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(54) Title: PROCESS FOR COATING A GLASS PLATE

(57) Abrégé/Abstract:

Process for the preparation of glass plates by applying a porous coating to the glass through a coating slit over the required width of the glass, such that a coating thickness of 50-400 nm is achieved after drying and curing, and the slit is at a distance of between 5-10,000 times the dry coating thickness.

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(54) Title: PROCESS FOR COATING A GLASS PLATE

(57) Abstract: Process for the preparation of glass plates by applying a porous coating to the glass through a coating slit over the required width of the glass, such that a coating thickness of 50-400 nm is achieved after drying and curing, and the slit is at a distance of between 5-10,000 times the dry coating thickness.

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PROCESS FOR COATING A GLASS PLATE

The invention relates to a process for making a coated glass plate, the glass plate having on at least a part of at least one of its surfaces a porous coating.

Coated glass plates are known. For example, anti-reflective coated plates are used in picture frames for framing photos, aquarelle or watercolour paintings, drawings, etches, posters and the like. Untreated glass plates show a strong light reflection generally of about 8% when looking at the glass at normal angle (90°). The reflection increases sharply at sharper angles. This reduces the clarity of the picture and is therefore unwanted.

The coatings are commonly applied in a dip-coating process: the glass plate is dipped in a container with a coating fluid, and withdrawn at a certain speed. Although this method is satisfactory in some cases it requires relatively stable coating fluids as the fluid in the container is used in only a very small percentage. In addition, the process is inefficient as the glass plates must be manipulated into the container and can only be coated a few at a time. Furthermore, the coating is applied to both sides of the glass which may be unnecessary.

The aim of the present invention is to provide a process for the preparation of a coated glass plate.

The present invention provides a process for the preparation of coated plates by applying a coating to the glass through a coating slit over the required width of the glass, such that a coating thickness of 50-400 nm is achieved after drying and curing, and the slit is at a distance of between 5-10,000 times the dry coating thickness.

In a preferred embodiment, the process present process relates to coating a glass plate with a porous coating, and in particular an anti-reflective coating.

A further preferred embodiment relates to a coating process used in-line on a float-glass line.

One of the problems encountered is that float glass can become contaminated during the fabrication process especially on the side that is contacted by the float bath. In one embodiment of the invention, the anti-reflective coating is applied directly after fabrication to the side which was not in contact with the float bath.

In another embodiment of the invention, the invention provides for a process of making a coated glass plate, the process comprises the steps of

(1) cleaning the glass, preferably only the side to be coated

(2) providing on at least a part of at least one side of the glass plate a coating through a coating slit over the required width of the plate, such that a coating thickness of 50-400 nm is achieved after drying and curing, and the slit is at a distance of between 5-10,000 times the dry coating thickness; the coating comprising nano size particles, a binder and a solvent

(3) drying the coating

Preferably, the coating layer has an arithmetic average roughness of 2-50 nm, and having per reflective coated side a minimum reflection at a wavelength between 425 and 675 nm of about 2% or less.

In an alternative embodiment, the present invention provides a process for the preparation of anti-reflective glass plates by applying a coating to the glass through a gravure coating process over the required width of the glass, such that a coating thickness of 50-400 nm is achieved after drying, and the gravure roll applies 1-8 μm wet coating thickness, while the coating chamber is designed to preclude substantial solvent evaporation.

It was unexpected that, with such gravure coating technique, thin coatings with very even thickness could be applied at relatively high speed. This technique is preferred for applications that require higher production rates but can accept a less even coating. An example of such an application is glass for mass-produced solar cells. It should be noted, however, that coating through a slit might also be used for solar cell production as it produces a very even coating thickness even if it is not as fast as the gravure technique.

In a preferred embodiment of the invention, the process for coating a glass plate with an anti-reflective layer in which the coating is applied through a gravure coating role is used in-line at a glass plant, preferably for glass for solar cells.

The embodiments as described herein for the coating through a slit can also be applicable to coating with a gravure role.

In one embodiment the thickness of the coating after curing is estimated by multiplying the wet thickness by the concentration of solids in the coating solution.

The transparency of the anti-reflective glass plate is preferably high. For common float glass, which has an absorbance of 1 to 1.5% at 2 mm thickness, the transparency is generally about 94% or higher at 2 mm thickness at wavelength between 425 and 675 nm, preferably about 96% or higher, more preferably about 97% or higher, even more preferably about 98% or higher.

