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(54) **Hard coating solution for optical plastic lenses**

(57) A hard coating solution for optical plastic lenses which contains at least one metal oxide and at least one silane coupling agent in an amount satisfying at least one of the following conditions (I) or (II):

$X/Y \geq 2.0$... (I)
 $x/y \geq 0.7$... (II)

in which X is the sum of the molar concentration of the metal oxide, Y is the sum of the molar concentration of the silane coupling agent, x is the sum of the solid content of the metal oxide, and y is the sum of the solid content of the silane coupling agent. The oxide may be SiO₂, Sb₂O₅, GeO₂, SnO₂, Al₂O₃, Te₂O₃, In₂O₃, TiO₂, ZrO₂ and/or WO₃ preferably in sol form.

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HARD COATING SOLUTION FOR OPTICAL PLASTIC LENSES

The present invention relates to a hard coating
5 solution or hard coat-forming solution for optical plastic
lenses.

Hitherto, a hard coating solution (which contains a sol
of metal oxide and a silane coupling agent as principal
10 components and also a surfactant, a curing catalyst, a
solvent and the like) has been used in the production of
optical plastic lenses having a hard-coated layer on a
surface thereof. A refractive index of the hard-coated layer
is determined depending upon the mixing ratio of the sol of
15 metal oxide and the silane coupling agent contained in the
hard coating solution. For example, if it is intended to
prepare a coating solution having the refractive index
"n" of 1.60, different amounts of the silane coupling agent
(n = about 1.4 to 1.5) must be used when the metal oxide sol
20 used in combination with the silane coupling agent has
different refractive indexes, namely, one metal oxide sol
has a refractive index "n" of about 2.5 and another one has
a refractive index "n" of about 2.0.

Furthermore, properties of the resulting hard-coated

layer can be varied depending on the type and mixing ratio of the metal oxide sol and the silane coupling agent used. In particular, if the mixing ratio of the metal oxide sol and the silane coupling agent is varied substantially, it is
5 difficult to predict the resulting properties of the hard-coated layer until the preparation of the hard coating solution has been completed, because the properties can be also vary substantially as a result of the large variation of the mixing ratio.

10 In addition, when the metal oxide sol and the silane coupling agent are mixed in an inappropriate ratio of amounts in the step of controlling a refractive index of the resulting coating solution, there is a problem that if, from any possible cause, a defect such as an abrasion or a scratch
15 is contained in the multicoated layer, cracks can be produced in the hard-coated layer due to the influence of ultraviolet radiation etc., and the cracks may extend further with time.

20 An object of the present invention is to provide a hard coating solution for optical plastic lenses, in which a suitable mixing ratio of the sol of metal oxide and the silane coupling agent can be easily determined, and which does not induce cracks in the resulting hard-coated layer

due to the influence of ultraviolet radiation etc., even if a scratch or other such defects are contained in the multicoated layer.

According to the present invention there is
5 provided a hard coating solution for optical plastic lenses which contains at least one metal oxide and at least one silane coupling agent in an amount which satisfies at least one of the following conditions (I) and (II):

10 $x/y \geq 2.0$. . . (I)

$x/y \geq 0.7$. . . (II)

in which

X is a sum of the molar concentration of the metal oxide,

15 Y is a sum of the molar concentration of the silane coupling agent,

x is a sum of the solid content of the metal oxide, and

y is a sum of the solid content of the silane coupling agent.

20

In the preparation of a hard coating solution embodying the present invention, the metal oxide and the silane coupling agent are incorporated so that the above-

described condition (I) is satisfied; that is, the ratio of the sum (X) of the molar concentration of the metal oxide and the sum (Y) of the molar concentration of the silane coupling agent is 2 or more. If the ratio X/Y is less than 2.0, when a scratch or other defect is produced in the multicoated layer from any possible cause during the production of lens products, having the applied multicoated layer as an antireflection layer and, if necessary, as a "watertarnish"-preventing layer, cracks in the hard-coated layer can be induced due to the influence of ultraviolet radiation etc. For the present invention, it is preferred in view of the properties of the resulting hard-coated layer that the ratio X/Y is 10 or less.

Alternatively, in the hard coating solution embodying the present invention, the metal oxide and the silane coupling agent may be contained so that the above-described condition (II) is satisfied, that is, the ratio of the sum (x) of the solid content of the metal oxide and the sum (y) of the solid content of the silane coupling agent is 0.7 or more. As in the above-described ratio X/Y, if the ratio x/y is less than 0.7, cracks in the hard-coated layer can be induced due to the influence of ultraviolet radiation and the like, when a scratch or the like is produced in the multicoated layer from any possible cause. Furthermore, it is preferred in view of the properties of the hard-coated layer that the

ratio x/y is 5 or less.

