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## Sascha SCHWINDT Spray-On Glass

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<http://www.nanopool.eu/en/core-competence/core-competence>

### **Liquid Glass is probably the world's most versatile new technology ?**

“SiO<sub>2</sub>- ultra thin layering” is the technical term for Liquid Glass. Apart from a select group of professionals, few people in the UK know about this stunning technology. If you walk around Ataturk's Mausoleum in Ankara you are walking on it; if you visit certain hospitals in the UK you are touching it. If you see an unusually clean train you are probably looking at it, and if you wonder how your white settee looks so clean, you may be sitting on it. All of these surfaces have been coated with invisible glass.

The flexible and breathable glass coating is approximately 100 nanometres thick (500 times thinner than a human hair), and so it is completely undetectable. It is food safe, environmentally friendly (winner of the Green Apple Award) and it can be applied to almost any surface within seconds . When coated, all surfaces become easy to clean and anti- microbially protected (Winner of the NHS Smart Solutions Award ). Houses, cars, ovens, wedding dress or any other protected surface become stain resistant and can be easily cleaned with water ; no cleaning chemicals are required. Amazingly a 30 second DIY application to a sink unit will last for a year or years, depending on how often it is used. But it does not stop there - the coatings are now also recognised as being suitable for agricultural and in-vivo application. Vines coated with SiO<sub>2</sub> don't suffer from mildew, and coated seeds grow more rapidly without the need for anti-fungal chemicals. This will result in farmers in enjoying massively increased yields . Trials for in-vivo applications are subject to a degree of secrecy, but Neil McClelland, the UK Project Manager for Nanopool GmbH, describes the results as “stunning”.

“Items such as stents can be coated, and this will create anti sticking features - catheters , and sutures which are a source of infection, will also cease to be problematic.”

When asked about how the technology works, Neil, said “In essence, we extract molecules of SiO<sub>2</sub> (the primary constituent of glass) from quartz sand, and then we add the molecules to water or ethanol. Unfortunately, as they say in the movies , if I told you any more .....”. Neil comments further, “The really clever part is that there are no added nano-particles , resins or additives- the coatings form and bond due to quantum forces. Our research informs us that in all probability, we offer the most versatile coating in the world. We are happy to hear about any other technology which offers the same range of applications. Very soon almost every product that you purchase will be protected with some form of easy -to -clean coating. It just so happens that we offer something that everyone finds fascinating . The concept of spray - on glass is just mind -boggling”.

This technology is now available for domestic use in Germany. Full scale retail availability in the UK will commence in early 2010

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<http://www.treehugger.com/files/2010/02/spray-on-liquid-glass-sio2-nanopool.php>

# Potentially Amazing Technology: Is Spray-On Liquid Glass About to Make Everything Greener?

by

**Michael Graham Richard**

liquid-glass-nanopool-image-01.jpg

"The fissure was induced in order present an image which shows the characteristics of the coating. The image shows the SiO<sub>2</sub> coating on a filament of a microfibre." Image: Nanopool

## **If it Works and is Safe, It Could Change the World**

A special coating technically known as "SiO<sub>2</sub> ultra-thin layering", but more memorably called "spray-on liquid glass", has been invented in Turkey at the Saarbrücken Institute for New Materials (the patent is owned by Nanopool). It is non-toxic promises to "protect virtually any surface against almost any damage from hazards such as water, UV radiation, dirt, heat, and bacterial infections [...] the coating is also flexible and breathable, which makes it suitable for use on an enormous array of products."

## **How Does it Work?**

The details are still secret, but based on the information that is available, it seems like a pretty simple process. They purify silicon dioxide (SiO<sub>2</sub>, which is basically what you find in regular glass) from quartz sand, add water or ethanol molecules, and then through an unknown process are able to spray this on surfaces and get a very thin film of glass (100 nanometers, or 15-30 molecules) to stick. "The really clever part is that there are no added nano-particles, resins or additives- the coatings form and bond due to quantum forces." They also claim that it is very safe (these is already a lot of these types of inert molecules out in the wild, though I think it stills needs to be rigorously tested for toxicity).

## **An Almost Unbelievable List of Applications**

Nanopool writes:

The flexible and breathable glass coating is approximately 100 nanometres thick (500 times thinner than a human hair), and so it is completely undetectable. It is food safe, environmentally friendly (winner of the Green Apple Award) and it can be applied to almost any surface within seconds . When coated, all surfaces become easy to clean and anti- microbially protected (Winner of the NHS Smart Solutions Award ). Houses, cars, ovens, wedding dress or any other protected surface become stain resistant and can be easily cleaned with water ; no cleaning chemicals are required. Amazingly a 30 second DIY application to a sink unit will last for a year or years, depending on how often it is used. But it does not stop there - the coatings are now also recognised as being suitable for agricultural and in-vivo application. Vines coated with SiO<sub>2</sub> don't suffer from mildew, and coated seeds grow more rapidly without the need for anti-fungal chemicals. This will result in farmers in enjoying massively increased yields . Trials for in-vivo applications are subject to a degree of secrecy, but Neil McClelland, the UK Project Manager for Nanopool GmbH, describes the results as "stunning". "Items such as stents can be coated, and this will create anti sticking features - catheters , and sutures which are a source of infection, will also cease to be problematic."

Physorg has a few more details: "Food processing companies in Germany have already carried out trials of the spray, and found sterile surfaces that usually needed to be cleaned with strong bleach to keep them sterile needed only a hot water rinse if they were coated with liquid glass. The levels of sterility were higher for the glass-coated surfaces, and the surfaces remained sterile for months. [...] A year-long trial of the spray in a Lancashire hospital also produced "very promising" results for a range of applications including coatings for equipment, medical implants, catheters, sutures and bandages. The war graves association in the UK is investigating using the spray to treat stone monuments and grave stones, since

trials have shown the coating protects against weathering and graffiti. Trials in Turkey are testing the product on monuments such as the Ataturk Mausoleum in Ankara. "

### **Promising, but Let's Wait and See**

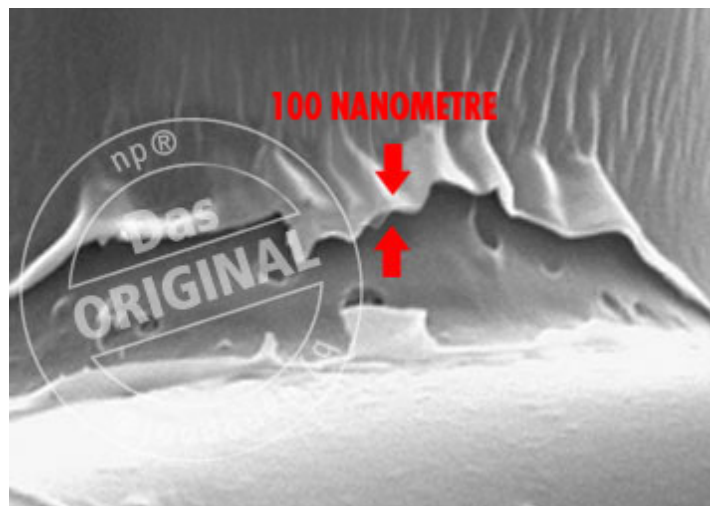
I'm still waiting for more tests (real-world and lab) before getting too excited. But if it works as promised, this could be a new super-material like graphene, with multiple applications in tons of different fields. And if it really makes things more durable and reduces or removes the need for strong chemicals to clean something, it could have a pretty significant positive environmental impact. But it could also have unforeseen effects, so let's not rush to put this everywhere.

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<http://www.physorg.com/news184310039.html>

## **Spray-on liquid glass is about to revolutionize almost everything**

February 2nd, 2010



The fissure was induced in order to present an image which shows the characteristics of the coating. The image shows the SiO<sub>2</sub> coating on a filament of a microfibre.

Spray-on liquid glass is transparent, non-toxic, and can protect virtually any surface against almost any damage from hazards such as water, UV radiation, dirt, heat, and bacterial infections. The coating is also flexible and breathable, which makes it suitable for use on an enormous array of products.

The liquid glass spray (technically termed "SiO<sub>2</sub> ultra-thin layering") consists of almost pure silicon dioxide (silica, the normal compound in glass) extracted from quartz sand. Water or ethanol is added, depending on the type of surface to be coated. There are no additives, and the nano-scale glass coating bonds to the surface because of the quantum forces involved. According to the manufacturers, liquid glass has a long-lasting antibacterial effect because microbes landing on the surface cannot divide or replicate easily.

Liquid glass was invented in Turkey and the patent is held by Nanopool, a family-owned German company. Research on the product was carried out at the Saarbrücken Institute for New Materials. Nanopool is already in negotiations in the UK with a number of companies and with the National Health Service, with a view to its widespread adoption.

The liquid glass spray produces a water-resistant coating only around 100 nanometers (15-30 molecules) thick. On this nanoscale the glass is highly flexible and breathable. The coating is environmentally harmless and non-toxic, and easy to clean using only water or a simple wipe with a damp cloth. It repels

bacteria, water and dirt, and resists heat, UV light and even acids. UK project manager with Nanopool, Neil McClelland, said soon almost every product you purchase will be coated with liquid glass.

Food processing companies in Germany have already carried out trials of the spray, and found sterile surfaces that usually needed to be cleaned with strong bleach to keep them sterile needed only a hot water rinse if they were coated with liquid glass. The levels of sterility were higher for the glass-coated surfaces, and the surfaces remained sterile for months.

Other organizations, such as a train company and a hotel chain in the UK, and a hamburger chain in Germany, are also testing liquid glass for a wide range of uses. A year-long trial of the spray in a Lancashire hospital also produced “very promising” results for a range of applications including coatings for equipment, medical implants, catheters, sutures and bandages. The war graves association in the UK is investigating using the spray to treat stone monuments and grave stones, since trials have shown the coating protects against weathering and graffiti. Trials in Turkey are testing the product on monuments such as the Ataturk Mausoleum in Ankara.

The liquid glass coating is breathable, which means it can be used on plants and seeds. Trials in vineyards have found spraying vines increases their resistance to fungal diseases, while other tests have shown sprayed seeds germinate and grow faster than untreated seeds, and coated wood is not attacked by termites. Other vineyard applications include coating corks with liquid glass to prevent “corking” and contamination of wine. The spray cannot be seen by the naked eye, which means it could also be used to treat clothing and other materials to make them stain-resistant. McClelland said you can “pour a bottle of wine over an expensive silk shirt and it will come right off”.

In the home, spray-on glass would eliminate the need for scrubbing and make most cleaning products obsolete. Since it is available in both water-based and alcohol-based solutions, it can be used in the oven, in bathrooms, tiles, sinks, and almost every other surface in the home, and one spray is said to last a year.

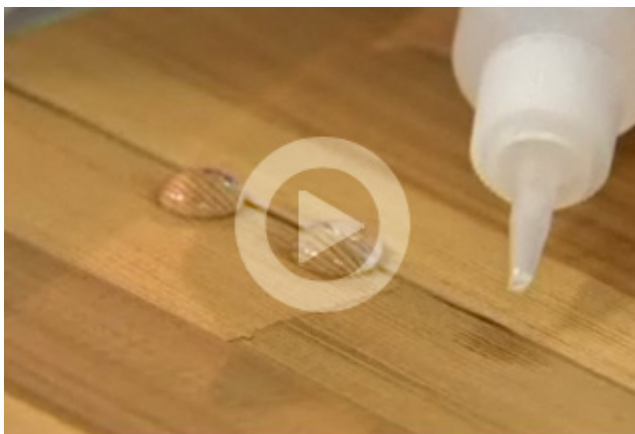
Liquid glass spray is perhaps the most important nanotechnology product to emerge to date. It will be available in DIY stores in Britain soon, with prices starting at around £5 (\$8 US). Other outlets, such as many supermarkets, may be unwilling to stock the products because they make enormous profits from cleaning products that need to be replaced regularly, and liquid glass would make virtually all of them obsolete.

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<http://www.nanopool.eu/en/downloads>

### Videos

<http://uk.reuters.com/news/video?videoId=47835540>



[http://svtplay.se/v/1909578/rapport/flytande\\_glas\\_skyddar\\_omtaliga\\_ytor](http://svtplay.se/v/1909578/rapport/flytande_glas_skyddar_omtaliga_ytor)



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[0001] The invention relates to a method for preparing a composition, is dispersed in an aqueous solution in which at least one gel-forming substance. The invention also relates to a composition, in particular for coating surfaces, which consists at least from an aqueous solution and at least one gel-forming substance.

[0002] Sol-gel processes are wet processes, which are for example the deposition of homogeneous, nano-crystalline ceramic oxide coatings or keramischorganischer used. The special feature of sol-gel process is that the production of coating each of a liquid sol state proceeds, which is converted by a sol-gel transformation into a solid gel state. As brine dispersions of solid particles in the size range be used between 1 nm to 100 nm, which are dispersed in water or organic solvents. Sol-gel process usually go out of brines based on organometallic polymers. The transition from a liquid sol is then used for coating each of the gel state, where there is a three-dimensional network of nanoparticles in the solvent, so that the gel is replaced by solid state properties. The transfer of the gel into a solid oxide coating is controlled by a heat treatment in air.

[0003] Sol-gel coatings influence the properties of surfaces. Depending on the nature of the brine and its impurities, hard and scratch-resistant surfaces are generated by such a coating. Sol-gel coatings can be performed on metals, glasses, synthetic and natural polymers. There exist in this area a number of patents and publications, both of which are only mentioned a few examples (HK Schmidt, Organically modified silicates as inorganic-organic polymers, RM Laine (Ed.), Inorganic and Organometallic Polymers with special properties, 297-317, 1992 Kluwer Academic Publishers, Netherlands; CJ Brinker and G. Scherer, Sol-Gel Science. The Physics and Chemistry of Sol-Gel Processing, Academic Press, Boston, MA (1990);

H. Böttcher, K.-H. Kallies, T. Textor, E. Schollmeyer, T. Bahnners, DE 197 56 906 A (1999); H. Böttcher, J. Trepte, K.-H. Kallies, DE 19839292 (2000).

[0004] The simultaneous hydrolysis of inorganic salts and organic silanes gives coatings with an adjustable flexibility to each other depending on the ratio of the inorganic and organic components (T. Textor, D. Knittel, T. Bahnners, E. Schollmeyer, Inorganic-organic hybrid polymers for coating textile materials, Current Trends in Polymer Science, Vol 8, 2003, page 127-133).

[0005] The chemical compounds that are capable of volatile and other organic compounds bind to, are known cyclodextrins. These are macrocyclic molecules, which are constructed from six, seven or eight [alpha]-D-glucose units. There are ring-shaped molecules that possess a hydrophobic cavity. In this cavity a number of organic molecules is deposited. This changes the physical and chemical properties of the embedded molecules. The embedded molecules possess, for example, compared to the free molecules, a much lower vapor pressure and an improved stability against degradation by light or oxygen. For this reason, cyclodextrins have been used for many years in the field of cosmetics and pharmaceuticals (J. Szejtli, Cyclodextrin Technology, Kluwer, Dordrecht, 1988).

[0006] A permanent fixation of cyclodextrins on various textile materials is known (for BH-J Buschmann, D. Knittel, E. Schollmeyer, DE 4036328; DE 40 35 378 A and DE 100 60 710 A). The binding of the cyclodextrins by chemical bonds or physical interactions, so that their removal by washing processes is not possible.

