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(54) **SUPERHYDROPHOBIC COATING**

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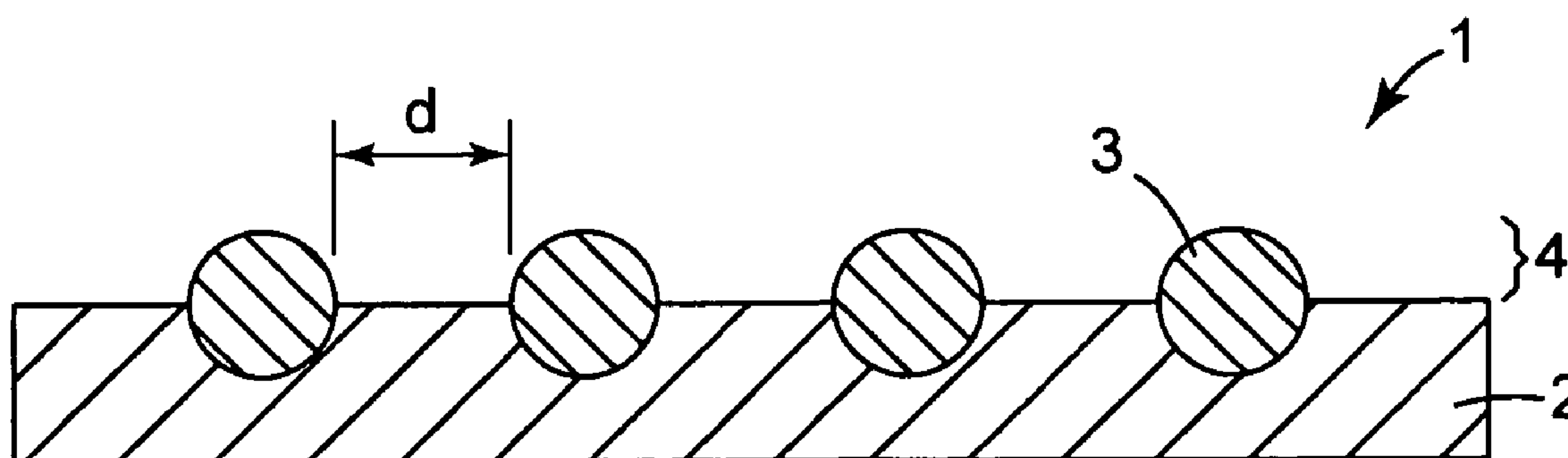
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(57) **ABSTRACT**

A coating comprises a polymer binder layer and a plurality of porous protrusions projecting from the surface of the polymer binder layer, the polymer binder layer and the protrusions independently (a) consisting essentially of at least one hydrophobic material; and/or (b) bearing a film that consists essentially of at least one hydrophobic material; wherein the distances between the protrusions are essentially shortest at the polymer binder layer surface.

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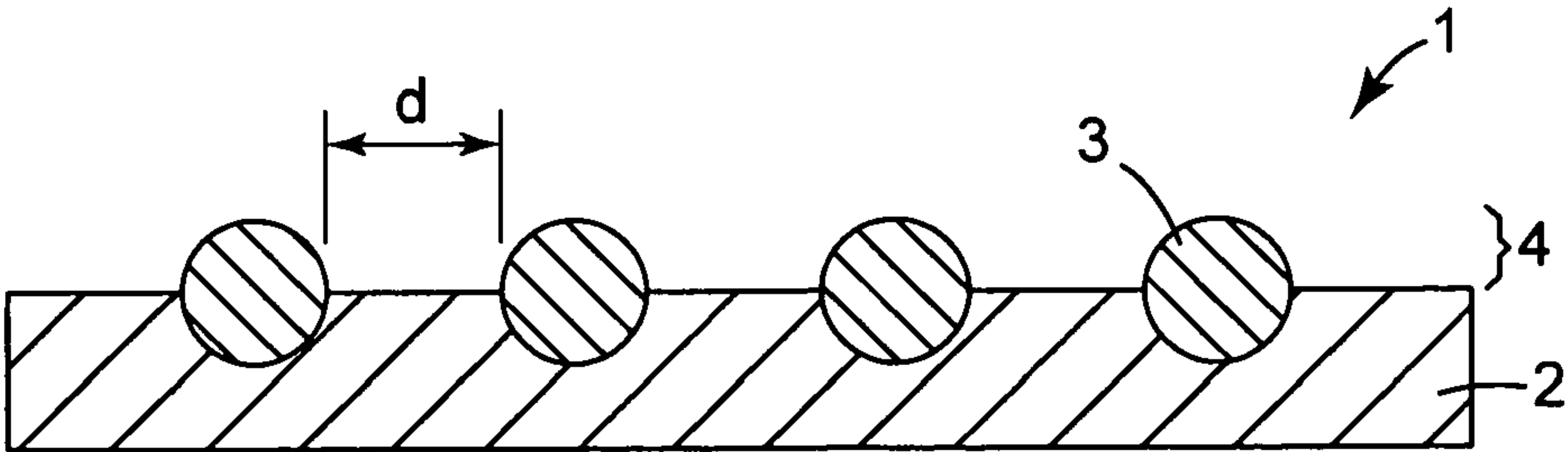


