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(54) Titre : PROCEDE DE PREPARATION DE CONDENSATS SOL-GEL A BASE D'ORGANOSILANES A FONCTIONS MULTIPLES, ET LEUR UTILISATION

(54) Title: METHOD FOR PRODUCING SOL-GEL CONDENSATES BASED ON POLYFUNCTIONAL ORGANOSILANES AND USE THEREOF

(57) Abrégé/Abstract:
The invention relates to a method for producing sol-gel condensates by using aqueous silica sols, in addition to the use thereof for coating inorganic or organic substrates.

ABSTRACT

The invention relates to a method for producing sol-gel condensates by using aqueous silica sols, in addition to the use thereof for coating inorganic or organic substrates.

Method for producing sol-gel condensates based on polyfunctional organosilanes and use thereof

The present invention relates to a method of producing sol-gel condensates using aqueous silica sols, and to the use thereof for coating organic or inorganic substrates.

Through cocondensation of SiO_2 nanoparticles with alkyltrialkoxysilanes, such as methyltrimethoxysilane, for example, it is possible to obtain sol-gel condensates which on plastic surfaces, for example, can be cured to inorganic coatings of high scratch resistance. These sol-gel condensates are produced by reacting methyltrimethoxysilane with an aqueous dispersion of SiO_2 nanoparticles (aqueous silica sol) in the presence of organic solvents, as described, for example, in US-4,476,281. The addition of organic solvent is needed because as a result of the hydrophobic alkyl radical neither the alkyltrialkoxysilanes employed nor their hydrolysis and condensation products are completely miscible with water.

In contrast to the above-described sol-gel condensates based on alkyltrialkoxysilanes, in which the organic radicals are attached exclusively at the ends, the use of polyfunctional organosilanes allows chemical linking of the organic radicals to the inorganic network. Polyfunctional organosilanes, as described for example in EP-A 0 947 520, are linear, branched or cyclic monomeric organosilanes possessing at least two silicon atoms with hydrolyzable and/or condensation-crosslinking groups, the silicon atoms each being connected via at least one carbon atom via a linking structural unit.

Polyfunctional organosilanes in which the linking structural unit is a cyclic siloxane, such as *cyclo*-$\{OSi[(CH_2)_2Si(OH)(CH_3)_2]\}_4$, are of particular interest as a starting material for the production of sol-gel condensates, since from them it is possible, for example, to produce sol-gel coatings having a scratch resistance

similar to that of glass (see EP-A 0 947 520). These scratch-resistance coatings are particularly of interest in connection with the production of automobile coatings. Furthermore, sol-gel coatings of this kind feature a pronounced water repellency, which allows them to be used, for example, to produce antigraffiti coatings or fouling release coatings (e.g. EP-A 96 72 53).

To produce sol-gel condensates suitable for coating surfaces the polyfunctional organosilane is usually reacted not on its own but rather in combination with metal oxides and/or nanoparticles. Through a suitable choice of the proportions it is thereby possible to tailor the water repellency and the hardness of the resultant coating to requirements. It was hitherto a major disadvantage that the reaction of the polyfunctional organosilanes with SiO_2 nanoparticles in the presence of metal alkoxides was possible only through the use of solventborne SiO_2 nanoparticle dispersions, referred to as organosols (e.g., EP A 0 947 520). The majority of polyfunctional organosilanes are completely immiscible with water and thus also incompatible with aqueous dispersions of SiO_2 nanoparticles (aqueous silica sols). Preparing organosols, however, is much more complicated than preparing corresponding aqueous silica sols, which are available on the market as commercially customary products (e.g. Levasil®, Bayer AG, Leverkusen).

It was an object of the present invention, therefore, to provide a method which allows aqueous silica sols to be incorporated into sol-gel condensates based on polyfunctional organosilanes.

It has now been found that by reacting an aqueous silica sol with a silicon alkoxide it is possible to obtain condensates which are miscible with polyfunctional organosilanes.

