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(54) Title: OPTICAL ARTICLE WITH IMPROVED ANTIREFLECTIVE COATING, METHODS FOR MAKING THE SAME

Fig.1a

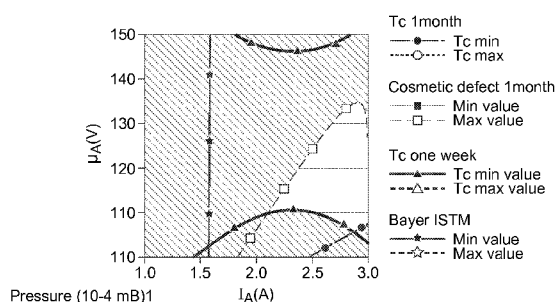
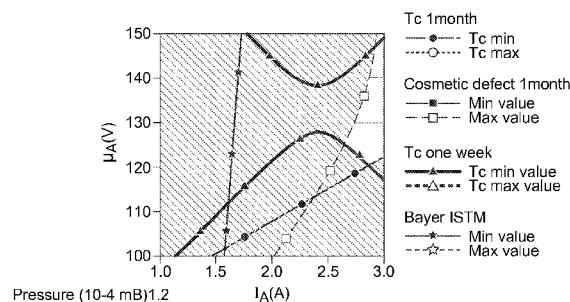


Fig.1b



(57) Abstract: The present invention relates to an optical article comprising a transparent substrate with a front main face and a rear main face, at least one of said main faces being coated with at least: a sub-layer with a main thick layer that is deposited in a vacuum chamber under a predetermined pressure and a multilayered antireflective coating comprising at least one HI layer having a refractive index higher than or equal 1.55, and at least one LI layer having a refractive index lower than 1.55, said multilayered antireflective coating - has a mean light reflection factor in the visible region R_v that is lower than or equal to 1.5 % for at least an angle of incidence lower than 35° and - a mean reflection factor R_{uv} between 280 nm and 380 nm, weighted by the function $W(\lambda)$ defined in the ISO 13666:1998 standard, that is equal to or lower than 5%, for an angle of incidence in the range 20° to 50° , wherein the at least one HI layer comprises at least one material selected from the group consisting of tantalum pentoxide (Ta_2O_5), and wherein said multilayered antireflective coating comprises no cosmetic defects evaluated visually in transmission.

Optical article with improved antireflective coating, methods for making the same**BACKGROUND OF THE INVENTION****1. Field of the invention**

The invention relates to an optical article, especially an ophthalmic lens, comprising an antireflective coating which strongly reduces reflection both in the visible region and in the UV-radiation range, while being able to develop no (or almost no) cosmetic defects over time, as well as to methods for making such an optical article.

2. Description of related art

It is a common practice in the art to coat at least one main surface of a lens substrate, such as an ophthalmic lens or lens blank, with several coatings for imparting to the finished lens additional or improved optical or mechanical properties. These coatings are designated in general as functional coatings.

Thus, it is usual practice to coat at least one main surface of a lens substrate, typically made of an organic glass material, with successively, starting from the surface of the lens substrate, an impact-resistant coating (impact-resistant primer), an abrasion- and/or scratch-resistant coating (hard coat), an anti-reflection coating and, optionally, an anti-fouling top coat. Other coatings such as a polarized coating, a photochromic or a dyeing coating may also be applied onto one or both surfaces of the lens substrate.

An anti-reflection coating is defined as a coating, which improves the anti-reflective properties of an optical article when deposited at its surface. It reduces reflection of light at the interface article-air on a relatively wide band of the visible spectrum.

Anti-reflection coatings are well known and classically comprise a single-layer or multi-layer stack of dielectric materials such as SiO₂, SiO, Al₂O₃, MgF₂, LiF, Si₃N₄, TiO₂, ZrO₂, Nb₂O₅, Y₂O₃, HfO₂, Sc₂O₃, Ta₂O₅, Pr₂O₃, and mixtures thereof. They are generally inorganic by nature.

It is also well known that anti-reflection coatings preferably are multi-layer coatings comprising alternatively high refractive index layers (HI) and low refractive index layers (LI).

It is also known to interleave a sub-layer between the substrate and the first anti-reflection layer in order to improve abrasion and/or scratch resistance of said coating and its adhesion to the substrate.

Generally, classical anti-reflection (AR) coatings have a satisfactory heat resistance up to about 70 °C. Above this temperature, cracks may appear in the AR stack, in particular at the surface of the substrate of the optical article, which damages the AR coating. In the present patent application, the temperature from which cracks are beginning to be observed in an article or coating is called the critical temperature (T_C).

In the case of organic glass substrates (synthetic resin), deposition of the anti-reflection coating (optionally comprising a sub-layer) has to be performed through moderate temperature processes so as to avoid deterioration of the substrate. Taking such precaution is useless in the case of mineral glass substrates.

The consequence of a lower temperature treatment is, generally, in the case of organic glass substrates, a lower durability of the AR coating.

Moreover, organic glass substrates (either coated or uncoated) have a higher thermal expansion coefficient than inorganic materials constituting layers or sub-layers of the anti-reflection coating. The consequence is that they lead to articles which may develop high stress. Such stress may generate naked eye visible cracks or exfoliation in the AR coating upon increasing temperature.

This phenomenon is particularly noticeable when the organic substrate is based on diethylene glycol bis(allyl carbonate) monomers, episulfide monomers (materials having a refractive index $n \geq 1.70$), or polythiourethane (materials having a refractive index n equal to or higher than 1.60).

In addition, during the edging and fitting of an eyeglass by an optician, the eyeglass undergoes mechanical deformations that may produce cracks in mineral interference coatings, in particular when the operation is not carried out with care. Similarly, thermal stresses (heating of the frame) may produce cracks in the anti-reflection coating. Depending on the number and the size of the cracks, the latter may mar the field of view of the wearer and prevent the eyeglass from being sold. Furthermore, while the treated organic eyeglasses are being worn, scratches may appear. In mineral anti-reflection coatings, certain scratches lead to cracking, making the scratches more visible because of scattering of light.

Different ways to improve the critical temperature of an optical article can be found in the literature.

US patent application 2005/0219724 describes an optical article coated with a multi-layer dielectric film, such as an anti-reflection coating, comprising alternate layers of high (TiO_2) and low (SiO_2 doped with a small amount of Al_2O_3 , $n = 1.47$) refractive indexes. According to this document, using $\text{SiO}_2/\text{Al}_2\text{O}_3$ mixtures instead of SiO_2 allows to decrease the stress in LI layers, and consequently the cracks appearance probability at the substrate surface.

The document US 2008/002260 describes an optical article having anti-reflection properties comprising a substrate having at least one main face coated with a multi-layer anti-reflection coating comprising a stack of at least one high refractive index layer and at least one low refractive index layer, wherein:

each low refractive index layer has a refractive index of 1.55 or less;

each high refractive index layer has a refractive index higher than 1.55 and does not comprise niobium pentoxide (Nb_2O_5);

said coated main face of the optical article has a mean luminous reflection factor $R_v \leq 1\%$; and:

(a) the low refractive index layer of the anti-reflection coating below the outermost layer of said coating each have a physical thickness < 100 nm, the ratio R_T

$$R_T = \frac{\text{sum of the physical thicknesses of the low refractive index layers of the anti-reflection coating}}{\text{sum of the physical thicknesses of the high refractive index layers of the anti-reflection coating}}$$

is higher than 2.1, and the anti-reflection coating does not comprise a sub-layer comprising niobium (Nb), or

(b) the anti-reflection coating comprises: at least one low refractive index layer having a physical thickness ≥ 100 nm which is not the outermost layer of the anti-reflection coating; and at least one high refractive index layer and at least one low refractive index layer, which are located above the low refractive index layer having a physical thickness ≥ 100 nm and not being the outermost layer of the anti-reflection coating which is the furthest from the substrate, and the ratio R_T

$$R_T = \frac{\text{sum of the physical thicknesses of the low refractive index layers of the anti-reflection coating}}{\text{sum of the physical thicknesses of the high refractive index layers of the anti-reflection coating}}$$

is higher than 2.1, with the proviso that the layers of the anti-reflection coating taken into account for the calculation of said ratio R_T are only the layers located above the low refractive index layer having a physical thickness ≥ 100 nm and not being the outermost layer of the anti-reflection coating which is the furthest from the substrate.

The particular multilayered interferential coating such as performed in this document improves the critical temperature of cracks appearance up to 98 to 110°C. However, even if this optical article is satisfactory, there is still a need to improve its robustness and its aesthetic appearance.

Hence, there is a need to provide a transparent optical article comprising an organic or mineral glass substrate bearing an inorganic anti-reflection coating, preferably a lens, and more preferably an ophthalmic lens for eyeglasses, having an improved resistance to heat and temperature variations, i.e., a high critical temperature, which would be an alternative to already known thermally resistant antireflective coated optical articles.

There is also a need to provide novel antireflective coatings having both very good antireflective properties at least in the visible region and in the UVA and UVB bands, while having at the same time robustness properties and aesthetic appearance, i.e.: developing no (or almost no) cosmetic defects over time.

The aim of the present invention is thus to provide a new optical article, that avoids all or some of the aforementioned drawbacks.

Another aim of this invention is to provide a process of manufacturing the above defined article, which could be easily integrated into the classical manufacturing chain.

SUMMARY OF THE INVENTION

The targeted aims are therefore achieved according to the invention by an optical article comprising a transparent substrate with a front main face and a rear main face, at least one of said main faces being coated with at least: a sub-layer with a main thick layer that is deposited in a vacuum chamber under a pre-determined pressure and a multilayered antireflective coating comprising at least one HI layer having a refractive index higher than or equal 1.55, and at least one LI layer having a refractive index lower than 1.55, said multilayered antireflective coating

- has a mean light reflection factor in the visible region R_v , as defined in the ISO 13666:1998 Standard and measured in accordance with the ISO 8980-4, that is lower than or equal to 1.5 % for at least an angle of incidence lower than 35° and

- a mean reflection factor R_{UV} between 280 nm and 380 nm, weighted by the function $W(\lambda)$ defined in the ISO 13666:1998 standard, that is equal to or lower than 5%, for an angle of incidence in the range 20° to 50°,

wherein the at least one HI layer comprises at least one material that is tantalum pentoxide (Ta_2O_5), and

wherein said multilayered antireflective coating comprises no cosmetic defects evaluated visually in transmission.

Due to its characteristics, the optical article, especially the ophthalmic lens according to the invention, comprises a transparent organic or mineral glass substrate coated with a multilayered antireflective coating possessing very good antireflective performances in the visible region and in the UV range, while guarantying both good aesthetics appearance (no or almost no cosmetic defects over time) and high robustness.

In addition, the optical article according to the invention has improved resistance to heat and temperature variations, i.e., a high critical temperature even after a long time, and is therefore an alternative to already known thermally resistant antireflective coated optical articles.

Such multilayered antireflective (AR) coating resistant to cracking would be particularly interesting if applied on the first face of a semi-finished lens, generally the front (convex) face, because it would then be possible to deposit by spin coating an AR coating on the second face of the lens (generally on the back side) followed by curing at elevated temperature without altering the AR on the front face.

As it will be shown in the experimental part below, the optical article according to the invention has generally a critical temperature equal to or higher than 80°C, preferably higher than or equal to 90°C, without compromising the economic and/or industrial feasibility of its manufacture and without compromising their robustness properties and their aesthetic appearance.

Furthermore, the optical article according to the invention offers the advantage of having high critical temperature, without decreasing the optical and mechanical performances of said optical article, such as color and anti-reflection performances, cleanability, adhesion of the layers to the substrate, abrasion resistance and corrosion resistance.