Note that the above-described conditions (I) and (II) are specified by using different methods of the expression. However, the condition referring to the molar concentration and the condition referring to the solid content can both be used in the calculation to obtain substantially the same results.

In order to prevent induction of cracks in the hard-coated layer, it is necessary to provide more than a predetermined number of metal oxide particles (colloid particles) in a surface of the lens to be coated by using 1 mole of a silane coupling agent. The inventors have found the above-described conditions (I) and (II) as a result of their studies for the conditions which enable provision of the above stated more than a predetermined number of metal oxide particles sufficient to prevent induction of cracks without the need to conduct a troublesome calculation of the metal oxide number.

In the hard coating solution embodying the present invention, the metal oxide is used to adjust and obtain a desired refractive index. Useful metal oxides include, for example, SiO_2 , Sb_2O_5 , GeO_2 , SnO_2 , Al_2O_3 , Tl_2O_3 , In_2O_3 , TiO_2 , ZrO_2 , WO_3 and the like, or their complexes (the core of which is composed of compounds TiO_2 and SiO_2 , and covering the outside

of the core compounds with ZrO_2 and SiO_2 , etc.). For the present invention, the above-listed metal oxides may be used alone, or may be used as a combination of two or more oxides, and it is preferred that metal oxide(s) having a high refractive index are used along with metal oxide(s) having a low refractive index. Generally, in the field of spectacle

lenses, a refractive index which is higher than about 1.6 is considered a high refractive index while a refractive index which is lower than about 1.6 is considered a low refractive index. Examples of metal oxides which have a high refractive index are antimony oxide, tungston oxide, zirconium oxide, titanium oxide, tin oxide, indium oxide, yttrium oxide etc.; examples of metal oxides which have a low refractive index are silicon oxide and aluminum oxide etc.

Furthermore, if the ratio of the metal oxide(s) having a high refractive index to the metal oxide(s) having a low refractive index in the coating solution is varied within the range of 1 : 0 to 0 : 1, it becomes possible to adjust a refractive index without largely changing the properties of the resulting layer.

Preferably, the metal oxide is used as a sol of the metal oxide containing fine particles of the metal oxide having an average particle diameter of about 1 to 200 μm in

an amount of not less than about 20 % based on total weight of the sol. When the average particle diameter of the metal oxide particles is less than $1\mu\text{m}$, there is a tendency that a dyeability and hardness of the coated layer is lowered due to poor stability of the sol itself. Furthermore, an average particle diameter above $200\mu\text{m}$ causes a reduction of the transparency of the layer and poor stability of the hard coating solution. Furthermore, it is preferred that the fine particles of metal oxide used have substantially the same particle diameter.

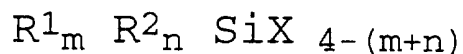
As an alternative, the particles of metal oxide may be used after they are coated with a silane coupling agent. Coating of the metal oxide particles with a silane coupling agent enables an easy and uniform dispersion of different metal oxides in the solution.

In the preparation of the metal oxide sol, water or an organic solvent is used. A useful organic solvent includes, for example, alcohols such as methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol and the like; cellosolves such as methyl cellosolve, ethyl cellosolve and the like, and others.

Furthermore, to assist in a stable dispersion of the metal oxide particles in the sol, acids such as nitric acid,

sulfuric acid, acetic acid, oxalic acid, tartaric acid, malic acid, citric acid and the like, or organic amines such as monoethanol amine, diethanol amine, isopropanol amine, ethylene diamine, isopropyl amine, diisopropyl amine, 5 triethanol amine, diaminopropane, aminoethyl ethanol amine and the like, may be added.

In the hard coating solution of the present invention, the silane coupling agent used is not restricted to the specific one, and therefore a wide variety of the silane 10 coupling agents may be used. For example, the compounds represented by the following general formula:



in which R^1 represents an alkyl group, an alkenyl group, a phenyl group or halogen, R^2 represents an epoxy 15 group, a glycidoxy group, an amino group, an amido group, a mercapto group, a methacryloyloxy group, a cyano group or an organic group containing a nucleosubstituted aromatic ring, X represents a hydrolyzable group such as halogen, an alkoxy group, an alkoxyalkoxy group, an acyloxy group and the like, 20 m and n each represents a number of 0 to 2, and $m + n \leq 3$, and a hydrolyzed product or partially condensed product thereof may be used as the silane coupling agent. Typical examples of these compounds include tetrafunctional silanes such as tetramethoxy silane and the like, trifunctional