The coated glass plates obtained with the process of the present invention are preferably used in framing such as frames for photo's, paintings, posters, etches, drawings, presentation cases, and the like.

In another embodiment of the invention, the glass plate is used in an architectural setting such as for a window, partition, or other glass structure.

In one embodiment, the glass is curved and can be multi-layered to improve strength.

In another embodiment, the glass is used for solar cells. The anti-reflective properties allow for a substantial higher efficiency, not only at around normal angle, but also at acute angles. The latter is an advantage in comparison to multi-layer anti-reflective coatings.

A glass plate is contemplated by the inventors to have a wide meaning, including quartz, polycarbonate or other plate like materials that have a high transparency, preferably a transparency of about 80% or more at 2 mm thickness, more preferably about 90% or more at 2 mm thickness.

Generally, the glass plate has a thickness of 0.5 mm or more, preferable 1 mm or more, most preferably, about 1.8 mm or more. In general, the glass plate has a thickness of about 10 mm or less, preferably 6 mm or less, more preferable about 4 mm or less, and most preferred, about 3 mm or less. However, the thickness of the glass is not critical, and could be 10 cm or less.

In another embodiment, the substrate is inorganic. More in particular ordinary glass or quartz. Ordinary float glass is most preferred, as it is a cheap and widely available material

An anti-reflective glass plate is meant to be a glass plate (as defined) with a light reflection reducing coating on at least part of at least one side of the glass.

The anti reflective glass plate will generally have a size of 10 cm by 10 cm or larger, preferably about 20 cm by 20 cm or larger. The maximum size is mainly dictated by practical considerations, and will generally be 2 by 3 meter or less. In one embodiment, the anti reflective glass plate preferably has a size of about 20 by 30 cm or multiples thereof, such as preferably 30 by 40 and most preferably 90 by 130 cm or the multiple thereof. In another embodiment, the anti reflective glass plate preferably has a size of about 30 by 40 inch (about 72 by 96 cm) or multiple thereof, such as for example about 60 by 40 inch (about 144 by 96 cm).

In one embodiment of the invention the coated glass is coated and then tempered. This embodiment offers the advantage that the tempering step also cures the coating hence saving energy.

Preferably at least part of the surface is coated with an anti-reflective coating. Generally about 20% or more of the width of a surface will be coated, preferably about 50% or more, even more preferably, about 90% or more of the width of the surface is coated with the anti-reflective coating.

Preferably the anti-reflective coating is such, that – measured for one coated side - at a wavelength between 425 and 675 nm (the visible light region) the minimum reflection is about 2% or less, preferably about 1.5% or less, and most preferably about 1% or less. The average reflection at one side, over the region of 425 to 675 nm generally will be about 2.5% or less, preferably about 2% or less, more preferred, about 1.5% or less, and , even more preferably about 1% or less. Generally, the minimum in the reflection will be at a wavelength between 425 and 675 nm, preferably at a wavelength of 450 nm or higher, and more preferred at 500 nm or higher. Preferably, minimum is at a wavelength of 650 nm or lower, more preferred at 600 nm or lower. The optimal wavelength for the human eye is a minimum reflection around 550 nm as this is the wavelength (colour) at which the human eye is most sensitive. In case a colour shade is required, a minimum at lower or higher wavelength can be chosen. The reflection can be measured with any suitable reflectometer or colorimeter as known to the skilled artisan. Generally, the reflection will show a slope or a curve over the 425-675 nm wavelength. The minimum is defined as either a minimum in a curve, or the lower end of the slope, being at 675 or at 425 nm.

Generally, at least one side of the glass plate needs to be coated e.g. in case a picture or a solar-cell substrate is glued to the other side of the glass. However, in one embodiment of the invention, the glass plate has an anti-reflective coating on both sides. This may be achieved by coating both sides of a glass plate. It is also possible to laminate two glass plates which are coated on one side, whereby the non-coated sides are laminated to each other. It is preferred, that the glass plate in use has on both outermost sides an anti-reflective coating. It is, however, also possible to combine different techniques to obtain various functionalities. Other useful functionalities include anti-fogging, anti-fouling, anti-stick, easy-clean, lubricious, antistatic, low-emission coatings (such as low-heat emission), and the like.

Preferably, the reflection of the glass plate (with a coating on two sides) at the wavelength exhibiting a minimum is about 3% or less, preferably about 2% or less, and more preferred about 1% or less. The average reflection over a 425-675 nm wavelength range is generally about 4% or less, preferably about 3% or less, and even more preferably about 2% or less.