Especially, another advantage is that the optical article has a good resistance to dipping in hot water followed by mechanical surface solicitations.

It is another object of the invention to provide a method of manufacturing an optical article, comprising at least the following steps:

(i) providing an optical article comprising a transparent substrate with a front main face and with a rear main face;

(ii) depositing by evaporation under vacuum, onto one of said main faces of said substrate,

- a sub-layer with a main thick layer that is performed at a pre-determined pressure;

- a multilayered antireflective coating comprising at least one HI layer having a

refractive index higher than or equal 1.55, and at least one LI layer having a refractive index

lower than 1.55, the at least one HI layer comprising at least one material that is tantalum pentoxide (Ta_2O_5), that is performed by ion-beam assisted deposition (IAD) in which a pre-determined anode current I_A that is ranging from 1 to 4 A and a pre-determined anode voltage U_A that is ranging from 80 to 200 V, are supplied, so as to form the stack S;

5 (iii) recovering the optical article.

The Applicant has discovered that specific experimental conditions during the deposition of the main thick layer of the sub-layer (such as the pressure) and during the deposition of the HI layer of the multilayered antireflective coating (such as the anode current I_A or the anode voltage U_A), combined with the use of HI layer(s) made of tantalum pentoxide, enable to obtain
10 in an easy manner an appropriate antireflective film coated onto a sublayer, and especially an appropriate antireflective coating comprising alternate HI and LI layers.

Indeed, the Applicant has found that from at least a specific mineral oxide that is tantalum pentoxide for forming at least one HI layer of the multilayered antireflective coating and from specific experimental conditions (pressure, anode current and anode voltage) and
15 deposition processes (evaporation under vacuum with or without ion-beam assisted deposition), it is possible to form a multilayered antireflective coating having an improved critical temperature, a reduced weakness to crazing and/or cracking, while having excellent antireflective and robustness properties, while being easy to implement.

The invention also relates to a method of optimizing the manufacture of an optical article
20 comprising a transparent substrate with a front main face and a rear main face, at least one of said main faces being coated with at least a multilayered antireflective coating comprising at least one HI layer having a refractive index higher than or equal 1.55, and at least one LI layer having a refractive index lower than 1.55, the at least one HI layer comprising at least one material that is tantalum pentoxide (Ta_2O_5),

25 said method of optimizing comprising the following steps:

(a) performing a plurality of times, the following steps (i) to (iii) by varying only three parameters that are : a pre-determined main thick layer of sub-layer pressure, a pre-determined anode current I_A and a pre-determined anode voltage U_A so as to obtain several optical articles having the same structure:

30 (i) providing an optical article comprising the transparent substrate with a front main face and a rear main face;

(ii) depositing by evaporation under vacuum, onto one of said main faces of said substrate,

- a sub-layer, the deposition of a main thick layer of which is performed at the pre-determined pressure;
- the multilayered antireflective coating, the deposition of the at least one HI layer is performed by ion beam assisted deposition (IAD) in which the pre-determined anode current I_A and the pre-determined anode voltage U_A are supplied, so as to form the stack S;

35

40 (iii) recovering the optical article;

(b) measuring at least one optical performance for each of the obtained optical articles including the critical temperature, so as to obtain optical performance data;

(c) selecting the combination(s) of said three parameters that enable(s) to obtain a critical temperature T_c equal to or higher than 80°C , preferably equal to or higher than 90°C , and more preferably equal to or higher than 95°C .

The Applicant has developed a method of optimizing the manufacture of an optical article, such as the one described above.

Indeed, he has found that by modifying the experimental conditions (such as the pressure, the anode current and the anode voltage) for the manufacture of the same determined stack comprising a sub-layer and a multilayer antireflective coating, it is possible to configure an abacus containing the best experimental parameters.

Other objects, features and advantages of the present invention will become apparent from the following detailed description. It should be understood, however, that the detailed description and the specific examples, while indicating specific embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

DETAILED DESCRIPTION OF THE INVENTION

AND PREFERRED EMBODIMENTS

1. Definitions

The terms "comprise" (and any grammatical variation thereof, such as "comprises" and "comprising"), "have" (and any grammatical variation thereof, such as "has" and "having"), "contain" (and any grammatical variation thereof, such as "contains" and "containing"), and "include" (and any grammatical variation thereof, such as "includes" and "including") are open-ended linking verbs. They are used to specify the presence of stated features, integers, steps or components or groups thereof, but do not preclude the presence or addition of one or more other features, integers, steps or components or groups thereof. As a result, a method, or a step in a method, that "comprises," "has," "contains," or "includes" one or more steps or elements possesses those one or more steps or elements, but is not limited to possessing only those one or more steps or elements.

Unless otherwise indicated, all numbers or expressions referring to quantities of ingredients, reaction conditions, etc. used herein are to be understood as modified in all instances by the term "about."

Also unless otherwise indicated, the indication of an interval of values « from X to Y » or "between X to Y", according to the present invention, means as including the values of X and Y.

In the present application, when an optical article comprises one or more coatings onto the surface thereof, the expression "to deposit a layer or a coating onto the article" is intended to mean that a layer or a coating is deposited onto the external (exposed) surface of the outer coating of the article, that is to say its coating that is the most distant from the substrate.

A coating, that is said to be "on" a substrate or deposited "onto" a substrate is defined as a coating, which (i) is positioned above the substrate, (ii) is not necessarily in contact with the substrate, that is to say one or more intermediate coatings may be arranged between the substrate and the coating in question, and (iii) does not necessarily completely cover the substrate.

In a preferred embodiment, the coating on a substrate or deposited onto a substrate is in direct contact with this substrate.

When "a layer 1 is lying under a layer 2", it is intended to mean that layer 2 is more distant from the substrate than layer 1.

By outermost layer of the multilayered antireflective coating, it is meant the layer of the anti-reflection coating which is the furthest from the substrate.

By innermost layer of the multilayered antireflective coating, it is meant the layer of the anti-reflection coating which is the closest to the substrate.

By inner layer of the multilayered antireflective coating, it is meant any layer of the anti-reflection coating except for the outermost layer of said AR coating.

Also, unless stated otherwise, all thicknesses disclosed in the present application relate to physical thicknesses.

The terms multilayered antireflective coating or AR coating and AR stack have the same meaning.

Unless otherwise specified, the refractive indexes referred to in the present application are expressed at 25 °C at a wavelength of 550 nm.

The multilayered antireflective coating according to the invention may be formed on at least one of the main faces of a bare substrate, i.e. an uncoated substrate, or at least one of the main faces of the substrate already coated with one or more functional coatings, such as an anti-abrasion coating.

As used herein, the rear (or the inner or Concave or CC) face of the substrate is intended to mean the face which, when using the article, is the nearest from the wearer's eye. It is generally a concave face. On the contrary, the front face of the substrate (or Convex or CX), is the face which, when using the article, is the most distant from the wearer's eye. It is generally a convex face.

Also, as used herein, a "transparent substrate" means a substrate that, in at least one angle of incidence in the visible light ranges (380-780 nm), has a light absorption up to 0.2%. Indeed, above 0.2%, a substrate is considered to be opaque.

The term cosmetic appearance means that there is no, or almost no, cosmetic defects over time evaluated visually in transmission and is preferably measured under an arc lamp.

The term "robustness" of an optical article, such as an ophthalmic lens, in the present invention is defined as the ability of this lens to resist change despite the variations induced by its manufacture process. These variations depends, for instance, on the type of substrate which is used, the setting of the manufacturing machine (temperature schedule, appropriate time,

setting of the electron gun...) and/or its usage mode, the replacement of said manufacturing machine by another one.

Indeed, when a multilayered antireflective coating is manufactured at industrial scale, some thickness variations for each layer generally occur. These variations lead to different reflection performance, and especially different perceived residual reflected color of the multilayered antireflective coating. If the perceived residual reflected color of the antireflective coating of two lenses is different, these lenses will appear different and will not be able to be associated in pair.

As previously mentioned, in the present patent application, the temperature from which cracks are beginning to be observed in an article or coating is called the critical temperature (T_c).

According to the invention, the "angle of incidence (symbol θ)" is the angle formed by a ray light incident on an ophthalmic lens surface and a normal to the surface at the point of incidence. The ray light is for instance an illuminant light source, such as the standard illuminant D65 as defined in the international colorimetric CIE $L^*a^*b^*$ (1976). Generally the angle of incidence changes from 0° (normal incidence) to 90° (grazing incidence). The usual range for angle of incidence is from 0° to 75° .

The colorimetric coefficients of the optical article of the invention in the international colorimetric system CIE $L^*a^*b^*$ (1976) are calculated between 380 and 780 nm, taking the standard illuminant D 65 and the observer into account (angle of 2°). The observer is a "standard observer" as defined in the international colorimetric system CIE $L^*a^*b^*$.

The T_v factor, also called "luminous transmission" of the system, is such as defined in the standard ISO 13666:1998 and relates to an average in the 380-780 nm wavelength range that is weighted according to the sensitivity of the eye at each wavelength of the range and measured under D65 illumination conditions (daylight).

In the present description, unless otherwise specified, transmittances/transmissions are measured at the center of the optical article for a thickness ranging from 0.7 to 2 mm, preferably from 0.8 to 1.5 mm, at an angle of incidence ranging from 0° to 15° , preferably 0° . As used herein, the light transmitted refers to light arriving on the front main face of the optical article and that went through the lens.

Herein, the "luminous reflectance" noted R_v , is such as defined in the ISO 13666:1998 Standard, and measured in accordance with the ISO 8980-4, i.e. this is the weighted spectral reflection average over the whole visible spectrum between 380 and 780 nm. R_v is usually measured for an angle of incidence lower than 17° , typically of 15° , but can be evaluated for any angle of incidence.

In the present application and unless otherwise specified, R_v factor has been measured at an angle of incidence of 15° .

The mean reflection factor R_{UV} on the rear main face between 280 nm and 380 nm, weighted by the function $W(\lambda)$ defined in the ISO 13666:1998 standard, is lower than 7 %, preferably lower than 5 %, more preferably lower than or equal to 4.5%, even better lower than

or equal to 4% for an angle of incidence of 35° (on the rear face). In another embodiment, the mean reflection factor R_{UV} on the rear main face between 280 nm and 380 nm, weighted by the function $W(\lambda)$ defined in the ISO 13666:1998 standard, is preferably lower than 5 % for both an angle of incidence of 30° and for an angle of incidence of 45°. Said mean reflection factor R_{UV} is defined through the following relation:

$$R_{UV} = \frac{\int_{280}^{380} W(\lambda) \cdot R(\lambda) \cdot d\lambda}{\int_{280}^{380} W(\lambda) \cdot d\lambda}$$

wherein $R(\lambda)$ represents the lens spectral reflection factor at a given wavelength, and $W(\lambda)$ represents a weighting function equal to the product of the solar spectrum irradiance $E_s(\lambda)$ and the efficiency relative spectral function $S(\lambda)$. In certain embodiments, this factor may be measured at an angle of incidence that ranges from 30° to 45° on the rear face.

The spectral function $W(\lambda)$, enabling to calculate the ultraviolet radiation transmission factors, is defined according to the ISO 13666:1998 Standard. It makes it possible to express the ultraviolet solar radiation distribution tempered by the relative spectral efficiency of such radiation for the wearer, since it simultaneously takes both the solar spectral energy $E_s(\lambda)$ into account, which does globally emit less UVB-rays as compared to UVA-rays, and the spectral efficiency $S(\lambda)$, UVB-rays being more harmful than UVA-rays. The values for those three functions in the ultraviolet region are given in the table disclosed at page 6 of the publication WO 2012/076714.