silanes such as methyltrimethoxysilane,
methyltriethoxysilane, γ -chloropropyltrimethoxysilane,
vinyltrimethoxysilane,
 γ -methacryloyloxypropyltrimethoxysilane,
5 β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane,
 γ -Glycidoxypropyltrimethoxysilane,
 γ -mercaptopropyltrimethoxysilane,
 γ -aminopropyltrimethoxysilane,
N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane,
10 γ -ureidopropyltrimethoxysilane,
 γ -cyanopropyltrimethoxysilane,
 γ -morpholinopropyltrimethoxysilane,
N-phenylaminopropyltrimethoxysilane and the like, and also
bifunctional silanes, i.e. a part of the above-described
15 trifunctional silanes is substituted with an alkyl group, a
phenyl group, a vinyl group and the like, such as
dimethyldimethoxysilane, phenylmethyldimethoxysilane,
vinylmethyldimethoxysilane,
 γ -chloropropylmethyldimethoxysilane,
20 γ -glycidoxypropylmethyldiethoxysilane and the like.
Furthermore, hydrolyzed products, partially condensed
products and the like of these compounds may be used.

In addition to the metal oxide and silane coupling agent in an amount satisfying the conditions (I) or (II), the hard coating solution of the present invention may contain additives which are normally used in a hard coating solution, for example, a surfactant, a curing catalyst, a solvent, an ultraviolet-absorbing agent, and also organic polymeric compounds such as epoxy resin, acrylic resin and the like for the purpose of improvement of hardness and others, within the range of not deteriorating the desired properties.

There is no specific limitation to the curing catalyst used for the purpose of shortening a time for forming a coating. A wide variety of compounds may be used as the curing catalyst, and they include, for example, organic amines such as triethylamine, n-butylamine and the like, metal acetylacetonates such as aluminum acetylacetonate, indium acetylacetonate, chromium acetylacetonate, titanium acetylacetonate, cobalt acetylacetonate and the like, metal salts of organic acid such as zinc acetate, copper acetate, barium acetate, cobalt naphthenate, lead naphthenate, manganese naphthenate, calcium naphthenate, aluminum naphthenate, zinc naphthenate, zirconium naphthenate, cobalt octylate, lead octylate, iron octylate, zinc octylate and the like, Louis acids such as stannous chloride, aluminum

chloride, ferric chloride, titanium chloride, zinc chloride, antimony chloride and the like, peroxides such as calcium peroxide, manganese peroxide, hydrogen peroxide and the like, and others.

5 The surfactant added for the purpose of improving the fluidability of the solution during coating and the flatness of the resulting coating to thereby reduce a friction coefficient of the coating surface includes, for example, a silicone surfactant, a block copolymer or graft copolymer of
10 dimethyl siloxane and alkylene oxide and also a fluorine surfactant, and others.

 In the application of the hard coating solution of the present invention onto a lens substrate, a solvent may be added to the solution to thereby control its viscosity in
15 view of controlling the workability and thickness of the coating. The solvent which can be used herein includes, for example, water, alcohols such as methanol, n-propyl alcohol, isopropyl alcohol and the like, esters such as ethyl acetate, butyl acetate and the like, ethers such as diethyl
20 ether, diisopropyl ether, diethyleneglycol dimethyl ether and the like, cellosolves such as methyl cellosolve, ethyl cellosolve and the like, halogen compounds such as chloroform, 1,2-dichloroethane, trichloroethylene, chlorobenzene and the like, ketones such as methyl ethyl

ketone, cyclohexanone and the like, hydrocarbons such as pentane, hexane, octane, benzene, toluene and the like, and others. If necessary, these solvents may be used as a mixture. Among these solvents, in particular, alcohols and
5 cellosolves can be preferably used.

The hard coating solution of the present invention can be applied to any substrate of the optical plastic lenses to thereby form a hard-coated layer having excellent properties without producing cracks.

10 As the means for coating the hard coating solution onto a lens substrate, any conventional coating method such as brush coating, dip coating, roll coating, spray coating, spinner coating, flow coating and the like can be easily used.

15 In consideration of retaining an adhesion strength, a hardness etc, the hard coating solution of the present invention is preferably coated at a layer thickness of 1 to 10 μm , more preferably at a layer thickness of 2 to 5 μm . A layer thickness above 10 μm causes deterioration of the
20 thermal resistance of the coated layer, and a thickness less than 1 μm causes deterioration of the adhesion property and scratch resistance of the layer.

After completion of the coating as mentioned above, the

hard coating solution is subjected to a drying or heating treatment to harden it. The heating temperature is in the range of 60 to 150°C, preferably 80 to 130°C. If the heating is at a temperature less than 60 °C, it does not ensure a satisfactory hardening, and a temperature above 150 °C has the possibility of the substrate of the plastic lenses being deformed.

