

Antireflection filter for display apparatus

Field of the Invention

This invention relates to an antireflection filter for a display apparatus which filter has excellent stain resistance, scratch resistance and processing resistance. The filter is also used as a front surface for CRT.

Prior Art

When an object is watched through a transparent material, strong reflected light or clear reflected image is troublesome. For example, a reflected image called ghost or flare appears in the eyeglass lenses, which gives discomfort to our eyes. A reflected light on a glass surface also causes the problem that owing to the light, the reflection in a looking glass becomes unclear.

The reflection has so far been prevented by covering a substrate with a substance having a reflective index different from that of the substrate by the vacuum deposition or the like method. In the above method, it is known to be important to select the thickness of a substance covering the substrate in order to obtain the highest antireflective effects. For example, it is known that in a single layer, the minimum reflective index, in other words, maximum transmission is brought about when the optical film thickness of a substance having a refractive index lower than that of a substrate is selected to be the one fourth of the wavelength of the target light or multiple thereof by an odd number.

The term "optical film thickness" used herein means the product obtained by multiplying a refractive index of a film-forming material by said film. It is also possible to form a multi-layer antireflection layer and for it, several proposals are made for the selection of the film thickness (refer to "Optical Technique Contact", Vol.9, No. 8, pp17(1971)). On the other hand, described in Japanese Patent Application Laid-Open Nos. SHO 58-46301, SHO 59-49501 and SHO 59-50401 are a method of forming a multi-layer antireflection film, which can satisfy the above-described conditions for the

optical film thickness, by using a liquid composition. In recent years, antireflection optical products using glass as a substrate are devised and put into industrial use by making use of its advantages such as weighing safety and handling ease. Many of such optical products adopt as their structure a film having silicon dioxide on its outermost layer.

Problems Sought for Solution by the Invention

The antireflection film formed by the deposition method adopts a film-forming material composed mainly of an inorganic oxide or inorganic halide. When used for a glass substrate, the antireflection film containing such an inorganic substance essentially has a high surface hardening but is accompanied with the problems that stains by hand, finger print, hair liquid or hair spray appear clearly and moreover, they cannot be removed easily. It also involves the problem that inferior slip properties on the film surface make a scar bigger. It is accompanied with further problems that wettability with water is large so that rain drops or water splash attaching to the film spreads thereover and, for example, an object reflected on eyeglass lenses looks distorted over a wide area.

In antireflection films described in Japanese Patent Application Laid-Open Nos. SHO 58-46301, 59-49501 and 59-50401, it is necessary to incorporate an inorganic substance typified by fine silica particles in an amount not smaller than 30 wt.% in the outermost layer of the film in order to impart the surface with high surface hardness. The antireflection film available from such film composition is accompanied with the problem that due to inferior surface slip properties, the film tends to be damaged by the abrasion with a cloth or the like.

Various surface treating agents are proposed and put on the market with a view to overcoming the above-described problems. Since any one of them is soluble in water or a solvent, the effects once imparted to the surface are transient and lack in durability. It is also reported in Japanese Patent Application Laid-Open No. HEI 3-266801 that a fluorine base resin layer is formed to impart a film with water repellency. The formation of the fluorine base resin layer heightens water repellency but does not bring about satisfactory results against friction or abrasion.

It has been found that the surface treatment with a perfluoropolyether compound exhibits high effects for the improvement of friction or abrasion resistance or stain characteristics, but concerning chemical stability, these effects lower markedly, for example, by the treatment with a solvent. This is considered to be caused by the mutual action with SiO_2 on the surface.

Means for the Solution of the Problems

The present inventors have carried out an extensive investigation with a view to overcoming the above problems, leading to the present invention which will be described below. Described specifically, the present invention has the following constitution.

An object of the present invention is to overcome the problem concerning abrasion resistance or stain resistance of an antireflection filter for a display apparatus by applying onto the surface of a single-layer or multi-layer antireflection film, said film having an outermost layer mainly composed of silicon dioxide and being disposed on a glass substrate, with a perfluoropolyether-containing alkoxysilane compound represented by the following formula 1: $\text{R}_f\text{COR}_1\text{-R}_2\text{-Si(OR}_1\text{)}$, wherein R_f represents a perfluoropolyether group, R_1

generally represents an atom or atomic group of O, NH, S or the like, R_1 represents an alkylene chain which is not particularly limited in the number of carbon atoms, and R_2 represents an alkyl group which is not particularly limited in the number of carbon atoms, and then drying the uncoated surface under heat, thereby covering the surface with the compound.

