Abstract:

An antimicrobial coating prepared by the sol-gel method onto the surface of the substrate, comprising a binding agent that forms a coating layer oriented with respect to the substrate, and a polyhexamethylene guanidine salt or a mixture of these as an antimicrobiological component that is bound to the surface of the substrate by means of the above-mentioned binding agent. Furthermore, the invention relates to a coating solution for forming an antimicrobiological sol-gel coating, as well as a method for preparing and regenerating the coating.
ANTIMICROBIOLOGICAL COATING, COATING SOLUTION, AND METHOD FOR MANUFACTURING AND REFORMING THE COATING

Field of the invention

The invention relates to an antimicrobiological coating prepared by the sol-gel method. The invention also relates to a coating solution to be applied onto the surface of a substrate to form an antimicrobiological sol-gel coating. Furthermore, the invention relates to a method for forming an antimicrobiological sol-gel coating onto a substrate, as well as a method for regenerating the antimicrobiological activity of a coating on a substrate.

Background of the invention

The ease of cleaning various surfaces and the coating of surfaces to provide an antimicrobiological effect are of particular importance, for example, in hospitals, in food industry and in mass catering services, as well as in various public facilities. Conventionally, easily cleanable surfaces have been provided by means of coatings with a low surface energy, for example by means of various fluorine compounds (such as PFTE, i.e. Teflon), waxes, and silicones. These components that enhance cleanliness have been added into various paints for a long time. Various active components, for example biocides, such as silver or titanium oxide, have also been added into paints to provide a property to repel bacteria and other microbes.

However, the suitability of paint-type coatings for coating various types of materials is limited. Typically, paints are opaque in nature and they change the appearance and character of the surface to be coated. In many cases, a thick, film-like paint also sets constraints and demands on the quantity and quality of additives, such as biocides, to be used. The required cleanliness or the effect of the antimicrobiological agent will often remain insufficient as the paint film conceals the active ingredients in it. For an effective paint-based coating, a large quantity of additives is normally required.
To destroy microbes from surfaces, it is also possible to use various disinfectants that contain biocides. The action of conventional disinfectants is one-off, and in spite of their effectiveness, their action is of short duration.

Contamination of the surface to a lesser degree and, on the other hand, the easier cleanability of the contaminated surface together with the antimicrobial effect are desired properties of a coating in many uses. Furthermore, the coating to be applied should be wear-proof and provide protection from microbiological contamination for as long a time as possible, but without altering the properties of the surface to be coated.

**Brief summary of the invention**

It is an aim of the present invention to provide a novel type of antimicrobiological coating that is suitable for several surface materials and is prepared by the sol-gel method, and is unnoticeable, durable, maintains the original character of the surface and enhances the cleanliness of the surface, and also enables an effective long-term antimicrobiological effect on the surface to be treated.

To achieve this aim, the antimicrobiological coating of the invention, made by the sol-gel method, is primarily characterized in that the coating comprises

- a binding agent that forms a coating layer oriented with respect to the substrate, and
- as an antimicrobiological component, a polyhexamethylene guanidine salt or a mixture of these, bound to the surface of the substrate by means of the above-mentioned binding agent.

The coating solution according to the invention, to be applied onto a substrate to form an antimicrobiological sol-gel coating, is, in turn, primarily characterized in that the coating solution comprises at least a
solvent, a binding agent and, as an antimicrobiological component, a polyhexamethylene guanidine salt, or a mixture of these.

The method according to the invention for forming an antimicrobiological sol-gel coating on a substrate is, in turn, primarily characterized in that the above-described coating solution is applied onto the substrate, wherein the binding agent in the coating solution forms a coating layer oriented with respect to the substrate and binds the polyhexamethylene guanidine salt that acts as an antimicrobiological component, to the surface of the substrate.

The functionality of the coating according to the invention is based on the interaction of the suitable sol-gel coating and the applied active antimicrobiological component or biocide, resulting in a significant improvement in the duration of action of the biocide on the substrate coated with said coating, and good antimicrobiological effect even with a very small quantity of added biocide.