The present invention accordingly provides a method of producing sol-gel condensates, characterized in that

A1.) an aqueous silica sol is first reacted with a silicon alkoxide, and then

A2.) the condensate obtained from A1.) is reacted with a polyfunctional organosilane.

In one preferred embodiment of the method of the invention

B1.) a silicon alkoxide is dissolved in a solvent and, with stirring, the aqueous silica sol is added, and then

B2.) the condensate obtained from B1.) is reacted with a polyfunctional organosilane.

In the first step of the method of the invention, A1. or B1., the alkoxysilyl groups of the silicon alkoxide are hydrolyzed. The silanol (Si-OH) groups formed as a result are able either to react with themselves or to undergo condensation with extant alkoxysilyl groups, with the elimination of water or alcohol, to form Si-O-Si bonds. The SiO_2 nanoparticles present in the silica sol, however, have a reactive surface which is likewise available for reaction with the silicon alkoxides or their hydrolysis products. Particles are obtained which can be referred to as being surface-modified and are therefore miscible with polyfunctional organosilanes.

Suitable polyfunctional organosilanes for the method of the invention are linear, branched or cyclic monomeric organosilanes which have at least two silicon atoms with hydrolyzable and/or condensation-crosslinking groups, the silicon atoms each being connected via at least one carbon atom via a linking structural unit.

Preferred polyfunctional organosilanes have the general formula (I)

$$[(R^1O)_{3-a}(R^2)_aSi(CH_2)_e]_c\text{-}X\text{-}[(CH_2)_fSi(OR^3)_{3-b}(R^4)_b]_d \qquad (I)$$

in which

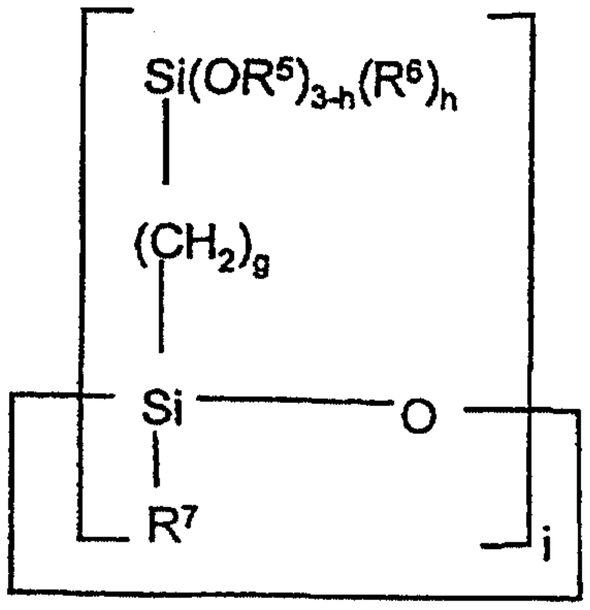
R^1, R^2, R^3 and R^4 independently are C_1-C_8 alkyl radicals or phenyl radicals, R^1 and R^3 also possibly being H,

a and b independently are 0.1 or 2 and also

c, d and, respectively e and f independently are greater than or equal to 1, and

X is the bridging structural unit, a linear, branched or cyclic siloxane, carbosilane or carbosiloxane.

Particular preference is given to using cyclic carbosiloxanes of the general formula (II) in which



(II)

R^5, R^6 and R^7 independently are C_1-C_4 alkyl radicals, R^5 also possibly being H,

h is 0.1 or 2, and also

g is an integer from 1 to 4, and

i is an integer from 3 to 10.

