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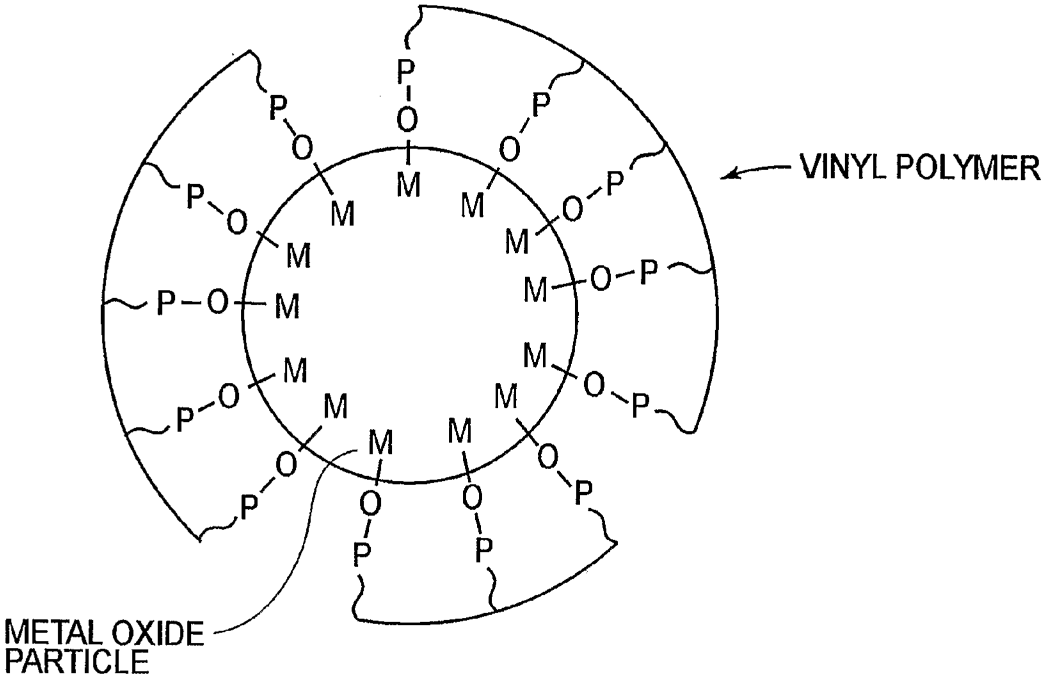
(54) Title: NANO-OXIDE PARTICLES AND PRODUCTION PROCESS THEREOF



(57) Abstract: Nano-oxide particles are surface-protected with a polyvinyl monomolecular film having a binding functional group. The surface-protected nano-oxide particles are produced through vinyl polymerization of a vinyl monomer having a binding functional group in a solution containing nano-oxide particles, the vinyl monomer having the binding functional group, and a dispersion medium. The dispersion medium is contained in the solution in an amount of 70 wt. % or more.

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DESCRIPTION

NANO-OXIDE PARTICLES AND PRODUCTION PROCESS THEREOF

[TECHNICAL FIELD]

The present invention relates to nano-oxide particles for imparting characteristics such as a desired refractive index and transparency to a composite material comprising an oxide and an organic polymer and a process for producing the nano-oxide particles. The present invention also relates to a transparent optical resin material and an optical material which employ the nano-oxide particles.

[BACKGROUND ART]

Amorphous thermoplastic resins such as styrene-based resin, acrylic resin and polycarbonate resin and curable resins such as unsaturated polyester resin and diallyl phthalate resin are general-purpose transparent resin materials having good transparency to light of wavelengths in the visible region. Compared with inorganic glass materials, these resin materials have low specific gravity and an excellent characteristic well-balanced in terms of mechanical characteristics such as moldability, mass-productivity, toughness, flexibility, and shock resistance. However, refractive indices of these resin materials are determined by their constituents, so that the resin materials have a narrow variable region of optical characteristics compared with conventional optical glass materials.

In order to increase a refractive index of a transparent resin material, attempt to incorporate fine particles of metal oxide, metal sulfide, or the like having a high refractive index into the resin matrix has been made.

Japanese Laid-Open Patent Application (JP-A) Hei 1-306477 has disclosed a coating agent, for an optical material, comprising an oxide sol such as an antimony oxide sol and siloxane as a matrix component. In this case, a silane coupling agent or siloxane contributes to dispersion of the colloid. However, a bonding property between siloxane and fine oxide particles is deteriorated by the existence of water so that it is difficult to sufficiently suppress agglomeration among the fine oxide particles. Such a composite material is therefore limited to application of a thin film, and thas not yet been used as a bulk material.

As an attempt to improve dispersibility of the oxide particles in the matrix, studies on a dispersant acting on surfaces of the oxide particles and on introduction of a component acting on the fine oxide particles into the matrix have been made.

JP-A Hei 5-25320 has disclosed a curable composition comprising a thermosetting resin such as acrylic resin or unsaturated polyester resin, an inorganic filler of fine powder, such as titanium oxide or the like, and a dispersant consisting of a phosphate compound having a terminal aryl group. JP-A 2002-55225 has disclosed an active energy-polymerizable resin layer, as a hard coating surface layer of an optical filter, containing inorganic particles treated with an organic compound having an active energy-curable group and an acidic group such as phosphoric group, sulfonic group or carboxylic group. JP-A (Tokuhyo) 2004-524396 has disclosed a composite composition, as an electric or optic device, comprising inorganic particles and a polymer having a side-chain containing oxysilane group, phosphonate group, sulfide group, amino group, or sulfonate group. JP-A 2002-105325 has disclosed a composition prepared by dispersing semiconductor ultrafine particles in a resin matrix having a polymer chain copolymerized with radical-polymerizable phosphine oxide as a ligand for the fine particles.

In the fields of utilizing nanometer oxides for the purpose of increasing a refractive index of an optical material, uniform dispersion of fine particles at nanometer level has become increasingly important. In addition to the optical material, a dispersing technique of nano-oxide particles is also required for an inorganic-organic composite material strengthened with the nano-oxide particles, a shielding material for radiation, ultraviolet rays, visible rays, or infrared rays on the basis of absorbency of the nano-oxide particles, a nonlinear material based on plasmon in the nano-oxide particles, etc.

However, in the techniques disclosed in the above described documents, interaction between a surface of inorganic fine particle and a functional group such as phosphoric group, phosphine oxide or carboxyl group is ensured but a resultant bonding strength is not sufficient. Accordingly, with a decrease in size of the inorganic fine particles, agglomeration among colloid particles cannot be sufficiently suppressed, so that it is difficult to sufficiently uniformly disperse the fine particles of nanometer level. In the case of requiring thermal moldability, it is required that dispersibility of nano-oxide particles is not destroyed by flow of a thermoplastic matrix, so that a surface treating technique of the oxide fine particles becomes further difficult.