The alkoxysilane compound having a perfluoropolyether group represented by the above formula 1 contains in its molecular structure an alkoxy silane group so as to impart an interaction with an SiO_2 surface. By heating, sol-gelation reaction occurs on the surface, whereby a firm bond is formed. In this way, the problems of the conventional antireflection film such as unsatisfactory solvent resistance can be overcome. In addition, the compound according to the present invention contains a fluorine compound in its molecule so that by the application of the compound, the surface is imparted with water repellency and thereby has improved water stain resistance. Instead of a perfluoropolyether group, the use of a perfluoroalkyl-containing silano group is considered but it is not satisfactory in abrasion resistance and friction characteristics. Satisfactory abrasion resistance or friction characteristics can be obtained by using an alkoxysilane

compound containing in its molecular structure a perfluoropolyether group excellent in tribology properties.

Modes for Embodying the Invention

The single layer or multi-layer antireflection film of the present invention formed on a substrate has an outermost layer composed mainly of silicon dioxide, but the constitution is not limited thereto and various combinations can be employed. In particular, the constitution of the substances which form layers below the outermost layer should be determined experimentally according to necessary performances, for example, heat resistance, anti-reflective properties, color of reflected light, durability and surface hardening.

Examples of the forming method of various inorganic substances, such as silicon dioxide, into film for the formation of the antireflection film as described above include various PVD methods (physical vapor deposition method) typified by vacuum deposition method, ion plating method and sputtering method. Preferred examples of the inorganic substance suited for the PVD method include, in addition to SiO_2 , inorganic oxides such as Al_2O_3 , ZrO_2 , TiO_2 , Ta_2O_5 , SiO , HfO_2 , ZnO , $\text{In}_2\text{O}_3/\text{SnO}_2$, TiO , Ti_2O_3 , Y_2O_3 , Sb_2O_3 , MgO and CeO_2 .

The outermost layer of the antireflection film formed by the above-exemplified PVD method is preferably composed of silicon dioxide. If it is not composed of silicon dioxide, sufficient surface hardness cannot be obtained, improvements in stain resistance and scratch resistance, which are the objects of the present invention, are not attained and durability of these performances do not appear eminently. The present invention relates to a material which covers an antireflection layer so that a deposition material is not particularly limited to silicon dioxide.

The thickness of the outermost layer should be determined according to the necessary performances other than the anti-reflective effects. For the purpose of bringing about the maximum anti-reflective effects, it is preferred to select an optical thickness of the outermost layer to be the one fourth of the wavelength of the target light or multiple thereof by an odd number because such selection provides the minimum reflective index, in other words, the maximum transmittance.

No particular limitation is imposed on the lower portion of the outermost layer. It is possible to form the outermost

layer directly on the substrate but in order to attain more eminent anti-reflective effects, it is effective to cover the substrate with at least one layer having a refractive index higher than that of the outermost layer. Concerning the film thickness of the multi-layer antireflection film and the selection of a refractive index, there are some proposals (refer to "Optical Technique Contact", Vol. 9, No. 8, pp17, (1971)).

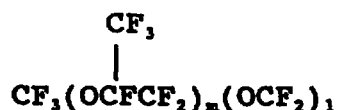
In the present invention, the surface of a single layer or multi-layer antireflection film having an outermost layer substantially formed of silicon dioxide is coated with an alkoxysilane compound containing a perfluoropolyether group having lubricating action and then the coated film is subjected to drying treatment, whereby covering is effected. No particular limitation is imposed on the molecular weight of the perfluoropolyether compound but the compound having a number-average molecular weight of 500 to 10,000, more preferably 500 to 2,000 is used in consideration of stability and handling ease.

Examples of the recurring unit structure in the perfluoropolyether group of the present invention include, but

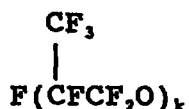
not limited to, the following ones.



Chemical formula 1



Chemical formula 2



wherein 1, m, n, k, p and q in the chemical structure of the perfluoropolyether group each stands for an integer of 1 or larger.

No particular limitation is imposed on the thickness of the film composed of a perfluoropolyether-containing alkoxysilane compound, but 0.5 nm to 50 nm is preferred from the viewpoint of the relationship between surface hardness and the balance of antireflective properties with a contact angle of repose.

In the present invention, it is preferred that the surface of the antireflection film to be coated is cleaned prior to the application of the perfluoropolyether-containing alkoxysilane

compound. Upon cleaning, stain removal by a surfactant, degreasing by an organic solvent, steam cleaning by Freon or the like is applied. It is also effective to subject the antireflection film to various pre-treatments for the purpose of improving adhesion and durability. Examples of the particularly preferred method include treatment with an activating gas and treatment with a chemical such as an acid or alkali.

