Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).
The present invention relates to an antibacterial composition comprising an inorganic antibacterial agent and a hydrophilic substance. The antibacterial composition of the invention may be molded alone or in a composite form, or may be laminated on an inorganic or organic substrate, giving antibacterial moldings such as antibacterial fibers, antibacterial fabrics, antibacterial sheets, antibacterial films, antibacterial plastics moldings, antibacterial binders and the like.

Background

Thermoplastic resins, typically polyethylene, polypropylene, polyvinyl chloride, polyvinylidene chloride, nylon, polyethylene terephthalate and polyethylene naphthalate have superior physical and chemical properties and are used for fibers, plastics, films, sheets, adhesives and the like. In recent years, antibacterial goods having an inorganic and/or organic antibacterial agent incorporated therein or applied thereto are becoming available in the market.

Main antibacterial agents currently under investigation or in use include natural antibacterial agents such as chitin, chitosan, wasabi extracts, mustard extracts, hinokitiol and tea extracts, inorganic compounds such as titanium oxide particles (catalytic in photooxidation), fine particles of zinc oxide, silver-containing zeolite and silver-containing zirconium phosphate, and synthetic antibacterial agents such as organic ammonium salt compounds and organic phosphonium salt compounds.

Natural antibacterial agents and inorganic antibacterial agents, typically silver, are now attracting attention in view of their safety from toxicity. The following inventions have been disclosed.


EP-A-O 663 409 describes polymers used to form antibacterial contact lenses based on a phosphonium salt-containing polymer. The polymerisable monomers do not contain metal ions or oxides.

US-A-5 079 004 relates to an antimicrobial superabsorbent composition of a crosslinked hydrophilic sodium salt of a partially neutralised acrylic acid-based polymer gel having a silane covalently bonded thereto. The presence of metal ions or oxides on the polymer is mentioned.

A stopwatch is made of a polyester which is a polyethylene terephthalate, polybutylene terephthalate or poly(1,4-cyclohexane dimethylene terephthalate). It is copolymerised with an ester-forming sulphonic acid phosphonium salt in the presence of polyalkylene glycol. The abstract makes no mention of antibacterial activity or of any association with metal ions or oxides.

JP-A- 06 041408 describes a film made of a polyester which is a polyethylene terephthalate, polybutylene terephthalate or poly(1,4-cyclohexane dimethylene terephthalate). It is copolymerised with an ester-forming sulphonic acid phosphonium salt in the presence of polyalkylene glycol. The abstract makes no mention of antibacterial activity or of any association with metal ions or oxides.

JP-A- 05 310820 describes antibacterial compounds based on monomers having carboxyl, phosphate, sulphone, sulphoxide and phenolic OH groups. The polymerised polymers are based on dimethyl terephthalate containing a phosphonium salt or a polyester containing the phosphonium salt, but metal ions or oxides are not mentioned.

Films, sheets, fibers and plastics were prepared according to the techniques of these publications and were tested for antibacterial properties against Staphylococcus aureus, Escherichia coli and the like. The results show that if the antibacterial agent was used in a relatively small amount to retain the clarity of the moldings, the moldings showed a low degree of antibacterial activity. However, an improvement in antibacterial activity required sacrifice of clarity. Thus, it was found that the moldings disclosed in the publications remained to be improved for practical use.

On the other hand, synthetic organic antibacterial agents are generally superior in antibacterial activity against fungi compared with natural antibacterial agents and inorganic antibacterial agents. However, if the synthetic organic antibacterial agent is applied to the surface of a substrate such as a film or incorporated thereinto, the antibacterial agent is easily evaporated, released or separated from the surface of the substrate because the antibacterial agent is of low molecular weight. Hence, the application or incorporation of such antibacterial agent is undesirable in terms of prolonged stability of antibacterial activity and safety of human bodies.

When an antibacterial agent is used for a film or the like, it is desirable from the viewpoints of prolonged stability of antibacterial properties and safety of human bodies that the antibacterial agent be undissolved in water, an organic solvent or the like, becoming difficult to release, give off, peel or separate from the film surface. In such situation, recently an immobilized type of antibacterial agent was disclosed. The disclosed antibacterial agent contains an organic antibacterial agent attached, due to ionic bond or covalent bonding, to a polymer used as a raw material for films or fibers.

Japanese Unexamined Patent Publication JP-A-86584/1979 discloses an antibacterial material predominantly comprising a high molecular substance which contains an antibacterial component having a quaternary ammonium salt group attached, due to ionic bond, to an acid group such as a carboxyl group or a sulfonic acid group. Japanese Unexamined Patent Publication JP-A-245378/1986 describes fibers composed of a polyester copolymer containing an antibacterial component having a base group such as an amidine group and a quaternary ammonium salt group.


[0016] Japanese Unexamined Patent Publication JP-A-41408/1994 discloses a modified polyester and a film formed therefrom, the modified polyester comprising a polyester copolymer prepared from a phosphonium salt of sulfonic acid and polyalkylene glycol, the modified polyester being used as a support for photographic purposes, or usable for wrapping, for general industrial purposes or for magnetic tape, although without reference to the antibacterial activity thereof. The alkyl group attached to the phosphonium salt described in said patent specification includes, for example, a butyl group, a phenyl group and a benzyl group all of which have relatively few carbon atoms, unlike the group disclosed in Japanese Unexamined Patent Publication No.310820/1993.

[0017] Based on Japanese Unexamined Patent Publications JP-A-266912/1992; 814365/1992 and 310820/1993, a vinyl polymer containing a phosphonium salt group and a polyester (copolymer) were prepared according to Examples described in the publications, and were molded into fibers, films, sheets and the like. Then, fibers, films, sheets and the like were coated with the disclosed antibacterial polymer to provide a laminate. The antibacterial properties of the laminate were evaluated and found unsatisfactory. A polyester having at least 50 mole% of tri-n-butylmethoxy phosphonium salt group attached thereto was prepared in an attempt to improve the antibacterial properties, and was molded into films, sheets and the like. The moldings showed insufficient antibacterial properties as well as colored polymers and lowered mechanical properties due to the drop in the glass transition point.

