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(54) **Method for producing composition for vapor deposition, composition for vapor deposition, and method for producing optical element with antireflection film**

Verfahren zur Herstellung einer Verbindung zur Vakuum-Beschichtung, Verbindung zur
Vakuumbeschichtung und Herstellungsverfahren für ein optisches Element mit Antireflexschicht

Méthode de fabrication d'une composition pour dépôt sous vide, composition pour dépôt sous vide et
méthode de fabrication d'un élément optique avec revêtement anti-réfléchissant

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EP-A- 1 184 686 EP-A- 1 205 774
US-A- 4 940 636 US-A- 5 858 519

• **PATENT ABSTRACTS OF JAPAN vol. 2000, no.**
07, 29 September 2000 (2000-09-29) -& JP 2000
119062 A (JAPAN ENERGY CORP), 25 April 2000
(2000-04-25)

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).

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| <ul style="list-style-type: none">• NASU H ; SATO M ; MATSUOKA J ; KAMIYA K :
"Sol-gel preparation and third-order optical nonlinearity of amorphous Bi₂O₃-TiO₂ and Nb₂O₅-TiO₂ films " J. CERAM. SOC. JPN. (JAPAN) , vol. 104, no. 8, August 1996 (1996-08), pages 768-771, XP008023029 | <ul style="list-style-type: none">• C.K. NARULA: "Ceramic Precursor Technology and Its Applications" , MARCEL DEKKER INC. , 1995 XP002257211 * page 307, right-hand column - page 309, right-hand column * |
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Description

Description of the Invention

5 Technical Field of the Invention

[0001] The present invention relates to a composition for vapor deposition, and to a method for producing an optical element with an antireflection film and to an optical element. In particular, the invention relates to a method for producing a composition for vapor deposition and to a composition for vapor deposition capable of forming a high-refraction layer even in low-temperature vapor deposition, and therefore ensuring an antireflection film having good scratch resistance, good chemical resistance and good heat resistance, of which the heat resistance lowers little with time; and also relates to a method for producing an optical element having such an antireflection film, and to the resulting optical element.

15 Prior Art

[0002] For improving the surface reflection characteristics of an optical element that comprises a synthetic resin, it is well known to form an antireflection film on the surface of the synthetic resin. To enhance the antireflectivity of the film a laminate of alternate low-refraction and high-refraction is generally used. In particular, for compensating for the drawback of synthetic resins that are easy to scratch, silicon dioxide is often used for the vapor source to form low-refraction layers on the substrates, as the film formed is hard. On the other hand, zirconium dioxide, tantalum pentoxide and titanium dioxide are used for the vapor sources to form high-refraction layers on the substrates. Especially for forming an antireflection film of lower reflectivity, selected are substances of higher refractivity for the high-refraction layers of the antireflection film. For this, titanium dioxide is generally used.

Nasu H et al, J. Ceram. Soc. Jpn. (Japan), vol. 104, pp. 777 - 780 (1996) discloses sol-gel preparation of amorphous Nb_2O_5 - TiO_2 films which contain titanium dioxide and niobium pentoxide with the ratios of mol% of TiO_2 to that of Nb_2O_5 being 90:10, 80:20, 70:30, 60:40, and 50:50. After drying, the films were heat-treated at 300° and 500°, respectively. 90:10 mol% TiO_2 - Nb_2O_5 composition which is equivalent to the TiO_2 : Nb_2O_5 weight ratio of approximately 2.7:1, has also been disclosed by US 4 940 636 A (column 6, lines 25-33).

One of the manufacturing methods of TiO_2 : Nb_2O_5 layers involved evaporating simultaneously titanium and niobium as metals in two crucibles with the aid of electron beams and co-deposited onto a heated substrate in a reactive oxygen atmosphere. Such layers were then used as high-refractive index layers in an optical interference filter alternated with amorphous SiO_2 layers.

JP 2000119062 discloses a sputtering target composed of 0.01-10 wt.% of glass-forming oxides consisting of Nb_2O_5 , V_2O_5 , B_2O_3 , SiO_2 and P_2O_5 , 0.01-20 wt.% of Al_2O_3 + Ga_2O_3 , and, as necessary, 0.01-5 wt.% of ZrO_2 and/or TiO_2 , for producing an optical disk-protective film of low reflectivity with high light transmittance through diminishing particle generation during sputtering operation, thereby reducing the frequency of suspending or stopping the sputtering operation to effect raising film production efficiency.

However, the vapor source prepared by sintering titanium dioxide powder, when heated with electron beams for vaporizing it to be deposited on substrates, is decomposed into $\text{TiO}_{(2-x)}$ and generates oxygen gas. The thus-formed oxygen gas exists in the atmosphere around the vapor source, and oxidizes the vapor of $\text{TiO}_{(2-x)}$ from the source before the vapor reaches the substrates. Therefore, a film of little light absorption is formed on substrates from the vapor source. On the other hand, however, the oxygen gas interferes with the vapor component that runs toward the substrates, and therefore retards the film formation on the substrates. In addition, when the vapor source, prepared by sintering titanium dioxide powder, is heated with electron beams, it melts, and is therefore generally used as a liner. At this stage, the electroconductivity of the $\text{TiO}_{(2-x)}$ vapor increases, and the electrons of the electron beams applied to the vapor source therefore escape to the liner. This causes electron beam loss, and the vapor deposition system therefore requires a higher power which is enough to compensate for the loss. On the other hand, when pellets only made of titanium dioxide are used for vapor deposition, the speed of film formation is low. When electron beams are applied, it was problematic in that the pellets are readily cracked.