After a hard-coated layer has been formed using the hard coating solution of the present invention, a multicoated layer can be formed thereon in accordance with conventional methods.

"Multicoated-layer" is a generic term for a multiple coating which can exhibit an anti-reflection effect by the depositing of multi-layers of metal oxides having different refractive indexes. In the formation of the multicoated layer, its outmost layer (located on the atmospheric side) is generally deposited from a metal oxide having a low refractive index and a hydrophilic property, and therefore suffers from a so-called "watertarnish", i.e., fixation of the impurities on the multicoated layer upon adhesion of water droplets containing said impurities onto said layer. Moreover these impurities can not be swept and removed from the multicoated layer. It is believed that the adhesion and retention of the impurities on the multicoated layer was

caused as a result of bonding between the impurities and the hydrophilic metal oxide.

To generally avoid the watertarnish problem, a watertarnish-preventing layer has been applied from a fluorine resin over the antireflection layer. The
5 watertarnish-preventing layer is intended to obtain a water repellency without varying the resulting interference color by coating the layer at a layer thickness which does not affect the antireflection layer. Ideally, the watertarnish-
10 preventing layer should be 2 to 5 nm thick. Due to its water repellency, the watertarnish-preventing layer ensures water droplets have difficulty in remaining, and even if impurities are adhered to the surface of the watertarnish-
preventing layer, they can be easily swept from the surface.
15 Furthermore, since the watertarnish-preventing layer is made from a fluorine resin, it shows a small surface friction, and therefore it becomes possible to protect it from any defect such as abrasion or scratches. Furthermore, since the watertarnish-preventing layer is remarkably thinner than the
20 antireflection layer, the generation of damages, cracks etc. in only the watertarnish-preventing layer can be prevented.

EXAMPLES

The present invention will be further described with reference to its working examples. Note, however, that the
25 present invention should not be restricted to these

examples. Optolake 1120Z mentioned in the examples below has an average particle diameter of 5 to 15nm and a refractive index of 2.10. Oscal, also mentioned in the examples below, has an average particle diameter of 5-25nm
5 and a refractive index of 1.42.

It should be noted that Optolake 1120Z explained in the specification corresponds to the sol containing particles of metal oxide compound. The core of the metal oxide compound is composed of compounds TiO_2 and SiO_2 , and the core is
10 covered with the compounds of ZrO_2 and SiO_2 . Furthermore, Optolake 1120Z explained in the specification corresponds to the sol containing metal oxide particles coated with silane coupling agent.

Example 1:

15 300g of TiO_2-ZrO_2 sol is a sol containing particles of metal oxide compound. The core of the metal oxide compound is composed of compounds TiO_2 and SiO_2 , and the core is covered with the compounds of ZrO_2 and SiO_2 , etc. The sol is commercially available from Shokubai-Kasei
20 Kabushikikaisha under the trade name "Optolake 1120Z" (S7.A8), having a solid content of 21.7% by weight and molecular weight (MW) of 60, and 100g of hydrolyzed γ -glycydoxypropyltrimethoxysilane having a solid content (after hydrolysis) of 58.5% by weight and MW of 167.3 were

mixed, and 5g of a silicone surfactant and 2g of aluminum acetylacetonate (curing catalyst) were added to the mixture to make a hard coating solution.

In this example, the mixing ratio of the sol and silane coupling agent used satisfies the above-described conditions (I) and (II) as described below.

Condition (I):

$$\begin{aligned} X & \text{ (sum of molar concentration of metal oxide)} \\ & = \text{(amt. of sol added} \times \text{solid cont.)} / \text{MW of metal} \\ & \text{oxide} \\ & = 300 \times 0.217 / 60 = 1.85 \text{ moles} \end{aligned}$$

$$\begin{aligned} Y & \text{ (sum of molar conc. of silane coupling agent)} \\ & = \text{(amount of coupling agent added} \times \\ & \text{solid content)} / \text{MW of coupling agent} \\ & = 100 \times 0.585 / 167.3 = 0.3497 \text{ moles} \end{aligned}$$

That is, $X/Y = 1.085/0.3497 = 3.1023$.

Condition (II):

$$\begin{aligned} x & \text{ (sum of solid content of metal oxide)} \\ & = \text{amount of sol added} \times \text{solid content} \\ & = 300 \times 0.217 = 65.1\text{g} \end{aligned}$$

$$\begin{aligned} y & \text{ (sum of solid cont. of silane coupling agent)} \\ & = \text{amt. of coupling agent added} \times \text{solid cont.} \end{aligned}$$

$$= 100 \times 0.585 = 58.5\text{g}$$

That is, $x/y = 65.1/58.5 = 1.11282$.