2. Figure

The present invention will be described in more detail by referring to the appended drawing, wherein Figure 1 shows a graph obtained thanks to the Minilab software with the experiment conditions of example 1 with a pressure of 10^{-4} mBar (a) and $1.2 \cdot 10^{-4}$ mBar (b).

3. The optical article

The optical article according to the present invention is a transparent optical article, preferably a lens or lens blank, and more preferably an ophthalmic lens or lens blank. The optical article may be coated on its convex main side (front side), concave main side (back side), or both sides with the multilayered antireflective layer of the invention.

Generally speaking, the interferential multilayered coating of the optical article according to the invention, which may be an antireflective coating (called hereafter AR coating), may be deposited onto any substrate, and preferably onto organic lens substrates, for example a thermoplastic or thermosetting plastic material.

Substrate

The substrate of the article according to the invention is preferably an organic eyeglass, for example made of thermoplastic or thermosetting plastic. This substrate may be chosen from the substrates mentioned in patent application WO 2008/062142.

5 In particular, thermoplastic materials may be selected from, for instance: polyamides, polyimide, polysulfones, polycarbonates and copolymers thereof, poly(ethylene terephthalate) and polymethylmethacrylate (PMMA).

Thermoset materials may be selected from, for instance: cycloolefin copolymers such as ethylene/norbornene or ethylene/cyclopentadiene copolymers ; homo- and copolymers of allyl
10 carbonates of linear or branched aliphatic or aromatic polyols, such as homopolymers of diethylene glycol bis(allyl carbonate) (CR 39®) ; homo- and copolymers of (meth)acrylic acid and esters thereof, which may be derived from bisphenol A ; polymer and copolymer of thio(meth)acrylic acid and esters thereof, polymer and copolymer of allyl esters which may be derived from Bisphenol A or phthalic acids and allyl aromatics such as styrene, polymer and
15 copolymer of urethane and thiourethane, polymer and copolymer of epoxy, and polymer and copolymer of sulphide, disulfide and episulfide, and combinations thereof. As used herein, a (co)polymer is intended to mean a copolymer or a polymer. As used herein, a (meth)acrylate is intended to mean an acrylate or a methacrylate.

According to another embodiment of the invention, particularly recommended substrates
20 have a water uptake rate equal to or greater than 0.6% by weight relative to the total weight of said substrate, preferably equal to or greater than 0.7%, the water uptake rate being measured after predrying said substrate and storing it for 800 hours in a chamber at 50° C under 100% relative humidity and at atmospheric pressure. The inventors have observed indeed that the substrates with a water uptake rate lower than 0.6% by weight under the hereabove indicated
25 test conditions did not result in the formation of cosmetic defects.

Determining the water uptake rate of a substrate requires traditional procedures which are well known from the person skilled in the art and can be easily implemented. They are described in detail in the experiment part hereunder.

For instance, the following substrates are suitable for the present invention, especially if
30 they satisfy the hereabove mentioned water uptake rate characteristic: (meth)acrylic (co)polymers, in particular poly(methyl methacrylate) (PMMA), thio(meth)acrylic (co)polymers, polyvinyl butyral (PVB), polyurethanes (PU), poly(thiourethanes), polyol allylcarbonate (co)polymers, thermoplastic ethylene/vinyl acetate copolymers, polyesters such as poly(ethylene terephthalate) (PET) or poly(butylene terephthalate) (PBT), polyepoxides,
35 polycarbonate/polyester copolymers, cycloolefin copolymers such as ethylene/norbornene or ethylene/cyclopentadiene copolymers, and combinations thereof. Of course the substrates may be obtained through polymerization of monomer mixtures, or may also comprise mixtures of such polymers and copolymers.

Particularly preferred classes of substrates include poly(thiourethanes), polyurethane,
40 polyepisulfides and resins resulting from the polymerization or copolymerization of

alkyleneglycol bis allylcarbonates, polycarbonate, provided they have a water uptake rate equal to or greater than 0.6%.

Examples of substrates to be suitably used in the present invention include those obtained from MR6®, MR7®, MR8®, MR174® and MR10® resins (thermosetting polythiourethane resins). The various substrates based on polythiourethane resins are marketed by the Mitsui Toatsu Chemicals company and these substrates as well as the monomers used for their preparation are especially described in the patents U.S. Pat. No. 4,689,387, U.S. Pat. No. 4,775,733, U.S. Pat. No. 5,059,673, U.S. Pat. No. 5,087,758 and U.S. Pat. No. 5,191,055.

Still another organic material which is suitable for the substrate-forming optical article is that marketed under trade name Trivex® by PPG Industries company, and which is obtained from nitrogen-enriched urethane-based pre-polymer.

The substrates obtained through (co)polymerization of the diethyleneglycol bis allyl carbonate are also suitable (lenses ORMA® ESSLOR). The monomer acting as the synthesis basis is sold, for example, under the trade name CR-39® by the PPG Industries company. According to an embodiment of the invention, the substrate of the optical article is however not obtained through (co)polymerization of the diethyleneglycol bis allyl carbonate and especially is not selected from homo- and copolymers of allyl carbonates of linear or branched aliphatic or aromatic polyols (such as homopolymers of diethylene glycol bis(allyl carbonate) (CR 39®)) and/or homo- and copolymers of (meth)acrylic acid and esters thereof.

Examples of substrates that do not present a water uptake rate lower than 0.6% are mineral substrates (silica-based glasses), the 1.74® substrate, based on a polyepisulfide resin, and substrates based on a bisphenol-A homopolycarbonate resin, marketed especially by the TEIJIN company under the trade name PANLITE®, by GENERAL ELECTRIC COMPANY under the trade name LEXAN®, by the BAYER company under the trade name BAYBLEND®, by MOBAY CHEMICAL Corp. under the trade name MAKROLON® and by DOW CHEMICAL Co. under the trade name CALIBRE®.

The preferred substrates according to the invention are for instance the substrates obtained from MR6®, MR7®, MR8®, MR10®, MR174® resins and Trivex® product or polycarbonate. As used herein, a polycarbonate (PC) is intended to mean either homopolycarbonates or copolycarbonates and block copolycarbonates

The Applicant has discovered that these materials enable to obtain substrate that have improved resistance to heat and temperature variations.

Pre-treatment of the substrate

Before the multilayered interferential coating is deposited on the substrate, which is optionally coated, for example with an anti-abrasion and/or anti-scratch coating, it is common to subject the surface of said optionally coated substrate to a physical or chemical activation treatment intended to increase the adhesion of said multilayered interferential coating.

This pretreatment is generally carried out under vacuum. It may be carried out through bombardment with energetic and/or reactive species, for example an ion beam (ion pre-cleaning

or IPC) or an electron beam, a corona discharge treatment, a glow discharge treatment, a UV treatment or treatment in a vacuum plasma, generally an oxygen or argon plasma. It may also be carried out through an acidic or basic surface treatment and/or a treatment with solvents (water or organic solvent(s)). Several of these treatments may be combined. By virtue of these cleaning treatments, the cleanliness and the reactivity of the surface of the substrate are optimized.

The term "energetic species" (and/or "reactive species") is particularly understood to mean ionic species having an energy ranging from 1 to 300 eV, preferably from 1 to 150 eV, better still from 10 to 150 eV and even better still from 40 to 150 eV. The energetic species may be chemical species, such as ions, radicals, or species such as photons or electrons.

The preferred pre-treatment of the surface of the substrate is an ion bombardment treatment carried out by means of an ion gun, the ions being particles formed from gas atoms from which one or more electrons have been stripped. Argon is preferably used as the ionized gas (Ar^+ ions), though oxygen or a mixture of oxygen and argon may also be used, under an acceleration voltage generally ranging from 50 to 200 V, a current density generally contained between 10 and 100 $\mu\text{A}/\text{cm}^2$ at the activated surface, and generally under a residual pressure in the vacuum chamber possibly ranging from 8×10^{-5} mbar to 5×10^{-4} mbar.

Multilayered AR coating

The optical article of the invention comprises a multilayer antireflection coating that may be formed on an abrasion-resistant coating.

Especially, the optical article of the invention comprises a transparent substrate such as defined above with a front main face and a rear main face, at least one of said main faces being coated with at least: a sub-layer with a main thick layer that is deposited in a vacuum chamber under a pre-determined pressure and a multilayered antireflective coating comprising at least one HI layer having a refractive index higher than or equal to 1.55, and at least one LI layer having a refractive index lower than 1.55, said multilayered antireflective coating

- has a mean light reflection factor in the visible region R_v that is lower than or equal to 1.5 % for at least an angle of incidence lower than 35° and

- a mean reflection factor R_{UV} between 280 nm and 380 nm, weighted by the function $W(\lambda)$ defined in the ISO 13666:1998 standard, that is equal to or lower than 5%, for an angle of incidence in the range 20° to 50° ,

wherein the at least one HI layer comprises at least one material selected from the group consisting of tantalum pentoxide (Ta_2O_5) and preferably is constituted of tantalum pentoxide (Ta_2O_5), and

wherein said multilayered antireflective coating comprises no cosmetic defects evaluated visually in transmission, preferably evaluated visually under an arc lamp.

It is worth noting that, in the present application, single-layer or multi-layer sub-layers are not considered to be part of the anti-reflection coating. In general, they do not contribute to the anti-reflection properties of the optical article.

Hence, the multilayered antireflective coating of the invention comprises a stack of at least one layer with a high refractive index comprising at least tantalum pentoxide (named hereafter the "first HI layer") and of at least one layer with a low refractive index named hereafter the "first LI layer").

5 More preferably, it comprises at least two layers with a low refractive index (LI) and at least two layers with a high refractive index (HI). It is here a simple stack, since the layer total number in the antireflective coating is higher than or equal to 3, preferably higher than or equal to 4, and preferably higher than or equal to 5. In general, the layer total number in the antireflective coating is lower than or equal to 8, preferably lower than or equal to 7, and more
10 preferably lower than or equal to 6 layers. For instance, the layer total number in the antireflective coating (including the sublayer) is 5.

As used herein, a layer of the antireflective coating is defined as having a thickness higher than or equal to 1 nm. Thus, any layer having a thickness lower than 1 nm will not be considered when counting the number of layers in the antireflective coating.

15 HI layers and LI layers don't need to alternate with each other in the stack, although they also may, according to one embodiment of the invention. Two HI layers (or more) may be deposited onto each other, as well as two LI layers (or more) may be deposited onto each other.

In the present application, a layer of the antireflective coating is said to be a layer with a high refractive index (HI) when its refractive index is higher than or equal to 1.55, preferably
20 higher than or equal to 1.6, even more preferably higher than or equal to 1.7, even more preferably higher than or equal to 1.8 and most preferably higher than or equal to 1.9, such as higher than or equal to 2.0. Said HI layer preferably has a refractive index lower than 3.

A layer of an antireflective coating is said to be a low refractive index layer (LI) when its refractive index is lower than 1.55, preferably lower than or equal to 1.50, more preferably lower
25 than or equal to 1.48. Said LI layer preferably has a refractive index higher than 1.1.