A light reflection reducing (or anti-reflective) coating is a coating that reduces the reflection of light from an article at least one wavelength between 425 and

675 nm, as measured at the normal incident angle. Measurements are carried out on the coated and uncoated article. Preferably the reduction in reflection is about 30% or more, preferably about 50 % or more, more preferably about 70% or more, even more preferably about 85% or more. The reduction in reflection as expressed in a percentage is equal to 100x(reflection of the uncoated article - the reflection of the coated article)/ (reflection of uncoated article).

The arithmetic average roughness can be measured by Atomic Force Microscopy (AFM) and is preferably about 2 nm or larger, more preferably about 5 nm or larger, even more preferably about 10 nm or larger, even more preferably still about 20 nm or larger. The arithmetic average roughness generally will be about 50 nm or lower, preferably 45 nm or lower.

The coating of the present invention can exhibits voids in the coating thereby having a nano-porous structure. The voids aid in obtaining anti-reflective properties. Generally, the coating comprises about 20 volume% or more of void volume. Void volume is herewith defined as open space between the particle/binder in principle filled with ambient air. Preferably the voids represent about 30 volume% or more, even more preferably the voids represent about 40 volume% or more; still more preferably, the voids represent about 50 vol.% or more. Generally, the coating exhibits voids in the coating of about 90% or less, in another embodiment about 80 volume% or less; and in a further embodiment about 70 vol.% or less.

The process for making the present coated glass plate preferably comprises the steps of

(1) producing the glass on a float-glass line,
(2) optionally cleaning the glass,
(3) providing on at least a part of at least one side of the glass plate a coating, the coating being applied through a coating slit over the required width of the plate such that a coating thickness of 50-400 nm is achieved after drying and curing, and the slit is at a distance of between 5-10,000 times the dry coating thickness; the coating comprising nano sized particles, a binder and a solvent,
(4) drying and, if necessary, curing the coating.

Preferably the coating layer has an arithmetic average roughness of 2-50 nm, and having per reflective coated side a minimum reflection at a wavelength between 425 and 675 nm of about 2% of less.

For many coating processes, cleaning is an important step, as small amounts of contaminant such as dust, grease and other organic compounds cause the anti reflective coating, or other coatings to show defects. Cleaning can be done in a number of ways, such as firing (heating up to 600-700 °C; applicable if an inorganic substrate is used); and/or cleaning with a cleaning fluid such as soap in demineralised water, alcohol, or acidic or basic detergent systems. When using a cleaning fluid, generally, the glass plate is dried at a temperature between 20 °C and 400 °C, optionally with applying an air flow.

However, cleaning may be dispensed with where the glass is clean enough already or where the intended application of the coated glass does not require a high quality coating.

The coating is provided on at least a part of at least one side of the glass plate. In the process of the present invention, the coating is applied via a slit over the required width of the plate such that a coating thickness of 50-400 nm is achieved after drying and curing, and the slit is at a distance of between 5-10,000 times the dry coating thickness. With this coating technique it is possible to use in a continuous or semi-continuous process. Furthermore, it is an advantage that it is unnecessary to use large amounts of coating composition. In addition, the coating composition can be used continuously with less quality control issues or prolonged storage times. Therefore it is possible to use less stable coating solutions. This is a clear advantage, as normal silica-based coatings tend to have a shelve life of 1-4 weeks. After such time it is necessary to replace the solution which can be difficult and can cause substantial waste problems.

The coating generally has a thickness of 1-5 µm before drying. The required wet thickness is dependant on the solid content of the coating, and is not important as such. The coating thickness generally is measured after drying and curing, but may be measured after drying only, i.e. after evaporation of the non-reactive solvent(s). The thickness of the wet coating is influenced by the viscosity of the coating, the width of the slit, the distance of the slit to the glass plate, the pressure put on the coating while flowing through the slit, and the speed of coating. The thickness of the coating when substantially dry (i.e. with about 20 wt% or less of non-reactive solvent relative to the solid material) is preferably about 300 nm or less, preferably about 200 nm or less, most preferred about 170 nm or less. Generally, the dry, uncured coating will have a thickness of about 50 nm or more, preferable about 60 nm or more, most preferably about 70 nm or more. Thickness is measured either spectroscopically (reflectometery or ellipsometery) or by directly observing a fracture surface by electron microscopy.

The slit of the coating apparatus has the length of the part that is required to be coated. Generally, the whole length of a plate will be coated. In one embodiment, only the outer mm. is not coated. Generally, the slit will be straight, but it can or needs to be curved if necessary, in order to keep that the distance to the plate substantially the same across the coated length.