FIG. 1

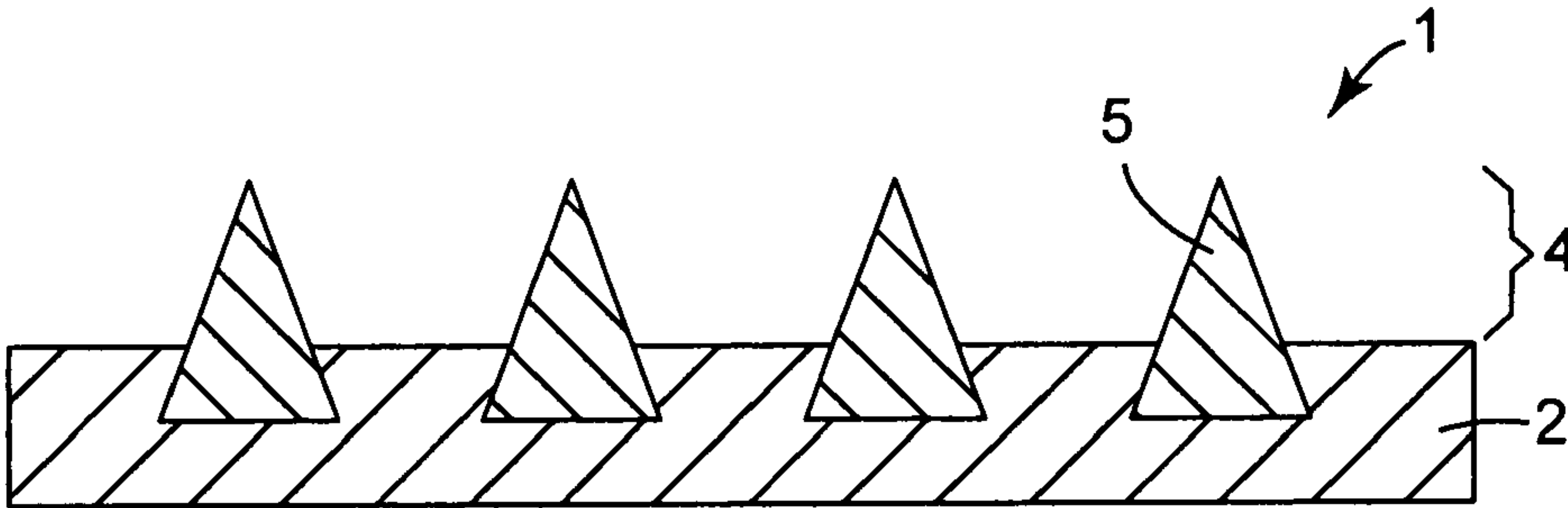


FIG. 2

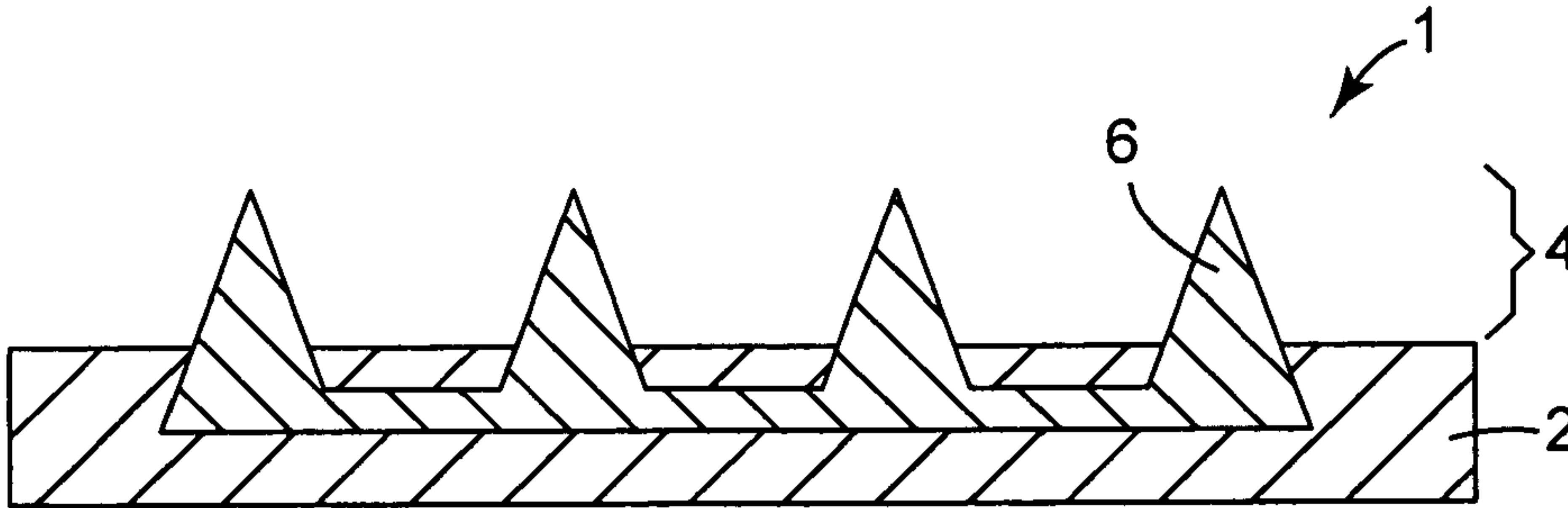


FIG. 3

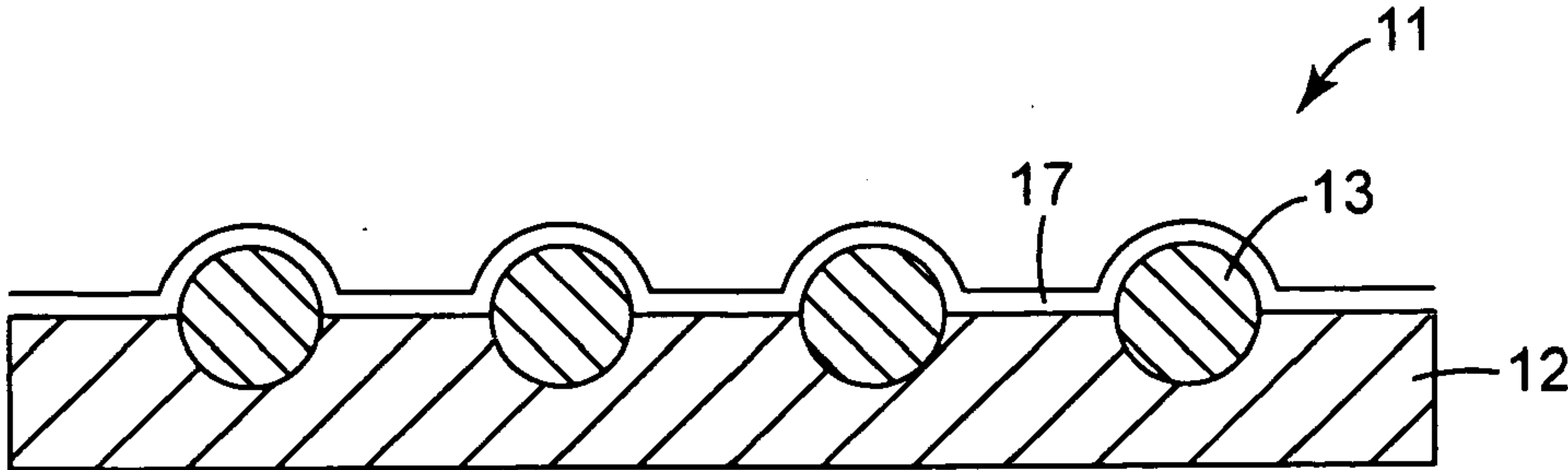


FIG. 4

SUPERHYDROPHOBIC COATING

FIELD

[0001] This invention relates to coatings for imparting water repellency and/or self-cleaning properties to substrates (for example, glass, metal, and plastic) and to articles comprising such coatings.

BACKGROUND

[0002] Self-cleaning surfaces are highly desirable in various industrial fields and in aspects of daily life. When rendered superhydrophobic (for example, ultra-water-repellent to the extent of having water contact angles greater than about 150°), surfaces exhibit a self-cleaning effect and an ability to maintain surface properties that are often detrimentally affected by water.

[0003] Control of the wettability of solid surfaces has conventionally been addressed by chemical modification of the surface, such as by the introduction of water-repellent functionalities (for example, fluoroalkyl groups). In order to achieve superhydrophobicity and its accompanying self-cleaning characteristics, however, both a low surface energy and a degree of surface micro-roughness or micro-texture are necessary.

[0004] Such combinations can be found in nature. Lotus leaves, for example, are self-cleaning due to an inherently low surface energy coupled with a microstructured surface comprising pyramidal elevations spaced a few micrometers apart.

[0005] In attempting to mimic such natural characteristics, there have been various different approaches to the production of self-cleaning surfaces. Superhydrophobic surfaces have been prepared, for example, by plasma processes, by vapor deposition, and by photolithography. Such methods have often not been suitable for industrial manufacturing, however, due to the need for multiple process steps and/or lengthy processing times. In addition, some of the surface textures resulting from these and other methods can be fragile and easily damaged.

[0006] Other approaches have employed coating compositions (for example, particle-containing binders), but coatings comprising hydrocarbon binders have tended to be somewhat lacking in chemical resistance and/or photoresistance. Fluoropolymer-based coatings have generally exhibited greater chemical stability and/or photostability but have often been difficult to bond to hydrocarbon substrates and therefore sometimes lacking in durability. Still other approaches have lacked heat resistance or have required high temperature treatment (and substrates that can withstand such treatment).

SUMMARY

[0007] Thus, we recognize that there is a need for industrially useful coatings for imparting durable superhydrophobicity to substrates (for example, glass, metals, and organic polymers).