[DISCLOSURE OF THE INVENTION]

In view of the above described problems, a principal object of the present invention is to provide nano-oxide particles capable of being uniformly dispersed in a general-purpose resin matrix to sufficiently reduce a degree of agglomeration among particles.

Another object of the present invention is to provide a transparent optical resin material containing the nano-oxide particles for the purpose of realizing a high refractive index or the like and a lens using the transparent optical resin material.

According to an aspect of the present invention, there is provided nano-oxide particles comprising particles each surface of which is coated with a polyvinyl monomolecular film having a binding functional group.

According to another aspect of the present invention, there is provided a production process of surface-protected nano-oxide particles, comprising:

polymerizing a vinyl monomer having a binding functional group in a solution containing nano-oxide particles, the vinyl monomer having the binding functional group, and a dispersion medium,

wherein the dispersion medium is contained in the solution in an amount of 70 wt. % or more.

The nano-oxide particles of the present invention are coated with the polyvinyl monomolecular film having the binding functional group, so that the nano-oxide particles exhibit high dispersibility and can be dispersed at a high concentration in an optical resin material, a polymerizable monomer for an optical material, or a curable oligomer for the optical material. As a result, it is possible to realize an optical material or an optical lens which has a high refractive index and excellent transparency. It is also possible to realize a high-strength composite material containing nano-oxide particles dispersed therein.

These and other objects, features and advantages of the present invention will become more apparent upon a consideration of the following description of the preferred embodiments of the present invention taken in conjunction with the accompanying drawings.

[BRIEF DESCRIPTION OF THE DRAWINGS]

Figure 1 is a schematic view for illustrating a nano-oxide particle according to the present invention.

Figure 2 is a schematic view for illustrating a lens molded from a transparent optical resin material in which nano-oxide particles of the present invention are dispersed.

[BEST MODE FOR CARRYING OUT THE INVENTION]

Preferred embodiments of the present invention will be described in detail.

The nano-oxide particles of the present invention are characterized in that agglomeration among the nano-oxide particles is suppressed by coating a surface of each nano-oxide particle with a polyvinyl monomolecular film having a binding functional group. The binding functional group derived from a vinyl monomer having a binding functional group bonds to the surface of nano-oxide particle. The vinyl monomer is polymerized to provide a vinyl polymer (polyvinyl compound). Hydrocarbon linkages (bonds) are exposed at an outermost surface of nano-oxide particle to form a monomolecular film. Figure 1 schematically illustrates a nano-oxide particle of the present invention. Referring to Figure 1, M represents a metal atom located at the nano-oxide particle surface. In the case where the binding functional group is phosphoric group, as shown in Figure 1, phosphorus atom forms P-O-M linkage (bond) with associated metal oxide located at the nano-oxide particle surface. At the same time, a vinyl group of each molecule is polymerized.

Generally, the "monomolecular film" means a film, such as LB (Langmuir-Blodgett) film, in which a monomer (one molecule) is placed in such a state that hydrophobic groups and hydrophilic groups are uniformly arranged. However, in the present invention, a monomer before its vinyl group is polymerized is regarded as one molecule and a film in which a chain after the polymerization binds to the oxide particle through the binding functional group is referred to as a "polyvinyl monomolecular film". More specifically, at the surface of the oxide particle, the vinyl monomer is polymerized and present as a polymer while the binding functional group derived from the vinyl monomer binds to the oxide surface.

In the present invention, the nano-oxide particles means oxide particles having a particle size of 100 nm or less.

The binding functional group of the polyvinyl monomolecular film acts on metal ion and hydroxyl group at the oxide particle surface and attracts the polyvinyl monomolecular film to the oxide particle surface. The action may be attributable to covalent bond, ionic bond, hydrogen bond, and chelate bond. Herein, the binding functional group means a functional group capable of binding to the oxide particle surface. The binding functional group is not particularly limited and can be used in the present invention so long as a functional group binds to metal ion of the oxide. Examples of the binding functional group may include primary amino group, secondary amino group, tertiary amino group, hydroxyl group, epoxy group, organic group having β-diketone structure, organic group having β-ketoester, carboxyl group, sulfonic group, phosphoric group, and thiol group.

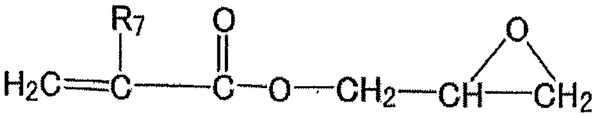
The polyvinyl monomolecular film having the binding functional group used in the present invention is prepared by polymerizing a vinyl monomer having the binding functional group, a vinyl monomer mixture containing the vinyl monomer, or a polymerizable oligomer of the vinyl monomer.

Specific examples of the vinyl monomer having the binding functional group will be described.

Examples of the amino group-containing vinyl monomer may include $H_2C{=}CHCH_2NH_2$, $H_2C{=}CHCH_2NHCH_3$, $H_2C{=}C(CH_3)COOC_2H_4NH_2$, $H_2C{=}C(CH_3)COOC_2H_4NHCH_3$, $H_2C{=}C(CH_3)COOC_2H_4N(CH_3)_2$, $H_2C{=}C(CH_3)COOC_2H_4N(C_2H_5)_2$, $H_2C{=}(CH_3)COOC_3H_6NH_2$, $H_2C{=}C(CH_3)COOC_3H_6NHCH_3$, $H_2C{=}CHCOOC_2H_4NH_2$, $H_2C{=}CHCOOC_2H_4NHCH_3$, and $H_2C{=}CHCOOC_2H_4N(CH_3)_2$.

Examples of the hydroxyl group-containing vinyl monomer may include $H_2C{=}CHCH_2OH$, $H_2C{=}C(CH_3)COOC_2H_4OH$, $H_2C{=}C(CH_3)COOC_3H_6OH$, $H_2C{=}C(CH_3)COOCH_2CHOHCH_3$, $H_2C{=}C(CH_3)COOCH_2CHOHCH_2CH_3$, $H_2C{=}CHCOOC_2H_4OH$, $H_2C{=}CHCOOC_3H_6OH$, $H_2C{=}CHCOOCH_2CHOHCH_3$, and $H_2C{=}CHCOOCH_2CHOHCH_2CH_3$.

Examples of (meth)acrylic monomer having the epoxy group may include a vinyl monomer represented by the following formula (3):

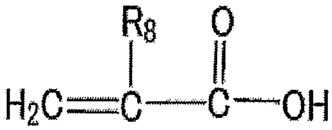


(3)

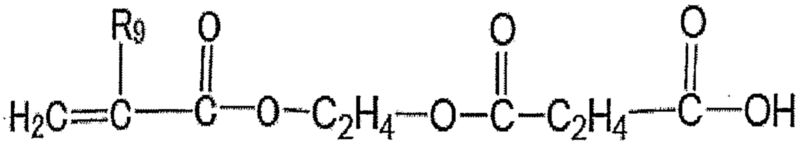
wherein R_7 represents hydrogen atom or methyl group.