[0018] Further, fibers, fabrics, films, sheets, plastics and the like were formed using said inorganic and organic antibacterial agents either singly or in combination and were tested for antibacterial properties against Staphylococcus aureus, Escherichia coli and the like. The moldings were found to have a low antibacterial activity and were unsuitable for use.

Disclosure of the Invention

[0019] The present invention was accomplished to overcome the foregoing prior art problems. The primary object of the present invention is to provide an antibacterial composition having a high activity, more specifically, to improve the antibacterial activity of the composition without marked increase in the amount of an inorganic antibacterial agent to be incorporated in or applied to a substrate. The secondary object of the invention is to provide an antibacterial laminate having superior antibacterial properties and prepared by laminating the antibacterial composition on an inorganic or organic substrate.

[0020] According to the present invention, there is provided (1) an antibacterial composition comprising an inorganic antibacterial agent and a hydrophilic substance. The invention includes a mixture of the antibacterial agent and the hydrophilic substance. Some modifications of the invention are as follows.

(2) The antibacterial composition as defined in item (1) is characterized in that the inorganic antibacterial agent is an inorganic compound which carries the particles and/or ions of at least one metal selected from the group consisting of silver (Ag), zinc (Zn) and copper (Cu), and/or an organic compound having said metallic ions attached thereto.

(3) The antibacterial composition as defined in item (1) or (2), characterized in that the inorganic antibacterial agent contains a metallic oxide having the capability of photooxidation catalyst.

(4) The antibacterial composition as defined in item (3), characterized in that said metallic oxide contains at least one of titanium oxide (TiO₂) and zinc oxide (ZnO₂).

(5) The antibacterial composition as defined in any one of items (1) to (4), characterized in that the hydrophilic substance is a high molecular compound containing at least one member selected from the group consisting of a hydroxyl group, an amino group, an amido group, a carboxyl group or an alkali metal salt thereof, a sulfonic acid group or an alkali metal salt thereof, a quaternary ammonium salt group, an amine salt group, a polymer chain and a polyamine chain.

(6) The antibacterial composition as defined in any one of items (1) to (5), characterized in that the hydrophilic substance is at least one member selected from the group consisting of glycerin, polyglycerin, polyglycerin derivatives, polyalkylene glycol, polyalkylene glycol derivatives and polyester prepared by copolymerizing 1 to 10 mole% of an alkali metal salt and/or ammonium salt of sulfoisophthalic acid.

(7) An antibacterial laminate prepared by laminating the antibacterial composition as defined in any one of items 1 to 6 on at least one surface of an inorganic or organic substrate.
(8) The antibacterial laminate as defined in item (7), characterized in that the inorganic substrate is a metal plate.

(9) The antibacterial laminate as defined in item (7), characterized in that the organic substrate is a molded product prepared from a thermoplastic resin.

(10) The antibacterial laminate as defined in item (9), characterized in that the molded product of thermoplastic resin is molded from at least one member selected from the group consisting of polyvinyl chloride, polyvinylidene chloride, polyethylene, polypropylene, polylamide, polystyrene, polycrylonitrile, polyester and polyurethane.

(11) The antibacterial laminate as defined in item (10), characterized in that the molded product is a film or a sheet.

[0021] The present invention is described below in more detail.

[0022] The term "inorganic antibacterial agent" used herein is a general term for inorganic compounds which contain a metal or metal ions and which show antibacterial activity against Staphylococcus aureus and Escherichia coli. The form of the inorganic antibacterial agent can be, for example, any of a gas, liquid and solid and is preferably a solid in view of the durability of the antibacterial agent. Examples of the inorganic antibacterial agent to be used are fine particles having particles or ionic species of metals such as silver, zinc or copper which have antibacterial properties, the metal particles or metal ionic species being supported on an inorganic substance such as silica or like metal oxides, zeolite, synthetic zeolite, zirconium zeolite, aluminosilicates, aluminophosphates, aluminophosphate, titanium dioxide, carbon black, and the like; thin films of sol-gel material or fine particles of metal oxides having the capability of photooxidation catalyst such as zinc oxide and titanium oxide; and composite particles prepared by surface-treating a thin film of sol-gel material or fine particles thereof with an inorganic or organic compound reagent, or by laminating, applying or embedding (for enclosure) such inorganic oxides or composite oxides on or into the surface thereof by a sol-gel processing or the like. Also useful as the inorganic antibacterial agent is a composite antibacterial agent prepared by adding said inorganic antibacterial agent to a metal halide coated used as a raw material in forming a metal sol-gel material.

[0023] More specific examples of such inorganic antibacterial agents are Novaron (product of Toagosei Co., Ltd.), Bactekiller (product of Kanebo Kasei Co., Ltd.), fine particles of antibacterial spherical ceramics S1, S2, S5 (products of Adomatex Co., Ltd.), Horonkiller (product of Nikko Co., Ltd.), Zeomitic (product of Sinagawa Fuel Co., Ltd.), Amenitop (product of Matsushita Electric Industrial Co., Ltd.), Ionpure (product of Ishizuka Glass Co. Ltd.) and like silver-based antibacterial agents, Z-Nouve (product of Mitsuishi Mining & Smelting Co., Ltd.) and like zinc-based antibacterial agents, fine particles of antibacterial spherical ceramics S1, S2, S5 (product of Nippon Aerosil Co., Ltd.), ST-135 (product of Ishihara Sangyo Co., Ltd.) and like fine particles of titanium dioxide and sol-gel materials thereof. Useful composite particles include, for example, fine particles of titanium dioxide coated with silica, GYT (product of Goyoshoiki Co., Ltd.).