Generally, the coating will be forming a bead on top of the slit, either by capillary forces, or by slight pressure, e.g. because the surface of the coating material in the storage tank is slightly above the height of the slit. The bead is than brought into contact to the plate, and the coating adheres to the glass, as the adhesive forces are larger than the cohesive forces within the bead. The plate can than be drawn along the slit, or the slit can be drawn along the plate, or both movements can be made, as to coat the required length of the plate.

In order to increase the capillary force, for e.g. higher flow speed, it is preferred to coat the slit with a high surface tension material, such as for example PTFE, or other fluorinated materials. A high surface tension causes a larger bead, and thereby an easier coating process.

In a preferred embodiment, the substrate is at an angle which helps a liquid coating 'flow' causing a more equal coating. The angle preferably is about 2 degrees or higher, more preferably about 5 degrees or higher, and even more preferably 10 degrees or higher. The angle may be as high as about 90 degrees (i.e. vertical). In one embodiment, the plate is preferably approximately vertical as an optimal leveling of the coating on the glass plate may take place.

The width of the slit is preferably about 0.1 mm or larger, more preferably about 0.25 mm or larger, even more preferably, about 0.5 mm or larger. Preferably, the width of the slit will be about 5 mm or smaller, even more preferably 2mm or smaller.

Preferably, the distance between the slit and the surface to be coated will be about 5 times the dry coating thickness or more, preferably about 10 times, and more preferably about 20 times the dry coating thickness. Preferably, the distance is about 10,000 times or less, preferably about 1000 times or less.

In a preferred embodiment of the invention measures are taken to increase the evaporation of the solvent and/or to withdraw the evaporated solvent off after coating of the glass. For example, a hood and/or air flow can be used to aid removal of the solvent.

In one embodiment, the coated and dried plate is subjected to a curing step.

In another embodiment, the process comprises a further step, the coated glass plate being subjected to a quality control step after coating and drying, but before curing the coating. After coating, but before curing, the antireflective properties are discernable although slightly different from the cured coated plate. For example, upon cure, the coating may shrink, causing a shift in wavelength at minimum reflection. If glass plates would be not within specifications, these plates can be taken out before curing, thereby saving the costs of curing. Furthermore, these plates can be cleaned, and used again in the process of the invention.

The coating used in this invention comprises nano sized particles, a binder and a solvent.

Examples of suitable particles are particles comprising lithium fluoride, calcium fluoride, barium fluoride, magnesium fluoride, titanium dioxide, zirconium oxide, antimony doped tin oxide, tin oxide, aluminum oxide, and silicon dioxide. Preferably particles comprising silicon dioxide, most preferably particles consisting for at least for 90 wt.% of silicon dioxide are used.

In one embodiment of the invention, the coating comprises particles having an average aspect ratio larger than 1.5, as the glass plate shows an advantageous low reflection of light.

Preferably the aspect ratio of the particles is larger than 2, more preferably larger than 4, even more preferably larger than 6, even still more preferably larger than 8, most preferably larger than 10. Generally, the aspect ration will be about 100 or lower, preferably about 50 or lower.

The sizes of the particles may be determined by spreading a dilute suspension of the particles over a surface and measuring the sizes of individual particles by using microscopic techniques, preferably scanning electronic microscopy (SEM) or atomic force microscopy (AFM). Preferably the average sizes are determined by measuring the sizes of 100 individual particles. The aspect ratio is the ratio between the length and the width of a particle. In case of rods and worm-like particles the length is the largest distance between two points in the particle and the width is the largest diameter as measured perpendicular to the central axis of the particle, both the length and the width are measured of the projection of the particles as observed under the microscope.

In one embodiment, rod-like and/or worm-like particles, preferably worm-like particles, are used. Worm-like particles are particles having a central axis that deviates from a straight line. Examples of worm-like particles are known by the trade name Snowtex (IPA-ST-UP, particles have a diameter of 9-15 nm with a length of 40-300 nm), as delivered by Nissan Chemical.

Preferably the particles are nano particles. Preferably the nano particles have a length of less than 1000 nm, more preferably of less than 500 nm, even more preferably of less than 350nm.

