



(51) International Patent Classification:

G02B 1/11 (2015.01)

(21) International Application Number:

PCT/EP2019/078406

(22) International Filing Date:

18 October 2019 (18.10.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

18306373.4 18 October 2018 (18.10.2018) EP

(71) Applicant: **ESSILOR INTERNATIONAL** [FR/FR]; 147 rue de Paris, 94220 CHARENTON-LE-PONT (FR).

(72) Inventors: **MOYSAN, Yannick**; c/o Essilor International, 147 rue de Paris, 94220 CHARENTON LE PONT (FR). **ALBUQUERQUE DA SILVA, José**; c/o Essilor International, 147 rue de Paris, 94220 CHARENTON LE PONT (FR). **FELTEN, Yohann**; c/o Essilor International, 147 rue de Paris, 94220 CHARENTON LE PONT (FR). **MAITRE, Nicolas**; c/o Essilor International, 147 rue de Paris, 94220 CHARENTON LE PONT (FR). **VALENTI, Christophe**; c/o Essilor International, 147 rue de Paris, 94220 CHARENTON LE PONT (FR).

(74) Agent: **CHAUVIN, Vincent** et al.; JACOBACCI CORALIS HARLE, 32 rue de l'Arcade, 75008 PARIS (FR).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH,

GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: OPTICAL ARTICLE HAVING AN INTERFERENTIAL COATING WITH A HIGH ABRASION-RESISTANCE

$$R_D = \frac{\text{thickness of the outermost low refractive index layer(s) of the interferential coating}}{\text{thickness of the outermost high refractive index layer(s) of the interferential coating}} \quad (I)$$

(57) Abstract: The invention relates to an optical article having a Bayer value determined in accordance with the ASTM F735-81 standard higher than or equal to 7, comprising a substrate having at least one main face successively coated with a monolayer sub-layer having a thickness higher than or equal to 250 nm and a multilayer interferential coating comprising a stack of at least one high refractive index layer having a refractive index higher than 1.55 and at least one low refractive index layer having a refractive index of 1.55 or less. The ratio: (I) is higher than or equal to 1.5, and/or the deposition of the high refractive index layer of the interferential coating having a refractive index higher than 1.55 and a thickness higher than or equal to 15 nm that is the furthest from the substrate has been carried out under ionic assistance.



Optical article having an interferential coating with a high abrasion-resistance

The invention relates to an optical article comprising a substrate coated with a multilayer transparent interferential coating, typically an antireflection coating, having an improved abrasion resistance and good thermal resistance, in particular an ophthalmic lens, and a method of manufacturing such optical article.

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

The various coatings that may be used to impart a plurality of mechanical and/or optical properties may be impact-resistant coating layers, abrasion- and/or scratch-resistant coating layers, anti-reflection and/or reflective coating layers, and/or anti-fouling layers and/or anti-fog layers.

Different ways to improve the abrasion resistance of an optical article, which is sensitive to scratches from environment, can be found in the literature. For instance, it has been proposed to increase the total thickness of the anti-reflection coating, such as in JP 2003-195003 and JP 2003-294906, where a lens coated with a primer coating, a hard coat and a 7-layer anti-reflection coating comprising alternated layers of SiO_2 and TiO_2 , the latter being deposited with ion assistance and known to be sensitive to photo-degradation, is described.

US 8982466 relates to an optical lens having a hard coat and a multilayer anti-reflection coating in which the high-refractive-index layers, made of TiO_2 , together have a thickness of less than 40 nm.

EP 2775341 discloses an eyeglass lens having a hard coat layer, a 360-390 nm thick SiO_2 sub-layer and a 4-layer interferential coating made of SiO_2 , ZrO_2 and/or Ta_2O_5 , in which the layers have a specific nanoindentation hardness and compressive stress, and have generally been deposited by ion-assisted vapor deposition. This deposition technique increases compressive stress and as a result may lead to delamination.