[0024] The term "hydrophilic substance" used herein refers to a substance which is superior in affinity for water and which can be dissolved or dispersed in water and can retain water or moisture and can swell with water. The hydrophilic substance is an organic compound or a high molecular compound containing at least one of a hydroxyl group, amino group, amide group, carboxyl group or alkali metal salts thereof, sulfonic acid group or alkali metal salts thereof, quaternary ammonium salt group and amine salt group, or an organic compound or a high molecular compound containing at least one of a polyether chain and a polyamine chain. The polyether is a high molecular compound containing at least two ether bonds in one molecule. Typical examples are polyoxyethylene monochiain, polyoxyethylene chain and polyoxypropylene chain. The polyamine is a polymer having basic nitrogen atoms in the principal chain, typically polyethyleneimine and polyalkylene polyamine (such as polyethylene polyamine).

[0025] Specific examples of the hydrophobic substance are polyvinyl alcohol, polyacrylamide, poly(N,N-dimethylaminomethyl acrylamide), poly(N,N-dimethacrylamide), poly(N,N-dimethylaminoethyl acrylate), poly(N,N-dimethylaminoethyl methacrylate), polyvinylamine, polyvinyl pyridine, polyvinyl pyrrolidone, polyvinyl imidazole, homopolymers or copolymers of polyacrylic acid, homopolymers or copolymers of poly(methacrylic acid), homopolymers or copolymers of maleic anhydride (e.g. maleic anhydride-styrene copolymer), polyvinyl sulfonate or copolymers thereof or alkali metal salts thereof, polystyrenesulfonic acid or copolymers thereof or alkali metal salts thereof, derivatives of quaternary ammonium salt of polystyrene, polyvinyl imidazoline salt, polyallylamine salt, polyethylene glycol (alias, polyethylene oxide), polypropylene glycol, polyethylene/ propylene glycol, polytetramethylene glycol and like polyalkylene glycols, glycerin, polyglycerin and like polyols or polymers thereof and polyesters prepared by copolymerizing 1 to 10 mole% of an alkali salt or ammonium salt of sulfoisoephthalic acid. The hydrophilic substance to be used further includes, for example, polyether derivatives composed of such polyalkylene glycol or polyglycerin with a terminal thereof protected with an alcohol, alkanol, fatty acid, amine or the like. Examples of the polyether derivatives are polyethylene glycol monomethyl ether, polyethylene glycol dimethyl ether, polyglycerol alkylene oxide addition reaction product, fatty acid ester thereof or aliphatic alcohol ether, polyglycerin fatty acid ester, polyglycerin fatty acid alcohol ether, polyglycerin glycidyl ether and reaction products thereof. Among them, polyethylene glycol, polyglycerin and derivatives thereof are preferred in view of the improvements in the compatibility with a polyester and in antibacterial properties.

[0026] The methods of incorporating the hydrophilic substance into an inorganic antibacterial agent are not limited. Any desired method can be selected according to the method of preparing an inorganic antibacterial agent and the chemical and physical properties thereof. The incorporation can be done, as by mixing or melt-kneading, or through the
formation of ionic-bond or covalent bonding, copolymerization or the like.

Specific examples of mixing methods employable in the invention are a method comprising heating the inorganic antibacterial agent and the hydrophilic substance and mixing the melt using an extruder or the like; and a method comprising dissolving or dispersing the inorganic antibacterial agent and the hydrophilic substance in a suitable solvent such as water, a water/alcohol solvent mixture, or an organic solvent such as acetone, methyl ethyl ketone or the like, followed by evaporation of the solvent to dryness. The hydrophilic substance may exist with the inorganic antibacterial agent in any form of covalent bonding, ionic bond, copolymer or mixture within the antibacterial composition obtained by said processes.

To inhibit the bleedout of the hydrophilic substance out of the system, namely to maintain the high antibacterial activity of the antibacterial composition of the invention for a long time, it is preferable to cause the hydrophilic substance (monomer) to bind to the principal chain or the side chain of the antibacterial component-containing polymer such as a polyester, polyamide or polyolefin, examples of the hydrophilic substance being glycols, polyols, alkali salts or ammonium salts of sulfoisophthalic acid, vinyl pyrrolidone, acrylic acid and styrenesulfonic acid which are all copolymerizable. There is no limitation on the molecular weight of the hydrophilic substance to be combined (mixed or copolymerized) with the antibacterial agent. Yet, the number average molecular weight of polyethylene glycol used as such substance is preferably 200 to 30,000, more preferably 1,000 to 25,000.

Although the amount of the hydrophilic substance to be added (in case of a copolymer, the hydrophilic substance in the copolymer) is limitless, the amount of polyethylene glycol used as such substance is 0.1 to 20% by weight, preferably 0.5 to 10% by weight, more preferably 1 to 5% by weight, based on the total amount of inorganic antibacterial agents. Less than 0.1% by weight of the substance fails to satisfactorily increase the antibacterial activity, whereas above 20% by weight of the substance lowers the mechanical properties, heat resistance and weatherability of antibacterial composition, and is undesirable.

The antibacterial composition of the invention may contain other components to improve the slidability, resistance to abrasion and to blocking, hiding power and other physical properties. The components include inorganic particles, such as particles of calcium carbonate (CaCO₃), calcium phosphate, apatite, barium sulfate (BaSO₄), calcium fluoride (CaF₂), talc, kaolin, silicon oxide (SiO₂), alumina (Al₂O₃), titanium dioxide, zirconium oxide (ZrO₂), iron oxide (Fe₂O₃) and alumina/silica composite oxide; and organic particles such as particles of polystyrene, polymethacrylate, polyacrylate, copolymers thereof and crosslinked products thereof. The foregoing particles are described below in more detail.

