

[54] SURFACE PROTECTIVE COATING ON AN ARTICLE AT LEAST SURFACE OF WHICH IS FORMED OF A SYNTHETIC RESIN

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[51] Int. Cl. **B44d 5/00**; B32b 3/10; B32b 7/02

[58] Field of Search 117/37 R, 38, 138.8 R, 117/138.8 PV, 138.8 UA, 70 A, 70 R, 69, 72, 73, 75; 161/146, 71 R; 350/61, 175; 351/62, 66

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[57] ABSTRACT

An inorganic protective coating of a thickness of from 400 A. to 5 microns is applied to a surface of an article at least the surface of which is formed of a synthetic resin to increase the surface hardness of the said article without any sacrifice in the inherent properties of the said article. The protective coating comprises discrete islets of an inorganic solid each having an area of at most 7×10^4 square microns and being firmly deposited on the synthetic resinous substrate, and being formed by evaporating an inorganic material through a shadow mask or screen onto the surface of the said article.

62 Claims, 16 Drawing Figures

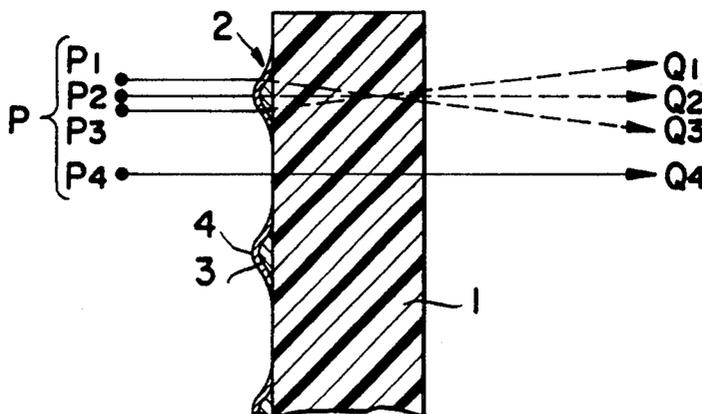


FIG. 1

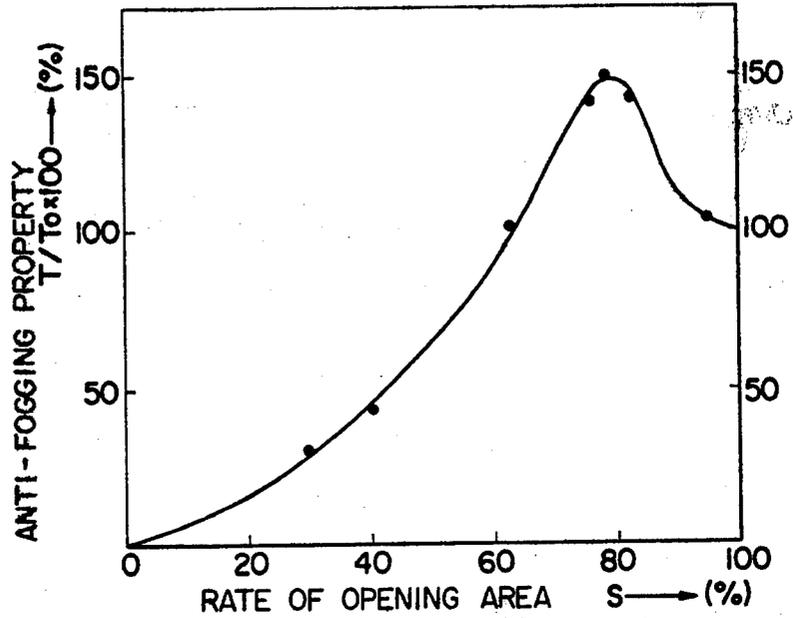


FIG. 2

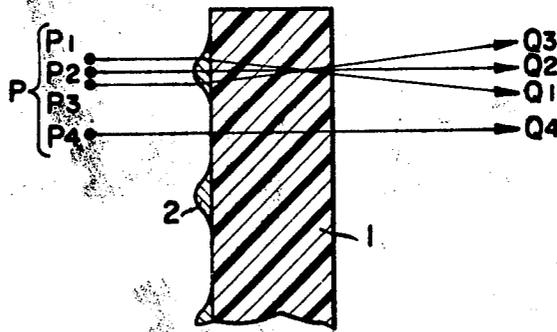


FIG. 3

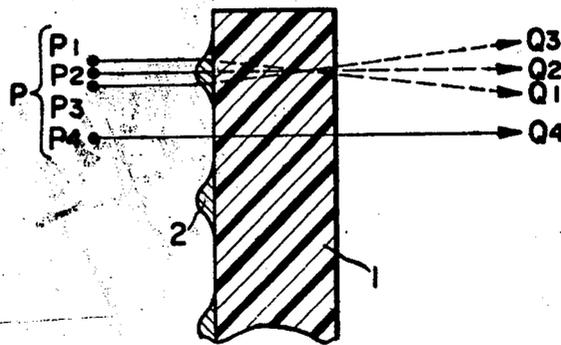


FIG. 4

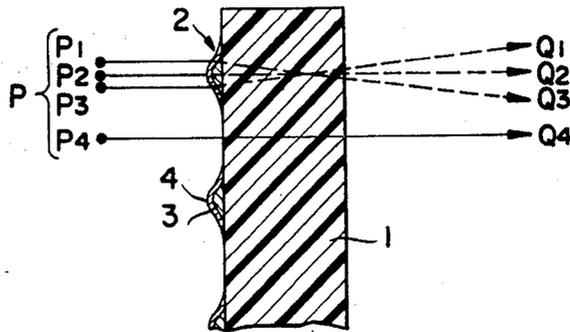


FIG. 5

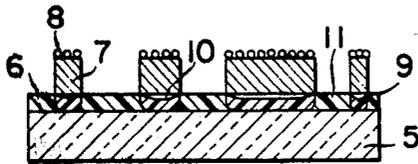


FIG. 6

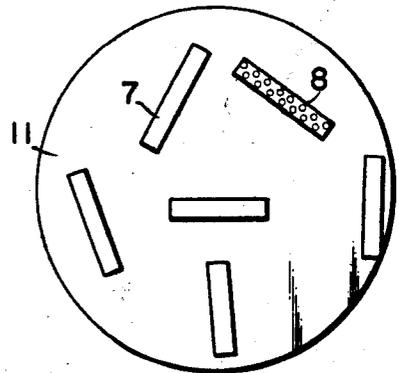


FIG. 7

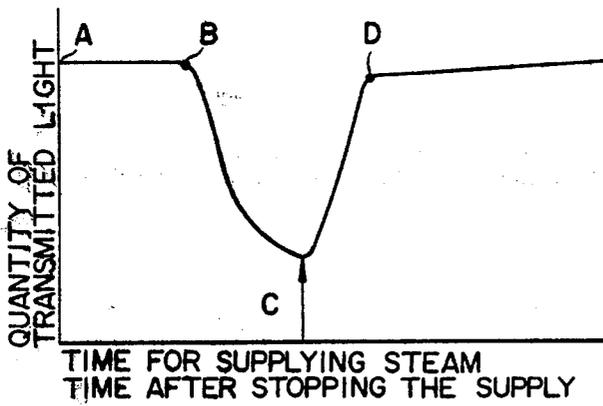


FIG. 8

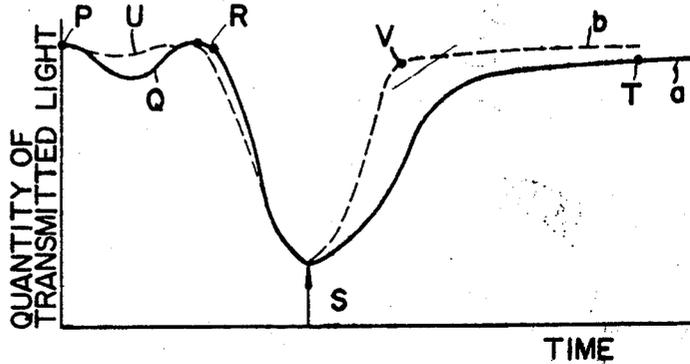


FIG. 9

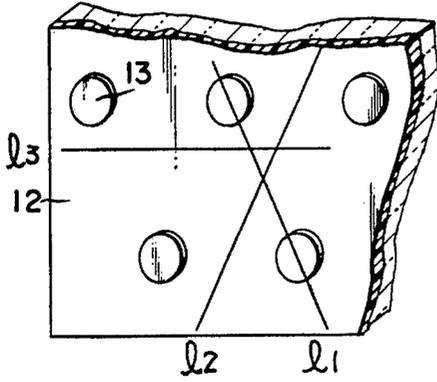


FIG. 10(a)

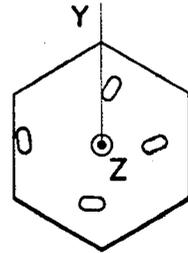


FIG. 10(b)

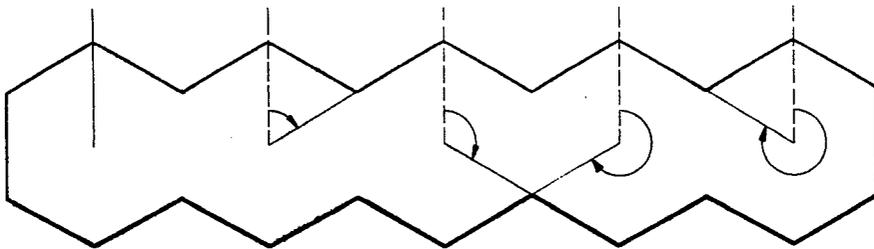


FIG. 12

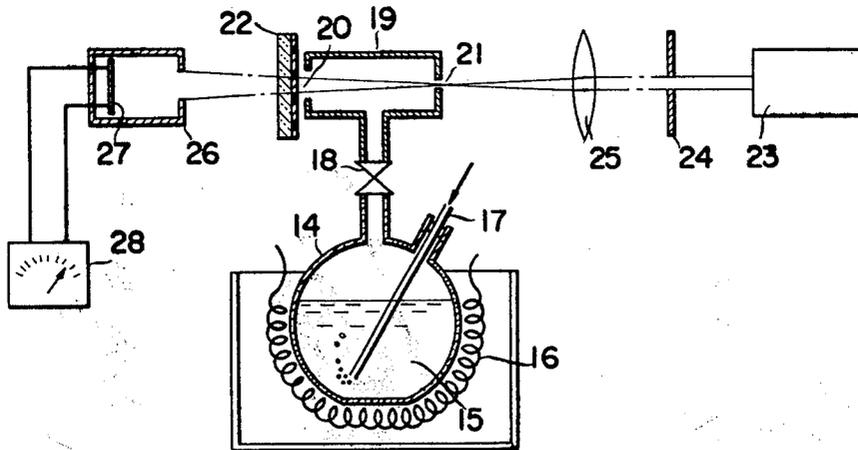


FIG. 11.