[0008] Briefly, in one aspect, this invention provides such a coating, which comprises a polymer binder layer and a plurality of porous protrusions projecting from the surface of the polymer binder layer, the polymer binder layer and the

protrusions independently (a) consisting essentially of at least one hydrophobic material (that is, a material having a water contact angle of at least 90°); and/or (b) bearing a film that consists essentially of at least one hydrophobic material; wherein the distances between the protrusions are essentially shortest at the polymer binder layer surface. Preferably, both the polymer binder layer and the protrusions consist essentially of at least one hydrophobic material, and no film is present.

[0009] It has been discovered that by properly controlling the shapes of irregularities (in the form of protrusions) formed on a water repellent coating, the coating can exhibit not only water repellency (or hydrophobicity) but also a water-shedding or self-cleaning property that can be retained even after immersion of the coating in water. By forming protrusions on the surface of a water repellent material and appropriately adjusting the shapes of the protrusions, it can be possible to achieve a relatively high water-shedding ability, even for fine water droplets such as mist, and to retain this property over prolonged periods. Surprisingly, such characteristics can be achieved even without the use of fluorochemical materials.

[0010] Water repellency, as referenced herein, means “static” water repellency (which can be determined by measuring the contact angle of a coating with water), while the above-mentioned water-shedding property is “dynamic” water repellency (which can be measured by determining the angle at which a water droplet that is deposited on a horizontal coated surface begins to roll when the surface is tilted (“rolling angle”). Depending on the shapes of their irregularities, some prior art coatings or films (even some that exhibit relatively high contact angles with water) do not exhibit a water-shedding property for fine water droplets such as mist. Others initially exhibit a water-shedding property but, after prolonged immersion in water, gradually undergo a loss of their water-shedding property.

[0011] Unlike such prior art coatings, the coating of the invention can be durably superhydrophobic (that is, durably water repellent and durably water-shedding or self-cleaning) and, thus, can be used to impart superhydrophobic characteristics that are stable and long-lasting to various substrates. From a process standpoint, the coating can be relatively easily formed on substrate surfaces. Thus, at least some embodiments of the coating of the invention can meet the need in the art for industrially useful coatings.