The particles of calcium carbonate are classified according to its crystal structure into three crystal forms, namely, calcite (trigonal or hexagonal system), aragonite (orthorhombic system) and vaterite (hexagonal or pseudohexagonal system). The calcium carbonates in any crystal form can be used in the invention. The shape of calcium carbonate to be used can be selected as desired from the shapes of connected globes, cubes, spindles, pillars, needles, spheres, eggs, etc.

The kaolin particles useful in the invention can be any of calcined or uncalcined natural kaolin and synthetic kaolin and can be in any shape selected as desired from the shapes of plates, pillars, spheres, spindles and eggs.

The alumina to be used in the invention includes, for example, hydrated crystalline alumina such as gibbsite, bayerite, nordstrandite, boehmite, diaspore and toddite, hydrated amorphous alumina such as amorphous gels, boehmite gels and bayerite gels; and mid-activated alumina such as \( \rho \), \( \eta \), \( \chi \), \( \delta \) or \( \theta \) type, and \( \alpha \)-type alumina.

The average diameter of the particles is not limited since the particles of varied diameters are to be used according to the purpose. Generally a preferred average diameter of primary particles is 0.01 \( \mu \)m to 5 \( \mu \)m. The amount of the particles to be added is preferably 5% by weight or less. If the amount exceeds 50,000 ppm, coarse particles noticeably exist in the inorganic and/or organic antibacterial agent, and projections markedly appear over the surface of antibacterial film, so that the particles are likely to come off, diminishing the film quality.

There is no limitation on the methods of incorporating the particles into the antibacterial composition.

A stage for addition of particles can be determined depending on the kind of particles to be used, the diameter of the particles, concentration of chloride ions, slurry concentration, slurry temperature and the like. Usually it is preferred to add the particles prior to the initiation of polymerization reaction for synthesis of a polyester or in the course of production of an oligomer. When the slurry is added to the reaction system, preferably the slurry is heated to the boiling point of ethylene glycol to increase the dispersibility of particles. In adding the particles to the antibacterial composition, a specific thermoplastic resin containing the particles can be mixed with the inorganic antibacterial agent. The antibacterial composition of the invention used alone can be molded to provide a molded article. Optionally the antibacterial composition of the invention may be mixed with a suitable thermoplastic or thermosetting resin before molding operation. Examples of useful thermoplastic or thermosetting resins are polyethylene, polypropylene, poly(4-methylpentene), polybutene-1, ethylene copolymers and like polyolefins, polyvinyl chloride, polyvinylidene chloride, polyvinyl alcohol, ethylene-vinyl alcohol copolymers and like vinyl polymers, 6-nylon, 6,6-nylon, nylon 11, nylon 12 and like polyamides, aliphatic polyester, polyethylene terephthalate, polyethylene naphthalate and like aromatic polyesters, polycarbonate, polystyrene, acrylic resins, polyurethane resins, aminoaalkyd resins, acryl silicone resins, melamine resins, etc.

The antibacterial composition of the invention can be used as mixed with water-insoluble alkali silicate, orga-
noalkoxysilane, tetrasilane zirconium alkoxide or like inorganic compounds, or emulsions of alkali silicate, organoalkoxysilane melamine resins, tetrasilane zirconium alkoxide polyurethane resin or like hybride materials.

[0039] The foregoing mixture can be laminated by melt extrusion or by its application to at least one surface of fibers, fabrics, non-fabrics, films, sheets, synthetic papers, filters, plastics, papers, wood and like organic substrates or glass plates, stainless steel plates, steel plates, aluminum plates, aluminum foil, thin films of metals, thin films of metallic oxides, pottery and like inorganic substrates. In this case, the surface strength can be increased by mixing a crosslinkable substance with the antibacterial composition to provide an antibacterial composition laminate with a three-dimensionally crosslinked structure. It is also possible to apply a thin film of gelatin or like natural high molecular substance, polyester, polyamide or like linear or crosslinking synthetic high molecular substance to the surface of the antibacterial composition layer. Antibacterial fibers, antibacterial films, antibacterial sheets or antibacterial polymer laminated metal plates prepared using the antibacterial composition of the invention may be in stretched or unstretched form. The stretched films may be either monaxially oriented or biaxially oriented. The thickness of the film is not limited.

[0040] The antibacterial films or sheets prepared using the antibacterial composition of the invention are suitable for use, for example, as a film or sheet for wall papers, a film or sheet for wrapping foods, a shrink film, a shrink label, a base film for magnetic tape, a film for wrapping semi-conducting or electronic materials, magnetic card, OHP, a support for photographic materials, heat-sensitive papers, etc.

Embodiments of the Invention

(Examples)

[0041] The present invention is described below in more detail with reference to the following Examples and Comparative Examples.

[0042] Given below are methods for evaluating the antibacterial properties and other properties of the antibacterial compositions and laminates obtained in the Examples and Comparative Examples.

(1) Test for antibacterial properties

[0043] A 0.1 ml quantity of a suspension (conc. 10^7 cells/ml) containing S. aureus (Staphylococcus aureus) and diluted with a 1/50 broth was dropped onto an autoclaved film, 5 cm X 6 cm. An autoclaved Saran wrapping film was superposed on the film to give a laminate (test piece).

[0044] The test piece was placed on a sterilized Petri dish and was incubated at 37°C for 24 hours. Then the test piece was washed with 10 ml of an SCDLP medium. The washings were diluted ten-fold and spread over a nutrient agar plate. Twenty-four hours later, the number of cells was counted.

(2) Evaluation of laminate clarity

[0045] The clarity of the laminate was measured using a turbidimeter (trade mark “NDH-1001DP” manufactured by Nihon Denshoku Kogyo Co., Ltd.). The results were expressed in a haze value.