JP 2002-122820 describes a hard-coated substrate coated with a SiO_2 sub-layer having a physical thickness of 89-178 nm (optical thickness: $0.25-0.5 \lambda$ at 520 nm) and a 4-layer anti-reflection coating ($\text{ZrO}_2/\text{SiO}_2/\text{ZrO}_2/\text{SiO}_2$). According to this document, high critical temperatures can be reached by being able to balance coating thickness and stress between the layers of the various materials. However, the only parameter which was studied was the thickness of the sub-layer. Its thickness should be such that the ratio (sum of the physical thicknesses of the SiO_2 layers, including the sub-layer) / (sum of the physical thicknesses of the ZrO_2 layers) ranges from 2 to 3. Higher ratios are said to be undesirable because the durability of the anti-reflection coating is decreased.

US 7692855 discloses an optical article having anti-reflection properties and high thermal resistance, comprising a substrate having at least one main face coated with a multilayer anti-reflection coating in which the ratio of physical thickness of low refractive index layers / high refractive index layers is generally higher than 2.1.

US 2008/206470 relates to a process for manufacturing an optical article having antireflection or reflective properties, comprising a sub-layer a sub-layer and a multilayer stack. In order to increase the abrasion resistance of the optical article, the sub-layer has to be deposited in a vacuum chamber with an additional gas supply during the deposition step, and the exposed surface of the sub-layer has to be submitted to an ionic bombardment treatment prior to depositing the multilayer stack.

European patent application EP3392680 suggests the control of the thicknesses of the layers in an interferential coating in order to increase abrasion resistance of an optical article, i.e., the use of a ratio of physical thickness of external low refractive index layer(s) / external high refractive index layer(s) higher than or equal to 2.

An objective of the current invention is to provide a transparent optical article comprising an organic or mineral glass substrate bearing an interferential coating, preferably a lens, and more preferably an ophthalmic lens for eyeglasses, having an improved abrasion resistance, a good adhesion to the substrate and a good resistance to heat and temperature variations, i.e., a high critical temperature, which would be an alternative to already known reflective or antireflective coated optical articles. These properties should be obtained without decreasing the optical performances and other mechanical performances of said article, such as anti-reflection or reflection performances.

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 and would avoid heating the substrate.

The inventors identified several levers that allow in particular to boost the abrasion resistance of the optical article, and found that the above objectives could be achieved by combining those levers: the use of a thick sub-layer, selecting a specific ratio of (physical thickness of outermost low refractive index layer(s) of the interferential coating) / (physical thickness of outermost high refractive index layer(s) of the interferential coating) and/or depositing the high refractive index layer of the interferential coating having a thickness higher than or equal to 15 nm that is the furthest from the substrate under ionic assistance, and optionally depositing the sub-layer in a vacuum chamber under a low pressure (a pressure preferably lower than 1.6×10^{-4} mBar), more preferably without supplying any supplementary gas during said deposition. Combining the highest number of abrasion resistance boosters leads to the highest abrasion resistance improvement, generally in a synergistic manner.

Compared to classical interferential coatings, inventive interferential coatings have a higher critical temperature, a better adherence and a higher abrasion resistance.

Thus, the present invention relates to an optical article having a Bayer value determined in accordance with the ASTM F735-81 standard (Bayer sand) higher than or equal to 7, comprising a substrate having at least one main face successively coated with:

- a monolayer sub-layer having a thickness higher than or equal to 250 nm,

- a multilayer interferential coating comprising a stack of at least one high refractive index layer having a refractive index higher than 1.55 and at least one low refractive index layer having a refractive index of 1.55 or less, wherein:

a) the ratio:

$$R_D = \frac{\text{thickness of the outermost low refractive index layer(s) of the interferential coating}}{\text{thickness of the outermost high refractive index layer(s) of the interferential coating}}$$

is higher than or equal to 1.5, and/or

b) the interferential coating comprises at least one high refractive index layer having a refractive index higher than 1.55 and a thickness higher than or equal to 15 nm, and the deposition of the high refractive index layer of the interferential coating having a refractive index higher than 1.55 and a thickness higher than or equal to 15 nm that is the furthest from the substrate has been carried out under ionic assistance by bombarding by means of an ion beam said high refractive index layer while it is being formed.

