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(54) **Title:** FIXED-AMOUNT SPRAY-TYPE AEROSOL PRODUCT

(54) 発明の名称: 定量噴射型エアゾール

(57) **Abstract:** The present invention relates to a fixed-amount spray-type aerosol product having a pressure-proof container and an aerosol composition filled in the pressure-proof container, a fixed amount of aerosol composition being sprayed in one spray operation, wherein the aerosol composition contains a room-temperature solid drug, a solvent, and a propellant, and the latent heat of vaporization of the mixture of the solvent and the propellant is 10.00 kcal/mol or less.

(57) 要約: 本発明は、耐圧容器と、前記耐圧容器に充填されたエアゾール組成物とを有し、1回の噴射操作で一定量のエアゾール組成物を噴射する定量噴射型エアゾールであって、前記エアゾール組成物が常温固体状薬剤と溶剤と噴射剤とを含み、前記溶剤及び前記噴射剤からなる混合物の蒸発潜熱が10.00 kcal/mol以下である、定量噴射型エアゾールに関する。



WO 2023/106385 A1

DESCRIPTION

Title of Invention:

METERED-SPRAY AEROSOL

Technical Field

[0001] The present invention relates to a metered-spray aerosol.

Background Art

[0002] Aerosol compositions containing chemical agents such as pest control components are common as pest control agents to be used indoors or the like. For example, Patent Literature 1 describes an aerosol composition containing an insecticide which is volatile at room temperature as an active component and describes that the concentration of the active component in the air can be kept for a long time by spraying a small amount of the aerosol composition.

Citation List

Patent Literature

[0003] Patent Literature 1: JP-A-2002-3302

Summary of Invention

Technical Problem

[0004] As in the above Patent Literature 1, when the active component is volatile at room temperature, the effect can be maintained by volatilizing it even after spray particles adhere to indoor walls or indoor floors.

On the other hand, when the chemical agent that is an active component is in a solid state at room temperature, the active component does not volatilize at room temperature and precipitates on a treatment surface, so the adhesion state directly affects the effect.

Thus, there was room to study the means of effectively treating the chemical agent that is in a solid state at room temperature.

[0005] Also, as an aerosol, general continuous spray aerosols and metered-spray aerosols are common. Here, in the metered-spray aerosol, the amount of a chemical agent ejected by one spraying operation is fixed. Especially in the metered-spray aerosol, there was room to study

the means of treating the chemical agent that is in a solid state at room temperature for more widely spraying and enhancing the effect.

[0006] An object of the present invention is to provide a means that can enhance the effect of a chemical agent that is in a solid state at room temperature in the treatment using a metered-spray aerosol.

Solution to Problem

[0007] As a result of intensive studies, the present inventors have found that the effect of a chemical agent that is in a solid state at room temperature can be enhanced by using a metered-spray aerosol in which the sprayed amount by one spraying operation is fixed and a latent heat of evaporation of a mixture of a solvent and a propellant in the aerosol composition is within a specific range.

[0008] That is, the present invention relates to the following (1) to (3).

(1) A metered-spray aerosol comprising a pressure-resistant container and an aerosol composition with which the pressure-resistant container is filled, from which a fixed amount of the aerosol composition is sprayed by one spraying operation,

wherein the aerosol composition comprises a chemical agent that is in a solid state at room temperature, a solvent, and a propellant, and

a latent heat of evaporation of a mixture of the solvent and the propellant is 10.00 kcal/mol or less.

(2) The metered-spray aerosol according to (1), wherein the chemical agent that is in a solid state at room temperature is a pest control component that is in a solid state at room temperature.

(3) The metered-spray aerosol according to (1) or (2), wherein the solvent is a volatile solvent.

Advantageous Effects of Invention

[0009] In the present invention, by using a metered-spray aerosol from which a fixed amount of an aerosol composition is sprayed by one spraying operation, in which a latent heat of evaporation of a mixture of the sprayed solvent and propellant is within a specific range, the chemical agent that is in a solid state at room temperature is widely and uniformly adhered to a treatment surface. This can enhance the effect of the chemical agent that is in a solid state at room temperature.

Brief Description of the Drawings

[0010] Fig. 1 is a microscope photograph showing the precipitation state of the chemical agent after aerosol spray in Example 1.

Fig. 2 is a microscope photograph showing the precipitation state of the chemical agent after aerosol spray in Example 2.

Fig. 3 is a microscope photograph showing the precipitation state of the chemical agent after aerosol spray in Example 3.

Fig. 4 is a microscope photograph showing the precipitation state of the chemical agent after aerosol spray in Example 4.

Fig. 5 is a microscope photograph showing the precipitation state of the chemical agent after aerosol spray in Example 5.

Fig. 6 is a microscope photograph showing the precipitation state of the chemical agent after aerosol spray in Example 6.

Fig. 7 is a microscope photograph showing the precipitation state of the chemical agent after aerosol spray in Example 7.

Fig. 8 is a microscope photograph showing the precipitation state of the chemical agent after aerosol spray in Example 8.

Fig. 9 is a microscope photograph showing the precipitation state of the chemical agent after aerosol spray in Example 9.

Fig. 10 is a microscope photograph showing the precipitation state of the chemical agent after aerosol spray in Example 10.

Fig. 11 is a microscope photograph showing the precipitation state of the chemical agent after application of the chemical agent solution in Comparative Example 1.

Fig. 12 is a microscope photograph showing the precipitation state of the chemical agent after aerosol spray in Comparative Example 2.

Fig. 13 is a microscope photograph showing the precipitation state of the chemical agent after aerosol spray in Comparative Example 3.

Fig. 14 is a microscope photograph showing the precipitation state of the chemical agent after application of the chemical agent solution in Comparative Example 4.

Fig. 15 is a microscope photograph showing the precipitation state of the chemical agent after application of the chemical agent solution in Comparative Example 5.

Description of Embodiments

[0011] Hereinafter, embodiments of the present invention are described in more detail.

[0012] (Metered-spray aerosol)

The metered-spray aerosol in the present invention includes a pressure-resistant container and an aerosol composition with which the pressure-resistant container is filled.

[0013] (Aerosol Composition)

The aerosol composition includes a chemical agent that is in a solid state at room temperature (hereinafter also referred to as "chemical agent"), a solvent, and a propellant. Being in a solid state at room temperature means that it is in a solid state at room temperature, i.e., around 25°C, and it is preferable that a vapor pressure at 25°C is 25 mPa or less. Examples of being in a solid state at room temperature include, for example, being in a crystalline solid state, being in a powdered solid state, and the like. The active component refers to something that exhibits some effect when using the metered-spray aerosol. The chemical agent that is in a solid state at room temperature as an active component is not particularly limited, and examples thereof include a pest control component, a fragrance component, a deodorant component, and a disinfecting/sterilizing component, those are in a solid state at room temperature.

Hereinafter, each component is described.

[0014] The pest control component is a component that can kill, repel (including flushing out), knock down a target pest, for example. The kind of the pest control component is not particularly limited as long as the pest control component is in a solid state at room temperature, and a pest control component having a vapor pressure at 25°C being 25 mPa or less is preferable. Also, common compounds can be used.

Specific examples of the pest control component that is in a solid state at room temperature include pyrethroid compounds such as phthalthrin, etofenprox, bifenthrin, and fenpropathrin, carbamate compounds such as propoxur, organophosphorus compounds such as trichlorfon, bromophos, calcrofos, pyridaphenthion, and chlorpyrifos methyl, oxadiazole compounds such as metoxadiazone, neonicotinoid compounds such as dinotefuran, meta-diamide compounds such as broflanilide, phenylpyrazole compounds such as fipronil, and others such as pyriproxyfen, diflubenzuron, hydramethylnon, and amidoflumet, and the like. These can be used alone or in combination of two or more thereof.

[0015] The pest control component may be appropriately selected according to the kind of the target pest. Examples of the target pest include flying pests such as mosquitoes, flies,

moths, bees, horseflies, blackflies, sand flies, chironomids, and leafhoppers, creeping pests such as cockroaches, bed bugs, mites, stink bugs, ants, spiders, wood louses, lice, centipedes, caterpillars, ticks, millipedes, termites, bark beetles, ground beetles, earwigs, book worms, fleas, assassin bugs, longicorns, carpet beetles, psocids, clothes moths, and webbing clothes moths, and the like, and creeping pests are preferred.

[0016] Examples of the deodorant component that is in a solid state at room temperature include sodium hypochlorite, baking soda, catechins (such as epicatechin gallate and epigallocatechin gallate), flavonoids, polyphenols, plant extracts (such as persimmon tannin, green tea extract, grapefruit seed extract, yuzu seed extract), metal-based deodorants using metals such as silver, copper or zinc, and the like. These may be used alone or in combination of two or more thereof.

[0017] The disinfectant/sterilizing component that is in a solid state at room temperature is a component that removes or kills microorganisms, molds, or bacteria. Examples of the disinfectant/sterilizing component include isopropylmethylphenol, chlorinated isocyanurate, cetylpyridinium chloride, thymol, hinokitiol, triclosan, methylparaben, ethylparaben, propylparaben, butylparaben, 4-chloro-3,5-dimethylphenol, orthophenylphenol, benzalkonium chloride, benzalkonium saccharinate, polyhexamethylene biguanide, 1,4-bis[3,3'-(1-decylpyridinium)methoxy]butane dibromide, enilconazole, thiabendazole, 3-iodo-2-propyl-N-butylcarbamate (IPBC), benzisothiazolinone, zinc pyrithione, sodium pyrithione, diiodomethyl-p-tolylsulfone, monocaprin, monocaprylin, tebuconazole, metal-based disinfectant/sterilizing agent using metals such as silver, copper, or zinc, and the like. These may be used alone or in combination of two or more thereof.

[0018] The above-mentioned chemical agents can be used in combination with components that exhibit different effect.

[0019] The content of the chemical agent is preferably 0.01 to 90 mass/volume % relative to the total amount of the chemical agent and the solvent (hereinafter also referred to as "stock solution"). In the case where the content of the chemical agent is 0.01 mass/volume % or more relative to the stock solution, a sufficient effect of the chemical agent can be obtained, and in the case where the content is 90 mass/volume % or less, it can be sufficiently dissolved or dispersed in the solvent. In terms of the lower limit, the content of the chemical agent is more preferably 0.1 mass/volume % or more, even more preferably 0.3 mass/volume % or more, particularly preferably 0.5 mass/volume % or more, most preferably 1 mass/volume % or more, and in terms of the upper limit, the content is more preferably 80 mass/volume % or

less, even more preferably 65 mass/volume % or less, particularly preferably 50 mass/volume % or less, most preferably 15 mass/volume % or less.

