spherical and fiber-form particles refers to their diameter.

The silicate composition is especially resistant to attacks by acids, if the filler substance is also resistant to acid. As a crystalline filler substance, quartz or silicates are preferred. Glass powder is preferred as

an amorphous filler substance.

It is understood that as the filler substance also mixtures of different crystalline and/or amorphous substances can be employed. By selecting suitable filler substances, the coefficient of thermal expansion of a coating formed of a cured silicate composition can be adapted to the coefficient of expansion of the substrate such that no cracking occurs in the coating with temperature changes.

An especially crack-free silicate composition with a smooth surface is obtained if the binder matrix comprises a crystalline filler substance from the class of stratified silicates. The filler substance can comprise for example mica or a mixture of different stratified silicates.

The silicate composition has especially high tensile strength if it comprises fiber-form filler substances.

~~For adaptation to a desired color, the silicate composition can be dyed through with color pigments. Suitable pigments are mineral pigments such as iron oxide or titanium dioxide. It is understood that colored filler substances, in particular colored glass powder, can also be used for dyeing. Organic pigments such as phthalocyanine, quinacridone or the like can be used if these are introduced in conformance with DE-C 195 33 081.~~

In the following, a preferred method for the production of the silicate composition according to the invention will be described.

For the production of the silicate composition an aqueous silicate mixture is used, which is subsequently dried. The aqueous silicate mixture can comprise an alkaline silica sol with more than 25 moles silicon dioxide for each mole of alkali oxide and with a silicon dioxide content in the range of 15 to 65 percent by weight, preferably 30 to 60 percent by weight, as well as for every 1000 g silicon dioxide in uniform distribution 10 g to 150 g of a silicon-containing hydrophobing additive which can be integrated in order to form the amorphous binder matrix, and for every 1000 g silicon dioxide 400 g to 7000 g filler substance with a thickness of less than 200 μm .

It was found that in order to attain high stability in storage of the aqueous silicate mixture, the pH value of the silica sol must be matched to the fraction of the hydrophobing additive. At a low content of hydrophobing additive a silica sol with 500 moles silicon dioxide for each mole of alkali oxide can

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It was found that in order to attain high stability in storage of the aqueous silicate mixture, the pH value of the silica sol must be matched to the fraction of the hydrophobing additive. At a low content of hydrophobing additive a silica sol with 500 moles silicon dioxide for each mole of alkali oxide can be employed. At higher contents of hydrophobing additive, the fraction of alkali oxide can be higher.

The particles of the silica sol have on average advantageously a specific surface (BET) in the range of 35 m^2/g to 600 m^2/g , preferably of 50 m^2/g to 300 m^2/g .

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~~be employed. At higher contents of hydrophobing additive, the fraction of alkali oxide can be higher.~~

~~The particles of the silica sol have on average advantageously a specific surface (BET) in the range of 35 m²/g to 600 m²/g, preferably of 50 m²/g to 300 m²/g.~~ Especially advantageous is an average specific surface (BET) of 160 m²/g.

Especially suitable is a silica sol, whose particles have at least a bimodal particle size distribution. In this way, an especially weathering resistant silicate composition is obtained.

A bimodal silica sol has been found to be suitable in which approximately 40 to 80 percent by weight of the particles have a specific surface (BET) in the range of 30 m²/g to 100 m²/g and approximately 20 to 60 percent by weight of the particles a specific surface (BET) in the range of 200 m²/g to 600 m²/g. Preferred is a bimodal silica sol, in which approximately 60 percent by weight of the particles have a specific surface (BET) of 50 m²/g and approximately 40 percent by weight of the particles a specific surface (BET) of 300 m²/g.

To produce a colored silicate composition, the aqueous silicate mixture can contain color pigments. Inorganic color pigments can be added directly into the aqueous silicate mixture.

Dyeing with organic color pigments, such a phthalocyanine, quinacridone or the like is possible if to the aqueous silicate mixture is added an organic color pigment which is dispersed in an aqueous polymer dispersion compatible with the silicate mixture. As polymer dispersions are in particular suitable aqueous polymer dispersions based on styrene and/or pure acrylate. The ratio of weight of organic color pigment to the polymer should not exceed the value 1. Due to the integration into the polymer dispersion, the organic color pigment is permanently fixed in the matrix.

The silicate composition can serve as a surface coating, for example as a weathering-resistant protective layer, if the above described aqueous silicate mixture is applied onto a substrate and is dried. The coating has a porosity of less than 20%.