[0007] The removal of odors and the fragrance of textile materials with the aid of cyclodextrins or cyclodextrin derivatives is also known (eg, T. Trinh, JM Gardlik, TJ Banks and F. Benvegno U.S. 5,094,761, JM Gardlik, T. Trinh, TJ Banks and F. Benvegno 5.23461 million U.S., T. Trinh, JM Gardlik, TJ Banks and F. Benvegno EP 0392607 and JM Gardlik, T. Trinh, TJ Banks and F. Benvegno, EP-A-0 392 606). The used cyclodextrins have no affinity for the fiber material so that they do not adhere to the textile materials.

[0008] The adsorptive accumulation of cyclodextrins with substituted polyethylene glycols of various materials, such as hair and textile materials is well known (A. Schmidt, O. Lammerschop and H. Küster, DE 103 44 967 A). These cyclodextrin derivatives can partly be a normal household washing process removed from the surface of materials.

[0009] The object of the invention to provide cyclodextrins for sol-gel process and available to provide an improved method and an alternative composition for coating surfaces.

[0010] This object is inventively achieved by a method for preparing a composition of the aforementioned kind in which the dispersion is at least one cyclodextrin added.

[0011] In an advantageous embodiment of the inventive method provides that the cyclodextrin at a final concentration of 0.1 to 20 wt.-%, preferably 0.1 to 15 wt.-%, more preferably 0.1 to 10 wt.-%, especially 0.1 to 5 wt.-% is added.

[0012] In an alternative advantageous embodiment of the inventive method provides that the cyclodextrin derivative in a final concentration of 1 to 20 wt.-%, preferably 5 to 20 wt.-%, preferably 10 to 20 wt.-%, especially 15 to 20 weight.-% is added.

[0013] In an alternative advantageous embodiment of the inventive method provides that the cyclodextrin at a final concentration of 0.1 to 15 wt.-%, preferably 5 to 10 wt.-%, particularly preferably from 1 to 5 wt.-%, especially 2 to 4 wt.-% is added.

[0014] According to the invention it is particularly advantageous when the partially methylated cyclodextrin [beta]-cyclodextrin and / or hydroxypropyl-[beta]-cyclodextrin is added to /.

[0015] Here, the cyclodextrin in the dispersion may be dissolved or dispersed.

[0016] To cyclodextrins for use in a sol-gel method to make use of, d.h. the cyclodextrins to embed in a coating is advantageously provided that a cyclodextrin is prepared by reacting with polyvinylamines, polyethyleneimines aminosiloxanes, alkylamines with 3 to 12 carbon atoms in the alkyl group, chitosan, polyvinyl alcohols and / or Perfluoroalkylaminen.

[0017] The novel cyclodextrin derivatives can be fixed in the coating, such as a silicon oxide coating, by their substituents, which act almost as anchor molecules. Due to the inventive derivatization or modification of cyclodextrins is also advantageously able to handle these useful materials in a sol-gel process and permanently integrate into an ultra-thin coating.

[0018] In a further advantageous embodiment of the inventive method is provided that can be stored in the Cyclodextrinderivatmoleküle organic substances. It may be, for example to insecticides, fungicides, biostatic or biocidal agents, fragrances and / or therapeutic agents.

[0019] In an advantageous embodiment of the inventive method is further provided that is dispersed as a gel-forming material at least one metal oxide or a mixture of metal oxides in aqueous solution, preferably SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub> and / or R VerSiOn with R = H , alkyl, aryl, epoxy-alkyl, aminoalkyl, and n = 1.5 or 1

[0020] According to the invention the object is also achieved by following the methods described above prepared composition. Such a composition is advantageously used for coating surfaces in a sol-gel method.

[0021] The object is further achieved by a composition of the type that includes at least one cyclodextrin. Such a composition is also advantageously used for coating surfaces in a sol-gel method.

[0022] In an advantageous embodiment of the inventive composition is provided that the cyclodextrin at a final concentration of 0.1 to 20 wt.-%, preferably 0.1 to 15 wt.-%, more preferably 0.1 to 10 wt.-%, especially 0.1 to 5 wt.-% is included.

[0023] In an alternative embodiment of the inventive composition is provided that the cyclodextrin derivative in a final concentration of 1 to 20 wt.-%, Preferably 5 to 20 wt.-%, preferably 10 to 20 wt.-%, especially 15 to 20 wt.-% is included.

[0024] In an alternative embodiment of the inventive composition is provided that the cyclodextrin at a final concentration of 0.1 to 15 wt.-%, preferably 5 to 10 wt.-%, particularly preferably from 1 to 5 wt.-%, especially 2 to 4 weight.-% is included.

[0025] Preferably, the cyclodextrin derivative according to the invention a partially methylated [beta]-cyclodextrin or hydroxypropyl-[beta]-cyclodextrin.

[0026] In an advantageous manner can be stored more organic substances in the novel cyclodextrin derivative, preferably insecticides, fungicides, biostatic or biocidal agents, fragrances and / or therapeutic agents. As therapeutic agents, for example, anti-inflammatory and / or wound-healing agents.

[0027] In an advantageous embodiment of the inventions according to the composition is further provided that the gel-forming substance is at least one metal oxide or a mixture of metal oxides, preferably SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub> and / or R VerSiOn with R = H, alkyl, aryl , epoxy-alkyl, aminoalkyl, and n = 1.5 or 1

[0028] The invention also relates to a method for coating surfaces, in which a sol is applied from an aqueous solution, at least one gel-forming substance and at least one cyclodextrin derivative to a surface and then dried. This method is particularly advantageous when the coating is at least partly from the composition of the invention is or has been made of this. The cyclodextrin derivatives according to the invention are derivatized so that they can be processed in a sol-gel process and permanently incorporated into a coating produced in this process.



[0029] Preferably the sol is sprayed onto either the surface or the surface immersed in the sol. In both cases, advantageously produces an ultra-thin coating that uniformly covers the so-coated article.

[0030] The sol can be applied for example to a textile material, a nonwoven fabric made of natural or synthetic polymers or mixtures of these polymers. Alternatively, the sol can also be applied to an inorganic fiber material, preferably glass fibers, carbon fibers and / or ceramic fibers, or metallic, ceramic, glass-like and / or cellulosic materials. In a particularly preferred embodiment of the invention, the sol also on plastics or plastic-like materials are applied.

[0031] The inventive composition is particularly suitable for coating of textile materials and / or leather, preferably clothing, shoes, diapers, wound dressings or office equipment, interior trim and other interior fittings of motor vehicles, trains and airplanes. In these applications, in particular, the odor-binding properties of the composition and the ability to store active substances in the cyclodextrin advantage of

[0032] Also advantageous is the use of the composition for coating plastics, preferably sanitation or interior trim and other interior fittings of motor vehicles, trains and airplanes. Examples are toilet lids and seats and plastic components in motor vehicles, the latter being bound in a coated form not only smell, but no self-interference, due to production have more odor. Is also particularly advantageous to coat the plastic housings of mobile phones with coatings that are embedded in the antimicrobial substances and / or fragrances.

[0033] The invention also includes any object with a nonstick surface, which was prepared by the method of the invention and / or in which the coated surface comprises the composition of the invention.

[0034] The invention relates for example, ultra-thin coatings that are produced by a sol-gel process and have the addition to the known properties still an odor-reducing properties. Likewise, a storage of insecticides, fungicides or other agents into the possible in the sol-gel coating located Cyclodextrinderivate. The embedding of the active ingredients in the cyclodextrin their stability to degradation by exposure to light and oxygen is greatly increased. For drugs that have a higher vapor pressure, evaporation is prevented by the incorporation in the cavities of the cyclodextrin.

[0035] According to the invention has been shown that some of cyclodextrin so in a sol-gel matrix can be stored, that the cavities of the cyclodextrins remain still accessible. This can produce sol-gel coatings that have both a protective layer, or another functional layer formed on the surfaces of textile materials, woven fabrics, glass fibers, metals, ceramics or wood and have the same odor-reducing properties. In addition, a variety of organic compounds are incorporated into the cyclodextrins, which are released only by moisture and get back to the surface of the coating.

[0036] Known brine based on pure aqueous solutions or mixtures of water and alcohols. It can be used preferably metal oxide xerogels of  $\text{SiO}_2$ ,  $\text{R}_2\text{SiO}_n$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$  or mixtures thereof, where  $\text{R} = \text{H}$ , alkyl, aryl, epoxy-alkyl, aminoalkyl, and can be  $n = 1.5$  or  $1$ . As unsuitable for incorporation into the starting sols has been shown [beta]-cyclodextrin. Its solubility in the brine is too low. Sols in alcoholic form [alpha]-, [beta]- and [gamma]-cyclodextrin precipitation. Such solutions are not suitable for the sol-gel process.

[0037] The invention therefore relates to the production example, cyclodextrin-salt, which can be in a conventional sol-gel process as thin or very thin coating is applied uniformly to different materials.

[0038] The invention also relates, for example brine containing 0.1 weight -% contained, a cyclodextrin derivative -% to 10 wt -%, preferably 1 wt -% to 5 wt. These solutions can be applied both in a dipping process as well as by spraying onto the desired substrate. After drying, a coating has formed on the basis of polymerized  $\text{SiO}_2$ .

[0039] are in principle the following cyclodextrin derivatives for incorporation in the composition of the invention: partially methylated [beta]-Cyclodextrin (CAVASOL <(R)> W7 M, Wacker-Chemie) and hydroxypropyl-[beta]-Cyclodextrin (CAVASOL <(R)> W7 HP, Wacker-Chemie). Starting with a

cyclodextrin derivative with a reactive group, such as monochlorotriazin substituted [beta]-cyclodextrin (CAVATEX W7MCT, Wacker Chemie GmbH, Burghausen) or other cyclodextrin derivative with a reactive group (A. Schmidt, H.-J. Buschmann, E. Schollmeyer, DE 101 55 781 A) or the reaction product of acrylic acid or an acrylic acid derivative with an unsubstituted cyclodextrin, for example, this polyvinylamine (ZD1168/69-3, BASF, Ludwigshafen, Germany), polyethylenimine (Chemos GmbH), amino siloxane (DMS-A12, ABCR), alkylamines (Merck), dialkyl amines (Fluka), chitosan (Sigma-Aldrich), polyvinyl alcohol (Fluka), Perfluoralkylamin (Perfluorononylamin, Fluka), amino acids such as glycine (Fluka), implemented. Among cyclodextrins [alpha] are - to understand and [gamma]-cyclodextrin -, [beta]. The above-mentioned reactive derivatives formed, for example by reaction of [alpha] -, [beta] - and [gamma]-cyclodextrin with cyanuric chloride and acrylic acid or acrylic acid derivatives.

[0040] The reaction products are water-soluble cyclodextrin derivatives mentioned above can be added to the sol as a concentrated solution or as a pure substance. After a homogeneous solution is formed, it can go no further preparations for the application. Of the non-water-soluble cyclodextrin derivatives, is produced using ultrasound, a dispersion. This is mixed with the corresponding sol and applied to a homogenisation of the surface to be equipped.

[0041] The inventive method has the advantage that the sol-gel process is combined with equipment to adsorb odors and other organic substances. Through the use of cyclodextrin derivatives described the effect of odor control is permanent. These cyclodextrin derivatives are anchored by their substituents at the silicon oxide coating. On the other hand, the accessibility of the cyclodextrin cavities is guaranteed, leaving the complex-forming properties of the cyclodextrins.

[0042] The cyclodextrin-salt can be applied to metallic and ceramic surfaces by a dipping or spraying. After drying, a thin layer has formed on the surface that is mechanically stable against external influences.

[0043] The cyclodextrin composition is also suitable for the impregnation of porous inorganic materials. By immersion of these materials into suitable brine, they reach into all the pores by capillary forces. After centrifugation, excess sol from the pores are removed. After drying, the surfaces of the pores are coated by the sol, the pores of the material has been preserved.

[0044] Natural materials such as wood and paper can be impregnated by dipping into the corresponding cyclodextrin-sol. In this case the brine one hydrophobization the surface. In addition, the cyclodextrins can be chemical agents against pests are stored. This leads to an improved wood preservation.

[0045] Insulating materials that are made from mineral or natural fiber materials can be impregnated by immersion in a brine cyclodextrin. After drying, the cyclodextrin cavities with organic substances, such as insecticides and fungicides are loaded. By coating with the sol, the combustibility of the insulating material is reduced from natural fiber materials. The loading of the cyclodextrins with insecticides and / or fungicides reduce the pest infestation and / or infestation by fungi. Another advantage is that do not evaporate at high temperatures, the active ingredients from the cyclodextrin cavities. This ensures that occurs does not pollute the air by these substances.

[0046] Flexible materials such as films, nonwovens and textile fabrics, can be fitted by spraying or by a dipping process with the cyclodextrin-sols. Depending on the amount of the sol is applied to the flexible structure of the material received. The sol in fixed cyclodextrins are able to store chemical substances from the air. They may, for example by spraying as with perfumes and other fragrances are loaded.

[0047] A load of other organic substances such as insecticides, fungicides, bactericide or biostatically acting substances or pharmaceutical active substances is possible. By deposition of insecticides and fungicides, for example, a parasitic infestation of the materials is prevented.

[0048] After the finishing of nonwovens and / or textile fabrics with cyclodextrin brines can be loaded onto the cyclodextrin derivatives with pharmaceutical and / or cosmetic agents. Come such a finished

textile materials in contact with human skin, so the stored substances are released by the moisture on the skin surface of the skin. The sol-gel coating prevents their hydrophobic properties, the growth of skin cells, if such fabrics are used as wound dressings. By the release of substances that have been stored in the cyclodextrins, the healing process of wounds is accelerated.

[0049] The embedding of the cyclodextrin derivatives in a sol-gel coating ensures that the cyclodextrins can be removed by washing processes or similar processes from the surface of the treated materials. It is therefore considered a permanent modification of the surface of the corresponding materials.

[0050] The invention is further illustrated by the following embodiments as an example.

### **Example 1**

[0051] To a mixture of 50 ml of tetraethoxysilane, 15 ml of 3-glycidyloxypropyltrimethoxysilane and 40 ml of ethanol are added 10 ml of 0.01 N HCl and stirred at room temperature for 10 hours. Then 20 ml of a 10 wt -% solution added to the polyvinylaminsubstituierten cyclodextrin and stirred an additional hour. The result is a water-clear sol. To this sol, a 10 wt -% solution of  $ZrOCl_2 \cdot 8H_2O$  in 50 weight -% ethanol added. This sol is applied to a polypropylene film and dried.

[0052] By applying a drop of an alkaline phenolphthalein solution on the surface, the accessibility of the cavity of [beta]-cyclodextrin can be detected. They observed a discoloration of the drop, which occurs only in the presence of cyclodextrin (K. Beermann, H.-J. Buschmann, D. Knittel, E. Schollmeyer, methods of determination of cyclodextrins in textile materials, textile finishing, 37 (2002) 17).

### **Example 2**

[0053] To a mixture of 30 ml of tetraethoxysilane, diethoxysilane dimethyl-30 ml, 20 ml of 3-glycidyloxypropyltrimethoxysilane, 60 ml of ethanol are added dropwise 15 ml of 0.01 N HCl in 50 ml ethanol and stirred at room temperature for 10 hours. Then 20 ml of a 15 wt -% solution added to the polyethylenaminsubstituierten cyclodextrin and stirred an additional hour. The result is a water-clear sol. % Ethanol added - to this sol, a solution of 10 wt -%  $Al_2(OH)_2 \cdot 3H_2O$  in 5Cl \* 90 wt. The resulting sol is using a padding applied to a wool fabric (wet pickup 80 weight -%) and the tissue dried.