Detailed description of the invention

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, ranges, reaction conditions, etc. used herein are to be understood as modified in all instances by the term "about."

When an optical article comprises one or more surface coatings, the phrase "to deposit a coating or layer onto the optical article" means that a coating or layer is deposited onto the outermost coating of the optical article, i.e. the coating which is the closest to the air.

A coating that is "on" a side of a lens is defined as a coating that (a) is positioned over that side, (b) need not be in contact with that side, i.e., one or more intervening coatings may be disposed between that side and the coating in question (although it is preferably in contact with that side) and (c) need not cover that side completely.

The term "coating" is understood to mean any layer, layer stack or film, which may be in contact with the substrate and/or with another coating, for example a sol-gel coating or a coating made of an organic resin. A coating may be deposited or formed through various methods, including wet processing, gaseous processing, and film transfer.

The optical article prepared according to the present invention is a transparent optical article, preferably an optical lens or lens blank, and more preferably an ophthalmic lens or lens blank. The optical article may be coated on its convex main face (front side), concave main face (back/rear side), or both faces with the multilayer interferential coating according to the invention, preferably on the convex (front) main face. As used herein, the rear face of the substrate is intended to mean the face which, when using the article, is the nearest from the wearer's eye, in the cases of lenses. It is generally a concave face. On the contrary, the front face of the substrate is the face which, when using the article, is the most distant from the wearer's eye. It is generally a convex face. The optical article can also be a plano article.

Herein, the term "lens" means an organic or inorganic glass lens, comprising a lens substrate, which may be coated with one or more coatings of various natures.

The term "ophthalmic lens" is used to mean a lens adapted to a spectacle frame, for example to protect the eye and/or correct the sight. Said lens can be chosen from afocal, unifocal, bifocal, trifocal and progressive lenses. Although ophthalmic optics is a preferred field of the invention, it will be understood that this invention can be applied to optical articles of other types, such as, for example, lenses for optical instruments, in photography or astronomy, optical sighting lenses, ocular visors, optics of lighting systems, etc.

In the present description, unless otherwise specified, an optical article/material is understood to be transparent when the observation of an image through said optical article is perceived with no significant loss of contrast, that is, when the formation of an image through said optical article is obtained without adversely affecting the quality of the image. This definition of the term "transparent" can be applied to all objects qualified as such in the description, unless otherwise specified.

A substrate, in the sense of the present invention, should be understood to mean an uncoated substrate, and generally has two main faces. The substrate may in particular be an optically transparent material having the shape of an optical article, for example an ophthalmic lens destined to be mounted in glasses. In this context, the term "substrate" is understood to mean the base constituent material of the optical lens and more particularly of the ophthalmic lens. This material acts as support for a stack of one or more coatings or layers.

The substrate may be made of mineral glass or organic glass, preferably organic glass. The organic glasses can be either thermoplastic materials such as polycarbonates and thermoplastic polyurethanes or thermosetting (cross-linked) materials such as diethylene glycol bis(allylcarbonate) polymers and copolymers (in particular CR-39[®] from PPG Industries), thermosetting polyurethanes, polythiourethanes, preferably polythiourethane resins having a refractive index of 1.60 or 1.67, polyepoxides, polyepisulfides, such as those having a refractive index of 1.74, poly(meth)acrylates and copolymers based substrates, such as substrates comprising (meth)acrylic polymers and copolymers derived from bisphenol-A, polythio(meth)acrylates, as well as copolymers thereof and blends thereof. Preferred materials for the lens substrate are polycarbonates (PC) and diethylene glycol bis(allylcarbonate) polymers, in particular substrates made of polycarbonate.

Specific examples of substrates suitable to the present invention are those obtained from thermosetting polythiourethane resins, which are marketed by the Mitsui Toatsu Chemicals company as MR series, in particular MR6®, MR7® and MR8® resins. These substrates as well as the monomers used for their preparation are especially described in the patents US 4,689,387, US 4,775,733, US 5,059,673, US 5,087,758 and US 5,191,055.