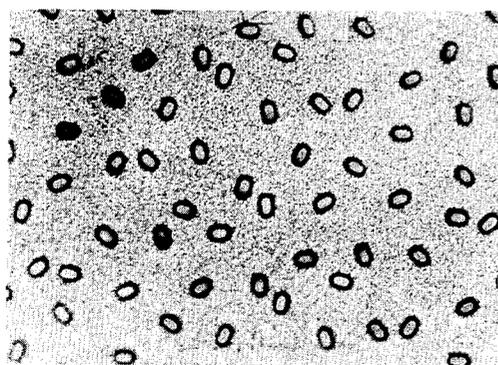


FIG. 13.

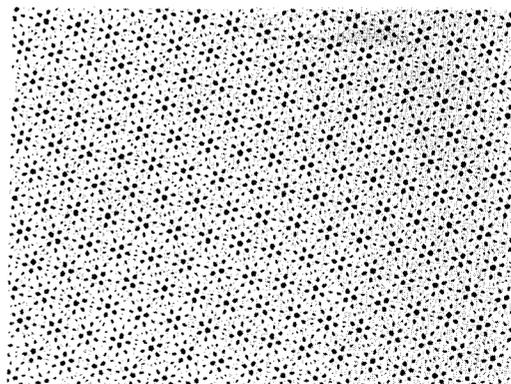


FIG. 14.

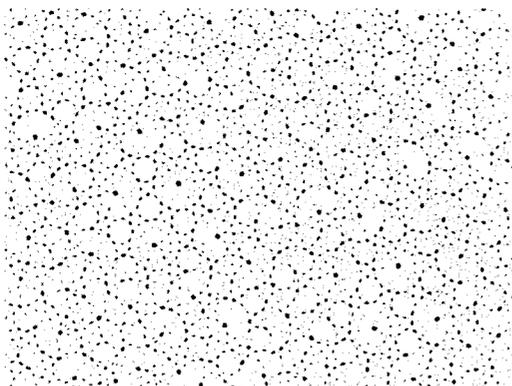
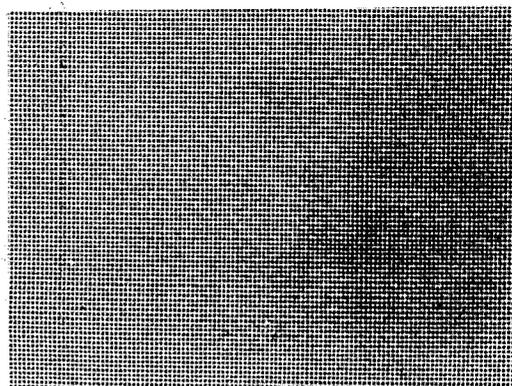


FIG. 15.



**SURFACE PROTECTIVE COATING ON AN
ARTICLE AT LEAST SURFACE OF WHICH IS
FORMED OF A SYNTHETIC RESIN**

This invention relates to a surface protective coating for shaped article formed of, at least in their surface portion, synthetic resins and a method of forming it. In particular, it concerns a surface protective coating for an article at least a surface of which is formed of a synthetic resin, particularly of a hydrophilic polymer, which possesses many desirable characteristics, e.g. non-fogging property, and increases the surface hardness of the aforesaid body without sacrifice in inherent desirable physical properties of the aforesaid article.

Recently, the use of transparent plastics as window glass for buildings, automobiles, trains or aeroplanes or as doors has been attempted and in some fields of applications plastic windows or doors have already been put to practical use. However, the plastic windows or doors have the drawback of being easy to scratch due to their poor surface hardness. It has also been attempted to apply a transparent hydrophilic polymer coating to the surface of an inorganic window glass of a building, automobile, train or aeroplane, eyeglasses, goggles or optical lenses to render them non-fogging through absorption by the coating of water droplets deposited on their surfaces. However, such coated films of hydrophilic polymers are easy to scratch even in the dried state as are ordinary plastics moldings because of poor surface hardness and this is much more so in the moistened state because a hydrophilic polymer film is swelled by absorption of water.

It is known to improve the surface hardness of plastic substrates by application to their surfaces an inorganic protective coating of a metallic oxide, nitride, fluoride or silicide or other inorganic solid. However, a continuous film of such an inorganic substance, even if it has a sufficient initial surface hardness, is cracked or otherwise injured by internal stress due to difference in the thermal expansion coefficient between the coating film and the substrate when put to practical use or subjected to weathering, boiling, repeated heating and cooling or exposure test. The crack or other injury results in a decreasing of the surface hardness, voids in the film and, finally, scaling-off of the film from the substrate.

At present the problem of the internal stress has been solved at least partly by applying a protective coating to a substrate heated to an elevated temperature, by heat treatment in vacuo or in air treatment just after application of the protective coating to minimize the internal stress, or by incorporation of one or more additives in the coating to minimize the difference in thermal expansion coefficient between the coating and the substrate. However, it is difficult to eliminate completely the internal stress by the former method and, in addition, the former method is inadequate for plastic substrates because of insufficient thermal resistance of plastic substrates for a sufficient heat treatment. The latter method has poor practicality because of the necessity of determining the composition of a coating in each case.

The prior protective coating films are completely continuous throughout the surface, so that, in the case where the coating material is opaque, the body coated therewith becomes non-transmissible. When such an opaque protective coating is applied to a body consisting of a glass substrate having thereon a coating layer

of a hydrophilic polymer, the body loses its photo transmissibility and, in addition, the aforesaid hydrophilic polymer layer cannot exhibit its defogging effect since it is completely isolated from the air by the continuous protective coating film.

Accordingly, it is an object of the present invention to provide an improved protective coating film for an article at least the surface of which is formed of synthetic resins.

It is another object of the present invention to provide a protective coating film for a transparent synthetic resin article which has substantially no adverse effect on the photo transmissibility of the article.

It is a further object of the present invention to provide a non-fogging protective coating film for an article of which at least the surface is formed of a hydrophilic polymer.

It is a still further object of the present invention to provide a method of enhancing the surface hardness of shaped bodies having a relatively poor surface hardness.

It is a separate object of the present invention to provide a surface protective coating film having a reduced haze.

In accordance with the present invention, these objects are accomplished by an inorganic protective coating film of a thickness of from 400 angstroms to 5 microns comprising discrete islets of an inorganic solid each having an area of 7×10^4 square microns or less leaving openings therebetween interconnecting the surface of an article to the air.

Thus, to the surface of a synthetic resin article having a poor surface hardness there is applied an inorganic film having a sufficient hardness consisting of discrete islets leaving therebetween uniformly distributed openings interconnecting with the air, so that the surface hardness of the aforesaid body is enhanced without sacrifice in the inherent properties of the body, such as transparency and the hydrophilic property and there is no risk of scaling-off of the coating film.

The invention will be readily understood from the following description, when read together with the accompanying drawings, wherein;

FIG. 1 is a curve indicating the relationship between the anti-fogging property and the percentage of opening area of a protective coating film in accordance with the present invention formed on the surface of a hydrophilic plastics body,

FIG. 2 to 4 are cross-sectional views of coated articles indicating the principle of development and reduction of haze,

FIG. 5 is an enlarged cross-sectional view of an article having a protective coating film in accordance with the present invention,

FIG. 6 is a plan view of the aforesaid article,

FIG. 7 is a curve indicating the change of quantity of transmitted light through a specimen of a sheet of a hydrophilic resin having no protective coating film determined by continuously supplying steam onto the specimen and then stopping the supply,

FIG. 8 is a curve indicating the similar change in the quantity of transmitted light obtained on a specimen having a protective coating film in accordance with the present invention,

FIG. 9 is a diagonal view of a specimen having a protective coating of the present invention consisting of

regularly arranged circular elements, indicating the anisotropy in abrasion hardness,

FIGS. 10(a) and 10(b) show an example of formation of a pattern on a shadow mask to be employed in the practice of the method of the present invention,

FIG. 11 is a microscopic photograph indicating an example of an evaporating mask or shadow mask,

FIG. 12 is a rough sketch of an apparatus for determination of the anti-fogging property, and

FIGS. 13 to 15 show examples of patterns on the masks for use in the formation of the protective coating film in accordance with the present invention.