(3) Coloring degree of laminate

[0046] The coloring degree of the laminate was measured using a color-difference meter (trade mark “Z-300A” manufactured by Nihon Denshoku Kogyo Co., Ltd.). The measurements were expressed in a color b value.

Reference Example 1 (not according to the invention)

[0047] Heated at 140 to 220°C were 9 moles of dimethyl terephthalate, 1 mole of tri-n-butylhexadecyl phosphonium salt of dimethyl 5-sulfoisophthalate, 22 moles of ethylene glycol, and zinc acetate in a concentration of 200 ppm calculated as zinc (Zn) relative to a theoretical amount of obtained polyester copolymer. Ester exchange reaction was carried out while distilling off the obtained methanol from the reaction system.

[0048] After completion of ester exchange reaction, the reaction product was mixed at 250°C with 0.12 mole of polyethylene glycol having a molecular weight of 10,000 (product of Nacalai Tesque Co., Ltd.), antimony oxide in a concentration of 250 ppm calculated as antimony (Sb) relative to a theoretical amount of obtained polyester copolymer and trimethyl phosphate in a concentration of 80 ppm calculated as P relative thereto. The mixture was stirred for 15 minutes, followed by addition of spherical particles of silica 0.9 μm in average particle diameter in a concentration of 2,000 ppm. The mixture was subjected to polycondensation reaction under vacuum at 260°C for 60 minutes, giving a polyester resin having an intrinsic viscosity (η) of 0.50.
With the use of a twin screw extruder, the obtained polymer was melted at 250°C and the melt was extruded. The obtained extrudate was cooled with a cooling roll at 30°C to give an unstretched film of about 180 μm thickness. The unstretched film was longitudinally stretched to 3.5 times the original length as placed between a pair of rolls heated to 80°C and having different circumferential speeds, and was transversely stretched to 3.5 times the original width at 1200°C by a tenter. Thereafter the film was thermally fixed at 190 to 200°C to produce a biaxially stretched film of polyester copolymer having a thickness of 14.5 μm.

Reference Example 2 (not according to the invention)

(A) Preparation of substrate film

Fine particles of calcium carbonate 0.5 μm in average particle diameter in a concentration of 4,000 ppm were dispersed in polyethylene terephthalate. The dispersion was melted at 290°C. The melt was extruded at 290°C and cooled with a cooling roll at 30°C to give an unstretched film of about 180 μm thickness. The unstretched film was longitudinally stretched to 3.5 times the original length as placed between a pair of rolls heated at 85°C and having different circumferential speeds, producing a film useful as a substrate.

(B) Preparation of coating fluid of antibacterial composition

An antibacterial composition was prepared in the same manner as in Reference Example 1 with the exception of using a mixture of 5 moles of dimethyl terephthalate and 4 moles of dimethyl isophthalate in place of 9 moles of dimethyl terephthalate. The obtained antibacterial composition was dissolved in methyl ethyl ketone (commercially available guaranteed reagent) to give a 3% by weight of a solution.

(C) Preparation of laminated polyester film

A coating fluid comprising the antibacterial composition obtained above in step (B) was passed through a filter having a mesh size of 1.0 μm. The filtrate was applied to the surface of the substrate film prepared above in step (A) by a bar coater method. The coated substrate film was dried by hot air at 70°C. The film was transversely stretched to 3.5 times the original width at 130°C by a tenter. Thereafter the film was thermally fixed at 200 to 210°C to produce a biaxially stretched laminated polyester film having a thickness of 14.5 μm.

| Table 8 |
|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Ex. 34| Ex. 35| Com.Ex.14| Com.Ex.15| Com.Ex.16| Com.Ex.17| Com.Ex.18 |
| Polyester A Wt %| A-1| 75 | A-2| 75 | None| A-1| 100| A-1| 97 | A-3| 75 | A-1| 75 |
| Graft poly mer B Monomer Wt %| B-1| Acrylic acid 8.75 Ethyl acrylate 16.25 | B-2| Acrylic acid 8.75 Ethyl acrylate 16.25 | None| None| B-4| Acrylic acid 1.05 Ethyl acrylate 1.95 | B-3| Acrylic acid 8.75 Ethyl acrylate 16.25 | B-5| Vinyl acetate 21.25 Ethyl acrylate 3.75 |
| Initial cell number Cell number 24 hours later| 3.6X10⁶| 2.4X10²| 3.6X10⁶| 2.0X10²| >10⁸| 3.6X10⁶| 3.6X10⁶| 3.6X10⁶| 3.6X10⁶| 4.6X10⁴| 2.2X10⁴ |

Example 1

One part by weight of silver/zirconium phosphate antibacterial filler, i.e. Novaron (product of Toagosei Co., Ltd.) was added to 100 parts by weight of a terephthalic acid/ethylene glycol/polyethylene glycol (molecular weight...
1000) (100//95/5 mole ratio) copolymer wherein fine particles of calcium carbonate 0.5 μm in average particle diameter in a concentration of 4000 ppm are dispersed. The mixture was heated to 280°C and the melt was extruded at 280°C. The obtained extrudate was cooled with a cooling roll at 30°C to give an unstretched film of about 180 μm thickness. The unstretched film was longitudinally stretched to 3.5 times the original length as placed between a pair of rolls heated to 85°C and having different circumferential speeds, and was transversely stretched to 3.5 times the original width at 130°C by a tenter. Thereafter the film was thermally fixed at 200 to 210°C to produce a biaxially stretched film of polyester having a thickness of 14.5 μm. The antibacterial test result of the obtained film is shown in Table 1.

Examples 2 and 3

[0055] Antibacterial films were formed in the same manner as in Example 1 with the exception of using the inorganic antibacterial agent shown in Table 1 in place of the silver/zirconium phosphate antibacterial filler. The antibacterial properties of the films were evaluated in the same manner as in Example 1. The test results are shown in Table 1.