Example 2:

230g of "Optolake 1120Z", having a solid content of
 5 21.7% by weight and molecular weight (MW) of 60, 80g of SiO₂
 sol, commercially available from Shokubai-Kasei
 Kabushikikaisha under the trade name "Oscal (S7.A8), having
 a solid content of 20.5% by weight and MW of 60, and 100g of
 hydrolyzed γ -glycydoxypropyltrimethoxysilane having a solid
 10 content (after hydrolysis) of 58.5% by weight and MW of
 167.3 were mixed, and 5g of a silicone surfactant and 2g of
 aluminum acetylacetonate (curing catalyst) were added to the
 mixture to make a hard coating solution.

In this example, the mixing ratio of the sol and silane
 15 coupling agent used satisfies the above-described conditions
 (I) and (II) as described below.

Condition (I):

$$\begin{aligned} & X \text{ (sum of molar concentration of metal oxide)} \\ & = (\text{amt. of 1120Z sol added} \times \text{solid cont.}) / (\text{MW} \\ & \text{20 of metal oxide}) + (\text{amt. of SiO}_2 \text{ sol added} \times \\ & \text{solid cont.}) / (\text{MW of SiO}_2) \\ & = (230 \times 0.217 / 60) + (80 \times 0.205 / 60) \\ & = 1.105 \text{ moles} \end{aligned}$$

$$\begin{aligned}
 Y & \text{ (sum of molar conc. of silane coupling agent)} \\
 & = \text{(amt. of coupling agent added} \times \text{solid cont.)} \\
 & \quad / \text{ MW of coupling agent} \\
 & = 100 \times 0.585 / 167.3 = 0.3497 \text{ moles}
 \end{aligned}$$

5 That is, $X/Y = 1.105/0.3497 = 3.159$.

Condition (II):

$$\begin{aligned}
 x & \text{ (sum of solid content of metal oxide)} \\
 & = \text{(amt. of 1120Z sol added} \times \text{solid cont.)} + \\
 & \text{(amt. of SiO}_2 \text{ sol added} \times \text{solid cont.)} \\
 10 \quad & = (230 \times 0.217) + (80 \times 0.205) = 66.31\text{g} \\
 y & \text{ (sum of solid cont. of silane coupling agent)} \\
 & = \text{amt. of coupling agent added} \times \text{solid cont.} \\
 & = 100 \times 0.585 = 58.5\text{g}
 \end{aligned}$$

That is, $x/y = 66.31/58.5 = 1.1335$.

15 Example 3:

320g of SiO_2 sol, commercially available from Shokubai-Kasei Kabushikikaisha under the trade name "Oscal (S7.A8), having a solid content of 20.5% by weight and MW of 60, and 100g of hydrolyzed γ -glycydoxypropyltri-
 20 methoxysilane having a solid content (after hydrolysis) of 58.5% by weight and MW of 167.3 were mixed, and 5g of a silicone surfactant and 2g of aluminum acetylacetonate

(curing catalyst) were added to the mixture to make a hard coating solution.

In this example, a mixing ratio of the sol and silane coupling agent used satisfied the above-described conditions (I) and (II) as described below.

Condition (I):

$$\begin{aligned}
 & X \text{ (sum of molar concentration of metal oxide)} \\
 & = (\text{amt. of sol added} \times \text{solid cont.}) / \text{MW of metal} \\
 & \text{oxide} \\
 10 \quad & = 320 \times 0.205 / 60 = 1.0933 \text{ moles}
 \end{aligned}$$

$$\begin{aligned}
 & Y \text{ (sum of molar conc. of silane coupling agent)} \\
 & = (\text{amt. of coupling agent added} \times \text{solid} \\
 & \quad \text{cont.}) / \text{MW of coupling agent} \\
 & = 100 \times 0.585 / 167.3 = 0.3497 \text{ moles}
 \end{aligned}$$

$$15 \quad \text{That is, } X/Y = 1.0933/0.3497 = 3.1267.$$

Condition (II):

$$\begin{aligned}
 & x \text{ (sum of solid content of metal oxide)} \\
 & = \text{amount of sol added} \times \text{solid content} \\
 & = 320 \times 0.205 = 65.6\text{g} \\
 20 \quad & y \text{ (sum of solid cont. of silane coupling agent)} \\
 & = \text{amt. of coupling agent added} \times \text{solid cont.} \\
 & = 100 \times 0.585 = 58.5\text{g}
 \end{aligned}$$

That is, $x/y = 65.6/58.5 = 1.1213$.

