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(54) **Eljárás hidrofób felületek előállítására**

Az európai szabadalom ellen, megadásának az Európai Szabadalmi Közlönyben való meghirdetésétől számított kilenc hónapon belül, felszólalást lehet benyújtani az Európai Szabadalmi Hivatalnál. (Európai Szabadalmi Egyezmény 99. cikk(1))

A fordítást a szabadalmas az 1995. évi XXXIII. törvény 84/H. §-a szerint nyújtotta be. A fordítás tartalmi helyességét a Szellemi Tulajdon Nemzeti Hivatala nem vizsgálta.

METHOD FOR PRODUCING HYDROPHOBIC SURFACES

The invention relates to a method for producing hydrophobic surfaces and also to a hydrophobic surface obtainable by the method of the invention.

There are a wide variety of applications in industry and/or everyday life where it is desirable to provide extremely hydrophobic and/or soil-rejecting properties to surfaces of any kind. Surface properties are here determined using particularly the measurement of the contact angle of a water droplet on the surface, as described for example in Physical Chemistry of Surfaces, Chapter X, A.W. Adamson, A.P. Gast, John Wiley & Sons, Inc., 1997.

Surfaces are termed hydrophilic when the contact angle is < 90°, while surfaces having a contact angle > 90° are termed hydrophobic. A contact angle of 180° denotes perfect unwettability, whereas a contact angle of 0° denotes complete wetting. However, neither limiting case occurs in nature. The relationship between the contact angle α and the interfacial tensions between water and air (σ_{lV}), solid bodies and water (σ_{SL}) and also solid bodies and air (σ_{SV}) is described by Young's equation:

$$\sigma_{SV} - \sigma_{SL} = \sigma_{LV} \cdot \cos\alpha$$

The lower the interfacial tension σ_{SV}, the greater the unwettability of the surface.

Considering the simplest case of a planar, i.e. smooth surface, then the contact angle of the water droplet on the surface is determined by the selection of the material (see Adamson, p. 365). If, for example, the contact angle on paraffin is measured, contact values of 110° are typically found. Polyethylene exhibits a 103° contact angle with respect to water.

Even more pronounced hydrophobic properties are encountered on switching to perfluorinated compounds. PTFE (polytetrafluoroethylene) is found to have a water contact angle of 112°. Although perfluorinated compounds are employed in industry, including for instance textile treatment, to hydrophobicize surfaces, disadvantages are firstly the high costs, secondly the oftentimes poor processability and thirdly the environmental incompatibility of the starting components, which can also end up in the wastewater and in landfills.

Still higher contact angles (>>110°) are attainable by employing a microstructured, hydrophobic surface. Superhydrophobicity is then said to be concerned. Systems of this type are found in nature on the leaves of the lotus plant for example. The term "lotus effect" has accordingly become established for a contact angle α of about 130° or more. This effect is caused in the lotus plant by the presence on the leaf surface of rods – known as papillae – 10 to 20 µm high and 10 to 15 µm apart in addition to secreted waxes. Owing to the microstructure, water is no longer able to get into the interstitial spaces of the leaf surface, dramatically reducing the contact area between the water and the surface. Only about 2-3% of the droplet surface is in contact with the plant surface, the latter displaying extremely low wettability as a result. In extreme cases, the contact area obtained may even be just 0.6% or thereabouts. Owing to this minimal adherence between leaf surface and water droplet, the water is easily able to bead off, carrying with it and removing particles of soil on the leaf surface, which likewise have but a small contact area. This phenomenon is therefore also referred to as a so-called self-cleaning surface. In plants, the benefit of this effect resides in the plant being protected from colonization by microorganisms, pathogens and germs, e.g. fungal traces, or the growth of algae. Similar surfaces are also found in animals, for example butterflies and dragonflies, in places unreachable with their legs for cleaning.

Following the detailed elucidation of the so-called lotus effect, there have been many studies also using artificial systems to establish a superhydrophobic surface and deploy same for technical applications. A self-cleaning paint for application to building exteriors is thus commercially available under the tradename of Lotusan®. An up to date review of superhydrophobic surfaces is found in R. Frenzel et al. Ultrahydrophobe Oberflächen durch gezieltes Grenzflächendesign [Ultrahydrophobic Surfaces via Precise Interfacial Design], Chemie Ingenieur Technik 2010, 82 No. 3, 297-308. Most of the systems disclosed to date consist of a combination of hydrophobic particles with a matrix formed of a hydrophobic polymer or compound. This construction is said to enable the modification of a multiplicity of surfaces with one coating formulation. Alternatively, superhydrophobic surfaces are also obtainable on specific substrates by first establishing the desired roughness required for the later attainment of superhydrophobicity and then merely hydrophobicizing the surface by means of a coating. Care must be taken here to ensure that such coatings do not affect the previously established surface roughness. In the extreme case, surface coatings with monolayers of hydrophobic compounds are sufficient here. Examples of such superhydrophobic surfaces where a custom-tailored surface roughness is established in a first step and hydrophobic coating is carried out in a subsequent step are surfaces of anoxidized aluminium coated with alkyl phosphonates, and also modified plasma-etched PTFE surfaces (see also R. Frenzel et al. Ultrahydrophobe Oberflächen durch gezieltes Grenzflächendesign [Ultrahydrophobic Surfaces via Precise Interfacial Design], Chemie Ingenieur Technik 2010, 82 No. 3, 297-308).

The WO 96074123 patent to Wilhelm Barthlott describes self-cleaning surfaces of objects and also methods of making same. Self-cleaning surfaces are protected of objects displaying an artificially produced surface structure comprising elevations and depressions wherein the elevations are spaced from 5-20 μm apart and are 5-100 μm high. At least the elevations, if not the entire system, consist of hydrophobic polymer or durably hydrophobicized materials, and the elevations are not detachable by means of water or by means of water comprising detergents. This patent to Wilhelm Barthlott, the discoverer of the self-cleaning effect of superhydrophobic micro- and nanostructured surfaces, is the first to refer to the lotus effect and lays claim to any superhydrophobic surfaces established by a microstructured system.

The EP 0933388 patent describes structured surfaces having hydrophobic properties. The surfaces according to the invention display large edge angles with water, are scarcely wetted by water and therefore have a self-cleaning effect. Methods of producing the structured surfaces and using same further form part of the subject-matter of this invention. The claims specify certain aspect ratios, i.e. the ratio of structure width to structure height. More particularly, structured surfaces are claimed in Claim 1 as being characterized in that they display elevations having an average height of 50 nm-10 μm and an average spacing of 50 nm-10 μm and also surface energies of 10-20 mN/m for the unstructured material. This invention more particularly describes microstructured polymers which are obtained via a casting process and thereby acquire their microstructuring. They are hydrophobicized in a second step.

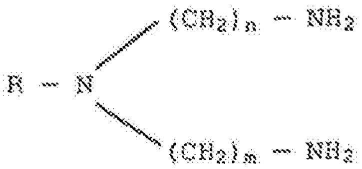
The CH 268258 patent describes a method wherein structured surfaces are created by application of powders, such as kaolin, talc, clay or silica gel. The powders are fixed on the surface by oils or resins based on organosilicon compounds. Using other materials such as waxes or polyethylene or polypropylene, which might serve as a matrix for the soil-rejecting particles and the microstructured systems, are not described here.

The EP 0909747 patent describes a method of creating a self-cleaning property for surfaces which include specifically those of roof tiles. The surface displays hydrophobic elevations 5-200 µm high in distributed form. To create these elevations, a surface is wetted with a dispersion of powdered particles of inert material in a siloxane solution and the siloxane is subsequently hardened. The powdered particles preferably represent a ceramic material.