Prior to depositing the sub-layer, the interferential coating or other functional coatings, the surface of the article is usually submitted to a physical or chemical surface activating and cleaning pre-treatment, so as to improve the adhesion of the layer to be deposited, such as disclosed in WO 2013/013929. This pre-treatment is generally performed on the surface of an abrasion- and/or scratch-resistant coating (hard coat).

This pre-treatment is generally carried out under vacuum. It may be a bombardment with energetic species, for example an ion beam method ("Ion Pre-Cleaning" or "IPC") or an electron beam method, a corona treatment, an ion spallation treatment, an ultraviolet treatment or a plasma treatment under vacuum, using typically an oxygen or an argon plasma. It may also be an acid or a base surface treatment and/or a solvent surface treatment (using water or an organic solvent) with or without ultrasonic treatment. Many treatments may be combined. Thanks to these cleaning treatments, the cleanliness of the substrate surface is optimized.

By energetic species, it is meant species with an energy ranging from 1 to 300 eV, preferably from 10 to 150 eV, and more preferably from 10 to 150 eV and most preferably from 40 to 150 eV. Energetic species may be chemical species such as ions, radicals, or species such as photons or electrons.

The interference coating may be virtually any interference coating conventionally used in the field of optics, in particular ophthalmic optics. The interference coating may be, in a non-limiting manner, an anti-reflection coating, a reflective (mirror) coating, an infrared filter or an ultraviolet filter, but is preferably an anti-reflection coating.

An anti-reflection coating is a coating, deposited on the surface of an article, which improves the anti-reflection properties of the final article. It reduces the reflection of light at the article/air interface over a relatively broad portion of the visible spectrum.

The multilayer interferential coating of the invention comprises a stack of at least one high refractive index layer having a refractive index higher than 1.55 and at least one low refractive index layer having a refractive index of 1.55 or less.

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). The total number of layers in the interferential coating is preferably higher than or equal to 3, more preferably higher than or equal to 4, and preferably lower than or equal to any one of the following values: 8, 7, more preferably lower than or equal to 6, even more preferably lower than or equal to 5, and most preferably equal to 5 layers.

As used herein, a layer of the interferential 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 interferential coating. The sub-layer and

optional impedance layers either are not considered when counting the number of layers of the interferential coating or when indicating its thickness.

HI layers and LI layers do not necessarily 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 interferential coating is said to be a layer with a high refractive index (HI) when its refractive index is higher than 1.55, preferably higher than or equal to 1.6, even more preferably higher than or equal to 1.8 or 1.9 and most preferably higher than or equal to 2. Said HI layers preferably have a refractive index lower than or equal to 2.2 or 2.1. A layer of an interferential coating is said to be a low refractive index layer (LI) when its refractive index is lower than or equal to 1.55, preferably lower than or equal to 1.52, more preferably lower than or equal to 1.48 or 1.47. Said LI layer preferably has a refractive index higher than or equal to 1.1.

The HI layer 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), La_2O_3 , Nb_2O_5 , Y_2O_3 , with the proviso that TiO_2 is not present in the outermost high refractive index layer(s) of the interferential coating. In some aspects of the invention, the outermost high refractive index layer(s) of the interferential coating do(es) not comprise titanium oxide. In a preferred embodiment, the interferential coating does not comprise any layer comprising TiO_2 , or more generally, titanium oxide. As used herein, titanium oxide is intended to mean titanium dioxide or a substoichiometric titanium oxide (TiO_x , where $x < 2$). Titanium oxide-containing layers are indeed sensitive to photo-degradation.

Optionally, the HI layers may further contain silica or other materials with a low refractive index, provided they have a refractive index higher than 1.55 as indicated hereabove. The preferred materials include ZrO_2 , PrTiO_3 , Nb_2O_5 , Ta_2O_5 , Y_2O_3 and mixtures thereof.