Examples of the sulfonic group-containing vinyl monomer may include $CH_2=CHSO_3H$, $CH_2=CHCH_2SO_3H$, $H_2C=C(CH_3)COOC_3H_4OSO_3H$, $H_2C=C(CH_3)COOC_3H_6SO_3H$, $H_2C=C(CH_3)COOC_2H_4OCOC_5H_{10}OSO_3H$, $H_2C=CHCOOC_2H_4OCOC_5H_{10}OSO_3H$, and $H_2C=CHCOOC_{12}H_{24}(1,4\text{-}pH)SO_3H$.

Examples of the carboxyl group-containing vinyl monomer may include those represented by the following formulas (4) and (5):



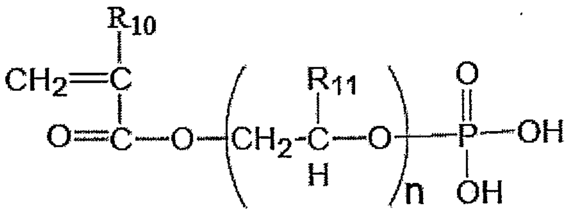
$$H_2C=\overset{R_8}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-OH \qquad (4)$$



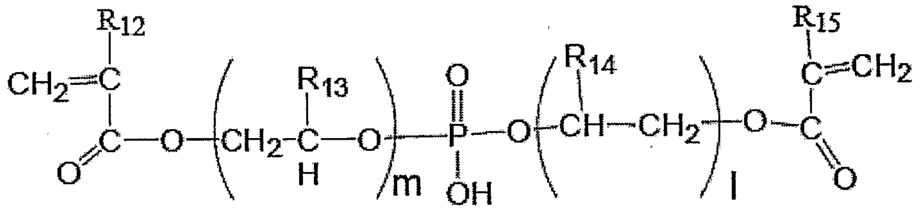
$$H_2C=\overset{R_9}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-C_2H_4-O-\overset{O}{\overset{\|}{C}}-C_2H_4-\overset{O}{\overset{\|}{C}}-OH \qquad (5)$$

wherein R_8 and R_9 represent hydrogen atom or methyl group.

Examples of the phosphoric group-containing vinyl monomer may include (meth)acrylate monomer having phosphoric group represented by the following formulas (6) and (7):



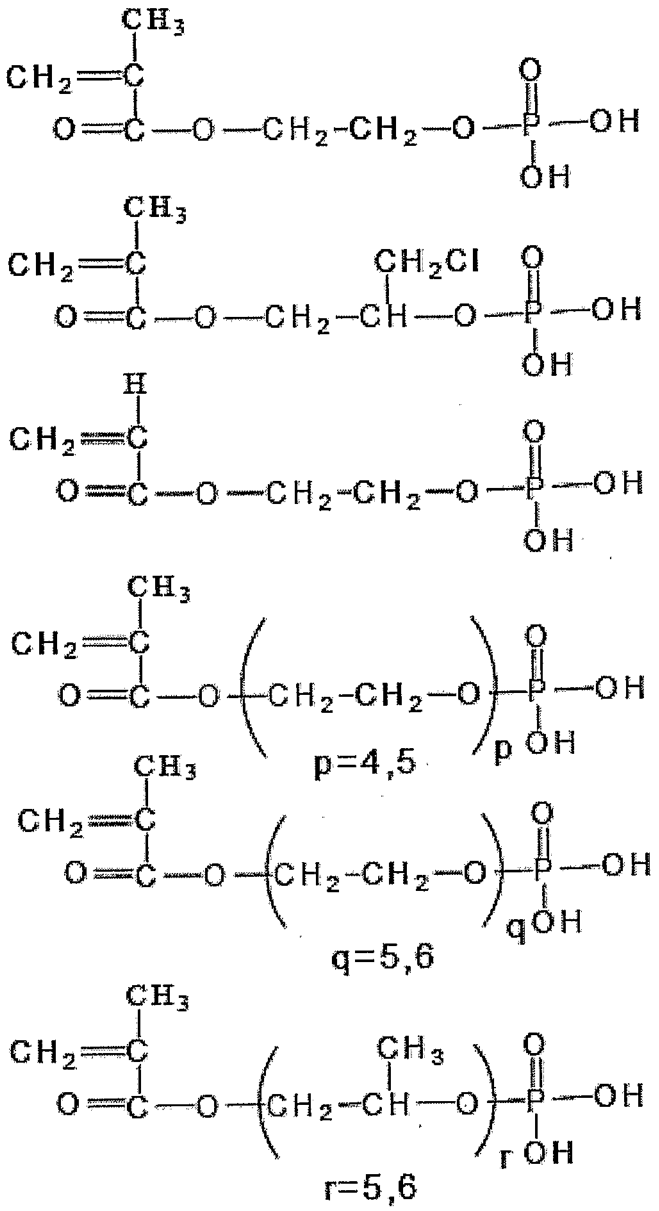
$$CH_2=C(R_{10})-C(=O)-O-\left(CH_2-\underset{H}{C}(R_{11})-O\right)_n-P(=O)(OH)-OH \quad (6)$$



$$CH_2=C(R_{12})-C(=O)-O-\left(CH_2-\underset{H}{C}(R_{13})-O\right)_m-P(=O)(OH)-O-\left(CH(R_{14})-CH_2\right)_l-O-C(=O)-C(R_{15})=CH_2 \quad (7)$$

wherein R_{10}, R_{12} and R_{15} independently represent hydrogen atom or methyl group; R_{11}, R_{13} and R_{15} independently represent hydrogen atom or alkyl group; and n, m and l are an integer of 1 or more.

Commercially available phosphoric group-containing vinyl monomer may include those represented by the following formula (8):



$$CH_2{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}CH_2{-}O{-}P({=}O)(OH){-}OH$$

$$CH_2{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}CH(CH_2Cl){-}O{-}P({=}O)(OH){-}OH$$

$$CH_2{=}C(H){-}C({=}O){-}O{-}CH_2{-}CH_2{-}O{-}P({=}O)(OH){-}OH$$

$$CH_2{=}C(CH_3){-}C({=}O){-}O{-}(CH_2{-}CH_2{-}O)_p{-}P({=}O)(OH){-}OH \quad p=4,5$$

$$CH_2{=}C(CH_3){-}C({=}O){-}O{-}(CH_2{-}CH_2{-}O)_q{-}P({=}O)(OH){-}OH \quad q=5,6$$

$$CH_2{=}C(CH_3){-}C({=}O){-}O{-}(CH_2{-}CH(CH_3){-}O)_r{-}P({=}O)(OH){-}OH \quad r=5,6$$

(8)

Examples of the thiol group-containing vinyl monomer may include $CH_2{=}CHCH_2SH$ and $CH_2{=}CHCH_2CH_2SH$.