The WO 0058410 patent describes a method of producing self-cleaning detachable surfaces displaying elevations and depressions, the elevations being spaced 0.1-200 µm apart and 0.1-100 µm high. These surfaces are formed by applying a solution, dispersion or emulsion comprising a hydrophobic material which on evaporation of the solvent self-assembles into a self-cleaning surface and then drying. The applied material is detergent detachable.

The DE 10/2005 052404 A1 *offenlegungsschrift* in the name of Goldschmidt GmbH describes a method of producing detachable biostatic sheetlike coatings on different objects wherein hydrophobic particles are applied to the surface of the objects in the coating step to thereby create on the surface of the objects a surface structure comprising elevations. The layer consists of hydrophobic particles embedded in a volatile siloxane optionally comprising a silicone wax dissolved therein. The starting formulation is applied to the surfaces in the form of a suspension. The next step is to remove the volatile siloxane. For instance, a siloxane wax having a molecular weight of 13 000 g/mol and a recrystallization point of < 5°C is dissolved in decamethylcyclopentasiloxane. A hydrophobicized pyrogenous silica having a BET surface area of 220 m^2/g (Aerosil® R 812 S from Evonik Degussa) is subsequently admixed under intensive agitation. These formulations are sprayed onto solid surfaces, and the formation of microbial impurities is tracked as a function of time, a distinctly lower colonization with microorganisms being found for the coating adduced in this patent.

WO 2009/040596 discloses a liquid composition for cleaning hard surfaces which by way of constituents comprises an at least partly aqueous vehicle, one or more surfactants and an effective amount of a certain compound conforming to formula I.



(I)

There is further described a liquid composition for coating substrates with a hydrophobic film that by way of constituents comprises a liquid vehicle and an effective amount of the compound of formula I. A hydrophobic coating film comprising a compound of formula I for at least partially coating a substrate is finally also disclosed. Insofar as a liquid composition for cleaning hard surfaces is concerned, "inorganic particles" are disclosed as further constituents. Suitable inorganic particles are selected from the group of phosphates, oxides, silicates, carbonates, hydroxides and mixtures thereof.

WO 2005/071023 relates to a waterborne coating composition comprising, in addition to an organic binder, a "stain blocking agent", which comprises at least one type of inorganic nanoparticle having a layered structure and a crystalline structure having positively charged layers. The nanoparticles referred to are preferably selected from anionic clays and salts of layered double hydroxides. A method of coating specific substrates wherein the composition described is employed is also disclosed. Cationic clays may additionally also be used therein as nanoparticles.

WO 2010/139586 relates to an aqueous coating composition comprising between 10 to 50 wt% of a water-miscible and hydrophobic polyester resin, between 50 and 90 wt% of a metal salt of a fatty acid, and a base in an amount of 70 to 130% of the number of carboxyl groups in the resin. The composition may further comprise tallow or some other cationically charged mineral such as hydrotalcite in an amount between 10 to 45 wt% based on the metal salt of the fatty acid. A substrate coated with the composition described is finally also disclosed.

While a whole series of formulations to produce soil-repellent, hydrophobic and superhydrophobic coatings are already known, there continues to be a need for improvement.

Improvements are needed particularly with regard to the environmental compatibility of the coatings, but also with regard to a simplification of the production method and finally with regard to the durability of adherence to very different substrates. For instance, the formulation based on silicone and hydrophobic silica particles has the disadvantage that such hydrophobic silica particles obtained by flame pyrolysis are spherical and therefore but minimally adherent to planar substrates. Coatings of this type are removed even by relatively minimal mechanical stress. At the same time, coatings utilizing silicones are not unconcerning healthwise and hence also under environmental aspects. One example thereof is described in "Adhesion and friction studies of silicon surfaces processed using a microparticle-based method", authors Yilei Zhang and Sriram Sundararajan, Tribology Letters, Vol. 23, No. 1, July 2006.

It has now been found that, surprisingly, layered double hydroxides are very useful in the manufacture of hydrophobic and superhydrophobic, i.e. soil-rejecting, coatings. Layered double hydroxides are typically employed in a technically completely different field, namely as absorbents in the processing of PVC.

The present invention in a first aspect accordingly provides a method for producing a hydrophobic surface, said method comprising the steps of:

- preparing a composition comprising at least one layered double hydroxide, and

- applying the composition to a surface,

wherein the at least one layered double hydroxide is provided at least one hydrophobic coating, and wherein the hydrophobic surface has a contact angle of 100 to 175°.

The composition comprising the at least one layered double hydroxide preferably comprises, in the context of the present invention, a dispersion, a matrix, in particular a polymeric matrix or a matrix comprising a wax, or a varnish.

Insofar as the composition comprises a dispersion, preferred dispersions in the context of the present invention comprise water, alcohols (preferably ethanol), ketones such as acetone and mixtures thereof. Besides these it is also possible to use other solvents, for example aliphatic and aromatic solvents, and also solvent mixtures. These should be easy to volatilize. An example thereof is Stoddard Solvent (white spirit). Likewise possible are supercritical carbon dioxide and environmentally compatible ionic liquids.

The preference overall is for solvents having melting points of not more than 100°C, preferably not more than 95°C, more preferably not more than 90°C, yet more preferably not more than 80°C, yet still more preferably not more than 70°C, yet still even more preferably not more than 65°C and most preferably not more than 60°C.

Insofar as the composition comprises a polymeric matrix, the present invention provides that the polymer is preferably selected from the group consisting of thermoplastic polymers such as polyolefins, preferably from polar thermoplastic polymers such as, for example, acrylic ester-styrene-acrylonitrile (ASA), acrylonitrile-butadiene-styrene (ABS), casein plastics, cellulose acetate, liquid crystal polymers (LCPs), high impact polystyrene (HIPS), cellulose hydrate, cellulose nitrate, cycloolefin copolymers (COC), perfluoroalkoxyalkane, polyamides (PA), polyesters such as polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polymethylene terephthalate, polycarbonate (PC), polyether block amide (PEBA), polyetherimide (PEI), polyether ketone (PEK, PEEK), polyether sulphone (PES), polyhydroxybutyrate (PHB), polyimide (PI), polylactide (PLA), polymethacrylmethylimide (PMMI), polymethyl methacrylate (PMMA), polyoxymethylene (POM), polyacetal, polyphenylene ether (PPO), polyphenylene sulphide (PPS), polyphthalamide, polystyrene(s), polysulphone, polyvinyl acetal (PVAc), polyvinyl chloride(s) (PVC), polyvinylidene fluoride, styrene-acrylonitrile (SAN), thermoplastic starch or thermoplastic polyurethane (TPU, TPE). Preference is similarly given to copolymers comprising comonomer units of the thermoplastic polymers recited.

Particular preference is given to oligomers and/or low molecular weight fractions of the thermoplastic polymers recited, which in addition to a comparatively low molecular weight (M_w = 1000-20 000, preferably 1500-15 000, most preferably 2000-12 000) also have comparatively low melting ranges and/or softening temperatures and/or dripping ranges. These include polyethylene waxes such as, for example, the commercially available Luwax A (from BASF) (melting range/DSC 101-109°C (DIN 51007; ASTM D 3418)); dripping range/Ubelohde 107-114°C (DIN 51801; ASTM D-3954) and also the polyethylene (PE) and polypropylene (PP) waxes of the Licocene range (from Clariant) having melting ranges – according to type – from 70°C to 140°C and dripping ranges from 75°C to 145°C. Also suitable, however, are fully and partially oxidized waxes and also mixtures of esters of long-chain carboxylic acids such as products of natural origin, for instance those known by the name of montan waxes.

Embedding may finally also be effected into appropriate intermediates. To this end, the layered double hydroxides are imported into precursors, for example monomers which are polymerized onto the carrier via thermal or photochemical initiation.