[0056] The antibacterial properties of P-25-containing films were evaluated by irradiation with black light (0.25 mw/cm²) at a distance of 40 cm away.

Comparative Examples 1 to 3

[0057] Antibacterial films were prepared and the antibacterial properties were rated in the same manner as in Examples 1, 2 and 3 except that polyethylene terephthalate PET was used in place of the copolymer.

Table 1

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Inorganic antibacterial agent</th>
<th>Type of hydrophilic substance (copolymer)</th>
<th>Evaluation of antibacterial properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Type</td>
<td>Amount (wt %)</td>
<td>Initial cell number</td>
</tr>
<tr>
<td>Ex. 1</td>
<td>Novaron</td>
<td>1.0</td>
<td>T//EG/PEG1000</td>
</tr>
<tr>
<td>Com. Ex. 1</td>
<td>Novaron</td>
<td>1.0</td>
<td>PET</td>
</tr>
<tr>
<td>Ex. 2</td>
<td>Z-Nouve</td>
<td>1.0</td>
<td>T//EG/PEG1000</td>
</tr>
<tr>
<td>Com. Ex. 2</td>
<td>Z-Nouve</td>
<td>1.0</td>
<td>PET</td>
</tr>
<tr>
<td>Ex. 3</td>
<td>P-25</td>
<td>20</td>
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<tr>
<td>Com. Ex. 3</td>
<td>P-25</td>
<td>20</td>
<td>PET</td>
</tr>
</tbody>
</table>

Novaron: trade name for a silver-based antibacterial agent manufactured by Toagosei Co., Ltd.
Z-Nouve: trade name for a zinc-based antibacterial agent manufactured by Mitsui Mining & Smelting Co., Ltd..
P-25: trade name for titanium dioxide manufactured by Nippon Aerosil Co., Ltd. ND refers to no detection of bacteria.

Example 4

(A) Preparation of sulfonic acid group-containing polyester and aqueous dispersion

[0058] A sulfonic acid group-containing polyester was prepared by the following process. Ninety-five mole% of dimethyl isophthalate and 5 mole% of sodium 5-sulfoisophthalate as a dicarboxylic acid component and 100 mole% of diethylene glycol as a glycol component were subjected to ester exchange reaction and to polycondensation in the conventional manner. The obtained sulfonic acid group-containing polyester (PES-SO₃Na) had a glass transition point of 69°C.

[0059] The sulfonic acid group-containing polyester (300 parts) and 150 parts of n-butyl cellosolve were heated with stirring to give a viscous solution. Water (550 parts) was gradually added with stirring, giving a uniform pale white aqueous dispersion with a 30% solids content.

[0060] The dispersion was added to a 1 : 1 mixture of water and isopropanol, giving an aqueous dispersion of sulfonic acid group-containing polyester with a 5% solids content.
(B) Preparation of mixed coating fluid

[0061] A silver/zirconium phosphate antibacterial filler (0.1 part by weight), i.e. Novaron (product of Toagosei Co., Ltd.) was added to 100 parts by weight of the aqueous dispersion of sulfonic acid group-containing polyester (A). The former was minutely dispersed to produce a coating fluid.

(C) Formation of film

[0062] A substrate film was produced in the same manner as in Reference Example 2 with the exception of using a different coating fluid, whereby a laminated film was formed. The amount of the coating fluid deposited on the film was about 0.5 g/m². The antibacterial test result of the film is shown in Table 2.

Examples 5 and 6

[0063] Antibacterial films were produced in the same manner as in Example 4 except that the inorganic antibacterial agents shown in Table 2 were used in place of the silver/zirconium phosphate antibacterial filler (product of Toagosei Co., Ltd.). The antibacterial properties of the films were evaluated in the same manner as in Example 1. The test results are shown in Table 2.

[0064] The antibacterial properties of P-25-containing films were evaluated by irradiation with black light (0.25 mW/cm²) at a distance of 40 cm away.

Table 2

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Inorganic antibacterial agent Type</th>
<th>Amount (wt %)</th>
<th>Type of hydrophilic substance (copolymer)</th>
<th>Evaluation of antibacterial properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex. 4</td>
<td>Novaron</td>
<td>1.0</td>
<td>PES-SO3Na</td>
<td>Initial cell number: 5.6 X 10⁵</td>
</tr>
<tr>
<td>5</td>
<td>Z-Nouve</td>
<td>1.0</td>
<td>PES-SO3Na</td>
<td>Cell number 24 hr.later: 2.5 X 10³</td>
</tr>
<tr>
<td>6</td>
<td>P-25</td>
<td>20</td>
<td>PES-SO3Na</td>
<td></td>
</tr>
</tbody>
</table>

Novaron: trade name for a silver-based antibacterial agent manufactured by Toagosei Co., Ltd.
Z-Nouve: trade name for a zinc-based antibacterial agent manufactured by Mitsui Mining & Smelting Co., Ltd.
P-25: trade name for titanium dioxide manufactured by Nippon Aerosil Co., Ltd.

Example 7

[0065] Five parts by weight of polyethylene glycol (molecular weight 20,000) and 2 parts by weight of silver/zirconium phosphate antibacterial filler (product of Toagosei Co., Ltd.) were added to 95 parts by weight of polyethylene terephthalate (PET, molecular weight 20,000) wherein fine particles of calcium carbonate 0.5 μm in average particle diameter in a concentration of 4000 ppm were dispersed. The mixture was heated to 280°C and the melt was extruded. The obtained extrudate was cooled with a cooling roll at 30°C to give an unstretched film of about 180 μm thickness. The unstretched film was longitudinally stretched to 3.5 times the original length as placed between a pair of rolls heated to 85°C and having different circumferential speeds, and was transversely stretched to 3.5 times the original width at 130°C by a tenter. Thereafter the film was thermally fixed at 200 to 210°C to produce a biaxially stretched film of polyester having a thickness of 14.5 μm. The antibacterial test result of the obtained film is shown in Table 3.