It is also possible to add another vinyl monomer in an amount of 80 wt. % or less on the basis of starting material as a copolymerization component to the binding functional group-containing vinyl monomer so long as a binding force between the polyvinyl monomolecular film and the oxide particle is not impaired.

Examples of such a vinyl monomer may include acrylates, methacrylates, acrylonitrile, methacrylonitrile, styrene, nuclear-substituted styrenes, alkyl vinyl ethers, alkyl vinyl esters, perfluoroalkyl vinyl ethers, perfluoroalkyl vinyl esters, maleic acid, maleic anhydride, fumaric acid, itaconic acid, maleimide, and phenylmaleimide.

As another method of obtaining the polymer having the binding functional group, it is also possible to impart the above described binding functional group to a polyvinyl compound having a reactive functional group. For example, when the reactive functional group is epoxy group or hydroxyl group, the polyvinyl compound is reacted with P_2O_5 or H_3PO_4 to change the reactive functional group of the polyvinyl compound into the phosphoric group.

The polyvinyl monomolecular film may preferably contain the acrylic monomer component in an amount of 20 wt. % or more, particularly 50 wt. % or more on the monomer basis. This is because when the amount of the acrylic monomer component is increased, an affinity for a general purpose transparent resin material is increased, thus leading to good transparency of nano-oxide particle-dispersed composite material.

The above described binding functional group may preferably be thiol group, carboxyl group, sulfonic group, or phosphoric group, particularly phosphoric group. In this case, the binding functional group forms strong ionic bond with metal ion at the oxide particle, so that a binding force of the polyvinyl monomolecular film onto the oxide particle surface is increased. In the case of the phosphoric group, it forms P-O-M bond (M: metal ion of the oxide) with the metal ion located at the oxide particle surface remains attached on the oxide particle surface in many environments including moisture environment. In addition, it causes less light absorption in the visible region. Further, from the viewpoints of economy and an affinity for the matrix, it is more preferable that the phosphoric group-containing acrylates represented by the above described formula (8) are used.

The nano-oxide particles may preferably have a particle size in a range of 0.5 - 30 nm, more preferably 1 - 10 nm. When the particle size is 0.5 nm or larger, a characteristic attributable to the oxide can be obtained. When the particle size is 30 nm or smaller, light scattering by the particles is less, so that it is possible to obtain a high-transparency composite material when the nano-oxide particles are combined with a transparent resin matrix. Herein, the particle size means a crystallite size of primary particles and can be determined by direct observation through a transmission electron microscope (TEM) or the like.

In the present invention, any nano-oxide particles except for nano-oxide particles of alkali metal can be used. Examples of oxides for the nano-oxide particles of the present invention may include magnesium oxide, aluminum oxide, iron oxide, titanium oxide, gallium oxide, niobium oxide, tin oxide, indium oxide, zirconium oxide, lanthanum oxide, cadmium oxide, hafnium oxide, erbium oxide, neodymium oxide, cerium oxide, dysprosium oxide, and a mixed oxide of these oxides. From the viewpoint of stability, it is preferable that aluminum oxide, iron oxide, titanium oxide, galium oxide, niobium oxide, tin oxide, indium oxide, zirconium oxide, lanthanum oxide, cadmium oxide, hafnium oxide, erbium oxide, neodymium oxide, cerium oxide, dysprosium oxide, and a mixed oxide of these oxides are used. Such oxide particles of nano-size ordinarily have many hydroxyl groups at their surfaces and are stabilized in many cases by electric double layer created by acid or base or by a surface treatment agent. Further, the oxide particles used in the present invention may also include a partially hydroxylated particles such as oxide particles containing hydroxyl group in their crystal lattices.

The nano-oxide particles of the present invention can be present in a dispersed state in an organic dispersion medium. The dispersion medium can be selected, depending on the application therefor, from alcohols such as methanol, ethanol, propanol, iso-propanol, butanol, sec-butanol, and tert-butanol; ketons such as acetone and methyl ethyl ketone; and aromatic solvents such as toluene and xylene. Further, it is also possible to use a mixture solvent of water with these organic solvents, as desired. It is further possible to use the nano-oxide particles in other dispersion states in which they are dispersed in a monomer solution, an oligomer solution, or a mixture solution of the monomer solution and the oligomer solution.

A specific production process of the nano-oxide particles which have been surface-protected or coated according to the present invention will be described.

The nano-oxide particles of the present invention can be obtained by binding the polymer having the binding functional group and a polyvinyl main chain to the surfaces of the oxide particles to form a polyvinyl monomolecular film at each oxide particle surface. The polyvinyl monomolecular film can also be formed by in-situ vinyl polymerization of the vinyl monomer in a dispersion state at the oxide particle surfaces. In this case, formation of the bond between the binding functional group and the oxide particle surface and the polymerization of the vinyl monomer proceed at the same time to form the polyvinyl monomolecular film at the oxide particle surface.

More specifically, in a dispersion solution containing the oxide particles and the vinyl monomer having the binding functional group, the polymerization is performed in a state in which an amount of the dispersion medium in the entire dispersion solution is 70 wt. % or more. When the amount of the dispersion medium in the entire dispersion solution is 70 wt. % or more, by the interaction of the binding functional group-containing vinyl monomer with the oxide particle surface, the probability of polymerization at the oxide particle surface is larger than the probability of polymerization between vinyl monomer components in the dispersion medium to permit dominant formation of the polyvinyl monomolecular film at the oxide particle surface. Further, the polymerization between the vinyl monomer components having the binding functional group proceeds at a moderate speed and with a degree of the polymerization, a degree of contribution to stabilization of entropy at the oxide particle surface inreases, so that a tendency of binding to the oxide particle is more enhanced. Accordingly, the polymerization product in the dispersion medium can also contribute to formation of the monomolecular film at the oxide particle surface. As a polymerization condition, the amount of the dispersion medium in the dispersion solution may more preferably be 80 wt. % or more.

Further, the polyvinyl monomolecular film may also be formed at the oxide particle surface by using a dispersion solution containing another vinyl monomer or a polymerizable oligomer as desired. Further, if necessary, it is also possible to employ a process of adsorbing and attaching the binding functional group-containing vinyl monomer to the oxide particle surface in advance of the polymerization. This process may, e.g., be an oxidative decomposition process of a colloidal surface stabilizing component other than the binding functional group-containing vinyl monomer or a dissociation process using a method such as dialysis or substitution of the solvent with a solvent different in affinity.

The dispersion medium used in the present invention is not particularly limited so long as it can disperse the nano-oxide particles having the dispersibility in the above described polymerizable monomer but may preferably be a hydrophilic organic dispersion medium such as alcohols or ketones or a mixture solvent of the hydrophilic organic dispersion medium with water from the viewpoint of stability of the nano-oxide particles. Examples of alcohols may include methanol, ethanol, propanol, butanol, etc. In the case where the oxide particle surface is coated with the binding functional group-containing monomer, as the dispersion medium, it is also possible to use a hydrophobic dispersion medium such as toluene or xylene. In the case of using an aqueous dispersion solution of the nano-oxide particles, an aqueous dispersion medium may preferably be partly replaced with the hydrophilic organic dispersion medium in order to ensure the stability of the dispersion solution. The replacement with the hydrophilic dispersion medium may be performed before or during the vinyl polymerization.