Insofar as the composition comprises a wax-containing matrix, the present invention provides that the wax is preferably selected from the group consisting of fully oxidized, partially oxidized or unoxidized paraffin waxes, montan waxes, carnauba wax, beeswax, amide waxes and mixtures thereof.

It is similarly possible for fatty acids, long-chain ketones, aldehydes and amides and also long-chain hydrocarbons (more than 12 carbon atoms) having a combination of the recited polar functions and also mixtures thereof to constitute suitable matrices for the purposes of the present invention. Likewise possible are sorbitan fatty acid esters such as, for example, sorbitan tristearate (commercially available under the tradename "Span 65").

Claim is further laid to mixtures of the recited thermoplastic polymers including of any polyolefins with waxes including nonfunctionalized paraffin waxes and/or long-chain hydrocarbons. The wax content is commonly between 1 and 25 wt%, preferably between 2 and 15 wt%, more preferably between 3 and 10 wt%.

The composition for the purposes of the present invention may also comprise a varnish. The term "varnish" is for the purposes of the present invention to be understood as meaning any composition comprising at least one pigment and at least one solvent. Preferred varnishes further comprise at least one binder, at least one filler and/or at least one additive.

Preferred layered double hydroxides for the purposes of the present invention are preferably selected from the group consisting of the class of hydrotalcite compounds. Insofar as the layered double hydroxide comprises a hydrotalcite, this hydrotalcite is preferably selected from the group consisting of $[Mg_xAl(OH)_{2x+2}]+[0.5CO_3*nH_2O]$ (where x=2, x=3) such as hydrotalcite, manasseite, $[Mg_xFe(OH)_{2x+2}]+[0.5CO_3*nH_2O]$ (where x=3) such as pyroaurite, sjörgrenite, $[Mg_xCr(OH)_{2x+2}]+[0.5CO_3*nH_2O]$ (where x=3) such as stichtite, barbertonite, $[Mg_xMn(OH)_{2x+2}]+[0.5CO_3*nH_2O]$ (where x=3) such as dessautelsite, $[Mg_xFe(OH)_{2x+2}]+[OH*2H_2O]$ (where x=3) such as meixenite and

$[Ni_xAl(OH)_{2x+2}]+[0.5CO_3/OH*4H_2O]$ such as takovite. It is also possible in the context of the present invention to employ mixtures of two or more layered double hydroxides, preferably mixtures of two or more hydrotalcites. Particular preference in the context of the present invention is given to hydrotalcites, which may in principle comprise natural or synthetic hydrotalcites or else compounds having a hydrotalcite-similar structure and mixtures thereof. These are more preferably employed in a composition comprising 7-15% Al, 10-28% Mg and optionally 5-15% Zn, while aluminium-magnesium hydroxycarbonate comprising 9-12% Al and 20-24% Mg and also aluminium-magnesium-zinc hydroxycarbonate comprising 8-13% Al, 12-18% Mg and 9-13% Zn are particularly preferable. These particularly preferable hydrotalcites are also marketed by Süd-Chemie AG under the tradenames "SORBACID® 911" and "SORBACID® 944" respectively.

A layered double hydroxide very useful for the method of the present invention is further characterizable via a BET surface area of less than 20 m^2/g, preferably less than 15 m^2/g, more preferably less than 12 m^2/g and most preferably less than 10 m^2/g. A very useful layered double hydroxide for the method of the present invention further preferably has a pH of 5.5-10, preferably of 7 to 9.5, in a 5% suspension of ethanol. A very useful layered double hydroxide for the method of the present invention likewise preferably has a moisture content of 0.05 to 0.75%, preferably 0.25 to 0.55% and most preferably of 0.5%. Layered double hydroxides useful for the method of the present invention further preferably have a particle size distribution of D50 0.01 µm to 2 µm, preferably 0.1 µm to 1.5 µm and most preferably 0.75 µm to 1 µm and D90 1 µm to 20 µm, preferably 2.5 µm to 15 µm and most preferably of 5 µm to 10 µm, as measured by dynamic light scattering.

The layered double hydroxides employed in the method of the present invention preferably comprise particles having a primary structure in the form of a platelet structure. The terms "platelet structure" and "platelet-shaped structure" are used interchangeably in the context of the present invention.

When the layered double hydroxides employed in the method of the present invention are in the form of a "platelet structure", the composition will adhere particularly well to the surface to be coated. Moreover, the coating obtained will be of particular durability and long-term stability.

The term "platelet structure" is to be understood in the context of the present invention as meaning any three-dimensional structure where the first dimension and possibly the second dimension each amount to a multiple of the third dimension. Applying this definition to the structure of a cuboid, the cuboid would have a platelet structure in accordance with the present invention when the length amounts to a multiple of the height and the width of the cuboid is between the height and the length and the width is not more than the length of the cuboid.

Layered double hydroxides preferred for the purposes of the present invention, which have a platelet structure, are not limited, however, to a cuboid shape or a cuboid-similar shape. On the contrary, any three-dimensional structure may be concerned provided it satisfies the above-specified proviso, namely that one or two dimensions are each a multiple of the third dimension. Where the three-dimensional structure is a structure that does not permit exact measurement of length, width and height, the respective average length, width and height must be used. Where the three-dimensional structure is a structure without a defined length or width - tablet-shaped structures for example - then the "platelet structure" criterion is likewise satisfied for the purposes of the present invention when the average diameter of the plane formed by a first and second dimension amounts to a multiple of the height of the three-dimensional structure. In principle, this plane formed by the first and second dimensions may have any desired contour. Nor for the purposes of the present invention need this plane be solely defined by two axes in space; on the contrary, it is likewise possible for this plane to be defined by three or more axes in space and to comprise a singly or multiply undulating structure with and without concave and/or convex portions.

The "platelet structure" criterion of the present invention is likewise satisfied by any three-dimensional structure which – provided it is imported into a cuboid structure such that every side of the cuboid touches the structure at a single point – satisfies the following definition:

The length L (corresponds to the longest lateral length) of the resulting cuboid must not be less than two times the height H (corresponds to the shortest lateral length) of the resulting cuboid, preferably is two to one thousand times, more preferably ten to one hundred times.

The platelet-shaped structures of the present invention are preferably structures that are completely filled out by the layered double hydroxide. In further embodiments, however, the platelet-shaped structures of the present invention may also be interrupted by pores or hole-type structures having dimensions < 1.0 µm. In principle, however, the present invention requires that the three-dimensional platelet-shaped structure be filled out at least 20 vol% by the double layered hydroxide, preferably 30 vol%, more preferably 50 vol%, yet more preferably 60 vol%, yet still more preferably 75 vol%, yet still even more preferably 90 vol% and most preferably 99 to 100 vol%.

Examples of platelet-shaped structures in accordance with the present invention are structures in scale, shell, leaf, tablet or tile form or else structures in the form of cornflakes. Preference is given to platelet shapes that are hexagonal and/or rounded-off hexagonal.

In one preferred embodiment, the length L or the average diameter D of the plane formed by the first and second dimensions amounts to from five to thirty times the height H. Preferred measurements are subject to the following ratio:

L or D: H from 5:1 to 30:1

Preferred platelet measurements are in the range of

L or D = 0.1 to 15 μm and H = 0.01 to 1 μm.

The layered double hydroxides employed in the method of the present invention may further – even before application to the surface – be combined into a secondary structure in the form of agglomerates or else stacks of primary structure particles ("platelet structure"). It is possible in this connection for all the layered double hydroxides to be applied to already be combined into agglomerates and/or stacks even before application to the surface, but preferably less than 95%, more preferably less than 80%, yet more preferably less than 65%, yet still more preferably less than 50% and most preferably less than 35%.