Example 4:

190g of "Optolake 1120Z", having a solid content of 21.7% by weight and MW of 60, 15g of SiO₂ sol, commercially available from Shokubai-Kasei Kabushikikaisha under the trade name "Oscal (S7.A8)", having a solid content of 20.5% by weight and MW of 60, and 100g of hydrolyzed γ -glycydoxy propyl-trimethoxysilane having a solid content (after hydrolysis) of 58.5% by weight and MW of 167.3 were mixed, and 5g of a silicone surfactant and 2g of indium acetylacetonate (curing catalyst) were added to the mixture to make a hard coating solution.

In this example, a mixing ratio of the sol and silane coupling agent used satisfied the above-described equations (I) and (II) as described below.

Condition (I):

$$\begin{aligned}
 X & \text{ (sum of molar concentration of metal oxide)} \\
 & = (\text{amt. of 1120Z sol added} \times \text{solid cont.}) / (\text{MW} \\
 & \text{ of metal oxide}) + (\text{amt. of SiO}_2 \text{ sol added} \times \\
 & \text{solid cont.}) / (\text{MW of SiO}_2) \\
 & = (190 \times 0.217 / 60) + (15 \times 0.205 / 60) \\
 & = 0.7384 \text{ moles} \\
 Y & \text{ (sum of molar conc. of silane coupling agent)}
 \end{aligned}$$

$$= (\text{amt. of coupling agent added} \times \text{solid cont.}) / \text{MW of coupling agent}$$

$$= 100 \times 0.585 / 167.3 = 0.3497 \text{ moles}$$

That is, $X/Y = 0.7384/0.3497 = 2.1115$.

5 Condition (II):

$$x (\text{sum of solid content of metal oxide})$$

$$= (\text{amt. of 1120Z sol added} \times \text{solid cont.}) +$$

$$(\text{amt. of SiO}_2 \text{ sol added} \times \text{solid cont.})$$

$$= (190 \times 0.217) + (15 \times 0.205) = 44.305\text{g}$$

10 y (sum of solid cont. of silane coupling agent)

$$= \text{amt. of coupling agent added} \times \text{solid cont.}$$

$$= 100 \times 0.585 = 58.5\text{g}$$

That is, $x/y = 44.305/58.5 = 0.7573$.

Example 5:

15 200g of "Optolake 1120Z", having a solid content of 21.7% by weight and MW of 60, and 100g of hydrolyzed γ -glycydoxypropyltrimethoxysilane having a solid content (after hydrolysis) of 58.5% by weight and MW of 167.3 were mixed, and 5g of a silicone surfactant and 2g of calcium

20 peroxide (curing catalyst) were added to the mixture to make a hard coating solution.

In this example, a mixing ratio of the sol and silane

coupling agent used satisfied the above-described conditions (I) and (II) as described below.

Condition (I):

$$\begin{aligned} X & \text{ (sum of molar concentration of metal oxide)} \\ 5 \quad & = (\text{amt. of sol added} \times \text{solid cont.}) / \text{MW of sol} \\ & = 200 \times 0.217 / 60 = 0.7233 \text{ moles} \end{aligned}$$

$$\begin{aligned} Y & \text{ (sum of molar conc. of silane coupling agent)} \\ & = (\text{amount of coupling agent added} \times \\ & \quad \text{solid content}) / \text{MW of coupling agent} \\ 10 \quad & = 100 \times 0.585 / 167.3 = 0.3497 \text{ moles} \end{aligned}$$

$$\text{That is, } X/Y = 0.7233/0.3497 = 2.0684.$$

Equation (II):

$$\begin{aligned} x & \text{ (sum of solid content of metal oxide)} \\ & = \text{amount of sol added} \times \text{solid content} \\ 15 \quad & = 200 \times 0.217 = 43.4\text{g} \end{aligned}$$

$$\begin{aligned} y & \text{ (sum of solid cont. of silane coupling agent)} \\ & = \text{amt. of coupling agent added} \times \text{solid cont.} \\ & = 100 \times 0.585 = 58.5\text{g} \end{aligned}$$

$$\text{That is, } x/y = 43.4/58.5 = 0.7418.$$

20 Comparative Example 1:

300g of "Optolake 1120Z", having a solid content of 21.7% by weight and MW of 60, and 180g of hydrolyzed γ -

glycydoxypropyltrimethoxysilane having a solid content (after hydrolysis) of 58.5% by weight and MW of 167.3 were mixed, and 5g of a silicone surfactant and 2g of aluminum acetylacetonate (curing catalyst) were added to the mixture
5 to make a hard coating solution.