The vinyl polymerization is performed by using a polymerization initiator. Examples of the polymerization initiator may include azo-type initiators such as 2,2-azobisisobutyronitrile, 2,2-azobis(2,4-dimethylvaleronitrile), dimethyl 2,2-azobis(2-methylpropionate), and dimethyl 2,2-azobisisobutylate; and peroxide-type initiators such as lauryl peroxide, benzoyl peroxide, and tert-butyl peroctoate. In the aqueous dispersion medium, it is possible to use an aqueous initiator such as potassium persulfate.

Further, it is also possible to initiate radical copolymerization only by light irradiation. As a photodegradable radical initiator, it is possible to use, e.g., aminoacetophenones such as α-aminoacetophenone and 2-benzyl-2-dimethylamino-1-(4-morphorinophenyl)-butane-1; benzyldimethylketals; and glyoxylates.

As the oxide particles used in the present invention, from the veiwpoints of uniformity in particle size and stability of the dispersion solution, oxide particles synthesized through hydrothermal method may preferably be used. More specifically, a hydroxide is formed by a known method such as ion exchanging method, deflocculating method or hydrolysis method, and then is heated to form a stable oxide colloid sol, which is used as the oxide particles.

Examples of the ion exchanging method may include a method in which acidic salt of metal is treated with hydrogen-type cation exchange resin and a method in which basic salt of metal is treated with hydrogen-type anion exchange resin.

Examples of the deflocculating method may include a method in which a gel obtained by neutralizing the acidic salt of metal with base or the basic salt of metal with acid is washed and then is deflocculated with an acid or a base.

Examples of the hydrolysis method may include a method in which alkoxide of metal is hydrolyzed and a method in which unnecessary acid is removed after the basic salt of metal is hydrolyzed under heating.

The oxide particles may preferably be surface-modified with acid, base, an organic compound, a surfactant, or the like during or after the hydrothermal synthesis. The oxide particles may also be surface-modified with the binding functional group-containing monomer or oligomer.

The nano-oxide particles of the present invention are finally covered with the polyvinyl monomolecular film having the binding functional group, so that dispersion stability thereof does not basically vary depending on the above described pre-treatment for the oxide particles. When the oxide particle is once protected by the polyvinyl monomolecular film having the binding functional group, it is easy to achieve solvent replacement by another desired organic dispersion medium.

An amount of the monomer required for forming a stable organic surface layer changes depending on the particle size of the oxide particles, so that a weight ratio of (vinyl monomer)/(oxide particles) may appropriately be adjusted depending on the kind of the monomer and the particle size. It is ordinarily preferable that the weight ratio of (vinyl monomer)/(oxide particles) is set in a range of 1/10 to 10/1.

The nano-oxide particles of the present invention can be introduced into a desired organic optical matrix. The organic optical matrix is not particularly limited so long as it is transparent but may be a thermoplastic resin material or a thermosetting resin material. Examples of the thermoplastic resin material may suitably include styrene-based resin, acrylic resin, aromatic polycarbonate resin, and amorphous polyolefin resin. Examples of the thermosetting resin material may include polyurethane, polythiourethane, and polysiloxane.

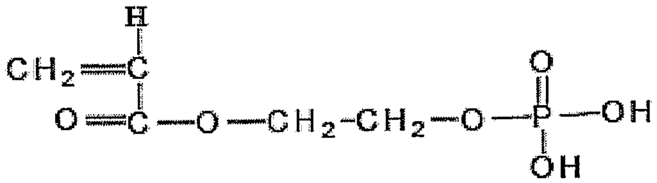
As a method of introducing the nano-oxide particles into the resin material, formation of a composite material between the nano-oxide particles and the resin material is performed through an appropriate liquid state depending on a characteristic of the resin material. For example, with respect to a resin material soluble in the organic solvent, the resin material is dissolved in the organic solvent in advance and mixed with a dispersion solution of the nano-oxide particles to prepare a uniform dispersion solution. Thereafter, the organic solvent is removed from the dispersion solution to obtain a resin material in which the nano-oxide particles are dispersed. Further, it is also possible to employ a method in which a resin material is dissolved in the dispersion solution of the nano-oxide particles containing a solvent in which the resin material is soluble and thereafter the solvent is removed. Further, it is also possible to obtain a resin material, in which the nano-oxide particles are dispersed, by introducing the nano-oxide particles into a monomer for forming the resin material and then polymerizing the monomer. As necessary, it is also possible to carry out the polymerization by using the resin material-forming monomer、an oligomer having a polymerizable functional group、or two or more species of polymerizable oligomers as starting materials for the resin material. In the case of forming a composite material of the nano-oxide particles with the thermoplastic resin material, the nano-oxide particles have high dispersibility and interaction of the nano-oxide particles with the resin matrix is minimized, so that it is possible to apply a conventional molding method utilizing thermoplasticity. In this case, the resultant composite material shows high transparency since the surface organic layer is not detached from the oxide particle keeping the dispersibility of the particles at a high level. As the thermoplastic resin material, acrylic resin and aromatic polycarbonate resin are particularly preferred.

The above described transparent optical resin material in which the nano-oxide particles are dispersed is applicable to an optical material such as a lens. Figure 2 shows a lens prepared by molding the transparent optical resin material in which the nano-oxide particles of the present invention are dispersed. By dispersing the nano-oxide particles of the present invention, it is possible to obtain a lens having transparency and high refractive index.

Hereinbelow, the present invention will be described more specifically based on Examples. In the following Examples, "%" represents "wt. % (% by weight)".

(Example 1)

A mixture solution was prepared by mixing 40 g of aqueous TiO_2 dispersed sol (solid content: 6 %, average particle size: 5 nm) and 60 g of 1 %-aqueous solution of phosphate represented by the following formula (10):



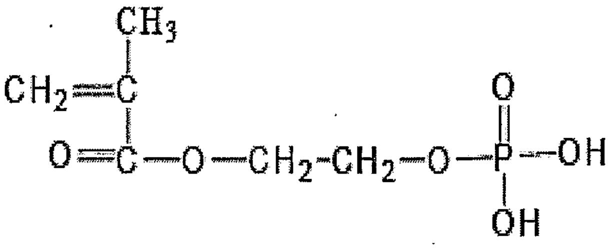
$$CH_2{=}CH{-}C({=}O){-}O{-}CH_2{-}CH_2{-}O{-}P({=}O)(OH){-}OH \qquad (10)$$

The mixture solution was placed in a flask and solvent substitution with propanol was performed under heating. At a time when a total amount of the dispersion solution was 110 g and a concentration of propanol in the solvent reached about 50 % (about 97 % of the dispersion medium), 0.01 g of potassium persulfate ($K_2S_2O_8$) was added as a polymerization initiator. After the resultant mixture was polymerized for 10 hours at 50 °C, the polymerization mixture was cooled and added in a hollow membrane, which was externally washed sufficiently with a 50 %-aqueous propanol solution to remove unnecessary components. While heating the hollow membrane, the solvent was substituted with methyl ethyl ketone (MEK). Finally, concentration was performed to obtain about 50 g of nano-titanium oxide fine particles (solid content: about 6.5 %) which were surface-protected with a monomolecular film.