By way of example of cyclic carbosiloxanes mention may be made of compounds of the formulae (IIIa) to (IIIe), in which R^8 represents methyl or ethyl:

(IIIa) *cyclo*-{$OSi[(CH_2)_2Si(OH)(CH_3)_2]$}$_4$

(IIIb) *cyclo*-{$OSi[(CH_2)_2Si(OR^8)(CH_3)_2]$}$_4$

(IIIc) *cyclo*-{$OSi[(CH_2)_2Si(OH)_2(CH_3)]$}$_4$

(IIId) *cyclo*-{OSi[$(CH_2)_2Si(OR^8)_2(CH_3)$]}$_4$

(IIIe) *cyclo*-{OSi[$(CH_2)_2Si(OR^8)_3$]}$_4$.

The oligomers of the cyclic carbosiloxanes mentioned, which are disclosed in WO 98/52992, can of course also be used as polyfunctional organosilanes in the method of the invention. It is likewise possible to use mixtures of different cyclic monomeric or else oligomeric carbosiloxanes.

Aqueous silica sols suitable for the method of the invention consist essentially of a dispersion of amorphous, predominantly SiO_2-containing nanoparticles having an average primary particle size of preferably 5 to 500 nm, which additionally are present very largely as individual particles. To produce transparent coatings, average primary particle sizes of 5 to 100 nm are particularly preferred. The aqueous silica sols may have been stabilized acidically or basically. By adding acids or bases it is possible to adjust the pH of the silica sols where appropriate.

In order to minimize the water content of the sol-gel condensates produced in accordance with the invention the concentration of the aqueous silica sols used can be raised by distillation under atmospheric pressure and elevated temperature or under reduced temperature and optionally elevated temperature. Preferably, therefore, the amount of SiO_2 nanoparticles in the aqueous silica sols is 20 to 80% by weight, more preferably 30 to 60% by weight.

Suitable silicon alkoxides which can be reacted by the method of the invention with the aqueous silica sol are preferably those of the general formula (IV)

$$(R^9)_aSi(OR^{10})_{4-a} \qquad \text{(IV)}$$

in which

a is 0, 1, 2 or 3,

R^9 represents an optionally substituted alkyl or aryl radical, and

R^{10} is a C_1 to C_3 alkyl radical.

Particularly preferred silicon alkoxides of the formula (IV) are those in which

$$(R^9)_aSi(OR^{10})_{4-a} \qquad (IV)$$

a is 0 or 1,

R^9 represents a methyl radical and

R^{10} is a methyl or ethyl radical.

By way of example mention may be made of the following silicon alkoxides of the formulae (Va) to (Vc), where R^{11} is a methyl or ethyl radical:

(Va) $Si(OR^{11})_4$

(Vb) CH_3-$Si(OR^{11})_3$

(Vc) C_6H_5-$Si(OR^{11})_3$.

In one preferred embodiment of the method of the invention in the first step (A1/B1) the silicon alkoxide is first dissolved in a suitable solvent such as alcohol, then, with stirring, the aqueous silica sol is added. After the end of the addition the reaction mixture is stirred until it is homogeneous, i.e., it is no longer an emulsion or no precipitate is visible. Finally, in the second step, the polyfunctional organosilane is added, possibly having been dissolved beforehand in a suitable solvent where appropriate.

By means of the method of the invention it is possible to vary the composition of sol-gel condensates formed from polyfunctional organosilanes, metal alkoxides, and SiO_2 nanoparticles over a wide range. The sol-gel condensates produced in accordance with the invention preferably have the following theoretical composition, calculated assuming complete hydrolysis and condensation:

10 to 90% by weight of polyfunctional organosilane,
90 to 10% by weight of hydrolysis product of the metal alkoxide(s) and SiO_2 nanoparticles, the hydrolysis products of the metal alkoxide(s) and SiO_2 nanoparticles being used in a weight ratio of from 10:1 to 1:10.

With particular preference the sol-gel condensates used in accordance with the invention have the following composition:

15 to 60% by weight of polyfunctional organosilane,
85 to 40% of hydrolysis product of the metal alkoxide(s) and SiO_2 nanoparticles, which are used in a weight ratio of from 8:1 to 1:5.

