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(54) Title: METHOD FOR PRODUCING AN ANTIMICROBIAL COATING ON A TECHNICAL SURFACE

(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG EINER ANTIMIKROBIELL WIRKENDEN BESCHICHTUNG AUF EINER TECHNISCHEN OBERFLÄCHE

(57) Abstract: The invention relates to a method for producing a microbial substance-releasing layer on a technical surface. The inventive method comprises three steps: a) producing a solution from polyvinylacetate, a preservative agent and a solvent, b) applying the solution to the technical surface, and c) drying the solution applied to the technical surface while forming the layer. The inventive method is characterized by using benzoic acid, sorbic acid, natamycin, bacteriocines, plant extracts or mixtures thereof as the preservative agent and an ethanol/water mixture, ethyl acetate or acetone as the solvent.

(57) Zusammenfassung: Beschrieben wird ein Verfahren zur Herstellung einer antimikrobielle Wirkstoffe freisetzenden Schicht auf einer technischen Oberfläche. Das erfindungsgemäße Verfahren umfasst drei Verfahrensschritte: a) Herstellen einer Lösung aus Polyvinylacetat, einem Konservierungsmittel und einem Lösungsmittel, b) Aufbringen der Lösung auf die technische Oberfläche, und c) Trocknen der auf die technische Oberfläche aufgetragenen Lösung unter Ausbildung der Schicht. Das Verfahren zeichnet sich weiterhin dadurch aus, dass vorzugsweise als Konservierungsmittel Benzoesäure, Sorbinsäure, Natamycin, Bacteriocine, Pflanzenextrakte oder deren Gemische und als Lösungsmittel ein Ethanol-Wasser Gemisch, Ethylacetat oder Aceton verwendet werden.

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METHOD FOR PRODUCING AN ANTIMICROBIAL COATING ON A  
TECHNICAL SURFACE

**Technical field**

The invention relates to a method for producing an antimicrobial coating on a technical surface. The method is used in the food and packaging industry, in particular for packing perishable food products. It is also possible to apply the method in all fields in which it is necessary to protect surface regions from contamination with bacteria, fungi, rickettsia or germs, e.g. in medicine, the pharmaceutical industry, biology, in consumer goods, in the household or in the textile industry.

**State of the art**

Coatings of the above-mentioned type are used in an intrinsically known manner in food packaging materials for protecting the packed food products from attack by microorganisms such as bacteria, fungi or other germs. Perishable food products in particular can be stored for a long time in a high quality condition when packaging materials with an antimicrobial coating are used. In addition, the risk of the occurrence of pathogens on or in the packed food products is reduced.

Antimicrobial coatings typically have a carrier layer in a matrix design with active substances or inhibitors embedded in it, which, if they come into contact with microorganisms, kill them or inhibit or prevent their growth. At present two principles of operation of antimicrobial coatings are essentially known:

The first principle of operation is characterised in that the antimicrobial active substances and inhibitors have volatile properties and are first embedded in a carrier layer of a matrix design, but are released in time from the matrix material. The antimicrobial action therefore takes place not only in the close region above the coated surface, but the active substances and inhibitors develop their antimicrobial action throughout the packaging volume by release

from the carrier layer. Suitable antimicrobial active substances for this principle of operation may be used for food applications in the European area (for example chlorine dioxide, since it is toxic, or ethanol, since it has adverse sensory properties).

5 The second principle of operation is significantly more widespread and is characterised in that the antimicrobial active substances and inhibitors are spatially fixed in the carrier layer in such a manner that they not able to escape from the carrier layer independently. The antimicrobial action of the active substances and inhibitors embedded in the coating material of a matrix design is developed, in particular, by contact of the food products with the antimicrobially coated surface. Here the active substances and inhibitors can diffuse through the surface of the matrix material into the surface of the food product so that the antimicrobial action of the coating is determined essentially by the diffusion kinetics.