The other HI layer (s) (other than the above-mentioned first HI layer comprising at least tantalum pentoxide Ta_2O_5) may be traditional high refractive index layer, that is well known in the art. It generally comprises one or more metal oxides such as, without limitation, zirconia (ZrO_2), titanium dioxide (TiO_2), alumina (Al_2O_3), tantalum pentoxide (Ta_2O_5), neodymium oxide (Nd_2O_3), praseodymium oxide (Pr_2O_3), praseodymium titanate (PrTiO_3), lanthanum oxide (La_2O_3), niobium oxide (Nb_2O_5), yttrium oxide (Y_2O_3). Optionally, the HI layers may further
30 contain silica or other materials with a low refractive index, provided they have a refractive index higher than or equal to 1.55 as indicated hereabove. The preferred materials include TiO_2 , PrTiO_3 , ZrO_2 , Al_2O_3 , Y_2O_3 , Ta_2O_5 and mixtures thereof and more preferably Ta_2O_5 .

35 Ta_2O_5 -based HI layer

In one particular embodiment of the invention, at least two HI layer of the antireflection coating is a Ta_2O_5 -based layer, the high refractive index of which is particularly interesting. In addition, this material Ta_2O_5 has a natural compressive stress (contrary to ZrO_2 that has a tensile stress) which helps to increase the critical temperature T_c of the optical article according
40 to the invention.

In general, at least two HI layers, preferably all the HI layers, of the antireflection coating (except the electrically conductive layer that will be described below) are Ta₂O₅-based layers and typically are constituted only of Ta₂O₅.

IAD during Ta₂O₅-based HI layer deposition

5 In another particular embodiment of the invention, the first HI layer made of at least Ta₂O₅ or constituted of Ta₂O₅ is deposited by ion-assisted deposition (IAD). This deposition method enables indeed to increase the compression of this layer and therefore its refractive index. Preferably, the other HI layer(s) is (are) also deposited by IAD. IAD does not require any heating of the substrates, which is interesting for coating heat-sensitive substrates such as
10 glass or plastic substrates.

The IAD operation may be performed by means of an ion gun (the Commonwealth of the type Mark II for example), where ions are particles composed of gas atoms from which one or more electron(s) is or are extracted. It does preferably consist in bombarding the surface to be treated with oxygen ions. Other ionized gases may be used either combined with oxygen, or
15 not, as for example argon, nitrogen, in particular a mixture of O₂ and argon according to a volume ratio ranging from 2:1 to 1:2.

Preferably, the first HI layer is deposited in a vacuum chamber by ion beam assisted deposition (IAD) with a pre-determined anode current I_A ranging from 1 to 4 A. The IAD is also performed at a pre-determined anode voltage U_A that is preferably ranging from 80 to 200 V.

20 As used herein, "a pre-determined anode current I_A ranging from 1 to 4 A" includes the followings values and any intervals between them: 1; 1.5 ; 2; 2.5 ; 3 ; 3.5 ; 4 and "a pre-determined anode voltage U_A ranging from 80 to 200 V" includes the followings values and any intervals between them: 80; 90; 100; 110; 120; 130; 140; 150; 160; 170; 180; 190; 200.

Hence, said first HI layer is deposited in a vacuum chamber by ion beam assisted
25 deposition (IAD) with a current density typically ranging from 10 μA/cm² to 200 μA/cm², preferably from 30 to 100 μA/cm² on the activated surface and typically under a residual pressure in the empty chamber which may vary from 6.10⁻⁵ mbar to 1.3.10⁻⁴ mbar, preferably from 8.10⁻⁵ mbar to 1.3.10⁻⁴ mbar.

Generally, all the HI layers of said multilayered antireflective coating (preferably
30 composed of Ta₂O₅) are deposited in a vacuum chamber by ion beam assisted deposition (IAD) with the pre-determined anode current I_A and the pre-determined anode voltage U_A.

Experimental conditions

According to a characteristic of the invention, the optical article is obtained with the following experimental conditions:

- 35
- said pre-determined sub-layer pressure ranges from 0.4×10^{-4} mbar to 1.5×10^{-4} mbar, preferably from 0.5×10^{-4} mbar to 1.3×10^{-4} mbar;
 - said pre-determined anode current I_A ranges from 2 to 3 A;
 - said pre-determined anode voltage U_A ranges from 100 to 150 V.

The inventors have observed that, in the AR coating of the invention, the use of Ta₂O₅
40 for forming the HI layer(s) associated with the IAD deposition method enable to improve the

critical temperature of the optical article of the invention and to obtain a reduced weakness to crazing and/or cracking, while having excellent antireflective properties, no or almost no cosmetic defects and while being easy to implement.

LI layers

5 LI layers are also well known and may comprise, without limitation, SiO_2 , MgF_2 , ZrF_4 , AlF_3 , and their combinations, preferably SiO_2 , which contributes to increase the thermal resistance of the antireflection coating. Optionally, the LI layers may further contain materials with a high refractive index, provided the refractive index of the resulting layer is lower than 1.55.

10 Preferably, the at least one LI layer comprises at least one material selected from SiO_2 that is not doped with alumina (Al_2O_3), and/or the sub-layer comprises SiO_2 that is not doped with alumina (Al_2O_3).

In a preferred embodiment, the outermost layer of the multi-layer AR coating is a low refractive index layer.

15 In general, LI layer(s) is (are) not deposited by IAD.

Preferably, the multilayered antireflective coating comprises at least two HI layers composed of tantalum pentoxide (Ta_2O_5) and at least two LI layers composed of silicon dioxide (SiO_2).

Sub-layer

20 As mentioned above, the antireflective coating is deposited onto a sub-layer comprising at least a main thick layer.

As used herein, a sub-layer comprising at least a main thick layer or thick sub-layer (or adhesion layer) is intended to mean a relatively thick coating, used in order to improve the mechanical properties such as the abrasion resistance and/or the scratch resistance of said AR
25 coating and/or so as to reinforce its adhesion to the substrate or to the underlying coating.

Because of its relatively high thickness, the sub-layer does not generally take part to the antireflective optical activity, especially when it has a refractive index close to that of the underlying coating (which is generally the anti-abrasion and anti-scratch coating) or to that of the substrate, if the sub-layer is directly deposited onto the substrate.

30 The sub-layer should have a thickness that is sufficient for promoting the abrasion resistance of the antireflective coating, but preferably not to such an extent that a light absorption could be caused, which, depending on the sub-layer nature, could significantly reduce the relative transmission factor τ_v . Its thickness is generally lower than 300 nm, more preferably lower than 200 nm, and is generally higher than 90 nm, more preferably higher than
35 100 nm and may be ranging from 90 to 300 nm.

The sub-layer preferably comprises a SiO_2 -based layer, this layer comprising preferably at least 80% by weight of silica, more preferably at least 90% by weight of silica, relative to the layer total weight, and even more preferably consists in a silica layer. The thickness of such silica-based layer is generally lower than 300 nm, more preferably lower than 200 nm, and is
40 generally higher than 90 nm, more preferably higher than 100 nm.

Preferably, this SiO₂-based layer is a silica layer that is not doped with alumina. Indeed, the inventors have found that SiO₂-based layer doped with alumina may produce cosmetic defects.

Single-layered sublayer

5 In a particular embodiment, the sub-layer comprising at least a main thick layer consists in a SiO₂ layer.

A sub-layer of the single-layer type will be preferably used.

Multilayered sublayer

10 However, the sub-layer may be laminated (multilayered), especially when the sub-layer and the underlying coating (or the substrate, if the sub-layer is deposited directly onto the substrate) have a substantially different refractive index. This applies especially when the underlying coating, which is generally an anti-abrasion and/or anti-scratch coating, or the substrate, have a high refractive index, i.e. a refractive index higher than or equal to 1.55, preferably higher than or equal to 1.57.

15 In this case, the sub-layer may comprise, in addition to a 90-300 nm-thick layer, called herein the main thick layer, preferably at most three additional layers, more preferably at most two additional layers, interleaved between the optionally coated substrate and such 90-300 nm-thick layer, which is generally a silica-based layer.

20 These additional layers are preferably thin layers, which function aims at limiting the reflections at the sub-layer / underlying coating interface or sub-layer / substrate interface, as appropriate.

A multilayered sub-layer preferably comprises, in addition to the main thick layer, a layer with a high refractive index and with a thickness lower than or equal to 80 nm, more preferably lower than or equal to 50 nm and most preferably lower than or equal to 30 nm. Such layer with
25 a high refractive index is directly contacting the substrate with a high refractive index or the underlying coating with a high refractive index, as appropriate. Of course, this embodiment may be used even if the substrate (or the underlying coating) has a refractive index lower than 1.55.

As an alternative, the sub-layer comprises, in addition to the main thick layer and to the previously mentioned layer with a high refractive index, a layer made of a SiO₂-based material
30 (that is to say comprising preferably at least 80% by weight of silica) with a refractive index lower than or equal to 1.55, preferably lower than or equal to 1.52, more preferably lower than or equal to 1.50, and with a thickness lower than or equal to 80 nm, more preferably lower than or equal to 50 nm and even more preferably lower than or equal to 30 nm, onto which is deposited said layer with a high refractive index. Typically, in this instance, the sub-layer
35 comprises, deposited in this order onto the optionally coated substrate, a 25-35 nm-thick SiO₂ layer, a 0-10 nm, preferably 0-5 nm -thick ZrO₂ or Ta₂O₅ layer and thereafter the sub-layer main thick layer as described above.

In particular, the main thick layer of the sub-layer (either of the single-layered or multilayered type) is deposited under vacuum at a predetermined pressure that is preferably

ranging from 0.4×10^{-4} mbar to 1.5×10^{-4} mbar, preferably from 0.5×10^{-4} mbar to 1.3×10^{-4} mbar.

Antistatic properties

5 The optical article of the invention may be made antistatic, that is to say not to retain and/or develop a substantial static charge, by incorporating at least one charge dissipating conductive layer into the stack present on the surface of the article.

The ability for a glass to evacuate a static charge obtained after rubbing with a piece of cloth or using any other procedure to generate a static charge (charge applied by corona...) may be quantified by measuring the time it takes for said charge to dissipate. Thus, antistatic
10 glasses have a discharge time of about a few hundred milliseconds, preferably 500 ms or less, whereas it is of about several tens of seconds for a static glass. In the present application, discharge times are measured according to the method exposed in the French application FR 2 943 798.

As used herein, an "electrically conductive layer" or an "antistatic layer" is intended to
15 mean a layer which, due to its presence on the surface of a non- antistatic substrate (i.e. having a discharge time higher than 500 ms), enables to have a discharge time of 500 ms or less after a static charge has been applied onto the surface thereof.

The electrically conductive layer may be located on various places in the stack, generally in or in contact with the antireflective coating, provided the anti-reflective properties thereof are
20 not affected. It is preferably located between two layers of the antireflective coating, and/or is adjacent to a layer with a high refractive index of such antireflective coating. Preferably, the electrically conductive layer is located immediately under a layer with a low refractive index of the antireflective coating, most preferably is the penultimate layer of the antireflective coating by being located immediately under the silica-based outer layer of the antireflective coating.

25 The electrically conductive layer should be thin enough not to alter the transparency of the antireflective coating. The electrically conductive layer is preferably made from an electrically conductive and highly transparent material, generally an optionally doped metal oxide. In this case, the thickness thereof preferably varies from 1 to 15 nm, more preferably from 1 to 10 nm. Preferably, the electrically conductive layer comprises an optionally doped
30 metal oxide, selected from indium, tin, zinc oxides and mixtures thereof. Tin-indium oxide ($\text{In}_2\text{O}_3:\text{Sn}$, tin-doped indium oxide), indium oxide (In_2O_3) and tin oxide (SnO_2) are preferred. In particular, the electrically conductive and optically transparent layer is a indium-tin oxide layer, noted ITO layer or a tin oxide layer (SnO_2).