In order to prevent the sol-gel condensates gelling too rapidly the solids content is adjusted by adding an organic solvent to 10 to 50% by weight, preferably to 15 to 45% by weight. The addition of this solvent, which ought to be at least partly miscible with water, is made preferably before or during the inventive production of the sol-gel condensate. The resultant solids content of the sol-gel condensate can be calculated beforehand from the weight fractions of the individual components, taking into account the weight loss of the polyfunctional organosilane and of the metal alkoxide through hydrolysis and condensation (the theoretical weight loss of $Si(OC_2H_5)_4$, for example, is 72% by weight).

The addition of organic solvents is of advantage furthermore for the production of homogeneous coatings from the sol-gel condensates produced in accordance with the invention. Particularly in the case of sol-gel condensates having a high aqueous silica sol content the addition of organic solvents prevents separation occurring in the (inorganic) coating which forms. Particularly advantageous in this context is the addition of those organic solvents which are at least partly miscible with water and have a boiling point of at least 80°C. With particular preference these solvents form azeotropic mixtures with water, whereby the sol-gel condensates can be freed from excess water by azeotropic distillation under atmospheric pressure and

elevated temperature or in vacuo at optionally elevated temperature. In addition to the removal of water by means of azeotropic distillation, the solvent of the sol-gel condensate can be changed in this way by removal of highly volatile solvents.

The sol-gel condensates produced by the method of the invention from one or more polyfunctional organosilanes are especially suitable for coating organic or inorganic substrates. Following application, which may take place by any common techniques (e.g. spreading, spraying, rolling, spin coating, dipping), the volatile constituents are evaporated at -10°C to 200°C and the sol-gel condensate is cured on the surface. On metals, ceramics, glass, wood, and plastics it is possible in this way to obtain inorganic coatings of high weathering stability, scratch resistance, and chemical resistance. Particularly substrates which already have an organic coating such as a polyurethane coat, for example, can be coated with the sol-gel condensates produced in accordance with the invention. Owing to the nanoparticles present in the sol-gel condensates the coatings produced with the sol-gel condensates obtained in accordance with the invention are highly resistant to cracking as a result of moisture and/or fluctuations in temperature. This cannot be achieved with other inorganic clearcoat materials on moisture-absorbing substrates, such as polyurethane coatings, for example, since cracking occurs there as a result of swelling. The sol-gel condensates produced in accordance with the invention can be used, for example, to coat vehicles, which are then significantly less sensitive to instances of scratching (due for example to cleaning in a wash unit).

The sol-gel condensates produced in accordance with the invention can be used, moreover, for the inorganic modification of organic polymers, which are then used, for example, as moldings or coatings. Mention may be made preferably of organic polymers or polymer mixtures based on polyacrylates, polyesters, polyisocyanates, polyurethanes and epoxides, which are used to produce coatings.

For example, either the sol-gel condensate of the invention can be mixed directly with the organic polymers or else the condensate (A1 or B1) obtained from the

reaction of an aqueous silica sol with a silicon alkoxide is first mixed with the organic polymers and only then reacted, in accordance with the invention, with a polyfunctional organosilane.

Preferably, the condensate A1 or B1 is mixed with the organic polymers and only then reacted with a polyfunctional organosilane.

The fraction of the organic polymers in the cured coating or in the moldings is preferably between 10 and 90%, more preferably between 30 and 70%.