The shaped article to which a protective coating is applied in accordance with the present invention may be formed of any hydrophilic and hydrophobic polymer. The hydrophobic polymers includes, e.g., polycarbonates, poly(methyl methacrylate), polyvinyl chloride, polystyrene, polypropylene, polyethylene and unsaturated polyester resins. The hydrophilic polymers includes, e.g., hydrophilic acrylate and methacrylate polymers, polyvinyl alcohol, polyvinyl acetal, polyacrylamides, polyvinylpyrrolidone, poly(ethylene oxide), poly(ethylene imine), hydroxyethylcellulose and regenerated cellulose. These materials may form shaped bodies by themselves or form the surfaces of shaped bodies of other plastics, glass, metal, wood, concrete or porcelain. As the hydrophilic polymer there are preferably used water-insoluble, hydrophilic acrylate, and methacrylate polymers.

The hydrophilic acrylate and methacrylate polymers are exemplified by, e.g., polymers of hydroxy-lower alkyl acrylates, hydroxy-lower alkyl methacrylates, hydroxy-lower alkoxy-lower alkyl acrylates and hydroxy-lower alkoxy-lower alkyl methacrylates, such as of 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, diethyleneglycol monoacrylate, diethyleneglycol monomethacrylate, triethyleneglycol monoacrylate, triethyleneglycol monomethacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl acrylate, 3-hydroxypropyl methacrylate, dipropyleneglycol monoacrylate and dipropyleneglycol methacrylate.

The aforesaid polymer may be crosslinked, if necessary, by copolymerization of 0.05 to 20, preferably 0.1 to 2.5% of a crosslinking agent, such as, e.g., ethyleneglycol diacrylate, ethyleneglycol dimethacrylate, propyleneglycol diacrylate, propyleneglycol dimethacrylate, divinylbenzenes and N,N'-methylene-bis-acrylamide.

The aforesaid polymer may be modified, if necessary, by copolymerization with, e.g., acrylic acid, methacrylic acid, itaconic acid, fumaric acid or mono-2-hydroxypropyl itaconate.

As the polyvinyl alcohol there may be used partially saponified polyvinyl acetate other than the complete saponification product. The polyvinyl acetals includes polyvinyl formal, polyvinyl acetoacetal, and polyvinyl butyral. The polyacrylamides includes polymers of acrylamide, methacrylamide, N-methylol acrylamide, N-methylol methacrylamide, diacetone acrylamide, diacetone methacrylamide and like acrylamide and methacrylamide derivatives.

The protective coating film in accordance with the present invention formed on a hydrophilic polymer body combines the effect of enhancing surface hardness and the advantages that there is no fear of scaling-off and it is air permeable and photo transmissible.

Namely, the protective coating film of the present invention on an article of which at least the surface is formed of a hydrophilic polymer has a structure comprising discrete dots or stripes or otherwise figured islands of an inorganic solid and openings or interstices therebetween interconnecting the surface of the substrate with the air; this structure prevents the scaling-off of the protective coating film and deformation of the film by thermal stress and allows gaseous molecules to reach the surface of the hydrophilic polymer body. The discrete structure should be of a pitch smaller than the diameter of fibers of the cloth to be used for cleaning the surface or of abrasive grains. This structure is obtainable by forming an inorganic protective coating film through a sheet of perforated mask or combination of several sheets of perforated mask on the surface of a shaped body of which at least the surface is formed of a plastic by an evaporating method, such as, e.g., resistance heating method, electron beam method or sputtering method.

In the resistance heating method, a material to be evaporated is heated by Joule's heat generated by application of an intensive electric current to a wire or foil of a high melting point and the bond between the protective coating and the substrate is attributable mainly to physical adsorption and van der Waals forces. In this case, since the bonding strength is not sufficiently high, it is desirable to preheat the substrate prior to evaporation or activate it by means of ion bombardment to enhance adhesion.

In the electron beam method, the material is heated by collision of a beam of a large number of electrons accelerated to a high speed. In the sputtering method, the material is bombarded by cations generated by glow discharge, low pressure glow discharge in a magnetic field or high frequency electric field, low pressure plasma, ion beam or like physical or chemical sputtering means. In the electron beam method and sputtering method, particles of a metal or metal oxide shot out of a target have a very high level of energy (10 - 100 eV) compared with particles evaporated in the resistance heating method (about 0.2 eV), so that they locally heat the surface of the substrate and form a substantially complete chemical bond with the surface.

Therefore, through depending on the melting point and decomposition point of the material being used, in general it is preferred to process a material of a low melting point in the resistance heating method and a material of a high melting point in the electron beam or sputtering method. In all cases, however, the temperature of the substrate should carefully be controlled to prevent the substrate from thermal decomposition. A fairly strong bond between the substrate and protective coating is attained by cleaning the surface of the substrate by ion bombardment. This is believed to be attributable to formation of oxygen linkages on the polymer molecules.

The protective coating film may be formed by a chemical method other than the above mentioned physical methods.

A protective coating film of a desired percentage area of openings or interstices and a desired pattern of stripes or islands is made by use of a mask consisting of one or several sheets of a masking sheet having numerous through-holes having a desired contour or numerous slits. The contour of through-holes or stripes and their arrangement are not critical. It may be of discrete

islands or stripes and arranged regularly or at random. The area of each preferably is 7×10^4 square microns, or less, more desirably 3×10^4 square microns or less, because if it exceeds 3×10^4 square microns transmitted light becomes nonuniform and there occasionally occurs fluctuation of transmitted light and the coating film becomes fragile. In particular in case of hydrophilic polymer bodies, it is preferred the area to be 8×10^3 square microns or less from the point of view of non-fogging and hygroscopicity. The thickness of the aforesaid coating consisting of numerous discrete islands preferably is 400 angstroms to 5 microns, because a film of a thickness of less than 400 angstroms does not have sufficient function and, on the other hand, one of a thickness exceeding 5 microns has a haze and is poor in adhesion to the substrate.

The shape or contour of each element of the protective coating film may be circle, oval or stripe, though it is preferred that the ratio of its short axis to its long axis ranges between 0.1 and 1.0.

It is preferred that openings or interstices between islands or stripes be uniformly distributed throughout the surface to be protected. The percentage area of openings may be varied depending on desire, though normally is 5 to 99%. In case of a hydrophilic polymer body, a percentage area of openings of 30 to 99% is preferred to attain the object of surface protection without sacrifice in the desirable properties of the body, and, in case of a hydrophobic polymer body, a range from 5% to 70% is preferred because, in the latter case, the protective coating is applied for the purpose of surface protection only.

The term "percentage area of openings" means the percentage of an area obtained by subtracting the total area of islands from the total area of the substrate covered by the protective coating. Usually, for instance, it is represented by the following equation in the case of a two-dimensional zig-zag pattern,

$$S (\%) = (1 - 2\pi r^2 / \sqrt{3} l^2) \times 100$$

where S is the percentage area of openings, r is the diameter of an island and l is the average distance between two adjacent islands.

As the result of more detailed experiments, we have found that, in case of hydrophilic polymer bodies, the anti-fogging property takes its highest value when the percentage area of openings is in the range of from 60 to 99%.

In theoretical point of view, it is believed that, when the aforesaid protective coating film is applied to the surface of a hydrophilic polymer, the anti-fogging property deteriorates as the total area of the islands increases, in other words, the percentage area of openings decreases, whereas, surprisingly, it has been found that, as the result of experiments as indicated by FIG. 1, a coated body having a protective coating film of a percentage area of opening of 60 to 99% is superior in anti-fogging property to one of a percentage area of opening of 100% (a body having no protective coating film). The hump of the curve in FIG. 1 indicates this. The curve in FIG. 1 is obtained by plotting the anti-fogging property T/T_0 vs. the percentage area of openings, as determined by the method as set forth hereinafter on coated bodies prepared by evaporating silicon oxide through various masks on to substrates to form thereon a protective coating film of a thickness of 1,000 to 1,500 angstroms. The percentage area of

openings is determined by measuring the total area of islands by microscopic photography, since the pattern of the protective film is not always identical with that of the mask used because of imperfect contact between the surface of the substrate and the mask.

Thus, the present invention is based on the discovery contrary to the ordinary idea that an uncoated hydrophilic plastic body is superior in non-fogging property to an at least partially coated one. While the exact mechanism is uncertain, it is believed that diffusion of water deposited on the surface into the inside of the hydrophilic plastic body is delayed by the porous protective coating film and this delay results in an enhancement of the anti-fogging property.

In the practice of the present invention there may be used various inorganic substances in the formation of a protective coating film, and for the formation of a transparent protective coating film there are used oxides, nitrides, fluorides and sulfides of various metals. The material may be applied to a substrate in an appropriate process according to the material used.

For example, the material suitably applied in the resistance heating method includes, e.g., tin oxide, cadmium oxide, indium oxide, zinc oxide, bismuth oxide, antimony oxide, silicon monoxide, cadmium sulfide, zinc sulfide, magnesium fluoride, beryllium fluoride, calcium fluoride, lithium fluoride, sodium fluoride, thulium fluoride, cerium fluoride and cryolite.

The material suitably applied in the electron beam or sputtering method includes, e.g., thorium oxide, beryllium oxide, calcium oxide, strontium oxide, barium oxide, aluminum oxide, magnesium oxide zirconium oxide, cerium oxide, silica, niobium oxide, titanium oxide, tantalum oxide, lanthanum oxide, hafnium oxide, niobium nitride, boron nitride, aluminum nitride and silicon nitride.

Both transparent and opaque materials are employed in accordance with the object to form a protective coating film of the present invention, but when a transparent protective coating film is formed on a transparent substrate, there is sometimes observed the phenomenon of becoming cloudy due to scattering of light, so called haze. It is desired to avoid development of haze in the case especially of lenses. The haze is attributable to scattering of light at the periphery of or center of each element or island of a protective coating film.