[0054] The proof is the accessibility of the cyclodextrin cavities with an alkaline phenolphthalein.

### **Example 3**

[0055] To a mixture of 70 ml of tetraethoxysilane, 30 ml of methyl triethoxysilane, 400 ml of ethanol are added 20 ml of 0.01 N HCl in portions and [deg.] Stirred at 25 C for several hours. To this sol after which a solution of 10 weight -%  $Al_2(OH)_2 \cdot 3H_2O$  in 5Cl \* 80 weight -% ethanol and 30 ml of an aqueous dispersion (20 wt -%) added to the aminosiloxansubstituierten cyclodextrin. The resulting dispersion is applied to a cotton fabric using a sprayer and dried.

[0056] The proof is the accessibility of the cyclodextrin cavities with an alkaline phenolphthalein.

### **Example 4**

[0057] To a mixture of 30 ml of tetraethoxysilane, diethoxysilane dimethyl-30 ml, 20 ml of 3-glycidyloxypropyltrimethoxysilane, 60 ml of ethanol are added dropwise 15 ml of 0.01 N HCl in 50 ml ethanol and stirred at room temperature for 10 hours. Then 20 ml of a 15 wt -% solution added to the partially methylated [beta]-cyclodextrin and stirred an additional hour. The result is a water-clear sol. To this sol, a solution of 10 weight -%  $Al_2(OH)_2 \cdot 3H_2O$  \* 5Cl in 90 wt- Added% ethanol. By dipping a piece of wood in the resulting sol is impregnated them. After drying, the piece of wood at room temperature, the sample is sprayed with a Permethrinlösung in acetone. After drying, the wood is dipped briefly in acetone to remove adsorbed permethrin. Evidence of complex formation of cyclodextrin with permethrin is done by an aqueous extraction of the wood piece. In the extract permethrin by GC-MS

analysis is proven.

## **QUOTES INCLUDED IN THE DESCRIPTION**

[0058] This list of documents cited by the applicant was automatically generated and is included solely to better inform the reader. The list is not part of the German patent or utility model application. The DPMA is not liable for any errors or omissions.

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## **WO 2009033635**

### **SOL-GEL COATING OF SUBSTRATE MATERIAL SURFACES WITH ODOR-ABSORBING PROPERTIES**

The invention relates to sol-gel coatings, which additionally has known about the properties still an odor-reducing properties. Likewise, a storage of insecticides, fungicides or other agents in the in the sol-gel coating located cyclodextrins possible. The embedding of the active ingredients in the cyclodextrins their stability to degradation by exposure to light and oxygen is greatly increased. For drugs that have a higher vapor pressure, evaporation is prevented by the incorporation in the cavities of the cyclodextrins.

The production and application of sol-gel coatings on different materials is discussed below.

Sol-gel coatings influence the properties of surfaces. Depending on the nature of the brine and its impurities, hard and scratch-resistant surfaces are generated by such a coating. Sol-gel coatings can be performed on metals, glasses, synthetic and natural polymers. There exist in this field a number of patents and publications, both of which are only mentioned a few examples (HK Schmidt, Organically modified silicates as inorganic-organic polymers, RM Laine (Ed.), Inorganic and Organometallic Polymers with

special properties, 297 - 317, 1992 Kluwer Academic Publishers, Netherlands; CJ Brinker and G. Scherer, Sol-gel Science: The Physics and Chemistry of Sol-Gel Processing. Academic Press, Boston, MA (1990); H. Böttcher, K.-H. Kaili, T. Textor, E. Schollmeyer, T. Bahnners, DE 19756906 (1999); H. Böttcher, J. Trepte, K.-H. Kaili, DE 19839292 (2000). By the simultaneous hydrolysis of inorganic salts and organic silanes gives coatings with an adjustable flexibility to each other depending on the ratio of the inorganic and organic components (T. Textor, D. Knittel, T. Bahnners, E. Schollmeyer, Inorganic-organic hybrid polymers for coating textile materials, Current Trends in Polymer Science, Vol.8, 2003, Page 127-133; Bahnners T., T. Textor, E. Schollmeyer, Surface functionalization of textile fibers with reactive silanes, in KL Mittal (Ed.), Silanes and Other Coupling Agents, Vol 4 "s. 141-152, VSP, Leiden (2007)). Coatings by the sol-gel method with a deodorizing effect can be produced by the installation of catalytic additives (T. Benthien, P. Faber, G. Jonschker, p. Sepeur, H. Schmidt, P. Stossel, DE 19,915,377 (1999)). These catalysts are able to decompose organic substances at high temperatures.

As chemical compounds that are able to bind and other volatile organic compounds, cyclodextrins are known. These are macrocyclic molecules, which are constructed from six, seven or eight [ $\alpha$ ]-D-glucose units. There are ring-shaped molecules that possess a hydrophobic cavity. In this cavity a number of organic molecules is deposited. This changes the physical and chemical properties of the embedded molecules. The embedded molecules possess as compared to the free molecules, a much lower vapor pressure and an improved stability against degradation by light or oxygen. For this reason, cyclodextrins have been used for many years in the field of cosmetics and pharmaceuticals (J. Szejtli, Cyclodextrin Technology, Kluwer, Dordrecht, 1988).

Permanent fixation of cyclodextrins on various textile materials is known (eg H.-J. Buschmann, D. Knittel, E. Schollmeyer, DE 4036328 and DE 4035378 and DE 10.06071 million). The binding of the cyclodextrins by chemical bonds or physical interactions, so that their removal by washing processes is not possible.

The removal of odor or fragrance of textile materials with the aid of cyclodextrins or Cyclodextrin is also known (eg, T. Trinh, JM Gardlik, TJ. Benvegno F. Banks and U.S. 5,094,761, JM Gardlik, T. Trinh, TJ. Benvegno F. Banks and 5.23461 million U.S., Trinh T., JM Gardlik, TJ. Banks and F. Benvegno EP 0392607 and JM Gardlik, T. Trinh, TJ. Benvegno F. Banks and EP 0392606). The used cyclodextrins have no affinity for the fiber material so that they do not adhere to the textile materials.

Adsorptive accumulation of cyclodextrins with substituted polyethylene glycols of various materials, such as hair and textile materials is well known (A. Schmidt, O. and H. Küster Lammerschop DE 10,344,967). These cyclodextrin derivatives can be partly through normal household washing process removed from the surface of materials.

The use of cyclodextrins in the preparation of sol-gel coatings is described in the literature on principle. Thus, the embedding of native [ $\alpha$ ] -, ss- and [ $\gamma$ ]-cyclodextrins described in a matrix of amorphous silicon dioxide (F. Mizukami, M. Toba and S. Niwa U.S. 4,781,858 (1988) The embedding of the cyclodextrins. the matrix improves the thermal stability of cyclodextrins. coatings by the sol-gel method can also include cyclodextrins, which act as carriers for active ingredients (M. Dreja, W. Rybinski of DE 10,126,966 (2001)). Here, the drug-loaded cyclodextrins are already used in the manufacture of coatings. These agents can be re-released from the cyclodextrin cavities. It is, however, described no release mechanism. According to current knowledge, one must assume, however, assume that the described in the application of the matrix, drying the water molecules are removed almost quantitatively. Small amounts of water are required to produce drugs and other substances such as perfumes, from the cyclodextrin cavities release (J. Szejtli, Cyclodextrin Technology, Kluwer (1988), pages 188-190).

According to the invention has been shown that some of cyclodextrin derivatives, eg with one or two substituents such as polyvinyl amine, polyallylamine, polyethyleneimine, polyethylene glycol and polyvinyl alcohols so in a sol-gel matrix can be stored, that the cavities of the cyclodextrins remain still accessible. These substituted cyclodextrins are almost infinitely soluble in water or aqueous alcoholic solutions, so that the disadvantages of low solubility of ss-cyclodextrin in water and the native

cyclodextrins ([alpha] -, ss-and [gamma]-CD) in aqueous alcoholic solutions no longer exist. It is possible to produce coatings, sol-gel, both a protective layer or other functional layer formed on the surfaces of textile materials, woven fabrics, glass fibers, metals, wood or wood-like products such as paper, cardboard, etc., leather or ceramics and have the same odor-reducing properties. The coatings are formed even at room temperature. A thermal treatment at temperatures above 40 [deg.] C is not required, which allows the use even in very thermally sensitive materials. Since the coatings formed are porous, can subsequently a variety of organic compounds in the cyclodextrins are stored, which are released only by moisture and then get back onto the surface of the coating. Since the accessibility of the cyclodextrin cavities in the sol-gel coatings is given, the cyclodextrins in the matrix chemical compounds bind in the air. Thus, the coating has an odor-reducing properties. By treatment with an aqueous solution can remove all the odor molecules from the cyclodextrin, whereby the odor-reducing effect of the coating with the cyclodextrin is restored.

Since the charge of cyclodextrins after formation of the sol-gel coating is applied, is an influence of the sol-gel process through the use of cyclodextrin avoided. In aqueous and aqueous ethanolic solutions dissociate the cyclodextrin used, so that by the previously may be adversely affected in the cyclodextrins bound substances and active ingredients of the sol-gel process. This drawback is not with the approach described in this application given.

The used cyclodextrin derivatives have an effect biostatic. Therefore, the use of additional chemical substances are not required to obtain a biostatic or biocidal effect of the coating. This makes it possible to produce sol-gel coatings, which have simultaneously a biostatic or biocidal and an odor-reducing effect. Known brine based on pure aqueous solutions or mixtures of water and alcohols. Here are preferably made of Si metal-oxide xerogels [theta] 2, R-SiON, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, Ti [theta] 2 [theta] using the mixtures thereof, where R = H, alkyl, aryl, epoxy-alkyl, aminoalkyl, and n can be 1, 5 or 1. As unsuitable for incorporation into the starting sols has proven ss-cyclodextrin. Its solubility in the brine is too low. Sols in alcoholic form [alpha] -, ss-and [gamma]-cyclodextrin precipitation. Such solutions are not suitable for the sol-gel process.

The invention therefore relates to the provision of a coating on a substrate, which is produced by the sol-gel method from a cyclodextrin and brine can be as thin or very thin coating is applied uniformly to different materials.

This problem is solved by a cyclodextrin-salt, are used in the specific cyclodextrin in a special weight percent interval in which the cyclodextrin is dissolved in the sol or dispersion.

The invention therefore relates to a coating of a substrate by the sol-gel process by cyclodextrin-salt, which is characterized in that the 0.1 wt -% to 10 wt-% Containing a cyclodextrin derivative that is dissolved or dispersed in the sol.

These solutions / dispersions can be applied either in an immersion process and by spraying or similar methods to the desired substrate. After drying, a coating has formed on the basis of polymerized SiO<sub>2</sub>.

According to a preferred embodiment, the coating is characterized in that the cyclodextrin derivatives are prepared by reaction with polyvinylamine, polyallylamine, polyethyleneimine, aminosiloxanes, alkylamines with 3 to 12 carbon atoms in the alkyl group, chitosan, polyvinyl alcohols and / or Perfluoroalkylamine. In principle, the following cyclodextrin derivatives suitable for incorporation in brine: partially methylated ss-cyclodextrin (CAVASOL (R) W7 M, Wacker-Chemie) and hydroxypropyl-ss-cyclodextrin (CAVASOL (R) W7 HP, Wacker-Chemie). Starting with a cyclodextrin derivative with a reactive group, such as monochlorotriazin substituted ss-cyclodextrin (CAVATEX W7MCT, Wacker Chemie GmbH, Burghausen) or other cyclodextrin derivative with a reactive group (A. Schmidt, H.-J. Buschmann, E. Schollmeyer, DE 10155781) or the reaction product of acrylic acid or an acrylic acid derivative with an unsubstituted cyclodextrin, is this example, with polyvinyl (ZD1168/69-3, BASF, Ludwigshafen, Germany), polyethylenimine (Chemos GmbH), amino siloxane (DMS-A12, ABCR), alkylamines (Merck), dialkyl amines (Fluka), chitosan (Sigma-Aldrich), polyvinyl alcohol (Fluka), Perfluoroalkylamin (Perfluorononylamin, Fluka), amino acids such as glycine (Fluka),



implemented. Among cyclodextrins [alpha] are - to understand, and ss-[gamma]-cyclodextrin. The above-mentioned reactive derivatives are formed for example by reaction of [alpha] -, ss- and gamma-cyclodextrin with cyanuric chloride and acrylic acid or acrylic acid derivatives.

The reaction products are water-soluble cyclodextrin derivatives mentioned above can be added to the sol as a concentrated solution or as a pure substance. After a homogeneous solution is formed, it can go on to further preparations for the application. Of the non-water-soluble cyclodextrin derivatives, a dispersion is produced using ultrasound, and this is mixed with the corresponding sol, and applied to a homogenisation of the surface to be equipped.

The great advantage of the described coating or finish is that the sol-gel process is combined with equipment to adsorb odors and other organic substances. Through the use of cyclodextrin derivatives described the effect of odor control is permanent. These cyclodextrin derivatives are permanently anchored by their substituents at the silicon oxide coating. On the other hand, the accessibility of the cyclodextrin cavities is guaranteed, leaving the complex-forming properties of the cyclodextrins. According to a preferred embodiment, the coating is characterized by the fact that this 1 wt % to 5 wt %, contains a cyclodextrin derivative that is dissolved or dispersed in the sol.

According to a preferred embodiment, the coating is characterized in that the formation of the sol-gel matrix [deg.] At temperatures between 15 °C and 40 °C takes place.

According to a preferred embodiment, the coating is characterized in that the cyclodextrin permanently in the sol-gel matrix is anchored.

According to a preferred embodiment, the coating is characterized in that the sol-gel matrix in the cyclodextrin molecules subsequently incorporated 0.1 weight % of organic substances are stored - up to 10% by weight.

According to a preferred embodiment, the coating is characterized in that the sol-gel matrix in the cyclodextrin molecules subsequently incorporated 0.1 weight % up to 10% by weight % insecticides, fungicides and / or biostatic and biocidal substances are stored.

According to a preferred embodiment, the coating is characterized in that the carrier material is a textile material, a nonwoven fabric made of natural or synthetic polymers or mixtures of these polymers.

According to a preferred embodiment, the coating is characterized in that the carrier material consists of inorganic substances.

According to a preferred embodiment, the coating is characterized in that the carrier material contains glass fibers, carbon fibers and / or ceramic fibers. According to a preferred embodiment, the coating is characterized in that the carrier material includes metal, ceramic, glass-like and / or cellulosic materials.

According to a preferred embodiment, the coating is characterized in that the carrier material, wood and / or wood chip plant substances.

According to a preferred embodiment, the coating is characterized in that the carrier material has a surface of plastics or plastic-like materials.

According to a preferred embodiment, the coating wherein the coating has a thickness of  $1 \times 10^{-6}$  m to  $50 \times 10^{-6}$  m (very thin) or a thickness of  $100 \times 10^{-6}$  m to  $1000 \times 10^{-6}$  m (thin) has.

The cyclodextrin-salt can be applied to metallic and ceramic surfaces by a dipping or spraying. After drying at room temperature, a thin layer has formed on the surface that is mechanically stable against external influences.

The cyclodextrin-salts are also used for impregnation of porous inorganic materials. By immersion of these

materials into suitable brine they reach into all the pores by capillary forces. After centrifugation, excess sol is removed from the pores. After drying at room temperature, the surfaces of the pores are coated by the sol, the pores of the material has been preserved. The coating is permanent.