Examples

Remarks

The D4 diethoxide oligomer used, a condensation product of monomeric *cyclo*-$\{OSi[(CH_2)_2Si(OEt)_2(CH_3)]\}_4$ was prepared as described in WO 98/52992; *cyclo*-$\{OSi[(CH_2)_2Si(OH)(CH_3)_2]\}_4$ was prepared in accordance with the teaching of US-A 5 880 305. The aqueous silica sols used were Levasil® 200/30 and 200S/30, from Bayer AG, Leverkusen, Germany. Levasil® 200/30 is an anionically stabilized dispersion of amorphous SiO_2 nanoparticles (30% by weight of SiO_2 in the supplied form), the average particle size being 15 nm and the BET surface area 200 m^2/g. Prior to use, the pH of Levasil® 200/30 was adjusted from 9 to 2 by addition of concentrated hydrochloric acid. Levasil® 200S/30 is a corresponding dispersion stabilized cationically using aluminum salts. Prior to use, the pH of Levasil® 200S/30 was adjusted from 3.8 to 2 by addition of concentrated hydrochloric acid. The aqueous silica sols of higher solids content were prepared by removing water by condensation in vacuo (rotary evaporator). This allowed solids contents of 45 to 55% by weight SiO_2 to be set without the aqueous silica sol gelling. Tetraethyl orthosilicate (= TEOS), and also 1-methoxy-2-propanol, 1-butanol and 2-butanol (all from Aldrich), were used without further purification.

Desmophen A665 BA/X is a polyacrylate-based polyol used for polyurethane coatings, from Bayer AG, Leverkusen, Germany.

The solids content was determined by evaporating one g of the sample in a crystallizing dish (Ø = 7.5 cm) at 130°C (1 h) in a forced air oven. The moisture resistance of the inorganic coatings produced from the sol-gel condensates was tested by applying them to a test panel with a coat system typical of that in automotive finishing (= metal automobile panel) and storing the test panel in distilled water at 50°C. An assessment was made of the cracking (visually). The pencil hardness was determined as specified in ASTM D 3363-92a. The organic polymers modified with the sol-gel condensates were tested by applying them to a test panel having a coat system typical of that in automotive finishing but where, instead of the topcoat (clearcoat), the inorganically modified polymer was applied.

Example 1

Preparation of a sol-gel condensate with 4.5% by weight of SiO_2 nanoparticles

a) With stirring, 17.5 g of 0.1 N aqueous p-toluenesulfonic acid solution were added to 204.2 g of TEOS and 50 g of ethanol. The reaction mixture was stirred at room temperature for 1 h; then 25 g of Levasil® 200 (pH = 2, 30% by weight SiO_2) diluted with 8 ml of ethanol were added dropwise and stirring was continued for 2 h. The solids content of the resulting TEOS-Levasil condensate was 29.8% by weight.

b) With stirring, 50 g of D4 diethoxide oligomer and 8 g of 0.1 N aqueous p-toluenesulfonic acid solution were added to 100 g of the TEOS-Levasil condensate obtained according to a). The mixture was then stirred at room temperature for 1 h. This gave a homogeneous, weakly opaque sol-gel

condensate containing (calculated on the solids) 4.5% by weight of SiO_2 nanoparticles from the Levasil® 200 used.

Example 2

Production of inorganic coatings from the sol-gel condensate from Example 1 and testing of the moisture resistance.

The sol-gel condensate obtained according to Example 1 was applied by spraying to a metal automotive panel and, after being left to stand at room temperature for 10 minutes, was finally cured at 80°C for 10 minutes and at 130°C for 30 minutes (dry film thickness approximately 3 µm). After cooling, the test panel was stored in distilled water at 50°C for 7 days. No cracks occurred in the transparent inorganic top coat.

Example 3

Preparation of sol-gel condensate containing 24.8% by weight SiO_2 nanoparticles.

a) Over the course of 2 hours, with vigorous stirring, 106.5 g of TEOS were added dropwise to a mixture of 74.3 g of Levasil® 200 (pH = 2; 50.2% by weight SiO_2) and 100 g of 1-methoxy-2-propanol. The temperature of the reaction mixture rose to 35°C. After the end of the addition the mixture was stirred for 90 minutes. The solids content of the resulting TEOS-Levasil condensate was 28.2% by weight.

b) With stirring, 3.7 g of 1-butanol and 2.2 g of D4 diethoxide oligomer were added to 5 g of the TEOS-Levasil condensate obtained according to a). The mixture was then stirred at room temperature for 30 min. Addition of 4 drops of 1 N aqueous p-toluenesulfonic acid solution and a further 60 min

of stirring gave, finally, a homogeneous, weakly opaque sol-gel condensate containing (calculated on the solids) 24.8% by weight of SiO_2 nanoparticles from the Levasil® 200 used.