[0020] In the present invention, since the chemical agent is in a solid state at room temperature, it is preferable from the viewpoint of handling that the chemical agent is dissolved or dispersed in the solvent in the stock solution. As such a solvent, a volatile solvent is particularly preferable because such a solvent is required to dissolve or disperse the chemical agent in the aerosol composition and to gradually volatilize and precipitate the chemical agent after the aerosol composition is sprayed.

Specific examples of the volatile solvent include organic solvents such as glycol ether solvents, hydrocarbon solvents, alcohol solvents, aromatic solvents, and ester solvents, and water. The volatile solvent is not particularly limited as long as it has volatility at room temperature, but it is preferable that a volatile solvent having a vapor pressure at 25°C being 50 Pa or more, more preferably 100 Pa or more, and particularly preferably 1000 Pa or more. In addition, a surfactant may be used.

[0021] Examples of glycol ether solvents include propylene glycol monopropyl ether, propylene glycol monobutyl ether, dipropylene glycol monopropyl ether, dipropylene glycol monobutyl ether, dipropylene glycol dimethyl ether, ethylene glycol monoisobutyl ether, diethylene glycol monoisobutyl ether, diethylene glycol dibutyl ether, diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, and the like.

Examples of hydrocarbon solvents include aliphatic hydrocarbons and cycloaliphatic hydrocarbons, such as paraffin hydrocarbons and naphthenic hydrocarbons, and kerosene such as JIS No. 1 kerosene is preferable. Specific examples thereof include normal paraffin and isoparaffin. Examples of normal paraffin include those having 8 to 16 carbon atoms, such as NEO-CHIOZOL manufactured by Sanko Chemical Industry Co., Ltd. and Normal Paraffin MA manufactured by ENEOS Corporation. Examples of isoparaffin include those having 8 to 16 carbon atoms, such as IP Clean LX manufactured by Idemitsu Kosan Co., Ltd.

Examples of alcohol solvents include lower alcohols such as ethanol, normal propanol, isopropanol, polyhydric alcohols such as ethylene glycol, and the like.

Examples of aromatic solvents include toluene, xylene, and the like.

Examples of ester solvents include isopropyl myristate, hexyl laurate, isopropyl palmitate, and the like.

Among these, alcohol solvents are preferable because they have excellent solubility or dispersibility for the chemical agent that is in a solid state at room temperature, and lower

alcohols such as ethanol, normal propanol, and isopropanol are more preferable.

The above solvents can be used alone or in combination of two or more thereof.

[0022] The stock solution may contain other components as long as the effects of the present invention are not impaired. Examples of the other components include a preservative, a pH adjuster, an ultraviolet absorbent, an inorganic substance, a surfactant, and dissolution aid.

[0023] The content of the stock solution in the aerosol composition can be appropriately changed according to the purpose of use of the metered-spray aerosol and the combination with the propellant, and is not particularly limited, but for example, the content can be 1 to 90 volume% in the aerosol composition. In the case where the content of the stock solution in the aerosol composition is 1 volume% or more, the surface area of the chemical agent remaining on the treatment surface increases, so the amount of chemical agent taken up by pests and the frequency of contact with the chemical agent can be increased, and as a result, sufficient pest control effect can be obtained. In the case where the content of the stock solution in the aerosol composition is 90 volume% or less, the stock solution can be sprayed as spray particles, so for example, the chemical agent can be sufficiently and uniformly adhered to the target area. As a result, it is possible to effectively prevent initial adhesion such as biofilm formation by bacteria and adhesion and hyphal elongation of mold spores, and to obtain sufficient disinfection/sterilization effects. The content of the stock solution is more preferably 5 volume% or more in terms of the lower limit and is more preferably 70 volume% or less in terms of the upper limit, in the aerosol composition.

[0024] The propellant is a medium for spraying the stock solution composed of the above-mentioned chemical agent and solvent, and a pressure-resistant container is filled with the propellant together with the chemical agent and solvent under pressure. As the propellant, for example, one or two or more kinds of liquefied petroleum gas (LPG) such as propane, propylene, n-butane and isobutane, liquefied gas such as dimethyl ether (DME), carbon dioxide gas, nitrogen gas, compressed gas such as compressed air, and halogenated carbon gas such as HFC-152a, HFC-134a, HFO-1234yf, HFO-1234ze can be used. The propellant to be used can be appropriately selected according to the solubility with the stock solution and the container members such as the aerosol valve.

[0025] The content of the propellant in the aerosol composition can be appropriately changed according to the purpose of use of the metered-spray aerosol and the combination with the stock solution, and is not particularly limited, but for example, the content can be 10 to 99 volume% in the aerosol composition. In the case where the content of the propellant in

the aerosol composition is 10 volume% or more, the stock solution can be sprayed as spray particles, so for example, the chemical agent can be sufficiently and uniformly adhered to the target area, and the effect of the chemical agent is likely to last. In the case where the content of the propellant is 99 volume% or less, sufficient effect can be obtained. The content of the propellant is more preferably 30 volume% or more in terms of the lower limit and is preferably 95 volume% or less in terms of the upper limit, in the aerosol composition.

[0026] The volume ratio of the stock solution and the propellant in the aerosol composition is preferably 1:99 to 90:10, more preferably 3:97 to 80:20, and even more preferably 5:95 to 70:30. By setting such a volume ratio, it is possible to obtain a sufficient effect of the chemical agent.

[0027] In the aerosol composition, the latent heat of evaporation of the mixture of the solvent and the propellant is 10.00 kcal/mol or less, and preferably 9.80 kcal/mol or less. In the case where the latent heat of evaporation of the mixture of the solvent and the propellant is 10.00 kcal/mol or less, the chemical agent in the composition is less likely to aggregate on the treatment surface, and such a case is preferable. In addition, the latent heat of evaporation of the mixture of the solvent and the propellant is preferably 1.00 kcal/mol or more. In the case where the latent heat is 1.00 kcal/mol or more, the chemical agent in the composition can spread sufficiently on the treatment surface, and such a case is preferable.

The above latent heat of evaporation is a value at 0°C (273.15K).

In addition, the above latent heat of evaporation can be calculated based on the following formulae 1 to 3. In the formulae 1 to 3, a polar liquid refers to a liquid composed of molecules with polarity, such as ethanol, isopropanol, isopropyl myristate, water, or dimethyl ether. On the other hand, a non-polar liquid refers to a liquid composed of molecules without polarity, such as normal paraffin, isoparaffin, propane, butane, or ethane.

*Formula 1: Latent heat (kcal/mol) of evaporation of mixture of solvent and propellant = Latent heat (kcal/mol) of evaporation of solvent × Molar ratio (mol%) of solvent + Latent heat (kcal/mol) of evaporation of propellant × Molar ratio (mol%) of propellant

*Formula 2: For a case where the solvent or propellant is a polar liquid,

Latent heat (kcal/mol) of evaporation of solvent or propellant = Temperature (K) × 27.98 × (Vapor pressure (mmHg) of solvent or propellant at temperature (K)/Temperature (K))^{-0.105}

*Formula 3: For a case where the solvent or propellant is a non-polar liquid,

Latent heat (kcal/mol) of evaporation of solvent or propellant = Temperature (K) ×

$23.61 \times (\text{Vapor pressure (mmHg) of solvent or propellant at temperature (K)}/\text{Temperature (K)})^{-0.119}$

In the above formulae 1 to 3, the latent heat of evaporation was calculated from the vapor pressure based on Hildebrand's law. The vapor pressure was calculated based on Antoine equation or Karinger-Davis's equation.

The latent heat of evaporation can be adjusted by changing the kind and amount of the solvent and the propellant, and the blending ratio.

[0028] (Metered-Spray Aerosol)

The metered-spray aerosol in the present invention includes a pressure-resistant container and the above-mentioned aerosol composition with which the pressure-resistant container is filled. The opening of the pressure-resistant container is closed by an aerosol valve.

The metered-spray aerosol is an aerosol for spraying a fixed amount of the aerosol composition by one spray operation. In the metered-spray aerosol, when a spraying member attached to the aerosol valve (hereinafter, also referred to as a spraying button) is operated by a user, a fixed amount of the aerosol composition in the pressure-resistant container is sprayed through the aerosol valve, and the stock solution is converted into particles by the propellant and sprayed as spray particles.

[0029] (Aerosol Valve)

The aerosol valve includes an opening and closing member for switching communication and shutoff between the inside and outside of the pressure-resistant container through operation of the spraying member by a user, a housing to which the opening and closing member is attached, and a mount member for holding the housing at a predetermined position of the pressure-resistant container. The opening and closing member includes a stem that slides up and down in conjunction with the spraying member. The sliding of the stem switches communication (spraying state) and shutoff (non-spraying state) of the aerosol composition. At the aerosol valve, a housing hole for taking in the aerosol composition from the pressure-resistant container, and a stem hole for sending the taken-in aerosol composition to the spraying member are formed. The path from the housing hole to the stem hole constitutes an internal passage through which the aerosol composition passes.

[0030] In the present invention, the aerosol valve is a metered type aerosol valve that sprays a fixed amount by operating the spraying member once. The spraying amount of the aerosol valve can be set in the range of 0.1 mL or more per spraying operation, preferably in the range

of 0.2 mL to 5 mL, and more preferably in the range of 0.2 mL to 3 mL. By setting the spraying amount in the above range, the chemical agent can be efficiently spread on the treatment surface while keeping the amount of the chemical agent sprayed small. The spraying amount of the aerosol valve can be appropriately set to a predetermined spraying amount as long as it falls within the above range.

[0031] (Spraying Member)

The spraying member (spraying button) is a member to be attached to the pressure-resistant container via the aerosol valve. At the spraying button, a passage in the operation unit in which the aerosol composition taken in from the pressure-resistant container passes through the stem hole of the aerosol valve, and a nozzle port through which the aerosol composition is sprayed are formed. The spraying button may be a button type that is pressed from above, or it may be a trigger type for ease of operation.

[0032] The inner diameter of the nozzle port (nozzle port hole diameter) of the spraying button is preferably $\phi 0.45$ to 3.0 mm, more preferably $\phi 0.5$ to 2.0 mm, and still more preferably $\phi 0.6$ to 1.6 mm from the viewpoint of controlling the spraying time to a desired range.