Natural materials such as wood and paper can be impregnated by dipping into the corresponding cyclodextrin-sol. In this case the brine one hydrophobization the surface. In addition, the cyclodextrins can be chemical agents against pests are stored. This leads to an improved wood preservation. In the manufacture of wood particle materials of different sizes of wood chips with a binder are pressed together. After manufacture the fittings by dipping or spraying with a cyclodextrin-salt impregnated. This causes a hydrophobization the surface. Simultaneously, the cyclodextrin molecules capable of chemical components that can be released from the binders are too complex. Thus, the emission of substances that can cause an odor nuisance is reduced considerably.

Insulation, made from mineral or natural fiber materials can be impregnated by immersion in a brine cyclodextrin. After drying, the cyclodextrin cavities with organic substances such as insecticides and fungicides are loaded. The coating with the sol, the combustibility of the insulating material is reduced from natural fiber materials. The loading of the cyclodextrins with insecticides and / or fungicides reduce the pest infestation and / or infestation by fungi. Another advantage is that vaporize at high temperatures, the active ingredients are not from the cyclodextrin cavities, since the formed cyclodextrin complexes are thermally stable. This ensures that occurs does not pollute the air by these substances.

Flexible materials such as films, nonwovens and textile fabrics, can be fitted by spraying or by dipping process with the cyclodextrin-sols. Depending on the amount of the sol is applied to the flexible structure of the material received. The sol in fixed cyclodextrins are able to store chemical substances from the air. They may also, by spraying, eg with perfumes and other fragrances that are loaded. A load of other organic substances such as insecticides, fungicides, bactericide or biostatically acting substances or pharmaceutical active substances is possible. By deposition of such insecticides and fungicides, a parasitic infestation of the materials is prevented.

After the finishing of nonwovens and / or textile fabrics with cyclodextrins, the cyclodextrin-sols with pharmaceutical and / or cosmetic active ingredients are loaded. Come such a finished textile materials in contact with human skin, so the stored substances are released by the moisture on the skin surface of the skin. The sol-gel coating prevents their hydrophobic properties, the growth of skin cells, if such fabrics are used as wound dressings. By the release of substances that have been stored in the cyclodextrins, the healing process of wounds is accelerated.

By the incorporation of cyclodextrin into a sol-gel coating ensures that the cyclodextrins can not be removed by washing processes or similar processes from the surface of the treated materials. It is therefore considered a permanent modification of the surface of the corresponding materials. The invention further relates to the use of a cyclodextrin-brine as equipment / impregnation of support materials.

This invention concerns such as the use of a sol-gel method for the cyclodextrin-produced brine containing 0.1 to 10 wt % containing a cyclodextrin derivative that is dissolved or dispersed in the sol according to the type as described above equipment / impregnation of inorganic or organic support materials.

The present invention is explained by examples.

### **Example 1**

To a mixture of 50 ml of tetraethoxysilane, 15 ml of 3-glycidoxypolytrimethoxysilane and 40 ml of ethanol are added 10 ml of 0.01 N HCl and stirred at room temperature for 10 hours. Then 20 ml of a 10 wt % solution added to the polyvinylamin substituted cyclodextrin and stirred an additional hour. The result is a water-clear sol. To this sol, a 10 wt % solution of  $\text{H}_2\text{O}$   $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  in 50 weight % ethanol added. This sol is applied to a polypropylene film and dried at room temperature. By applying a drop of an

alkaline phenolphthalein solution on the surface, the accessibility of the cavity of  $\alpha$ -cyclodextrin can be detected. They observed a discoloration of the drop, which occurs only in the presence of cyclodextrin (K. Beermann, H.-J. Buschmann, D. Knittel, E. Schollmeyer, methods of determination of cyclodextrins in textile materials, textile finishing, 37 (2002) 17).

### Example 2

To a mixture of 30 ml of tetraethoxysilane, diethoxysilane dimethyl-30 ml, 20 ml of 3-glycidioxypropyltrimethoxysilane, 60 ml of ethanol are added dropwise 15 ml of 0.01 N HCl in 50 ml ethanol and stirred at room temperature for 10 hours. Then 20 ml of a 15 wt-% solution added to the polyethyleniminsubstituierten cyclodextrin and stirred an additional hour. The result is a water-clear sol. To this sol, a solution of 10 weight-%  $\text{Al}_2(\text{OH})_5 \cdot 2-3 \text{H}_2\text{O}$  in 90 wt-% ethanol. The resulting sol is using a padding applied to a wool fabric (wet pickup 80 weight-%) and the tissue dried at room temperature.

The proof of the accessibility of the cyclodextrin cavities is carried out using an alkaline phenolphthalein.

### Example 3

To a mixture of 70 ml of tetraethoxysilane, 30 ml of methyl triethoxysilane, 400 ml of ethanol are added 20 ml of 0.01 N HCl in portions and [deg.] Stirred at 25 C for several hours. To this sol, then a solution of 10 wt%  $\text{Al}_2(\text{OH})_5 \cdot 2-3 \text{H}_2\text{O}$  in 80 wt% ethanol and 30 ml of an aqueous dispersion (20 wt-%) added to the aminosiloxansubstituierten cyclodextrin. The resulting dispersion is applied to a cotton fabric using a sprayer and then [deg.] At 30 C dried.

The proof of the accessibility of the cyclodextrin cavities is carried out using an alkaline phenolphthalein. Example 4

To a mixture of 50 ml of tetraethoxysilane, 15 ml of 3-glycidioxypropyltrimethoxysilane and 40 ml of ethanol are added 10 ml of 0.01 N HCl and stirred at room temperature (20 <0> C) for 10 hours. Then 20 ml of a 10 wt-% solution added to the polyvinylaminsubstituierten cyclodextrin and stirred an additional hour. The result is a water-clear sol. To this sol, a 10 wt-% solution of  $\text{H}_2\text{O} \cdot \text{ZrOCl}_2 \cdot 8$  in 50 weight-% ethanol added. The resulting sol is using a padding applied to a cotton fabric (wet pickup 80 weight-%) and the fabric is dried at room temperature.

The cotton fabric is coated with the Formazantests (mp Altman Prog Histochem Cytochem 9 (1976);.. W. Oppermann, R. Gutmann, S. Schmitt, E.-held hair dryer, textile finishing, 37, 19 (2003)) on his biostatic / biocidal efficacy investigated. The efficacy is 99%, iether there is no metabolism by microorganisms in the tissue determined.

### Example 5

From the fitted cotton fabric in Example 4 is a 2 x 2 cm <2> large piece in a petri dish on a given nutrient agar standardization. After the inoculation, with half a milliliter of E. coli culture is a storage of the sample at 37 [deg.] C for 24 hours. A visual inspection shows that no growth of microorganisms on the finished textile sample has taken place. It has formed around the sample and no yard. This shows that the cyclodextrin biostatic not diffused out of the sol-gel matrix.

### Example 6

From the fully equipped in Example 4 is a round piece of cotton fabric with a diameter of 5 cm placed on a watch glass and placed in a desiccator. In the desiccator is a petri dish with approximately 20 ml benzyldimethylamine. After 7 days, the textile sample is released some time in order to remove adsorbed benzyldimethylamine, and then into a sample vial for headspace gas chromatography transferred. After the addition of a few microliters of water, the sample is at 80 [deg.] C water bath. Subsequently, the gas is analyzed by gas chromatography. The benzyldimethylamine can be clearly demonstrated.

### Example 7

From the fully equipped in Example 4 is a round piece of cotton fabric with a diameter of 5 cm placed on a watch glass and placed in a desiccator. In the desiccator is a petri dish with approximately 20 ml of hexanal. After 3 days, the textile sample is released some time in order to remove adsorbed hexanal, and then into a sample vial for headspace gas chromatography transferred. After the addition of a few microliters of water sample at 80 [deg is.] C water bath. Subsequently, the gas is analyzed by gas chromatography. The hexanal can be clearly demonstrated.

### Example 8

From the fully equipped in Example 6 is a round piece of cotton fabric with a diameter of 5 cm placed on a watch glass and placed in a desiccator. In the desiccator is a petri dish with approximately 20 ml benzyldimethylamine. After 5 days of the textile sample is released some time in order to remove adsorbed benzyldimethylamine. It is given a 2 x 2 cm <2> large piece in a petri dish on a standard 1 nutrient agar. After the inoculation, with half a milliliter of E. coli culture is a storage of the sample at 37 [deg.] C for 24 hours. A visual inspection shows that no growth of microorganisms on the finished textile sample has taken place. However, over the textile sample formed a courtyard, in which there are no microorganisms. By the existing water obviously a release of benzyldimethylamine has taken place.

### Example 9

Of the vessel equipped in Example 2 is a circular piece of wool fabric with a diameter of 5 cm placed on a watch glass and placed in a desiccator. In the desiccator is a petri dish containing about 5 ml of lemongrass oil. After 2 days the textile sample is released some time in order to remove adsorbed Lemon grass oil. After a slight moistening significantly, the smell of lemon grass can be perceived.

### Example 10

From the fitted wool fabric in Example 2 is a round piece with a diameter of 5 cm placed on a watch glass and placed in a desiccator. In the desiccator is a petri dish containing about 5 ml of lavender oil. After 2 days the textile sample is released some time to adsorbed lavender oil. to remove. After a slight moistening of the smell of lavender can clearly be seen.

### Example 11

To a mixture of 30 ml of tetraethoxysilane, diethoxysilane dimethyl-30 ml, 20 ml of 3 - glycidyoxypropyltrimethoxysilane, 60 ml of ethanol are added dropwise 15 ml of 0.01 N HCl in 50 ml of ethanol and at room temperature (20 <0> C) 10 hours stirred. Then 20 ml of a 15 wt -% solution added to the partially methylated ss-cyclodextrin and stirred an additional hour. The result is a water-clear sol. % AI2 (OH) 5ci x 2-3 H2O in 90 wt - - To this sol, a solution of 10 wt% ethanol added. By dipping a piece of wood in the resulting sol this is impregnated. After drying, the piece of wood at room temperature, the sample is sprayed with a Permethrinlösung in acetone. After drying, the wood is dipped briefly in acetone to remove adsorbed permethrin. Evidence of complex formation of cyclodextrin with permethrin is done by an aqueous extraction of the wood piece. In the extract permethrin by GC-MS analysis is proven.

### Example 12

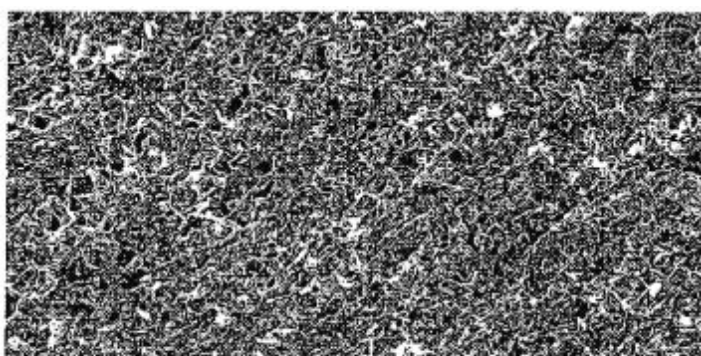
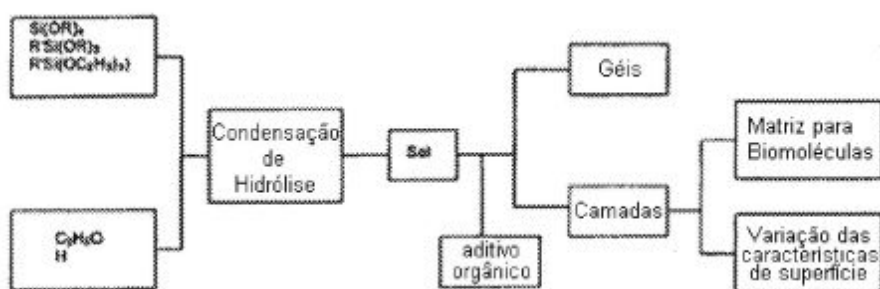
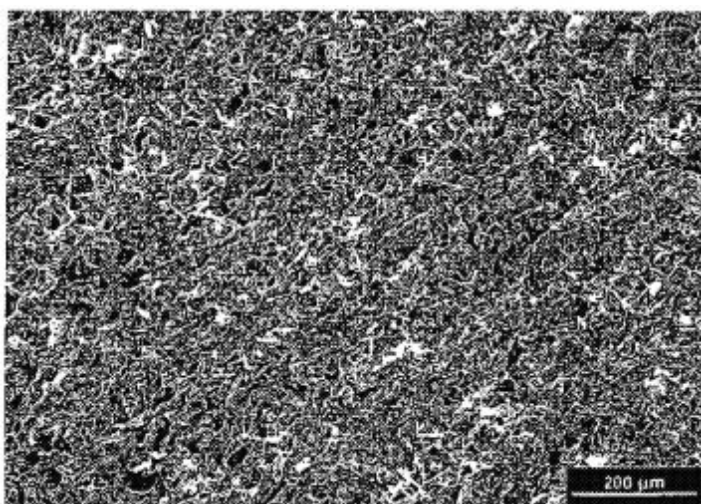
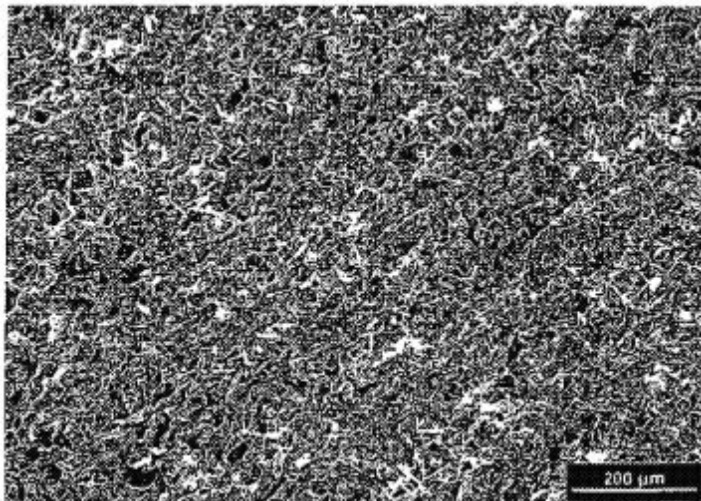
The sol prepared in Example 4 is used to a piece of wood floors (36 x 17 cm) to be sprayed. For comparative purposes, an equally large piece of wood parquet with a 10 wt -% solution of cyclodextrin polyvinylaminsubstituierten sprayed. After drying, both samples dropped onto a drop of water using a pipette. In the case of the sample sprayed with the sol is no wetting of the surface. Contrast, one observes a complete wetting in a short time, in the sample with the sprayed polyvinylaminsubstituierten cyclodextrin.