The adhesive used in the coating is, particularly, a silane, siloxane, metal alcoxide, silasane, or a mixture of these. The cleanliness of the coating can be improved particularly by using fluorosilane as the adhesive.

The biocide or antimicrobiological component used in the coating is a polyhexamethylene guanidine salt or a mixture of them, whose antimicrobial effect is based on an electrical charge. In particular, poly(hexamethylenediamine guanidium chloride) (PHMG) is used. By means of the binding agent, the water-soluble PHMG can be maintained on the surface of the substrate without a thick film-like coating and in such a way that the antimicrobiological effect of the PHMG is maintained in the coating even with small quantities of PHMG. In other words, the thin sol-gel coating according to the invention anchors the biocide in itself without blocking out the effect of the biocide. In this way, even a small quantity of biocide provides an effective and long-term antimicrobiological property on the surface of a substrate treated with the coating according to the invention. The
coating according to the invention has an antimicrobiological effect under both moist and dry conditions.

The coating solution according to the invention can be easily applied onto the substrate to be coated. The binding agent of the coating adheres chemically to the substrate material, if the chemistry of the substrate is suitable or the substrate has been treated to have suitable chemistry. Covalent metal-oxygen bonds are formed between the coating and the substrate material. Particularly when fluorosilane is used as the binding agent, the oriented structure of the binding agent with respect to the substrate will also make the binding agent form a hydrophobic and oleophobic surface onto the coating, resulting in a coating that is resistant to contamination and easily cleanable.

Among the binding agents of the coating according to the invention, it is particularly fluorosilane that forms a thin and non-film-like coating on the surface of the substrate to be coated. Consequently, fluorosilane does not block out the effect of the biocide used, but the biocide is on the surface of the coating, wherein even small quantities of biocide in the coating will provide a good antimicrobial effect. Furthermore, when fluorosilane is used, the coating can be provided with a hydrophobic surface that prevents the dissolution of very water-soluble PHMG from the coating.

The coating according to the invention adheres very well to stainless steel and other metal surfaces as well as glass and various ceramic surfaces. Painted surfaces and plastic materials can also be coated with a coating according to the invention. The surfaces can be pre-treated before coating to improve the adhesion of the coating. One advantage of the sol-gel coating is the ease of modifying the coating to be suitable for the use.

The coating according to the invention can be easily renewed, for example, in connection with cleaning. Consequently, the invention also relates to a method for regenerating the antimicrobiological activity of a coating already applied onto the surface of a substrate, in which method a porous or worn-out coating on the substrate is renewed or
the porous parts are refilled with the above-described coating solution that contains a polyhexamethylene guanidine salt or a mixture of them as an antimicrobiologically active component.

In addition to the ease of cleaning and the soil-repellent surface, the surface according to the invention has the advantages of good chemical and mechanical strength. Other advantages include unnoticeability and invisibility compared with paint coatings. The coating is also easy to prepare on site and to apply onto the surfaces to be treated. The coating has a short drying time at room temperature; in other words, it does not require separate thermal treatment. Furthermore, the long duration of the antimicrobiological effect of the coating according to the invention will reduce the need for cleaning chemicals.

The coating according to the invention can be applied widely in various uses, and the coating can also be easily adopted to new applications. Particularly hospitals, food industry and catering services are advantageous uses for the coating according to the invention, but the coating can also be widely used, for example, in process industry and packaging industry. Moreover, suitable uses include various public facilities, schools, day-care centres, offices and spas, in which the ease of cleaning and the antimicrobial property of surfaces are desired. Furthermore, the coating according to the invention can also be used, for example, in ventilation systems to prevent microbiological contamination.

On the basis of experiments carried out, the coating according to the invention is effective and easy to use for the treatment of even large surfaces. The coating resists various conditions well (chemical conditions, temperatures), which makes it suitable for many even demanding uses. Consequently, the coating is also resistant to various cleaning chemicals and washing conditions.

By means of the coating according to the invention, it is possible to reduce significantly, for example, the quantity of the meticillin-resistant bacteria *Staphylococcus aureus* (MRSA) and *Pseudomonas*
aeruginosa on the surface of stainless steel in a hospital environment. The difference between coated and uncoated steel is significant under both dry and moist conditions.