Into 10 g of a 2 %-polymethyl methacrylate (PMMA) solution in MEK, 10 g of the above obtained sol of nano-titanium oxide fine particles was added and stirred for 2 hours. Thereafter, the mixture was placed in a glass mold which had been subjected to water-repellent treatment and dried for 48 hours at 80 °C to obtain a transparent composite film containing the nano-titanium oxide fine particles. When refractive index of the thus obtained composite film was measured by Abbe refractometer, the refractive index was 1.77.

(Example 2)

A mixture solution was prepared by mixing 20 g of aqueous SnO_2 dispersed sol (solid content: 10 %, average particle size: 2 nm), 25 g of 4 %-aqueous solution of phosphate represented by formula (11) shown below, and 25 g of 1 %-methacrylic acid solution:



$$CH_2{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}CH_2{-}O{-}P({=}O)(OH){-}OH$$

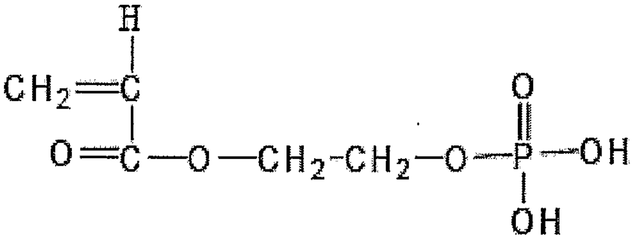
(11)

The mixture solution was placed in a flask and solvent substitution with propanol was performed under heating. At a time when a total amount of the dispersion solution was 95 g and a concentration of propanol in the solvent reached about 50 % (about 96 % of the dispersion medium), 0.01 g of potassium persulfate ($K_2S_2O_8$) was added as a polymerization initiator. After the resultant mixture was polymerized for 10 hours at 50 °C, the polymerization mixture was cooled and added in a hollow membrane, which was externally washed sufficiently with a 50 %-aqueous propanol solution to remove unnecessary components. While heating the hollow membrane, the solvent was substituted with MEK. Finally, concentration was performed to obtain about 60 g of nano-tin oxide fine particles (solid content: about 4.5 %) which were surface-protected with a monomolecular film.

Into 30 g of a 2 %-PMMA solution in MEK, 20 g of the above obtained sol of nano-tin oxide fine particles was added and stirred for 2 hours. Thereafter, the mixture was placed in a glass mold which had been subjected to water-repellent treatment and dried for 48 hours at 80 °C to obtain a composite film containing the nano-tin oxide fine particles. The thus obtained composite film was transparent. When a refractive index of the composite film was measured by Abbe refractometer, the refractive index was 1.57.

(Example 3)

A mixture solution was prepared by mixing 20 g of aqueous ZrO_2 dispersed sol (solid content: 10 %, average particle size: 5 nm) and 50 g of 1 %-aqueous solution of phosphate represented by the following formula (12):



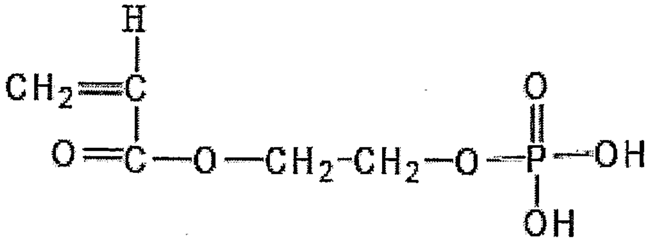
$$CH_2{=}CH-C({=}O)-O-CH_2-CH_2-O-P({=}O)(OH)-OH \qquad (12)$$

The mixture solution was placed in a flask and solvent substitution with propanol was performed under heating. At a time when a total amount of the dispersion solution was 80 g and a concentration of propanol in the solvent reached about 50 % (about 96 % of the dispersion medium), 0.3 g of methyl methacrylate (monomer) was added and stirred for 5 hours. Thereafter, to the mixture, 0.01 g of potassium persulfate ($K_2S_2O_8$) was added as a polymerization initiator. After the resultant mixture was polymerized for 10 hours at 50 °C, the polymerization mixture was cooled and added in a hollow membrane, which was externally washed sufficiently with a 50 %-aqueous propanol solution to remove unnecessary components. While heating the hollow membrane, the solvent was substituted with MEK. Finally, concentration was performed to obtain about 50 g of nano-zirconium oxide fine particles (solid content: about 5.5 %) which were surface-protected with a monomolecular film.

Into 10 g of a 2 %-PMMA solution in MEK, 10 g of the above obtained sol of nano-zirconium oxide fine particles was added and stirred for 2 hours. Thereafter, the mixture was placed in a glass mold which had been subjected to water-repellent treatment and dried for 48 hours at 80 °C to obtain a transparent composite film containing the nano-zirconium oxide fine particles. When a refractive index of the thus obtained composite film was measured by Abbe refractometer, the refractive index was 1.65.

(Example 4)

A mixture solution was prepared by mixing 20 g of aqueous AlOOH dispersed sol (solid content: 20 %, average particle size: 5 nm) and 10 g of 1 %-aqueous solution of phosphate represented by the following formula (13):



(13)

$$\mathrm{CH_2{=}CH{-}C({=}O){-}O{-}CH_2{-}CH_2{-}O{-}P({=}O)(OH){-}OH} \qquad (13)$$

The mixture solution was placed in a flask and solvent substitution with propanol was performed under heating. At a time when a total amount of the dispersion solution was about 125 g and a concentration of propanol in the solvent reached about 50 % (about 96 % of the dispersion medium), 0.5 g of methyl methacrylate (monomer) was added and stirred for 5 hours. Thereafter, to the mixture, 0.01 g of potassium persulfate ($K_2S_2O_8$) was added as a polymerization initiator. After the resultant mixture was polymerized for 10 hours at 50 °C, the polymerization mixture was cooled and added in a hollow membrane, which was externally washed sufficiently with a 50 %-aqueous propanol solution to remove unnecessary components. While heating the hollow membrane, the solvent was substituted with MEK. Finally, concentration was performed to obtain about 100 g of nano-aluminum oxide fine particles (solid content: about 5.5 %) which were surface-protected with a monomolecular film.