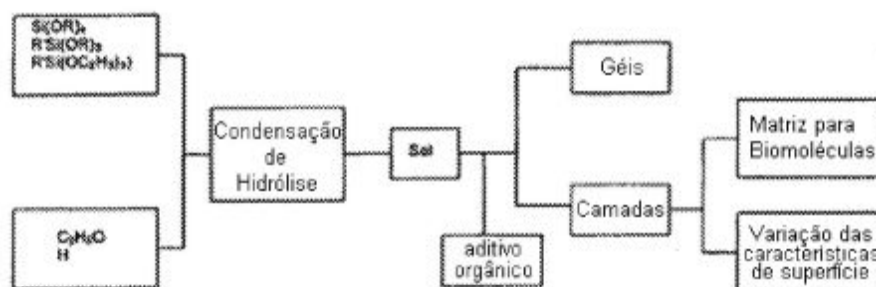
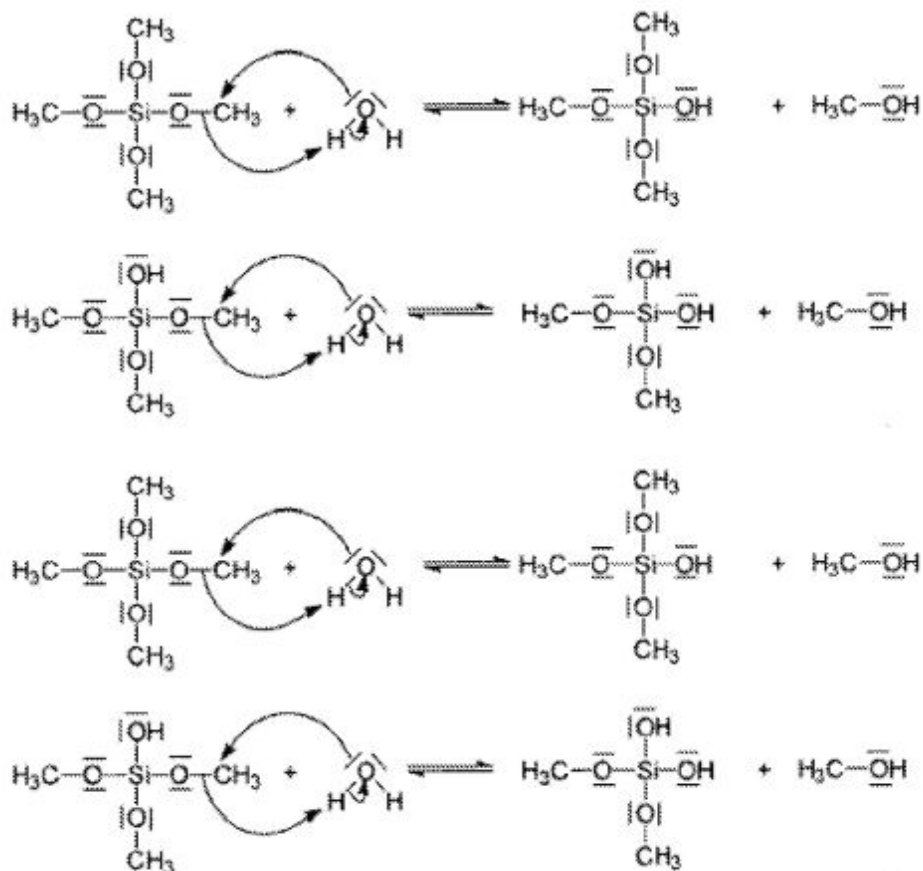
The complexation of substances leached from the wood floor is determined according to DIN ISO 16006-3. This is quantitatively measured in a test chamber after a day the concentration of formaldehyde in the air. It gives the following values: a) wood flooring (untreated): 0.24 [ppm] b) wood floor (sol with

cyclodextrin): 0.07 [ppm] c) Holparkett (only with cyclodextrin): 0.03 [ppm]

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**PT 1826248**  
**CONTAINER FASTENING COATING COMPOSITION, CONTAINER FASTENING COATING,**  
**ITS MANUFACTURE AND APPLICATION**





CA 2709191

WO 2009/074124

# PROTECTIVE LAYER FOR PLANTS AND TREES, THE PRODUCTION THEREOF AND USE THEREOF

2009-06-18

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Classification: - European: A01N25/04; A01N25/34; A01N43/16

The invention relates to a method for producing a protective layer on a surface of a plant, a protective coating for a surface of a plant, a plant coated with this protective layer, a composition for carrying out the process and the production of the protective layer and uses of that composition.



## Background of the Invention

Every year the world's agriculture caused billions in damage by plant pests such as fungi or Frassschädlinge that infect the leaves of crops and damage. Previously, these pests were controlled by herbicides, pesticides, according to the directory (Federal Office for Consumer Protection and Food Safety, as of 01.11.2007) to the areas

Herbicides to control weeds,  
Insecticides against insect pests,  
Fungicides to control fungal pathogens,  
Rodenticides against rodents,  
Nematicides against nematodes (roundworms)  
Acaricides against mites / spiders,  
Molluscicides against slugs,  
Bactericidal against bacteria,  
Agents against viroids,  
Agents against viruses  
Resources for the processing of Obstund Rebveredelung and ornamental trees,  
Tool for preventing wildlife damage  
Means for Wound closure / wound treatment,  
Growth regulator,  
Seeds and Propagating Material for the treatment of seed potatoes and  
Means of soil decontamination

belong. All means and substances in common is that they are either the protected plant to encourage appropriate defensive measures or kill the pests. The plant leaf is next to the stem axis and the root of one of three basic institutions of higher plants and is known as a body type Phyllom. Leaves are lateral outgrowths of the node (nodes) of the stem. The original functions of leaves photosynthesis (structure of organic materials with the aid of light) and transpiration (water evaporation, important for nutrient uptake, and - transport). Leaves occur only in plants sprout, that is, at fern-like plants (Pteridophyta) and seed plants (Spermatophyta). However, they are absent in mosses and algae, at the <"> phallus, however, may experience leaf-like structures, but these are provided as an analogy of the leaves. The variety of leaf shapes is enormous. In some cases, in the course of evolution were also leaf organs, the with the original function of the leaf, namely, photosynthesis and transpiration, have nothing to do more: for example, petals, leaf spines and leaf tendrils, and bud scales.

The sheet includes the outside with a final tissue from the epidermis, which consists of only one cell layer. The epidermis has a waterproof layer of wax to the outside cuticle that prevents unregulated evaporation. The cells of the epidermis usually have no chloroplasts (the cell components, in which photosynthesis takes place). Exceptions are the epidermis of hygro, HeIound hydrophytes and partially shade leaves, especially the guard of the stomata (stomata), which always contain chloroplasts. The stomata are the regulation of gas exchange, primarily of water vapor. After the distribution of stomata, a distinction is hypo-matic (stomata on the leaf base, most common form), amphistomatische (stomata on both sides of the leaf) and epistomatische leaves (stomata on the leaf surface, suchExample, in floating leaves). The attachments are formed by the epidermis hairs (trichomes) called. Are involved in the formation and subepidermal cell layers, it is called Emergence: Examples are spikes or glandular. When mesophyll tissue called the Assimilation. It is usually in the structured under the upper epidermis and palisade parenchyma located below it spongy. The palisade parenchyma consists of an elongated or three layers, perpendicular to the leaf surface vertical, chloroplastenreicher cells. In the palisade, whose main task is to photosynthesis, there are about 80 percent of chloroplasts. The spongy parenchyma is composed of irregularly shaped cells that form the basis of their form large intercellular spaces. The main task of the spongy parenchyma is to ensure the ventilation of the parenchymatous tissue. The cells are relatively poor in chloroplasts. The vascular bundles are often located on the border between the upper Palisadenund spongy spongy. The structure resembles that of the vascular bundles in the shoot axis and is usually collateral. The vascular bundles branch off from the shoot axis and pass by without turning the petiole into the blade. This includes the xylem to leaf surface, the phloem to the leaves. Large vascular bundles

are often surrounded by an endodermis, which is here called bundle sheath. The bundle sheath controls the material exchange between vascular bundles and mesophyll. The vascular bundles end blindly in the mesophyll. Here, the vascular bundles are reduced still more, that is, the first sieve tubes become less and fall out, then remain in the xylem only part Schraubentracheiden ending ultimately blind. The entire leaf is usually so dense interspersed with vascular bundles, leaf cell is that no more than seven cells from a vascular bundle. The resulting small fields between the vascular bundles are called areoles or intercostal fields. The function of the vascular bundles is the delivery transport of water and minerals into the leaves (through the xylem) and the transport of photosynthates from the leaf (through the phloem).

So far, no methods are known which generate as protection against fungi and a Frassinsekten whatsoever layer on the surface of the plant or leaf surface. So far, it was expected to affect the physiology of a coating plant leaf and thereby harm the plant would. A coating plant leaf as a protective layer must therefore meet two conditions. Had a sufficiently large translucency is required to provide the information contained in the plant leaf chloroplasts with radiation in the range of 320 to 700 nm. A in this wavelength range adsorptive or reflective coating acts would affect the energy supply of the plant cell. Inside the chloroplasts located as plasmatic phase of the stroma. This is interspersed with stroma thylakoid membranes (Membraneinstülpungen), the multi-roll-like superimposed is the Granum. This may in the membranes as a pigment chlorophyll is now embedded in turn absorb light from the above-mentioned wavelength range and use this energy for the production of ADP (adenosine triphosphate) from ADP (adenosine diphosphate) and phosphate.

The second requirement is to meet a nanoscale protective layer must plant leaf, the orderly functioning of the stomata. Through the stomata (Greek stoma, mouth) or stomata, gas exchange is a plant. The stomata are usually of two bean-shaped cells called guard-formed, which enclose an opening, the gap. Counting the cells that surround the guard around, add more, we speak of stomatal apparatus (stomatal complex). The pores themselves are, strictly speaking, the actual gap openings. Guard-cells are usually in the lower epidermis of plant leaves, the grasses on both sides of the leaf, and floating leaf plants only at the top. The gas exchange with the surrounding air is especially important for the supply of CO<sub>2</sub>. Carbon dioxide is absorbed by plants through the processes of photosynthesis from the air. Thus, the diffusion through the cell walls function optimally, it must be as thin or permeable. Such cells evaporate but plenty of water, land plants would wither quickly with such leaves. About the separation of the intercellular space in the Journal of the dry outside air through the stomata, the plant receives control over the water loss. Through the pores by evaporation (stomatal transpiration or evaporation) instead, which creates a suction transported by water from the roots to the leaves: further points are important for the stomata. With the water are transferred from the soil and nutrients are concentrated in the leaves. In addition, the evaporation cools the leaves, this overheating in bright sunshine and not the specific temperature optimum, the enzymes in the leaf tissues, are not exceeded....

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**SI1825752**

**Coating compound made of an agent which generates SiO<sub>2</sub> with at least two antibacterial agents**

Inventor: JURGENS RALF [DE]; SCHWINDT SASCHA [DE]

[0001] The invention relates to an antibacterial coating composition, on base of a silicon dioxide-producing means, an application set, a nanoskalige coating on the base of polymerized SiO<sub>2</sub>, the preparation of the coating, the subsequent treatment of the coating as well as a multiplicity of uses, like appended more near explained.

**State of the art**

[0002] DE 102004014483 A1 concerns a porous inorganic oxide layer with at least a cationic polysaccharide contained in it. Here chitosan, becomes Chitosansalze, a cationic Chitosanderivat with

amino and ammonium functional groups and an alkyl or an acyl modified chitosan mentioned as bioactive ingredient. From the present invention this document differs by the different surface structure, those non porous is and and. A. deacetylated Chitosan derivatives begin.

[0003] US 6306835 A1 describes 3-Trimethylammonium-2-hydroxypropyl-N-chitosan (CHI-Q188) as antimicrobial active ingredient. It becomes described that to the preparation more homogeneous, transparent layers the use is pure aqueous nano-brine of advantage, since in these the antimicrobial cationic polysaccharides are good soluble. Around the fact it is provided that the first formed alcoholic nano-brine by careful removal of the alcohol in aqueous nano-brine converted become.

[0004] DE 20 2004 019,687 A1 concerns the use of particles, whose at least partly consist surface of metallic silver, with a diameter of less than 100 Nm, and, which as clearcoat formed is in accordance with claims. With the described layers it essentially acts around substantial thicker lacquer layers within the range of 1 m to 100 m.

[0005] DE 20 2005 006,784 A1 describes, a porous Sol gelcoating with antimicrobial effective substances/compounds those, prepared after the Sol gelprocess, selected is from the group, existing from Ag, Zn, Cu, Sn, I, width unit, Gr, CR, their ions as well as their compounds and mixtures of it, in particular silver-organic compounds, silver-inorganic compounds, zinc-organic compounds, zinc-inorganic compounds as well as their salts and oxides. These compounds are not subject-matter of the present invention. Furthermore this Patent Laid open describes the presence of carbon in detectable amount in the Sol gellayer, when case of planar is not desired here.

[0006] The disadvantage of the before described antimicrobial substances in the state of the art is in case of the cationic polysaccharides in only the effect limited to negative charged surfaces of bacteria, to cationic or nonionic microorganisms becomes only insufficient because of the growth hindered and/or killed. After newest studies a resistance adjusts itself against silver ions, the effectiveness of the antimicrobial component diminishes thus after few weeks, from a durable antimicrobial effect cannot thus not the speech be with certain microbial organisms.

[0007] Disadvantages in DE 20 2005 006,784 A1 described organometallic compounds are their strong polluting effect, since excluded due to the porous structure of the Sol gelcoating an erosion and thus an entry are not into the environment. These active ingredients are found increased in the food chain up to the humans and are to a considerable degree harmful for the humans and the environment, thereby. Tributylzinn is erbgutschädigend.

[0008] It is already known, antibacterial and/or. antimicrobial active ingredients to the destruction and/or. Growth inhibition of bacteria, funguses, to use algae and viruses and to the protection of materials and foods against microbial impurity. The environmental, microbial contamination through approx. 2 to 3 billion different microorganisms, of it alone approx. a steady increasing health Gefährdungspotenzial represents 15.000, which can spread over the air and settle thus almost any surface. In the following the term becomes "antimicrobial" used, thus is in particular the biocides and/or for the effect of the substances. biostatic effect on microorganisms meant.

[0009] It is known to produce Sol gellayers by means of a Sol gelprocess. Metallic oxide xerogels become preferably from SiO<sub>2</sub>, R-SiOn, R<sub>2</sub>SiOn, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub> or their mixtures used, whereby R = H, alkyl, aryl, Epoxy alkyl, Aminoalkyl and n = 1.5 or 1 can be. One by the hydrolysis and condensation reactions receive these gels from silicon alkoxides. The molecules become connected with one another due to the polymerization taken place during the process. The total volume of the sols becomes polymerized thereby. The polymerized silicon oxides form a SiO<sub>2</sub>-Gel (see. J.C. Brinker, G.W. Sheared one, sol gel Science, Academic press, London 1990).

[0010] The continuous condensation bottom alcohol splitting off leads to spherical increasing of the particles, which itself starting from a thickness of approx. 70 Nm due to the light scattering at the particles (Tyndall effect) to prove leave. By a procedure referred as gelation sols can change into gels. The particles continue to grow, until they touch themselves and network by other condensation. Finally thereby a solid

phase is formed which is penetrated with a liquid phase. As gels form beständige, light deformable disperse systems rich at liquid become referred, which of a solid, irregular three-dimensional network and a liquid to consist.

The functionalization become the sol from tetraethoxysilanes aliphatic and aromatic aldehydes, carbonic acids or aminocarbonic acids an added. Alternative one becomes organic modified by changed substituents at the Precursor ( $R'Si(OC_2H_5)_3$ ) the  $SiO_2$ -Netzwerk. Likewise for it the synthesis of various Alkyltriethoxysilane with Azomethinbindung becomes by the conversion of aminopropyltriethoxysilanes with Benzaldehydderivaten and/or. Acetylacetone used.