In this comparative example, a mixing ratio of the sol and silane coupling agent used did not satisfy the above-described conditions (I) and (II) as described below.

Condition (I):

10 X (sum of molar concentration of metal oxide)
= (amt. of sol added X solid cont.) / MW of metal
oxide

$$= 300 \times 0.217 / 60 = 1.085 \text{ moles}$$

Y (sum of molar conc. of silane coupling agent)

15 = (amount of coupling agent added X
solid content) / MW of coupling agent
= 180 X 0.585 / 167.3 = 0.6294 moles

That is, $X/Y = 1.085/0.6294 = 1.7238$.

Equation (II):

20 x (sum of solid content of metal oxide)
= amount of sol added X solid content
= 300 X 0.217 = 65.1g

y (sum of solid cont. of silane coupling agent)

= amt. of coupling agent added X solid cont.

= 180 X 0.585 = 105.3g

That is, $x/y = 65.1/105.3 = 0.6182$.

Comparative Example 2:

5 320g of SiO₂, commercially available from Shokubai-
Kasei Kabushikikaisha under the trade name "Oscal (S7.A8),
having a solid content of 20.5% by weight and MW of 60,
and 180g of hydrolyzed γ -glycydoxypropyltrimethoxysilane
having a solid content (after hydrolysis) of 58.5% by weight
10 and MW of 167.3 were mixed, and 5g of a silicone surfactant
and 2g of aluminum acetylacetonate (curing catalyst) were
added to the mixture to make a hard coating solution

In this comparative example, a mixing ratio of the sol
and silane coupling agent used did not satisfy the above-
15 described conditions (I) and (II) as described below.

Condition (I):

X (sum of molar concentration of metal oxide)

= (amt. of sol added X solid cont.) / MW of metal
oxide

20 = 320 X 0.205 / 60 = 1.0933 moles

Y (sum of molar conc. of silane coupling agent)

= (amt. of coupling agent added X solid
cont.) / MW of coupling agent

$$= 180 \times 0.585 / 167.3 = 0.6294 \text{ moles}$$

$$\text{That is, } X/Y = 1.0933/0.6294 = 1.7370.$$

Condition (II):

x (sum of solid content of sol)

$$5 \quad = \text{amount of sol added} \times \text{solid content}$$

$$= 320 \times 0.205 = 65.6\text{g}$$

y (sum of solid cont. of silane coupling agent)

$$= \text{amt. of coupling agent added} \times \text{solid cont.}$$

$$= 180 \times 0.585 = 105.3\text{g}$$

$$10 \quad \text{That is, } x/y = 65.6/105.3 = 0.6229.$$

Test Example:

A lens consisting of a copolymer of m-xylene diisocyanate and 4-mercaptomethyl-3,6-dithia-1,8-octane diol and having a refractive index of 1.67 commercially available
 15 from Mitsui Toatsu Kagaku Kabushikikaisha under the trade name "MR-7" was coated with the hard coating solution prepared in each of the above-described Examples 1 to 5 and Comparative Examples 1 and 2 in accordance with a dip coating method to form a hard-coated layer having a layer
 20 thickness of $2 \mu\text{m}$. A multicoated layer consisting of SiO_2 to the thickness of $\lambda/4$, ZrO_2 to $\lambda/4$ and SiO_2 to $1/4\lambda$, was then deposited onto the hard-coated layer followed by the

forming of a watertarnish-preventing layer consisting of a fluorine-containing silicone and having a layer thickness of 2 nm in accordance with a dip coating method. The fluorine-containing silicone is fluoroalkylsilane coating solution commercially available from Toshiba Silicon Col, Ltd under the trade name of XC98-A5479.

The thus obtained lenses were tested in accordance with the following methods.

(1) Determination of Cracks

10 The lenses with the applied multicoated layers were run over horse hair, sliding under a load of 1 kg 50 times, marring the multicoated layer. Then the lens was contained and retained in a sunshine weatherometer, and, after 30 hours, its multicoated layer and hard-coated layer were
15 evaluated in a visual inspection and in a microscopic inspection under illumination of a Zr lamp to ascertain whether cracks were produced in the layers. After completion of the inspection, the lens was stored in a room, and, after about one month, the multicoated layer and hard-coated layer
20 were again evaluated in a visual inspection to examine how the cracks had extended with time. The evaluation of the cracks was made with reference to the following criteria:

- no crack was produced in the hard-coated layer;
- ~△ cracks in the range of 10 lines or less were

produced in the hard-coated layer; and

X cracks in the range of more than 10 lines were produced in the hard-coated layer. The results of the evaluation are summarized in the following Table 1.