Detailed description of the invention

In this context, "sol-gel coating" refers to a coating formed of a suspension of colloid particles or macromolecules.

An antimicrobiological coating made by the sol-gel method onto the surface of a substrate comprises a binding agent that forms a coating layer on the substrate, oriented with respect to the substrate, and a polyhexamethylene guanidine salt or a mixture of them as an antimicrobiological component that is bound to the surface of the substrate by means of the binding agent. The binding agent to be used in the coating is preferably a silane, a siloxane, a metal alcoxide, a silasane, or a mixture of these.

In particular, a hydrolysable silane is used. In the coating, fluorosilane is advantageously used, which forms a hydrophobic surface onto the surface of the substrate, wherein a soil-repellent coating that is also easy to clean can be formed. As the binding agent, it is also possible to use alcoxides which are formed by all metals. Metal alcoxides have generally the form M(OR)_x in which M represents a metal or a non-metal, and R represents an alkyl or a corresponding group (for example CH₃, C₂H₅, C₃H₇, or C₄H₉).

To the above-mentioned binding agents, it is also possible to add an organic molecule, depending on the use and function of the coating.

Examples to be mentioned of such organic components include acrylates, epoxies, vinyl esters, and urethanes.

As the antimicrobiological component, a polyhexamethylene guanidine salt or a mixture of them is used. In particular, the antimicrobiological component used is poly(hexamethylenediamine guanidium chloride) (PHMG), whose CAS number is 57028-96-3. PHMG is also called polyhexamethylene guanidine.
As examples of other polyhexamethylene guanidine salts, polyhexamethylene guanidine phosphate and polyhexamethylene guanidine hydrochloride can be mentioned.

The content of the antimicrobiological component in the coating may vary, depending on the use and the desired antimicrobiological effect. Because the antimicrobiological agent can be bound to the surface of the coating, even small doses of the antimicrobiological agent provide an effective long-term antimicrobiological effect. Furthermore, PHMG is an effective antimicrobiological agent, so that also for that reason even small doses will provide an effective long-term antimicrobiological effect against, for example, gram-negative and gram-positive bacteria, fungi, germs, viruses, moulds, and yeasts. The effectiveness of PHMG is based on its positive electrical charge that reacts with the negative charge of the cell membrane of microbes, destroying the cell membrane. The mechanism of action of PHMG is physical and not chemical, for which reason it is an effective biocide against microbes.

In the coating, the content of polyhexamethylene guanidine salt or a mixture of them varies from 0.1 to 40 wt-% of the binding agent content; preferably, the content of polyhexamethylene guanidine salt is 1 to 15 wt-% of the binding agent content. In the coating, the water-soluble antimicrobiological component is bound to a matrix formed by the binding agent in such a way that the antimicrobiological component is on the surface of the coating.

Thanks to the high molecular weight of PHMG, the molecule comprises several active points which react with the cell membrane of microbes. The molecular weight varies from 8,000 to 10,000. However, PHMG is a safe antimicrobiological agent with a low toxicity, so that it can be used in a variety of applications. PHMG has an antimicrobial action in both dry and moist conditions.

The coating solution to be applied onto the substrate to form the antimicrobiological sol-gel coating also contains various catalysts and auxiliary agents as well as a solvent. Water, alcohol, other organic
solvents, or mixtures of them are used as the solvent. By the content and quality of the solvent, it is possible to influence, among other things, the thickness and orientation of the film to be formed. When the coating is applied onto the substrate, the solvent evaporates off, resulting in the formation of a thin coating film. The thickness of the finished sol-gel coating is less than 20 µm; preferably, the thickness of the film is less than 1 µm.

In addition to polyhexamethylene guanidine salts, it is also possible to use, if necessary, inorganic antimicrobiological agents, such as silver or titanium oxide or other corresponding biocides, in the coating.