In a preferred embodiment, the coating comprises particles are largely spherical (i.e. having an aspect ratio of about 1.2 or lower, preferably of about 1.1 or lower), and generally have a size of about 10 nm or larger, preferably 20 nm or larger, and most preferred 40 nm or higher. Generally, the particles will have a size of 200 nm or smaller, preferably 150 nm or smaller, and most preferred about 100 nm or smaller. With respect to other characteristics, the description of the non-spherical particles described above is equally applicable to the spherical particles. The advantage of using largely spherical particles is that the volume nano-pores resulting from the space between spherical particles is small relative to the space between non-spherical particles and thus the coatings derived from spherical particles suffer less from filling of the nano-pores via capillary forces leading to a loss in anti-reflective performance.

In another embodiment, the coating comprises mixtures of above described particles.

The coating preferably comprises a binder, which has as main function to keep the particles attached and adhered to the glass plate. Preferably, the binder forms covalent bonds with the particles and the substrate. For this purpose, the binder – before curing - preferably contains inorganic compounds with alkyl or alkoxy groups, but other compounds may be suitable as well. Further, the binder preferably polymerises itself to form a continuous polymeric network.

In one embodiment of the invention the binder of the coating consists substantially of an inorganic binder, as such coating shows good mechanical properties and good adhesion to the substrate, resulting in, for example, high puncture resistance, high scratch resistance and good wear resistance.

The inorganic binder preferably comprises one or more inorganic oxides, for example silicon dioxide. The binder preferably is a crosslinked inorganic material that covalently links the particles and the substrate.

The inorganic binder may result after the cross-linking reaction and heating of the non-reacted binder, for example an alkoxy silane, an alkyl silicate or a sodium silicate. As alkoxy silanes preferably tri and tetra alkoxy silanes are used. Preferably, ethyl silicate binders are used. Due to the heating step these silicium compounds are converted into silicon dioxide.

In another embodiment, the binder is an organic coating, wherein the particles bear reactive organic groups, and optionally, further coating material is present which has groups, reactive with the reactive groups on the particles. This embodiment is preferred in case the glass plate is of organic nature, and cannot withstand baking temperatures of up to 400 °C. In one embodiment, the reactive groups on the particles are (meth)acrylate, and the reactive groups on the further coating material is of ethylenic unsaturated, preferably (meth)acrylate. Examples of suitable coatings are described in WO2004/104113.

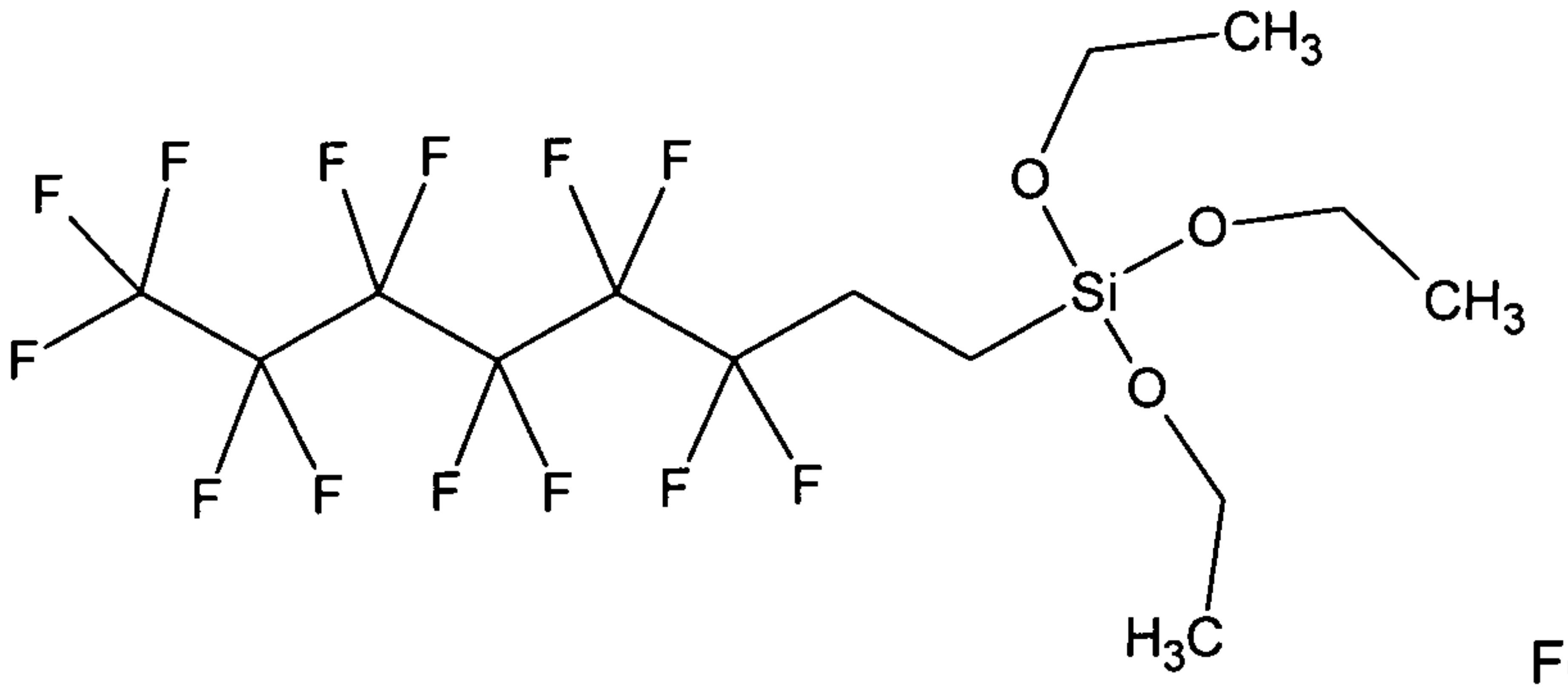
Preferably, the coating comprises an amount of non-reactive solvent to adjust the viscosity of the particles and binder to such a value, that thin layers can be applied on the glass plates. Preferably the viscosity of the coating is about the value of the neat non-reactive solvent, and is the amount of solids in the coating about 5 wt% or less, preferably, about 4% or less, more preferred about 3% or less. To have an economic process, the amount of solids generally will be about 0.5 wt% or more, preferably about 1 wt% or more, more preferably about 2 wt% or more. Preferably, the viscosity will be about 2.0 mPa.s or more, preferably 2.2 mPa.s or more and even more preferably about 2.4 mPa.s or more. Generally, the viscosity is about 20 mPa.s or less, preferable about 10 mPa.s or less, more preferably about 6 mPa.s or less, and even more preferred about 3 mPa.s or less. The viscosity can be measured with a Ubbelohde PSL ASTM IP no 1 (type 27042)