Applying the aqueous silicate mixture for coating a substrate can take place by brushing, rolling, pouring, immersion or preferably by spraying. Optimum processing properties can be attained through the addition of commercially available additives such as thickeners, auxiliary dispersing agents, defoaming agents and/or wetting agents. During the subsequent drying the aqueous silicate

mixture cures to form a silicate composition forming the coating. The substrate can be, for example, metal, unset concrete or a hard mineral base such as cured concrete or plaster. On a porous surface, such as that of foam mortar, a closed coating is also formed, which is water-repellent, however, permeable to water vapor.

The substrate can be a roofing pantile. Due to the low temperature in the production of the silicate composition, it is particularly suitable for coating concrete roofing tiles. The thickness of the coating on average can be between 20 μm and 2 mm, the thickness is preferably 0.1 mm.

The silicate composition according to the invention is also singularly suitable for coating granulates, sands or filler substances for decorative purposes.

The silicate composition is not only suitable for coatings, but also for many applications in which currently other materials are employed, for example for filling and sealing joints or for bonding building materials. It has been found that a silicate composition according to the invention comprising pulverized chamotte as a filler substances can replace the currently customary joint/gap filling composition, which is used when caulking inner pipes of chimneys. Herein primarily the high temperature resistance and the good acid resistance of the cured silicate composition has a particularly advantageous effect. Tests have surprisingly shown that even after the burning-out of chimneys, wherein temperatures of up to 1100°C can occur, the tightness and strength of the joints continues to be ensured. For these applications silicate composition with a small fraction of a hydrophobing additive are advantageous.

In addition, the silicate composition can be employed to attain decorative purposes or decorations. By using silicate mixtures having different colors, a marbling effect can be attained in the silicate composition.

The production of silicate compositions according to the invention, which are of different composition, and their application will be described in the following in conjunction with 22 embodiment examples.

The silica sols described in the following are products of Bayer AG, Leverkusen. In the description of polysiloxanes the symbols customary for silicon structure units are specified, such as described for example in the work by Walter Noll "Chemie und Technologie der Silicone", Verlag Chemie, Weinheim, 1968, page 3. "M" denotes monofunctional, "D" difunctional, "T" trifunctional structural

units of organopolysiloxanes, and "Me" denotes methyl groups. The polysiloxane preparations described in the following are products of GE Bayer Silicones GmbH & CO KG, Leverkusen.

Embodiment Example 1

Into 360 g of an aqueous silica sol with an SiO_2 content of 50 percent by weight, a molar ratio of 190 moles SiO_2 for each mole of Na_2O and an average particle size with a specific surface (BET) of $150 \text{ m}^2/\text{g}$ with a bimodal particle size distribution, wherein 60 percent by weight of the sol particles have a specific surface (BET) of $50 \text{ m}^2/\text{g}$ and 40 percent by weight have a specific surface (BET) of $300 \text{ m}^2/\text{g}$, is stirred as a color pigment 20 g red iron oxide pigment having a particle size of less than $1 \mu\text{m}$. Subsequently as a filler substance 160 g mica with an average particle size of $35 \mu\text{m}$ are added and dispersed for 10 minutes at high shearing speeds of 12 m/s to 15 m/s with the aid of a dissolver. Subsequently as a hydrophobing additive 40 g of an aqueous dispersion having a content of 50 percent by weight of a hydroxy-functional alkyl polysiloxane with low to medium branching was added and thoroughly mixed at a low shearing speed of approximately 3 m/s . As the hydroxy-functional alkyl polysiloxane was used "Baysilone Imprägnieremulsion 3657" having the structure $\text{T}(\text{Me})_{60}\text{D}(\text{Me})_{40}$.

It was found that the dispersing of pigment and filler substance can be accomplished faster at higher viscosity. Therefore in embodiment example 2 initially only $2/3$ of the total quantity of silica sol was charged and, after dispersing pigment and filler substance, the remaining third of the total quantity of silica sol was added.

Application Example 2

Into 240 g of the aqueous silica sol described in embodiment example 1 were stirred as a color pigment 20 g red iron oxide pigment having a particle size of less than $1 \mu\text{m}$. Subsequently as a filler substance 160 g mica with an average particle size of $35 \mu\text{m}$ were added and dispersed for 5 minutes at high shearing speeds of 12 m/s to 15 m/s with the aid of a dissolver. Subsequently at a low shearing speed of approximately 3 m/s an additional 120 g of the aqueous silica sols and as hydrophobing additive 40 g of the aqueous alkyl polysiloxane dispersion described in embodiment example 1 were added and mixed thoroughly.