The problem with optical elements comprising a synthetic resin is that the heating temperature in vapor deposition for the structures cannot be increased. Because of this limitation, therefore, the density of the film formed from titanium dioxide in such optical elements cannot be made satisfactory, and the film refractivity is not satisfactorily high. In addition, the scratch resistance and the chemical resistance of the film are also not satisfactory. To compensate for the drawbacks, ion-assisted vapor deposition is generally employed, but the ion gun unit for it is expensive, therefore increasing the production costs.

Optical elements comprising a synthetic resin, especially lenses for spectacles, are generally planned so that an organic hard coat film is formed on a plastic lens substrate for improving the scratch resistance of the coated lenses, and an inorganic antireflection film is formed on the hard coat film. For spectacle lenses, new optical elements having an

antireflection film of superior antireflectivity are now desired, in which the antireflection film is desired to have superior abrasion strength and good heat resistance, and its heat resistance is desired not to lower with time.

Object of the Invention

[0003] We, the present inventors, have made the invention in order to solve the problems as outlined above. The first object of the invention is to provide a composition which is suitable for vapor deposition; of which the advantages are such that the composition can form a high-refraction layer even on synthetic resin substrates that must be processed for vapor deposition thereon at low temperatures, within a short period of time and without using an ion gun unit or a plasma unit; not detracting from the good physical properties intrinsic to the high-refraction layer formed, that the high-refraction layer formed has high refractivity; that the antireflection film comprising the high-refraction layer formed on such synthetic resin substrates has good scratch resistance, good chemical resistance and good heat resistance, and that the heat resistance of the antireflection film lowers little with time.

The second object of the invention is to provide an optical element comprising a synthetic resin substrate with an antireflection film formed thereon, in which the antireflection film has good scratch resistance, good chemical resistance and good heat resistance, and the heat resistance of the antireflection film lowers little with time, and also to provide a method for the manufacture thereof.

Summary of the Invention

[0004] We, the present inventors, assiduously studied to develop plastic lenses for spectacles having the above-mentioned desired properties, and as a result, have found that, when an antireflection film is formed through vapor deposition on a plastic lens substrate from a vapor source prepared by sintering a mixture of titanium dioxide niobium pentoxide and zirconium dioxide and/or yttrium pentoxide as mandatory constituents then we can attain the above-mentioned objects, leading to the invention.

Specifically, the invention provides a composition obtainable by sintering a powder mixture essentially consisting of

(i) 70-100 wt.-% of a mixture of

(a) 100 parts by weight of TiO_2 and Nb_2O_5 in a weight ratio of $\text{TiO}_2:\text{Nb}_2\text{O}_5$ of 30:70 to 75:25,

(b) 3-46 parts by weight of ZrO_2 and/or Y_2O_3 and

(ii) up to 30 wt.-% of other metal oxides.

titanium dioxide and niobium pentoxide; and provides a composition that contains titanium dioxide and niobium pentoxide. The invention also provides a method for producing an optical element with an antireflection film, which comprises vaporizing the composition and depositing the generated vapor on a substrate to form thereon a high-refraction layer of an antireflection film.

Detailed Description of the Invention

[0005] The invention is described in detail hereunder.

[0006] The method for producing the present composition for vapor deposition comprises sintering a powder mixture essentially consisting of

(i) 70-100 wt.-% of a mixture of

(a) 100 parts by weight of TiO_2 and Nb_2O_5 in a weight ratio of $\text{TiO}_2:\text{Nb}_2\text{O}_5$ of 30:70 to 75:25,

(b) 3-46 parts by weight of ZrO_2 and/or Y_2O_3 and

(ii) up to 30 wt.-% of other metal oxides.

The method for producing an optical element of the invention comprises vaporizing the composition and depositing the generated vapor on a substrate to form thereon a high-refraction layer of an antireflection film.

[0007] The method for preparing the present composition comprises the sintering of a mixture containing, among others, titanium dioxide powder and niobium pentoxide powder. The composition containing titanium dioxide and niobium

pentoxide can be prepared by mixing titanium dioxide powder and niobium pentoxide powder. In this method, niobium pentoxide melts first as its melting point is low, and thereafter titanium dioxide melts. In the melting and vaporizing process, since the vapor pressure of the molten titanium dioxide is higher than that of the molten niobium pentoxide, the amount of titanium dioxide vapor that reaches the substrate is generally higher than that of the niobium pentoxide vapor. In addition, since the oxygen gas partial pressure resulting from the titanium dioxide decomposition is low, rapid film formation on the substrate is possible even if the power of electron beams applied to the vapor source is low. The compositional ratio of titanium dioxide to niobium pentoxide is such that the amount of titanium dioxide (calculated in terms of TiO_2) therein is from 30 to 75 % by weight, preferably from 30 to 50 % by weight, and that of niobium pentoxide (calculated in terms of Nb_2O_5) is from 25 to 70 % by weight, preferably from 50 to 70 % by weight.

If the composition ratio of niobium pentoxide is larger than 70 % by weight, the amount of niobium pentoxide that reaches the substrate in lack of oxygen increases, and, in addition, the oxygen gas resulting from titanium dioxide decomposition decreases. Below this value, it may be possible to achieve a particularly low light absorption of the antireflection film.