The LI layer is also well known and may comprise, without limitation, SiO_2 , MgF_2 , or a mixture of silica and alumina, especially silica doped with alumina, the latter contributing to increase the interferential coating thermal resistance. The LI layer is preferably a layer comprising 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.

Optionally, the LI layers may further contain materials with a high refractive index, provided the refractive index of the resulting layer is lower than or equal to 1.55.

When a LI layer comprising a mixture of SiO_2 and Al_2O_3 is used, it preferably comprises from 1 to 10%, more preferably from 1 to 8 % and even more preferably from 1 to 5 % by weight of Al_2O_3 relative to the $\text{SiO}_2 + \text{Al}_2\text{O}_3$ total weight in such layer.

For example, SiO_2 doped with 4 % Al_2O_3 by weight, or less, or SiO_2 doped with 8 % Al_2O_3 may be employed. $\text{SiO}_2/\text{Al}_2\text{O}_3$ mixtures, that are available on the market may be used, such as LIMA[®] marketed by the Umicore Materials AG company (refractive index $n = 1.48$ -

1.50 at 550 nm), or L5[®] marketed by the Merck KGaA company (refractive index $n = 1.48$ at 500 nm).

The interferential coating external layer, i.e., its layer that is the furthest from the substrate is generally a silica-based layer, comprising preferably at least 80 % by weight of silica, more preferably at least 90% by weight of silica (for example a silica layer doped with alumina), relative to the layer total weight, and even more preferably consists of a silica layer.

Generally, the HI and LI layers have a physical thickness ranging from 10 to 120 nm, preferably from 20 to 110 nm.

Generally, the total thickness of the interferential coating plus the thickness of the sub-layer plus the thickness of the impedance layers (defined later in this application) if present is lower than 1 micrometer, preferably lower than or equal to 800 nm, more preferably lower than or equal to any one of the following values: 700 nm, 650 nm, 600 nm. The interferential coating total thickness is generally higher than 100 nm, preferably higher than 200 nm.

In one embodiment of the invention, the R_D ratio of the present interferential coating is higher than or equal to 1.5, and preferably higher than or equal to any one of the following values: 1.6, 1.7, 1.8, 1.9, 2, 2.05, 2.1, 2.15, 2.2, 2.25, 2.3, 2.35, 2.4, 2.5, 2.6, 2.7, 2.8, 3, 3.25, and 3.5. R_D is defined as:

$$R_D = \frac{\text{thickness of the outermost low refractive index layer(s) of the interferential coating}}{\text{thickness of the outermost high refractive index layer(s) of the interferential coating}}$$

By outermost high or low refractive index layer(s) of the interferential coating, it is meant the layer(s) of the interferential coating that is (are) the furthest from the substrate. Generally, there is only one outermost high (or low) refractive index layer in the interferential coating, i.e., when high refractive index layers and low refractive index layers alternate with each other in the stack. However, in some embodiments, there can be two or more adjacent high (or low) refractive index layers in outermost position in the interferential coating. In this case, it is considered that there is a plurality of outermost high (or low) refractive index layers in the interferential coating, and this is taken into account by adding their respective thicknesses for the calculation of the R_D ratio.

When a high refractive index layer of the interferential coating is an electrically conductive layer, especially a conductive oxide layer (such as an ITO, SnO_2 layer) and is positioned as the outermost high refractive index layer but is not adjacent to one or more non conductive high refractive index layers (such as a ZrO_2 , Ta_2O_5 layer), such high refractive index conductive layer is not taken into account for the calculation of R_D and is not considered as being part of the interferential coating.

As an example, for an interferential coating comprising the following layers: Air/hydrophobic coating/ SiO_2 (thickness a)/ITO (thickness b)/ SiO_2 (thickness c)/ ZrO_2 (thickness d)/ SiO_2 ..., $R_D = (a + c)/d$.

The thicknesses of the two SiO₂ layers are added, as the conductive layer is not considered as being part of the coating. Consequently, the above defined general rules for the calculation are applied.