Inorganic-oxidic gels become frequent by conversion of element alkoxides with alcohol-water mixtures or in pure water prepared. The alcohol serves here the generation of an homogeneous reaction mixture and can become by other per tables or aprotic solvents replaced. The flexibility and porosity of the Sol gellayers can be changed by modification of the prescriptions. A higher portion of  $R-SiOn$  and/or  $R_2SiOn$  improves the flexibility of the layers, by the formation of composite oxides such as  $Al_2O_3$ ,  $ZrO_2$ ,  $TiO_2$  can the abrasion stability and specific hardness amplified become.

## **Invention**

### **Antibacterial coating composition**

[0011] An object of the invention is it first to make a novel antibacterial coating composition available.

[0012] This object becomes by the combination of the  $SiO_2$  of producing means as well as particular portions of particular antimicrobial agents dissolved, those from a selection of two by three different material classes made.

[0013] The invention relates to so an antibacterial coating composition, contained 50 Gew % to 99.9 Gew %, preferably 80 Gew % to 99 Gew %, a  $SiO_2$ -erzeugenden of means, whereby the coating composition contains 0.1 Gew % to 50 Gew %, preferably 1 Gew % to 20 Gew %, related to the total composition, at least an antibacterial active ingredient in the form of cationic, anionic or nonionic deacetylierten chitosans and Chitosanderivaten and/or phenols of the group of the halogenated Dihydroxydiphenylmethane, - sulfides, and - ether and/or substituted quaternary ammonium salts of the alkylated phosphoric acid, whereby the antibacterial active ingredient selected from at least 2 compounds of the 3 appended connecting classes in the form of cationic, anionic or nonionic deacetylierten chitosans and Chitosanderivaten and/or phenols of the group of the halogenated Dihydroxydiphenylmethane, - sulfides, and - ether and/or substituted quaternary ammonium salts of the alkylated phosphoric acid.

[0014] An other preferred embodiment of the present invention concerns a composition of the before-described type, with that the  $SiO_2$ -erzeugenden means selected is out

0 to 100 Gew %, preferably to Gew % tetraethoxysilanes,

0 to 100 Gew %, preferably to Gew % Trimethoxymethylsilan, and

0 to 100 Gew %, preferably to Gew % Dimethoxydimethylsilan.

[0015] An other preferred embodiment of the present invention concerns a composition of the before-described type, with which means producing the  $SiO_2$  contains  $Al_2O_3$ ,  $TiO_2$ ,  $ZrO_2$ ,  $MgO$  and/or  $V_2O_5$  further up to 20 Gew %, whereby these additives are in arbitrary mixing ratios present, preferably in mixing ratios between 0,1 Gew % and 50 Gew % from the group of the  $Al_2O_3$ ,  $TiO_2$ ,  $ZrO_2$ ,  $MgO$  and  $V_2O_5$ , particularly preferred in mixing ratios between 1 Gew % and 20 Gew % from the group of the  $Al_2O_3$ ,  $TiO_2$  and  $ZrO_2$ .

[0016] An other preferred embodiment of the present invention concerns a composition of the before-described type, with that the active ingredient as halogenated Dihydroxydiphenylmethan, - sulfide and -

ether selected is hydroxy more diphenylether from 5,5' - Dichlor-2,2' dihydroxy diphenylmethan, 3,5,3',5' - Tetrachlor-4,4' dihydroxy diphenylmethan, 3,5,6,3',5',6' - Hexachlor-2,2' dihydroxy diphenylmethan, 5,5' - Dichlor-2,2' dihydroxy diphenylsulfid, 2,4,5,2',4',5' Hexachlordihydroxydiphenylsulfid, 3,5,3',5' - Tetrachlor-2,2' Dihydroxy diphenylsulfid, 4,4' - Dihydroxy-2,2'dimethyl-diphenylmethan, 2' 2-Dihydroxy-5',5-diphenylether or 2,4,4' Trichlor-2'.

[0017] These phenols are available as 5,5' - Dichlor-2,2' dihydroxy diphenylmethan (Preventol of dd, Bayer AG), 3,5,3',5' - Tetrachlor-4,4' dihydroxy diphenylmethan (Monsanto corporation), 3,5,6,3',5',6' - Hexachlor-2,2' dihydroxy diphenylmethan (Hexachlorophen), 5,5' - Dichlor-2,2' dihydroxy diphenylsulfid (Novex, Boehringer Mannheim), 2,4,5,2',4',5' hexadecimale chlorine dihydroxy diphenylsulfid, 3,5,3',5' - Tetrachlor-2,2' Dihydroxydiphenylsulfid (Actamer, Monsanto), 4,4' - Dihydroxy-2,2'dimethyl-diphenylmethan, 2' 2-Dihydroxy-5',5-diphenylether (Unilever), 2,4,4' Trichlor-2' hydroxy more diphenylether (Irgasan DP 300, Ciba-Geigy).

[0018] An other preferred embodiment of the present invention concerns a composition of the before-described type, with which it concerns with the phenol 2,4,4' Trichlor-2' hydroxy more diphenylether.

[0019] An other preferred embodiment of the present invention concerns a composition of the before-described type, with which it concerns with the active ingredients cationic, anionic or nonionic deacetylierten chitosans and Chitosanderivate, preferably around Trimethylchitosaniumchlorid, the Dimethyl-N-C2. to C12-alkylchitosaniumiodid, quaternary Chitosansalze with anions of the phosphoric acid, O-Carboxymethylchitin-sodium salts, O-Acylchitosan, N, O-Acylchitosan, N-3-Trimethylammonium-2-hydroxypropyl-chitosan and O-TEAE-Chitiniodid.

[0020] An other preferred embodiment of the present invention concerns a composition of the before-described type, with which the chitosans and Chitosanderivate are low molecular chitosans and Chitosanderivate, whereby the molecular weights between  $1,0 \times 10^5$  g/mol and  $3,5 \times 10^6$  g/mol, preferably between  $2,5 \times 10^5$  g/mol and  $9,5 \times 10^5$  g/mol lie.

[0021] An other preferred embodiment of the present invention concerns a composition of the before-described type, with which the active ingredients are quaternary ammonium salts of the alkylated phosphoric acid, whereby each of the alkyl radicals exhibits, independently 1 to 12 carbon atoms and/or halogenated ammonium salts, preferably the Cetyltrimethylammoniumbromid, the Didecyldimethylammoniumchlorid, the Hexadecylpyridiniumchlorid and the Polyoxyalkyltrialkylammoniumchlorid. With these substituted quaternary ammonium salts of the alkylated phosphoric acid, their biostatic effect is in numerous publications documented. Paths of the very good water solubility of these salts their integration is particularly favourable into the SiO<sub>2</sub>-Matrix. Also halogenated quaternary ammonium salts like the Cetyltrimethylammoniumbromid, knew its antimicrobial effect bottom evidence provided and into the SiO<sub>2</sub>-Matrix to the use to come.

[0022] An other preferred embodiment of the present invention concerns a composition of the before-described type, with which the microbial active ingredients in mixing ratios between 0,1 Gew % to 99,9 Gew %, preferably 1 Gew % to 99 Gew %, in particular 5 Gew % to 95 Gew % are present.

[0023] The mixing ratio of the antimicrobial active ingredients chitosan, 2,4,4' Trichlor-2' hydroxy more diphenylether (triclosan) and quaternary ammonium salts in the sols among themselves should become set as follows. In sum the antimicrobial active ingredients between 0,1 Gew % and 50 Gew % can constitute, preferably 1 to 20% related to the total composition of the sols. The portion of the respective antimicrobial active ingredients can be thereby between 1 volume % and 98 volume %. By different prescriptions (quantities) the antimicrobial effect can become on the respective microbe population the purpose of the highest effect set.

[0024] An other preferred embodiment of the present invention concerns a composition of the before-described type further contained conventional auxiliary and additives, in particular acidic and basic polycondensation catalysts and/or Flouridionen.

[0025] The invention the object continues to be the basis, an application set to make available, which finds both with industrial application as well as in the DO it yourself range application.

[0026] This object becomes dissolved by the selection of the coating composition as well as particular application means.

[0027] The invention relates to therefore an other application set, the contained composition of the before-described type as well as application means for the purification and preparation of the substrates which can be coated, as well as in the form of individual packaged Sachet cloths. The aforementioned application means can cover bundle-large between 0,25 I to 800 I

### **Nanoskalige coating on carriers**

[0028] The invention is the basis the other object, a nanoskalige, and antimicrobial, to create in particular biocides coating on base of an inorganic polymerized SiO<sub>2</sub>-Schicht on arbitrary organic or inorganic supports which different than the layers in the state of the art porous are not and besides both hydrophobic as well as oleophobic is.

[0029] This object becomes by the combination of the SiO<sub>2</sub> of producing means as well as particular portions of particular antimicrobial agents dissolved, those from three different material classes alone or preferably as combination of at least two material classes made.

[0030] The invention relates to therefore further nanoskalige, in particular 50 Nm an antibacterial coating thick to 500 Nm, preferably between 120 Nm and 250 Nm, a contained not porous inorganic polymerized SiO<sub>2</sub>-Schicht, applied on a support material, whereby the coating 0.1 Gew % to 50 Gew %, preferably 1 Gew % to 20 Gew %, related to the total composition, at least an antibacterial active ingredient in the form of cationic, anionic or nonionic deacetylierten chitosans and Chitosanderivaten and/or phenols of the group of the halogenated Dihydroxydiphenylmethane, - sulfides, and - ether and/or substituted quaternary ammonium salts of the alkylated phosphoric acid, whereby the antibacterial active ingredient selected from at least 2 compounds of the 3 appended connecting classes in the form of cationic, anionic or nonionic deacetylierten chitosans and Chitosanderivaten contains and/or Phenols of the group of the halogenated Dihydroxydiphenylmethane, - sulfides, and - ether and/or substituted quaternary ammonium salts of the alkylated phosphoric acid.

[0031] The layers can become in varying thickness from 50 Nm to 500 prepared, preferably however in layers between 120 Nm and 250 Nm, there the SiO<sub>2</sub>-Nanopartikel used in the spraying method on the not-lung-common size of > 100 Nm set become.

[0032] Also preferred is a coating of the before-described type, with which the SiO<sub>2</sub>-Schicht at least partly consists of R-SiOn, and/or R<sub>2</sub>-SiOn, whereby R = H, alkyl, aryl, Epoxy alkyl or Aminoalkyl and n = 1.5 is larger or.

[0033] Also preferred is a coating of the aforementioned type, with which the SiO<sub>2</sub> contains layer Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, MgO and/or V<sub>2</sub>O<sub>5</sub> in arbitrary mixing ratios, preferably in mixing ratios between 0,1 Gew % and 50% Gew % from the group of the Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, MgO and V<sub>2</sub>O<sub>5</sub>, particularly preferred in mixing ratios between 1 Gew % and 20 Gew % from the group of the Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub>.

[0034] The advantages of the antimicrobial coating according to invention and/or. Surface refinement essentially consist of the subsequent points:

1. Very high hydrophobic and Oleophobicwerte, more comparable with the values of coatings, which become generated by means of fluorine carbon resins. Thus an extreme strong antiadhesive effect, which still exceeds those of the ptfе, goes it becomes contact angles of 139,5 deg. achieved (Institut high stone). This is favourable, in order to prevent the Erstbesiedlung of the surfaces by microorganisms, which test before the settlement of the substrate by the delivery of a tacky secretion quasi whether the surface for a settlement is suitable. Since this secretion on the oleophoben surface remains hardly clinging, it does not



come only at all in many cases to a settlement and into sequence to a colony formation.

2. The very good adhesive coating can be laid on because of the very good ductile properties on substrates of most different geometry and nature.

3. The SiO<sub>2</sub>-Matrix (glass) is very abrasion-stable and is characterised by not measurable abrasion and one much high hardness. Due to the ultradünnen layers of < the glass layer their very good flexible properties keeps 250 Nm.

4. The immobilization of the antimicrobial active ingredients the prevented elution and dilution of the active ingredients and thus removing the antibacterial activity.

5. The coating composition consists of non-toxic compounds, which are more degradable biological. Silicates like the SiO<sub>2</sub> are the most frequently occurring compounds of the earth's crust.

6. With most different fabrics Waschversuche became the determination of the permanence of the coating performed. A requirement of the textile industry became after a resistance to washing of > 50 laundries continuous achieved, provided that the substrate is not likewise after this number of washing processes degradiert.

7. By the mixture of most different antimicrobial substances a broadband Antimikrobiotikum can become prepared that suitable is to fight also strong heterogeneous populations. The prescription can become the respective ambienten requests adapted. Like that it is possible, particular prescriptions for fabrics, for hygiene-sensitive surfaces in hospitals to manufacture for breathing air filters or for aquatic environments and to obtain thus the optimum growth blockade. Training of resistances becomes more other (e.g. MRSA) prevented.

[0035] Other subject-matter of the invention is a coating of the aforementioned type as coating for hard surfaces, in particular as Antifouling means.

[0036] Object of the invention is it likewise to make a novel Antifouling coating available which overcomes the disadvantages comparable coatings to the state of the art, hydraulic and oleophobe properties exhibits, so that an effective protection of endangered surfaces before adhesion of biopolymers and microorganisms, with simultaneous indulgence of the environment is, ensured and the abrasion-stable for a lasting protection and thus is wasserunbelastend.

[0037] This object becomes according to invention dissolved by the fact that the surfaces a polymerized SiO<sub>2</sub> - matrix exhibits into which antimicrobial active ingredients and/or metal oxides are storable, whereby these active ingredients not eluierbar and immobilized is applicable into the SiO<sub>2</sub>-Matrix.

[0038] The coating is due to their polymerized SiO<sub>2</sub> matrix glass-similar. With use in moved waters from this an high hydrodynamic efficiency, which leads to an effective self cleaning, results. By the SiO<sub>2</sub> matrix is the coating furthermore abrasion-stable, scratching and scheuerfest.

[0039] This is the use of the coating composition of the aforementioned type as Antifouling means for with water, in particular with sea and sea water in compound standing surfaces.

[0040] An other object of the invention concerns therefore the use of the coating for with water, in particular with sea and sea water in compound standing surfaces to the protection before Biofouling causing biopolymers and/or microorganisms as well as a method to the preparation of a such coating.

[0041] Surfaces in aquatic habitats are the formation of tacky biopolymers exposed, which introduce a Biofoulingprozess. Bottom Biofouling understands one the deposition of living organisms on material surfaces in aqueous environment, which their physical surface properties negative affect. Each Foulingprozess in the water starts with the attachment of organic molecules at a surface. Its solidification the possible other settlement of bacteria, Diatomeen, shells and cancers etc. In marine environment

experiences each surface Biofouling, which leads to one of the largest problems with the surfaces in the marine technology. Particular surface coatings, “Antifouling coatings so mentioned”, are to prevent the vegetation at hulls, sea water constructions, oil platforms, harbor facilities and tubes, as well as at other artificial underwater structures. It is known, hulls, to provide oil platforms and harbor facilities with Antifouling coatings.

[0042] The TRGS516 (technical rules for dangerous materials, Antifouling, output 1996) shows the conditions of the safety-relevant, as well as ergonomical requests according to industrial medicine and hygienic to dangerous materials regarding Inverkehrbringen and handling. It regulates the use of very toxic, toxic and Antifouling colors injurious to health. Known Antifouling coatings are based either on forms of the mechanical purification or on the discharged one of toxic biocides from matrix coatings or on a combination of both. The mechanical purification strong slippery surfaces become generated by the use of Teflons or silicone in the coating, which prevent the attachment of Foulingstoffen.