The spraying button may have one or more nozzle ports with such an inner diameter.

[0033] (Spraying Force)

In the aerosol of the present invention, as described above, the pressure-resistant container for aerosols is filled with the aerosol composition, and by operating the spraying member, a fixed amount of the aerosol composition is sprayed by one operation.

The spraying force of the aerosol composition at a position 20 cm away from the nozzle port at 25°C is preferably 1 gf to 60 gf, and more preferably 5 gf to 40 gf. With the spraying force in the above range, it is possible to set the spraying time within a desired range.

[0034] The spraying force can be determined by measuring the maximum value when the aerosol composition is sprayed once towards the center of a circular flat plate with ϕ 60 mm attached to a digital force gauge (for example, made by Imada Co., Ltd., model number: DS2-2N) at a position of 20 cm away from the nozzle port of the metered-spray aerosol under the conditions of room temperature being 25°C.

[0035] (Method of observing precipitate of chemical agent)

In the present invention, the aerosol composition that is ejected in particle form by spraying adheres to the treatment surface, coagulates while the solvent evaporates, and the

chemical agent that is in a solid form at room temperature precipitates. The precipitate of the chemical agent can be observed under the following conditions.

Conditions: The aerosol composition is sprayed from a distance of 15 cm towards the center of a vinyl chloride plate having a size of 15 cm × 15 cm under the condition of about 15°C, followed by air drying for 1 hour. An arbitrary section is set at a position of 2.5 cm to 10 cm from the center of the plate, and a state of the crystals in the section is photographed. The crystals are photographed using a digital microscope (for example, digital microscope VHX-900 manufactured by KEYENCE Corporation).

[0036] (Average Particle Diameter)

The aerosol of the present invention also preferably has an average particle diameter (D50) of the aerosol composition being 3 μm to 300 μm at a spraying distance of 50 cm under the condition of about 25°C, from the viewpoint of the volatility of the spray particles. The average particle diameter of the aerosol composition can be measured by a laser light scattering particle size measuring device (for example, "LDSA-1400A" manufactured by MicrotracBEL Corporation). The average particle diameter of the aerosol composition can be adjusted by the internal pressure, nozzle port hole diameter, or the like.

[0037] As described above, with the metered-spray aerosol of the present invention, it is possible to enhance the effect of the chemical agent that is in a solid state at room temperature. This is thought to be because the chemical agent can be uniformly adhered to the treatment surface in a wide range by using the metered-spray aerosol of the present invention. In particular, regarding the state of the precipitate of the chemical agent on the treatment surface after evaporation of the solvent, it is characterized by the fact that the particle size distribution of the precipitate of the chemical agent is within a narrow range, the difference between the maximum and minimum particle sizes of the precipitate of the chemical agent is small, i.e., the size of the precipitate of the chemical agent is uniform, and the precipitate of the chemical agent can be adhered evenly without bias or gaps. This can, for example, increase the probability of contact between the pest and pest control component adhered to the treatment surface when the chemical agent is a pest control component, making it easier to exhibit the pest control effect.

Examples

[0038] The present invention is further described by examples and comparative examples, but the present invention is not limited to the following examples.

[0039] 1. Production of metered-spray aerosol (Examples 1 to 13, and Comparative Examples 2 and 3)

The pest control components that were in a solid state at room temperature and solvents shown in Tables 1 and 2 below were mixed to prepare a stock solution so that the concentration of the pest control components was as shown in Tables 1 and 2.

A pressure-resistant can for aerosol (capacity 220 mL) was filled with the stock solution in the amount shown in Tables 1 and 2, and the pressure-resistant can for aerosol was closed with an aerosol valve so that the spraying amount per operation was as shown in Tables 1 and 2. Then, a propellant was added thereto under pressure in the amount shown in Tables 1 and 2.

A spraying button having the nozzle port hole diameter and the number of nozzle ports shown in Tables 1 and 2 was attached to the aerosol valve, and the metered-spray aerosols in Examples 1 to 13 and Comparative Examples 2 and 3, which had the spraying amount and the treatment amount of the pest control component per operation as shown in Table 1, were obtained.

[0040] 2. Preparation of chemical agent solution of pest control component that is in solid state at room temperature (Comparative Examples 1, 4, 5)

The pest control components that were in a solid state at room temperature and solvents shown in Table 2 below were mixed to prepare a chemical agent solution having the concentration of the pest control components shown in Table 2.

[0041] 3. Production of hand pump (Comparative Example 6)

The pest control components that were in a solid state at room temperature and solvents shown in Table 2 below were mixed to prepare a chemical agent solution having the concentration of the pest control components shown in Table 2, and a hand pump composition was produced. A polypropylene container for hand pump (capacity 400 mL) was filled with the stock solution shown in Table 2, and the container was closed with a trigger for hand pump so that the spraying amount per operation was as shown in Table 2.

[0042] 4. Average particle diameter of aerosol composition and hand pump composition

Under the condition of about 25°C, the average particle diameter of the aerosol composition and the hand pump composition at a spray distance of 50 cm was measured using "LDSA-1400A" manufactured by MicrotracBEL Corporation.

[0043] 5. Observation of precipitate of chemical agent

As for the metered-spray aerosols produced in Examples 1 to 10 and Comparative

Examples 2 and 3, the precipitates of the chemical agents were observed. The aerosol composition was sprayed in the spraying amount shown in Tables 1 and 2 under the condition of about 15°C toward the center of a vinyl chloride plate having a size of 15 cm in height and 15 cm in width, which was placed at a position of 15 cm away from the nozzle port of the metered-spray aerosol in a straight line in the spray direction (horizontal direction), by operating the spraying button once. After one hour, the state of the precipitate of the chemical agent precipitated on the surface of the vinyl chloride plate was observed using a microscope.

[0044] As a comparison, the chemical agent solutions in Comparative Examples 1, 4, and 5 were dropped onto the center of one surface of a vinyl chloride plate having a size of 15 cm in height and 15 cm in width using PIPETMAN (manufactured by Gilson, Inc.). The amount of the chemical agent solution dropped was such that the treatment amount of chemical agent on the plate surface was the same as that of the corresponding example. Immediately after dropping, the plate was tilted to spread the liquid over the entire plate. After one hour at room temperature, the state of the precipitate of the chemical agent precipitated on the surface of the vinyl chloride plate was observed using a microscope.

[0045] 6. Test for confirming insecticidal effect against German cockroaches

A chemical agent was treated on a vinyl chloride plate having a size of 15 cm in height and 15 cm in width by the following method.

For the method of chemical agent treatment in the case of the metered-spray aerosols in the examples and comparative examples, the metered-spray aerosol was operated once (one push) toward the center of the plate from a distance of 15 cm, followed by air-drying for one hour.

For the method of chemical agent treatment in the case of the chemical agent solution in the comparative example, 0.3 mL of the chemical agent solution was dropped onto the center of one surface of the plate using PIPETMAN (manufactured by Gilson, Inc.). Immediately after dropping, the plate was tilted to spread the liquid over the entire plate, followed by air-drying for one hour.

Then, a plastic cup (diameter 13 cm, height 10 cm) was placed on the vinyl chloride plate upside down, and 10 German cockroaches were released into it and allowed to contact the vinyl chloride plate for a predetermined time.

After standing for a certain time, the test insects were transferred to a clean cup, and the knockdown rate after 3 hours and the mortality rate after 24 hours were measured.

[0046] 7. Test for confirming insecticidal effect against black cockroaches

The test was conducted in the same manner as the test for confirming the insecticidal effect against German cockroaches, except that 10 black cockroaches were used instead of 10 German cockroaches.

[0047] 8. Test for confirming insecticidal effect against bed bugs

The test was conducted in the same manner as the test for confirming the insecticidal effect against German cockroaches, except that 5 bed bugs were used instead of 10 German cockroaches and a glass bottle (diameter 6 cm, height 9 cm) was used instead of the plastic cup.

[0048] 9. Test for confirming insecticidal effect against house dust mites

(*Dermatophagoides pteronyssinus*)

A vinyl chloride plate having a size of 15 cm in height and 15 cm in width with the outer edge of which vaseline was applied to prevent escape of the test mites was prepared, and a chemical agent was treated by the following method.

For the method of the chemical agent treatment in the case of the metered-spray aerosols in Examples 7, 10, and 11 to 13, the metered-spray aerosol was operated once (pushed once) toward the center of the plate set at an angle of 45° from a distance of 75 cm, followed by air-drying for one hour.

For the method of the chemical agent treatment in Comparative Example 6, the hand pump equipped with a trigger (model number T-95, manufactured by Canyon Co., Ltd.) that had a spraying amount of 1.0 mL per operation was operated once toward the center of the plate set at an angle of 45° from a distance of 75 cm, followed by air-drying for one hour.

Then, 30 to 300 house dust mites (*Dermatophagoides pteronyssinus*) were placed on the center of the vinyl chloride plate and allowed to contact the vinyl chloride plate overnight.

The same operation was also performed using a vinyl chloride plate without chemical agent treatment.

After overnight, all the tested house dust mites (*Dermatophagoides pteronyssinus*) were collected. All the collected house dust mites (*Dermatophagoides pteronyssinus*) were observed using a stereomicroscope (manufactured by Olympus Corporation), and the number of surviving mites and dead mites was counted, and the mortality rate in the chemical agent-treated area was determined. The same operation was also performed using a vinyl chloride plate without chemical agent treatment, and the mortality rate in the chemical agent-untreated area was determined, and the corrected mortality rate (%) was calculated from the following formula.

Corrected mortality rate (%)

= (Mortality rate in chemical agent-treated area - Mortality rate in chemical agent-untreated area) / (1 - Mortality rate in chemical agent-untreated area) × 100

[0049] The results are shown in Tables 3 to 10 below.

In addition, the photos showing the state of the precipitates of the chemical agent by the microscope are shown in Fig. 1 to Fig. 15.

[0050] Notes for Tables 1 and 2

IPA: Isopropanol

DME: Dimethyl ether

LPG 0.20MPa: Liquefied petroleum gas

Latent heat of evaporation of aerosol composition: Calculated based on the above formulae 1 to 3.