In a further preferred embodiment, the composition prepared in the method of the present invention further comprises a hydrophobic solution. Preferred hydrophobic solutions for the purposes of the present invention shall be selected from the group consisting of solutions comprising one or more than one thermoplastic polymer, fatty acid, surfactant, natural lipid such as phospholipid, wax, preferably long-chain phosphonate or long-chain HO-, aldehyde- or amine-functionalized hydrocarbon or functionalized hydrophobic silane, or mixtures thereof as hydrophobic constituent and water and/or an alcohol, preferably ethanol, supercritical carbon dioxide and/or ionic liquids as solvent. Suitable surfactants are specifically anionic surfactants, e.g. alkyl sulphates, alkyl phosphates, alkyl phosphonates or ether sulphates. It is alternatively also possible to employ mixtures of anionic and nonionic surfactants.

Also suitable are, finally, hydrophobic polymers, for example acrylate polymers having alkyl side chains.

In the embodiment according to the invention, the layered double hydroxides are provided a single or multiple hydrophobic coating. The coating in a particularly preferred embodiment of the present invention comprises one or more than one thermoplastic polymer, fatty acid, surfactant, wax, preferably oxidized paraffin wax, montan wax and/or amide wax, long-chain phosphonate, long-chain HO-, aldehyde- or amine-functionalized hydrocarbon, long-chain ketone, long-chain aldehyde and/or long-chain amide or functionalized silane, or mixtures thereof, wherein in the case of a multiple coating each layer may comprise different hydrophobic constituents and it is likewise possible that one layer comprises a single hydrophobic constituent, whereas a second (or third etc.) layer comprises two or more hydrophobic constituents. Suitable surfactants are specifically anionic surfactants, e.g. alkyl sulphates, alkyl phosphates, alkyl phosphonates and ether sulphates. It is alternatively also possible to employ mixtures of anionic and nonionic surfactants. Also suitable are, finally, hydrophobic polymers, for example acrylate polymers having alkyl side chains.

The hydrophobic coating may be applied to the layered double hydroxides in any manner known to be suitable by a person skilled in the art. Preferably, the hydrophobic coating is applied to the layered double hydroxides by these being ground together with one or more hydrophobic constituents, for example fatty acid, wax, preferably an oxidized paraffin wax, montan wax and/or an amide wax, a phosphonate or a surfactant, or being coated in micronized form.

It is therefore in principle possible for the purposes of the present invention to import the layered double hydroxides into the composition when they are already in a hydrophobic-coated form.

However, the layered double hydroxides may also be imported into the composition without any hydrophobic coating. When the composition in a preferred embodiment still contains a hydrophobic solution, it is particularly preferable for the layered double hydroxides to be provided a hydrophobic coating by the hydrophobic constituents of the hydrophobic solution. When previously hydrophobic-coated layered double hydroxides are employed, it is particularly advantageous to provide these a further hydrophobic layer through the simultaneous employment of a hydrophobic solution in the course of the step preparing the composition.

The method of the present invention preferably comprises the composition as more particularly defined above being applied to a solid surface by spraying, dipping, blade coating, melting, sublimation or spincoating. In principle, however, the composition may be applied to the solid surface in any manner known to be suitable by a person skilled in the art.

The solid surface may comprise any material known to be suitable by a person skilled in the art, but the method of the present invention is very useful for surfaces made of glass, wood, metal, plastic, ceramic or a mineral surface for example in the form of building inside or outside surfaces.

The temperature at which the composition is applied in the present invention is preferably 0-150°C, more preferably 11-120°C, yet more preferably 15-100°C, yet still more preferably 18-50°C, most preferably 19-30°C.

In a further aspect, the present invention provides a hydrophobic surface comprising at least one layered double hydroxide, wherein the at least one layered double hydroxide is provided at least one hydrophobic coating, and wherein the hydrophobic surface has a contact angle of 100 to 175°.

The hydrophobic surface of the present invention preferably comprises a layered double hydroxide as defined above for the method of the present invention, more preferably at least one layered double hydroxide comprising at least one hydrotalcite, particularly preference being given to hydrotalcites as defined above.

In a preferred embodiment, the at least one layered double hydroxide is provided at least one hydrophobic coating comprising one or more than one thermoplastic polymer, fatty acid, surfactant, wax, preferably oxidized paraffin wax, montan wax, carnauba wax, beeswax, amide wax, long-chain phosphonate or long-chain HO-, aldehyde- or amine-functionalized hydrocarbon or mixtures thereof. In particularly preferred embodiments, the coating is a coating formed as defined above.

In a further preferred embodiment, the layered double hydroxide is present on the solid surface in particles having a primary structure in the form of a platelet structure, the term "platelet structure" being construed as defined above.

In a particularly preferred embodiment, the platelets have measurements of L and/or D = 5 to 15 µm and H = 0.01 to 1.5 µm.

In a further preferred embodiment, the layered double hydroxide is present on the solid surface in the form of a secondary structure in the form of agglomerates and/or stacks of primary particles.

In a further particularly preferred embodiment, the hydrophobic surface has a contact angle of 140 to 160° and most preferably a contact angle of 150°.

The term "contact angle" of liquids on surfaces as it is also being used in the context of the present invention is described for example in Physical Chemistry of Surfaces, Chapter X, A.W. Adamson, A.P. Gast, John Wiley & Sons, Inc., 1997. A method of measuring the contact angle as used in the context of the present invention is described hereinbelow.

In a further aspect, the present invention provides a hydrophobic surface obtained by the method of the invention and as more particularly defined hereinabove.

Methods

Particle size determination by laser diffraction (Malvern):

A Mastersizer 2000 from Malvern Instruments Ltd, UK was employed in accordance with the manufacturer's instructions. The measurements were carried out in ethanol having a hydrotalcite content of 5 wt% to determine the values (such as the average particle size D50) which are based on the sample volume. To completely disperse the samples, the dispersion of the hydrotalcite in ethanol was additionally ultrasonicated for 5 min before measurement.

The D90 value indicates the value at which 90% of the particles in the sample measured have a smaller or equal particle diameter. Correspondingly, the D100 value, the D50 value and the D10 value each indicate the value at which respectively 100%, 50% and 10% of the particles in the measured sample have a smaller or equal particle diameter.

Determination of bulk weight:

A graduated cylinder cut off at the 100 ml mark is weighed. The in-test sample is then powder-funnelled into the graduated cylinder in one fell swoop so as to form a cone of repose above the rim of the graduated cylinder. The cone of repose is smoothed off with a ruler dragged across the opening of the graduated cylinder, and the filled graduated cylinder is reweighed. The difference corresponds to the bulk weight.

Water content:

The water content of the products at 120°C was determined by using the DIN/ISO 787/2 method.

Measurement of contact angle:

Contact angle was measured for the different coatings obtained by using a Krüss DSA 100 contact angle meter from Krüss, Hamburg. The basis for determining the contact angle is the picture of the droplet on the surface of a planar solid body. First a cannula 1.8 mm in diameter is used to place a water droplet onto the desired surface. The circle fitting method of Drop Shape Analysis 1.8 software can be used to determine the contact angle resulting from applying a baseline between the surface and the drop contour.

Elemental analysis:

This analysis is based on total digestion of the layered double hydroxide and/or of the corresponding product in hydrochloric acid. After dissolution of the solids, specific methods of analysis, for example ICP, are used to analyze and quantify individual components.

Determination of pH:

The pH value is determined with a pH meter in an aqueous/ethanolic suspension. A 1:1 mixture of water and ethanol (95%) is prepared for this purpose. A 50 g quantity of the water-ethanol mixture is weighed out accurately to 0.1 g in a vessel. A 1 g quantity of layered double hydroxide is weighed out accurately to 1 mg and then transferred quantitatively into the glass beaker containing the ethanol-water mixture. This is followed by 5 min of stirring before the pH is read off on the instrument.