Example 4

Production of inorganic coatings from the sol-gel condensate from Example 3 and testing of the pencil hardness

The sol-gel condensate from Example b) was applied by knife coating (gap width 120 µm) to a glass plate and subsequently cured at room temperature for 10 minutes and at 130°C for 1 h. This gave a homogeneous, highly transparent inorganic coating which had a pencil hardness of 5 H.

Example 5

Production of the sol-gel condensate in analogy to Example 3 using 1-pentanol, and production and testing of an inorganic coating.

As Example 3 described, a sol-gel condensate was produced for which, however, 1-pentanol was used as solvent instead of 1-butanol. Application and curing as described in Example 4 gave a homogeneous, highly transparent inorganic coating which had a pencil hardness of 4 H.

Example 6

Preparation of sol-gel condensate containing 26.8% by weight SiO_2 nanoparticles.

a) Over the course of 1 hour, with vigorous stirring, 79.9 g of TEOS were added dropwise to a mixture of 77.7 g of Levasil® 200 (pH = 2; 48.0% by

weight SiO_2) and 100 g of 1-methoxy-2-propanol. The temperature of the reaction mixture rose to 32°C. After the end of the addition the mixture was stirred until the reaction mixture had cooled to room temperature (approximately 1 h). The solids content of the resulting TEOS-Levasil condensate was 25.8% by weight.

b) With stirring, 2.5 g of 1-pentanol and 1.6 g of D4 diethoxide oligomer were added to 3.5 g of the TEOS-Levasil condensate obtained according to a). Addition of 4 drops of 1 N aqueous p-toluenesulfonic acid solution and a further 60 min of stirring gave, finally, a homogeneous, weakly opaque sol-gel condensate containing (calculated on the solids) 26.8% by weight of SiO_2 nanoparticles from the Levasil® 200 used.

Example 7

Preparation of sol-gel condensate containing 30.1% by weight SiO_2 nanoparticles.

a) Over the course of 1 hour, with vigorous stirring, 59.9 g of TEOS were added dropwise to a mixture of 70.7 g of Levasil® 200 (pH = 2; 52.7% by weight SiO_2) and 100 g of 1-methoxy-2-propanol. The temperature of the reaction mixture rose to 33°C. After the end of the addition the mixture was stirred until the reaction mixture had cooled to room temperature (approximately 1 h). The solids content of the resulting TEOS-Levasil condensate was 26.5% by weight.

b) With stirring, 3.7 g of 1-pentanol and 2.2 g of D4 diethoxide oligomer were added to 5 g of the TEOS-Levasil condensate obtained according to a). Addition of 4 drops of 1 N aqueous p-toluenesulfonic acid solution and a further 60 min of stirring gave, finally, a homogeneous, weakly opaque sol-

gel condensate containing (calculated on the solids) 30.1% by weight of SiO_2 nanoparticles from the Levasil® 200 used.