[0008] To prepare the composition for vapor deposition of the invention, the vapor source mixture may be pressed by any suitable conventional method. For example, a pressure of at least 200 kg/cm² may be used, and the pressing speed can be controlled such that the pressed blocks contain no air gaps therein. The temperature at which the pressed blocks are sintered varies, depending on the compositional ratio of the oxide components of the vapor source composition, but may be in the range of from 1000 to 1400°C. The sintering time may be determined, depending the sintering temperature, etc., and may be generally in the range of from 1 to 48 hours.

[0009] When heated with electron beams, the composition for vapor deposition that comprises titanium dioxide and niobium pentoxide melts and often forms bumps and/or splashes. The splashes of the composition, if formed in the process of forming an antireflection film from the composition, reach the substrates that are being processed into coated products, thereby to cause pin holes, film peeling and deficiency by foreign matters. In addition, the splashes lower the properties including the chemical resistance and the heat resistance of the antireflection film formed. To prevent the composition from forming bumps and splashes, zirconium oxide and/or yttrium oxide are added to a mixture of titanium dioxide powder and niobium pentoxide powder, and to sinter the resulting mixture into the composition for vapor deposition of the invention. The total amount of zirconium oxide (calculated in terms of ZrO_2) and/or yttrium oxide (calculated in terms of Y_2O_3) to be added is from 3 to 46 parts by weight, preferably from 10 to 20 parts by weight, relative to 100 parts by weight of the total amount of titanium dioxide and niobium pentoxide.

[0010] Regarding its layer constitution, the antireflection film includes a two-layered film of $\lambda/4 - \lambda/4$ (in this patent application, unless otherwise specified, λ is generally in the range of 450 to 550 nm. A typical value is 500 nm), and a three-layered film of $\lambda/4 - \lambda/4 - \lambda/4$ or $\lambda/4 - \lambda/2 - \lambda/4$. Not being limited thereto, the antireflection film may be any other four-layered or multi-layered film. The first low-refraction layer nearest to the substrate may be any of known two-layered equivalent films, three-layered equivalent films or other composite films.

[0011] The substrate of the optical element of the invention is preferably formed of a synthetic resin. For this, for example, methyl methacrylate homopolymers are usable, as well as copolymers of methyl methacrylate and one or more other monomers, diethylene glycol bisallyl carbonate homopolymers, copolymers of diethylene glycol bisallyl carbonate and one or more other monomers, sulfur-containing copolymers, halogen-containing copolymers, polycarbonates, polystyrenes, polyvinyl chlorides, unsaturated polyesters, polyethylene terephthalates, polyurethanes, etc.

[0012] For forming an antireflection film on such a synthetic resin substrate, it is desirable that a hard coat layer containing an organosilicon polymer is first formed on the surface of the synthetic resin substrate in a method of dipping, spin coating or the like, and thereafter the antireflection film is formed on the hard coat layer. Hard coat layers and their preparation are disclosed in EP 1 041 404. For improving the adhesiveness between the synthetic resin substrate and the antireflection film, the scratch resistance, etc., it is desirable to dispose a primer layer between the synthetic resin substrate and the antireflection film or between the hard coat layer formed on the surface of the synthetic resin substrate and the antireflection film. The primer layer may be, for example, a vapor deposition film of silicon oxide or the like. Suitable primer layers are disclosed in EP 0 964 019.

[0013] The antireflection film may be formed, for example, in the manner mentioned below.

Preferably, silicon dioxide is used for the low-refraction layers of the antireflection film for improving the scratch resistance and the heat resistance; and the high-refraction layers can be formed by heating pellets that are prepared by mixing titanium dioxide (TiO_2) powder, niobium pentoxide (Nb_2O_5) powder, and zirconium oxide (ZrO_2) powder and/or yttrium oxide (Y_2O_3) powder, then pressing the resulting mixture and sintering it into pellets, and evaporating it, for example, with electron beams to thereby deposit the resulting vapor onto a substrate. In that manner, the antireflection film is formed on the substrate. Using such sintered material is preferred, as the time for vapor deposition can be shortened. If desired, the composition for vapor deposition of the invention may further contain any other metal oxides such as Ta_2O_5 , Al_2O_3 and the like as long as they are not detracting from the above-mentioned effects of the composition. Preferably, the total amount of other metal oxides is in the range of 2 to 30 wt%.

[0014] In the method of producing an optical element in the invention, for example, the high-refraction layers may be formed by vaporizing the composition by using any method of vacuum evaporation, sputtering, ion plating or the like

under ordinary conditions. Concretely, the composition for vapor deposition is vaporized to form a mixed oxide vapor, and the resulting vapor is deposited on a substrate.

The composition for vapor deposition of the invention can form high-refraction layers even on a synthetic resin substrate which should be kept at low temperatures ranging from 65 to 100°C during the vapor deposition, and the scratch resistance, the chemical resistance and the heat resistance of the antireflection film thus formed are all good, and, in addition, the heat resistance of the antireflection film lowers little with time.

[0015] The composition for vapor deposition of the invention may be used not only as an antireflection film for lenses for spectacles but also for lenses for cameras, monitor displays, windshields for automobiles, and even for optical filters, etc.