In the method for forming an antimicrobiological sol-gel coating on the surface of a substrate, the above-described coating solution is applied on the substrate, and the binding agent in the coating solution is bound to the surface, forming a thin oriented surface layer and binding the antimicrobiological component to the surface of the substrate. The formed coating is a thin molecular film on the surface of the substrate to be treated, wherein the antimicrobiological component is on the surface of the coating and is thereby active and efficient against microbes. With the coating, it is possible to reduce significantly the quantity of bacteria and other microbes on the surface treated with the coating. The solvent in the coating solution evaporates when the coating becomes dry.

The formed coating is thin and colourless, and it does not alter the visual properties of the surface to be treated. The coating adheres chemically to the substrate, if the chemistry of the substrate is suitable or the substrate has been treated to have suitable chemistry. Covalent metal-oxygen bonds are formed between the coating and the substrate material, resulting in the formation of the oriented structure of the coating. The surface of the coating is hydrophobic outwards, which is also a result of the orientation of the adhesive on the surface of the substrate. Furthermore, the surface of the coating is oleophobic when fluorosilane is used as the adhesive.
The coating is particularly suitable for substrates to which the coating can adhere by covalent metal-oxygen bonds. Suitable substrates are preferably metal surfaces, particularly stainless steel surfaces as well as ceramic surfaces and glass surfaces. Surfaces that do not enable the direct adherence of the coating must be pre-treated to be chemically suitable before applying the coating. For example, plastic and paint surfaces may require pre-treatment of the surface. The coating is also suitable for use on porous surfaces in which the coating is partly absorbed into the substrate to be coated but it still forms a durable and uniform coating film on the surface of the substrate.

Pre-treatment of the surfaces refers to treating the surface of the substrate before it is coated, to achieve the desired processing and the properties of the coating. The pre-treatment of the surface may include reducing the amount of contaminants to an acceptable level or, in other words, cleaning, modifying the physical and chemical properties of the surface, and activating the surface to enhance the reactions. To achieve a smooth and defect-free sol-gel coating, the surface to be coated must be clean. Therefore, before applying the coating, the surfaces to be protected should be cleaned from all contaminants. The applied pre-treatments do not affect the properties of the coating, but they are significant in view of the coatability, adhesion and durability of the surface.

The coating can be applied onto the substrate easily by sweeping, brushing, spraying, rubbing, dipping, or in another way, to provide a thin coating layer on the surface to be treated. By the composition of the coating solution, it is possible to modify the spreading properties of the coating and the thickness of the coating film to be formed. The coating is dried and cured at room temperature without separate thermal treatment, so that it is also easy and quick to prepare on site. The drying time of the coating varies from a few minutes to a few hours, depending on the surface to be treated. On the surface of a hard and smooth substrate, the coating is dried faster than on the surface of a porous substrate.
The coating is preferably formed by applying a coating solution that contains at least a solvent, a binding agent, and a polyhexamethylene guanidine salt or a mixture of them, onto the substrate. The coating solution may also comprise two components which are mixed first on site just before coating the substrate. Alternatively, the antimicrobiological feature of the coating may be prepared first on the surface to be coated, wherein a coating is first formed on the surface of the substrate, and the antimicrobiological component is then rubbed into the coating.

The durability and service life of the coating will depend on the use and the conditions. However, the coating enables a long-term effect against microorganisms, which may last from weeks to several months. In some cases, this feature may last even for years, depending on the quality and wear of the surface. The molecular structure of the coating will resist even high temperatures without impairing the effect of the coating. The coating also resists various chemical conditions well; for example use in a wide pH range is possible, because PHMG is stable in the pH range from 1 to 10. The coating also resists various chemicals well. Consequently, the washability of the coating is good.

Particularly when fluorosilane is used as the binding agent, the coating formed on the substrate is also water and fat repellent, wherein the surface also remains cleaner and the surface can be cleaned more easily, which reduces significantly the need for cleaning chemicals and also contributes to the durability of the coating. Thanks to the hydrophobic surface, water-soluble PHMG can also be kept in the coating.