The hydrotalcites hereinbelow were used as starting material, the commercial source being reported in each case although the preparation of corresponding layered double hydroxides is also readily possible by methods familiar to a person skilled in the art (see above).

BET surface area/pore volume after BJH and BET:

Surface area was determined using a fully automatic nitrogen porosimeter of the ASAP 2010 type from Micromeritics.

The sample is cooled down to the temperature of liquid nitrogen in a high vacuum. Nitrogen is subsequently metered continuously into the sample chambers. The adsorbed amount of gas is captured as a function of pressure and used to determine an adsorption isotherm at constant temperature. In a degassing procedure, the analytical gas is incrementally removed and a desorption isotherm recorded.

To determine the specific surface area and the porosity according to BIT theory, the data are analyzed according to DIN 66131.

Hydrotalcites employed:

The hydrotalcites employed are the Süd-Chemie materials Sorbacid® 911 and Sorbacid® 944. Their characteristic data are shown in the table which follows.

Table 1: Properties of hydrotalcites used

	Sorbacid® 911	Sorbacid® 944
Type	Mg-Al hydroxycarbonate	Mg-Al-Zn hydroxycarbonate
Chemical analysis		
Al	9-12%	8-13%
Mg	20-24%	12-18%
Zn	--	9-13%
Physical analysis		
pH (5% suspension, EtOH)	7.0-9.5	≤ 9.5
Moisture content (105°C, 2 h)	≤ 0.5%	≤0.5%
BET surface area	≤ 15 m^2/g	≤ 15 m^2/g
Particle size distribution (volumetric)		
D50	≤ 1 µm	≤ 1 µm
D90	≤ 10 µm	≤ 10 µm

SEM measurement:

The hydrophobic surfaces obtained are sputter coated to prepare the samples for scanning electron micrographs. Specifically, a sputter coater (EMITECH K 550) is used to apply an 80% gold and 20% palladium coating to the surface at a current strength of 15 mA and 0.15 mbar in the course of 1.5 min at a coating rate of 13 nm/min.

The hydrophobic surfaces thus prepared are measured in an ESEM Quanta 400 FEG SEM instrument.

Sputter coater: EMITECH K 550, from Emitech, England

Separation between object table and target: 25 mm

Sputtering time: 1.5 min

Current strength: 15 mA at 0.15 mbar

Coat thickness (deposition): ca 13 nm/min

Target: gold/palladium 80%/20%

ESEM Quanta 400 FEG: from FEI, Czechia

Schottky emitter cathode system

Everhart-Thornley detector

Semiconductor back scattered electron detector

Resolution: 2.0 nm at 30 keV

Magnification: up to 1 000 000x

Figures and examples

The method of the invention will now be more particularly described with reference to the described figures and examples. It must be emphasized here that both the figures and the examples are merely illustrative and shall not restrict the scope of the invention in any way.

Fig. 1 shows a scanning electron micrograph of an inventive coated surface comprising the product Sorbacid 944.

Fig. 2 shows a scanning electron micrograph of an inventive coated surface comprising the product Sorbacid 911.

Fig. 3 shows a scanning electron micrograph of an inventive coated surface comprising the product Sorbacid 944.

Fig. 4 shows a scanning electron micrograph of an inventive coated surface comprising the product Sorbacid 911.

Fig. 5 shows a schematic depiction of an inventive layered double hydroxide primary particle in platelet structure introduced into a cuboid. Figure 5 serves to clarify the definition of the term "platelet structure".

Example 1

1 g of Sorbacid® 911 and also Sorbacid® 944 (Süd-Chemie AG, Moosburg) were in each case weighed into 9 g of acetone (Carl Roth acetone > 99.5% for synthesis) and suspended/dispersed with a magnetic stirbar for 2 minutes and applied to a microscope slide (standard microscope slide from Roth). The dispersion was applied to the microscope slide such that the surface was homogeneously covered by the suspension. The subsequent drying took place for 15 min at 20°C in the airstream of a laboratory fume cupboard. The acetone evaporated to leave a turbid, white coating. The measurements of the contact angle are reported in Table 1. For comparison, Tegotop® 210 was coated onto the glass microscope slide (drying time about 4 h at 70°C). Tegotop® 210 is a system consisting of a silicone polymer and a hydrophobic silica. For comparison, contact angle measurements were additionally carried out with untreated glass microscope slides and also with glass microscope slides coated with stearic acid from a 20% stearic acid ethanol solution.

Table 1: Contact angle particulars

Coating system	Contact angle [°]
Sorbacid® 911	150°
Sorbacid® 944	146°

Tegotop® 210	140°
stearic acid	86°
untreated microscope slide (comparative measurement)	42°

The data confirm a universal usability of inventive hydrophobic layered double hydroxides on solid surfaces, and show that these are very useful for production of soil-repellent coatings of high contact angle.

What the scanning electron micrographs which are shown in the figures show in respect of the coatings is a structured occupancy of the glass slides by hydrotalcite particles wherein the distances between the elevations is similar to the average width of the elevations. This is a principal condition for establishing superhydrophobic surfaces (see: R. Fürstner, W. Barlhlott, C. Niehuis, P. Walzel, Wetting and Self-Cleaning Properties of Artificial Superhydrophobic Surfaces, Langmuir 2005, 21, 956-961). The high contact angles measured are thus in harmony with the structure of the coatings.

Example 2

In a 250 ml glass beaker, 21.5 g of Sorbacid® 911, 7.1 g of coloured varnish (OBI CLASSIC acrylic-based coloured varnish – water thinnable) and 35.7 g of Stoddard Solvent (Acros Organics) were heated at 90°C and homogenized by stirring. Then, 35.7 g of water at 90°C were admixed followed by further stirring to form a homogeneous suspension. After cooling, the suspension was applied to surfaces. The drying at 20°C in the airstream of a laboratory fume cupboard took 5 hours because of the high-boiling Stoddard Solvent. After drying, a mechanically strong, hydrophobic surface was obtained. It had a 143° contact angle with water. The surface coated with the acrylic varnish only merely had a contact angle of 84°.

Eljárás hidrofób felületek előállítására

Szabadalmi igénypontok

1. Eljárás hidrofób felület előállítására, mely eljárás magában foglalja a következő lépéseket:

– legalább egy réteges kettős hidroxid előállítása, és

– a készítmény felhordása egy felületre,

ahol a legalább egy réteges kettős hidroxid legalább egy hidrofób bevonattal van ellátva, és ahol a hidrofób felület kontaktszöge 100-175°.

2. Az 1. igénypont szerinti eljárás, ahol a készítmény tartalmaz egy diszperziót, egy mátrixot, közelebbről egy polimer mátrixot vagy egy olyan mátrixot, amely tartalmaz egy viaszt, vagy egy lakkot.

3.A 2. igénypont szerinti eljárás, ahol a diszperzió tartalmaz egy diszperziót, amely tartalmaz vizet, alkoholt, ketonokat, alifás és aromás oldószereket és azok elegyeit, szuperkritikus szén-dioxidot, ionos folyadékokat és azok elegyeit.

4. A 2. igénypont szerinti eljárás, ahol a mátrix tartalmaz egy polimer mátrixot, amely a termoplasztikus polimerek közül kiválasztott legalább egy polimert tartalmaz, vagy egy olyan mátrixot, amely a teljesen oxidált, részlegesen oxidált vagy nem oxidált paraffin viaszok, montánviaszok, amidviaszok, karnaubaviaszok, méhviaszok, illetve ezek keverékei közül kiválasztott legalább egy viaszt tartalmaz

5. Az előző igénypontok bármelyike szerinti eljárás, ahol a legalább egy réteges kettős hidroxid tartalmaz legalább egy hidrotalcitot.