Examples

[0016] The invention is described in more detail with reference to the following Examples, which, however, are not intended to restrict the scope of the invention. Examples 1 to 3, and Comparative Example 1 (Production of composition for vapor deposition):

Titanium dioxide, niobium pentoxide, zirconium oxide and yttrium oxide were mixed in a composition ratio as in Table 1, pressed, and sintered at 1250°C for 1 hour, to prepare pellets as a composition for vapor deposition.

Using the pellets, a single-layered high-refraction film was formed, having a thickness of $1/2 \lambda$ ($\lambda = 500 \text{ nm}$) on a flat glass substrate in a mode of vacuum evaporation. According to the test methods mentioned below, the samples were tested for (1) the melt condition of the composition for vapor deposition, (2) the attachment condition of fine particles, (3) the absorbance, (4) the refractivity, and (5) the speed of film formation. The results are given in Table 1.

(1) Melt condition of composition for vapor deposition:

[0017] The melt condition of the composition for vapor deposition during deposition was checked and evaluated according to the following criteria:

UA: Not splashed.

A: Splashed a little.

B: Splashed frequently.

C: Always splashed.

In the context of the present invention, "splashing" is defined as the formation of droplets that are thrust out of the melt.

(2) Attachment condition of fine particles:

[0018] After vapor deposition, the attachment condition of fine particles on the flat glass substrate by splashing, etc in vapordeposition was checked and evaluated according to the following criteria:

UA: No fine particles found.

A: 1 to 5 fine particles found.

B: 6 to 10 fine particles found.

C: 11 or more 11 fine particles found.

"Fine particles" are defined in this context as particles adhering to the coated surface which have a diameter of 0.05 to 3 mm, and which may be formed, for instance, by splashing. The number of fine particles is based on the total surface of the lens, which was used in the test, having a circular shape with a diameter of 70 mm.

(3) Absorbance:

[0019] The spectral transmittance and the spectral reflectance of the substrate coated with the single-layered $1/2 \lambda$ film were measured with a spectrophotometer. From the measured data, the luminous transmittance and the luminous reflectance were obtained. The absorbance was obtained according to a numerical formula, $100 \% - (\text{luminous transmittance} + \text{luminous reflectance})$.

(4) Refractive index:

[0020] Using a spectrophotometer, the spectral reflectance of the single-layered $1/2 \lambda$ film formed on the flat glass

substrate was measured. The refractive index of the glass substrate, the distributed data and the measured data were used as input in an optimized program.

(5) Speed of film formation:

[0021] In the process of forming the single-layered $1/2 \lambda$ film, electron beams were applied to the film under the condition mentioned below, and the thickness of the film formed on the glass substrate was measured with a spectrophotometer. The data was divided by the actual time spent for the film formation to obtain the speed of film formation ($\text{\AA}/\text{sec}$).

Condition for exposure to electron beams:

Electronic gun used: JST-3C made by JEOL Ltd.

Accelerating voltage: 6 kV

Filament current: 190 mA

Initial vacuum degree: 2.0×10^{-5} Torr

[0022] Table 1

Table 1

	Example 1	Example 2	Example 3	Comparative Example 1
Titanium dioxide (parts by weight)	59.5	42.5	30.0	100.0
Niobium pentoxide (parts by weight)	25.5	42.5	55.0	0.0
Zirconium oxide (parts by weight)	10.0	10.0	10.0	0.0
Yttrium oxide (parts by weight)	5.0	5.0	5.0	0.0
Melt condition	UA	UA	UA	B
Attachment condition of fine particles	UA	UA	UA	A
Absorbance (%)	0.5	0.34	0.43	0.44
Refractive index (500 nm)	2.178	2.197	2.232	2.119
Speed of film formation ($\text{\AA}/\text{sec}$)	3.66	5.19	6.23	2.57

[0023] As in Table 1, Examples 1 to 3 are all superior to Comparative Example 1 with respect to the melt condition, the attachment condition of fine particles, the refractive index and the speed of film formation. Examples 2 and 3 are particularly good with respect to the refractive index and the speed of film formation.

Example 4 (Production of optical element with antireflection film) :

[0024] For the synthetic resin to be provided with an antireflection film, a plastic lens (CR-39: substrate A) was prepared that was made of diethylene glycol bisallyl carbonate (99.7 % by weight) as a major component and containing a UV absorbent, 2-hydroxy-4-n-octoxybenzophenone (0.03 % by weight), and having a refractive index of 1.499.

The plastic lens was dipped in a coating solution containing 80 mol% of colloidal silica and 20 mol% of γ -glycidoxypolytrimethoxysilane, and cured to form thereon a hard coat layer (having a refractive index of 1.50).

The plastic lens coated with the hard coat layer was heated at 65°C , and a first layer of low refractivity (having a refractive index of 1.46 and a thickness of 0.5λ ($\lambda = 500 \text{ nm}$)) was formed thereon through vacuum evaporation of SiO_2 (at a vacuum degree of 2×10^{-5} Torr). The first layer is nearest to the substrate. Next, a second layer of high refractivity (having a thickness of 0.0502λ) was formed thereon through vapor deposition of the pellets that had been prepared in Example 1, for which the pellets were heated with an electronic gun (current: 180 to 190 mA); and a third layer of low refractivity (having a refractive index of 1.46 and a thickness of 0.0764λ) was formed thereon also through vacuum evaporation of SiO_2 . With that, a fourth layer of high refractivity (having a thickness of 0.4952λ) was formed thereon through vapor deposition of the pellets that had been prepared in Example 1, for which the pellets were heated with the electronic gun (current: 180 to 190 mA); and a fifth layer of low refractivity (having a refractive index of 1.46 and a thickness of 0.2372λ) was formed thereon also through vacuum evaporation of SiO_2 to form an antireflection film. Further, the back of the thus-coated plastic lens was also coated with an antireflection film of the same constitution. Both surfaces of the plastic lens were thus coated with the 5-layered antireflection film.