Example 8

Preparation of sol-gel condensate containing 32.4% by weight SiO_2 nanoparticles.

a) Over the course of 1 hour, with vigorous stirring, 44.9 g of TEOS were added dropwise to a mixture of 77.7 g of Levasil® 200 (pH = 2; 52.7% by weight SiO_2) and 100 g of 1-methoxy-2-propanol. The temperature of the reaction mixture rose to 31°C. After the end of the addition the mixture was stirred until the reaction mixture had cooled to room temperature (approximately 1 h). The solids content of the resulting TEOS-Levasil condensate was 24.6% by weight.

b) With stirring, 3.7 g of 1-pentanol and 2.2 g of D4 diethoxide oligomer were added to 5 g of the TEOS-Levasil condensate obtained according to a). Addition of 4 drops of 1 N aqueous p-toluenesulfonic acid solution and a further 60 min of stirring gave, finally, a homogeneous, weakly opaque sol-gel condensate containing (calculated on the solids) 32.4% by weight of SiO_2 nanoparticles from the Levasil® 200 used.

Example 9

Preparation of sol-gel condensate containing 25.8% by weight of SiO_2 nanoparticles, production of an inorganic coating, and testing of the state of dispersion of the SiO_2 nanoparticles (for TEM picture see Figure 1):

a) Over the course of approximately 2 h 106.5 g of TEOS were added dropwise with stirring to a mixture of 74.3 g of Levasil® 200 (pH = 2; 50.2% by weight SiO_2) and 100 g of 1-methoxy-2-propanol. The

temperature rose to about 35°C. After the end of the addition the homogeneous reaction mixture was stirred for a further 90 min.

b) Then 117 g of butanol and 44.3 g of D4 diethoxide oligomer were added with stirring to 100 g of the TEOS-Levasil condensate obtained according to a), and 48.9 g of volatile constituents (predominantly n-butanol and water) were removed on a rotary evaporator.

c) Finally, 0.3 g of an aqueous p-toluenesulfonic acid solution was added with stirring to 10 g of the sol-gel condensate obtained according to b). After 1 h of stirring of the reaction mixture at room temperature a polycarbonate panel and a glass panel were then coated by knife coating (120 µm gap width). After the cure (10 min at room temperature, 60 min at 130°C in a forced air oven) a homogeneous film was obtained of outstanding transparency and high hardness (pencil hardness 4H on glass).

The coating on the polycarbonate panel was investigated by TEM, and excellent distribution of the SiO_2 nanoparticles in the inorganic matrix comprising TEOS and D4 diethoxide oligomer was found. For illustration, the TEM pictures are documented in the appendix.

Example 10

Modification of an organic polymer with an inventively produced sol-gel condensate, and production and testing of a coating therefrom

a) With stirring, 17.5 g of 0.1 N aqueous p-toluenesulfonic acid solution were added to 204.2 g of TEOS and 50 g of ethanol. The reaction mixture was stirred at room temperature for 1 h; then 25 g of Levasil® 200S (pH = 2, 30% by weight SiO_2) diluted with 10 g of ethanol were added dropwise, stirring was continued for 15 min, and 200 g of 2-butanol were added.

Thereafter, under atmospheric pressure, 243 g of solvent were distilled off and the residue was adjusted by adding 1.9 g of 2-butanol to an amount of 265.6 g, giving a theoretical (calculated) solids content of 25%. The product was subsequently filtered through a pressure suction filter (0.6 µm). This gave a homogeneous, weakly opaque condensate.

b) 198.5 g of the condensate prepared under a) was mixed with 109.5 g of Desmophen A 665 BA/X and the mixture was stirred for 15 min. This gave a homogeneous, storage-stable mixture.

c) 88.0 g of the mixture prepared under b) were admixed with stirring with 6.2 g of a 50% strength *cyclo*-{$OSi[(CH_2)Si(OH)(CH_3)_{2]}\}_4$ in 2-butanol and 5.8 g of a 0.1 N aqueous p-toluenesulfonic acid solution and the mixture was stirred for a further 2 h. This gives a polymer modified with an inventively produced sol-gel condensate.

d) The inorganically modified polymer produced according to c) was applied in place of the conventional topcoat (clearcoat) to a metal automobile panel by spraying and was subsequently cured at room temperature for 5 min and at 140°C for 30 min. After cooling, the test panel was stored in distilled water at 50°C for 7 days. No cracks occurred in the transparent coating.