[0012] In another aspect, this invention also provides a coated sheet comprising a base film and the coating of the invention on at least a portion of at least one surface of the base film.

BRIEF DESCRIPTION OF THE DRAWING

[0013] These and other features, aspects, and advantages of the present invention will become better understood with regard to the following description, appended claims, and accompanying drawing, wherein:

[0014] FIGS. 1-4 show, in sectional view, various embodiments of the coating of the invention.

[0015] These figures, which are idealized, are not drawn to scale and are intended to be merely illustrative and nonlimiting.

DETAILED DESCRIPTION

Definitions

[0016] As used in this patent application:

[0017] “contact angle” means contact angle with water (the value obtained by measurement with distilled water using a contact angle meter, for example, a FACE Contact Angle Meter Model CA-A available from Kyowa Interface Science Co., Ltd.), unless otherwise specified;

[0018] “essentially shortest at the polymer binder layer surface” (in reference to the distance between coating protrusions) means that not necessarily all of the distances between the protrusions of the coating are shortest at the polymer binder layer surface, but that a sufficient number are for the coating to exhibit a rolling angle (for a deposited water droplet of at least 0.02 mL) of 25° or less;

[0019] “hydrophobic material” means a material having a contact angle of at least 90°; and

[0020] “rolling angle” means the angle at which a water droplet of at least 0.02 mL that is deposited on a horizontal coated surface begins to roll when the surface is tilted.

Description of Preferred Embodiments

[0021] Referring to FIG. 1, in a preferred embodiment 1 of the coating of the invention, a polymer binder layer 2 anchors a plurality of particles 3 by the particles being partially embedded in the polymer binder layer. Part of each particle projects from the surface of the polymer binder layer to form a plurality of protrusions 4 (the parts of the particles that project from the surface of the polymer binder layer) on the surface of the polymer binder layer.

[0022] Particles and polymer binder layers that are suitable for use in the coating of the invention include those that consist or consist essentially of at least one material that exhibits a contact angle of 90° or greater. (The particles and polymer binder layers can “consist essentially” of such material(s), in that one or more materials having contact angles less than 90° can be present in either or both, provided that the contact angle of the overall mixture or blend of materials in both is 90° or greater (preferably, at least 100°; more preferably, at least 110°)). If the contact angle of the mixture or blend is less than 90°, it can be difficult or impossible to achieve superhydrophobicity solely by control of the shapes of the protrusions on the coating surface.) Although a larger contact angle is generally preferred, it will usually be no greater than 140°.

[0023] Polymer binders suitable for use in forming the polymer binder layer of the coating of the invention include hydrophobic materials (that is, materials that exhibit water repellency with a contact angle of 90° or greater) that are capable of anchoring particles or are otherwise capable of forming protrusions. The polymer binder preferably contains essentially no fluorine. Examples of suitable polymer binders include silicone-based adhesives and silicone-based resins, such as addition reaction-type silicones, polyurethanes, polyureas, polyepoxides, and the like, and mixtures thereof (with silicone-based adhesives, silicone-based resins, polyurethanes, and mixtures thereof being preferred).

[0024] Preferably, the particles contain essentially no fluorine. Examples of suitable particle materials include polyethylene, polypropylene, polystyrene, and the like, and mixtures thereof.

[0025] Useful particles include porous particles, aggregates of particles, and mixtures thereof. Non-porous particles generally exhibit less good water-shedding ability than their more porous counterparts. Porous particles include those having small openings or holes in the particle surface, whereby the apparent contact angle of the particle is higher than the actual contact angle of the material composing it. For example, the particles can have a specific surface area of 10-200 m²/g and a pore size of 150-200 Å. Aggregates of particles are particles that are grouped together and that thereby exhibit porosity that is similar to that of porous particles.

[0026] In the preferred embodiment of FIG. 1, the particles 3 are substantially spherical (including, for example, spheres and spheroids). Useful particles also include, however, conical and pyramidal particles 5 as shown in FIG. 2, for example, and truncated conical and truncated pyramidal particles, and the like, and mixtures thereof. The particles can be microparticles. Useful particle sizes include average diameters of 0.05-500 μm (preferably, 0.1-300 μm; more preferably, 3-100 μm; where “diameter” refers not only to the diameter of substantially spherical particles but also to the longest dimension of non-spherical particles).

[0027] Instead of separate particles as shown in FIGS. 1 and 2, the protrusions 4 can be formed on the polymer binder layer surface using a protrusion structure 6 having projecting sections that are connected together at the base of the structure, with the base being embedded in the polymer binder layer 2, as shown in FIG. 3. In the embodiments of FIGS. 2 and 3, the particles 5 and the protrusion structure 6 can be formed of the same material(s) as the particles 3 in FIG. 1, and the protrusions 4 are porous. The heights of the protrusions formed using such a protrusion structure are preferably 3-100 μm, and the density of the protrusions on the polymer binder layer surface (that is, the ratio of the area of the protrusions to that of the polymer binder layer, as measured from above) is preferably 10-85%.

[0028] The water-shedding property of the polymer binder layer can be enhanced by providing protrusions on its surface and controlling the shapes of the protrusions. Specifically, the distance (d in FIG. 1) between the protrusions can be controlled so as to be essentially shortest at the polymer binder layer surface, as compared to the distances between the protrusions at other locations. This can result in the formation of spaces between protrusions that widen from the polymer binder layer surface toward the exposed tops of the protrusions. If, rather than widening, such spaces were to narrow, water and especially fine mist can be trapped near the polymer binder layer surface and shed less easily.

[0029] The coating of the present invention exhibits a water contact angle that can be greater than the water contact angles of its components (preferably, the coating exhibits a water contact angle of 140° or more; more preferably, 150° or more). The coating exhibits a rolling angle of 25° or less (preferably, 10° or less; more preferably, 5° or less).