10 With regard to the packing of food products with antimicrobially coated food packaging materials, a multiplicity of active substances and inhibitors, as well as release mechanisms, have been investigated in recent years. The publication: "Review of antimicrobial food packaging", by Paola Appendini and Joseph H. Hotchkiss, in Innovative Food Science & Emerging Technologies 3 (2002) 113–126, gives an overview of these substances.

15 However, the methods of prior art for producing an antimicrobial coating suffer from the disadvantage that the coating is either technically complicated to produce, and is therefore expensive, or the raw materials used are not available in sufficient quantity or the raw materials and/or the resultant product substances do not meet the legal requirements.

20 A reference herein to a patent document or other matter which is given as prior art is not to be taken as an admission that that document or matter was known or that the information it contains was part of the common general knowledge as at the priority date of any of the claims.

25 Throughout the description and claims of the specification, the word "comprise" and variations of the word, such as "comprising" and "comprises", is not intended to exclude other additives, components, integers or steps.

#### **Representation of the invention**

30 One aspect of the invention is to indicate as low cost a method as possible for producing an antimicrobial coating on a technical surface, which method is

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5 technically simple and meets the existing legal requirements. It will be possible, in particular, to implement the invention in the production of antimicrobial coatings on food packaging materials and on technical surfaces which are of relevance in medicine, the pharmaceutical industry, biology, in consumer goods, in the household or in the textile industry, and which are to be protected from colonisation by microorganisms such as bacteria, fungi or germs. It will also be possible to carry out the method with conventional systems, which means that coating systems already in use may be resorted to.

10 One desired feature of the invention is indicated in claim 1. Other desired features of the inventive concept may be deduced from the dependent claims and the further description.

Accordingly, in one aspect the present invention provides a method for producing an antimicrobial substance-releasing layer on a technical surface, comprising the following method steps:

- 15
- producing a solution from polyvinyl acetate, a preservative agent and a solvent,
  - electrically polarizing the technical surface,
  - applying the solution to the technical surface, and
  - drying the solution applied to the technical surface while forming the layer.

20 In a further aspect, the present invention provides a method for producing an antimicrobial substance-releasing layer on a technical surface comprising:

- a) producing a solution which has the following components in fully dissolved form: polyvinyl acetate, a preservative agent and a solvent,
- b) applying the solution to the technical surface, and
- 25 c) drying the solution applied to the technical surface while forming the antimicrobial layer.

30 In the first method step a solution is produced which has the components polyvinyl acetate, a preservative agent and a solvent. 100% ethyl acetate, or preferably an ethanol-water mixture with an ethanol/water mixing ratio of between 80:20 and 100:0 percent by weight is used as the solvent. The ethanol-water mixture serves as a technical, physiological and environmentally harmless solvent which can be evaporated and largely recovered. Acetone is also suitable as a solvent.

35 Polyvinyl acetate is first added to the solvent and completely dissolved in the solvent. Polyvinyl acetate has been shown to be an ideal substance for the matrix-type carrier layer of the antimicrobial coating to be produced, since it

easily soluble in a solvent, has very good release properties as a carrier layer for the antimicrobial active substances or inhibitors embedded in it, and forms a transparent, flexible, film-like carrier layer after it is applied to a technical surface. The solution preferably contains up to 60 percent by weight of polyvinyl acetate related to the quantity of solvent.

The preservative agent is then added to the solvent. The preservative agent corresponds to the actual antimicrobial active substance or inhibitor. In principle a multiplicity of such active substances or inhibitors that can be used in this method are known (cf. Paola Appendini and Joseph H. Hotchkiss, *Innovative Food Science & Emerging Technologies* 3 (2002), page 115, Table 2). Benzoic acid, sorbic acid, natamycin, bacteriocines (e.g. nisin or pedicin), plant extracts or mixtures thereof have proved to be ideal active substances or inhibitors. Benzoic acid and sorbic acid in particular are legally licensed both for food products and for plastics used for food packaging and have a broad antimicrobial spectrum of action against different groups of microorganisms, for example bacteria, yeasts or moulds. In polyvinyl acetate films both these substances also remain dissolved up to high concentration ranges without their affecting the transparency of the polyvinyl acetate films due to their own crystallisation. As indicated, however, other well known preservative agents or mixtures thereof, licensed according to food legislation, may also be used. The solution, with the components solvent, polyvinyl acetate and preservative agent, preferably contains up to 40 percent by weight of preservative agent related to the quantity of polyvinyl acetate contained in the solution.