5 (2) Other Properties

Other properties of the lenses with the applied multicoated layer were determined in accordance with the following methods.

The scratch resistance of the lens was determined by
10 wiping the lens with steel wool under the load of 1 kg thereby making scratches on the surface of the multicoated layer. The scratch resistance was determined by measuring the wiped lens using a haze-measuring device.

An adhesion property of the lens was determined with
15 regard to adhesion in warm water and humidity adhesion.

A weather resistance of the lens was determined in accordance with the test method using a sunshine weatherometer.

A heat resistance of the lens was determined by leaving
20 the multi-coated lens to stand for 2 days after completion of the multi coating and then heating the lens at a specified temperature for 10 minutes. The multicoated layer and hard-coated layer were inspected to ascertain whether cracks were produced therein.

The values obtained upon the above determination processes were totally evaluated based on the following criteria.

- no crack was produced in the hard-coated layer;
- 5 X formation of cracks was observed in the hard-coated layer. The results of the evaluation are also summarized in Table 1.

Table 1

	<u>Examples</u>					<u>Comp. Ex.</u>	
	1	2	3	4	5	1	2
10							
Refractive Index	1.67	1.60	1.49	1.61	1.64	1.59	1.49
Value of Eq. (I)	3.1	3.1	3.1	2.1	2.1	1.7	1.7
15 Value of Eq. (II)	1.1	1.1	1.1	0.7	0.7	0.6	0.6
Cracks	○	○	○	○~△	○~△	×	×
Other Properties	○	○	○	○	○	○	○

20

As can be appreciated from the above descriptions, with the present invention, it becomes possible to

easily determine a suitable mixing ratio of the metal oxide sol and the silane coupling agent in the preparation of the hard coating solution. Further, the incorporation of the sol and the coupling agent in the thus determined mixing ratio
5 enables the production of optical plastic lenses having high qualities without affecting properties of the hard-coated layer such as scratch resistance, adhesion property, weathering resistance, heat resistance and the like. Furthermore, even if any defect such as an abrasion or a
10 scratch is contained in the multicoated layer, no formation of cracks due to the influence of ultraviolet radiation etc is induced in the hard-coated layer.

Although the invention has been described with reference to particular means, materials and embodiments, it
15 is to be understood that the invention is not limited to the particulars disclosed and extends to all equivalents within the scope of the claims.

CLAIMS:-

1. A hard coating solution for optical plastic lenses, which solution contains at least one metal oxide and at least one silane coupling agent in an amount which satisfies at least
5 one of the following conditions (I) and (II):

$$X/Y \geq 2.0 \quad \dots \text{ (I)}$$

$$x/y \geq 0.7 \quad \dots \text{ (II)}$$

in which

X is the sum of the molar concentration of the metal
10 oxide,

Y is the sum of the molar concentration of the silane coupling agent,

x is the sum of the solid content of the metal oxide, and

y is the sum of the solid content of the silane coupling
15 agent.

2. A hard coating solution for optical plastic lenses according to claim 1 which contains at least a first metal oxide having a first refractive index and a second metal oxide having a second refractive index different from said
20 first refractive index as said metal oxide.

3. A hard coating solution for optical plastic lenses according to claim 2 in which said first metal oxide and said second metal oxide have substantially the same particle diameter.

4. A hard coating solution for optical plastic lenses according to any preceding claim in which said at least one metal oxide comprises metal oxide particles having coated thereon said at least one silane coupling agent.

5 5. A hard coating solution for optical plastic lenses according to any preceding claim wherein said metal oxide is used as a metal oxide sol.

6. A hard coating solution for optical plastic lenses according to claim 5 wherein said metal oxide sol contains
10 not less than about 20% by weight of fine particles of the metal oxide having an average particle diameter of about 1 to 200 μm .

7. A hard coating solution for optical plastic lenses according to any preceding claim which satisfies at least one
15 of the following conditions:

$$X/Y \leq 10$$

$$x/y \leq 5$$

8. A hard coating solution for optical plastic lenses substantially as herein described.



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Application No: GB 9726069.9
Claims searched: 1-8

Examiner: C A Clarke
Date of search: 2 March 1998

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.P): C1A (APG1A, APG1B, APG1C, APG1D, APG1E, APG1S); C2R (RSU)
Int CI (Ed.6): G02B 1/10,1/11
Other: ONLINE: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0379343 A SHIN-ETSU CHEMICAL see whole document	1 and 5 at least
X,P	Derwent Abstract 97-189325 & JP090049901A ASAHI OPTICAL	1 and 5 at least
X	Derwent Abstract 88-046408 & JP630004201A SEIKO EPSON	1 and 5 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
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