Furthermore, the coating can be easily renewed. The coating can be applied again on a surface that has already been treated before, without a need to remove the old coating. The new coating layer will adhere to the points where it has been rubbed off or become porous as a result of mechanical or chemical wear. The coating can be easily renewed, for example, in connection with normal cleaning. At the same time, the antimicrobiological activity of the coating can be renewed by refilling the porous or worn-out parts of the coating with a coating
composition which comprises at least a polyhexamethylene guanidine salt as an antimicrobiologically active component. The previous coating on the surface of the substrate does not need to be a sol-gel coating according to the invention, but the coating may be any coating made by the sol-gel method and to be renewed, or whose antimicrobiological effect is to be enhanced by including a polyhexamethylene guanidine salt, particularly PHMG, in the coating layer.

The coating according to the invention can be applied widely in various uses, and the coating can be easily transferred to new uses. The possibilities of using the coating are also increased by the fact that the agent used as the antimicrobiological agent is active in both dry and moist conditions. The coating can also be easily applied on surfaces that comprise complex shapes.

Particularly hospitals and food industry are advantageous uses for the coating according to the invention. In hospitals, the coating can be widely used on all surfaces that require antimicrobiological protection, including walls, doors, floors, as well as various pieces of furniture and equipment. In food industry, the use of the coating improves, for example, the shelf life of food, because the food is not exposed to microbes during the preparing and handling processes and thereby also the content of preservatives in the food itself can be reduced. In process industry, the coating can be used for coating either the production facilities or the production machinery.

The coating can be generally applied on any ceramic surfaces, for example in bathrooms and other sanitary facilities. It is also possible to coat wooden surfaces with said coating; in other words, the coating can be used as a wood preservative.

The coating can also be widely used in processing industry, for example in paper industry or packaging industry, to prevent microbiological contaminations. The coating can also be used for coating packages made of plastic or cardboard. Furthermore, the coating can be widely used in catering services, schools, day-care centres, public facilities, offices, and spas. On the basis of tests carried
out, the coating is efficient and easy to use for the treatment of even large surfaces. The coating according to the invention can also be used in ventilation systems to prevent microbiological contamination. Various applications relating to the treatment of water are also possible uses.

In the following example, the performance of the coating according to the invention on a steel surface and its effect on the number of bacteria found on coated surfaces particularly in a hospital environment were examined. An uncoated stainless steel surface was used as a reference.

The bacterial strains used in the test was the meticillin-resistant *Staphylococcus aureus* strain ATCC 33591 and *Pseudomonas aeruginosa* strain ATCC 15442 (under moist conditions only).

The coating solution used in the tests included 0.016 wt-% of PHMG as the antimicrobial component, about 0.3 wt-% of silanes as the binding agent, about 5 wt-% of water, and about 1.7 wt-% of an acid catalyst. The rest of the solution was a mixture of isopropanol and ethanol in a mixture ratio of 1:1.

The stainless steel surfaces were treated with the above-described coating solution and dried. The tests were carried out on both dry surface and moist surface. As a reference, an uncoated stainless steel surface was used.

The test was carried out by applying the EN13697 surface disinfectant standard. In a viability assay, 100 µl of a microbial solution (1 × 10^5 pmy/ml) was pipetted onto the surface, dried at 37°C for 2 h and sampled on a dish right away (before drying), 4 h, 24 h, and 48 h after the pipetting. Part of the steel surfaces were stored in dry conditions (at room temperature) and part in moist conditions (+37°C) for the time of the series of tests. Two parallel samples were taken of the tests. The samples were incubated at 37°C for 1 day.

In the test, it was found that the coating according to the invention reduces significantly the content of both MRSA and *Pseudomonas*
aeruginosa bacteria on the surface of stainless steel. The difference between steel coated with the coating according to the invention and uncoated steel is significant under both dry and moist conditions. The results of the test are shown in tables 1 and 2.

Table 1. Number of MRSA colonies on dishes (cfu/ml).

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<th>time (h)</th>
<th>uncoated steel, dry</th>
<th>coated steel, dry</th>
<th>uncoated steel, moist</th>
<th>coated steel, moist</th>
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<td>1</td>
<td>830000</td>
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Table 2. Number of *Pseudomonas aeruginosa* colonies on dishes (cfu/ml).