In both cases a sedimentation-stable viscous silicate mixture was obtained, which could be stored in a closed vessel for more than three months without change of properties.

Since mica has a thixotroping, and thus thickening, effect, a viscosity favorable for processing was obtained with the relatively small fraction of filler substance.

In a first coating test the silicate mixture was applied as a thin uniform layer by means of a spray gun onto a cured concrete roofing tile. The layer was already dry to the touch after 2 hours at ambient temperature and after approximately 24 hours at ambient temperature was cured completely.

In a second coating test the silicate mixture was applied onto a noncured concrete roofing tile as a thin uniform layer by means of a spray gun. Complete curing of the layer took place, together with the curing of the concrete roofing tile, within 6 hours at 60°C in a humid atmosphere.

In both coating tests a uniform, defect-free, red coating with a silky luster having an average thickness of 100 µm was obtained. Water drops rolled off the surface and virtually did not penetrate into the coating. The coating was resistant to weathering.

In all subsequent coating examples the silicate mixture was applied onto cured concrete roofing tiles.

Embodiment Example 3

This embodiment example corresponds to embodiment example 2, however as the hydrophobing additive 40 g of "Baysilone Imprägnieremulsion 3641", an aqueous dispersion having a content of 50 percent by weight of hydroxy-functional alkyl polysiloxane with the structure $T(Me)_{87}D(Me)_{10}M(Me)_3$ was used. A coating produced with this silicate mixture was weathering resistant, however was less stable during cycles of freezing and thawing than in embodiment example 2. The water absorption was low, however higher than in embodiment example 2.

Embodiment Example 4

~~This embodiment example corresponds to embodiment example 2, however as the hydrophobing additive were used 60 g of "Baysilone Imprägnieremulsion LD", an aqueous dispersion with a content of 33 percent by weight of methoxy-functional alkyl polysiloxane with the structure $T(Me)_nD(Me.dodecyl)_n$ with $n = 1$ to 10. A coating produced with this silicate mixture was resistant to weathering, however in cycles of freezing and thawing it was slightly less resistant than in embodiment example 2. The water absorption was low, however higher than in embodiment example 2. Water drops were rolling off the coating.~~

This embodiment example corresponds to embodiment example 2, however as the hydrophobing additive 60 g of "Baysilone Imprägnieremulsion LD" was used, an aqueous dispersion with a content of 33 percent by weight of methoxy functional alkyl polysiloxane with the structure $T(Me)_nD(Me.dodecyl)_n$ with $n = 1$ to 10. A coating produced with this silicate mixture was resistant to weathering, however in cycles of freezing and thawing it was slightly less resistant than in embodiment example 2. The water absorption was low, however higher than in embodiment example 2. Water drops were rolling off the coating.

Embodiment Example 5

This embodiment example corresponds to embodiment example 2, however as a hydrophobing additive were used 35 g of an aqueous dispersion with a content of 60 percent by weight of dimethyl polysiloxane with a viscosity of 500 mPa·s. A coating produced with this silicate mixture was comparable to that from embodiment example 2, however an increased tendency toward chalking could be observed.

Embodiment Example 6 in comparison with US 3 895 956 A

This embodiment example corresponds to embodiment example 2, however as a hydrophobing additive, instead of a hydroxy-functional alkyl polysiloxane, were used 80 g "Baysilone Imprägniermittel SK", a 25% aqueous solution of potassium methyl silicate. A coating produced with this silicate mixture was stable under weathering exposure, however, after cycles of freezing and thawing, was slightly less resistant than in embodiment example 2. The water absorption was low, however markedly higher than in embodiment example 2.

Based on the results obtained in embodiment examples 2 to 6, for the following embodiment examples that hydroxy-functional alkyl polysiloxane was used, which had been employed in embodiment examples 1 and 2 with the structure $T(Me)_{60}D(Me)_{40}$.

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Embodiment Example 5

This embodiment example corresponds to embodiment example 2, however as a hydrophobing additive 35 g of an aqueous dispersion with a content of 60 percent by weight of dimethyl polysiloxane with a viscosity of 500 mPa·s was used. A coating produced with this silicate mixture was comparable to that from embodiment example 2, however an increased tendency toward chalking could be observed.