Generally, the electrically conductive layer contributes, within the stack, but in a limited
35 manner, because of its low thickness, to obtaining antireflective properties and represents a layer with a high refractive index in the antireflective coating. This is the case for those layers made from an electrically conductive and highly transparent material such as ITO or SnO_2 layers.

Layer thickness

The antireflective coating does not comprise any layer with a thickness higher than or equal to 20 nm, preferably higher than 15 nm, based on tin oxide. When a plurality of indium oxide-based layers are present in the antireflective coating, their total thickness is preferably lower than 20 nm, more preferably lower than 15 nm. As used herein, an indium oxide-based layer is intended to mean a layer comprising at least 50% by weight of indium oxide relative to the layer total weight.

According to a preferred embodiment, the antireflective coating does not comprise any layer with a thickness higher than or equal to 20 nm, preferably higher than 15 nm, comprising indium oxide or tin oxide. When a plurality of layers comprising indium oxide, tin oxide or are present in the antireflective coating, their total thickness is preferably lower than 20 nm, more preferably lower than 15 nm.

Generally, each HI layer has a physical thickness ranging from 8 to 130 nm, preferably from 10 to 120 nm and typically ranging from 15 to 100 nm and each LI layer has a physical thickness ranging from 8 to 120 nm, preferably from 10 to 110 nm and typically ranging from 15 to 90 nm.

Preferably, the total thickness of the antireflection coating is lower than 1 micrometer, more preferably lower than or equal to 800 nm and even more preferably lower than or equal to 500 nm. The total thickness of the antireflection coating is typically higher than 100 nm, preferably higher than 150 nm.

Especially, the sub-layer has a physical thickness ranging from 75 nm to 250 nm, especially from 80 nm to 200 nm and typically from 100 to 180 nm and the multilayered antireflective coating comprises at least two HI layers and two LI layers and has especially, in the direction moving away from the substrate, the followings structure:

a first HI layer having a physical thickness ranging from 10 to 30 nm, preferably from 15 to 20 nm and typically from 17 to 22 nm;

a first LI layer having a physical thickness ranging from 10 to 35 nm, preferably from 15 to 30 nm and typically from 16 to 25 nm;

a second HI layer having a physical thickness ranging from 80 to 105 nm, preferably from 85 to 100 nm and typically from 88 to 95 nm;

an optional electrically conductive layer having a physical thickness lower than or equal to 10 nm (such as SnO_2);

a second LI layer having a physical thickness ranging from 60 to 90 nm, preferably from 65 to 85 nm and typically from 70 to 78 nm.

The present invention provides hence an antireflective coating with an improved conception, comprising a stack made of thin layers, the thicknesses and materials of which have been selected so as to obtain satisfactory antireflective performances both in the visible region and eventually in the ultraviolet region, while having both improved heat resistance, esthetic appearance and robustness properties.

Layer deposition

Except the first HI layer of the multilayered AR coating, and preferably except all the HI layers of the multilayered AR coating, that is (are) generally deposited by IAD, the various other layers of the antireflective coating and the sub-layer are preferably deposited by chemical vapor deposition, under vacuum, according to any of the following methods: i) by optionally ion-beam assisted, evaporation; ii) by ion-beam sputtering; iii) by cathode sputtering; iv) by plasma-assisted chemical vapor deposition. These various methods are described in the following references "Thin Film Processes" and "Thin Film Processes II," Vossen & Kern, Ed., Academic Press, 1978 and 1991, respectively. A particularly recommended method is the evaporation under vacuum.

Preferably, the deposition of the LI layer(s) of the multilayered AR coating and of the sub-layer are conducted by evaporation under vacuum. Preferably the deposition of the HI layer(s) of the multilayered AR coating are conducted by evaporation under vacuum with ion gun assistance (IAD),

Robustness

The Inventors have discovered that the multilayered antireflective coating of the invention has improved robustness properties and heat resistance properties.

In general, the multilayered antireflective coating has an optical robustness corresponding to the standard deviation of hue "σh" as defined in the international colorimetric CIE L*a*b* (1976) for an angle of incidence (θ) of 15° that is lower than or equal to 12°, preferably lower than or equal to 10°, in particular lower than or equal to 8°.

As used herein, "a standard deviation of hue "σh" lower than or equal to 12" includes the followings values and any intervals between them: 0; 0.5 ; 1 ; 1.5 ; 2; 2.5 ; 3 ; 3.5 ; 4 ; 4.5 ; 5 ; 5.5 ; 6 ; 6.5 ; 7 ; 7.5 ; 8 ; 8.5 ; 9 ; 9.5 ; 10 ; 10.5 ; 11; 11.5 ; 12.

Especially, the standard deviation of hue "σh" corresponds to the formula below and is measured such as explained in the experimental part (standard deviation of 500 values of hue generated by the Mac Leod software) :

$$\sigma h = \sqrt{\frac{\sum_{i=0}^{500} (\text{hue} - \text{hue}_{\text{average}})^2}{500}}$$

Critical temperature

Preferably, the optical article has a critical temperature Tc equal to or higher than 80°C.

As used herein, a critical temperature Tc equal to or higher than 80°C. includes the followings values and any intervals among them: 80; 81; 82; 83; 84; 85; 86; 87; 88; 89; 90; 91; 92; 93; 94; 95; 96; 97; 98; 99; 100; 101; 102; 103; 104; 105; 106; 107; 108; 109; 110; 111; 112; 113; 114; 115; 116; 117; 118; 119; 120; 121; 122; 123; 124; 125; etc.

Advantageously, the optical article has a critical temperature equal to or higher than 81°C, preferably equal to or higher than 85°C, more preferably equal to or higher than 90°C, especially equal to or higher than 93°C and typically equal to or higher than 100°C.

In general, T_c is measured as explained in the experimental part below, for instance at one month after the preparation of the optical article.

Rear face

Typically, an optical article, preferably an ophthalmic lens according to the invention
5 comprises a substrate that is successively coated on its rear face with an impact-resistant primer layer, an anti-abrasion and scratch-resistant layer, an anti-UV, antireflective coating according to the invention, and with a hydrophobic and/or oleophobic coating, or with a hydrophilic coating which provides antifog properties, or an antifog precursor coating. The ophthalmic lens according to the invention is preferably an ophthalmic lens for spectacles
10 (spectacle lens), or a blank for ophthalmic lenses. The lens may be a polarized lens, a photochromic lens or a solar lens, which may be tinted or not, be corrective, or not.

Front face

The front face of the substrate of the optical article may be successively coated with an impact-resistant primer layer, an abrasion-resistant layer and/or a scratch-resistant layer, an
15 antireflective coating which may be, or not, an anti-UV antireflective coating according to the invention, and with a hydrophobic and/or oleophobic coating.

In one embodiment, the optical article according to the invention does not absorb in the visible or not much, which means, in the context of the present application, that its transmission factor in the visible range τ_v , also called relative transmission factor in the visible range, is
20 higher than 90%, more preferably higher than 95%, even more preferably higher than 96% and most preferably higher than 97%.

The factor τ_v should be understood as defined by the international normalized definition (ISO 13666:1998 Standard) and is measured in accordance with the ISO 8980-3 Standard. It is defined in the wavelength range of from 380 to 780 nm.

25 Preferably, the light absorption of the article coated according to the invention is lower than or equal to 1%.

4. Method of manufacturing of an optical article

The invention also relates to a process for manufacturing an optical article, comprising at
30 least the following steps:

(i) providing an optical article comprising a transparent substrate with a front main face and with a rear main face;

(ii) depositing by evaporation under vacuum, onto one of said main faces of said substrate,

35 - a sub-layer with a main thick layer that is performed at a pre-determined pressure;

- a multilayered antireflective coating comprising at least one HI layer having a refractive index higher than or equal 1.55, and at least one LI layer having a refractive index lower than 1.55, the at least one HI layer comprising at least one material selected from the
40 group consisting of tantalum pentoxide (Ta_2O_5), that is performed by ion beam assisted

deposition (IAD) in which a pre-determined anode current I_A that is ranging from 1 to 4 A and a pre-determined anode voltage U_A that is ranging from 80 to 200 V, are supplied, so as to form the stack S;

(iii) recovering the optical article.

5 Of course, the characteristics of the optical article described above are reproduced here for the description of the method of manufacturing.

Therefore, the first HI layer of the multilayered AR coating made of at least Ta_2O_5 or constituted of Ta_2O_5 is deposited by ion-assisted deposition (IAD). More precisely, this HI layer is deposited by evaporation under vacuum assisted by bombarding the surface to be treated
10 with ions. This deposition method enables indeed to increase the compression of this layer and therefore its refractive index. Preferably, the other HI layer(s) is (are) also deposited by IAD. IAD does not require any heating of the substrates, which is interesting for coating heat-sensitive substrates such as glass or plastic substrates.

The IAD operation may be performed by means of an ion gun (the Commonwealth of the
15 type Mark II for example), where ions are particles composed of gas atoms from which one or more electron(s) is or are extracted. It does preferably consist in bombarding the surface to be treated with oxygen ions. Other ionized gases may be used either combined with oxygen, or not, as for example argon, nitrogen, in particular a mixture of O_2 and argon according to a volume ratio ranging from 2:1 to 1:2.

20 As used herein, "a pre-determined anode current I_A ranging from 1 to 4 A" includes the followings values and any intervals between them: 1; 1.5 ; 2; 2.5 ; 3 ; 3.5 ; 4 and "a pre-determined anode voltage U_A ranging from 80 to 200 V" includes the followings values and any intervals between them: 80; 90; 100; 110; 120; 130; 140; 150; 160; 170; 180; 190; 200.

Hence, said first HI layer of the multilayered AR coating is deposited in a vacuum
25 chamber by ion beam assisted deposition (IAD) with a current density typically ranging from to $10 \mu A/cm^2$ to $200 \mu A/cm^2$, preferably from $30 \mu A/cm^2$ to $100 \mu A/cm^2$ on the activated surface and typically under a residual pressure in the empty chamber which may vary from 6.10^{-5} mbar to $1,3 \cdot 10^{-4}$ mbar, preferably from 8.10^{-5} mbar to $1,3.10^{-4}$ mbar.

Generally, all the HI layers of said multilayered antireflective coating (preferably
30 composed of Ta_2O_5) are deposited in a vacuum chamber by ion beam assisted deposition (IAD) with the pre-determined anode current I_A and the pre-determined anode voltage U_A .

Preferably, the experimental conditions are as follows:

- said pre-determined main thick layer of sub-layer pressure ranges from 0.4×10^{-4} mbar to 1.5×10^{-4} mbar, preferably from 0.5×10^{-4} mbar to 1.3×10^{-4} mbar;

35 - said pre-determined anode current I_A ranges from 2 to 3 A;

- said pre-determined anode voltage U_A ranges from 100 to 150 V.

Such a process avoids heating the substrate, which is particularly interesting in the case of organic glasses.

Vacuum methods for the deposition of the different layers of the AR stack, especially the
40 LI layers, and the sublayer include: i) evaporation; ii) spraying with an ion beam; iii) cathode

sputtering; iv) plasma assisted chemical vapor deposition. These techniques are described in detail in "Thin Film Processes" and "Thin Film Processes II," Vossen & Kern, Ed., Academic Press, 1978 and 1991 respectively. The particularly recommended technique is vacuum evaporation.

5 The optional electrically conductive layer, which generally is a HI layer of the anti-reflection stack, may be deposited according to any appropriate method, for example by vacuum evaporation, preferably under ion assistance (IAD: Ion Assisted Deposition), or by a sputtering technique. The IAD method comprises packing said layer with heavy ions while it is being formed, so as to increase its density, adhesion and refractive index. It requires an ion
10 plasma in a gas atmosphere, such as argon and/or oxygen.