Into 10 g of a 2 %-PMMA solution in MEK, 10 g of the above obtained sol of nano-aluminum oxide fine particles was added and stirred for 2 hours. Thereafter, the mixture was placed in a glass mold which had been subjected to water-repellent treatment and dried for 48 hours at 80 °C to obtain a transparent composite film containing the nano-zirconium oxide fine particles. When a refractive index of the thus obtained composite film was measured by Abbe refractometer, the refractive index was 1.52. Further, when the composite film was observed through a transmission electron microscope (TEM), it was confirmed that the particles were uniformly dispersed.

(Comparative Example)

Solvent substitution with propanol was performed while heating 20 g of aqueous TiO_2 dispersed sol (solid content: 6 %, average particle size: 5 nm). The solvent substitution was continued until a concentration of propanol in the solvent reached about 50 %.

Into 10 g of 2 %-PMMA solution in MEK, when 10 g of the above obtained sol of nano-titanium oxide fine particles was added, the dispersion solution became white and turbid. After the dispersion solution was stirred for 2 hours, the dispersion solution was placed in a glass mold which had been subjected to water-repellent treatment and dried for 48 hours at 80 °C. As a result, an opaque composite film was obtained.

[INDUSTRIAL APPLICABILITY]

The nano-oxide particles of the present invention coated with the polyvinyl monomolecular film having the binding functional group, exhibit high dispersibility and can be dispersed at a high concentration in an optical resin material, a polymerizable monomer for an optical material, or a curable oligomer for the optical material. As a result, it is possible to realize an optical material or an optical lens which have a high refractive index and excellent transparency. It is also possible to realize a high-strength composite material containing nano-oxide particles dispersed therein.

While the invention has been described with reference to the structures disclosed herein, it is not confined to the details set forth and this application is intended to cover such modifications or changes as may come within the purpose of the improvements or the scope of the following claims.

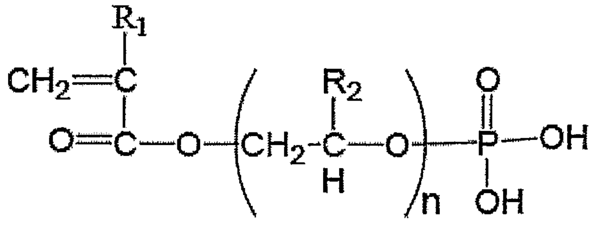
CLAIMS

1. Nano-oxide particles comprising particles each surface of which is coated with a polyvinyl monomolecular film having a binding functional group.

2. Particles according to Claim 1, wherein the polyvinyl monomolecular film having the binding functional group is polyacrylic polyvinyl monomolecular film having a binding functional group.

3. Particles according to Claim 1 or 2, where the binding functional group is selected from the group consisting of thiol group, carboxyl group, sulfonic group, and phosphoric group.

4. Particles according to any one of Claims 1 - 3, wherein the polyvinyl monomolecular film having the binding functional group is formed by polymerizing an acrylic monomer having a binding functional group represented by the following formula (1):



$$CH_2=C(R_1)-C(=O)-O-\left(CH_2-CH(R_2)-O\right)_n-P(=O)(OH)-OH \qquad (1)$$

wherein R_1 is hydrogen atom or methyl group; R_2 is alkyl group, halogen atom, or hydrogen atom; and n is an integer of 1 or more.

5. Particles according to any one of Claims 1 - 4, wherein the nano-oxide particles have a particle size of 1 nm or more and 30 nm or less.

6. Particles according to any one of Claims 1 - 5, wherein the nano-oxide particles are particles of an oxide selected from the group consisting of aluminum oxide, titanium oxide, niobium oxide, tin oxide, indium oxide, zirconium oxide, lanthanum oxide, cadmium oxide, hafnium oxide, erbium oxide, neodymium oxide, cerium oxide, dysprosium oxide, and a mixed oxide of these oxides.

7. A production process of surface-protected nano-oxide particles, comprising:

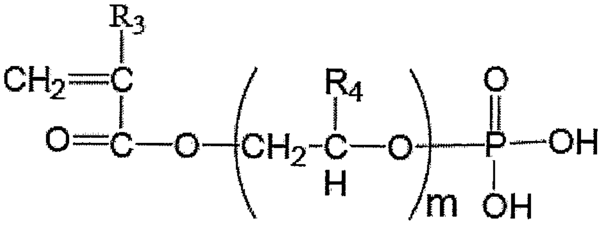
polymerizing a vinyl monomer having a binding functional group in a solution containing nano-oxide particles, the vinyl monomer having the binding functional group, and a dispersion medium,

wherein the dispersion medium is contained in the solution in an amount of 70 wt. % or more.

8. A process according to Claim 7, wherein the vinyl monomer having the binding functional group is acrylic monomer having a binding functional group.

9. A process according to Claim 7 or 8, where the binding functional group is selected from the group consisting of thiol group, carboxyl group, sulfonic group, and phosphoric group.

10. A process according to any one of Claims 7 - 9, wherein the vinyl monomer having the binding functional group is an acrylic monomer having a binding functional group represented by the following formula (2):



$$CH_2{=}C(R_3)-C({=}O)-O-\left(CH_2-CH(R_4)-O\right)_m-P({=}O)(OH)-OH \qquad (2)$$

wherein R_3 is hydrogen atom or methyl group; R_4 is alkyl group, halogen atom, or hydrogen atom; and m is an integer of 1 or more.

11. A process according to any one of Claims 7 - 10, wherein the nano-oxide particles are obtained by hydrothermal synthesis.

12. A process according to any one of Claims 7 - 11, wherein the nano-oxide particles have a particle size of 1 nm or more and 30 nm or less.

13. A process according to any one of Claims

7 - 12, wherein the nano-oxide particles are particles of an oxide selected from the group consisting of aluminum oxide, titanium oxide, niobium oxide, tin oxide, indium oxide, zirconium oxide, lanthanum oxide, cadmium oxide, hafnium oxide, erbium oxide, neodymium oxide, cerium oxide, dysprosium oxide, and a mixed oxide of these oxides.

14. A transparent optical resin material comprising:

a resin material; and

nano-oxide particles according to any one of Claims 1 - 7 dispersed in the resin material.

15. A lens comprising:

a transparent optical resin material, according to Claim 14, which has been molded.