Embodiment Example 6

This embodiment example corresponds to embodiment example 2, however as a hydrophobing additive, instead of a hydroxy-functional alkyl polysiloxane, were used 80 g "Baysilone Imprägniermittel SK", a 25% aqueous solution of potassium methyl silicate. A coating produced with this silicate mixture was stable under weathering exposure, however, after cycles of freezing and thawing, was slightly less resistant than in embodiment example 2. The water absorption was low, however markedly higher than in embodiment example 2.

Based on the results obtained in embodiment examples 2 to 6, for the following embodiment examples that hydroxy-functional alkyl polysiloxane was used, which had been employed in embodiment examples 1 and 2 with the structure $T(Me)_{60}D(Me)_{40}$.

Embodiment Examples 7 to 11

In the embodiment examples 7 to 11 described in the following the fraction of hydrophobing alkyl polysiloxane dispersion was varied.

For the silicate mixtures the same aqueous silica sol and the same aqueous alkyl polysiloxane dispersion as in embodiment example 1 was used. Into 2/3 of the total quantity of aqueous silica sol was stirred as a color pigment 20 g red iron oxide pigment with a particle size of less than 1 µm. Subsequently as a filler substance 400 g quartz powder with an average particle size of 30 µm and as a thickener 1.4 g Bentone EW by Rheox GmbH, Leverkusen, was added and dispersed for 5 minutes at high shearing speeds of 12 m/s to 15 m/s with the aid of a dissolver. Bentone EW is an ultrapurified magnesium stratified silicate. Subsequently at a low shearing speed of approximately 3 m/s, the remaining third of the aqueous silica sol and as a hydrophobing additive the aqueous alkyl polysiloxane dispersion is added and mixed thoroughly.

Embodiment Example 7

The silicate mixture contained 360 g silica sol and 40 g alkyl polysiloxane dispersion. The result was comparable to embodiment example 2: a cured coating showed very low water absorption and highly marked rolling-off of water drops. Due to the other filler substance, the surface was scratch-resistant, however had a matter finish than in embodiment example 2.

Embodiment Example 8

The silicate mixture contained 320 g silica sol and 80 g alkyl polysiloxane dispersion. The higher content of alkyl polysiloxane dispersion lead in a cured coating to even lower water absorption, however the hardness of the coating was less than in embodiment example 7.

Embodiment Example 9

The silicate mixture contained 380 g silica sol and 20 g alkyl polysiloxane dispersion. A cured coating showed a somewhat higher water absorption, in comparison to embodiment example 7, and marked rolling-off of water drops.

Embodiment Example 10

The silicate mixture contained 390 g silica sol and 10 g alkyl polysiloxane dispersion. The cured coating showed a still higher water absorption, in comparison to embodiment example 9, and less marked rolling-off of water drops.

Embodiment Example 11

This embodiment example was completed as a comparison test without a hydrophobing additive. The silicate mixture contained 400 g silica sol and no alkyl polysiloxane dispersion. The cured coating absorbed water, and water drops did not roll off. The coating was not resistant during the chalking test.

Embodiment examples 7 to 11 demonstrated that with increasing content of alkyl polysiloxane hardness and color intensity decrease. The best result was attained according to embodiment example 7.

Embodiment Example 12

For the silicate mixtures the same aqueous silica sol and the same aqueous alkyl polysiloxane

dispersion as in embodiment example 1 were used. Into 360 g of aqueous silica sol were stirred as a color pigment 20 g red iron oxide pigment having a particle size of less than 1 μm . As a filler substance 550 g quartz powder having an average particle size of 30 μm were subsequently added and dispersed for 10 minutes at high shearing speeds of 12 m/s to 15 m/s with the aid of a dissolver. Subsequently 6 g of a 50% KOH solution were stirred in as a thinner such that the molar ratio was 70 moles SiO_2 for each mole of alkali oxide. 40 g of the aqueous alkyl polysiloxane dispersion were subsequently added and mixed thoroughly at a low shearing speed of approximately 3 m/s. The coating produced therewith had a mineral-like matt finish and was highly resistant.