As the coating method, those employed in the ordinary coating work can be applied but spin-coating, dip coating and curtain flow coating are preferably employed from the viewpoints that they bring about uniform anti-reflective effects and can control reflection interference color. A method of impregnating a material such as paper or cloth in a liquid, followed by coating and casting is also preferably used from the viewpoint of operating efficiency.

These curable substances containing an organic material are generally coated after diluted in a volatile solvent. No particular limitation is imposed on the solvent but it should be determined after the stability of the composition, wettability with a silicon dioxide film, volatility or the like

is taken into consideration.

It is generally known that an acid base is used as a catalyst when a solution of the perfluoropolyether-containing alkoxy silane compound used in the present invention is prepared. Upon preparation, the addition of a carbonyl compound such as acetylacetone heightens the reactivity.

Examples of the glass substrate usable in the present invention include soda glass, lead glass, hard glass, quartz glass, liquid crystal glass ("Kagaku Benran" Introduction, P.I-537, ed. by The Chemical Society of Japan). For CRT, silicate glass containing strontium (St) or barium (Ba) is preferably employed, while an alkali-free glass is preferably used for a liquid crystal display device. Examples of the glass substrate are however not limited to the above-exemplified ones.

Examples

The characteristics of the present invention will hereinafter be shown clearly by Examples. It should however be borne in mind that the present invention is not limited to or by the following Examples. Incidentally, the designations

of part in the Examples indicate part by weight.

Examples 1-10

(1) Formation of an antireflection film

Onto the panel surface of a cathode ray tube, ITO (tin-oxide-doped indium oxide, Indium Tin Oxide) was deposited to give a thickness of 130 nm, followed by the deposition of SiO_2 to give a film thickness of 80 nm by the sputtering method, whereby an antireflection film was formed.

(2) Preparation of a coating composition which contains a perfluoropolyether-containing alkoxysilane compound

To 0.4 part of each of the perfluoropolyether-containing alkoxysilane compounds (having a number-average molecular weight of 2,000) described in Table 1 as Lubricants 1 to 10, 380 parts of hexane and 20 parts of an alcohol were added and mixed to form a uniform solution. The resulting solution was filtered through a membrane filter, whereby a coating composition was obtained.

Table 1

Lubricant	R_1	R_1	R_2	R_3
Lubricant 1	$F(CF_2CF_2CF_2O)_1CF_2CF_2CH_2$	O	C_3H_6	CH_3
Lubricant 2	$F(CF_2CF_2CF_2O)_1CF_2CF_2CH_2$	O	C_3H_6	CH_3
Lubricant 3	CF_3 $CF_3(OCF CF_2)_1O CF_2$	O	Ph*	CH_3
Lubricant 4	CF_3 $CF_3(OCF CF_2)_1O CF_2$	O	Bz	CH_3
Lubricant 5	$F(CF_2CF_2CF_2O)_1CF_2CF_2CH_2$	NH	C_3H_6	CH_3
Lubricant 6	CF_3 $CF_3(OCF CF_2)_1O CF_2$	NH	C_3H_6	C_2H_5
Lubricant 7	$F(CF_2CF_2CF_2O)_1CF_2CF_2CH_2$	NH	Ph	C_2H_5
Lubricant 8	CF_3 $CF_3(OCF CF_2)_1O CF_2$	NH	$C_{10}H_{20}$	C_2H_5
Lubricant 9	CF_3 $CF_3(OCF CF_2)_1O CF_2$	NH	Bz*	C_2H_5
Lubricant 10	$F(CF_2CF_2CF_2O)_1CF_2CF_2CH_2$	S	C_3H_6	C_2H_5

*Ph represents C_6H_5 and Bz represents $CH_2C_6H_4CH_2$.

(3) Coating and Drying

Onto the surface of the antireflection film obtained above in (1), the coating composition prepared in (2) was dip-coated at a drawing velocity of 5 cm/min and was then dried at 70°C to cover the film with the composition, whereby an optical product having anti-reflective properties was obtained.

(4) Performance evaluation

The performance of the optical product so obtained was tested concerning the below-described evaluation items (a) to (e). The test results are shown in Table 2. Incidentally, "before" and "after" in the table indicate the test results of solvent resistance before and after washing with ethanol, respectively.

(a) Test on stain resistance

On the surface of a filter, 5 ml of tap water were made fall in drops. After it was allowed to stand in the atmosphere of room temperature for 48 hours, remaining conditions of water stain after it was wiped with a cloth were observed. In the case where the water stain was removed, the evaluation was "good", while in the case where water stain was not removed, the evaluation was "poor".