Depending on the chemistry of the binder, many solvent are useful. Suitable examples of solvents include water, non-protic organic solvents, and alcohols.

In one embodiment, with an inorganic binder an organic solvent is used, more preferably a mixture of water and alcohol is used as the solvent. The concentration of solids in the coating composition may be between 1 and 20 weight (wt) %, preferably between 1 and 5 wt. %. The wt % of the particles, based on 100% of solids is for example more than 50 wt.%, preferably more than 60 wt.% and most preferably more than 70 wt.% in the final coating. The concentration of solids is the concentration of all components that don't evaporate after the application of the coating composition to the article.

The coating composition may comprise a compound to catalyze the conversion of the precursor into the binder. In case of alkoxy silane or ethyl silicate binders as the precursor preferably an acid, for example acetic acid is used as the catalyst. The catalyst preferably is added to the coating composition just prior to its application. In case of UV curable materials, a light sensitive initiator is generally used as catalyst.

The coating composition may also comprise a hydrophobic inorganic binder precursor. The addition of such a precursor can lead to hydrophobic and even super-hydrophobic properties of the resulting coating while retaining the anti-reflective function. Preferably a hydrophobic coating is obtained with static water contact angles of greater than 90°, more preferably with a static water contact angles of greater than 140°. An example of such a hydrophobic binder precursor additive binder can be, but is not limited to, 1H,1H,2H,2H-(Perfluorooctyl) triethoxysilane (see formula I)



Formula 1

For organic binders, a fully organic solvent system is preferred, although some water may be present. Examples of suitable solvents include 1,4-dioxane, acetone, chloroform, cyclohexane, diethylacetate, propanol, ethanol, methanol, butanol, methyl ethyl ketone, methyl propyl ketone, tetrahydrofuran, toluene and tetrafluoroisopropanol. Preferred solvents are methanol, methyl ethyl ketone, isopropanol or 1-methoxypropan-2-ol.

It is an advantage of the present invention that the coating is insensitive to moisture. Thus, in contrast to the three-layer coating, the space where the glass plates are coated need not to be humidity controlled, and humidity between for example 30 and 80% is acceptable. Further, the inorganic coating also is not sensitive to time delays between coating and curing. The organic UV curable coating is generally cured directly after application, although this is also not critical.