Examples 8 and 9

[0066] Antibacterial films were formed in the same manner as in Example 1 with the exception of using the inorganic antibacterial agents in Table 3 in place of the silver/zirconium phosphate antibacterial filler (product of Toagosei Co., Ltd.) in Example 7. The antibacterial properties of the films were evaluated in the same manner as in Example 1. The test results are shown in Table 3.

[0067] The antibacterial properties of P-25-containing films were evaluated by irradiation with black light (0.25 mW/cm²) at a distance of 40 cm away.
Comparative Examples 4 to 6

Antibacterial films were prepared and the antibacterial properties were rated in the same manner as in Examples 7, 8, and 9, respectively except that polyethylene terephthalate (PET) was used in place of the copolymer. The results in Table 3 were obtained.

Table 3

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Inorganic antibacterial agent</th>
<th>Hydrophilic substance</th>
<th>Evaluation of antibacterial properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Type</td>
<td>Amount (wt%)</td>
<td>Type</td>
</tr>
<tr>
<td>Ex. 7</td>
<td>Novaron</td>
<td>2</td>
<td>PEG#20000</td>
</tr>
<tr>
<td>Com. Ex. 4</td>
<td>Novaron</td>
<td>2</td>
<td>None</td>
</tr>
<tr>
<td>Ex. 8</td>
<td>Z-Nouve</td>
<td>2</td>
<td>PEG#20000</td>
</tr>
<tr>
<td>Com. Ex. 5</td>
<td>Z-Nouve</td>
<td>2</td>
<td>None</td>
</tr>
<tr>
<td>Ex. 9</td>
<td>P-25</td>
<td>20</td>
<td>PEG#20000</td>
</tr>
<tr>
<td>Com. Ex. 6</td>
<td>P-25</td>
<td>20</td>
<td>None</td>
</tr>
</tbody>
</table>

Novaron: trade name for a silver-based antibacterial agent manufactured by Toagosei Co., Ltd.
Z-Nouve: trade name for a zinc-based antibacterial agent manufactured by Mitsui Mining & Smelting Co., Ltd.
P-25: trade name for titanium dioxide manufactured by Nippon Aerosil Co., Ltd. PG: polyglycerin

Examples 10 to 21

Antibacterial films were produced in the same manner as in Examples 7, 8, and 9, respectively with the exception of using three types of polyglycerins as shown in Table 4, i.e. polyglycerin #310, polyglycerin #500, and polyglycerin #750 (products of Sakamoto Yakuhin Kogyo Co., Ltd.) and polyvinyl alcohol (PVA) as shown in Table 4 in place of the polyethylene glycol. The antibacterial properties of the films were evaluated with the results shown in Table 4.

Table 4

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Inorganic antibacterial agent</th>
<th>Hydrophilic substance</th>
<th>Evaluation of antibacterial properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Type</td>
<td>Amount (wt%)</td>
<td>Type</td>
</tr>
<tr>
<td>Ex. 10</td>
<td>Novaron</td>
<td>2</td>
<td>PG#310</td>
</tr>
<tr>
<td>11</td>
<td>Novaron</td>
<td>2</td>
<td>PG#500</td>
</tr>
<tr>
<td>12</td>
<td>Novaron</td>
<td>2</td>
<td>PG#750</td>
</tr>
<tr>
<td>13</td>
<td>Novaron</td>
<td>2</td>
<td>PVA</td>
</tr>
<tr>
<td>14</td>
<td>Z-Nouve</td>
<td>2</td>
<td>PG#310</td>
</tr>
<tr>
<td>15</td>
<td>Z-Nouve</td>
<td>2</td>
<td>PG#500</td>
</tr>
<tr>
<td>16</td>
<td>Z-Nouve</td>
<td>2</td>
<td>PG#750</td>
</tr>
<tr>
<td>17</td>
<td>Z-Nouve</td>
<td>2</td>
<td>PVA</td>
</tr>
<tr>
<td>18</td>
<td>P-25</td>
<td>20</td>
<td>PG#310</td>
</tr>
<tr>
<td>19</td>
<td>P-25</td>
<td>20</td>
<td>PG#500</td>
</tr>
<tr>
<td>20</td>
<td>P-25</td>
<td>20</td>
<td>PG#750</td>
</tr>
</tbody>
</table>
Claims

1. An antibacterial composition comprising an inorganic antibacterial agent and a hydrophilic substance as main components, wherein the inorganic antibacterial agent is an inorganic compound which carries particles and/or ions of at least one metal selected from the group consisting of silver (Ag), zinc (Zn) and copper (Cu) and/or an organic compound having said metallic ions attached thereto.

2. An antibacterial composition comprising an inorganic antibacterial agent and a hydrophilic substance as main components, wherein the inorganic antibacterial agent contains a metallic oxide having the capability of photooxidation catalyst.

3. The antibacterial composition according to claim 2, characterized in that the metallic oxide contains at least one of titanium oxide (TiO$_2$) and zinc oxide (ZnO$_2$).

4. The antibacterial composition according to any one of claims 1 to 3, characterized in that the hydrophilic substance is a high molecular compound containing at least one member selected from the group consisting of a hydroxyl group, an amino group, an amido group, a carboxyl group or an alkali metal salt thereof, a sulfonic acid group or an alkali metal salt thereof, a quaternary ammonium salt group, an amine salt group, a polyether chain and a polyamine chain.

5. The antibacterial composition according to any one of claims 1 to 4, characterized in that the hydrophilic substance is at least one member selected from the group consisting of glycerin, polyglycerin, polyglycerin derivatives, polyalkylene glycol, polyalkylene glycol derivatives and polyester prepared by copolymerizing 1 to 10 mole% of an alkali metal salt and/or ammonium salt of sulfoisophthalic acid.