Surface pre-treatments such as IPC (Ion pre-cleaning) are performed at a stage in which the outermost coating layer of the substrate is the hard coat.

The optical article to be coated with the AR coating of the present invention may be a finished lens or a semi-finished lens. One of its main faces may have previously been coated
15 with an appropriate coating stack (anti-reflection, hard coat, primer coating, impact resistant coating, etc.).

The process of the invention presents many advantages. For example, its implementation requires no modification of the original tweaking of the traditional process for depositing an AR coating, no modification of the deposition apparatus, no various additional
20 equipments.

5. Method of optimizing the manufacture of an optical article

The invention also relates to a method of optimizing the manufacture of an optical article comprising a transparent substrate with a front main face and a rear main face, at least one of
25 said main faces being coated with at least a multilayered antireflective coating comprising at least one HI layer having a refractive index higher than or equal 1.55, and at least one LI layer having a refractive index lower than 1.55,

said method of optimizing comprising the following steps:

(a) performing a plurality of times, the following steps (i) to (iii) by varying only three
30 parameters that are : a pre-determined sub-layer pressure, a pre-determined anode current I_A and a pre-determined anode voltage U_A so as to obtain several optical articles having the same structure:

(i) providing an optical article comprising the transparent substrate with a front main face and a rear main face;

35 (ii) depositing by evaporation under vacuum, onto one of said main faces of said substrate,

- a sub-layer, the deposition of a main thick layer of which is performed at the pre-determined pressure;

- the multilayered antireflective coating, the deposition of which is performed by ion beam assisted deposition (IAD) in which the pre-determined anode current I_A and the pre-determined anode voltage U_A are supplied, so as to form the stack S;

(iii) recovering the optical article;

5 (b) measuring at least one optical performance for each of the obtained optical articles including the critical temperature, so as to obtain optical performance data;

(c) selecting the combination(s) of said three parameters that enable(s) to obtain a critical temperature T_c equal to or higher than 80°C , such as 90°C , preferably equal to or higher than 93°C , and more preferably equal to or higher than 95°C .

10 Preferably, said optical performances are further selected from: transparency, abrasion properties thanks to the ISTM Bayer Test, optical losses, cosmetic defects, adhesion thanks to the $n \times 10$ blow test.

Especially,

15 - the transparency T_v (%) as defined by the international normalized standard ISO 8980-3 measured at a wavelength ranging from 380 to 780 nm is higher than or equal to 90 %, preferably 95 %; and/or

- the calculated optical losses OL (%) corresponding to the formula :

$$\text{OL (\%)} = 100\% - T_v (\%) - R_v (\%) \text{ (front main face)} - R_v (\%) \text{ (rear main face)};$$

- the ISTM Bayer value is higher than or equal to 9, preferably 10 according to ASTM
- 20 Standard F735-81; and/or
- the n_{10} blows value is higher than 12; and /or
- the cosmetic defects evaluated visually in transmission, preferably under an arc lamp.

Of course, the characteristics of the optical article described above or the characteristics of the method of manufacturing described above are reproduced here for the description of the

25 method of optimizing the manufacture of the optical article.

In general, step (c) is implemented through a computer means, such as a computer with the analyzing program using the Minitab software from Minitab Inc.

Indeed, the different parameters are entered in the software. Especially, the lower limit and the upper limit of each desired parameters are entered in the software that is able to

30 provide a graph defining the ideal process window for the different tested parameters (see Fig.1). Indeed, Fig.1 shows the ideal process window for different parameters, such as T_c at one week, T_c at one month, cosmetic defect, and ISTM Bayer value for a predetermined pressure (1×10^{-4} mBar; Fig.1(a) or 1.2×10^{-4} mBar; Fig.1(b)) and as function of different predetermined values of anode current I_A (A) and of anode voltage U_A (V). For that purpose,

35 minimal values and maximal values of these different parameters (T_c , ISTM Bayer value and cosmetic defect) are entered in the software.

EXAMPLES

The invention is further illustrated by the examples described below. These examples are meant to illustrate the invention and are not to be interpreted as limiting the scope of the invention.

5

1. Preparation of the lenses: general procedure

The optical articles used in the examples were semi-finished MR7[®] round lenses surfaced to a power of (-4.00) diopters and a diameter of 75 mm, coated with a hard coat layer of refractive index 1,6 (Elis Mithril 1.6 hardcoat) and coated on its front face with an sub-layer made of SiO₂.

10

The layers of the antireflective coating were deposited without heating the substrates by evaporation under vacuum (evaporation source: electron gun) in a Syrus 3 AR coater.

The deposition frame is a Leybold 1104 machine fitted with an electron gun (ESV14 (8kV)) for evaporating oxides, and provided with an ion gun (Commonwealth Mark II) for the deposition of all the HI Layer of the multilayered AR coating by IAD and the electrically conductive layer made of SnO₂ and for the preliminary phase to prepare the surface of the substrate (IPC). The ionized gas was Argon for IPC and O₂ for IAD for both SnO₂ & Ta₂O₅.

15

The thickness of the layers was controlled by means of a quartz microbalance. The spectral measurements were effected on a variable incidence-spectrophotometer Perkin-Elmer Lambda 850 with an URA accessory (Universal Reflectance Accessory).

20

2. Operating procedures

The method for making optical articles comprises the step of:

- introducing the substrate, a step of activating the surface of the substrate by means of an argon ion beam (anode current: 1 A, anode voltage: 100 V, neutralization current: 130 mA),
- turning the ion irradiation off, forming the vernis and the sub-layer on the substrate by evaporation (generally 33 nm of SiO₂, 5nm of Ta₂O₅ and 158 nm of SiO₂ at a predetermined pressure with O₂),
- then subsequently the various layers of the antireflective coating by successive evaporations and at last a ventilation step (HI layers being deposited with IAD with O₂ at a predetermined anode current and a predetermined anode voltage).

25

30

3. Characterization

***Determination of the abrasion resistance (Bayer test)**

The Bayer abrasion test is a standard test used to determine the abrasion resistance of curved/lens surfaces. Determination of the Bayer value was performed in accordance with the standards ASTM F 735-94 (Standard Test Method for Abrasion Resistance of Transparent Plastics and Coatings Using Oscillating Sand Method) and ISO CD 15258 (Bayer Abrasion test for ophthalmic lenses), with a higher Bayer value meaning a higher abrasion resistance.

35

Per this test, a coated lens is mounted and held tightly using clamps on the bottom of a tray next to an uncoated CR-39[®] reference lens of similar curvature, diameter, thickness and diopter. An abrasive powder (sand) of specified grain size is poured evenly over the lenses and the tray, and the tray is oscillated at a period of 100 cycles/minutes for two minutes. Oscillation is achieved using a motor that is connected to an oscillating plate through a revolving wheel. The coated lens and the reference are then removed and the haze and transmittance of both the reference and coated sample are measured with a Haze Guard Plus meter, in accordance with ASTM D1003-00, before and after the test has been performed. The results are expressed as a calculated ratio of the standard CR-39[®] test lens to the coated lens (haze gain caused by the abrading sand). The Bayer value is set to 1 for the reference CR-39[®] lens. Only fresh sand is used for each measurement.

Abrasion resistance results of some prepared lenses are reported in table 3 (the test was carried out with 12×3 lenses).

*** Heat-resistance test: determination of the critical temperature (T_c)**

The heat resistance test is performed one month after preparation of the lenses. The prepared lenses were put into an oven preheated to a selected temperature, and were left there for 1 hour. They were removed from the oven and visually evaluated by reflection in terms of the presence of cracks under a desk lamp. This experiment was performed at different temperatures, starting from 50 °C and raising the heating temperature in 10°C increments. The temperature was measured, at which the lenses could not withstand the heat treatment and were cracked after 1 hour. This temperature is given as the critical temperature in the tables below. When several lenses have been tested, the critical temperature mentioned is the average value.

*** Determination of the optical characteristics**

Mean reflection factors R_m and R_v throughout the visible range were recorded and allow to quantify performance of the AR coating and color of the residual reflection in the color space CIE L*a*b* (1976). Colorimetric coefficients were generated from these factors, taking into account standard illuminant D₆₅ (daylight) and standard colorimetric observer based on visual stimuli extending 10°. C* defines chroma, L* defines lightness and h represents hue angle. Optical characteristics of some prepared lenses are given in table 2.

*** Optical losses**

The calculated optical losses OL (%) correspond to the formula :

$$OL (\%) = 100\% - T_v (\%) - R_v (\%) \text{ (front main face)} - R_v (\%) \text{ (rear main face)}.$$

*** Evaluation of the Possible Occurrence of Cosmetic Defects**

There are localized optical defects.

Although such defects are perceptible to the naked eye, for the most pronounced of them, their examination is made easier by transmission with an arc lamp.

The possible presence of cosmetic defects on optical articles (articles of the invention or comparative articles) was evaluated visually under an arc lamp (high intensity lamp), after storage of the articles, immediately after their preparation (reference time t), in a "climatic"

chamber with a controlled environment (temperature 40° C., relative humidity 80%, atmospheric pressure), and for a limited period of time.

These storage conditions make it possible to prematurely age the optical articles and to accelerate the possible occurrence of cosmetic defects. The defects that could be observed under the arc lamp came as points or little filaments.

As used herein, the atmospheric pressure means a pressure of 1.01325 Bar.

The observation of cosmetic defects is either done visually in transmission with a test called R-17 (in standard mode) or with an arc lamp (in expert mode).

The test called R-17 used for the inspection is in fact the transmission test described in detail in WO2006136757 (Protocole of measurement of optical defects) which is incorporated herein by reference.

In addition to the protocole, WO2006136757 describes in detail the apparatus used for the inspection.

Inspection with an arc lamp is carried out by using a BT XL 75/ LIS//Lamp made by Bulbtronics Inc.

The light from the above lamp is directed towards the lens and the reflected light is projected on a screen. The image of the lens on the screen is visually inspected in order to see if there are optical defects.

The notation with the test R-17 (corresponding to the first column of the table) is as follows:

- Rating of 0: no defects
- Rating of 1: observable defects in reflection
- Note of 2: observable defects in transmission

The notation with the arc lamp (corresponding to the second column of the table) is as follows:

- Rating of 0: no defects
- Score of 1: defects on 25% of the glass surface
- Score of 2: defects on 50% of the glass surface
- Score of 3: defects on 75% of the glass surface
- Score of 4: defects on 100% of the glass surface

The final grade is an average of several glasses.

*** Evaluation of the adhesion properties of the coatings (n×10 blow test)**

A qualitative test was carried out using the procedure known as the "n×10 blow test." This procedure makes it possible to evaluate adhesion of a film deposited on a substrate, such as an ophthalmic lens. The test was performed such as described in international patent application WO 99/49097.

The operator checked the state of the tested lens every 3 cycles, by visually inspecting the lens. He noted the cycle number through which a defect appeared for the first time. Consequently, the higher the test value, the better the adhesion of the layers of the AR stack to

the substrate. For comparison purposes, a standard anti-reflection glass has $n \times 10$ blow values in the order of 12.

$n \times 10$ blow test results of some prepared lenses are reported in table 3 (the test was carried out with 30 identical lenses).

5

4. Example 1: optimization of the parameters

The following structure shown on table 1 has been reproduced several times according to the operating procedure described above and by varying different parameters such as the pressure during the deposition of the of SiO_2 thick main layer of the sub-layer "P_{UL}", the anode current " I_A " and the anode voltage " U_A " during the deposition of all the HI layers and the electrically conductive layer.