[0030] When the particles used are narrow conical or pyramidal shapes as shown in FIG. 2, in order to form the protrusion shapes so that the distances between the protrusions are essentially shortest at the polymer binder layer surface, the particles can be anchored with their bases situated in the polymer binder layer. In most cases anchoring of particles can be accomplished with 25-75%, preferably

30-70%, and more preferably 35-65%, of the average particle size embedded in the polymer binder layer, although this percentage can vary depending on the particle size distribution. When substantially spherical particles such as those shown in FIG. 1 are used, however, at least half of the particle size can generally be embedded in the polymer binder layer.

[0031] The coating of the invention can be produced, for example, by arranging particles or protrusion structures on a polymer binder layer of prescribed thickness, and embedding the particles in the polymer binder layer to a depth equal to a fraction of their particle size. The polymer binder layer can be formed by using conventional methods (for example, conventional coating methods such as knife coating, bar coating, dipping, and the like, and combinations thereof). The degree of embedding can be controlled by adjusting the thickness of the polymer binder layer relative to the particle size. Alternatively, the degree of particle embedding can be controlled by applied heat (which can change the viscosity of the polymer binder) or applied pressure, instead of by controlling the thickness of the polymer binder layer. Also, after partially embedding the particles in the polymer binder layer, a material with a contact angle of 90° or greater can be situated in the regions between the particles to further adjust the degree of embedding.

[0032] FIG. 4 is a sectional view of another embodiment of the coating of the invention. The embodiment 11 shown in FIG. 4 comprises a polymer binder layer 12 and a plurality of particles 13 anchored by being partially embedded in the polymer binder layer. The particles partially project from the surface of the polymer binder layer, forming a plurality of protrusions (particle portions projecting from the polymer binder layer surface) on the surface of the polymer binder layer. A film or overcoat 17 consisting or consisting essentially of a hydrophobic material is situated on the surface of the polymer binder layer and the protrusions.

[0033] The polymer binder of the polymer binder layer 12 can be essentially any material (preferably containing essentially no fluorine) that is capable of anchoring the particles 13 (or capable of otherwise forming protrusions). For example, the polymer binder can comprise silicone-based, urethane-based, acrylic-based, olefin-based, and rubber-based resins or adhesives, and the like, and mixtures thereof. The binder can be either hydrophobic or non-hydrophobic, as the film 17 is itself hydrophobic.

[0034] The particles 13 can be porous particles or particle aggregates (or mixtures thereof), as described above. Since the particles 13 are covered with a water-repellent film 17, they can comprise essentially any material (for example, useful non-hydrophobic materials include acrylic- and methacrylic-based resins, metals such as aluminum and iron, ceramics such as silica and alumina, and the like, and mixtures thereof). The particles 13 can also comprise one or more hydrophobic materials, such as those described above, in which case the use of film 17 can further enhance the water repellency and water-shedding properties of the coating. Preferably, however, the particles contain essentially no fluorine.

[0035] In FIG. 4, the particles 13 can be of any of the shapes and sizes described above, and they can also be replaced by or admixed with the above-described protrusion

structures. The heights of the formed protrusions and the density of the protrusions on the polymer binder layer surface can be essentially the same as those described above, and the shapes of the protrusions can also be controlled in essentially the same manner. The particles or protrusion structures can be anchored in the polymer binder layer as described above.

[0036] The film 17 consists or consists essentially of a hydrophobic material. (The film can “consist essentially” of such a material, in that one or more materials having contact angles less than 90° can be present in the film, provided that the contact angle of the overall mixture or blend of materials is 90° or greater (preferably, at least 100°; more preferably, at least 110°)). Preferably, however, it contains essentially no fluorine. Examples of useful hydrophobic materials include organic silicone derivatives (for example, condensed hydrolysates of methyltriethoxysilane, dimethyldiethoxysilane, or phenyltrimethoxysilane), and the like, and mixtures thereof.

[0037] The thickness of film 17 is preferably in the range of 0.001-5 μm . With a thickness of greater than 5 μm , the protrusions can become embedded in the film, such that a desired protrusion structure does not exist on the surface of the film, and the water-shedding property of the coating is reduced or eliminated. With a thickness of less than 0.001 μm , some sections of the polymer binder layer and/or the particles may not be covered with the film, which can be detrimental to the properties of the coating if the binder and/or the particles do not themselves comprise sufficiently hydrophobic material. The thickness of film 17 will also depend on the heights of the protrusions, as a greater protrusion height will allow the formation of a thicker film. Thus, the thickness of film 17 can generally be 0.1-30% of the size of the particles 13.

[0038] A superhydrophobic sheet can be obtained by, for example, situating a base film on the surface of the polymer binder layer that is opposite the surface on which the protrusions are formed. The base film can comprise essentially any commonly used material (for example, useful materials include polymer films (such as polyester, polyvinyl chloride, polyurethane, polypropylene, and the like, and combinations thereof), paper, metal, wood, concrete, ceramic, and the like, and combinations thereof). The above-described hydrophobic materials can also be used. Preferably, the base film is a polymer film.

[0039] The sheet can exhibit a water-shedding property, which can be measured by determining the angle at which a water droplet that is deposited on the coated side of the sheet begins to roll when the sheet is tilted (the rolling angle), as explained above. A sheet according to the invention can exhibit a rolling angle (for a deposited 0.02 mL water droplet) of 25° or less (preferably of 10° or less; more preferably of 5° or less). Preferred coatings can also exhibit a rolling angle, for a deposited 0.02 mL water droplet, of 25° or less after immersion in water for a period of one hour.