6. Az 5. igénypont szerinti eljárás, ahol a legalább egy hidrotalcit a következők közül van kiválasztva: alumínium-magnézium-hidroxikarbonát, amely 9-12 % Al-t és 20-24 % Mg-ot tartalmaz, valamint alumínium-magnézium-cink-hidroxikarbonát, amely 8-13% Al-t, 12-18 % Mg-ot és 9-13 % Zn-et tartalmaz.

7. Az előző igénypontok bármelyike szerinti eljárás, ahol a legalább egy réteges kettős hidroxid lemezke struktúrájú partikulumok formájában van jelen.

8. A 7. igénypont szerinti eljárás, ahol a lemezkék mérete a következő: hosszúság (L) vagy átmérő (D) = 0,1-15 μm, és magasság (H) = 0,01-1 μm.

9. Az előző igénypontok bármelyike szerinti eljárás, ahol a készítmény tartalmaz továbbá egy hidrofób oldatot.

10. A 9. igénypont szerinti eljárás, ahol a hidrofób oldat a következők közül egyet vagy többet tartalmaz: termoplasztikus polimer, zsírsav, felületaktív anyag, természetes lipid, például foszfolipid, viasz, hosszú láncú foszfonát vagy hosszú láncú HO-, aldehid- vagy amin funkciós csoportot tartalmazó szénhidrogén, vagy funkciós csoportot hordozó hidrofób szilán és ezek keverékei.

11. Az előző igénypontok bármelyike szerinti eljárás, ahol a hidrofób bevonat tartalmaz egy olyan bevonatot, amely tartalmaz termoplasztikus polimert, zsírsavat, felületaktív anyagot, természetes lipidet, például foszfolipidet, viaszt, hosszú láncú foszfonátot vagy hosszú láncú HO-, aldehid- vagy amin funkciós csoportot tartalmazó szénhidrogént vagy ezek keverékeit.

12. Az előző igénypontok bármelyike szerinti eljárás, ahol a készítmény porlasztással, merítéssel, olvasztással, centrifugál-bevonással, szublimálással van felhordva a felületre.

13. Az előző igénypontok bármelyike szerinti eljárás, ahol a készítmény 0-150 °C hőmérsékleten van felhordva a felületre.

14. Az előző igénypontok bármelyike szerinti eljárás, ahol a felület tartalmaz egy üvegfelületet, fémfelületet, műanyagfelületet, fafelületet, kerámiafelületet, ásványfelületet, például, egy épület belső vagy külső felületei formájában.

15. Hidrofób felület, amely tartalmaz legalább egy réteges kettős hidroxidot, ahol a legalább egy réteges kettős hidroxid legalább egy hidrofób bevonattal van ellátva, és ahol a hidrofób felület kontaktszöge 100-175°.

16. A 15. igénypont szerinti hidrofób felület, ahol a legalább egy réteges kettős hidroxid tartalmaz legalább egy hidrotalcitot.

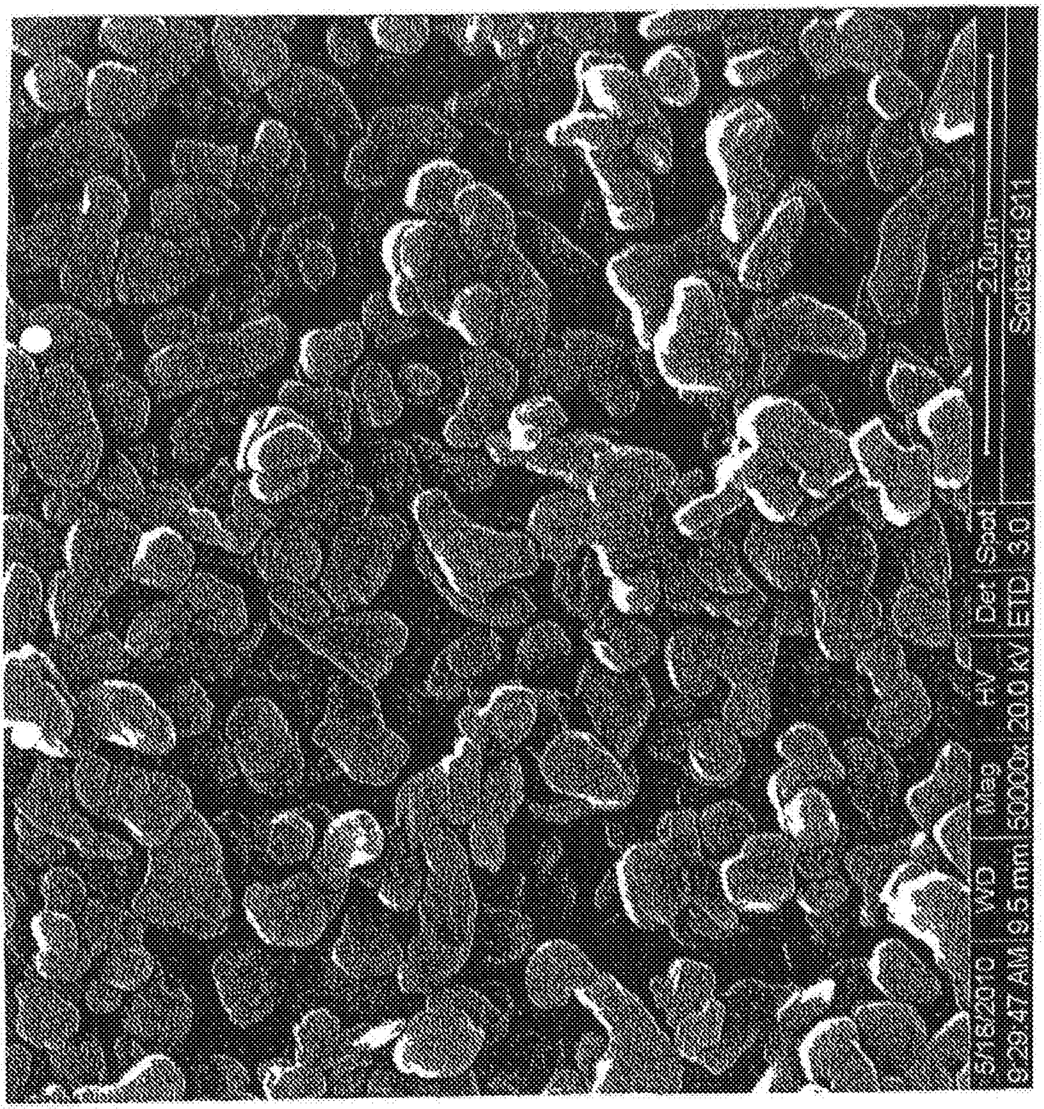
17. A 15. vagy 16. igénypont szerinti hidrofób felület, ahol a legalább egy réteges kettős hidroxid legalább egy bevonattal rendelkezik, amely bevonat a következők közül egyet vagy többet tartalmaz: termoplasztikus polimer, zsírsav, felületaktív anyag, viasz, hosszú láncú foszfonát vagy hosszú láncú HO-, aldehid- vagy amin funkciós csoportot tartalmazó szénhidrogén vagy ezek keverékei.

18. A 15-17. igénypontok bármelyike szerinti hidrofób felület, ahol a legalább egy réteges kettős hidroxid lemezkés szerkezetű.

19. A 18. igénypont szerinti hidrofób felület, ahol a lemezkék mérete a következő: hosszúság (L) és/vagy átmérő (D) = 5-15 μm, és magasság (H) = 0,01-1,5 μm.