[0043] In addition one differentiates between insoluble and soluble coatings. The insoluble Antifouling coatings exhibit an high abrasion resistance, soluble Antifouling coatings are eroding and become from flowing water slow removed. Known Antifouling coatings prevent the settlement phase of the Foulingprozesses by their biocides.

[0044] In that DE 101 17 945 becomes a Antifouling coating a without biocide described, which biomimetisch as dual Kompositsystem, constructed with cleaning, an hydrodynamic very smooth, a nano-structured surface pore size defined in form of of a pore-formed component with, which I after the particle size of tacky dirt particles arranges, and a pore-filling component, which exhibit gel-formed desert hydrophobic, the adhesive properties of the adhesive biopolymers adapted properties.

[0045] EP 1,446,011 A1 describes a Antifouling composition on the base of 4-Bromo-2 (4-Chlorophenyl) - 5 (Trifluoromethyl) - 1 H-Pyrrole-3-Carbonitril.

[0046] EP 1,457,531 A1 describes likewise a Antifouling composition on the base of a metalliferous copolymer and the active ingredient 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one.

[0047] EP 65 10 34 A1 describes a rot-preventing painting composition, which contains a copper oxide or a Kupferthiocyanat and a copper salt of 2-Pyridinthiol-1 as effective compound.

[0048] EP 64 66 30 describes a coating composition, which contains several Antifouling means as essential components or and or several copolymers, the available is from a monomer mixture, comprising monomer A of the formula (1)

<EMI ID=1.0>

[0049] Where R< 1> and R< 3> in each case a group is, selected from alkyl groups, cycloalkyl groups and aryl groups, and which can be identical or from each other various, and X is a Aryloxygruppe, a Methacryloxygruppe, a Maleinoyloxygruppe or a Fumaroyloxygruppe and a monomer B of the formula (2)

Y (CH<sub>2</sub>CH<sub>2</sub>O) NR< 4> (2)

where R< 4> an alkyl group, a cycloalkyl group or aryl group is, Y a Aryloxygruppe, a Methacryloxygruppe, a Maleinoyloxygruppe or a Fumaroyloxygruppe and a n is a whole number from 1 to 25, and the amount of the Antifoulingmittels amounts to 0.1 to 80 Gew % on base of the weight of the solid content of the coating composition.

With the biocides one differentiates between “metal-organic biocides”, like arsenics, coppers and Tributylzinn, and “natural biocides”, with which many marine organisms themselves protect their surface from Biofouling. They can antialgalen as biogenous active ingredients antibacterially, work antifungisch and makrofoulingverhindernd. However the need grows at altogether non-toxic vegetation protection methods due to stricter legislation

[0050] The antimicrobial active ingredients, like chitosan, 2,4,4'-Trichlor-2'-hydroxy more diphenylether and quaternary ammonium salts prevent the effective settlement of surfaces of the support material by bacteria, fungi, viruses, algae, Diatoms, shells and cancers in air environment, aqueous environment and air water systems, work thus antibacterially, antifungal, fungicidal, algicidal and virocidal.

[0051] The Antifouling coating is water and environmental neutral. It is simple in the processing and can by spraying (aerosol) or capers on the surfaces applied become. By storing the active ingredients into the SiO<sub>2</sub>-Matrix they cannot be washed dissolved or. Furthermore it is favourable that your effectiveness does not decrease over the time.

[0052] Further it is of advantage to bring metal oxides for example to Al<sub>2</sub>O<sub>3</sub> and/or TiO<sub>2</sub> into the SiO<sub>2</sub> matrix. This Antifouling coating according to invention is characterised with it by a strong hydrophobic and oleophobic effect.

[0053] One with the Antifouling coating according to invention treated surface represents a very poor clamping coat situation for polymers and/or for microorganisms, so that hardly colonies can form, biostatic active ingredients is antimicrobial acting substances, with whose contact the microorganisms adjust their growth. Beyond that it exhibits a thickness within the nanometer range and is acidic one and caustic solutions opposite very stable. Teflonhaltige and/or fluorcarbonhaltige or silikonhaltige coatings, which are to cause an attaching of microorganisms due to their smooth surface, are only hydrophobic ones, not however oleophobic, partially even oleophilic, so that microorganisms on the oil-wetted surfaces can quite settle and take place Biofoulingprozesse. Beyond that these coatings are not abrasion-stable and are subject therefore to strong wear. In the processing these coatings likewise critical are to be evaluated, since they contain alcohol-based solvents.

[0054] Metal-organic coatings, which contain arsenics, coppers, or Tributylzinn, are water-getting biocide dirty, strong and thus strong polluting. Furthermore Tributylzinn haltige colors are in the USA since 01.06.2005 even forbidden. Beyond that these not abrasion-stable coatings are eroding and become by flowing water removed. The active ingredients increased in the food chain are found to biocides up to the humans and are to a considerable degree harmful for the humans and the environment, thereby.

[0055] The nanoskalige Antifouling coating on SiO<sub>2</sub>-Basis however the satisfied requirement after both hydrophobic and oleophobic effect. Microorganisms cling only very heavier on this surface and can form so hardly colonies. By the complexation of the polymerized SiO<sub>2</sub>-Schicht by means of antibacterial chemicals a not eluierbares Antifouling becomes generated, which is water-neutral.

### **Cardboard box coating**

[0056] Other subject-matter of the invention is a coating of the aforementioned type in form of a packing coating.

[0057] An other object of the invention is it to make available a coating as well as methods to the protection before moisture of packages, like cardboard boxes on paper and sticking basis, like also on base of fabrics and tissues of most different type, before rains, snows, condensed water, sea water, extreme high relative humidity and microorganisms, with simultaneous retention of the breathing activity (diffusible) on the base of ultradünnen SiO<sub>2</sub>-Beschichtungen and simultaneous antimicrobial protection, as well as a method for this.

[0058] Packages, like cardboard boxes serve all type as waterproof package of goods and goods, in order to ensure as safe a transport of the cargo as possible, i.e. one strives to a Antifouling coating to reach.

[0059] Here the package is not only to protect the content against damages mechanical type, but the package is to protect the cargo also against impairment by waters or moisture. The cargoes are moisture of most different type, like e.g. Rain, snow, condensed water, sea water, extreme high relative humidity or wet pile documents, exposed. Moistened or wet-damaged cardboard boxes e.g. suffer depreciations. by linear deformations, twist features, changes in evenness and color, reduction of the mechanical tear

strength and. With the storage in the stack a Feuchtigkeitsüberschuss leads to swelling the fibers in the edge portions thereby among other things in their edges the wavy can. These damages are irreversible, there it with the later drying process to forgiven due to internal stresses with uneven distribution of the moisture within the sheet and for spotting (edges of drying) come. Charge sweat can particularly with travels from cold to warm and/or. with the deletion in tropical ports develop, if the good did not become sufficient heated during the journey and e.g. when opening the hatchways and/or. Container doors of the warm ambient air exposed becomes. A certain breathing activity is quite desired with some packages, if e.g. Products packaged become, which deliver moisture after packing still. In the range of the Pharma and medical technology industry some products e.g. become. warm and wet packaged. It exists thus the need at packages, which are in the layer, to deliver moisture from the inside outward simultaneous however from the outside inward waterproof is.

[0060] It is thus provided cardboard boxes on the outside with PL coatings (PE) too known, packages, in order to prevent the penetration of water in the form of rains, snows, condensed water, sea water, extreme high relative humidity or wet pile documents into the package. Simultaneous one however the prevented PL coating the diffusion of moisture, z. B. that residual moisture of the product which can be packed arrives, from the inside outward. From the outside applied PL coating works the moisture in and at the cardboard box condensed in this place like a vapor barrier. By the moisture absorption the stability of the carton, in particular from the inside becomes significant affected in the first 3-5 days. During this time the frequency of the TUL processes in such a way specified (transport, envelope, storage) is highest. Damages at the carton are preprogrammed thereby which has immense costs for remedy to the sequence.

[0061] Condensed water molecules are approx. 700-mal larger as vaporous water molecules, is called water vapor is in the layer by the coating to be diffused. Condensed molecules are substantial larger and become thus at the surface retained. The coating is glassy due to the polymerized SiO<sub>2</sub>-Matrix and favourable-proves thereby very abrasion-stable, acid and caustic solution-stable as well as scratch-proof.

[0062] Object of the invention is it to create a novel packing coating those the disadvantages of the polyethylene coating (vapor barrier) prevented, simultaneous wasserundurchlässige and breathe-active properties exhibits, hydrophobic and simultaneous oleophobic and antimicrobial is and the so inexpensive number of the damages reduced and but ensures that packages even multiple used to become to be able.

[0063] This object becomes dissolved by the use of the coating composition of the before-described type on/in packages, like cardboard boxes on paper and sticking basis, as also on base of fabrics and tissues and Gewirken.

### **Coating for aquariums/Terrarien**

[0064] Other subject-matter of the invention is a coating of the aforementioned type of aquariums or Terrarien, in particular from sea water or fresh water aquariums.

### **Coating of organic materials**

[0065] Other subject-matter of the invention is a coating, with that the support material from the organic materials, in particular wool, cotton (cellulose), fabrics, paper, paperboard, nature sponge, art sponge, leather, wood, carton and plastics exists.

[0066] As substrate surfaces used can become, exist those from plastic, wood, leather, textile tissues, felts, nonwoven fabrics, Non wovens and Gewirken. By the ductile properties of the coatings all geometric shapes can be treated, a very smooth, homogeneous surface of lowest surface tension always develops.

### **Coating of inorganic materials**

[0067] Other subject-matter of the invention is a coating of the aforementioned type, with which the support material exists metal, glass, artificial rock of the inorganic materials, in particular such as concrete, brick, tiles, fronts, finery.

[0068] Other subject-matter of the invention is a coating of the aforementioned type, with which the support material contains composite materials like glass-fiber reinforced plastic and/or metal plastic fabric.

### **Coating of plastics**

[0069] Other subject-matter of the vorliegenden invention is a coating of the aforementioned type, with which the support material artificial fibers, felts and tissue, in particular from polyester, contains polypropylene, polyethylene of high density, polyethylene low density, polyacrylonitrile, polyamide, Polyimid, Polyaramid, aramid, meta aramid, para aramid, polytetrafluoroethylene, polyvinylidene fluoride, polyphenylene sulfide

### **Preparation of the coating**

[0070] The present invention is the basis further the object to make a method available to the preparation of the before-described coating

[0071] The invention relates to such a method to the preparation of a coating of the before-described type, how in a first process step the formation of a Solgels also nano-potash towards particles in actual known manner by hydrolysis of a Prekursors in water performed becomes and in a second process step/the dispersed antimicrobial active ingredients of the before-described type of the sols supplied solved in an hydrophilic solvent become.

[0072] Here it is preferred that the Prekursor is selected from the group of the Alkyltriethoxysilane and the Aminopropyltriethoxysilane, that up to 20 Gew %  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{MgO}$  and/or  $\text{V}_2\text{O}_5$ , related to the total proportion at  $\text{SiO}_2$ , added are and that the conversion within 0,5 to 72 h, with temperatures of 5 deg. C to 60 deg. C made.

[0073] It is more other preferred that the hydrophilic solvent selected is from water and/or linear or branched alcohols with up to 6 carbon atoms, in particular water-contained alcohols, in particular ethanol.

### **Application of the coating**

[0074] The invention is the basis the other object to make available a method to the application of the coating.

[0075] The invention relates to therefore further a method to the application of the coating composition, on support materials of the before-described type by contacting the surface, in particular spraying, immersion, spinners, capers, Begiessen, Foulardierung, Filmbegiessen and spraying bars with at least a spray nozzle. The coating and/or. Surface refinement can take place via conventional methods such as a spraying (spray coating), immersion (dip coating), spinners (spin coating) capers, Begiessen. Likewise possible and established are industrial coating methods such as Foulardierung, Filmbegiessmaschinen, spraying bar with or several spray nozzles.

[0076] The present invention concerns finally various types of use of the application of the coating composition.

### **antifouling**

[0077] First the coating composition according to invention of the aforementioned type can become as Antifouling means for with water, in particular with sea and sea water in compound standing surfaces used.

### **Cardboard box coating**

[0078] More other the coating composition according to invention of the aforementioned type on/in

packages, like cardboard boxes on paper and sticking basis, can as also on base of fabrics and tissues and Gewirken used become.

### **Corrosion protection for technical apparatuses and containers**

[0079] The present invention concerns further the use of the aforementioned coating composition as corrosion protection of technical apparatuses or containers, in particular heat exchangers, evaporation radiators, Kesselrohren, heating surfaces, spraying adsorbents, spray dryers, refrigerators, chimneys from metal, catalysts, turbines, fans, reactors, silos for food, cement silo, lime silo, coal silo.

### **Corrosion protection for glass surfaces**

[0080] The present invention concerns further the use of the vorgenanten coating composition as corrosion protection before glass corrosion of glass surfaces, in particular windows, glass doors, devices and facade components from glass.

### **Stömungsverhältnisverbesserer**

[0081] The present invention concerns further the use of the vorgenanten coating composition as surface treatment to the improvement of flow conditions on surfaces of turbine wheels, turbine blades, heating snails, extruder screws, screws, injection nozzles, Windrädern, fans, compressor screws, compressor screws, turbocharger impellers.

### **Antimicrobial protective layer**

[0082] The present invention concerns further the use of the coating composition as antimicrobial protective layer of refrigerators, cooling resting and cooling spaces, in particular in commercial meat dismantling and processing plants.

[0083] The present invention concerns further the use of the coating composition as antimicrobial protective layer private spaces, in particular hospitals, used of surfaces in commercial or, senior hostels, meat-dismantling-operated, food production plants, large-scale catering establishments, and in vehicles, in particular aircrafts, person penalties, ships, trains and streetcars.

[0084] The present invention concerns further the use of the coating composition as antimicrobial protective layer of production machines in the food industry.

[0085] The aforementioned spaces and vehicles are always very susceptible due to the multiplicity of the users and the type of the processed stored foods to an increased occurrence of microorganisms, which establish themselves otherwise on the surfaces of the spaces. This can by the above mentioned. Coating (composition) reduced/avoided becomes.

### **Noise reduction**

[0086] The present invention concerns further the use of the coating composition as slipping layer for reduction/avoidance of noises, which result one on the other from rubbing surfaces.

### **Extensibility of the coating**

[0087] The composition according to invention is characterised finally by the fact that it exhibits an extensibility opposite the origin-large of up to 250%.

[0088] The present invention becomes subsequent first by embodiments in the form of manufacture examples and application examples more near explained.

### **Embodiment 1 “textile substrate”:**



## **1. Preparation aqueous biocides of a SiO<sub>2</sub> - Solgels**

[0089] Become 100 ml tetraethoxysilanes, 400 ml waters and 200 ml 0.01 N hydrochloric acid with ambient temperature (20 deg. C) mixed and continuous agitated (approx. 5 hours). An aqueous SiO<sub>2</sub> develops - for Solgel, with a solid content of approx. 4.5% SiO<sub>2</sub> with an average particle size of 6 Nm. Mixed in a second step 100 ml this Solgels with 100 ml 2% igen solution of the biocide combination (mixing ratio 50% chitosan 2s, 25% triclosan and 25% Cetyltrimethylammoniumbromid) in 5% acetic acid mixed and. The Solgel developed in such a way can become by means of various variants on textile substrates applied.