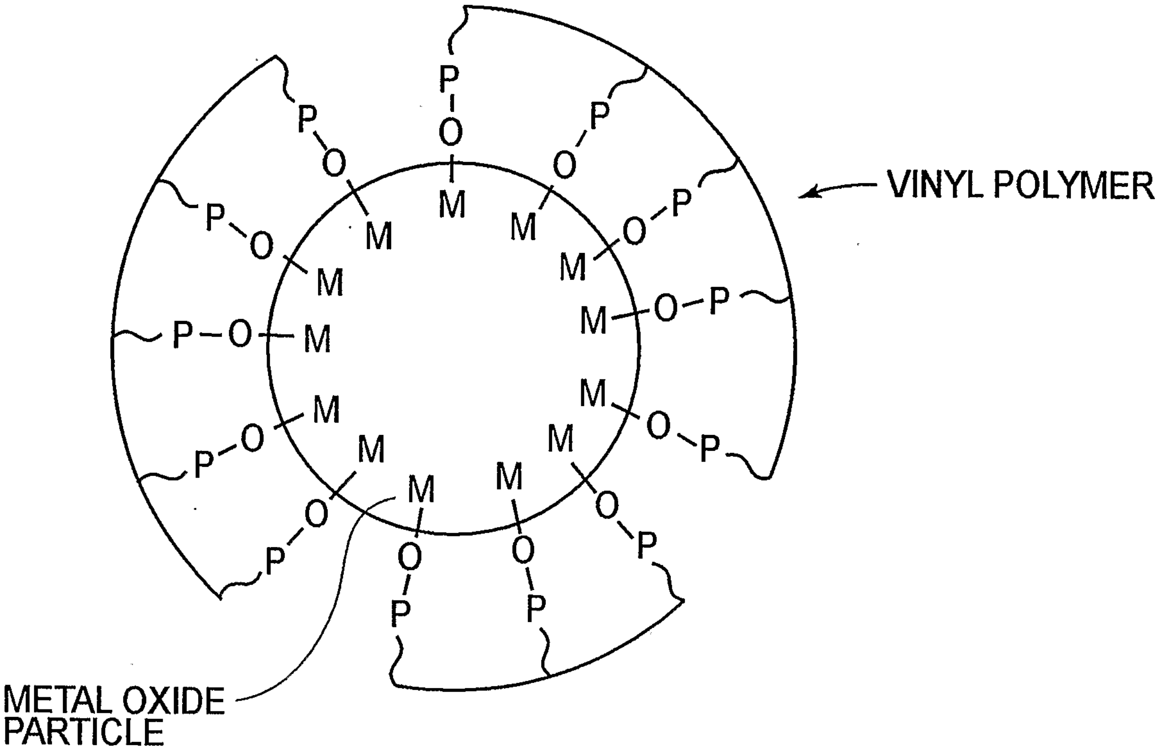

VINYL POLYMER
METAL OXIDE PARTICLE
P
O
M

FIG.1

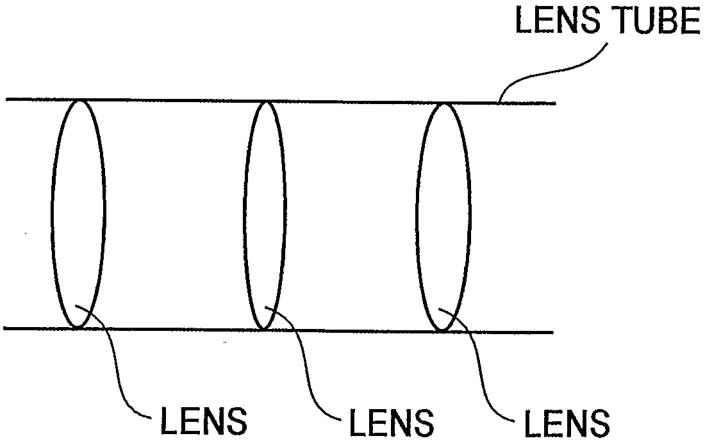

LENS TUBE
LENS
LENS
LENS

FIG.2

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2007/067350

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F292/00 C08K9/04 C08L51/10 C09D151/10 C08F290/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F C08L C09D B01J C09C C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 994 429 A (WIESERMAN LARRY F [US] ET AL) 19 February 1991 (1991-02-19) claims 1,12,13 column 6, lines 11-15 column 7, lines 1-4 column 6, line 46 column 6, lines 35-46 column 7, line 15 - column 11, line 53 claims 9,10 claims 4-8 column 2, lines 28-34 column 3, lines 31-33; claims 1-20 column 4, lines 1-38 -----	1-15
X	JP 56 147837 A (ASAHI CHEMICAL IND) 17 November 1981 (1981-11-17) * EPODOC & WPI abstracts * abstract -----	1-3,5-9, 12-14
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 8 November 2007	Date of mailing of the international search report 23/11/2007
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Hammond, Andrew

International application No
PCT/JP2007/067350

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/100630 A1 (YAMAGUCHI ET AL) 29 March 2003 (2003-03-29) claim 1 paragraph [0032] paragraph [0023] paragraph [0025] paragraph [0002]	1,3,5-7, 9,11-15
X	US 4 617 327 A (PODSZUN WOLFGANG [DE]) 14 October 1986 (1986-10-14) claims 1,4 column 2, lines 19-35 column 3, lines 10-58; claims 5,12	1,5-7, 11-13
A	EP 0 495 732 A (COATEX SA [FR]) 22 July 1992 (1992-07-22) abstract; claims 1-8 page 2, line 40 - page 12, line 45	1-15
A	JP 01 306477 A (SHINETSU CHEMICAL CO) 11 December 1989 (1989-12-11) cited in the application abstract	1-15
A	GB 1 156 653 A (ICI LTD [GB]) 2 July 1969 (1969-07-02) column 3, lines 83-91	1-15

4

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/JP2007/067350

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4994429 A	19-02-1991	NONE	
JP 56147837 A	17-11-1981	JP 1495365 C	16-05-1989
		JP 63045419 B	09-09-1988
US 2003100630 A1	29-05-2003	AT 286095 T	15-01-2005
		AU 3422601 A	31-07-2001
		CN 1416454 A	07-05-2003
		DE 60108073 D1	03-02-2005
		DE 60108073 T2	22-12-2005
		EP 1252239 A1	30-10-2002
		JP 2001200023 A	24-07-2001
		WO 0153420 A1	26-07-2001
		TW 262202 B	21-09-2006
US 4617327 A	14-10-1986	CA 1238996 A1	05-07-1988
		DE 3341888 A1	30-05-1985
		EP 0142784 A1	29-05-1985
		JP 1786978 C	10-09-1993
		JP 4077022 B	07-12-1992
		JP 60120703 A	28-06-1985
		JP 5105707 A	27-04-1993
EP 0495732 A	22-07-1992	DE 69206000 D1	21-12-1995
		DE 69206000 T2	04-07-1996
		FR 2671555 A1	17-07-1992
		JP 5025320 A	02-02-1993
		US 5412139 A	02-05-1995
JP 1306477 A	11-12-1989	JP 1979591 C	17-10-1995
		JP 6096691 B	30-11-1994
GB 1156653 A	02-07-1969	AT 286238 B	25-11-1970
		BE 682421 A	12-12-1966
		CH 471841 A	30-04-1969
		DE 1620887 A1	23-04-1970
		DK 128651 B	10-06-1974
		FI 45563 B	04-04-1972
		LU 51293 A	12-08-1966
		NL 6608072 A	12-12-1966
		SE 337683 B	16-08-1971