However, if the conductive layer identified as the outermost high refractive index layer is adjacent to one or more non conductive high refractive index layer(s) (plurality of adjacent high refractive index layers), the thicknesses of those plurality of high refractive index layers are added for the calculation of the R_D ratio.

As an example, for an interferential coating comprising the following layers Air/hydrophobic coating/SiO₂(thickness a')/ITO(thickness b')/ZrO₂(thickness c')/SiO₂...

$$R_D = a' / (b' + c')$$

It is to be noted that such high refractive index conductive layer (such as ITO or SnO₂) is generally thin or very thin (typically less than any one of the following thickness values: 20 nm, 15 nm, 10 nm).

In a preferred embodiment of the present invention, the interferential coating is designed with a ratio R_D higher than or equal to 2, and preferably as high as possible so as to increase the resistance to abrasion of the optical article. This is the first alternative means according to the invention to obtain an article having an improved abrasion resistance.

Indeed, a relationship has been established between abrasion resistance and the ratio R_D mentioned above. The inventors have found that limiting the thickness of the outermost layer(s) of high refractive index materials and/or increasing the thickness of the outermost layer(s) of low refractive index materials was beneficial to the abrasion resistance of the optical article. A standard Bayer abrasion test can be used to determine the abrasion resistance of the optical article.

Moreover, the optical article has a good resistance to heat and temperature variations, i.e., a high critical temperature, as defined in the experimental section. The critical temperature of an article coated according to the invention is preferably ≥ 50°C, more preferably ≥ 60°C, 65°C or 70°C.

It is also possible to define a R_T ratio, which is identical to the R_T ratio defined in US 7692855:

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

with the proviso that the layers of the antireflection coating taken into account for the calculation of said ratio R_T are only the layers located above the low refractive index layer (n ≤ 1.55) having a physical thickness ≥ 100 nm and not being the outermost layer of the antireflection coating which is the furthest from the substrate, when the antireflection coating comprises at least one low refractive index layer having a physical thickness ≥ 100nm which is not the layer of the antireflection coating that is the furthest from the substrate.

The ratio R_T is calculated on the whole antireflection coating unless at least one inner LI layer (i.e., not the LI layer that is the furthest from the substrate) having a thickness of 100 nm or more is present in the antireflection stack. Actually, if a high thickness LI layer (higher than

100 nm) is present inside the antireflection coating, it may block the propagation of cracks. In this case, the ratio R_T has to be calculated on the upper part of the stack, i.e., without taking into account said high thickness LI layer and the layers lying under. If several high thickness LI layers are present, R_T is calculated on the part of the stack located above the thick 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.

In one embodiment R_T is higher than or equal to 0.8, preferably higher than or equal to 1, 1.5, 1.9, 2, 2.2, 2.5, 3 or 3.4. In one embodiment, R_T is lower than 5, preferably lower than at least one of the following values 4.5, 4.0, 3.5. In another embodiment, R_T ranges from 0.8 to 3.5. It is preferable to have a high R_T ratio, in order to have an article showing a higher critical temperature, while exhibiting in the same time high abrasion resistance.

It is also possible to define a R1 ratio:

$R1 = \text{thickness of the outermost internal low refractive index layer(s) of the interferential coating} / \text{thickness of the outermost internal high refractive index layer(s) of the interferential coating}$

By outermost internal high or low refractive index layer(s) of the interferential coating, it is meant the layer(s) of the interferential coating that is (are) the furthest from the substrate but positioned just before the outermost low and high refractive index layer(s) of the interferential coating as defined previously. Generally, there is only one internal outermost high (or low) refractive index layer in the interferential coating, i.e., when high refractive index layers and low refractive index layers alternate with each other in the stack. However, in some embodiments, there can be two or more adjacent high (or low) refractive index layers in internal outermost position in the interferential coating. In this case, it is considered that there is a plurality of outermost high (or low) refractive index layers in the interferential coating, and this is taken into account by adding their respective thicknesses for the calculation of the R1 ratio.