Referring to FIG. 2, discrete elements or islands 2 are fixed to the surface of a substrate 1 having a relatively low surface hardness. In rays P incident upon the body, rays P_2 and P_4 go right on after passed through the body and arrive at Q_2 and Q_4 , respectively, namely unscattered and developing no haze, while rays P_1 and P_3 arrive at Q_1 and Q_3 , respectively, since they are refracted on the surface of the body. This is a reason for the development of haze in the transmitted rays. This results in the drawback that the visibility through the body is hindered somewhat though the surface hardness of the body is enhanced to a great extent by application of a discrete protective coating film thereto which is free from cracking and scaling-off.

As the result of further investigations, we have discovered that these drawbacks are eliminated by the following means.

In accordance with the present invention, haze is minimized by use as the coating material of an inorganic solid having a high hardness and a relatively low transparency, by first applying a discrete coating film

of an inorganic solid having a high transparency and a high adhesion to a substrate and applying thereover a solid having a relatively low transparency or by use of a blend of such high transparent and low transparent solids.

Illustrating in more detail, for instance, hitherto there has been used for forming a protective coating film silicon dioxide SiO_2 as a material having high transparency and hardness and excellent adhesion to a plastic substrate. In accordance with the present invention, haze is minimized to a great extent by applying a mixture of a small amount of a metal and SiO_2 or by applying a material having a low transmittance, such as, e.g., metallic aluminum, chromium or like material, over a coating of SiO_2 so as to reduce transmittance.

Namely, the present invention is characterized by reducing the quantity of transmitted light thereby to reduce the quantity of scattered light causing the haze by reducing the transmittance of the discrete protective coating film applied to a substrate so as to enhance surface hardness.

Illustrating the present invention referring to FIG. 3 and 4, to a substrate 1 to be protected there are applied elements 2 of a protective coating film consisting of a material having a low transmittance. The quantities of rays of light P_1 , P_2 and P_3 arrived at Q_1 , Q_2 and Q_3 are reduced or minimized to zero by the element, so that rays P_4 predominate in transmitted light through the body whereby haze is minimized to a great extent. In the embodiment as illustrated by FIG. 4, to a substrate 1 there is applied a transparent material 3 and thereover an opaque material 4 to form elements 2 of a protective coating film. In this case, in incident rays P_1 to P_4 , rays P_4 only pass through the body whereby haze is reduced to a great extent.

That is to say, the present invention intends to minimize haze by cutting off scattered light and allowing straight-forward light only to pass the body, so that the order of the transparent material 3 and opaque material 4 in FIG. 4 may be reversed, and the same result can be obtained by applying the opaque material annularly only to the peripheral section of each element or island of the transparent material. It is necessary for eliminating haze by minimizing or eliminating scattered light to reduce the transmittance of each element to 50% or less, preferably to 30% or less.

In the practice of the present invention there may be used the various transparent materials mentioned above for forming elements of a protective film and, on the other hand, there may be used as the opaque material to be used in combination with the transparent material, materials such as chromium, nickel, aluminum, gold, silver, tantalum, titanium or like metals; iron oxides, chromium oxide, cobalt oxide and like colored metallic oxides; and niobium nitride, chromium nitride, titanium nitride and like nitrides and carbides, silicides, fluorides and like so called refractories.

In the present invention, the protected areas of the surface of a substrate increase as the density of elements or islets scattered as to form a protective coating layer increase, while, on the other hand, the percentage area of openings on the substrate decreases to hinder the inherent desirable properties of the substrate, such as, e.g., hygroscopicity and the anti-fogging property in case of a hydrophilic resin. The present invention is of great value for enhancing the surface hardness of a shaped body of a hydrophilic plastic having insufficient

surface hardness, so that the present invention will be illustrated hereinafter in more detail with respect to such a substrate, but, of course, the present invention is applicable to any substrate in principle.

As shown in FIGS. 5 and 6, when each element or islet 7 formed on a substrate 5 and a coating layer 6 of a hydrophilic resin has a large area, there are formed water droplets 8 on the surface of each element due to lack of hygroscopicity of the protective coating itself to yield local fog upon exposure to steam or water vapour. To avoid this phenomenon it is desirable that each element has as small an area as possible. This is true of dehumidification of a hydrophilic plastic body after absorption of water. Namely, water 10 absorbed by plastic 9 just under an element 7 of a protective coating film must diffuse in the plastic layer to the naked section 11 to vaporize into the air. On this occasion, it is desirable for quick vaporizing of moisture that the area of each element 7 is as small as possible, because if moisture absorbed by the plastic just under an element 7 stays there indefinitely the element gives a faulty dehumidification response. The dehumidification response will be illustrated in detail with reference to FIG. 7.

FIG. 7 shows the change in quantity of light transmitted through a specimen of a hydrophilic or hygroscopic plastic layer having no protective coating film thereon determined by supplying steam at a constant flow rate thereto and continuing measurement after stop of the supply of steam. A laser beam is directed at a point of the surface of the plastic layer while supplying thereto steam. In the initial stage of supply of steam, the transmittance of the plastic layer for the laser beam passing straight through the specimen is not varied at all because of adsorption of steam by the hygroscopic resin. During continuous supply of steam for a long time, the resin is saturated with moisture, and thereafter there occurs condensation of a portion of the steam on the surface to form water droplets which cause fog. With progress of the condensation of steam, the quantity of light received by a light detector located on the optical axis of the laser beam is gradually decreased by scattering with the water droplets. In FIG. 7 the quantity of transmitted light arrived at the receiver is plotted as ordinate and the time of supply of steam as abscissa. In the graph, from point A to B there is no change in the quantity of transmitted light as steam is absorbed by the specimen so as not to form any water droplets thereon, while from point B to C the quantity decreases abruptly because of formation of fog on the surface, after the resin being saturated by moisture. When the supply of steam is stopped at point C, the quantity increases gradually thereafter because of evaporation of the water droplets into the air and the specimen reverts to the original transparent state at point D. The time elapsed from the point A and B is the value indicating the anti-fogging quality or property and the value represented by the time elapsed between the point C and D indicates dehumidification response.

In case of a specimen prepared by evaporating silicon dioxide onto a hydrophilic polymer sheet through a stainless steel mask having numerous circular through holes each of 100 microns ϕ at pitches of 200 microns to form a coating of a thickness of 200 angstroms consisting of discrete circular elements each of a diameter of about 100 microns, the quantity of transmitted light varies as indicated by the curve *a* (full line), in FIG. 8

(The symbol ϕ is used here and throughout the specification as the standard abbreviation of "diameter.") That is to say, the quantity somewhat decreases at point Q and reverts to point R and fog is formed as it decreases from point R to S. When application of steam is stopped at the point S, the transparency of the specimen reverts through point T to its original value. In this case, the decrease at the point Q corresponds to scattering of light caused by water droplets condensed on each elements of the protective coating and the reversion to R corresponds to formation of a transparent film of water resulting from condensation of a sufficient quantity of moisture. On the other hand, the reversion of the quantity of transmitted light after the stopping of application of steam takes a longer time than in case of an uncoated specimen and the quantity of light at the point T is smaller than that at the point D in FIG. 7. This seems, since the rate of application of steam is identical in both cases, to be attributable to difficulty in the escape of the moisture absorbed by the specimen just under the elements, the dehumidification response being not sufficiently high.

The curve *b* (dotted line) in FIG. 8, on the other hand, is one obtained on a specimen having a protective coating consisting of elements in accordance with the present invention in which each element has dimensions of 157 microns \times 50 microns (equal in area to the aforesaid circular element of 100 microns ϕ) and the density of the elements is equal to that in the aforesaid specimen having circular elements. In this case, the decrease in quantity of transmitted light at point U is smaller than that at point Q and reversion point V takes mean time and quantity of transmitted light of those of the point T on the curve *a* and of the point D in FIG. 3. It is believed to be a reason why the quantity of transmitted light at the point V is larger than that at the point T on the curve *a* and the time to V is shorter than that to T that the average distance which the moisture just below each element passes through until it reaches uncoated areas or openings is shorter resulting in a high dehumidification response. From this newly found fact, it will be concluded that, in enhancing the surface hardness of a surface of a hydrophilic plastic object by application of a protective coating consisting of numerous uniformly distributed discrete elements, the shape or contour of each element should be, if its area is fixed, other than circle.

Illustrating the abrasion resistance of a specimen having a protective coating in which elements are arranged in a pattern with a simple regularity, in FIG. 9 there is shown a pattern of a diagonal arrangement of elements. Numeral 12 indicates openings or interstices where the surface of a hydrophilic plastic is directly exposed to the air and 13 indicates elements of a protective coating. In this case, the coating film has sufficient hardness against abrasion in the direction of line l_1 since an abrasive passes over a number of hard protective elements, but in the direction of line l_2 and of l_3 it is easy to scratch since an abrasive passes over openings only. Thus, there is observed anisotropy in abrasion resistance with respect to patterns adopted. For assuring a sufficient abrasion resistance it is necessary to take notice of the pattern of rearrangement of elements.

The first rule is to arrange protective elements at random. However, in practical aspect, it is difficult to make a mask having a completely random pattern, so that it is reasonable to make a mask by providing a

number of unit patterns having one or few elements in a unit pattern, assembling a plurality of the unit patterns to form a block pattern and assembling a plurality of the block patterns in a regular arrangement. In this case, it is necessary to design the arrangement of the unit patterns and/or the elements that the elements may not be arranged with a simple regularity in the unit patterns and/or the block patterns. For instance, a hexagon as shown in FIG. 10(a) is regarded as a unit pattern in which few protective elements are arranged at random, and the unit pattern is turned around Z axis, perpendicular to the plane of the paper by 60°, five times to form a block pattern as shown in FIG. 10(b) in which elements are also arranged at random. A mask is made in a simple way by two dimensionally extending the block pattern by reversion, parallel movement or other transposition means, in which, in the finished mask, elements are arranged substantially randomly.