Preferably the coating composition is applied to the article in a thickness eventually resulting in a thickness after cure of about 50 nm or larger, preferably of about 70 nm or larger, more preferably about 90 nm or higher. Preferably, the thickness after cure will be about 300nm or less, preferably of about 200nm or less, more preferably about 160 nm or less, and most preferred about 140 nm or less.

In one embodiment of the process, the coating application is applied to a glass plate before a tempering step of that glass plate. The tempering step is normally carried to introduce internal stresses in an ordinary glass plate by virtue of which it will fragments in small pieces when the glass plate breaks. The tempering step is usually carried out as known to those skilled in the art and involves heating up to 600 °C. One advantage of the coating according to the invention is that the coating can withstand this tempering process and can be cured during the tempering process. In that case the curing and tempering process are thus carried out in one step.

In one embodiment of the invention, the coating is applied (semi-) continuous in line of a glass-plate manufacturer, and thereafter, the coating cured while the glass is subjected to a tempering step.

The invention will be further elucidated by the following examples, without being limited thereto.

Examples

The preparation of inorganic coatings systems based on particles both with a high and low aspect ratio is described in section A. Preparation of organic/inorganic hybrid coatings using UV curing are described in section B. The properties of the anti reflective coating systems are described in Section C.

The silica particles were delivered by Nissan Chemical and a summary of their properties is given in Table 1.

Table 1. Types and properties of silica particles.

Particle	particle Size (nm)	SiO_2 (wt%)	H_2O (%)	Viscosity (mPa.s.)	Specific Gravity	pH	Particle Shape	Solvent
MT-ST	10-15	30-31	< 2.0	< 5	0.98-1.02	2-4	Spherical	Methanol
IPA-ST-UP	9-15	15-16	< 1.0	< 20	0.85-0.90	2-4	Worm-like*	Iso-propanol

*worm-like particles have a high aspect ratio: a diameter of 9-15 nm and a length of 40-300 nm

Section A:

Coating formulations were prepared either by grafting reactive inorganic binder (alkoxy silanes) onto the surface of the silica particles (type IPA-ST-UP) and then mixing with a pre-hydrolysed binder (mixture B, see table 2) or by directly mixing the particles (type MT-ST) with the pre-hydrolysed binder.

Pre-hydrolysed alkoxy silane binder was made by adding an alkoxy silane, water and acetic acid to solvent. After 72 hours at room temperature the mixture was diluted with solvent to the desired concentration and hydrochloric acid was added to get a pH of 1 (mixture B). Table 2 shows the amounts of chemicals used.

Table 2.

Material	Mixture B
Tetraethylorthosilicate	11.9 wt-%
Water (hydrolysis agent)	10.9 wt-%
Acetic acid	1.2 wt-%
Isopropanol	75.8 wt-%
Hydrochloric acid	0.2 wt-%
Total	100 wt-%

Reactive inorganic binder precursor groups were grafted onto the worm like silica nano-particles by adding an alkoxy silane to a suspension of the oxide particles in solvent. Table 3 shows the amounts of chemicals used. After stirring, water was added to the mixture and the mixture was heated to 80°C and kept there for 4 hours. After cooling down the mixture was diluted with solvent to the desired concentration. At this point a certain amount of mixture B is added to the reaction mixture to get the desired final formulation suited for the dipping process (example formulation 1).

Example formulation 2 based on spherical nano-silica particles was prepared by adding pre-hydrolysed binder (mixture B) and water to a suspension of the spherical oxide particles in solvent. At this point the resultant mixture was diluted with solvent to the desired concentration for application to the substrate. Table 3 shows the amounts used.

Table 3. Compounds in weight percentage used for inorganic AR liquid coating formulations. Weight percentages of silica particles are given in equivalent dry weight, i.e. weight percentage solids.

Material	Formulation 1	Formulation 2
Isopropanol (solvent)	85.8 wt-%	75.9 wt-%
ST-UP particles	1.6 wt-%	
MT-ST particles		2.6 wt-%
Tetraethylorthosilicate	3.8 wt-%	
Water (hydrolysis agent)	5.0 wt-%	8.3 wt%

Mixture B	3.9 wt-%	13.2wt-%
Total	100 wt-%	100 wt-%

A2: Preparation of an inorganic AR coating or film on a substrate

Thin films of the formulations 1 and 2 are prepared on glass slides by the following procedure. A glass plate is washed and dried thoroughly to prepare it for the coating process. The glass slide is then coated with either formulation 1 or 2. The coating is applied through a slit of 2 mm which is drawn along the glass plate at a distance of 400 µm. The glass plate is kept at a 80° angle. After evaporation of the solvent the dried inorganic coating is cured in an oven for 4 hours at 450°C to ensure complete curing. The coating has a thickness of about 200 nm.