Claims

1, A method of producing sol-gel condensates, characterized in that

A1.) an aqueous silica sol is first reacted with a silicon alkoxide, and then

A2.) the condensate obtained from A1.) is reacted with a polyfunctional organosilane.

2. The method of claim 1, characterized in that

B1.) a silicon alkoxide is dissolved in a solvent and, with stirring, the aqueous silica sol is added, and then

B2.) the condensate obtained from B1.) is reacted with a polyfunctional organosilane.

3. The method of claim 1, characterized in that polyfunctional organosiloxanes are compounds of the general formula (I)

$$[(R^1O)_{3-a}(R^2)_aSi(CH_2)_e]_c\text{-}X\text{-}[(CH_2)_fSi(OR^3)_{3-b}(R^4)_b]_d \qquad (I)$$

in which

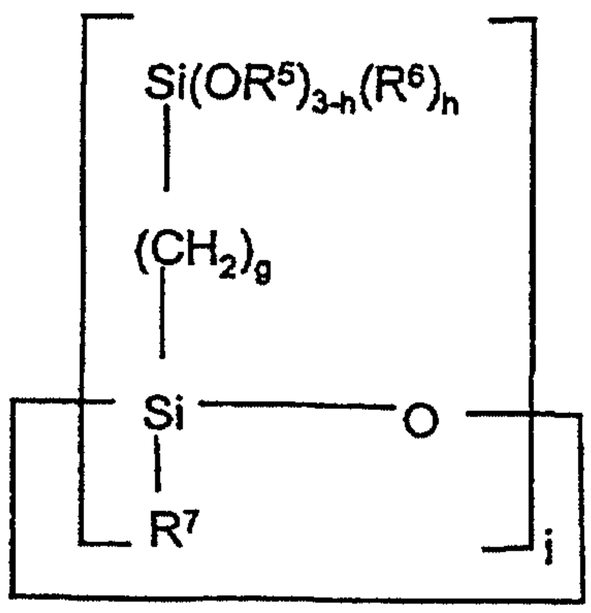
R^1, R^2, R^3 and R^4 independently are C_1-C_8 alkyl radicals or phenyl radicals,

a and b independently are 0.1 or 2 and also

c, d and, respectively e and f independently are greater than or equal to 1, and

X is the bridging structural unit, a linear, branched or cyclic siloxane, carbosilane or carbosiloxane.

4. The method of claim 1, characterized in that characterized in that poly-functional organosiloxanes are compounds of the general formula (II)



(II)

in which

R^5, R^6 and R^7 independently are C_1-C_4 alkyl radicals,

h is 0.1 or 2, and also

g is an integer from 1 to 4, and

i is an integer from 3 to 10.

5. The method of claim 1, characterized in that the silicon alkoxides are compounds of the general formula (IV)

$$(R^9)_aSi(OR^{10})_{4-a} \qquad (IV)$$

in which

a is 0, 1, 2 or 3,

R^9 represents an optionally substituted alkyl or aryl radical, and

R^{10} is a C_1 to C_3 alkyl radical.

6. The method of claim 1, characterized in that silicon alkoxides are compounds of the general formula (IV)

$$(R^9)_aSi(OR^{10})_{4-a} \qquad (IV)$$

in which

a is 0 or 1,

R^9 represents an methyl radical, and

R^{10} is a methyl or ethyl radical.

7. Sol-gel condensates obtainable by a method according to claim 1.

8. The use of sol-gel condensates of claim 7 for coating organic or inorganic substrates.

9. The use of sol-gel condensates of claim 8, characterized in that the substrate is selected from the group consisting of metals, ceramics, glass, wood, plastics, and substrates provided with organic coatings.

10. The use of sol-gel condensates of claim 7 for the inorganic modification of, organic polymers.

Application number / numéro de demande: EP02/00362

Figures: _____

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