Embodiment Example 13

For the silicate mixtures the same aqueous silica sol and the same aqueous alkyl polysiloxane dispersion as in embodiment example 1 were used. Into 360 g of the aqueous silica sol were stirred as a color pigment 20 g red iron oxide pigment having a particle size of less than 1 μm . As a filler substance subsequently 550 g quartz powder having an average particle size of 30 μm were added and dispersed for 10 minutes at high shearing speeds of 12 m/s to 15 m/s with the aid of a dissolver. Subsequently 10 g of a 50% KOH solution were stirred in as a thinner such that the molar ratio was 50 moles SiO_2 for each mole of alkali oxide. Subsequently 40 g of the aqueous alkyl polysiloxane dispersion were added and mixed thoroughly at a low shearing speed of approximately 3 m/s. The coating produced therewith had a mineral-like matt finish and was highly resistant.

Embodiment Example 14

For the silicate mixtures the same aqueous silica sol and the same aqueous alkyl polysiloxane dispersion as in embodiment example 1 were used. Into 360 g of the aqueous silica sol were stirred as a color pigment 20 g red iron oxide pigment having a particle size of less than 1 μm . Subsequently as a filler substance 140 g mica having an average particle size of 35 μm were added and dispersed for 10 minutes at high shearing speeds of 12 m/s to 15 m/s with the aid of a dissolver. Subsequently 21 g of a 50% KOH solution were stirred in as a thinner, such that the molar ratio was 26 moles SiO_2 for each mole of alkali oxide. 40 g of the aqueous alkyl polysiloxane dispersion were subsequently added and mixed thoroughly at a low shearing speed of approximately 3 m/s. A relatively liquid silicate mixture was obtained. The coating produced therewith had a strong silky luster.

Embodiment Example 15

The silicate mixture corresponds to that of embodiment example 7, however, as a thickener 0.5 g Kelzan by Monsanto, Hamburg, was used instead of Bentone EW. Kelzan is an organic thickener.

The molar ratio was 190 moles SiO_2 for each mole of Na_2O . Compared to the inorganic thickener used in embodiment example 7, a comparable viscosity of the silicate mixture with a smaller addition of thickener was obtained.

Embodiment Example 16

For the silicate mixtures the same aqueous silica sol and the same aqueous alkyl polysiloxane dispersion as in embodiment example 1 were used. Into 380 g of the aqueous silica sol were stirred as a color pigment 20 g red iron oxide pigment having a particle size of less than 1 μm . Subsequently 360 g quartz powder having an average particle size of 30 μm and 40 g wollastonite fibers having a diameter of less than 200 μm with needle form were added and dispersed for 10 minutes at high shearing speeds of 12 m/s to 15 m/s with the aid of a dissolver. The length of the wollastonite fibers was more than the 20-fold of the diameter. Subsequently as a hydrophobing additive 20 g of the aqueous alkyl polysiloxane dispersion were added and mixed thoroughly at a low shearing speed of approximately 3 m/s. Due to the fiber reinforcement, the coating produced from this silicate mixture had an especially high frost resistance.

Embodiment Example 17

Into 380 g of an aqueous silica sol with an SiO_2 content of 30 percent by weight, a molar ratio of 148 moles SiO_2 for each mole of Na_2O and an average particle size with a specific surface (BET) of 300 m^2/g were stirred as a color pigment 20 g red iron oxide pigment having a particle size of less than 1 μm . Subsequently as a filler substance 500 g quartz powder having an average particle size of 30 μm and as a thickener 1 g Bentone EW were added and dispersed for 10 minutes at high shearing speeds of 12 m/s to 15 m/s with the aid of a dissolver. Subsequently as a hydrophobing additive 20 g of the aqueous alkyl polysiloxane dispersion described in embodiment example 1 were added and mixed thoroughly at a low shearing speed of approximately 3 m/s. The use of an extremely fine-particle silica sol with a solids content of only 30% in connection with the large fraction of filler substance yielded a coating with a mineral-like matt finish.