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<th>time (h)</th>
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<tr>
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The invention is not intended to be limited to the embodiments or uses presented as examples above, but the invention is intended to be applied widely within the scope of the inventive idea as defined in the appended claims.
Claims:

1. An antimicrobiological coating prepared onto the surface of a substrate by the sol-gel method, characterized in that the coating comprises
   - a binding agent that forms a coating layer oriented with respect to the substrate, and
   - as an antimicrobiological component, a polyhexamethylene guanidine salt or a mixture of them, bound to the surface of the substrate by means of the above-mentioned binding agent.

2. The coating according to claim 1, characterized in that the binding agent is a silane, a siloxane, a metal alcoxide, a silasane, or a mixture of these.

3. The coating according to claim 1 or 2, characterized in that the binding agent is a hydrolysable silane.

4. The coating according to any of the preceding claims, characterized in that the binding agent is fluorosilane.

5. The coating according to any of the preceding claims 2 to 4, characterized in that another organic binding agent has been added into the binding agent.

6. The coating according to any of the preceding claims, characterized in that the coating comprises an inorganic antimicrobiological agent.

7. The coating according to any of the preceding claims, characterized in that the content of polyhexamethylene guanidine salt is 0.1 to 40 wt-% of the binding agent content.

8. The coating according to any of the preceding claims, characterized in that the content of polyhexamethylene guanidine salt is 1 to 15 wt-% of the binding agent content.
9. The coating according to any of the preceding claims, **characterized** in that the substrate is metal, glass, or ceramic material.

10. The coating according to any of the preceding claims, **characterized** in that the thickness of the coating is less than 20 µm.

11. The coating according to any of the preceding claims, **characterized** in that the thickness of the coating is less than 1 µm.

12. A coating solution to be applied onto the substrate to form an antimicrobiological sol-gel coating, **characterized** in that the coating solution comprises at least a solvent, a binding agent and, as an antimicrobiological component, a polyhexamethylene guanidine salt, or a mixture of these.

13. The coating solution according to claim 12, **characterized** in that the binding agent is a silane, a siloxane, a metal alcoxide, a silasane, or a mixture of these.

14. The coating solution according to claim 12 or 13, **characterized** in that the binding agent is a hydrolysable silane.

15. The coating solution according to any of the preceding claims 12 to 14, **characterized** in that the binding agent is fluorosilane.

16. The coating solution according to any of the preceding claims 12 to 15, **characterized** in that the content of polyhexamethylene guanidine salt is 0.1 to 40 wt-% of the binding agent content.

17. The coating solution according to any of the preceding claims 12 to 16, **characterized** in that the content of polyhexamethylene guanidine salt is 1 to 15 wt-% of the binding agent content.

18. The coating solution according to any of the preceding claims 13 to 17, **characterized** in that another organic binding agent has been added into the binding agent.
19. A method for forming an antimicrobiological sol-gel coating onto the surface of a substrate, characterized in that in the method, a coating solution according to any of the claims 12 to 18 is applied onto the substrate, the binding agent of the coating solution forming a coating layer oriented with respect to the substrate and binding the polyhexamethylene guanidine salt or a mixture of these, acting as the antimicrobiological component, to the surface of the substrate.

20. The method according to claim 19, characterized in that the surface of the substrate is pre-treated before the application of the coating solution.

21. A method for regenerating the antimicrobiological activity of a coating prepared by the sol-gel method on the surface of a substrate, in which method the porous or worn-out coating on the substrate is renewed or the porous points are filled with the coating solution according to any of the claims 12 to 18.
INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2008/050634

A. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC8: A01N, B05D, C09D

Documentation searched other than minimum documentation to the extent that such documents are included hi the fields searched

FI, SE, NO, DK

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI, XPAIP, XPESP, XPIOP, BIOSIS, COMPDX, EMBASE, INSPEC, MEDLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

Date of the actual completion of the international search
26 January 2009 (26.01.2009)

Date of mailing of the international search report
26 February 2009 (26.02.2009)

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