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[0025] The antireflection film-coated plastic lens was tested for (6) the scratch resistance, (7) the adhesiveness, (8) the luminous reflectance, (9) the luminous transmittance, (10) the absorbance, (11) the heat resistance and (12) the heat resistance with time, according to the methods mentioned below. The results are given in Table 2.

(6) Scratch resistance:

[0026] The surface of the plastic lens was rubbed with steel wool of #0000 and under a weight of 1 kg being applied thereto. After 10 strokes of rubbing, the surface condition of the lens was checked and evaluated according to the following criteria:

- A: Not scratched.
- B: Scratched slightly.
- C: Much scratched.
- D: Coating film peeled.

(7) Adhesiveness:

[0027] According to JIS-Z-1522, the surface of the antireflection film-coated plastic lens was cut to have 10 x 10 cross-cuts, and tested three times for cross-cut peeling with an adhesive tape, Cellotape (a trade name, produced by Nichiban Corp.). The number of the remaining cross-cuts of original 100 cross-cuts was counted.

(8) Luminous reflectance:

[0028] Using a automatic spectrophotometer, U-3410 made by Hitachi, Ltd., the luminous reflectance was measured.

(9) Luminous transmittance:

[0029] Using a spectrophotometer, U-3410 made by Hitachi, Ltd., the luminous transmittance was measured.

(10) Absorbance:

[0030] The absorbance was derived from the luminous transmittance of (8) and the luminous reflectance of (9). Concretely, the absorbance is represented by a numerical formula, $100 \% - (\text{luminous transmittance} + \text{luminous reflectance})$.

(11) Heat resistance:

[0031] Immediately after having been coated with the antireflection film through vapor deposition, the plastic lens was heated in an oven for 1 hour, and checked as to whether it was cracked or not. Concretely, it was heated first at 50°C over a period of 60 minutes, and the temperature was elevated at intervals of 5°C (of a duration of 30 minutes for each interval), and the temperature at which it was cracked was read.

(12) Heat resistance with time:

[0032] The plastic lens was, immediately after having been coated with the antireflection film, exposed to the open air for 2 months, and then heated in an oven for 1 hour and checked as to whether it was cracked or not. Concretely, it was heated first at 50°C over a period of 60 minutes, and the temperature was elevated at intervals of 5°C (of a duration of 30 minutes for each interval), and the temperature at which it was cracked was read.

Example 5 (Production of optical element with antireflection film):

[0033] In the same manner as in Example 4, both surfaces of the substrate were coated with a 5-layered antireflection film, for which, however, the pellets that had been prepared in Example 3 and not those prepared in Example 1 were used for forming the 2nd and 4th layers.

The antireflection film-coated plastic lens was tested for the properties (6) to (12) as described above. The results are given in Table 2.

Comparative Example 2 (Production of optical element with antireflection film):

[0034] In the same manner as described in Example 4, both surfaces of the substrate were coated with a 5-layered antireflection film, for which, however, the pellets that had been prepared in Comparative Example 1 and not those prepared in Example 1 were used for forming the 2nd and 4th layers. The antireflection film-coated plastic lens was tested for the properties (6) to (12) as described above. The results are given in Table 2.

Example 6 (Production of optical element with antireflection film) :

[0035] 142 parts by weight of an organosilicon compound, γ -glycidoxypolytrimethoxysilane, were put into a glass container, to which were dropwise added 1.4 parts by weight of 0.01 N hydrochloric acid and 32 parts by weight of water with stirring. After the dropwise addition, this was stirred for 24 hours to obtain a solution of hydrolyzed γ -glycidoxypolytrimethoxysilane. To the solution, 460 parts by weight of stannic oxide-zirconium oxide composite sol (dispersed in methanol, having a total metal oxide content of 31.5 % by weight and having a mean particle size of from 10 to 15 millimicrons) were added, 300 parts by weight of ethyl cellosolve, 0.7 parts by weight of a lubricant, silicone surfactant, and 8 parts by weight of a curing agent, aluminum acetylacetonate. After having been well stirred, this was filtered to prepare a coating solution.

A plastic lens substrate (a plastic lens for spectacles made by Hoya Corporation, EYAS (a trade name) having a refractive index of 1.60) was pretreated with an aqueous alkali solution, and dipped in the coating solution. After having been thus dipped therein, this was taken out at a pulling rate of 20 cm/min. Then, this was heated at 120°C for 2 hours, to form a hard coat layer.