Embodiment Example 18

Into 240 g of an aqueous silica sol with an SiO_2 content of 50 percent by weight, a molar ratio of 344 moles SiO_2 for each mole of Na_2O and an average particle size with a specific surface (BET) of 140 m^2/g with a trimodal particle size distribution, wherein 60 percent by weight of the sol particles have a specific surface (BET) of 50 m^2/g , 30 percent by weight a specific surface (BET) of 200 m^2/g and 10 percent by weight a specific surface (BET) of 500 m^2/g , were stirred as color pigment 20 g red

iron oxide pigment having a particle size of less than 1 μm . Subsequently as a filler substance 400 g quartz powder having an average particle size of 30 μm and as thickener 1.4 g Bentone EW were added and dispersed for 5 minutes at high shearing speeds of 12 m/s to 15 m/s with the aid of a dissolver. Subsequently, at a low shearing speed of approximately 3 m/s an additional 140 g of the aqueous silica sol and as hydrophobing additive 20 g of the alkyl polysiloxane dispersion described in embodiment example 1 were added and mixed thoroughly. The use of the trimodal silica sol with a solids content of 50% and the relatively high molar ratio of SiO_2 to Na_2O , after curing yielded a coating having a weak luster and being especially resistant to wiping in the chalking test.

Embodiment Example 19

Into 240 g of an aqueous silica sol with an SiO_2 content of 55.5 percent by weight, a molar ratio of 172 moles SiO_2 for each mole of Na_2O and an average particle size with a specific surface (BET) of 140 m^2/g with bimodal particle size distribution, wherein 70 percent by weight of the sol particles have a specific surface (BET) of 50 m^2/g and 30 percent by weight a specific surface (BET) of 200 m^2/g , was stirred as a color pigment 20 g red iron oxide pigment having a particle size of less than 1 μm . Subsequently, as a filler substance, 320 g quartz powder having an average particle size of 30 μm were added and dispersed for 5 minutes at high shearing speeds of 12 m/s to 15 m/s with the aid of a dissolver. Subsequently, at a low shearing speed of approximately 3 m/s an additional 120 g of the aqueous silica sol and as a hydrophobing additive 40 g of the alkyl polysiloxane dispersion described in embodiment example 1 were added and thoroughly mixed. The use of the bimodal silica sol with a solids content of 55.5 percent by weight and the relatively small fraction of filler substance yielded coatings which after curing had an especially strong luster.

Embodiment Example 20

For the silicate mixtures the same aqueous silica sol and the same aqueous alkyl polysiloxane dispersion as in embodiment example 1 were used. Into 360 g of the aqueous silica sol 40 g of uncoated white pigment Bayertitan A by Bayer AG, Leverkusen, with a titanium dioxide content of 99% and a particle size of less than 1 μm were stirred. Subsequently, as a filler substance 360 g limestone powder Calibrite SL by Omya, Köln, having an average particle size of 20 μm and 40 g mica having an average particle size of 35 μm as well as 2 g Kelcan and 2 g Bentone EW were added and dispersed for 5 minutes at high shearing speeds of 12 m/s to 15 m/s with the aid of a dissolver. Subsequently at a low shearing speed of approximately 3 m/s, 40 g of the aqueous alkyl polysiloxane dispersion were added and mixed thoroughly. This silicate mixture was used as an exterior paint and

yielded an intense white, chalking-resistant and weatherproof coating with a mineral-like matt finish of cement facing.

Embodiment Example 21

For the silicate mixtures the same aqueous silica sol and the same aqueous alkyl polysiloxane dispersion as described in embodiment example 1 were used. To 380 g of the aqueous silica sol were added as a filler substance 1060 g quartz powder having an average particle size of 30 μm and 160 g Mikrosilika UP 983 by Elkem GmbH, Düsseldorf, having a particle size of less than 45 μm and dispersed for 5 minutes at high shearing speeds of 12 m/s to 15 m/s with the aid of a dissolver. Subsequently 20 g of the aqueous alkyl polysiloxane dispersion were added and mixed thoroughly at a low shearing speed of approximately 3 m/s. This silicate composition with a very high solids content was used as a viscous free-flowing casting composition for the production of solid formed bodies. Strong plate-form monolithic formed bodies were produced which reproduce the contours of the casting mold precisely, are free of cracks and have very low porosity.

Embodiment Example 22

To 400 g of the bimodal silica sol described in embodiment example 1, which comprises 5% ethylene glycol to improve the properties of processibility and stability in storage at low temperatures to -5°C , were added as a filler substance 900 g pulverized chamotte having a particle size of less than 100 μm and as a thickener 2.4 g Bentone EW, and dispersed for 5 minutes at high shearing speeds of 12 m/s to 15 m/s with the aid of a dissolver. Subsequently, 20 g of the aqueous alkyl polysiloxane dispersion described in embodiment example 1 were added and mixed thoroughly at a low shearing speed of approximately 3 m/s. The silicate composition obtained thus is a viscous paste, which can be worked for example with a trowel. This paste is suitable in particular for connecting interior chamotte pipes when caulking house chimneys.