EXAMPLES

[0040] Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

Example 1

Preparation of a Silicone-Based, Superhydrophobic Coating Comprising Protruding Porous Particles

[0041] A solution of silicone adhesive (obtained under the trade designation “PSA518” from GE Toshiba Silicones, Tokyo, Japan) was diluted to 10 weight percent adhesive with toluene, and the resulting solution was coated on a sheet of poly(ethylene terephthalate) film. The thickness of the resulting coating was empirically determined to provide a dry coating thickness of approximately 4 micrometers. Porous poly(styrene) particles having a mean particle size of approximately 8 micrometers (obtained under the trade designation “SBP-8” from Sekisui Plastics Co., Ltd., Tokyo, Japan) were distributed over the entire surface of the coating and were allowed to become embedded in the coating. The coating was then dried by heating at 100° C. in a forced air oven for one hour to provide a coated sheet. The coating was then crosslinked by exposing it to ultraviolet radiation at a dose of approximately 96 millijoules per square centimeter using a Model UVL-2000N mercury lamp (available from Ushio America Inc., Cypress, Calif.). The resulting coated sheet was rinsed with water to remove any excess poly(styrene) particles and was then allowed to dry.

[0042] The coated sheet was placed on a stage that could be tilted or inclined (with respect to the horizontal) through a range of angles. A drop of water having a volume of approximately 0.02 mL was placed on the surface of the coating, and then the stage was slowly tilted. The angle of the stage (with respect to the horizontal) at which the water drop began to roll down the surface of the coating was determined to be less than 5°. The coated sheet was then immersed in water for 168 hours, after which time it was allowed to dry. A drop of water having a volume of approximately 0.02 mL was again placed on the surface of the coating, and then the stage was slowly tilted. The angle of the stage (with respect to the horizontal) at which the water drop began to roll down the surface of the coating was determined to be less than 5°.

Example 2

Preparation of a Silicone-Based, Superhydrophobic Coating Comprising Protruding Porous Particles

[0043] A sheet of coated poly(ethylene terephthalate) film was prepared essentially as described in Example 1, except that the dry coating thickness was approximately 6 micrometers. The hydrophobicity of the coated sheet was evaluated essentially as described in Example 1 by placing the coated sheet on a stage and determining the angle at which a water drop began to roll down the surface of the coating. The angle of the stage (with respect to the horizontal) at which the water drop began to roll down the surface of the coating was determined to be less than 5°.

[0044] The coated sheet was then immersed in water for 168 hours, after which time it was allowed to dry. A drop of water having a volume of approximately 0.02 mL was again placed on the surface of the coating and then the stage was slowly tilted. The angle of the stage (with respect to the horizontal) at which the water drop began to roll down the surface of the coating was determined to be less than 5°.

Comparative Example 1

Preparation of a Coating Comprising Protruding Non-Porous Particles

[0045] A solution of silicone adhesive (obtained under the trade designation “PSA518” from GE Toshiba Silicones, Tokyo, Japan) was diluted to 10 weight percent adhesive with toluene, and the resulting solution was coated on a sheet of poly(ethylene terephthalate) film. The thickness of the resulting coating was empirically determined to provide a dry coating thickness of approximately 4 micrometers. Non-porous poly(styrene) particles having a mean particle size of approximately 6 micrometers (obtained under the trade designation “SBX-6” from Sekisui Plastics Co., Ltd., Tokyo, Japan) were distributed over the entire surface of the coating and were allowed to become embedded in the coating. The coating was then dried by heating at 100° C. in a forced air oven for one hour to provide a coated sheet. The coating was then crosslinked by exposing it to ultraviolet radiation essentially as described in Example 1. The resulting sheet was rinsed with water to remove any excess poly(styrene) particles and was then allowed to dry.

[0046] The coated sheet was placed on a stage that could be tilted or inclined (with respect to the horizontal) through a range of angles. A drop of water having a volume of approximately 0.02 mL was placed on the surface of the coating, and then the stage was slowly tilted. The angle of the stage (with respect to the horizontal) at which the water drop began to roll down the surface of the coating was determined to be greater than 30°.

Comparative Example 2

Preparation of a Coating Comprising Fully Embedded Porous Particles

[0047] A solution of silicone adhesive (obtained under the trade designation “PSA518” from GE Toshiba Silicones, Tokyo, Japan) was diluted to 10 weight percent adhesive with toluene, and the resulting solution was combined with porous poly(styrene) particles having a mean particle size of approximately 8 micrometers (obtained under the trade designation “SBP-8” from Sekisui Plastics Co., Ltd., Tokyo, Japan) in proportion to provide a mixture that was equal parts by weight of silicone adhesive and poly(styrene) particles. The resulting mixture was coated on a sheet of poly(ethylene terephthalate) film. The thickness of the coating was empirically determined to provide a dry coating thickness of approximately 20 micrometers. The coating was then dried by heating at 100° C. in a forced air oven for one hour to provide a coated sheet. The porous poly(styrene) particles were observed to be essentially fully embedded in the silicone adhesive. Essentially no protrusions were observed to be projecting from the surface of the adhesive.

[0048] The coated sheet was placed on a stage that could be tilted or inclined (with respect to the horizontal) through a range of angles. A drop of water having a volume of approximately 0.02 mL was placed on the surface of the coating, and then the stage was slowly tilted. The angle of the stage (with respect to the horizontal) at which the water drop began to roll down the surface of the coating was determined to be greater than 40°.

Example 3

Preparation of a Silicone-Based, Superhydrophobic Coating Comprising Protruding Porous Particles

[0049] A sheet of coated poly(ethylene terephthalate) film was prepared essentially as described in Example 1, except that the coating was dried in a forced air oven at 100° C. before the particles were allowed to become as embedded in the adhesive, thereby resulting in a coating of silicone adhesive in which the particles were less embedded. The hydrophobicity of the coated sheet was evaluated essentially as described in Example 1 by placing the coated sheet on a stage and determining the angle at which a water drop began to roll down the surface of the coating. The angle of the stage (with respect to the horizontal) at which the water drop began to roll down the surface of the coating was determined to be less than 5°.