[0036] The plastic lens coated with the hard coat layer was heated at 80°C, and a first layer of low refractivity (having a refractive index of 1.46 and a thickness of 0.47λ ($\lambda = 500 \text{ nm}$)) was formed thereon through vacuum evaporation of SiO_2 (at a pressure of 2×10^{-5} Torr). The first layer is nearest to the substrate. Next, a second layer of high refractivity (having a thickness of 0.0629λ) was formed thereon through vapor deposition of the pellets that had been prepared in Example 1, for which the pellets were heated with an electronic gun (current: 180 to 190 mA); and a third layer of low refractivity (having a refractive index of 1.46 and a thickness of 0.0528λ) was formed thereon also through vacuum evaporation of SiO_2 . With that, a fourth layer of high refractivity (having a thickness of 0.4432λ) was formed thereon through vapor deposition of the pellets that had been prepared in Example 1, for which the pellets were heated with the electronic gun (current: 180 to 190 mA); and a fifth layer of low refractivity (having a refractive index of 1.46 and a thickness of 0.2370λ) was formed thereon also through vacuum evaporation of SiO_2 , to an antireflection film. Further, the back of the thus-coated plastic lens was also coated with an antireflection film of the same constitution. Both surfaces of the plastic lens were thus coated with the 5-layered antireflection film.

The antireflection film-coated plastic lens was tested for the properties (6) to (12) as specified above. The results are given in Table 3.

Example 7 (Production of optical element with antireflection film) :

[0037] In the same manner as in Example 6, both surfaces of the substrate were coated with a 5-layered antireflection film, for which, however, the pellets that had been prepared in Example 3 and not those prepared in Example 1 were used for forming the 2nd and 4th layers.

The antireflection film-coated plastic lens was tested for the properties (6) to (12) as specified above. The results are given in Table 3.

Comparative Example 3 (Production of optical element with antireflection film):

[0038] In the same manner as in Example 6, both surfaces of the substrate were coated with a 5-layered antireflection film, for which, however, the pellets that had been prepared in Comparative Example 1 and not those prepared in Example 1 were used for forming the 2nd and 4th layers.

The antireflection film-coated plastic lens was tested for the properties (6) to (12) as specified above. The results are given in Table 3.

Example 8 (Production of optical element with antireflection film) :

[0039] 100 parts by weight of an organosilicon compound, γ -glycidoxypolytrimethoxysilane was put into a glass container, to which were added 1.4 parts by weight of 0.01 N hydrochloric acid and 23 parts by weight of water with stirring. After the addition, this was stirred for 24 hours to obtain a solution of hydrolyzed γ -glycidoxypolytrimethoxysilane.

On the other hand, 200 parts by weight of an inorganic particulate substance, composite sol of particulates made of titanium oxide, zirconium oxide and silicon oxide as major components (dispersed in methanol, having a total solid content of 20 % by weight and having a mean particle size of from 5 to 15 nm - in this, the atomic ratio of Ti/Si in the core particles is 10, and the ratio by weight of the shell to the core is 0.25) was mixed with 100 parts by weight of ethyl cellosolve, 0.5 parts by weight of a lubricant, silicone surfactant, and 3.0 parts by weight of a curing agent, aluminum acetylacetonate. The resulting mixture was added to the hydrolyzed γ -glycidoxypolytrimethoxysilane, and well stirred. This was filtered to prepare a coating solution.

A plastic lens substrate (a plastic lens for spectacles made by Hoya Corporation, Teslalid (a trade name), having a refractive index of 1.71) was pretreated with an aqueous alkali solution, and dipped in the coating solution. After having been thus dipped therein, this was taken out at a pulling rate of 20 cm/min. Then, the plastic lens was heated at 120°C for 2 hours, to form a hard coat layer.

[0040] The plastic lens coated with the hard coat layer was heated at 80°C, and a first layer of low refractivity (having a refractive index of 1.46 and a thickness of 0.069λ ($\lambda = 500 \text{ nm}$)) was formed thereon through vacuum evaporation of SiO_2 (at a pressure of 2×10^{-5} Torr). The first layer is nearest to the substrate. Next, a second layer of high refractivity (having a thickness of 0.0359λ) was formed thereon through vapor deposition of the pellets that had been prepared in Example 1, for which the pellets were heated with an electronic gun (current: 180 to 190 mA); and a third layer of low refractivity (having a refractive index of 1.46 and a thickness of 0.4987λ) was formed thereon also through vacuum evaporation of SiO_2 . With that, a fourth layer of high refractivity (having a thickness of 0.0529λ) was formed thereon through vapor deposition of the pellets that had been prepared in Example 1, for which the pellets were heated with the electronic gun (current: 180 to 190 mA); a fifth layer of low refractivity (having a refractive index of 1.46 and a thickness of 0.0553λ) was formed thereon through vacuum evaporation of SiO_2 ; a sixth layer of high refractivity (having a thickness of 0.4560λ) was formed thereon through vapor deposition of the pellets that had been prepared in Example 1, for which the pellets were heated with the electronic gun (current: 180 to 190 mA); and a seventh layer of low refractivity (having a refractive index of 1.46 and a thickness of 0.2422λ) was formed thereon through vacuum evaporation of SiO_2 , to form an antireflection film. Further, the back of the thus-coated plastic lens was also coated with an antireflection film of the same constitution. Both surfaces of the plastic lens were thus coated with the 7-layered antireflection film.

The antireflection film-coated plastic lens was tested for the properties (6) to (12) as specified above. The results are given in Table 4.

Example 9 (Production of optical element with antireflection film):

[0041] In the same manner as in Example 8, both surfaces of the substrate were coated with a 7-layered antireflection film, for which, however, the pellets that had been prepared in Example 3 and not those prepared in Example 1 were used for forming the 2nd, 4th and 6th layers.