[0051]

Table 1

		Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6	Ex.7	Ex.8
Stock solution	Pest control component	Fipronil						Broflanilide	
	Concentration (w/v%)	1	1	1	1	3.3	10	3.3	3.3
	Solvent	IPA	IPA	IPA	IPA	IPA	Anhydrous ethanol	IPA	IPA
Propellant		DME	DME	LPG 0.20MPa (25°C)	DME	DME	DME	DME	DME
Aerosol composition	Liquid-Gas ratio (Stock solution:Propellant in volume ratio)	70:30	75:25	50:50	50:50	30:70	70:30	30:70	30:70
Photograph of precipitate of chemical agent		Fig.1	Fig.2	Fig.3	Fig.4	Fig.5	Fig.6	Fig.7	Fig.8
Nozzle port hole diameter (mm)		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Number of nozzle port		3	3	3	3	3	3	3	1
Spraying amount per operation (mL)		1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.2
Treatment amount of chemical agent per operation (mg)		7.0	7.5	5.0	5.0	9.9	70.0	9.9	1.98
Average particle diameter of aerosol composition (μm)		144	189	105	58	36	142	45	56
Spraying force (gf/20cm)		-	-	-	-	-	-	10	-
Latent heat of evaporation of mixture (kcal/mol, at 0°C)		9.46	9.72	9.16	8.47	7.40	8.96	7.40	7.40

Table 1 continued

		Ex.9	Ex.10	Ex.11	Ex.12	Ex.13
Stock solution	Pest control component	Metoxadiazone		Amidoflumet		
	Concentration (w/v%)	1	3.3	3.3	10	1
	Solvent	Anhydrous ethanol	IPA	IPA	IPA	Anhydrous ethanol
Propellant		DME	DME	DME	DME	DME
Aerosol composition	Liquid-Gas ratio (Stock solution:Propellant in volume ratio)	5:95	30:70	30:70	70:30	30:70
Photograph of precipitate of chemical agent		Fig.9	Fig.10	-	-	-
Nozzle port hole diameter (mm)		1.0	1.0	1.0	1.0	1.0
Number of nozzle port		3	3	3	3	3
Spraying amount per operation (mL)		1.0	1.0	1.0	1.0	1.0
Treatment amount of chemical agent per operation (mg)		0.5	9.9	9.9	70.0	3.0
Average particle diameter of aerosol composition (μm)		7	43	27	109	28
Spraying force (gf/20cm)		-	9.5	8.1	2.3	9.7
Latent heat of evaporation of mixture (kcal/mol, at 0°C)		6.34	7.40	7.40	9.30	7.60

[0052]

Table 2

		Comp. Ex.1	Comp. Ex.2	Comp. Ex.3	Comp. Ex.4	Comp. Ex.5	Comp. Ex.6
Stock solution	Pest control component	Fipronil			Broflanilide	Metoxadiazone	Amidoflumet
	Concentration (w/v%)	3.3	1	1	3.3	3.3	0.99
	Solvent	IPA	IPA	Anhydrous ethanol (50v/v%) + Glycerine	IPA	IPA	IPA
Propellant		-	LPG 0.20MPa (25°C)	DME	-	-	-
Aerosol composition	Liquid-Gas ratio (Stock solution:Propellant in volume ratio)	-	75:25	50:50	-	-	-
Photograph of precipitate of chemical agent		Fig.11	Fig.12	Fig.13	Fig.14	Fig.15	-
Nozzle port hole diameter (mm)		-	1.0	1.0	-	-	1.0
Number of nozzle port		-	3	3	-	-	1
Treatment method		Drop	Aerosol spray	Aerosol spray	Drop	Drop	Hand pump spray
Dropping amount/Spraying amount per operation (mL)		0.3	1	1	0.3	0.3	1
Treatment amount of chemical agent per operation (mg)		9.9	7.5	5.0	9.9	9.9	9.9
Average particle diameter of chemical agent solution or average particle diameter of aerosol composition (μm)		-	115	47	-	-	132
Spraying force (gf/20cm)		-	-	-	-	-	8.7
Latent heat of evaporation of liquid component excluding chemical agent in chemical agent solution or latent heat of evaporation of mixture (kcal/mol, at 0°C)		11.04	10.16	144.65	11.04	11.04	11.04

[0053]

Table 3

		Ex.2	Ex.3	Ex.5	Comp. Ex.1	Comp. Ex.2
Pest control component		Fipronil				
Insecticidal effect against German cockroaches	Knockdown rate (%)	85	70	75	25	40
	Mortality rate (%)	100	80	100	100	35

[0054]

Table 4

		Ex.7	Ex.8	Comp. Ex.4
Pest control component		Broflanilide		
Insecticidal effect against German cockroaches	Knockdown rate (%)	0	10	0
	Mortality rate (%)	100	90	40

[0055]

Table 5

		Ex.10	Comp. Ex.5
Pest control component		Metoxadiazone	
Insecticidal effect against German cockroaches	Knockdown rate (%)	100	0
	Mortality rate (%)	100	40

[0056]

Table 6

		Ex.2	Ex.3	Comp. Ex.2
Pest control component		Fipronil		
Insecticidal effect against black cockroaches	Knockdown rate (%)	45	35	20
	Mortality rate (%)	90	85	65

[0057]

Table 7

		Ex.8	Comp. Ex.4
Pest control component		Broflanilide	
Insecticidal effect against black cockroaches	Knockdown rate (%)	0	0
	Mortality rate (%)	90	0

[0058]

Table 8

		Ex.2	Ex.3	Ex.4	Ex.5	Comp. Ex.1	Comp. Ex.2	Comp. Ex.3
Pest control component		Fipronil						
Insecticidal effect against bed bugs	Knockdown rate (%)	40	60	55	80	20	30	40
	Mortality rate (%)	80	70	80	85	50	40	55

[0059]

Table 9

		Ex.7	Ex.8	Comp. Ex.4
Pest control component		Broflanilide		
Insecticidal effect against bed bugs	Knockdown rate (%)	70	50	0
	Mortality rate (%)	80	85	10

[0060]

Table 10

		Ex.11	Ex.12	Ex.13	Comp. Ex.6	Ex.7	Ex.10
Pest control component		Amidoflumet				Broflanilide	Metoxadiazone
Insecticidal effect against house dust mites (<i>Dermatophagoides pteronyssinus</i>)	Corrected mortality rate (%)	100	99	99	46	100	91

[0061] From the above results, for the German cockroach, it was found that, when the kind of the pest control component was the same and the treatment amount per operation was the same, at least one of the knockdown rate and mortality rate was improved in the examples as compared to the comparative examples, from the comparison between Example 2 and Comparative Example 2, the comparison between Example 5 and Comparative Example 1, the comparison between Example 7 and Comparative Example 4, and the comparison between Example 10 and Comparative Example 5.

For the black cockroach, it was found that, when the kind of the pest control component was the same and the treatment amount per operation was the same, at least one of the knockdown rate and mortality rate was improved in the examples as compared to the comparative examples, from the comparison between Example 2 and Comparative Example 2. Furthermore, it was found that, even when the treatment amount of the pest control component was small, at least one of the knockdown rate and mortality rate was improved in the examples as compared to the comparative examples, from the comparisons between Example 3 and Comparative Example 2, and the comparison between Example 8 and Comparative Example 4.

For bed bugs, it was found that, when the kind of the pest control component was the same and the treatment amount per operation was the same, at least one of the knockdown rate and mortality rate was improved in the examples as compared to the comparative examples, from the comparisons between Example 2 and Comparative Example 2, the comparison between Examples 3 and 4 and Comparative Example 3, the comparison between Example 5 and Comparative Example 1, and the comparison between Example 7 and Comparative Example 4. Furthermore, it was found that, even when the treatment amount of the pest control component was small, at least one of the knockdown rate and mortality rate was improved in the examples as compared to the comparative examples, from the comparison between Example 8 and Comparative Example 4.

For the house dust mites (*Dermatophagoides pteronyssinus*), it was found that, when the kind of the pest control component was the same and the treatment amount per operation was the same, the corrected mortality rate was improved in the examples as compared to the comparative examples, from the comparison between Example 11 and Comparative Example 6. Furthermore, regardless of the treatment amount of the pest control component, average particle size, and spraying force, it was found that the corrected mortality rate was improved in the examples as compared to the comparative examples, from the comparisons between

Examples 11 to 13 and Comparative Example 6. Moreover, regardless of the kind of the pest control component, the examples showed a high corrected mortality rate, from the results of Examples 7, 10, and 11.

Therefore, it was found that by using the metered-spray aerosol in which the latent heat of evaporation of the mixture is within a specific range, the efficacy of the chemical agent that is in a solid state at room temperature, which is a pest control component, could be enhanced against various pests.

[0062] In addition, by comparing the state of the precipitate of the chemical agent, it was found that the chemical agent crystals having a uniform size adhered to the plate surface in a state of covering the entire plate surface evenly without bias or gaps in the examples as compared to the comparative examples, from the comparison between Example 1 (Fig. 1) and Example 2 (Fig. 2) and Comparative Example 2 (Fig. 12), the comparison between Example 3 (Fig. 3) and Example 4 (Fig. 4) and Comparative Example 3 (Fig. 13), the comparison between Example 5 (Fig. 5) and Comparative Example 1 (Fig. 11), the comparison between Example 7 (Fig. 7) and Comparative Example 4 (Fig. 14), and the comparison between Example 10 (Fig. 10) and Comparative Example 5 (Fig. 15). In particular, it was found that even with the same dosage form of metered-spray aerosol, the state of adhesion of the chemical agent crystals to the plate surface changes due to the difference in latent heat of evaporation, from the comparisons between Example 1 (Fig. 1) and Example 2 (Fig. 2) and Comparative Example 2 (Fig. 12), and the comparison between Example 3 (Fig. 3) and Example 4 (Fig. 4) and Comparative Example 3 (Fig. 13).

From these results, it is inferred that, by using a metered-spray aerosol in which the latent heat of evaporation of the mixture of the solvent and propellant was within a specific range, the chemical agent crystals having a uniform size adhere to the plate surface in a state of covering the entire plate surface evenly without bias or gaps, thereby enhancing the efficacy of the chemical agent that is in a solid state at room temperature, which is a pest control component, against various pests.

[0063] Although the present invention is described in detail with reference to specific embodiments, it is obvious to those skilled in the art that various changes and modifications can be made without departing from the spirit and scope of the present invention. This application is based on Japanese Patent Application No. 2021-200095 filed on December 9, 2021, the contents of which are incorporated herein by reference.