B1. Modification of silica particles with polymerisable-groups

Radically polymerising groups were grafted onto worm like silica nano-particles by adding a trimethoxy-silane compound comprising an acrylate group (*e.g.,* 3-(trimethoxysilyl)propyl acrylate) together with p-methoxy-phenol, a compound that inhibits polymerization of the acrylate groups, an acid and a catalytic amount of water to a suspension of the silica nano-particles in an isopropyl alcohol. After each addition the formulation was shortly stirred. After the final addition the mixture was stirred for at least one hour at room temperature. Table 4 shows the amounts of chemicals used

Table 4. Compounds in weight percentage used for modification of worm-like silica nano- particles. Weight percentage of silica particles is given in equivalent dry weight, i.e. weight percentage solids.

Material	Modified nano-particle solution 1
IPA-ST-UP particles	14.9 wt%
3-(trimethoxysilyl)propyl acrylate	1.5 wt%
Hydroquinnone mono-methylether	0.004 wt%
Water	0.63 wt%
Isopropanol	83.0 wt%
Total	100 wt%

B2. Preparation of the inorganic/organic hybrid AR formulation

The acrylate modified silica particle solution was formulated to the example formulation 3 by adding various binders, photo-initiator, stabilizer and solvent. Table 5 shows the amounts of chemicals used. After stirring at room temperature for at least 6 hours the formulation 3 was ready for use.

Table 5. Example formulation 3.

Particle solution 1.	15.2 wt%
Trimethylolpropane propoxylate triacrylate	0.28 wt%
Trimethylolpropane-tris(3-mercapto-propionate)	0.06 wt%
2-methyl-4'-(methylthio)-2-morpholino-propiophenone	0.06 wt%
Propylgallate	0.002 wt%
1-methoxy-2-propanol	84.4 wt%
Total	100 wt%

B3. UV curable hard coat

The UV curable hard coat (HC) formulation (3) comprises (52 w-t% solids) acrylate surface modified silica particles (MT-ST, particles size 10-15nm), Dipentaerythritol pentaacrylate (28wt-% solids), Ethoxylated (9) trimethylolpropane triacrylate (18wt-% solids), photo-initiator Irgacure 184 from Ciba (2wt-% solids) and an amount of methanol as a solvent such that the final concentration of all solids is ca 50wt-%.

B4. Preparation of a coating or film on a substrate

Thin films of various mixtures are prepared on glass or polycarbonate plates by the following procedure. The glass or polycarbonate plates are washed and dried thoroughly to prepare it for the coating process. If preferred a hard coat can be applied before applying example formulation 3. The glass or polycarbonate plate is then coated with the hard coat formulation as described in example A2. After evaporation of the solvent the thin hard coat layer is cured with UV radiation (Fusion UV Systems, D-bulb) at a dose of 0.8 J/cm^2 in air. To apply example formulation 3 onto the hard coat or directly onto the glass or polycarbonate plate, the glass or polycarbonate plate is coated with formulation 3. After evaporation of the solvent the thin layer is cured with UV radiation (Fusion UV Systems, D-bulb) under nitrogen at a dose of 2.0 J/cm^2.

CLAIMS:

1. Process for the preparation of coated glass by applying a coating to the glass through a coating slit and drying the coating, wherein a coating thickness of 50-200 nm is achieved after drying, and the slit is at a distance of between 5-10,000 times the coating thickness after drying from the glass.
2. Process according to claim 1, wherein the process is used in-line on a float-glass line, and wherein the coating is applied directly after fabrication at the side which was not in contact with fluid metal.
3. Process according to claim 1 or 2, wherein the glass is at an angle relative to horizontal of about 10° or greater.
4. Process according to claim 1 or 2, wherein the width of the slit is from 0.1 mm to 2 mm.
5. Process according to claim 1 or 2, wherein the coating comprises nano-sized particles, a binder and a solvent.
6. The process according to claim 5, wherein the nano-sized particles comprise a metal oxide.
7. The process according to claim 5, wherein the nano-sized particles comprise silicon dioxide.
8. The process according to claim 5, wherein the binder contains inorganic compounds with alkyl or alkoxy groups.
9. The process according to any one of claims 1-8, wherein the coating has a concentration of solids between 1 and 5 wt%.
10. The process according to any one of claims 1-8, wherein the coating has a viscosity of 2.0 – 20 mPa.s.