(b) Surface slip properties

The scratched degree of the surface when 300 g of a load were applied to the point of a propelling pencil was evaluated. The judgment was made as follows:

O: no scratches Δ: small scratches x: marked scratches

(c) Test on abrasion resistance

Abrasion resistance was tested by confirming whether the surface of the antireflection film took scratches or not when rubbed 30 times with Steel Wool #0000 under a load of 200 g.

O: no scratches Δ: small scratches x: marked scratches

(d) Resistance to hand stain

Resistance to hand stain was visually evaluated.

O: not so marked stain Δ: easily removable stain x: marked stain

(e) Contact angle

The remaining ratio of the lubrication film or staining by water or oil was judged by measuring the contact angles of water and methylene iodide. The values before and after washing of the surface with ethanol were measured in order to

investigate resistance and stability against solvent.

Table 2

Ex.	Lubri-cant	Stain resistance		Surface slip properties		Abrasion resistance test		Hand-stain resistance		Contact angle (deg.)			
										H ₂ O	CH ₂ I ₂	H ₂ O	CH ₂ I ₂
		Before	After	Before	After	Before	After	Before	After	before ethanol washing		after ethanol washing	
Ex. 1	Lubri-cant 1	Good	Good	O	O	O	O	O	O	115	91	114	90
Ex. 2	Lubri-cant 2	Good	Good	O	O	O	O	O	O	113	93	112	93
Ex. 3	Lubri-cant 3	Good	Good	O	O	O	O	O	O	116	94	115	94
Ex. 4	Lubri-cant 4	Good	Good	O	O	O	O	O	O	112	92	113	91
Ex. 5	Lubri-cant 5	Good	Good	O	O	O	O	O	O	115	91	115	92
Ex. 6	Lubri-cant 6	Good	Good	O	O	O	O	O	O	114	94	113	94
Ex. 7	Lubri-cant 7	Good	Good	O	O	O	O	O	O	117	92	115	91
Ex. 8	Lubri-cant 8	Good	Good	O	O	O	O	O	O	115	95	116	94
Ex. 9	Lubri-cant 9	Good	Good	O	O	O	O	O	O	113	92	115	91
Ex. 10	Lubri-cant 10	Good	Good	O	O	O	O	O	O	115	94	114	93

Examples 11 to 15

Using the coating composition described in Example 6 and in a similar manner to Example 6 except that drying after

coating was effected within a temperature range of from 30 to 150°C, tests were conducted. Results are shown in Table 3. Incidentally, the stain resistance and surface slip properties were omitted because they resulted in good similar to the test results of the abrasion resistance and hand stain resistance. As can be understood from the test results, heating temperatures exceeding 100°C are satisfactory for properties but are not desired because owing to a large thermal capacity of a panel glass, it is difficult to raise the temperature and besides, they put thermal stress on the antireflection film, resulting in the formation of cracks on the film.

Table 3

Ex.	Lubri- cant	Reaction temperature (°C)	Hand-stain resistance		Abrasion resistance test		Contact angle (deg.)			
							H ₂ O	CH ₂ I ₂	H ₂ O	CH ₂ I ₂
			Before	After	Before	After	Before ethanol washing		After ethanol washing	
Ex. 11	Lubri- cant 1	30	O	O	O	O	112	89	105	81
Ex. 12	Lubri- cant 2	50	O	O	O	O	113	91	112	93
Ex. 13	Lubri- cant 3	70	O	O	O	O	114	94	113	94
Ex. 14	Lubri- cant 4	100	O	O	O	O	115	93	113	92
Ex. 15*	Lubri- cant 5	150	O	O	O	O	115	91	115	92

*Deformation of the substrate was found.

Comparative Examples 1 to 5

In Comparative Example 1, the antireflection film was not coated with a coating composition containing a perfluoropolyether-containing alkoxysilane compound, while in Comparative Examples 2 to 5, coating was conducted in a similar manner to Examples 1-10 except that the fluorine compound described in Table 4 was used instead of the compound described in Examples 1-10. Test results before washing with ethanol are shown in Table 4. As is apparent from these results, these antireflection films are inferior particularly in surface slip properties even before washing with ethanol.