CLAIMS

[Claim 1]

A metered-spray aerosol comprising a pressure-resistant container and an aerosol composition with which the pressure-resistant container is filled, from which a fixed amount of the aerosol composition is sprayed by one spraying operation,

wherein the aerosol composition comprises a chemical agent that is in a solid state at room temperature, a solvent, and a propellant, and

a latent heat of evaporation of a mixture of the solvent and the propellant is 10.00 kcal/mol or less.

[Claim 2]

The metered-spray aerosol according to claim 1, wherein the chemical agent that is in a solid state at room temperature is a pest control component that is in a solid state at room temperature.

[Claim 3]

The metered-spray aerosol according to claim 1 or 2, wherein the solvent is a volatile solvent.

FIG. 1

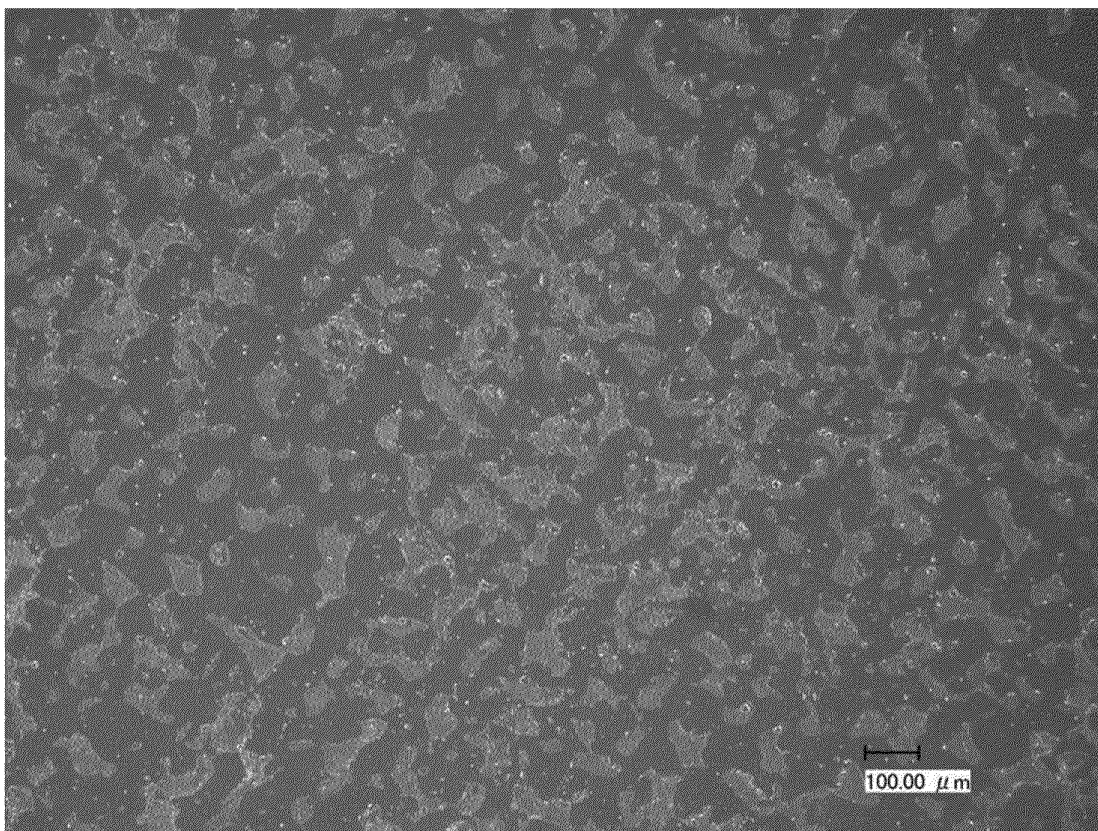


FIG. 2

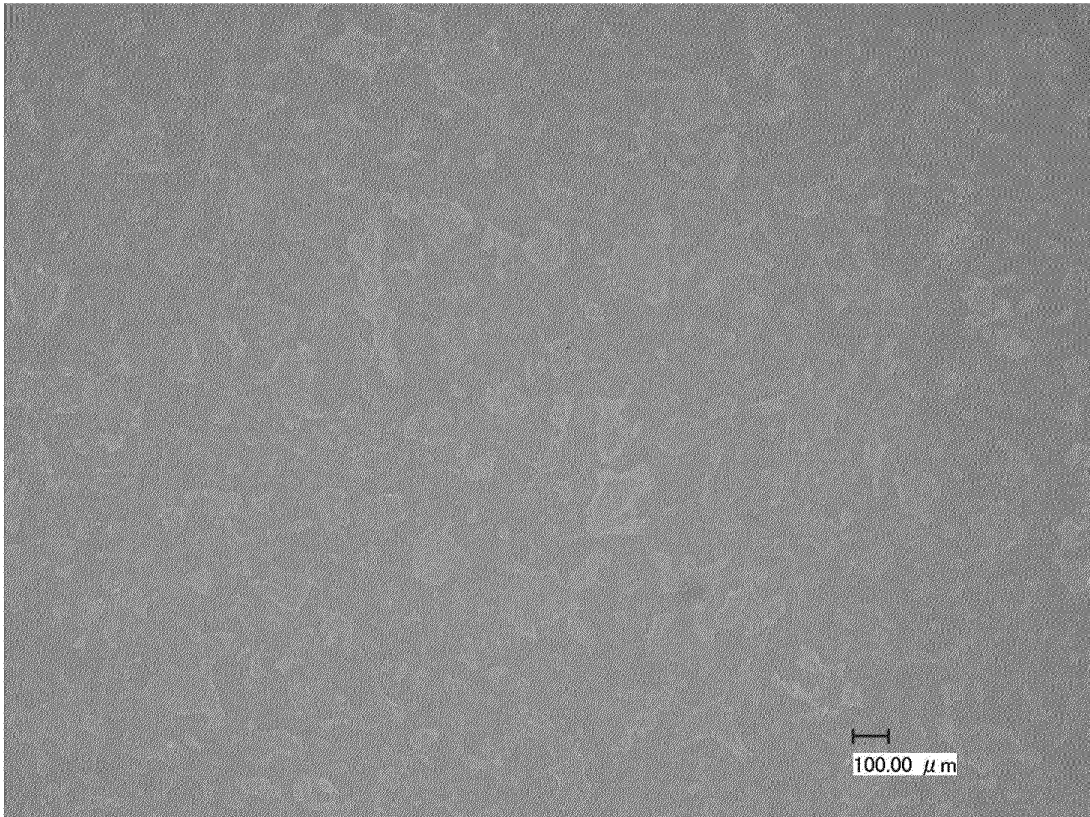


FIG. 3

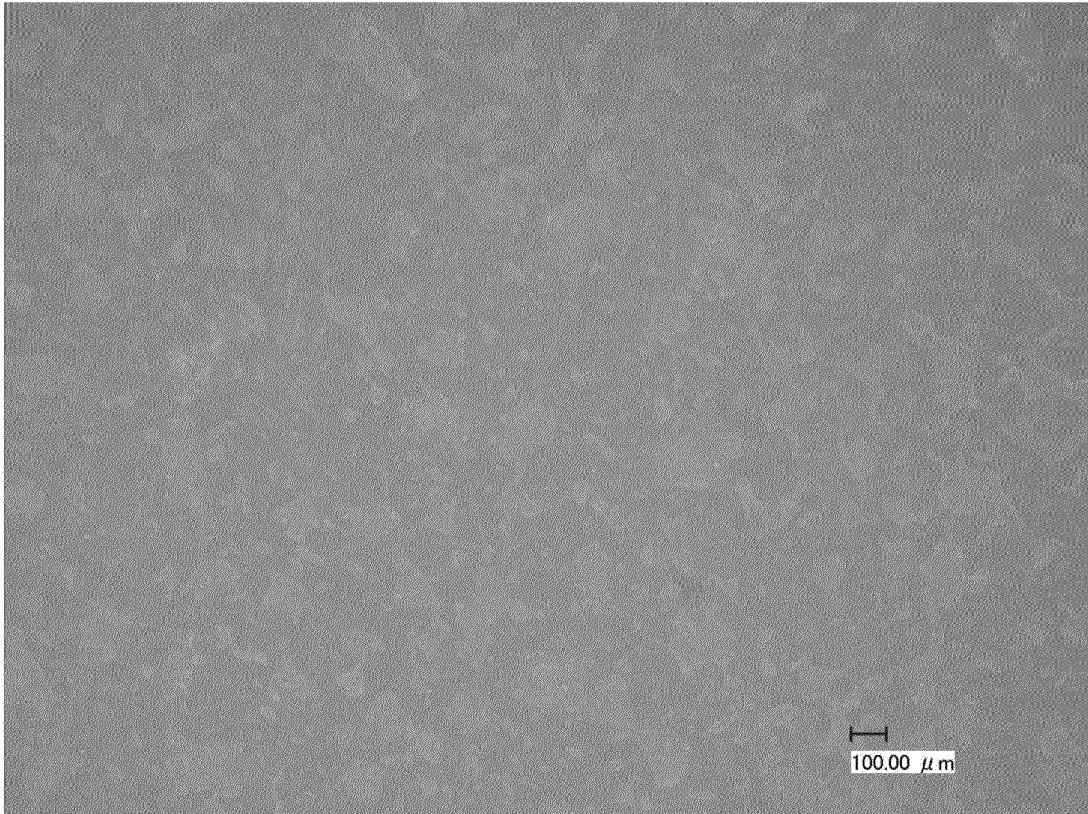


FIG. 4

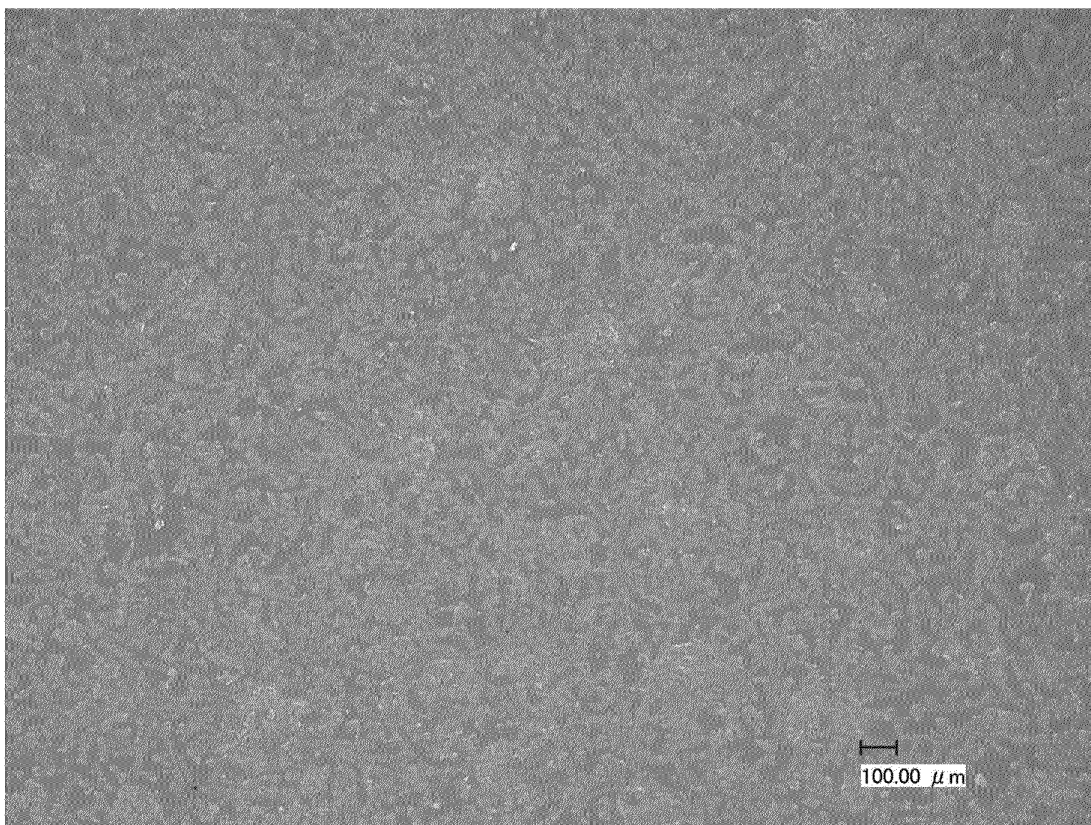


FIG. 5

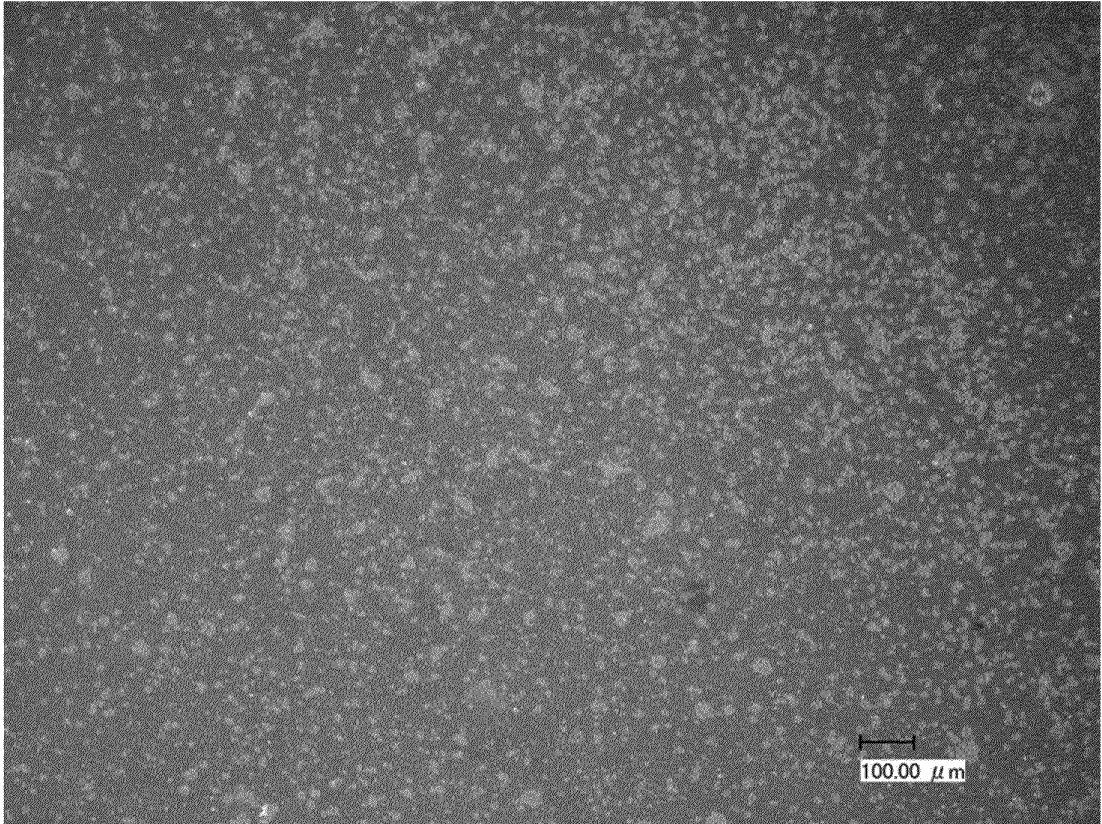


FIG. 6

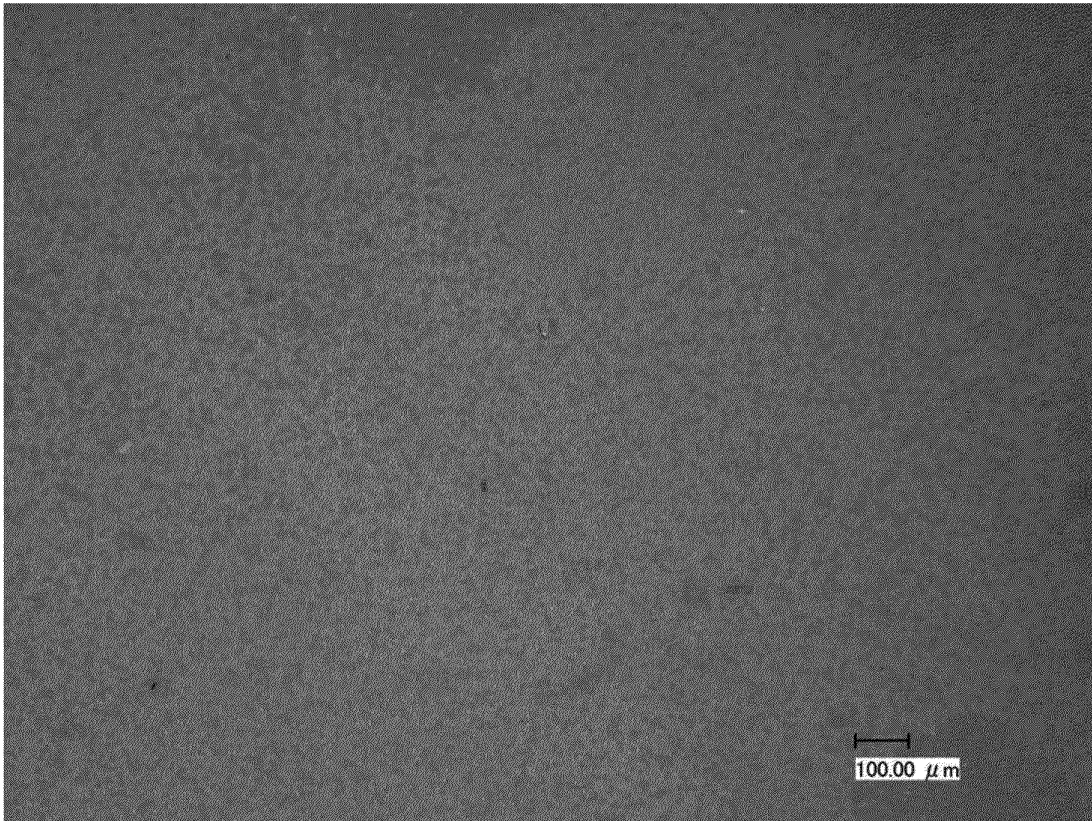


FIG. 7

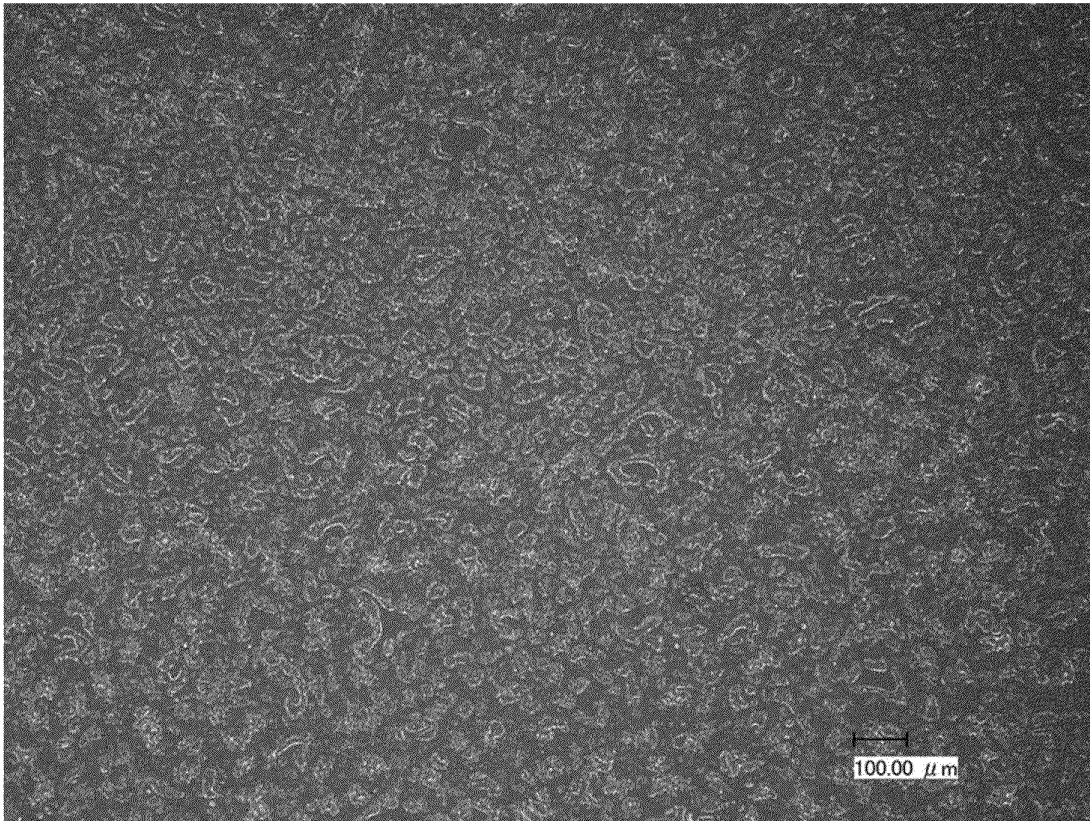