As will be understood from the above description, it also is an object of the present invention to provide a shape or contour of the protective element of a protective coating film and a pattern of arrangement of through-holes in a mask for use in the preparation of the protective coating film which (1) has not adverse effect on the inherent desirable characteristics of the substrate, such as, e.g., hygroscopicity and non-fogging quality, (2) enhances the moisture absorbing-and-desorbing response of a hygroscopic plastic and (3) has no anisotropy in abrasion.

Namely, the protecting method for enhancing the surface hardness of an object in accordance with the present invention is attained by studding randomly numerous fine, elongated or ellipse islets of an inorganic solid on a surface of a plastic, especially a hydrophilic, hygroscopic plastic substrate to form a coating layer having openings interconnecting the said surface with the air. A good result is obtainable by carrying out this using a mask formed of a plurality of block patterns in the manner as fully mentioned above.

Illustrating the preparation of the coating film in the method of the present invention in more detail, the percentage area of openings is appropriately chosen for providing a sufficient area of opening for the substrate resin as not to inhibit hygroscopicity and non-fogging quality, i.e. 40% or more, preferably 70% or more. For ensuring a high moisture absorption-and-desorption response and a high abrasion resistance, the element of protective coating layer must be of an elongated or elliptical form. And, for minimizing the isotropicity in abrasion resistance of a protective coating film, i.e., preventing the substrate being scratched or injured even if being rubbed in any direction, the elements are arranged randomly, i.e., arranged in a randomized pattern. Namely, the present invention is characterized by designing a pattern of a mask on the basis of the three fundamental rules as mentioned above as to ensure a sufficient enhancement of the surface hardness of an object.

An example of a pattern designed on these fundamental rules is shown in FIG. 11. First there is provided a hexagonal unit pattern of which the length of a side is 124 microns, the unit pattern having randomly arranged four through holes each consisting of a square of a side length of 15 microns and two hemi-circles of a diameter of 15 microns positioned on the opposite sides of the square, as shown in FIG. 10(a). The percentage area of openings for the substrate of the unit

pattern is 96%. The unit pattern is rotated five times by 60° to form a block pattern as shown in FIG. 10(b). A mask is formed by arranging alternately the block pattern and its mirror image. In FIG. 11 there is shown a microscopic photograph of a portion of a random pattern in the mask (direct magnification 400 × enlarging magnification 3). Thus, in this way, there is obtained with ease an evaporating mask with a random pattern which will provide an evaporation coating film having no isotropy in abrasion resistance.

As set forth above, it is very difficult for grains or particles of an abrasive to get into the openings between the islets or elements of a protective coating and, if got thereinto, it is rare that grains of an abrasive gotten into the openings are dragged over a long distance by fibers of an abrasive cloth to scratch the surface of a substrate since the islets or elements of the protective coating are dotted at very fine pitches on a plastic substrate, especially a hydrophilic plastic substrate. In fact, it is ascertained that a shaped body, especially of a hydrophilic plastic, thus applied with such a coating film has a highly enhanced surface hardness, is put to practical use without any trouble. When a specimen of a coated plastic body of the present invention was rubbed under a more severe rubbing than in practical use to injure the surface of the substrate for a test, it was ascertained by microscopic observation that only the surface of the protective coating film was injured and the surface of the substrate was not injured. This means that by the discrete coating film applied to the surface of a substrate defines the surface hardness of a coated object as a whole.

On the other hand, it is believed that since a protective coating film in accordance with the present invention is divided into numerous discrete islets or elements there occurs no local convergence of internal stress to cause destruction of the coating film, so that the protective coating film is prevented from breakage and scaling-off.

The discrete structure of the protective coating film in accordance with the present invention allows the surface of the substrate to directly contact the air and, accordingly, penetration into and evaporation from the surface of moisture. In other words, the protective coating film makes it possible to enhance the surface hardness of a plastic body, especially of a hydrophilic plastic body without sacrifice in its inherent properties, such as, e.g., hygroscopicity. A hydrophilic polymer layer is injured or deformed by lightly wiping it with a cloth when fully swollen by water as a result of absorption of moisture contained in the air, but the surface hardness of such a hydrophilic polymer layer is enhanced to a great extent without any sacrifice in its hygroscopicity by applying thereto a discrete protective coating film in accordance with the present invention.

In addition, the protective coating film allows free passage therethrough of light because it has openings uniformly distributed throughout its surface. Accordingly, in the case where an opaque protective film is applied to a transparent substrate, the transparency of the substrate is substantially not hindered and the substrate can exhibit its inherent photo transmitting quality.

Thus, in accordance with the present invention, there is obtained a protective coating film which is free from scaling-off and enhancement of the surface hardness of a substrate without sacrifice of the inherent transparency and hygroscopicity of the substrate firmly bonded

to the surface of building, automobile, train and airplane windows, doors, eyeglasses, goggles, optical lenses, sheet glasses for water tanks and mirrors made out of a plastic or made out of a glass or plastic coated with a hydrophilic plastic layer. Similar results are obtained by applying a protective coating film in accordance with the present invention to, e.g., window sashes, walls, concrete blocks, hulls and submarine structures.

The embodiments of the present invention will hereinafter be illustrated in more detail by the following examples.

The test methods as used in the examples are as follows:

15 Determination of non-fogging quality

Water 15 contained in a two-necked flask, 14, as shown in FIG. 12, is heated at (40° ± 0.5)°C by means of a mantle heater 16 and air at normal temperature is blown thereinto through a flow meter (not shown) at a rate of 1,000 ml/min to generate steam. The steam is introduced through a cock 18 into a thermally insulated T-pipe 19 one end of which has a through-hole 20 of a diameter of 10 mm and the other end has a through-hole 21 of a diameter of 3 mm. On front of the through-hole 20 there is set a specimen 22 at an interval of 2 mm for escape of steam.

A beam of light emitted from a He-Ne gas laser 23 (6328 Å., 1.0mW) passes through a slit 24, a lens 25, a through-hole 21, a through-hole 20, (the diameter of the beam is so adjusted that its diameter at the through-hole 20 is 10 mm), the specimen 22 and an iris 26 for eliminating scattered light and arrives at a photo cell 27 to yield an electric power. The electric power is read as voltage by means of a millivolt-meter 28.

First, the transmittance of the specimen before application to the specimen of steam in the state where the cock 18 is closed is determined. The measurement of the length of time is started concurrently with opening of the cock 18 and the length of time until the reading of the millivoltmeter reaches a value corresponding to a 10 % decrease of transmittance caused by deposition of water droplets on the surface of the specimen is determined. The specimen is, prior to the test, dehydrated by heating at 80°C for 30 minutes and cooled to room temperature in a desiccator. The relationship between the transmittance and the reading of the millivoltmeter employed in this method was determined by a calibration curve formed by measuring the transmittances and electromotive forces (milli-volts) in accordance with this test method on sheet glasses having different transmittances prepared by grinding separate pieces of a sheet glass with abrasives of different grain sizes for different grinding times.

55 Abrasion test

In Examples 4 to 9, a commercially available gauze is reciprocated under the load of 2 kg/cm² on a surface of a specimen until noticeable scratches are formed thereon, and the number of reciprocating cycles is counted.

In Examples 10 to 14, an uncoated specimen is rubbed at the intensity at which eyeglasses are usually wiped with a commercially available silicone cloth (Celite) or gauze. On this occasion, the view through the specimen is noticeably damaged when the specimen is rubbed about 400 cycles by the Celite or about 100 cycles by the gauze. The so rubbed uncoated specimen is regarded as a marginal specimen, and the abrasion

resistance of a coated specimen is indicated by the number of rubbing cycles by rubbing the specimen with the Celite or gauze until it is scratched on average to the same extent with the marginal specimen.

Determination of thickness of film

The thickness of a protective coating film is determined by means of Talysurf (Taylor-Hobson Co.).

EXAMPLE 1

Two polycarbonate plates of 50 mm × 50 mm × 3 mm were cleaned in an ultrasonic cleaning process and one of them was, as it was, and the other was, after being covered by a stainless steel mask having numerous circular holes of 300 microns ϕ arranged in a pattern as shown in FIG. 9 at a pitch of 500 microns, put in a vacuum evaporation apparatus. The vacuum chamber was evacuated to 1×10^{-6} Torr and silicon dioxide was evaporated on to the plates while heating the plates at about 100°C, in an electron beam evaporation process (accelerating voltage of 4 KV, beam current of 30 mA, evaporation time of 10 minutes and distance between the silicon dioxide source and the substrate of 120 mm) to form a uniform coating on the unmasked plate (B) and a discrete coating on the masked plate (C), both coating films being of a thickness of about 5 microns. The percentage area of openings of the coating film on (C) was 50% and the transparency of the coated plate (C) was substantially identical with that of the plate (B). There was also provided an uncoated polycarbonate plate (A).

The surface of the specimens A, B and C were lightly brushed by means of a wire brush consisting of a bundle of 30 copper wires of 0.2 mm ϕ to estimate their surface hardness. There were observed few scratches on the surface of specimen A after two or three touches, but on the surface of specimens B and C there was observed no scratch even after brushing of 100 times or more.

When specimens B and C were immersed in boiling water at 100°C, there occurred scaling-off of the protective coating film on specimen B after 30 minutes to 1 hour and the protective coating film almost disappeared after 1½ hours, while on specimen C there was observed no change even after boiling test for 3 hours.