6. An antibacterial laminate prepared by laminating the antibacterial composition as defined in any one of claims 1 to 5 on at least one surface of an inorganic or organic substrate.

7. The antibacterial laminate according to claim 6, characterized in that the inorganic substrate is a metal plate.

8. The antibacterial laminate according to claim 6, characterized in that the organic substrate is a molded product prepared from a thermoplastic resin.

9. The antibacterial laminate according to claim 8, characterized in that the molded product of thermoplastic resin is molded from at least one member selected from the group consisting of polyvinyl chloride, polyvinylidene chloride, polyethylene, polypropylene, polyamide, polystyrene, polyacrylonitrile, polyester and polyurethane.

10. The antibacterial laminate according to claim 9, characterized in that the molded product is a film or a sheet.

Patentansprüche

1. Antibakterielle Zusammensetzung, umfassend ein anorganisches antibakterielles Mittel und eine hydrophile Substanz als Hauptkomponenten, wobei das anorganische antibakterielle Mittel eine anorganische Verbindung, die Teilchen und/oder Ionen wenigstens eines Metalls, das aus der aus Silber (Ag), Zink (Zn) und Kupfer (Cu) besteht.
henden Gruppe ausgewählt ist, trägt, und/oder eine organische Verbindung mit den daran gebundenen metallischen Ionen ist.

2. Antibakterielle Zusammensetzung, umfassend ein anorganisches antibakterielles Mittel und eine hydrophile Substanz als Hauptkomponenten, wobei das anorganische antibakterielle Mittel ein Metalloxid mit der Fähigkeit eines Photooxidationskatalysators enthält.

3. Antibakterielle Zusammensetzung nach Anspruch 2, dadurch gekennzeichnet, dass das Metalloxid wenigstens entweder Titanoxid (TiO₂) oder Zinkoxid (ZnO₂) enthält.


5. Antibakterielle Zusammensetzung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, dass die hydrophile Substanz wenigstens entweder Titanoxid (TiO₂) oder Zinkoxid (ZnO₂) enthält.

6. Antibakterielles Laminat, hergestellt durch das Laminieren der in einem der Ansprüche 1 bis 5 definierten antibakteriellen Zusammensetzung auf wenigstens eine Fläche eines anorganischen oder organischen Substrats.

7. Antibakterielles Laminat nach Anspruch 6, dadurch gekennzeichnet, dass das anorganische Substrat eine Metallplatte ist.

8. Antibakterielles Laminat nach Anspruch 6, dadurch gekennzeichnet, dass das organische Substrat ein aus einem thermoplastischen Harz hergestelltes geformtes Produkt ist.


10. Antibakterielles Laminat nach Anspruch 9, dadurch gekennzeichnet, dass das geformte Produkt ein Film oder eine Folie ist.

Revendications

1. Composition antibactérienne comprenant un agent antibactérien inorganique et une substance hydrophile comme principaux composants, dans laquelle l'agent antibactérien inorganique est un composé inorganique qui porte des particules et/ou des ions d'au moins un métal choisi dans le groupe constitué par l’argent (Ag), le zinc (Zn) et le cuivre (Cu) et/ou un composé organique ayant lesdits ions métalliques fixés à celui-ci.

2. Composition antibactérienne comprenant un agent antibactérien inorganique et une substance hydrophile comme principaux composants, dans laquelle l’agent antibactérien inorganique contient un oxyde métallique ayant la capacité d’un catalyseur de photooxydation.

3. Composition antibactérienne selon la revendication 2, caractérisée en ce que l’oxyde métallique contient au moins un élément parmi l’oxyde de titane (TiO₂) et l’oxyde de zinc (ZnO₂).

4. Composition antibactérienne selon l’une quelconque des revendications 1 à 3, caractérisée en ce que la substance hydrophile est un composé à poids moléculaire élevé contenant au moins un élément choisi dans le groupe constitué par un groupe hydroxyle, un groupe amino, un groupe amido, un groupe carboxyle ou un sel de métal alcalin de celui-ci, un groupe acide sulfонique ou un sel de métal alcalin de celui-ci, un groupe sel d’ammonium quaternaire,
un groupe sel d’amine, une chaîne polyéther et une chaîne polyamine.

5. Composition antibactérienne selon l’une quelconque des revendications 1 à 4, caractérisée en ce que la substance hydrophile est au moins un élément choisi dans le groupe constitué par la glycérine, la polyglycérine, les dérivés de la polyglycérine, le polyalkylène glycol, les dérivés du polyalkylène glycol et le polyester préparé par copolymérisation de 1 à 10 % en mole d’un sel de métal alcalin et/ou d’un sel d’ammonium de l’acide sulfoisophtalique.

6. Stratifié antibactérien préparé en laminant la composition antibactérienne telle que définie dans l’une quelconque des revendications 1 à 5 sur au moins une surface d’un substrat inorganique ou organique.

7. Stratifié antibactérien selon la revendication 6, caractérisé en ce que le substrat inorganique est une plaque métallique.

8. Stratifié antibactérien selon la revendication 6, caractérisé en ce que le substrat organique est un produit moulé préparé à partir d’une résine thermoplastique.

9. Stratifié antibactérien selon la revendication 8, caractérisé en ce que le produit moulé en résine thermoplastique est moulé à partir d’au moins un élément choisi dans le groupe constitué par le polychlorure de vinyle, le polychlorure de vinylidène, le polyéthylène, le polypropylène, le polyamide, le polystyrène, le polycrylonitrile, le polyester et le polyuréthane.

10. Stratifié antibactérien selon la revendication 9, caractérisé en ce que le produit moulé est un film ou une feuille.