FIG. 8

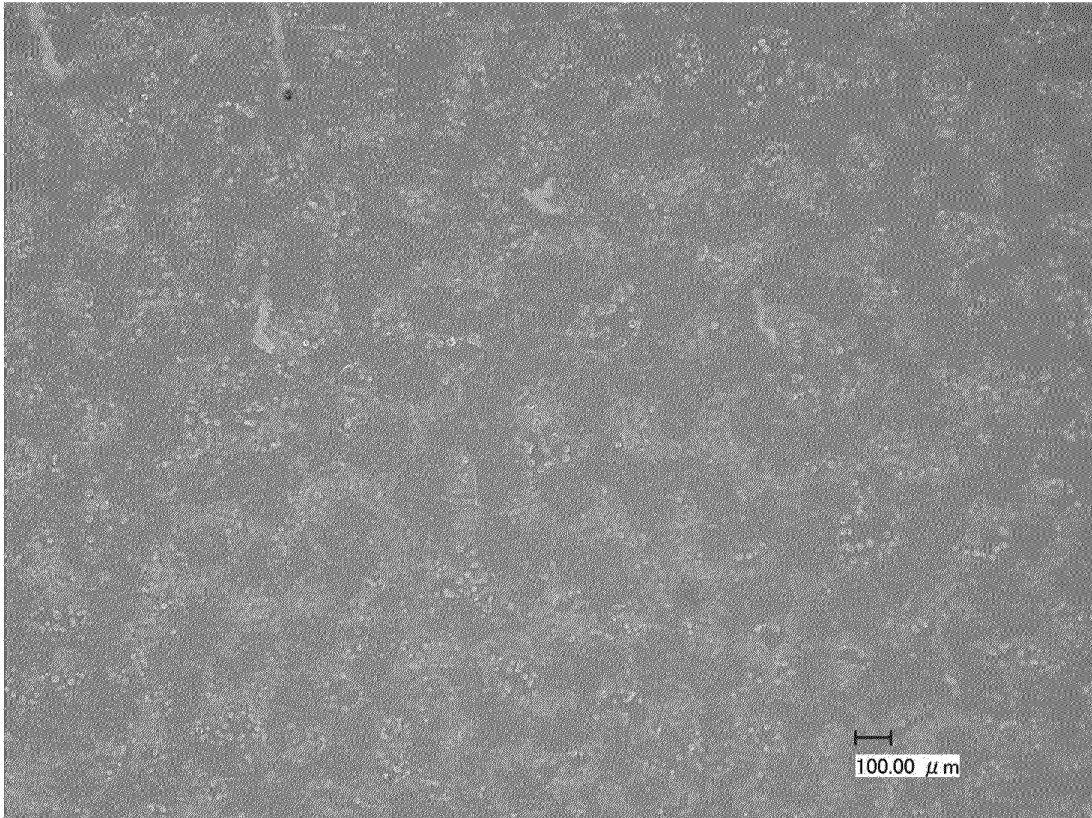


FIG. 9

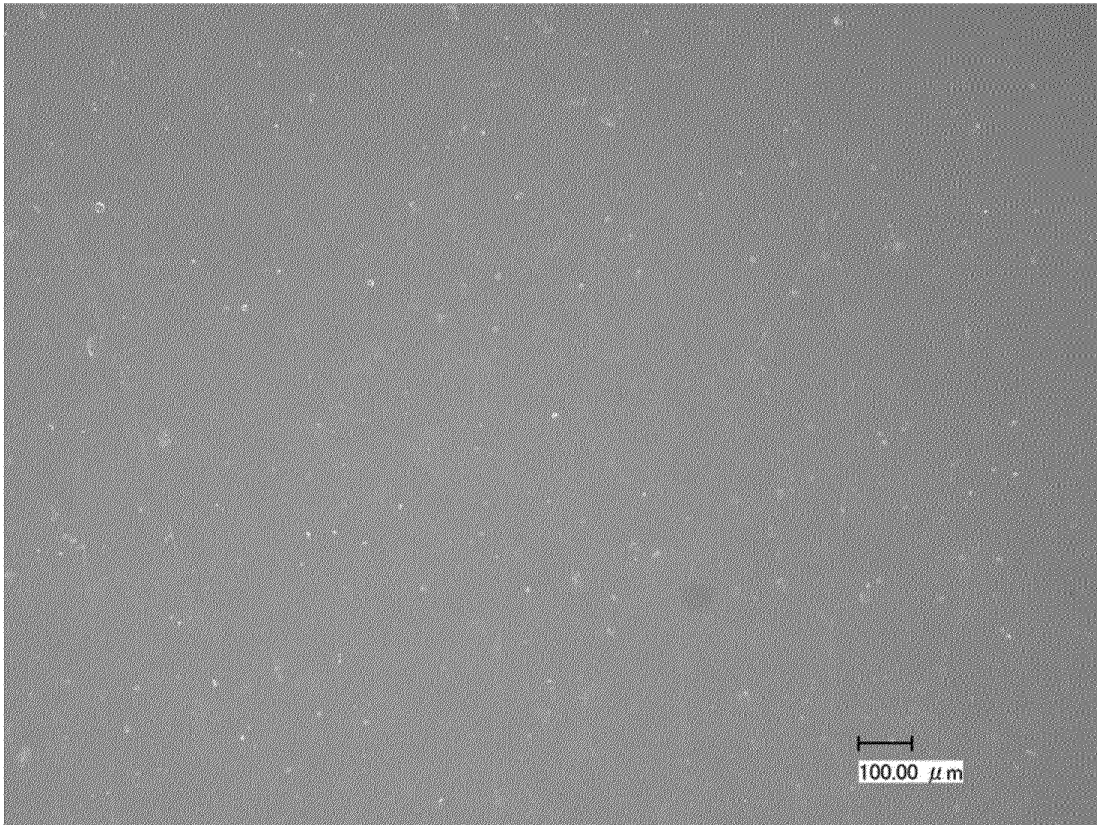


FIG. 10

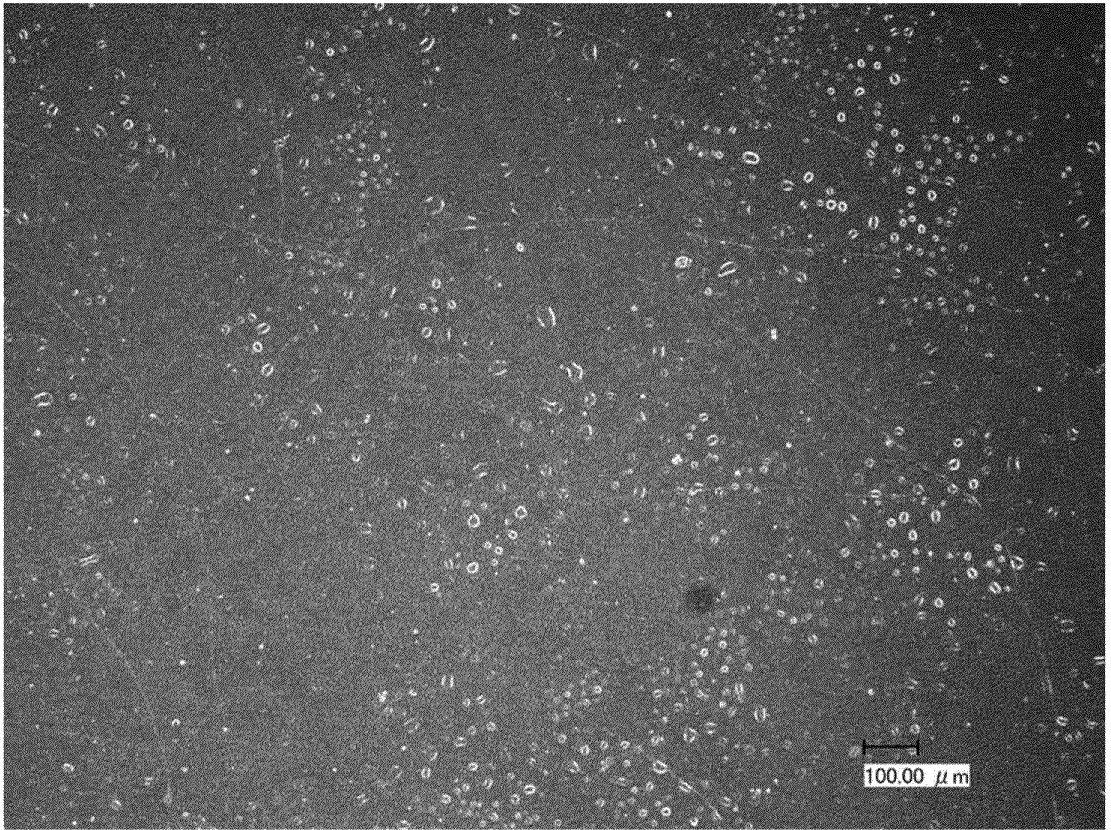


FIG. 11

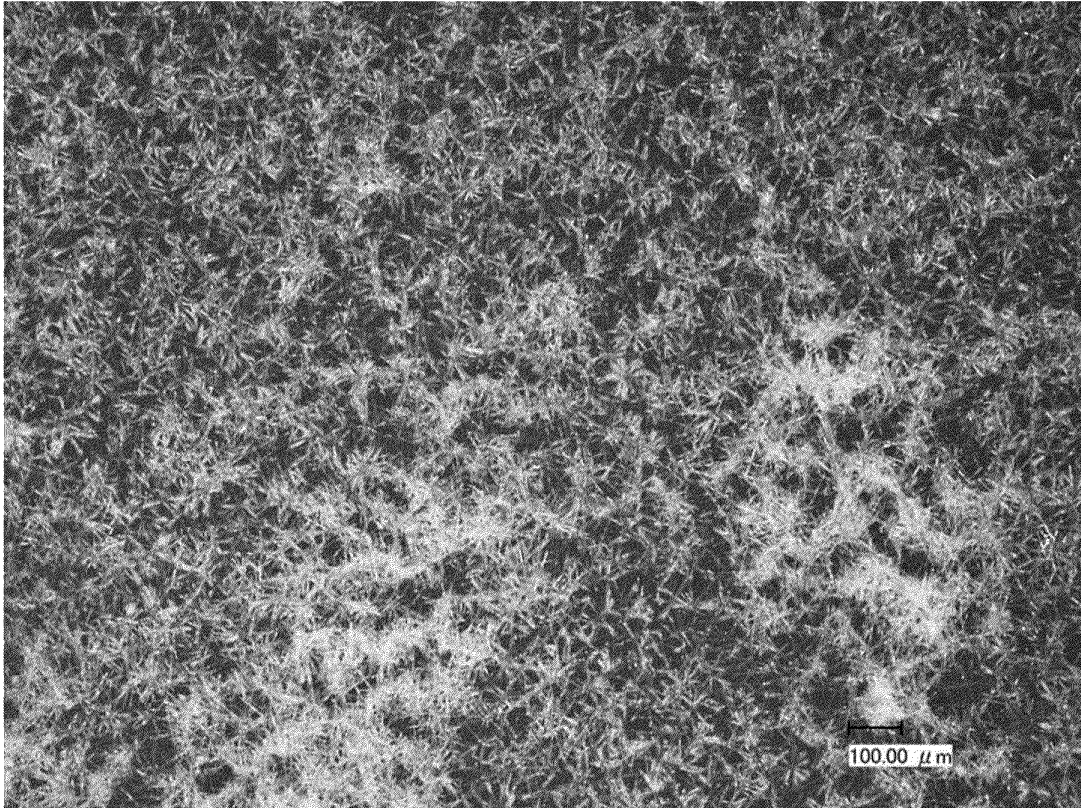


FIG. 12

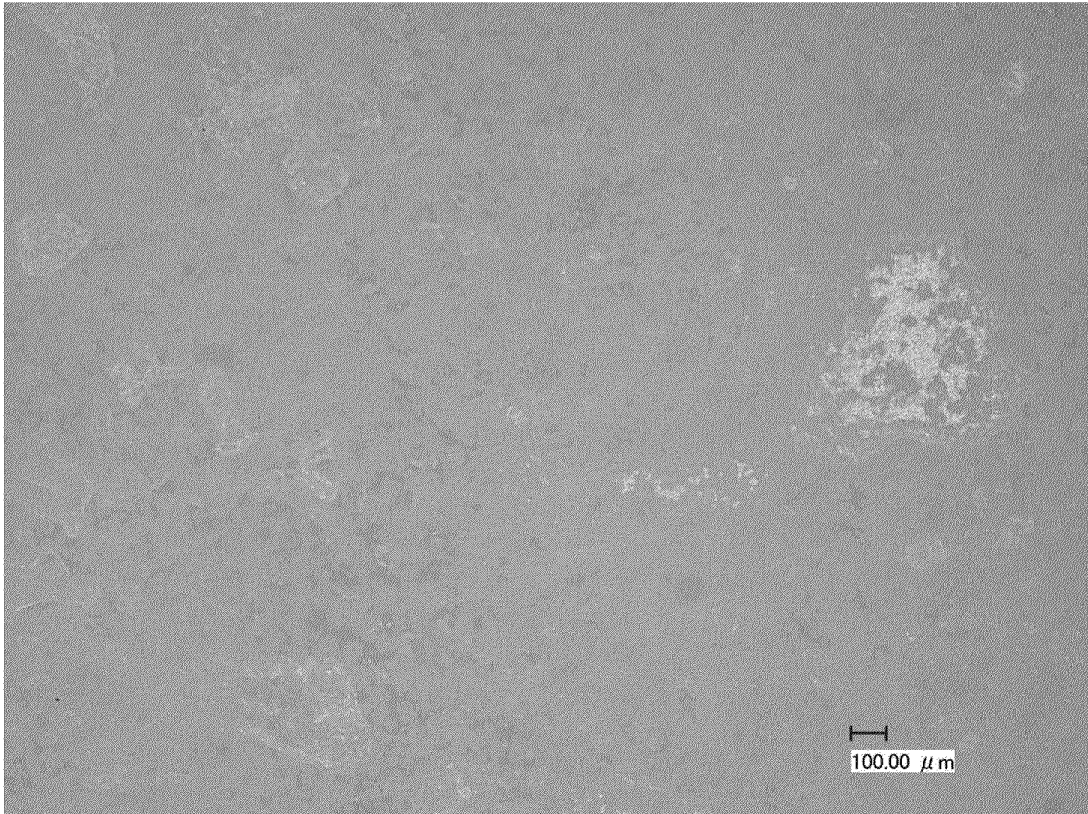


FIG. 13

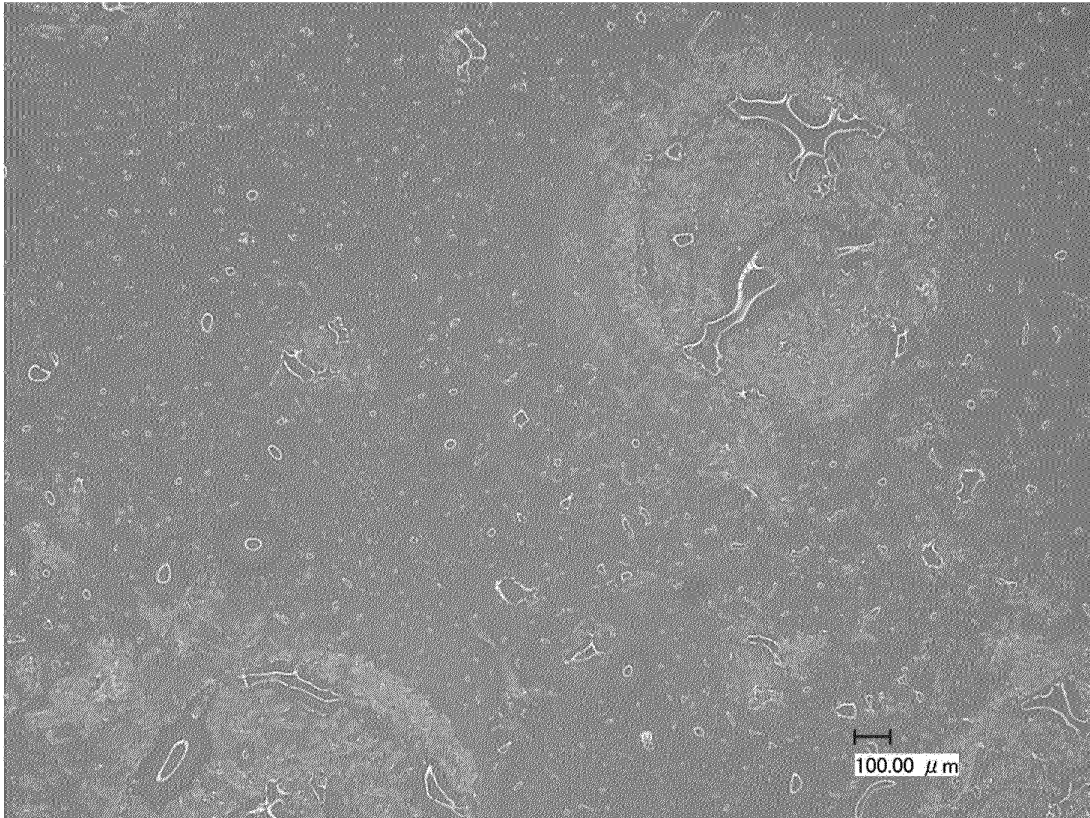


FIG. 14

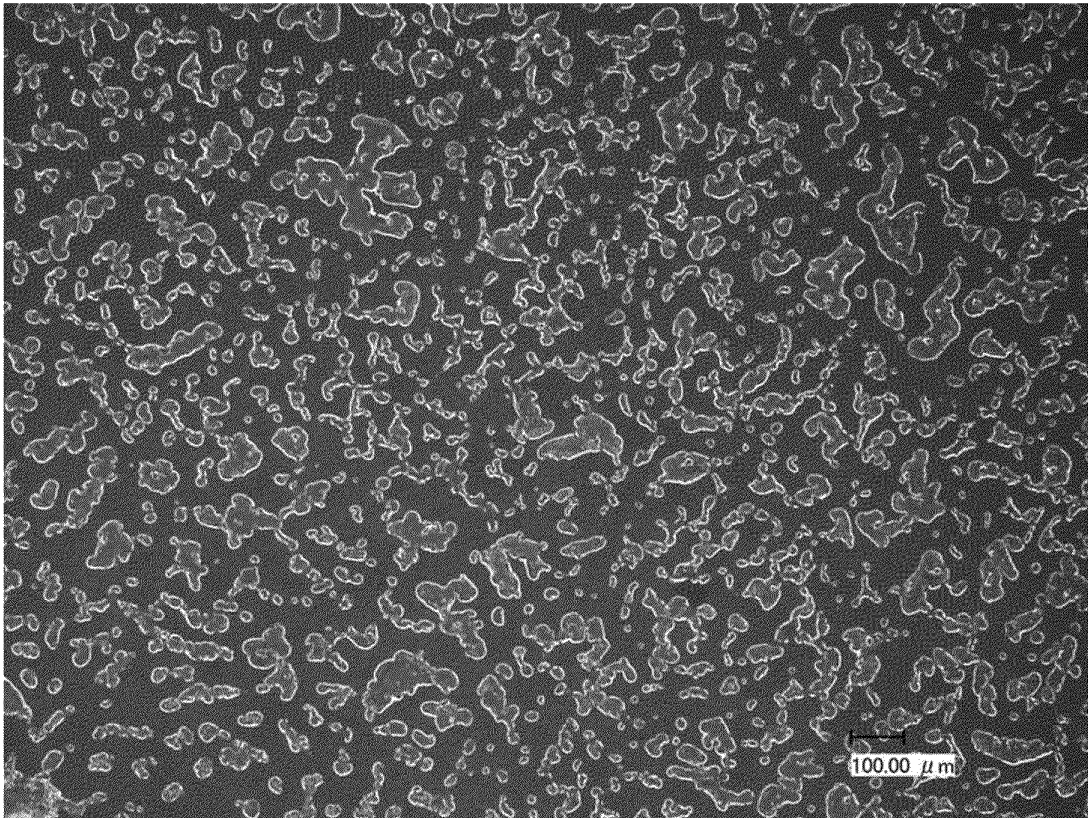


FIG. 15