Furthermore a so-called activity regulator can be added to the solution and has the function of setting the pH value of the technical surface and its immediate surroundings so that the preservative agent or agents is or are present in the solution in undissociated form. The preservative agents which correspond to the active substances or inhibitors, as mentioned above, can develop their antimicrobial action to the optimum degree in undissociated condition. The use of lactic acid or citric acid as activity regulator has surprisingly proved

particularly suitable when combined with benzoic and/or sorbic acid. The solution preferably contains up to 5 percent by weight of the activity regulator related to the quantity of preservative agent contained in the solution.

The solution is preferably produced with continuous agitation, maintaining a temperature level ranging between 20 and 50°C ideal for producing the solution.

In the second method step the mixed and, if necessary, tempered solution is applied to the technical surface. All the methods and techniques available for the specific application of a liquid medium to a technical surface are considered for this purpose, for example dipping, printing, painting or spraying methods and application of the solution by means of brushes, spreading knives or fluted rollers. The technique to be selected for applying the solution depends on the condition of the surface to be coated and the shape of the body having the surface. Conventional painting methods may be used for coating polymer films or paper, for example, whereas spraying techniques are more suitable for beaker-shaped containers.

It has been recognised as particularly advantageous if technical surfaces with a preferred electrical surface polarity were to be suitable for an internal composite between the surface and solution. The electrical polarity of technical surfaces may be produced or varied by electrical fields. The electrical polarisation of the technical surface preferably takes place before application of the solution by means of corona discharge.

In the third method step the solution applied to the technical surface is dried at temperatures below 60°C. As a result of drying the solvent is liquefied with the formation of the matrix-type carrier layer, consisting of polyvinyl acetate, with the preservative agents embedded in it, i.e. the antimicrobial active substances or inhibitors.

An antimicrobial coating can therefore be produced on a technical surface by the inventive method, which surface has polyvinyl acetate as the carrier layer, with one or a plurality of antimicrobial active substances or inhibitors embedded therein, which are released in time from the matrix material. Surfaces of food packaging materials, particularly film surfaces and/or containers produced from plastic, paper, metal or natural substances, are considered as technical surfaces for this purpose. Moreover, the coating according to the invention may also be used for technical surfaces in the areas of medicine, the pharmaceutical industry, biology, in consumer goods, in the household or in the textile industry, surfaces which are to be protected against colonisation by microorganisms such as bacteria, fungi or other germs.

It is also possible, with the inventive method, to apply antimicrobial coatings to technical surfaces by simple, conventional technical means using low cost raw materials available in any quantity and licensed according to the food legislation.

The invention is described in the following, without limiting the general inventive concept, with reference to a following exemplary embodiment.

First a clear solution is produced from 10 g of polyvinyl acetate, which is available in powder form or as a granulate, and 100 g of a solvent consisting of a mixture of ethanol and water in a mixing ratio of 95:5% by weight, with agitation and heating to 30 – 40°C, so that the polyvinyl acetate is present in fully dissolved form. 10% by weight of sorbic acid (preservative agent), related to the polyvinyl acetate contained in the solution, i.e. 1 g of sorbic acid, and 0.1% by weight of lactic acid, related to the quantity of preservative agent contained in the solution, i.e. 0.001 g of lactic acid, are then added to the solution. After a short time a clear solution is formed. The solution is now applied to a carrier film consisting of polyolefins, and spread on its surface by means of a spreading knife. Depending on the spreading knife used, coat thicknesses of the applied solution of between 40 and 100 µm were produced in

this case. For better adhesion of the applied solution to the carrier film it is advantageous to generate a surface tension of approximately 40 dynes/cm<sup>2</sup> on the carrier film by means of a corona process before applying the solution. In the case of the carrier film of polyolefins used here, this results in improved adhesion properties between the film and the applied solution.