On two sections of chamotte pipes divided lengthwise in half with a diameter of 170 mm and a wall thickness of 15 mm, onto one front face the above described silicate composition was applied in a thin layer, the pipe sections were placed one onto the other at the front side and silicate composition which had exuded laterally was scraped off. After drying for 24 hours at ambient temperature, in three-point bending tests at a span of 250 mm a breaking load of more than 1500 N was determined. The strength of the connection is not markedly impaired by storage in water nor by baking at temperatures up to 1100°C . The connection is resistant to acid.

Patent Claims

1. Silicate composition which comprises at least one amorphous binder matrix containing alkali oxide and silicon dioxide, wherein the alkali oxide is lithium, sodium and/or potassium oxide, characterized in
that the amorphous binder matrix comprises for each mole of alkali oxide more than 25 moles of silicon dioxide,
that the amorphous binder matrix comprises in addition for every 1000 g silicon dioxide in uniform distribution 10 g to 150 g of an integrated silicon-containing hydrophobing additive, and
that the silicate composition in addition comprises for every 1000 g silicon dioxide 400 g to 7000 g of a filler substance whose particles have a thickness of less than 200 μm .
2. Silicate composition as claimed in claim 1,
characterized in
that the hydrophobing additive comprises polysiloxane.
3. Silicate composition as claimed in claim 2,
characterized in
that the polysiloxane includes hydroxy-functional alkyl polysiloxane.
4. Silicate composition as claimed in claim 2 or 3,
characterized in
that the polysiloxane is a resin comprising a large fraction of linear siloxane chains with a low to medium degree of branching.
5. Silicate composition as claimed in at least one of claims 1 to 4,
characterized in
that the filler substance is resistant to acid.

6. Silicate composition as claimed in at least one of claims 1 to 5,
characterized in
that the filler substance is crystalline, preferably quartz or a silicate.
7. Silicate composition as claimed in at least one of claims 1 to 5,
characterized in
that the filler substance is amorphous, preferably glass powder.
8. Silicate composition as claimed in at least one of claims 1 to 7,
characterized in
that it comprises additionally color pigments.
9. Method for the production of the silicate composition as claimed in at least one of claims 1 to 8,
characterized in
that an aqueous silicate mixture is used and dried, wherein the aqueous silicate mixture comprises an alkaline silica sol with more than 25 moles of silicon dioxide for each mole of alkali oxide and with a silicon dioxide content in the range of 15 to 65 percent by weight, preferably 30 to 60 percent by weight, as well as for every 1000 g silicon dioxide in uniform distribution 10 g to 150 g of an integratable silicon-containing hydrophobing additive for the formation of the amorphous binder matrix, and for every 1000 g silicon dioxide 400 g to 7000 g of a filler substance whose particles have a thickness of less than 200 μm .
10. Method for the production of the silicate composition as claimed in claim 9,
characterized in
that the particles of the silica sol on average have a specific surface (BET) in the range of 35 m^2/g to 600 m^2/g , preferably of 50 m^2/g to 300 m^2/g .
- ~~11. Method for the production of the silicate composition as claimed in claim 9 or 10,
characterized in
that the particles of the silica sol have at least a bimodal particle size distribution.~~

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11. Method for the production of the silicate composition as claimed in claim 9 or 10, characterized in that the particles of the silica sol have at least a bimodal particle size distribution.
12. Method for the production of the silicate composition as claimed in claim 11, characterized in that approximately 40 to 80 percent by weight of the particles have a specific surface (BET) in the range of 30 m²/g to 100 m²/g and approximately 20 to 60 percent by weight of the particles have a specific surface (BET) in the range of 200 m²/g to 600 m²/g.
13. Method for the production of the silicate composition as claimed in one of claims 9 to 12, characterized in that the aqueous silicate mixture comprises in addition color pigments.
14. Use of the silicate composition as claimed in at least one of claims 1 to 8, characterized in that an aqueous silicate mixture is applied onto a substrate as a coating and is dried.
15. Use of the silicate composition as claimed in claim 14, characterized in that the substrate is a roofing pantile.
16. Use of the silicate composition as claimed in claim 14 or 15, characterized in that the thickness of the coating on average is between 20 µm and 2 mm, preferably is 0.1 mm.

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