EXAMPLE 2

Two poly(methyl methacrylate) plates were cleaned in an ultrasonic cleaning process and one of them was, at it was, and the other was, after being covered by a mask as shown in FIG. 13 consisting of two stainless steel masks each having circular hole 3 of 300 microns ϕ arranged in a pattern as shown in FIG. 9 at a pitch of 500 microns, said two masks being combined together at an angle of 45°. Each of the poly(methyl methacrylate) plates was then mounted on a specimen holder provided with a water cooling means in an RF sputtering apparatus. Since there was a risk of the plate being exposed to plasma and thermally decomposed, a vacuum grease was applied to the back of the plate so as to enhance thermal contact between the plate and the holder. To the cathode in the RF sputtering apparatus there was mounted a sintered plate of cerium oxide (CeO₂), the vacuum chamber was then evacuated to 1×10^{-5} Torr and thereafter dried gaseous argon was introduced thereinto to adjust the inner pressure to 3×10^{-3} Torr.

Sputtering was then carried out for 5 minutes at a RF voltage of 2.5 KV and plate current of 240 mA imposing a voltage from an 1 KW RF electric generator to deposit a CeO₂ film of a thickness of about 1,000 Å on the poly(methyl methacrylate) plate. Thus, there was formed a uniform film on the unmasked plate (B) and a discrete film having a moire pattern on the masked plate (C). The percentage area of openings of the protective film on the plate (C) was 65 % and the coated plate (C) was not different in transparency from the coated plate (B). There was also provided an uncoated poly(methyl methacrylate) plate (A).

The specimens A, B and C were subjected to the surface hardness test using a wire brush as in Example 1. Specimen A was injured by light brushing touches of only two or three times, while specimens C and B were scratched scarcely even if brushed 100 times or more. When specimens B and C were subjected to the boiling test as in Example 1, there occurred scaling-off of protective film on the specimen B after boiling for 20 to 30 minutes, while there was observed no change on specimen C even after boiling for 1 hour.

EXAMPLE 3

Two cast plates of an unsaturated polyester resin each of 50 mm × 50 mm × 3 mm were cleaned in an ultrasonic cleaning process, and one of them was, as it was, and the other was, after being covered by a stainless steel mask having a pattern as shown in FIG. 14 consisting of three stainless steel masks each having circular holes of 300 microns ϕ arranged in a pattern as shown in FIG. 9 at a pitch of 500 microns, the three unit masks being stacked one over another at angles of 22.5° and 45°, mounted in a vacuum chamber. In a molybdenum boat positioned below the plate in the vacuum chamber there was charged stannic oxide (SnO₂). The chamber was evacuated to 2×10^{-5} Torr and an electric current was applied to the molybdenum boat to evaporate SnO₂ on to the plate in a thickness of about 2,000 Å. Thus, there was formed a uniform coating on the unmasked cast plate (B) and a discrete coating of a pattern as shown in FIG. 14 on the masked plate (C). The percentage area of opening of specimen C was 75 % and there was no difference in transparency between specimens B and C. At the same time, there was provided an uncoated cast plate of unsaturated polyester resin (A).

Specimens A, B and C were subjected to the surface hardness test using a wire brush in a similar manner to Example 1. Few scratches were formed on specimen A when brushed one or two times, while no scratch was formed on specimens B and C even if brushed about 100 times. On a boiling test, there occurred scaling-off of the coating on specimen B after 30 to 40 minutes boiling, while no change was observed on specimen C even after 2 hours boiling.

EXAMPLE 4

To a commercially available eyeglass lens for short-sightedness of 63 mm ϕ there was applied a hydrophilic acrylic resin, polymer of 2-hydroxyethyl methacrylate (Hydron, trade name), in a thickness of about 7 microns and, after drying of the coating, the lens was covered with a stainless steel mask having circular holes of 300 microns ϕ arranged in a pattern as shown in FIG. 9 at a pitch of 500 microns and mounted in a vacuum evaporation chamber. A molybdenum boat was put

under the masked lens in the chamber and there was charged stannic dioxide in the boat. After evacuation of the chamber to 2×10^{-5} Torr, an electric current was applied to the molybdenum boat to evaporate stannic oxide on to the lens to form a discrete coating of a thickness of 500 A. The lens was then subjected to a test of its non-fogging quality and the abrasion test. The results obtained are summarized in the following Table 1 in comparison with those on an uncoated Hydron surface. The percentage area of openings of the protective film thus obtained was about 55%.

Table 1

Specimen	Non-fogging quality (sec)	Abrasion test
Uncoated	20	50
Coated	22	200

As indicated by the above Table, the protective film in accordance with the present invention enhanced abrasion resistance to a great extent without sacrifice in the non-fogging quality. The transparency of the lenses remained unchanged.

EXAMPLE 5

Two glass plates each of 50 mm \times 50 mm \times 3 mm were coated with a 2-hydroxyethyl methacrylate polymer (Hydron) respectively to form thereon a coating film of a thickness of 23 microns and, after drying, the coated surface of each plate was covered with a square section mask consisting of an 100 mesh standard wire netting and set in a vacuum evaporating chamber. An electric current was applied to a molybdenum boat containing therein silicon monoxide and located below the plate in the chamber after evacuation of the chamber to 2×10^{-5} Torr to form a discrete coating of silicon monoxide of a thickness of 500 A. on one of the plates and of 3,000 A. on the other plate. The specimens were subjected to determination of the nonfogging quality and the abrasion test.

The results of the tests were summarized in the following Table 2 in comparison with the properties of an uncoated Hydron surface. The percentage area of openings of the protective coating on the two specimens was about 60%.

Table 2

Specimen	Non-fogging quality (sec)	Abrasion test
Uncoated	160	50
Coated 500 A	150	500
Coated 3,000 A	170	Above 1,000

As indicated by the above Table, the protective films in accordance with the present invention enhanced the abrasion resistance without sacrifice in the non-fogging quality and transparency.

EXAMPLE 6

A flat glass plate of 3 mm \times 50 mm \times 50 mm was cleaned and coated with a hydrophilic polymer, polyvinyl alcohol PVA, in a thickness of about 5 microns. After fully drying the coating, the plate was set in a vacuum evaporation chamber. In this case, there was employed a combined mask consisting of three stainless steel panels each having circular holes of 300 microns ϕ arranged in a pattern as shown in FIG. 9 at a pitch

of 500 microns and stacked relationship to meet with each other at angles of 22.5° and 45° to form a pattern as shown in FIG. 14. In a molybdenum boat located in the lower section of the chamber there was charged bismuth trioxide (Bi_2O_3). After evacuation of the chamber to 2×10^{-5} Torr, there was applied an electric current to the molybdenum boat, to evaporate bismuth trioxide in a thickness of about 500 A. on to the plate. The PVA film having a protective film was subjected to the non-fogging quality test and abrasion test together with an unprotected PVA film for comparison to obtain the results summarized in the following Table 3. The percentage area of openings of the protective film was 80%.

Table 3

Specimen	Non-fogging quality (sec)	Abrasion test
Uncoated PVA	20	5
Coated PVA	18	300

EXAMPLE 7

The refractive index of PVA is usually 1.49 to 1.53, that of the PVA used in the above Example was about 1.51, so that the discrete protective film could be observed with careful observation because Bi_2O_3 has a high refractive index of 2.42. According to the field of application, it is desirable to make the protective film invisible, so that, in this Example, there was used a windshield glass having a substantially identical refractive index of 1.52. The glass plate was coated with a PVA as used in Example 6 and then coated with a glass film, which is used usually as a windshield, using a mask as used in Example 6 under a vacuum of 1×10^{-6} Torr with the aid of an electron beam of 20 mA accelerated by a voltage of 4 KV. The distance between the source and the surface of the substrate was 120 mm and the evaporating time was about 1 minute. On the PVA surface it was difficult to confirm the presence of a discrete coating film. The thickness of the coating film was 1,500 A. and the percentage area of opening was 80%. When subjected to the abrasion test, there was observed no scratch even after brushing 500 times and it was ascertained that the non-fogging quality is not hindered at all as indicated by fogging after exposure of about 23 seconds in the fogging test.

EXAMPLE 8

To a surface of a glass plate of 50 mm \times 50 mm \times 3 mm there was applied a 2-hydroxyethyl methacrylate polymer (Hydron) in a thickness of 5 microns and, after drying, the Hydron-coated surface was closely covered by a stainless steel mask having a number of slits of a width of 500 microns at a pitch of 700 microns. The plate was subjected to evaporation of silicon monoxide in the same manner as in Example 1 to form thereon a coating film of a thickness of 3,000 A. and a percentage area of openings of about 30%. The results of the non-fogging test and abrasion test on the specimen were as shown in the Table 4.

Table 4

Specimen	Non-fogging quality (sec)	Abrasion test
Uncoated	18	50
Coated	6	Above 1,000

EXAMPLE 9

A laminated glass plate of 100 mm × 100 mm, as usually used as a safety glass for an automobile windshield, was coated with a 2-hydroxyethyl methacrylate polymer (Hydron) to form a coating film of a dry thickness of about 7 microns and, after drying, it was set on an anode of cathode sputtering apparatus. A tin plate was set as a target on a cathode. Two masks each having holes of 50 microns ϕ at a pitch of 100 microns and stacked with each other at an angle of 45° were closely lapped thereover. After evacuation of the apparatus to 1×10^{-5} Torr, a gaseous mixture consisting of 95% of argon and 5% of oxygen was introduced therein to adjust the pressure to 2×10^{-2} Torr. A DC sputtering was carried out for about 4 minutes using a DC power source at a DC 5 KV and 200 mA to deposit on the glass plate a stannic oxide film of a thickness of about 2,000 Å. By incorporating gaseous oxygen, not only gaseous argon, in the inert gas to attain reactive sputtering, vapor of metallic tin emitted from the target was converted to stannic oxide. The percentage area of opening of the stannic oxide coating thus obtained was about 75%. The properties of the Hydron surface and of the SnO₂ coated Hydron surface were as follows.