## **2. Preparation that biocides SiO<sub>2</sub> - coating on a textile substrate**

[0090] A Polyphenylensulfidfilz in DIN A4-Format became coated by immersion in that bottom 1 described solution. Subsequent one became the substrate with ambient temperature 24 hours dried, after conclusion of the drying phase developed the coating of approx. 150 Nm layer thickness on the fibers (see fig 2). The sols became complete reacted into a gel, which the individual fibers of the felt structure complete coated.

## **3. Antimicrobial examination of the felt sample**

[0091] The determination biocides of the effect became following EN 1040 by Institut Fresenius performed. The test organisms staphylococci became aureus (ATCC 6538) and Pseudomonases aeruginosa (ATCC 15442) used. With the help of the dilution Neutralistions and diaphragm filtration method shown could become that on the coating surface a bacteria reduction around factor 10< 5> after an exposition time of 60 minutes to register was.

## **Embodiment 2 “substrate from plastic”:**

### **1. Preparation aqueous biocides of a SiO<sub>2</sub> - Solgels**

[0092] 100 ml tetraethoxysilanes, 400 become ml ethanol and 200 ml 0.01 N hydrochloric acid with ambient temperature (20 deg. C) mixed and continuous agitated (approx. 5 hours). A liquid SiO<sub>2</sub> develops - for Solgel, with a solid content of approx. 4.5% SiO<sub>2</sub> with an average particle size of 6 Nm. Mixed in a second step 100 ml this Solgels with 100 ml 2% igen solution triclosan in 5% acetic acid mixed and. The Solgel developed in such a way can become by means of various variants on substrates from plastic applied.

### **2. Preparation that biocides SiO<sub>2</sub> - coating on a plastic substrate**

[0093] A plastic plate from PVC in the dimension of 30 cms x 30 cms became coated by spraying with that bottom 1 described solution. Subsequent one became the substrate with ambient temperature 24 hours dried, after conclusion of the drying phase developed the coating of approx. 150 Nm layer thickness on the plastic plate. The surface of the plate became complete coated.

### **3. Antimicrobial examination of the plastic plate**

[0094] The determination biocides of the effect became following EN 1040 by Institut Fresenius performed. The bacteria “Corynebacterium became minutissimum (gram positive), Propionibacterium of acnes (gram positive), staphylococci aureus (gram positive), staphylococci epidermitis (gram positive), Streptococcus courage to (gram positive), Escherichia coli (gram negative) and Pseudomonases aeruginosa (gram negative) used. With the help of the dilution Neutralistions and diaphragm filtration method shown could become that on the coating surface a bacteria reduction around factor 10< 5> after an exposition time of 60 minutes to register was.

## **Embodiment 3 “comparative test”**

[0095] 8 plastic plates became after embodiment 2 for a comparative test prepared. In an initial step the plates with a strong cationic surfactant became purified, subsequent fine-purified with an isopropanol solution in a second step. The plates 1 to 8 became as follows coated:

- <tb> plate 1< September> uncoated (0-Probe)
- <tb> plate 2< September> SiO<sub>2</sub>-Beschichtung with Chitosan+Triclosan (2% industrial union)
- <tb> plate 3< September> SiO<sub>2</sub>-Beschichtung with Chitosan+Triclosan (5% industrial union)
- <tb> plate 4< September> SiO<sub>2</sub>-Beschichtung with Chitosan+Quats (2% industrial union)
- <tb> plate 5< September> SiO<sub>2</sub>-Beschichtung with Chitosan+Quats (5% industrial union)
- <tb> plate 6< September> SiO<sub>2</sub>-Beschichtung with Triclosan+Quats (2% industrial union)
- <tb> plate 7< September> SiO<sub>2</sub>-Beschichtung with Triclosan+Quats (5% industrial union)
- <tb> plate 8< September> SiO<sub>2</sub>-Beschichtung with Chitosan+Triclosan+Quats (2% industrial union)
- <tb> plate 8< September> SiO<sub>2</sub>-Beschichtung with Chitosan+Triclosan+Quats (5% industrial union)

[0096] The examination of the antibacterial activity of the different coatings against bacteria the shining bacteria test became after Dr. Prolonged one (DIN 38,412 L 34/341), which as test on the toxicity of effluents used becomes, applied. As test bacterium shining bacteria of the type “Vibrio became fischeri” (NRRL-B-11117, gram negative) used. This test is based on the ability of certain marine bacteria (v.a.Meeresbakterien) to shine. This lamps, which due to enzymatic, energy-metabolicdependent process (Luciferin luciferasesystem) runs off. If these organisms come however into a toxic medium, then their luminosity becomes inhibited. The toxicity of single substances, material mixtures or eluates becomes photometric determined as shining inhibition. From the degree of the inhibition of shining one can draw conclusions on the degree of the growth inhibition.

[0097] In an initial step the conserved shining bacteria of the type NRRL-B-11177 in a broth reactivated and output lights the photometric measured and thus the zero-sample defined become. Afterwards the shining bacteria solution becomes applied on the substrate which can be examined by means of a pipette. After in each case 20, 40, 60, 80, 100, 120 and 140 minutes luminosity becomes photometric measured and with the output value of the zero-sample compared. The decrease of luminosity becomes as %-value “growth inhibition related to the zero-sample” over the time applied.

Used one became the Dr. Prolonged LUMISTox measuring position, existing from the LUMISTox metre, which LUMISTherm Temperiergerät and the thermal printer see LD 100. e.g.  
<http://www.rz.fh-ulm.de/labore/chemie/AUSSTATTUNG/BIOLUM/Biolum.htm>

[0098] Fig 4 shows the growth inhibition of the various coating in % measured over the time.

[0099] The long-term effect regarding antimicrobial effect could become successful detected. Also after more than 12 months significant restrictions of growth could become from over 90% shown.

#### **Embodiment 4 “hull”**

[0100] 4 plates of 30 x each 30 cms, from an used yacht trunk the cut became, by the present Antifouling paints by sandblast freed. The paints became remote up to opening the Gelcoat layer. Subsequent one became the Gelcoat layer with filler verse lease ELT and polished. Afterwards the plates with a Vinyl primer treated and with a commercial bottom structure color (make became: Jotun Hardtop 2C) dual painted. It concerned a 2-components color on PU basis. After drying the color different coatings became 2 applied after embodiment. The subsequent biocide combinations became applied.

- <tb> plate 1< September> SiO<sub>2</sub>-Beschichtung with Chitosan+Triclosan (2% industrial union)
- <tb> plate 2< September> SiO<sub>2</sub>-Beschichtung with Chitosan+Quats (2% industrial union)
- <tb> plate 3< September> SiO<sub>2</sub>-Beschichtung with Triclosan+Quats (2% industrial union)-->
- <tb> plate 4< September> SiO<sub>2</sub>-Beschichtung with Chitosan+Triclosan+ Quats (2% industrial union)

[0101] The examination of the antimicrobial effect again that became bottom embodiments 3 described shining bacteria test performed. Almost identical results, like in fig 4 shown, could become observed.

## Embodiment 5 “cardboard gnawing”

[0102] 8 cardboard plates of 30 x each 30 cms, prepared became from a commercial cardboard box material with a basis weight of approx. 400 g/m<sup>2</sup>, after embodiment 1 with different biocide coatings equipped.

<tb> plate 1< September> uncoated (0-Probe)

<tb> plate 2< September> SiO<sub>2</sub>-Beschichtung with Chitosan+Triclosan (2% industrial union)

<tb> plate 3< September> SiO<sub>2</sub>-Beschichtung with Chitosan+Triclosan (5% industrial union)

<tb> plate 4< September> SiO<sub>2</sub>-Beschichtung with Chitosan+Quats (2% industrial union)

<tb> plate 5< September> SiO<sub>2</sub>-Beschichtung with Chitosan+Quats (5% industrial union)

<tb> plate 6< September> SiO<sub>2</sub>-Beschichtung with Triclosan+Quats (2% industrial union)

<tb> plate 7< September> SiO<sub>2</sub>-Beschichtung with Triclosan+Quats (5% industrial union)

<tb> plate 8< September> SiO<sub>2</sub>-Beschichtung with Chitosan+Triclosan+Quats (2% industrial union)

<tb> plate 8< September> SiO<sub>2</sub>-Beschichtung with Chitosan+Triclosan+Quats (5% industrial union)

[0103] Subsequent ones were submitted the cardboard plates to an antibacterial test. Again the shining bacteria test became also here after Dr. Prolonged to the application brought. It did not surprise that also with this test almost identical results were to be registered, like bottom fig 4 shown. Since the biological processes on that take place biocides coating, the nature of the substrate does not have any influence on the antibacterial activity.

## Embodiment 6 “noise reduction

[0104] With various laboratory tests surprising found became that surfaces, which became according to claim 1 coated with formulations a significant reduced noise shown. It is known that if two materials are located in contact and thereby by outside excitation relative move to each other, thus Knarz and screeching noises or undesirable friction behavior to develop can. The stick slip effect, which is major responsible for such phenomena, becomes minimized by the coating. Bottom stick slip effect understands one the permanent transition about detention on sliding friction in a movement motion. Various oscillations depending upon nature of the surfaces rubbing one on the other, which become of the resonancable surface radiated as noise, develop. It is obvious that the coating functions as release layer between the friction partner and contributes thus to the noise minimization.

### Example 6.1

[0105] A metal plate from stainless steel 1,4571 with the dimensions 25 x 40 cms was provided to the half along the longitudinal axis with the coating. Subsequent one became attempted to produce by means of a cork, piece a rubber, a polishing cloth, piece a wood and piece a metal on the uncoated and on the coated surface of the metal plate by friction with different pressure Knarz and screeching noises. With the fact found became that noise on the coated half of the metal plate was more perceptible smaller significant to nearly no longer present.

### Example 6.2

[0106] A plastic plate from PMMA with the dimensions 25 x 40 cms was provided to the half along the longitudinal axis with the coating. Subsequent one became attempted to produce by means of a cork, piece a rubber, a polishing cloth, piece a wood and piece a metal on the uncoated and on the coated surface of the metal plate by friction with different pressure Knarz and screeching noises. With the fact found became that noise on the coated half of the plastic plate was more perceptible smaller significant to nearly no longer present.

### Example 6.3

[0107] A glass plate from window glass with the dimensions 25 x 40 cms was provided to the half along the longitudinal axis with the coating. Subsequent one became attempted to produce by means of a cork,

piece a rubber, a polishing cloth, piece a wood and piece a metal on the uncoated and on the coated surface of the metal plate by friction with different pressure Knarz and screeching noises. With the fact found became that noise on the coated half of the glass plate was more perceptible smaller significant to nearly no longer present.

### **Embodiment 7 “extensibility**

[0108] As in embodiment described, became a polyamide fiber with approx. 0.80 mm diameters with the coating according to invention in addition, with a active substance-free coating provide and subsequent bent. With the fact significant is more recognizable that in both cases at the outer radius of the fiber no tears arise and develop at the inner radius of the fiber to only slight upsettings. The polymer structure of the SiO<sub>2</sub>-Beschichtung here exemplary for the fiber shown, leads ductility, elasticity and extensibility to properties, which are not from crystalline SiO<sub>2</sub>-Strukturen known, i.e. Dependent ones of the elasticity of the substrate are extensibilities of up to 250% more achievable.

[0109] The present invention becomes other more near explained by figs.

[0110] Show:

**Fig. 1:** : A rem receptacle of the coating in accordance with manufacture example 1 on a PPS fiber (1500x magnification)

**Fig. 2:** : a rem receptacle of the aforementioned coating on a PES fiber (1500x magnification)

**Fig. 3:** : a rem receptacle of the aforementioned coating on a metal substrate.

**Fig. 4:** : the antibacterial activity shows various coatings over the time.

**Fig. 5:** : the extension ability of the aforementioned coating shows on a Pa fiber.

[0111] Fig. 1 shows those much smooth surface of the coating, which shows at no location porosity. The pores located in the fiber become covered by the coating.

[0112] Fig. likewise the very smooth surface structure of the coating shows 2, as well as complete coating of the round fiber. Only the smooth surface in compound with one much low surface tension creates the hydrophobic and oleophoben properties, which contribute to the fact that the Erstbesiedlung is made more difficult by microorganisms. There is numerous microorganisms known, which test before the settlement of the substrate by the delivery of a tacky secretion quasi whether the surface for a settlement is suitable. Since this secretion on the oleophoben surface remains hardly clinging, it does not come only at all in many cases to a settlement and into sequence to a colony formation.

[0113] Fig. the coating shows 3 on a metal substrate out. It is clearer more recognizable the fact that the homogeneous layer does not exhibit any pores but shows a closed, dense surface.

[0114] Fig. the antibacterial activity of the coatings according to invention shows 4 to hard surfaces, here PVC a plate opposite an uncoated or a one only with silicon dioxide-coated plate over a period of up to 140 minutes with ambient temperature, i.e. in the comparison. approx. 20 deg. C. The uncoated plate shown in the frame of the measurement inaccuracy no growth inhibition and only with silicon dioxide-coated plate achieved after 60 min. a growth inhibition of 20% and after 140 min of 40%

[0115] Fig. a polyamide fiber with approx. shows 5. 0.80 mm diameters with the coating according to invention provided is and subsequent bent becomes. With the fact significant is more recognizable that at the outer radius of the fiber no tears arise and develop at the inner radius of the fiber to only slight upsettings.

[0011] An object of the invention is it first to make a novel antibacterial coating composition available.

[0012] This object becomes by the combination of the SiO<sub>2</sub> of producing means as well as particular portions of particular antimicrobial agents dissolved, those from a selection of two by three different material classes made.

[0013] The invention relates to so an antibacterial coating composition, contained 50 Gew % to 99.9 Gew %, preferably 80 Gew % to 99 Gew %, a SiO<sub>2</sub>-erzeugenden of means, whereby the coating composition contains 0.1 Gew % to 50 Gew %, preferably 1 Gew % to 20 Gew %, related to the total composition, at least an antibacterial active ingredient in the form of cationic, anionic or nonionic deacetylierten chitosans and Chitosanderivaten and/or phenols of the group of the halogenated Dihydroxydiphenylmethane, - sulfides, and - ether and/or substituted quaternary ammonium salts of the alkylated phosphoric acid, whereby the antibacterial active ingredient selected from at least 2 compounds of the 3 appended connecting classes in the form of cationic, anionic or nonionic deacetylierten chitosans and Chitosanderivaten and/or phenols of the group of the halogenated Dihydroxydiphenylmethane, - sulfides, and - ether and/or substituted quaternary ammonium salts of the alkylated phosphoric acid.

[0014] An other preferred embodiment of the present invention concerns a composition of the before-described type, with that the SiO<sub>2</sub>-erzeugenden means selected is out

0 to 100 Gew %, preferably to Gew % tetraethoxysilanes,

0 to 100 Gew %, preferably to Gew % Trimethoxymethylsilan, and

0 to 100 Gew %, preferably to Gew % Dimethoxydimethylsilan.

[0015] An other preferred embodiment of the present invention concerns a composition of the before-described type, with which means producing the SiO<sub>2</sub> contains Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, MgO and/or V<sub>2</sub>O<sub>5</sub> further up to 20 Gew %, whereby these additives are in arbitrary mixing ratios present, preferably in mixing ratios between 0,1 Gew % and 50 Gew % from the group of the Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, MgO and V<sub>2</sub>O<sub>5</sub>, particularly preferred in mixing ratios between 1 Gew % and 20 Gew % from the group of the Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub>.

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