Lens 1		
	Material	Thickness
	Substrate MR7 [®] + hardcoat 1.6	-
Sub-layer	SiO_2	33 nm
	Ta_2O_5 + IAD (I_A , U_A)	5 nm
	SiO_2 + P O_2 PUL	158 nm
AR coating	Ta_2O_5 + IAD (I_A , U_A)	19 nm
	SiO_2	20 nm
	Ta_2O_5 + IAD (I_A , U_A)	92 nm
	SnO_2	6.5 nm
	SiO_2	74 nm

Table 1

The results are illustrated on table 2 below.

Trial	I_A (A)	U_A (V)	PUL (10^{-4} mbar)	Optical losses (%)	ISTM Bayer	Critical temperature	Cosmetic defect	
						At 1 month	Cosmectic defect evaluation with test R17	Cosmectic defect evaluation with arc lamp
1	1	100	0.4	4.4	8.9	99°C	0	2.7
2	3	100	0.4	1.4	13.5	99°C	0	0
3	1	150	0.4	4.5	11.7	100°C	1.2	3.3
4	3	150	0.4	1.5	14.9	104°C	0	0.5
5	1	100	1	4.1	12.8	93°C	0	1.5
6	3	100	1	1.5	11.5	90°C	0	0
7	1	150	1	5.1	11.2	99°C	1.8	4
8	3	150	1	1.4	15.4	95°C	0	0
9	1	100	1.6	4.1	10.6	93°C	1.1	2.2
10	3	100	1.6	1.4	12.9	90°C	0	0
11	1	150	1.6	10	5.7	99°C	1.8	4

Trial	I_A (A)	U_A (V)	PUL (10^{-4} mbar)	Optical losses (%)	ISTM Bayer	Critical temperature	Cosmetic defect	
						At 1 month	Cosmectic defect evaluation with test R17	Cosmectic defect evaluation with arc lamp
12	3	150	1.6	1.4	13.7	90°C	0	0
13	2	125	1	1.6	14.7	96°C	0.3	1.1
14	2	125	0.4	1.5	15.7	96°C	0	0.7
15	2	125	1.6	1.4	13.6	90°C	0	0
16	2	100	1	1.5	14.7	90°C	0	0
17	2	150	1	1.5	13.2	96°C	0.7	1.8
18	1	125	1	5.6	6.3	95°C	1.7	3.7
19	3	125	1	1.4	14.5	90°C	0	0

Table 2

As used herein, "0" means that there are no cosmetic defects.

These different values are entered in the Minilab software. This software is able to generate graphs for a predetermined pressure: at 10^{-4} mbar (see Fig.1 (a)) and at $1.2 \cdot 10^{-4}$ mbar (see Fig.1(b)). These graphs Fig.1(a) and Fig.1(b) show the ideal window process of the anode current " I_A " and the anode voltage " U_A " for a predetermined pressure. In the present case, it has been shown that the optimized pressure during the deposition of the sub-layer is $1.2 \cdot 10^{-4}$ mbar and the optimized anode current " I_A " is 3A and the anode voltage " U_A " is 130V during the deposition of the HI layers and the electrically conductive layer.

Indeed, by using the optimized parameters, the tested lens has the following characteristics (table 3):

Criteria	MR7 + hardcoat 1.6
$C^* / \text{Hue} / Rv_{15^\circ} / Tv$	9 / 130° / 0.75% / 96.9%
RUV_{35°	2.8%
n_{10} blows	> 50
ISTM Bayer	14.7
Sand Bayer	6.1
Critical temperature at 1 month	90°C
Cosmetic defect	No AR tension defect

Table 3

5. Example 2: influence of other parameters

* Influence of the oxygen pressure during the deposition of the HI layer

The same structure of Lens 1 has been reproduced by varying another parameter such as the ionized gas during the IAD deposition (introduction of O_2) for two substrates (Orma® obtained through (co)polymerization of the diethyleneglycol bis allyl carbonate) and MR7®.

Especially, the tested structure is as follow (see table 4):

Lens 2			
	Material	Thickness	Deposition parameters
	Substrate MR7® + hardcoat 1.6	-	-
Sub-layer	SiO ₂	33 nm	
	Ta ₂ O ₅	5 nm	IAD (2A, 140V) with O ₂
	SiO ₂ + P O ₂	158 nm	P= 1.5 10 ⁻⁴ with O ₂
AR coating	Ta ₂ O ₅	19 nm	IAD (2A, 140V with O ₂ (trial 22, 23) without O ₂ (trial 20,21)
	SiO ₂	20 nm	
	Ta ₂ O ₅	92 nm	IAD (2A, 140V with O ₂ (trial 22, 23) without O ₂ (trial 20,21)
	SnO ₂	6.5 nm	IAD (1.2A, 120V with O ₂ (trial 22, 23) without O ₂ (trial 20,21)
	SiO ₂	74 nm	

Table 4

The results are illustrated on table 5 below:

Trial	Oxygen pressure (10 ⁻⁴ mbar)	Substrate	I _A (A)	U _A (V)	PUL (10 ⁻⁴ mbar)	Optical losses (%)	ISTM Bayer	Critical temperature At 1 month	cosmectic defect evaluation with test R17
20	1.1 (residual pressure)	MR7®	2	140	1.5	..		90°C	0
21		Orma®	2	140	1.5	0.3	15	60°C	0
22	1.5 PO ₂	MR7®	2	140	1.5	..		90°C	0
23		Orma®	2	140	1.5	0.3	14	60°C	0

Table 5

5 This table 5 shows that the presence/absence of the gas (O₂) during the deposition of the HI layers has no influence on the optical characteristics of the obtained lens (good optical performances).

This table 5 also shows that lens MR7® has an improved T_c as compared to Orma® lens.

10 * Influence of the substrate

The same structure of Lens 2 has been reproduced by varying another parameter such as the substrate.

The results are illustrated on table 6 below:

Trial	Substrate	I _A (A)	U _A (V)	PUL (10 ⁻⁴ mbar)	Optical losses (%)	ISTM Bayer	Critical temperature	Cosmetic defect	
							At 1 month	Cosmectic defect evaluation with test R17	Cosmectic defect evaluation with arc lamp
24	MR7	3	130	1.2	1.6	14.7	90°C	0	0
25	MR8	3	130	1.2	-	-	100°C	0	0

Table 6

This table 6 shows that these two substrates enable to obtain good optical characteristics.

5 * Influence of the two thin layers of the sub-layer

The same structure of Lens 2 has been reproduced except that the sub-layer is a single layer of SiO₂.

Especially, the tested structure is as follow (see table 7):

Lens 3			
	Material	Thickness	Deposition parameters
	Substrate MR7® + hardcoat 1.6	-	-
Sub-layer	SiO ₂ + P O ₂	158 nm	P= 1.3. 10 ⁻⁴ with O ₂
AR coating	Ta ₂ O ₅	19 nm	IAD (2.5A, 150V
	SiO ₂	20 nm	
	Ta ₂ O ₅	92 nm	IAD (2.5A, 150V
	SnO ₂	6.5 nm	IAD (2A, 120V
	SiO ₂	74 nm	

Table 7

10 The results are illustrated on table 8 below:

Trial	Substrate	I _A (A)	U _A (V)	PUL (10 ⁻⁴ mbar)	Optical losses (%)	ISTM Bayer	Critical temperature	Cosmetic defect	
							At 1 month		
26	MR7	2.5	150	1.3	~	-	100°C	0	
27	Orma	2.5	150	1.3	0.2	11.8	60°C	0	

Table 8

The assay shows that the two-thin layers of the sub-layers of lens 1 or lens 2 compared to lens 3 having a single layered sub-layer, have no influence for obtaining a lens having good optical characteristics.

15 Therefore, the specific choice of the three parameters of the method according to the invention (anode voltage, anode current and pressure of the underlayer) is not arbitrary and they have an influence for optimizing the manufacture of a lens having improved optical characteristics.

5. Example 3: robustness of the optical article of the invention (comparative example)

The robustness of Lens 1 according to the invention and of example 8 of the US 2008/0002260 has been tested.

	Lens 1 of the invention	Ex. 8 of US 2008/0002260
σ_{Hue}	5.1°	16.9°

Table 9

The robustness of an AR coating is theoretically determined thanks to Mac Leod software, by simulating 500 times (iterations) the predetermined antireflective coating and by randomly varying the thicknesses of each layer of this predetermined AR coating (+/- 4%) relative to the nominal thickness of said AR coating.

The robustness of the predetermined antireflective coating corresponds to the standard deviation of hue angle, also called "hue" or "h" of these 500 iterations. The greater the hue standard deviation " σ_{Hue} " is large, the worse the robustness is.

Here, table 9 shows that the lens according to the invention has an improved robustness as compared to the lens of the prior art document.

CLAIMS

1. Optical article comprising a transparent substrate with a front main face and a rear main face, at least one of said main faces being coated with at least: a sub-layer with a main thick
 5 layer that is deposited in a vacuum chamber under a pre-determined pressure and a multilayered antireflective coating comprising at least one HI layer having a refractive index higher than or equal 1.55, and at least one LI layer having a refractive index lower than 1.55, said multilayered antireflective coating

- has a mean light reflection factor in the visible region R_v that is lower than or equal to
 10 1.5 % for at least an angle of incidence lower than 35° and

- a mean reflection factor R_{UV} between 280 nm and 380 nm, weighted by the function $W(\lambda)$ defined in the ISO 13666:1998 standard, that is equal to or lower than 5%, for an angle of incidence in the range 20° to 50° ,

wherein the at least one HI layer comprises at least one material selected from the group
 15 consisting of tantalum pentoxide (Ta_2O_5), and

wherein said multilayered antireflective coating comprises no cosmetic defects evaluated visually in transmission.

2. Optical article according to claim 1, characterized in that said multilayered antireflective coating has an optical robustness corresponding to the standard deviation of hue "oh" as
 20 defined in the international colorimetric CIE $L^*a^*b^*$ (1976) for an angle of incidence (θ) of 15° that is lower than or equal to 12° , preferably lower than or equal to 10° , in particular lower than or equal to 8° .

3. Optical article according to claim 1 or 2, characterized in that it has a critical temperature T_c equal to or higher than $80^\circ C$.

25 4. Optical article according to any one of the preceding claims, characterized in that it has a critical temperature at one month after its preparation T_c equal to or higher than $81^\circ C$, preferably equal to or higher than $85^\circ C$, more preferably equal to or higher than $90^\circ C$, especially equal to or higher than $93^\circ C$ and typically equal to or higher than $100^\circ C$.

5. Optical article according to any one of the preceding claims, wherein said at least one HI
 30 layer being deposited in a vacuum chamber by ion beam assisted deposition (IAD) with a pre-determined anode current I_A ranging from 1 to 4 A and a pre-determined anode voltage U_A ranging from 80 to 200 V.

6. Optical article according to any one of the preceding claims, wherein all the HI layers of said multilayered antireflective coating are deposited in a vacuum chamber by ion beam
 35 assisted deposition (IAD) with the pre-determined anode current I_A and the pre-determined anode voltage U_A .

7. Optical article according to any one of the preceding claims, wherein

- said pre-determined main thick layer of the sub-layer pressure ranges from 0.4×10^{-4} mbar to 1.5×10^{-4} mbar, preferably from 0.5×10^{-4} mbar to 1.3×10^{-4} mbar;

40 - said pre-determined anode current I_A ranges from 2 to 3,5 A;

- said pre-determined anode voltage U_A ranges from 100 to 150 V.