Table 5

Specimen	Non-fogging quality (sec)	Abrasion test
Uncoated	60	50
Coated	55	Above 1,000

EXAMPLE 10

A commercially available eyeglass lens for shortsightedness made of glass of 63 mm ϕ was coated with a hydrophilic acrylic resin, 2-hydroxyethyl methacrylate polymer (Hydron), in a thickness of about 16 microns and, after drying, closely covered with a stainless steel mask having circular holes of 25 microns ϕ in a pattern as shown in FIG. 9 at a pitch of 110 microns. The lens was set in a vacuum chamber and a molybdenum boat containing therein silicon monoxide was placed below it. After the vacuum chamber had been evacuated to 2×10^{-5} Torr, an electric current was applied to the molybdenum boat to deposit silicon monoxide in a thickness of about 1,200 and 3,500 Å., on the lens. The percentage area of the openings was 79%. The results of non-fogging quality test and abrasion test were as summarized in following Table 6.

Table 6

Specimen	Non-fogging quality		Abrasion test	
	(sec)		Celite	Gauge
Uncoated	100		400	100
Coated 1,200 Å	About 140		>5,000	>1,000
Coated 3,500 Å	About 95		>10,000	>3,000

Thus, as indicated by the above Table, the protective films in accordance with the present invention enhanced surface hardness to a great extent and, in addition, the non-fogging quality.

EXAMPLE 11

A mask having circular holes of 15 microns ϕ in an

arrangement as shown in FIG. 9 at a pitch of 80 microns, instead of the mask 25 $\mu\phi$ - 110 μ pitch prescribed in Example 10, was used. The percentage area of opening, as determined by microscopic photographic observation on the resulting protective film, was 92%. Subjecting the specimen together with a specimen having no protective film to the non-fogging test and the abrasion test, there were obtained the results summarized in the following Table 7.

Table 7

Specimen	Non-fogging test		Abrasion test	
	T/To (%)		Celite	Gauge
Uncoated	100		400	100
Coated	130		>3,000	>1,000

EXAMPLE 12

A mask having circular holes of 15 microns ϕ in an arrangement as shown in FIG. 9 at a pitch of 100 microns instead of the mask 25 $\mu\phi$ - 110 μ pitch prescribed in Example 10, was used, to deposit a discrete film of stannic oxide of about 1,000 Å. thickness and of a percentage area of openings of 95%. The results on the specimen of non-fogging and abrasion tests were as summarized in the following Table 8.

Table 8

Specimen	Non-fogging test		Abrasion test	
	T/To (%)		Celite	Gauge
Uncoated	100		350	80
Coated	105		>1,000	100

EXAMPLE 13

To a 3 mm thick polycarbonate plate of 50 mm × 50 mm there was applied a hydrophilic resin (Hydron) in a thickness of about 7 microns and, after drying, the plate was set in a vacuum evaporating chamber together with a nickel mask having circular holes of a radius of 35 microns arranged in a pattern as shown in FIG. 9 at a pitch of 110 microns closely applied thereto. In the vacuum evaporating chamber there was set an electron gun and a block of an ordinary sheet glass was put in front of the electron gun as a target. The chamber was evacuated to 5×10^{-5} Torr and $5 \times$ electric current of 4 KV, 30 mA was imposed on the gun to melt and evaporate the block of glass. During evaporation of about 5 minutes there was formed a discrete coating film of a thickness of about 1.8 microns and a percentage area of openings of 61.0% was formed on the surface of the substrate plate.

Table 9

Specimen	Non-fogging quality		Abrasion test	
	T/To (%)		Celite	Gauge
Uncoated	100		400	100
Coated	113		>50,000	>10,000

EXAMPLE 14

To a surface of a 5 mm thick glass plate of 80 mm × 100 mm there was applied a hydrophilic resin (Hydron) in a thickness of about 5 microns and, after dry-

ing, the plate was closely covered with a nickel mask having circular holes of a radius of 40 microns arranged in a pattern as shown in FIG. 9 at a pitch of 150 microns and set in a sputtering chamber. The back side of the substrate plate was closely attached through a thin layer of a silicon grease to a cooled RF-anode (grounded) to effect cooling. On the opposite cathode there was set a silicon plate of 150 mm × 150 mm × 5 mm and the chamber was evacuated to 2×10^{-5} Torr. Gaseous nitrogen was then introduced into the chamber to adjust the pressure to 3×10^{-3} Torr. Then sputtering was carried out for 10 minutes at a voltage of 3.0 KV and an anode current of 250 mA to form a coating film of silicon nitride of a thickness of about 2,000 Å. The percentage area of opening of the film was 90%.

Table 10

Specimen	Non-fogging quality		Abrasion test	
	T/To (%)		Celite	Gauge
Uncoated	100		400	100
Coated	130		>3,000	>1,500

EXAMPLE 15

A cleaned poly(methyl methacrylate) plate of 10 cm × 10 cm × 3 mm was set in a vacuum evaporating chamber and metallic chromium was evaporated onto its surface through a nickel mask having circular holes of 15 microns ϕ at a pitch of 85 microns to form an about 1.0 micron coating in thickness. On to a substrate of the same quality there was evaporated silicon dioxide to form a coating film of an about 1.0 micron thickness through the same mask. The percentage area of openings of sample A (chromium coated) and of sample B (silicon dioxide coated) were both 96.5%, and the transmittance of each element itself of specimen A was about 7% and of sample B was about 92%. The haze of sample A, as determined by ASTM D-1003, was 0.62% and of B was 2.3%. The whole transmittance for visible rays of sample A was 87.6% and of sample B was 91.0%, any difference in transmittance between the two samples being indiscernible to the naked eye.

EXAMPLE 16

A cleaned polycarbonate plate of 10 cm × 10 cm × 3 mm was set in a vacuum evaporating chamber and a 0.8 micron thick film of silicon monoxide was evaporated onto its surface through a nickel mask having circular holes of 15 microns ϕ at a pitch of 85 microns and subsequently an about 0.2 micron thick metallic nickel film was evaporated thereover to form specimen A. An about 1.0 micron thick silicon monoxide film alone was evaporated on to a polycarbonate plate of the same dimensions to form sample B. The percentage area of coating of both samples was about 3%. The transmittance of each element itself of sample A was about 15%, while the haze of sample A was 0.83% and of sample B was 2.6% and the whole transmittance of sample A was 88.5% and of B was 90.5%, this indicating that there was no substantial difference in transmittance between the two samples.

EXAMPLE 17

To a surface of a cleaned glass plate of 10 cm × 10

cm × 3 mm there was applied an about 5 microns thick film of a hydrophilic resin, 2-hydroxyethyl methacrylate polymer (Hydron) and, after drying of the coating film, the plate was set in a vacuum evaporating chamber. On to the coated surface of the plate there were evaporated concurrently aluminum oxide Al_2O_3 and metallic aluminum from separate evaporating sources through a stainless steel mask having circular holes of 30 microns ϕ distributed uniformly at a pitch of 200 microns to form thereon a protective film of a thickness of about 0.6 micron (specimen A). In a similar manner, aluminum oxide alone was evaporated on to a cleaned glass plate of the same dimensions to form thereon an about 0.6 micron thick aluminum oxide film (specimen B). The percentage area of coating of specimen A and of B were both about 3% and the haze of specimen A was about 0.53% and of B was about 2.7%.

EXAMPLE 18

As a substrate there was provided a polarizing plate consisting of a polarizing frame interposed between two yellow colored poly(methyl methacrylate) plates and having a transmittance of about 80%. After cleaning, the substrate was covered with a mask having circular holes of 80 microns ϕ arranged in a pattern as shown in FIG. 9 at a pitch of 250 microns. The assembly was set in an RF sputtering chamber and subjected to a reactive sputtering in an atmosphere of gaseous nitrogen to form a discrete protective film of silicon nitride Si_3N_4 of a thickness of 3,000 Å. on a surface of the substrate (specimen A). A 3,000 Å. thick chromium-nitride discrete film was formed on another substrate of the same quality in a similar manner (specimen B). The Si_3N_4 was highly transparent but the CrN was brown in color. The transmittance for visible rays of the Si_3N_4 film itself (3,000 Å. in thickness) was about 90% and of the CrN was about 25%. The haze of specimen A was 1.65% and of specimen B was 0.45%.

EXAMPLE 19

An evaporation mask A was prepared by providing a unit pattern consisting of a regular hexagon having randomly distributed therein five rectangular holes of 40 microns × 12 microns, the length of a side of said hexagon being 124 microns, forming a block pattern on the basis of the unit pattern in the manner as fully described above with reference to FIG. 10(b) and rotating the block pattern two times. There was provided an evaporation mask B having circular holes of 25 microns ϕ arranged in a regular section pattern at pitches of 100 microns. On to separate substrates there was evaporated silicon dioxide through the mask A or B to form a coating film of a thickness of about 3,400 Å. Thus there were obtained coated specimens A and B, both having a percentage area of openings of about 92%. Specimens B and C and a specimen A of an uncoated substrate were subjected to an abrasion test and moisture absorption-desorption response test. The abrasion test was made employing a rotary abrasion tester provided with an abrasion tip consisting of a silicone rubber covered by a gauge. The abrasion resistance was determined by measuring the time until there was formed a distinctive scratch by abrasion under a load of 500 g/cm² at a speed of 30 rpm. The moisture absorption-desorption response was determined by measuring the quantity of transmitted light using a He-Ne laser beam while applying steam at 40 C to the surface of a speci-

men at a flow rate of 1,000 ml./min. The decrease of the quantity of transmitted light corresponding to the point Q and U in the curve as shown in FIG. 8 was indicated in relative value regarding that of specimen B as 1.0. The moisture desorption (dehumidification) response was expressed by the time until the transmittance of a specimen reversed to 99% of its initial value (before application of steam) after stopping the application of steam. The application of steam was made for the same time for all the specimens. The desorption response also was indicated in relative value to that of specimen C as 1.00.