When a high refractive index layer of the interferential coating is an electrically conductive layer, especially a conductive oxide layer (such as an ITO, SnO_2 layer) and is positioned as the outermost internal high refractive index layer but is not adjacent to one or more non conductive high refractive index layers (such as a ZrO_2 , Ta_2O_5 layer), such conductive layer is not taken into account for the calculation of R1 and is not considered as being part of the interferential coating.

As an example, for an interferential coating comprising the following layers: Air/hydrophobic coating/.../ SiO_2 (thickness a'')/ITO (thickness b'')/ SiO_2 (thickness c'')/ ZrO_2 (thickness d'')/ SiO_2 ..., $R1 = (a'' + c'')/d''$.

The thicknesses of the two internal SiO_2 layers are added, as the conductive layer is not considered as being part of the coating. Consequently, the above defined rules for the calculation are applied.

However, if the high refractive index conductive layer identified as the outermost internal layer is adjacent to one or more non conductive high refractive index layer (plurality of adjacent high refractive index layers), the thicknesses of those plurality of layers are added for the calculation of the R1 ratio.

As an example, for an interferential coating comprising the following layers Air/...../SiO₂(thickness a''')/ITO(thickness b''')/ZrO₂(thickness c''')/SiO₂... $R1 = a''' / (b''' + c''')$.

It is to be noted that such high refractive index conductive layer (such as ITO or SnO₂) is generally thin or very thin (typically less than one of the following thickness values: 20 nm, 15 nm, 10 nm).

In an embodiment R1 is higher than or equal to 1 preferably higher than or equal to 1.25, 1.4, 1.5, 1.75, 1.9, 2, 2.5 or 3. In an embodiment, R1 is lower than 5, preferably lower than at least one of the following values 4.5, 4.0, 3.5. Those values provide a good compromise of properties. In another embodiment, R1 ranges from 1 to 3.5.

In the present invention, the multilayer interferential coating is deposited onto a monolayer sub-layer having a thickness higher than or equal to 250 nm. It should be noted that such sub-layer does not belong to the interferential coating. Said sub-layer is preferably in direct contact with the interferential coating.

As used herein, an interferential coating sub-layer or adhesion layer is intended to mean a relatively thick coating, used in order to improve mechanical properties such as abrasion resistance and/or scratch resistance of the interferential 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 generally not take part to the reflective or anti-reflective optical activity of the interferential coating, especially when it has a refractive index close to that of the underlying coating (which is generally an impedance layer or an anti-abrasion and/or anti-scratch coating).

The sub-layer has a thickness that is generally lower than or equal to any one of the following values: 600 nm, 500 nm, 450 nm, 400 nm and is preferably lower than 375 nm, and is generally higher than or equal to 275 nm, more preferably higher than or equal to 300, 325 or 350 nm. Increasing the thickness of the sub-layer leads to an abrasion resistance improvement.

The sub-layer is preferably a SiO₂-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 of a silica layer. In another embodiment, this SiO₂-based layer is a silica layer doped with alumina, in amounts such as defined hereabove, preferably consists of a silica layer doped with alumina.

When designing an interference stack according to the invention, mechanical stresses are properties to be taken into account. The stress in the sub-layer is preferably negative, i.e., the sub-layer is under compression. This compressive stress is preferably lower than -250 MPa, more preferably lower than any one of the following values: -275 MPa, -290 MPa, -300 MPa, -350 MPa, -400 MPa, -450 MPa. It is preferably higher than -500 MPa. It is measured at a temperature of 20°C and under a relative humidity of 50% in the manner described in WO 2014/199103. The deposition conditions, in particular the pressure during the deposition of the sub-layer, allow these stress values to be achieved. The stress is measured for a thickness of the sub-layer of at least 150 nm, preferably at a thickness of the sub-layer of around 150 nm.