The solution applied to the carrier film is now dried at a temperature of 50°C for approximately 5 minutes. Further parameters, such as the quantity of air supplied or the humidity, must be taken into consideration according to the drying process used. A temperature of 60°C as a temperature limit should not be exceeded during the drying process. During drying a transparent, flexible coating is formed on the polymer film. After cooling, its antimicrobial action can be tested, for example, in a modified agar diffusion test which comprises the following four steps:

1. Supplying a Petri dish with a sterile agar layer,
2. Placing the test film with coated and uncoated areas onto the agar layer,
3. Applying agar, which contains a test germ, to the test film,
4. Incubation and evaluation.

The antimicrobial polyolefin film, i.e. the film coated with the solution, in the agar diffusion test described using the test organism *saccharomyces cerevisiae*, shows that no colonisations of microorganisms occur in the coated surface region of the test film. Coated films produced by the method described above also exert their inhibiting action against microorganisms of the type bacteria, gram positive and gram negative, fungi and other areas of microbiology. It was also shown by measurements that the coatings examined release approximately 20 – 40 mg/m<sup>2</sup> of the preservative agents used in 2 days.

The claims defining the invention are as follows:

1 A method for producing an antimicrobial substance-releasing layer on a technical surface, comprising the following method steps:

- producing a solution from polyvinyl acetate, a preservative agent and a solvent,
- electrically polarizing the technical surface,
- applying the solution to the technical surface, and
- drying the solution applied to the technical surface while forming the layer.

2. The method according to Claim 1, wherein antimicrobially acting substances or substance mixtures, in particular benzoic acid, sorbic acid, natamycin, bacteriocines, plant extracts or mixtures thereof, are used as preservative agents and an ethanol-water mixture or ethyl acetate or acetone is used as the solvent.

3. The method according to any one of Claims 1 or 2, wherein the solution contains lactic acid or citric acid as an activity regulator.

4. The method according to any one of Claims 1 to 3, wherein the solution contains up to 60% by weight of polyvinyl acetate related to the solvent.

5. The method according to any one of Claims 1 to 4, wherein the solution contains up to 40% by weight of preservative agent related to the polyvinyl acetate contained in the solution.

6. The method according to any one of Claims 1 to 5, wherein the solution contains up to 5% by weight of activity regulator related to the preservative agent contained in the solution.

7. The method according to any one of Claims 1 to 6, wherein the solvent consists of an ethanol-water mixture in a mixing ratio of 80:20 to 100:0% by weight.

8. The method according to any one of Claims 1 to 7, wherein the solution is produced at temperatures of 20° - 50°C by mixing.

9. The method according to any one of Claims 1 to 8, wherein the solution is applied to the technical surface by a dipping, printing, painting or spraying method, or by means of brushes, spreading knives or fluted rollers.

5 10. The method according to any one of Claims 1 to 9, wherein a surface of a means of food preservation, in particular a food packaging material, a consumer product or an agent used in the medial field.

10 11. The method according to Claim 10, wherein a film and/or containers produced from plastic, paper, metal or natural substances are used as mean for food preservation.

12. The method according to any one of claims 1 to 11, wherein the electrical polarisation is produced by means of the corona process.

15 13. The method according to any one of Claims 1 to 12, wherein the solution applied to the surface is dried at temperatures lower than 60°C.

20 14. An antimicrobial substance-releasing layer prepared by the process of any one of claims 1 to 13.

15. A method according to claim 1 substantially as hereinbefore described with reference to any one of the Examples.