[0050] The coated sheet was then immersed in water for a period of less than one hour, after which time it was allowed to dry. A drop of water having a volume of approximately 0.02 mL was again placed on the surface of the coating, and then the stage was slowly tilted. The angle of the stage (with respect to the horizontal) at which the water drop began to roll down the surface of the coating was determined to be greater than 60°.

Example 4

Preparation of a Silicone-Based, Superhydrophobic Coating Comprising Protruding Porous Particles

[0051] A sheet of coated poly(ethylene terephthalate) film was prepared essentially as described in Example 1, except that the dry coating thickness was approximately 1 micrometer. The hydrophobicity of the coated sheet was evaluated essentially as described in Example 1 by placing the coated sheet on a stage and determining the angle at which a water drop began to roll down the surface of the coating. The angle of the stage (with respect to the horizontal) at which the water drop began to roll down the surface of the coating was determined to be less than 5°.

[0052] The coated sheet was then immersed in water for a period of less than one hour, after which time it was allowed to dry. A drop of water having a volume of approximately 0.02 mL was again placed on the surface of the coating, and then the stage was slowly tilted. The angle of the stage (with respect to the horizontal) at which the water drop began to roll down the surface of the coating was determined to be greater than 60°.

Comparative Example 3

Preparation of a Coating Comprising Fully Embedded Porous Particles

[0053] A sheet of coated poly(ethylene terephthalate) film was prepared essentially as described in Example 1, except that the dry coating thickness was approximately 10 micrometers. The hydrophobicity of the coated sheet was evaluated essentially as described in Example 1 by placing the coated sheet on a stage and determining the angle at which a water drop began to roll down the surface of the coating. The angle of the stage (with respect to the horizon-

tal) at which the water drop began to roll down the surface of the coating was determined to be greater than 60°.

Example 5

Preparation of a Silicone-Based, Superhydrophobic Coating Comprising a Hydrophobic Film

[0054] A solution of silicone adhesive (obtained under the trade designation "PSA518" from GE Toshiba Silicones, Tokyo, Japan) was diluted to 10 weight percent adhesive with toluene, and the resulting solution was coated on a sheet of poly(ethylene terephthalate) film. The thickness of the resulting coating was empirically determined to provide a dry coating thickness of approximately 4 micrometers. Porous poly(styrene) particles having a mean particle size of approximately 8 micrometers (obtained under the trade designation "SBP-8" from Sekisui Plastics Co., Ltd., Tokyo, Japan) were distributed over the entire surface of the coating and were allowed to become embedded in the coating. The coating was then dried by heating at 100° C. in a forced air oven for two hours to provide a coated sheet. The coating was then crosslinked by exposing it to ultraviolet radiation essentially as described in Example 1. The resulting sheet was rinsed with water to remove any excess poly(styrene) particles and was then allowed to dry.

[0055] The sheet was then coated with approximately one gram of a solution that was prepared by combining methyltriethoxysilane (2 g), 0.1N aqueous hydrochloric acid (0.5 g), and water (1.5 g) with isopropyl alcohol (15 g). The resulting coated sheet was then dried in a forced air oven at 100° C. for two hours. The dried coated sheet was placed on a stage that could be tilted or inclined (with respect to the horizontal) through a range of angles. A drop of water having a volume of approximately 0.02 mL was placed on the surface of the coating, and then the stage was slowly tilted. The angle of the stage (with respect to the horizontal) at which the water drop began to roll down the surface of the coating was determined to be less than 3°.

[0056] The coated sheet was then immersed in water for 168 hours, after which time it was allowed to dry. A drop of water having a volume of approximately 0.02 mL was again placed on the surface of the coating, and then the stage was slowly tilted. The angle of the stage (with respect to the horizontal) at which the water drop began to roll down the surface of the coating was determined to be less than 3°.

Example 6

Preparation of a Silicone-Based, Superhydrophobic Coating Comprising Protruding Porous Particles

[0057] A solution of a two-part silicone adhesive (obtained under the trade designation "TSE3320" from GE Toshiba Silicones, Tokyo, Japan) was prepared by dissolving two grams of the silicone in ten grams of toluene. The resulting solution was coated on a sheet of poly(ethylene terephthalate) film. The thickness of the coating was empirically determined to provide a dry coating thickness of approximately 4 micrometers. Porous poly(styrene) particles having a mean particle size of approximately 8 micrometers (obtained under the trade designation "SBP-8" from Sekisui Plastics Co., Ltd., Tokyo, Japan) were distributed over the entire surface of the coating and were allowed to become embedded in the coating. The coating was then dried by

heating at 100° C. in a forced air oven for one hour to provide a coated sheet. The resulting coated sheet was rinsed with water to remove any excess poly(styrene) particles and was then allowed to dry.

[0058] The hydrophobicity of the coated sheet was evaluated essentially as described in Example 1 by placing the coated sheet on a stage and determining the angle at which a water drop began to roll down the surface of the coating. Before and after the sheet was immersed in water for 168 hours, the angle of the stage (with respect to the horizontal) at which the water drop began to roll down the surface of the coating was determined to be less than 3°.