The antireflection film-coated plastic lens was tested for the properties (6) to (12) as specified above. The results are given in Table 4.

Comparative Example 4 (Production of optical element with antireflection film):

[0042] In the same manner as in Example 8, both surfaces of the substrate were coated with a 7-layered antireflection film, for which, however, the pellets that had been prepared in Comparative Example 1 and not those prepared in Example 1 were used for forming the 2nd, 4th and 6th layers.

The antireflection film-coated plastic lens was tested for the properties (6) to (12) as above. The results are given in Table 4.

[0043] Table 2

Table 2

	Example 4	Example 5	Comparative Example 2
Scratch resistance	A	A	C
Adhesiveness	100	100	100
Luminous transmittance (%)	98.875	99.17	98.498
Luminous reflectance (%)	0.972	0.666	1.319
Absorbance (%)	0.153	0.164	0.183
Heat resistance (°C)	80	80	70
Heat resistance with time (°C)	65	65	50

[0044] Table 3

Table 3

	Example 6	Example 7	Comparative Example 3
Scratch resistance	A	A	C
Adhesiveness	100	100	100
Luminous transmittance (%)	98.874	99.164	98.545
Luminous reflectance (%)	0.937	0.648	1.284
Absorbance (%)	0.189	0.188	0.171
Heat resistance (°C)	120	120	110
Heat resistance with time (°C)	105	105	90

[0045] Table 4

Table 4

	Example 8	Example 9	Comparative Example 4
Scratch resistance	A	A	C
Adhesiveness	100	100	100
Luminous transmittance (%)	98.885	99.153	98.663
Luminous reflectance (%)	0.829	0.614	1.106
Absorbance (%)	0.286	0.233	0.231
Heat resistance (°C)	90	90	85
Heat resistance with time (°C)	80	80	70

[0046] As in Tables 2 to 4, the antireflection film-coated plastic lenses of Examples 4 to 9, for which the pellets of Example 1 or 3 were used, are better than the antireflection film-coated plastic lenses of Comparative Examples 2 to 4, for which the pellets of Comparative Example 1 were used, in the scratch resistance and the heat resistance, and, in addition, the heat resistance with time of the former lowered little after exposure to the weather, as compared with that of the latter. From the data of the antireflection film-coated plastic lenses of Examples 5, 7 and 9, for which the composition ratio of niobium pentoxide in the pellets of Example 3 was increased, it is understood that the refractivity and also the absorbance of the coated lenses are lowered.

The inventive examples of the present application describe preferred embodiments of the present invention. However, compositions having compositional ratios between the compositions of the examples are also preferred. Similarly, antireflection films having thicknesses between those disclosed in the examples are also preferred. Finally, optical elements, having layer structures between those disclosed in the examples are also preferred.

Advantages of the Invention

[0047] As described in detail hereinabove, the composition for vapor deposition of the invention can form a high-refraction layer even on synthetic resin substrates that must be processed at low temperatures for vapor deposition thereon, within a short period of time and without using an ion gun unit or a plasma unit, not detracting from the good physical properties intrinsic to the high-refraction layer formed, that the high-refraction layer formed has high refractivity; and the antireflection film comprising the high-refraction layer formed on such synthetic resin substrates has good scratch resistance, good chemical resistance and good heat resistance, and the heat resistance of the antireflection film lowers little with time.

In addition, the antireflection film-coated optical element obtained according to the method of the invention has good scratch resistance, good chemical resistance and good heat resistance, and its heat resistance lowers little with time. Specifically, the antireflection film that coats the optical element ensures good UV absorption of titanium dioxide therein, and the coated optical element is favorable for plastic lenses for spectacles.

Claims

1. Composition obtainable by sintering a powder mixture essentially consisting of

(i) 70-100 wt.-% of a mixture of

- (a) 100 parts by weight of TiO_2 and Nb_2O_5 in a weight ratio of $\text{TiO}_2:\text{Nb}_2\text{O}_5$ of 30:70 to 75:25,
- (b) 3-46 parts by weight of ZrO_2 and/or Y_2O_3 and

(ii) 0 - 30 wt.-% of other metal oxides.

2. Composition of claim 1, wherein ZrO_2 and/or Y_2O_3 are present in an amount of 10-20 parts by weight.

3. Composition of claim 1 or 2, wherein the other metal oxides (ii) are selected from Ta_2O_5 and Al_2O_3 .

4. Composition of any of claims 1-3, wherein the powder mixture is pressed into blocks prior to the sintering.

5. Composition of any of claims 1-4, wherein the sintering is conducted at a temperature of 1,000-1,400°C.

6. Method of producing an optical element having an antireflection film, comprising vaporizing a composition of any of claims 1-5 and depositing the generated vapor on a substrate.

7. Method of claim 6, wherein the substrate is a synthetic resin substrate.

8. Method of claim 7, wherein the substrate has a hard coat layer formed on the surface thereof.

9. Method of any of claims 6-8, wherein the substrate has formed thereon one or more coating layers.

10. Method of any of claims 6-9, wherein the antireflection film comprises in alternating fashion one or more layers of silicon dioxide and one or more layers obtained by vaporizing and depositing a composition of any of claims 1-5.

11. Optical element having an antireflection film, which is obtainable by the method of any of claims 6-10.

12. Optical element of claim 11, which is selected from lenses for spectacles or cameras, windshields for automobiles, and optical filters for word processor displays.