20. A 15. igénypont szerinti hidrofób felület, ahol a hidrofób felület kontaktszöge 140-160°.

21. Hidrofób felület, amely az 1-14. igénypontok bármelyike szerinti eljárással lett előállítva.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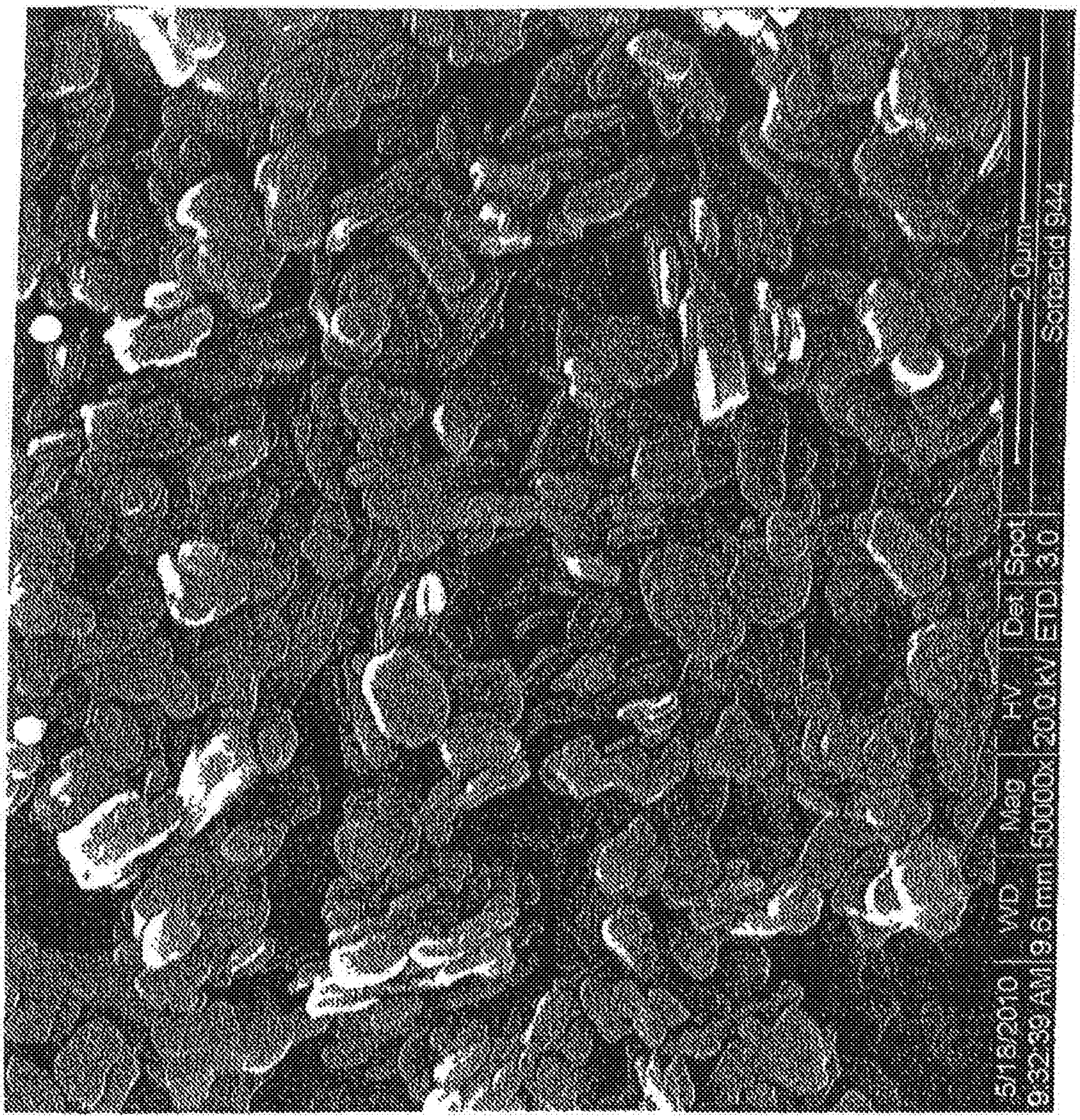