Table 11

Specimen	Abrasion test (min)	Decrease	Desorption response
A	90 - 100	About 0.25	About 1.15
B	30 - 40	1.00	About 1.50
C	5 - 10	—	1.00

The above Table indicates that specimens A and B both have far higher surface hardnesses than specimen C has, and specimen A is harder than specimen B while the former is less in decrease of transmitted light due to the protective coating film than the latter and, in addition, superior in desorption response, that is to say, that the process of the present invention is excellent as a process for enhancing surface hardness of a substrate.

EXAMPLE 20

A 460 microns square having randomly distributed therein 6 rectangular holes of 50 microns \times 157 microns as a unit pattern was rotated by 90° three times to form a block pattern consisting of 4 unit patterns. The block pattern was subjected to two turn-over operations to form an enlarged pattern thereby to form an evaporation mask D. There was provided an evaporation mask E having circular holes of 100 microns ϕ in a pattern as shown in FIG. 9 at pitches of 200 microns. On to a substrate there was evaporated an about 960 Å thick silicon monoxide film through mask D or E to obtain a specimen D or E, both having a percentage area of openings of about 92%. Specimens D and E and a specimen of an uncoated substrate were subjected to the same test as in Example 19 to obtain the results summarized in the following Table 12.

Table 12

Specimen	Abrasion test (min)	Decrease	Desorption Response
D	About 120	0.30	About 1.50
E	About 60	1.00	About 4.50
F	5 - 10	—	1.00

It is indicated by the above Table that a discrete protective film consisting of non-circular elements is superior in both surface hardness and moisture absorption-desorption response to a discrete protective film having circular elements even if both have the same percentage area of openings.

What is claimed is:

1. In an article of which at least the surface is formed of a synthetic resin, said article having an abrasion and scaling resistant inorganic film coating of a thickness of from 400 Å to 5 microns on said surface, the improvement comprising that the inorganic film is a discontinu-

ous film comprising discrete elements of such size and spacing that the article retains the abrasion resistance of a continuous film while avoiding scaling caused by stresses in a continuous film.

2. The article as defined in claim 1, in which the percentage area of uncoated areas in the film is from 5 to 99%.

3. The article as defined in claim 1, in which the inorganic film comprises numerous transparent elements.

4. The article as defined in claim 1 in which each of the discrete elements is of a transmittance of light of at most 50%.

5. The article as defined in claim 1 in which each element of the inorganic film is of a transmittance of light of at most 30%.

6. The article as defined in claim 1 in which each element of inorganic film consists of multilayers which comprise layers of transparent substances and/or layers of a transmittance of light of at most 50%.

7. The article as defined in claim 3 in which the transparent inorganic film is forced of at least one substance selected from the group consisting of oxides, nitrides, fluorides and sulfides of metals.

8. The article as defined in claim 4 in which the inorganic film is formed of a mixture of at least one substance selected from the group consisting of silicides, borides, nitrides and carbides and at least one substance selected from the group consisting of metals and colored oxides of metals.

9. The article as defined in claim 5 in which the inorganic film is formed of at least one substance of a transmittance of light of at most 30% selected from the group consisting of metals and colored oxides of metals.

10. The article as defined in claim 2 in which elements of the inorganic film are arranged in a regular pattern.

11. The article as defined in claim 2 in which elements of the inorganic film are arranged randomly.

12. The article as defined in claim 2 in which the ratio of the short axis to the long axis of each element of the inorganic film is from 0.1 to 1.

13. The article as defined in claim 12 in which the shape of each element of the inorganic film is a circle.

14. The article as defined in claim 12 in which the shape of each element of the inorganic film is oval or ellipse.

15. The article as defined in claim 12 in which the shape of each element of the inorganic film is a rectangle.

16. The article as defined in claim 2 in which the synthetic resin is a hydrophobic polymer.

17. The article as defined in claim 16 in which the percentage area of uncoated areas is from 5 to 70%.

18. The article as defined in claim 16 in which the area of each element of the inorganic film is at most 3×10^4 square microns.

19. The article as defined in claim 17 in which the hydrophobic polymer is a member of the group consisting of polycarbonates, poly(methyl methacrylate), polyvinyl chloride, polystyrene, polypropylene, polyethylene and unsaturated polyester resins.

20. The article as defined in claim 17 in which the hydrophobic polymer is a polycarbonate.

21. The article as defined in claim 17 in which the hydrophobic polymer is poly(methyl methacrylate).

22. The article as defined in claim 17 in which the hydrophobic polymer is an unsaturated polyester resin.

23. The article as defined in claim 17 comprising a panel for use as a door.

24. A protective film as defined in claim 17 comprising a sheet for use in goggles.

25. The article as defined in claim 2 in which the synthetic resin is a hydrophilic polymer.

26. The article as defined in claim 25 in which the percentage area of unreacted areas 30 to 99%.

27. The article as defined in claim 25 in which the percentage area of uncoated areas is 60 to 99%.

28. The article as defined in claim 25 in which the hydrophilic polymer is a member selected from the group consisting of hydrophilic acrylic and methacrylic polymers, polyvinyl alcohol, polyvinyl acetals, polyacrylamides, polyvinyl pyrrolidone, polyethyleneoxide, polyethyleneimine, hydroxyethylcellulose and regenerated cellulose.

29. The article, as defined in claim 25 in which the hydrophilic polymer is a hydrophilic acrylate or methacrylate polymer.

30. The article as defined in claim 29 in which the hydrophilic acrylate or methacrylate polymer is a polymer of at least one hydrophilic acrylate or methacrylate selected from the group consisting of hydroxy-lower alkyl acrylate, hydroxy-(lower alkyl) methacrylates, hydroxy-(lower alkoxy-lower alkyl) acrylates and hydroxy-(lower alkoxy-lower alkyl) methacrylates.

31. The article as defined in claim 29 comprising glass coated with the hydrophilic polymer.

32. The article as defined in claim 29 comprising glass coated with a hydroxyethyl acrylate or methacrylate polymer.

33. The article as defined in claim 31 comprising an eyeglass lens.

34. The article as defined in claim 31 comprising a window glass.

35. The article as defined in claim 31 comprising an automobile windshield.

36. The article as defined in claim 25 in which the hydrophilic polymer is polyvinyl alcohol.

37. An article having an abrasion resistant and antifogging surface comprising a substrate of which at least the surface is formed of a hydrophilic synthetic resin and a protective discontinuous inorganic film of a thickness of from 400 A. to 5 microns coated thereon, said film comprising discrete elements of such size and spacing that the article retains the abrasion resistance of a continuous film while presenting a sufficient portion of hydrophilic surface to the surrounding atmosphere to prevent fogging by absorbing moisture from the atmosphere.

38. The article of claim 37 having a percentage area of an uncoated area in the film from 5 to 99%.

39. The article of claim 38 wherein the inorganic film comprises numerous transparent elements.

40. The article of claim 37 in which each of the inorganic elements has a transmittance of light of at most 50%.

41. The article of claim 37 in which each element of the inorganic film has a transmittance of light of at most 30%.

42. The article of claim 37 wherein each element of inorganic film consists of a multilayer which comprise

layers of transparent substances, layers of a transmittance of light of at most 50% or mixtures of layers of transparent substances and layers of a transmittance of light of at most 50%.

43. The article of claim 39 in which the transparent inorganic film is formed of at least one substance selected from the group consisting of oxides, nitrides, fluorides and sulfides of metals.

44. The article of claim 40 in which the inorganic film is formed of a mixture of at least one substance selected from the group consisting of silicides, borides, nitrides, and carbides and at least one substance selected from the group consisting of metals and colored oxides of metals.

45. The article of claim 41 in which the inorganic film is formed of at least one substance of a transmittance of light of at most 30% selected from the group consisting of metals and colored oxides of metals.

46. The article of claim 38 in which the elements of the inorganic film are arranged in a regular pattern.

47. The article of claim 38 in which the elements of the inorganic film are arranged randomly.

48. The article of claim 38 in which the ratio of the short axis to the long axis of each element of the inorganic film is from 0.1 to 1.

49. The article of claim 48 in which the shape of each element of the inorganic film is a circle.

50. The article of claim 48 in which the shape of each element of the inorganic film is an oval or ellipse.

51. The article of claim 48 in which the shape of each element of the inorganic film is a rectangle.

52. The article of claim 38 in which the percentage area of uncoated area is 30 to 99%.

53. The article of claim 52 in which the percentage area of uncoated area is 60 to 99%.

54. The article of claim 38 in which the hydrophilic synthetic resin is a hydrophilic polymer which is a member selected from the group consisting of hydrophilic acrylic and methacrylic polymers, polyvinyl alcohol, polyvinyl acetals, polyacrylamides, polyvinyl pyrrolidone, polyethylene oxide, polyethyleneimine, hydroxyethyl cellulose and regenerated cellulose.

55. The article of claim 38 in which the hydrophilic synthetic resin is a hydrophilic acrylate or methacrylate polymer.

56. The article of claim 55 in which the hydrophilic acrylate or methacrylate polymer is a polymer of at least one hydrophilic acrylate or methacrylate selected from the group consisting of hydroxy-lower alkyl acrylates, hydroxy lower alkyl methacrylates, hydroxy lower alkoxy lower alkyl acrylates and hydroxy lower alkoxy lower alkyl methacrylates.

57. The article of claim 56 in which the hydrophilic acrylate or methacrylate is hydroxyethyl methacrylate.

58. The article of claim 55 in which the substrate is glass coated with the hydrophilic synthetic resin.

59. The article of claim 58 comprising an eyeglass lens.

60. The article of claim 58 comprising a window glass.

61. The article of claim 58 comprising an automobile windshield.

62. The article of claim 38 in which the hydrophilic synthetic resin is polyvinyl alcohol.

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