Example 7

Preparation of a Polyurethane-Based, Superhydrophobic Coating Comprising Protruding Porous Particles

[0059] A solution of a urethane adhesive was prepared by combining 255 parts by weight of a urethane precursor (obtained under the trade designation “SUMIDUR N75” from Sumitomo Bayer Urethane Co., Ltd., Tokyo, Japan) and 100 parts by weight of a multifunctional alcohol (available under the trade designation “TONE POLYOL 0301” from Sumitomo Dow Ltd., Tokyo, Japan) at a total concentration of 10 weight percent in toluene. The resulting solution was coated on a sheet of poly(ethylene terephthalate) film. The thickness of the coating was empirically determined to provide a dry coating thickness of approximately 4 micrometers. Porous poly(styrene) particles having a mean particle size of approximately 8 micrometers (obtained under the trade designation “SBP-8” from Sekisui Plastics Co., Ltd., Tokyo, Japan) were distributed over the entire surface of the coating. The particles were allowed to become embedded in the coating by placing a glass plate over the particles and heating the resulting construction at 155° C. in a forced air oven for two hours to provide a coated sheet.

[0060] The coating of the coated sheet was then covered with a thin film of a 0.1 weight percent solution of phenyltriethoxysilane in isopropyl alcohol and was allowed to dry. The hydrophobicity of the coated sheet was evaluated essentially as described in Example 1 by placing the coated sheet on a stage and determining the angle at which a water drop began to roll down the surface of the coating. Before and after the sheet was immersed in water for 168 hours, the angle of the stage (with respect to the horizontal) at which the water drop began to roll down the surface of the coating was determined to be less than 3°.

[0061] The referenced descriptions contained in the patents, patent documents, and publications cited herein are incorporated by reference in their entirety as if each were individually incorporated. Various unforeseeable modifications and alterations to this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention. It should be understood that this invention is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of example only, with the scope of the invention intended to be limited only by the claims set forth herein as follows:

We claim:

1. A coating comprising a polymer binder layer and a plurality of porous protrusions projecting from the surface of said polymer binder layer, said polymer binder layer and said protrusions independently (a) consisting essentially of at least one hydrophobic material; and/or (b) bearing a film that consists essentially of at least one hydrophobic material; wherein the distances between said protrusions are essentially shortest at said polymer binder layer surface.

2. The coating of claim 1, wherein both said polymer binder layer and said protrusions consist essentially of at least one hydrophobic material, and said film is absent.

3. The coating of claim 2, wherein said coating comprises a plurality of particles that are partially embedded in said polymer binder layer so as to partially project from the surface of said polymer binder layer to form said protrusions, said particles being selected from the group consisting of porous particles, particle aggregates, and mixtures thereof.

4. The coating of claim 2, wherein said polymer binder layer consists essentially of at least one hydrophobic material that contains no fluorine.

5. The coating of claim 2, wherein said polymer binder layer consists essentially of at least one hydrophobic material selected from silicone-based adhesives, silicone-based resins, polyurethanes, polyureas, polyepoxides, and mixtures thereof.

6. The coating of claim 3, wherein said particles consist essentially of at least one hydrophobic material that contains no fluorine.

7. The coating of claim 3, wherein said particles consist essentially of at least one hydrophobic material selected from polyethylene, polypropylene, polystyrene, and mixtures thereof.

8. The coating of claim 3, wherein said particles are selected from substantially spherical particles, conical particles, pyramidal particles, truncated conical particles, truncated pyramidal particles, and mixtures thereof.

9. The coating of claim 8, wherein said particles are substantially spherical particles.

10. The coating of claim 9, wherein said particles have at least 25% and less than 75% of their average particle size embedded in said polymer binder layer.

11. The coating of claim 3, wherein said particles are microparticles.

12. The coating of claim 1, wherein neither said polymer binder layer nor said protrusions consist essentially of at least one hydrophobic material, and said film is present.

13. The coating of claim 12, wherein said coating comprises a plurality of particles that are partially embedded in said polymer binder layer so as to partially project from the surface of said polymer binder layer to form said protrusions, said particles being selected from the group consisting of porous particles, particle aggregates, and mixtures thereof.

14. The coating of claim 12, wherein the polymer binder of said polymer binder layer comprises a material selected from silicone-based, urethane-based, acrylic-based, olefin-based, and rubber-based resins; silicone-based, urethane-based, acrylic-based, olefin-based, and rubber-based adhesives; and mixtures thereof.

15. The coating of claim 13, wherein said particles comprise a material selected from acrylic- and methacrylic-based resins, metals, ceramics, and mixtures thereof.

16. The coating of claim 13, wherein said particles are selected from substantially spherical particles, conical particles, pyramidal particles, truncated conical particles, truncated pyramidal particles, and mixtures thereof.

17. The coating of claim 16, wherein said particles are substantially spherical particles.

18. The coating of claim 17, wherein said particles have at least 25% and less than 75% of their average particle size embedded in said polymer binder layer.

19. The coating of claim 13, wherein said particles are microparticles.

20. The coating of claim 12, wherein said hydrophobic material of said film contains no fluorine.

21. The coating of claim 12, wherein said hydrophobic material of said film is selected from organic silicone derivatives and mixtures thereof.

22. The coating of claim 13, wherein the thickness of said film is 0.1-30 percent of the size of said particles.

23. The coating of claim 1, wherein said coating exhibits a rolling angle, for a deposited 0.02 mL water droplet, of 10° or less.

24. The coating of claim 1, wherein said coating exhibits a rolling angle, for a deposited 0.02 mL water droplet, of 25° or less after immersion in water for a period of one hour.

25. A coating comprising a polymer binder layer and a plurality of porous polystyrene microparticles partially embedded in and partially projecting from the surface of said polymer binder layer to form protrusions, said polymer binder layer consisting essentially of at least one hydrophobic material selected from silicone-based adhesives, silicone-based resins, polyurethanes, and mixtures thereof; wherein the distances between said protrusions are essentially shortest at said polymer binder layer surface.

26. A coated sheet comprising a base film and the coating of claim 1 on at least a portion of at least one surface of said base film.

27. A coated sheet comprising a base film and the coating of claim 25 on at least a portion of at least one surface of said base film.

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