8. Optical article according to any one of the preceding claims, wherein:

- the at least one LI layer comprises at least one material selected from SiO_2 that is not doped with alumina (Al_2O_3), and/or

5 - the sub-layer comprises SiO_2 that is not doped with alumina (Al_2O_3).

9. Optical article according to any one of the preceding claims, wherein the multilayered antireflective coating comprises at least two HI layers composed of tantalum pentoxide (Ta_2O_5) and at least two LI layers composed of silicon dioxide (SiO_2).

10. Optical article according to any one of the preceding claims, wherein

10 - the sub-layer has a physical thickness ranging from 75 nm to 250 nm, especially from 80 nm to 200 nm and typically from 100 to 200 nm;

- the multilayered antireflective coating comprises at least two HI layers and two LI layers and has especially, in the direction moving away from the substrate, the followings structure:

15 a first HI layer having a physical thickness ranging from 10 to 30 nm, preferably from 15 to 20 nm and typically from 17 to 22 nm;

a first LI layer having a physical thickness ranging from 10 to 35 nm, preferably from 15 to 30 nm and typically from 16 to 25 nm;

a second HI layer having a physical thickness ranging from 80 to 105 nm, preferably from 85 to 100 nm and typically from 88 to 95 nm;

20 an optional electrically conductive layer having a physical thickness lower than or equal to 10 nm;

a second LI layer having a physical thickness ranging from 60 to 90 nm, preferably from 65 to 85 nm and typically from 70 to 78 nm.

25 11. A process for manufacturing an optical article, comprising at least the following steps:

(i) providing an optical article comprising a transparent substrate with a front main face and with a rear main face;

(ii) depositing by evaporation under vacuum, onto one of said main faces of said substrate,

30 - a sub-layer having a main thick layer that is performed at a pre-determined pressure;

- a multilayered antireflective coating comprising at least one HI layer having a refractive index higher than or equal 1.55, and at least one LI layer having a refractive index lower than 1.55, the at least one HI layer comprising at least one material selected from the group consisting of tantalum pentoxide (Ta_2O_5), that is performed by ion beam assisted deposition (IAD) in which a pre-determined anode current I_A that is ranging from 1 to 4 A and a pre-determined anode voltage U_A that is ranging from 80 to 200 V, are supplied, so as to form the stack S;

(iii) recovering the optical article.

12. The process for manufacturing an optical article according to claim 11, wherein

- said pre-determined main thick layer of the sub-layer pressure ranges from 0.4×10^{-4} mbar to 1.5×10^{-4} mbar, preferably from 0.5×10^{-4} mbar to 1.3×10^{-4} mbar;
- said pre-determined anode current I_A ranges from 2 to 3 A;
- said pre-determined anode voltage U_A ranges from 100 to 150 V.

5 13. Method of optimizing the manufacture of an optical article comprising a transparent substrate with a front main face and a rear main face, at least one of said main faces being coated with at least a multilayered antireflective coating comprising at least one HI layer having a refractive index higher than or equal 1.55, and at least one LI layer having a refractive index lower than 1.55,

10 said method of optimizing comprising the following steps:

(a) performing a plurality of times, the following steps (i) to (iii) by varying only three parameters that are : a pre-determined main thick layer of the sub-layer pressure, a pre-determined anode current I_A and a pre-determined anode voltage U_A so as to obtain several optical articles having the same structure:

15 (i) providing an optical article comprising the transparent substrate with a front main face and a rear main face;

(ii) depositing by evaporation under vacuum, onto one of said main faces of said substrate,

- a sub-layer, the deposition of a main thick layer of which is performed at the pre-determined pressure;
- the multilayered antireflective coating, the deposition of which is performed by ion beam assisted deposition (IAD) in which the pre-determined anode current I_A and the pre-determined anode voltage U_A are supplied, so as to form the stack S;

(iii) recovering the optical article;

25 (b) measuring at least one optical performance for each of the obtained optical articles including the critical temperature, so as to obtain optical performance data;

(c) selecting the combination(s) of said three parameters that enable(s) to obtain a critical temperature T_c equal to or higher than 80°C , preferably equal to or higher than 90°C , and more preferably equal to or higher than 93°C .

30 14. Method of optimizing according to claim 13, wherein said optical performances are further selected from: transparency, abrasion properties thanks to the ISTM Bayer Test, optical losses, cosmetic defects, adhesion thanks to the $n \times 10$ blow test.

15. Method of optimizing according to claim 14, wherein

35 - the transparency T_v (%) as defined by the international normalized standard ISO 8980-3 measured at a wavelength ranging from 380 to 780 nm is higher than or equal to 90 %, preferably 95 %; and/or

- the calculated optical losses OL (%) corresponding to the formula :

$$\text{OL (\%)} = 100\% - T_v (\%) - R_v (\%) \text{ (front main face)} - R_v (\%) \text{ (rear main face)}$$

40 - the ISTM Bayer value is higher than or equal to 9, preferably 10 according to ASTM Standard F735-81; and/or

- the n₁₀ blows value is higher than 12; and /or
- there is no cosmetic defects evaluated visually in transmission.

Fig.1a

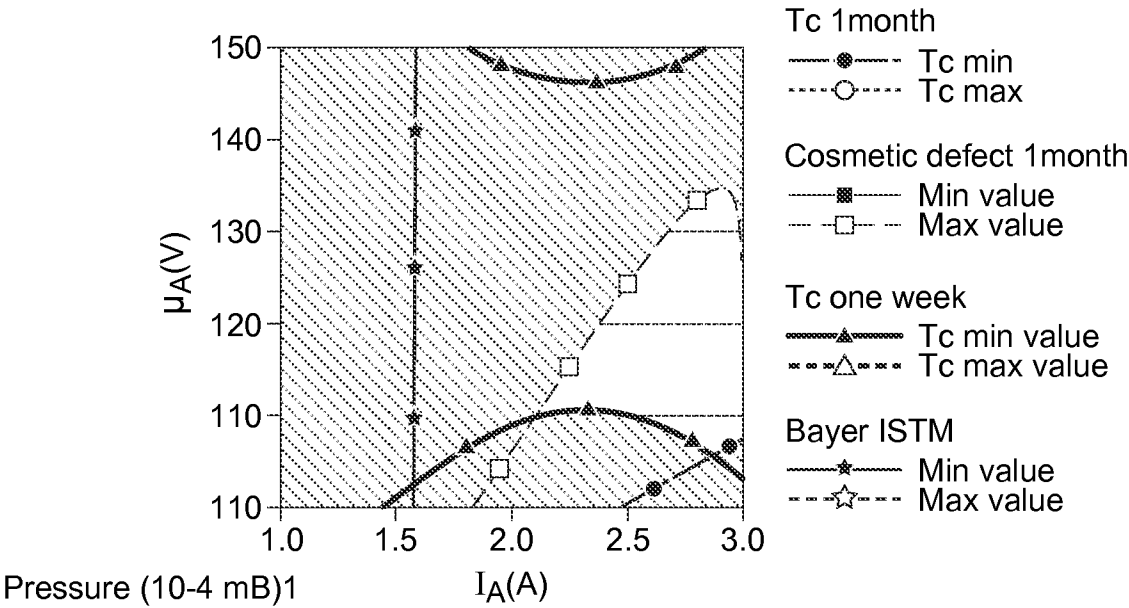
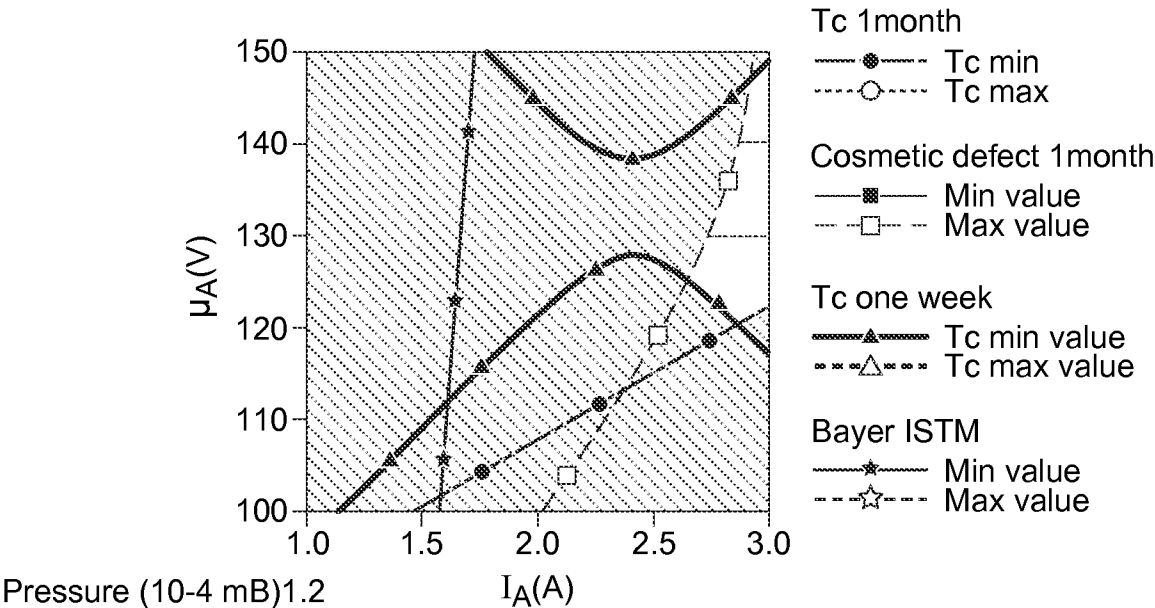


Fig.1b



INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/000921

A. CLASSIFICATION OF SUBJECT MATTER
INV. G02B1/115 G02C7/10 C23C14/00 C23C14/22
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G02B G02C C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/076714 A1 (ESSILOR INT [FR]; CADO HERVE [FR]; DE AYGUAVIVES FRANCISCO [FR]; POPHI) 14 June 2012 (2012-06-14) cited in the application	1,2,8-10
Y	page 3, lines 16-27 page 16, lines 21-29	7
X	----- WO 2016/151348 A1 (ESSILOR INT) 29 September 2016 (2016-09-29) page 2, line 18 - page 3, line 15; examples 8,9; table 3 page 7, lines 2-9	1-4,8-10
X	----- EP 3 182 177 A1 (ESSILOR INT [FR]) 21 June 2017 (2017-06-21) paragraphs [0051], [0054], [0055], [0061], [0068] ----- -/-	1,2

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

20 May 2019

Date of mailing of the international search report

31/05/2019

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/000921

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2016/146153 A1 (RUPP + HUBRACH OPTIK GMBH [DE]) 22 September 2016 (2016-09-22) page 3, lines 6-23 page 6, lines 36-39 page 8, lines 23-28 page 11, lines 17-23 -----	1,8
X	EP 3 203 274 A1 (ESSILOR INT [FR]) 9 August 2017 (2017-08-09) paragraphs [0061], [0079], [0082], [0088], [0090] -----	1,2
X	US 2016/003982 A1 (AVETISIAN HAMLET JOE [US] ET AL) 7 January 2016 (2016-01-07) paragraphs [0010], [0012], [0014], [0023], [0024], [0084] -----	1,4
X	US 2008/206470 A1 (THOMAS MICHELE [FR] ET AL) 28 August 2008 (2008-08-28)	11,12
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2018/000921

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1, 2, 8-10

multilayered antireflective coating having a defined optical robustness

2. claims: 3-7, 11-15

multilayered antireflective coating having a defined thermal robustness

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2018/000921

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Information on patent family members

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