Table 4

Lubricant		Stain resistance	Surface slip properties	Abrasion resistance test	Hand-stain resistance
Comp.Ex. 1	No coating agent	Poor	x	O	x
Comp.Ex. 2	Polytetrafluoroethylene	Good	Δ	O	O
Comp.Ex. 3	Polyvinylidene fluoride	Good	Δ	O	O

Comp.Ex. 4	Tetrafluoroethylene-ethylene copolymer	Good	Δ	O	O
Comp.Ex. 5	Chlorotrifluoroethylene-ethylene copolymer	Good	Δ	O	Δ

Comparative Examples 6 to 9

In Comparative Examples 6 to 9, the antireflection film was coated in a similar manner to Examples 1 to 10 except that compounds described in Table 5 were employed instead of the compounds described in Examples 1-10. Test results before washing with ethanol are shown in Table 5. When the compound is a perfluoroalkoxisilane compound as in Comparative Example 9, the film is inferior in the surface slip properties.

Table 5

Comp.Ex.	Molecular structure	Stain resistance	Surface slip properties	Abrasion resistance test	Hand-stain resistance
Comp.Ex. 6	$\text{RN}^+\text{H}_3\text{O}^+\text{OCCF}_2(\text{CF}_2\text{O})_n(\text{C}_2\text{F}_4\text{O})_m\text{CF}_2\text{COO}^-\text{N}^+\text{H}_3\text{R}^*$	Good	O	O	O
Comp.Ex. 7	$\text{F}(\text{CF}_2\text{CF}_2\text{CF}_2\text{O})_1\text{CF}_2\text{CF}_2\text{COO}^-\text{N}^+\text{H}_3\text{R}$	Good	O	O	O
Comp.Ex. 8	$\text{CF}_3\text{F}(\text{CF}_2\text{CF}_2\text{O})_1\text{CF}_2\text{CF}_2\text{COO}^-\text{N}^+\text{H}_3\text{R}$	Good	O	O	O
Comp.Ex. 9	$\text{C}_8\text{F}_{17}\text{C}_2\text{H}_4\text{Si}(\text{OC}_2\text{H}_5)_2$	Good	Δ	O	O

*R = $\text{C}_{16}\text{H}_{37}$

When the compound is a perfluoropolyether compound as in Comparative Examples 6 to 8, there are no problems in properties such as abrasion resistance or slip properties before washing with ethanol. The results of the measurement after washing with ethanol are shown in Table 6. As also apparent from these results, properties such as stain resistance, surface slip properties and hand-stain resistance show marked deterioration after washing with ethanol, compared with those before washing with ethanol.

Table 6

Comp. Ex.	Stain resistance	Surface slip properties	Abrasion resistance test	Hand-stain resistance
Comp.Ex. 6	Inferior	Δ	O	x
Comp.Ex. 7	Inferior	Δ	O	x
Comp.Ex. 8	Inferior	Δ	O	x

Advantages of the Invention

The antireflection filter for display apparatus according to the present invention, which is obtained by coating the surface with a perfluoropolyether-containing alkoxysilane compound and then drying and curing the coated surface, has the

characteristics as described below:

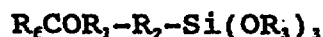
1. The filter is resistant to fingerprints or hand stain and does not show the stain. Such effects lasts eminently.
2. Even if the filter stained with fur is dried, the fur can be removed easily.
3. The filter has good surface slip properties.
4. The filter is resistant to the sticking of dust or the like so that it can be used conveniently.
5. The filter has durability against abrasion.

As described above, the antireflection filter for display apparatus according to the present invention is resistant to hand stain, fur or the like and does not show stains compared with the ordinary antireflection film. Furthermore, the lubrication properties of the perfluoropolyether-containing alkoxysilane compound make it possible to provide the filter with advantages that stains can be removed easily, the filter is resistant to scratches owing to its good surface slip properties, and the like. Because of good durability against abrasion, in addition to the above-described performances, the filter is excellent as a filter for CRT.

Claims

Claim 1. An antireflection filter for a display apparatus, wherein an outermost surface of a single layer or multi-layer antireflection film formed on a glass substrate has been covered with a perfluoropolyether-containing alkoxysilane compound represented by the following formula 1:

Formula 1



wherein R_f represents a perfluoropolyether group,

R_1 generally represents an atom or atomic group of O, NH, S or the like,

R_2 represents an alkylene chain, and

R_3 represents an alkyl group.

Claim 2. A filter for a display apparatus having antireflective properties according to claim 1, wherein the outermost surface is covered by applying a perfluoropolyether-containing alkoxysilane compound represented by the formula 1 on to the outermost surface and then drying at a temperature of 100°C or lower.



Claim 3 . A filter for a display apparatus having antireflective properties according to claim 1 or 2, wherein the outermost surface of the single layer or multi-layer antireflection film formed on the glass substrate is composed mainly of silicon dioxide.



* C L M S *