Patentansprüche

1. Zusammensetzung, die erhältlich ist durch Sintern einer Pulvermischung, die im wesentlichen aus folgendem besteht:

(i) 70-100 Gew.-% einer Mischung aus

- (a) 100 Gew.-Teilen TiO_2 und Nb_2O_5 in einem Gewichtsverhältnis von $\text{TiO}_2:\text{Nb}_2\text{O}_5$ von 30:70-75:25,
- (b) 3-46 Gew.-Teilen ZrO_2 und/oder Y_2O_3 und

(ii) 0-30 Gew.-% anderen Metalloxiden.

2. Zusammensetzung gemäss Anspruch 1, worin ZrO_2 und/oder Y_2O_3 in einer Menge von 10-20 Gew.-Teilen vorhanden ist/sind.

3. Zusammensetzung gemäss Anspruch 1 oder 2, worin die anderen Metalloxide (ii) ausgewählt sind aus Ta_2O_5 und Al_2O_3 .

4. Zusammensetzung gemäss mindestens einem der Ansprüche 1 bis 3, worin die Pulvermischung vor dem Sintern zu Blöcken gepresst wird.

5. Zusammensetzung gemäss mindestens einem der Ansprüche 1 bis 4, worin der Sintervorgang bei einer Temperatur von 1.000-1.400°C durchgeführt wird.
- 5 6. Verfahren zur Herstellung eines optischen Elements mit einer Antireflexionsschicht, das das Verdampfen einer Zusammensetzung gemäss mindestens einem der Ansprüche 1 bis 5 und Abscheidung des erzeugten Dampfs auf einem Substrat umfasst.
7. Verfahren gemäss Anspruch 6, worin das Substrat ein Kunstharzsubstrat ist.
- 10 8. Verfahren gemäss Anspruch 7, worin das Substrat eine auf seiner Oberfläche erzeugte Hartbeschichtung aufweist.
9. Verfahren gemäss mindestens einem der Ansprüche 6 bis 8, worin das Substrat eine oder mehrere darauf ausgebildete Beschichtungsschichten aufweist.
- 15 10. Verfahren gemäss mindestens einem der Ansprüche 6 bis 9, worin die Antireflexionsschicht in einander abwechselnder Weise eine oder mehrere Schichten aus Siliciumdioxid und eine oder mehrere Schichten, die erhalten werden durch Verdampfen und Abscheiden einer Zusammensetzung gemäss mindestens einem der Ansprüche 1 bis 5, umfasst.
- 20 11. Optisches Element mit einer Antireflexionsschicht, das erhältlich ist nach dem Verfahren gemäss mindestens einem der Ansprüche 6 bis 10.
12. Optisches Element gemäss Anspruch 11, das ausgewählt ist aus Linsen für Brillen oder Kameras, Windschutzscheiben für Automobile und optischen Filtern für Textverarbeitungsanzeigen.

Revendications

- 30 1. Composition qui peut être obtenue par frittage d'un mélange de poudre qui est essentiellement constitué de
 - (i) 70 à 100 % en poids d'un mélange de
 - (a) 100 parties en poids de TiO_2 et de Nb_2O_5 en un rapport en poids de $\text{TiO}_2 : \text{Nb}_2\text{O}_5$ de 30 : 70 à 75 : 25,
 - (b) 3 à 46 parties en poids de ZrO_2 et/ou de Y_2O_3 et
 - 35 (ii) 0 à 30 % en poids d'autres oxydes métalliques.
2. Composition selon la revendication 1, dans laquelle ZrO_2 et/ou Y_2O_3 sont présents en une quantité de 10 à 20 parties en poids.
- 40 3. Composition selon la revendication 1 ou 2, dans laquelle les autres oxydes métalliques (ii) sont choisis parmi Ta_2O_5 et Al_2O_3 .
- 45 4. Composition selon l'une quelconque des revendications 1 à 3, dans laquelle le mélange de poudre est pressé en blocs avant le frittage.
5. Composition selon l'une quelconque des revendications 1 à 4, dans laquelle le frittage est conduit à une température de 1 000 à 1 400°C.
- 50 6. Procédé de production d'un élément optique ayant un film antiréfléchissant, comprenant la vaporisation d'une composition selon l'une quelconque des revendications 1 à 5 et le dépôt de la vapeur générée sur un substrat.
7. Procédé selon la revendication 6, dans lequel le substrat est un substrat de résine synthétique.
- 55 8. Procédé selon la revendication 7, dans lequel le substrat comporte une couche de revêtement dure formée sur sa surface.
9. Procédé selon l'une quelconque des revendications 6 à 8, dans lequel le substrat a formé sur celui-ci une ou plusieurs

couches de revêtement.

5 10. Procédé selon l'une quelconque des revendications 6 à 9, dans lequel le film antiréfléchissant comprend de manière alternée une ou plusieurs couches de dioxyde de silicium et une ou plusieurs couches obtenues par vaporisation et dépôt d'une composition selon l'une quelconque des revendications 1 à 5.

11. Élément optique ayant un film antiréfléchissant, qui peut être obtenu par le procédé selon l'une quelconque des revendications 6 à 10.

10 12. Élément optique selon la revendication 11, qui est choisi parmi des verres de lunettes ou d'appareils photographiques, des pare-brises pour automobiles et des filtres optiques pour des affichages de traitement de texte.

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