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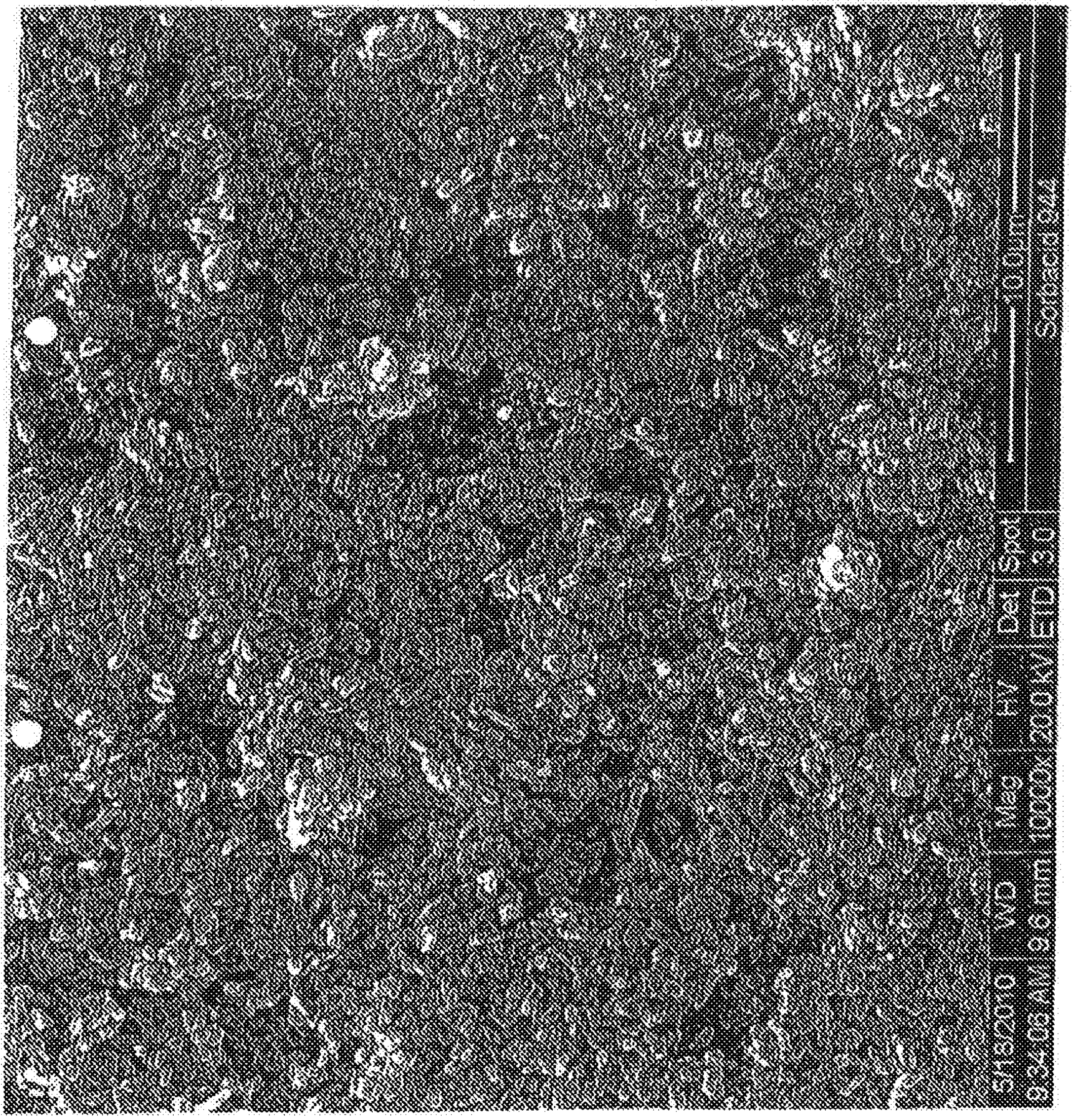
Sorbacid 944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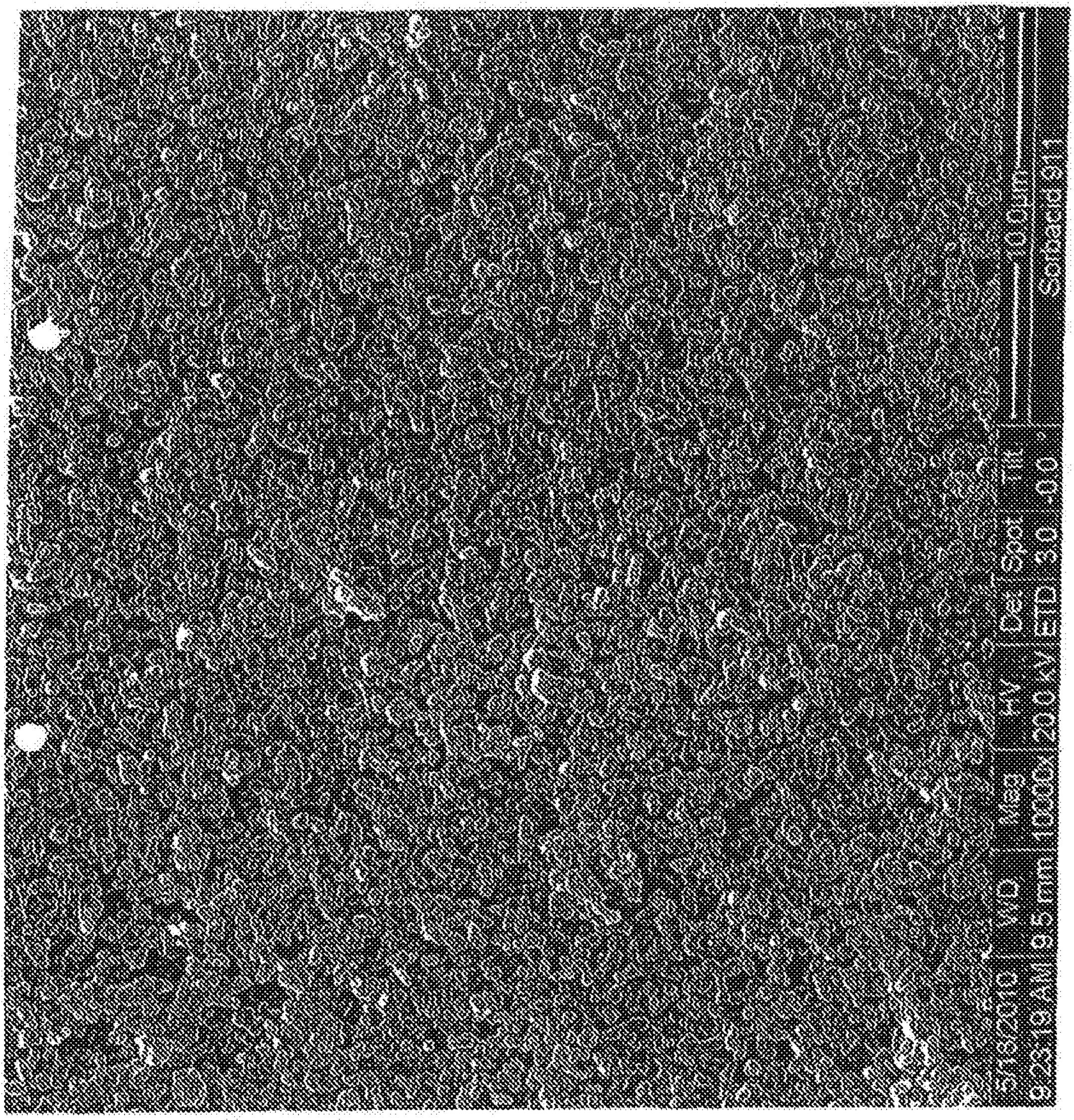
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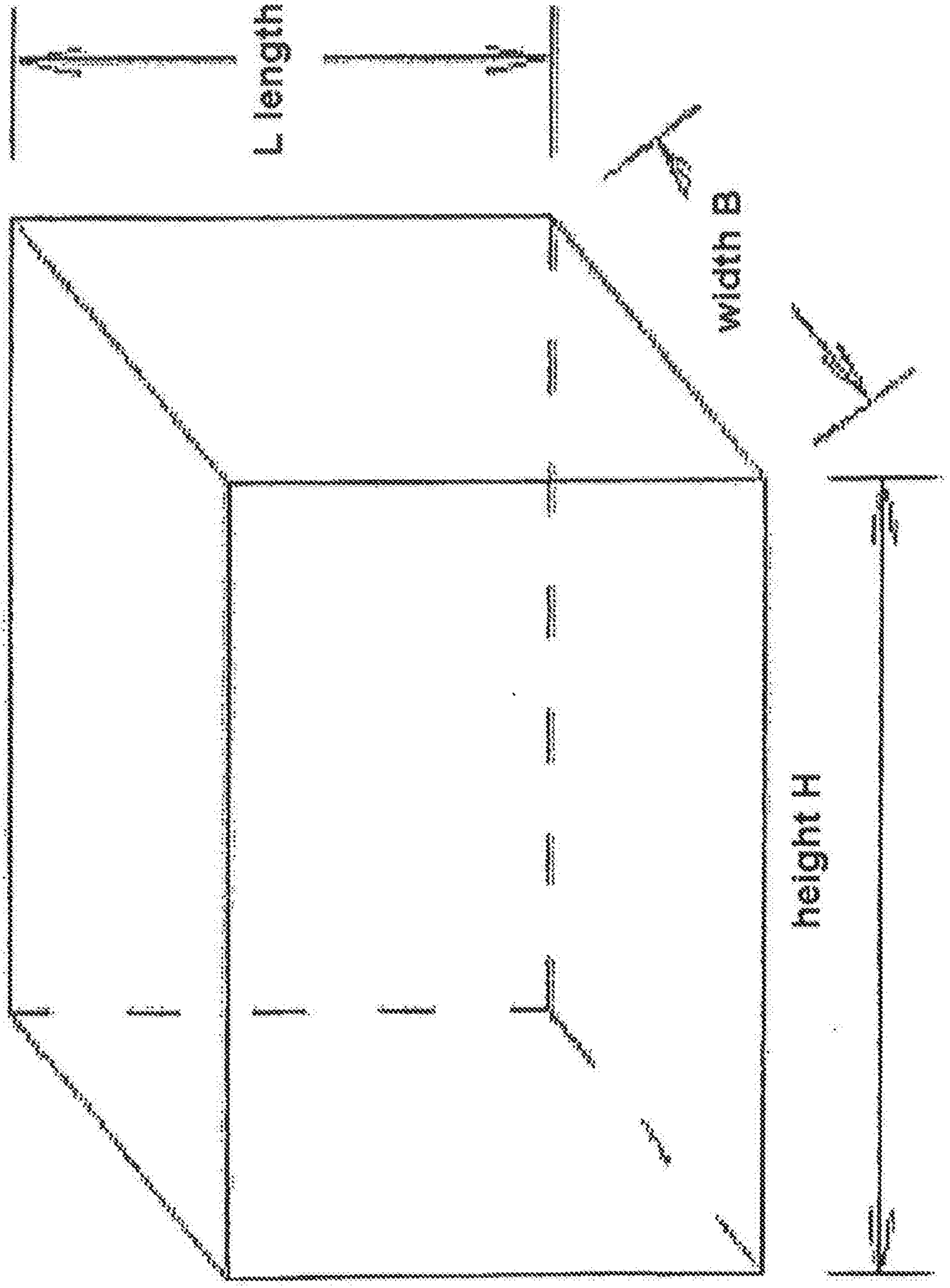
Sorbacid 911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