In some embodiments of the invention, especially when the sub-layer and the underlying coating (or the substrate, if there is no functional coating between the substrate and the sub-layer) have substantially different refractive indexes, one or more so-called "impedance layers" (or optical buffer layers or optical adjustment layers) can be interleaved between the underlying coating (or the substrate) and the sub-layer, thus forming an impedance coating that limits interference fringes due to differences of refractive indices between the sub-layer and the underlying coating or substrate. This embodiment is preferred when the underlying coating, which is generally an anti-abrasion and/or anti-scratch coating, or the substrate, has a high refractive index, i.e., a refractive index higher than 1.55, preferably higher than or equal to 1.57.

In this case, the optical article may comprise preferably at most three additional layers, more preferably at most two additional layers, interleaved between the optionally coated substrate and the sub-layer. These additional/intermediate layers are preferably thin layers, the function of which is to limit the reflections at the sub-layer / underlying coating interface or sub-layer / substrate interface, as the case may be, by interferential effect.

In one embodiment, the impedance coating comprises, preferably consists of 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, 20 or 10 nm. Such layer with a high refractive index is preferably in direct contact with 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 or equal to 1.55.

As an alternative, the impedance coating comprises, in addition to the previously mentioned layer with a high refractive index, a SiO₂-based layer made of a material (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 45 nm, onto which said layer with a high refractive index is deposited. Typically, in this instance, the impedance coating comprises, deposited in this order onto the optionally coated substrate, a 4-50 nm-thick SiO₂ layer (preferably a 20-40 nm thick layer), and a 3-12 nm-thick ZrO₂ or Ta₂O₅ layer, which is in contact with the sub-layer.

At least one thin (1 nm to several nm thickness) adhesion layer can be applied on the substrate before applying the impedance layers or the sub-layer such as a chromium based or a niobium based layer or any other layer known by the person skilled in the art to improve adhesion.

A sub-layer of an interferential coating is a category of layer that is well-identifiable and well-known to those of ordinary skill in the art, and cannot be confused with an abrasion-resistant and/or scratch-resistant coating (hard coat), described later in the present application.

Optionally, the exposed surface of the sub-layer may be submitted, prior to depositing the first layer of the interferential coating, to a physical or a chemical activation treatment which

may be selected from the pre-treatments the substrate may undergo prior to depositing the sub-layer and which have already been mentioned hereabove. The preferred pre-treatment is an ion bombardment, for example by using an ion gun-generated argon ion beam. Such physical or chemical activation treatments (preferably an ionic bombardment treatment) may also be performed on the exposed surface of one or more layer(s) of the multilayer interference coating, prior to depositing the subsequent layer of said multilayer interferential coating.

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 electrically conductive layer into the stack present on the surface of the article, preferably in the interferential coating.

The ability for a lens 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 lenses 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 lens. In the present application, discharge times are measured according to the method exposed in the French application FR 2943798.

As used herein, an "electrically conductive layer" or an "antistatic layer" is intended to mean a layer which, due to its presence on the surface of a substrate, decreases the ability of the optical article to attract dust/particles due to charge accumulation. Preferably, when applied onto a non-antistatic substrate (i.e. having a discharge time higher than 500 ms), the antistatic layer enables the optical article not to retain and/or develop a substantial static charge, for example to have a discharge time of 500 ms or less after a static charge has been applied onto the surface thereof, so that small dust is prevented from adhering to the optical article due to prevention of static effects.

The electrically conductive layer may be located at various places in the stack, generally in or in contact with the interferential coating, provided that the reflective or anti-reflective properties thereof are not affected. It is preferably located between two layers of the interferential coating, and/or is preferably adjacent to a layer with a high refractive index of such interferential coating. In an embodiment, the electrically conductive layer is located immediately under a layer with a low refractive index of the interferential coating, most preferably is the penultimate layer of the interferential coating by being located immediately under the LI external layer of the interferential coating.

The electrically conductive layer should be thin enough not to alter the transparency of the interferential 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 ranges from 1 to 15 nm, more preferably from 1 to 10 nm, ideally from 2 to 8 nm. Preferably, the electrically conductive layer comprises an optionally doped 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), aluminum-doped zinc oxide ($\text{ZnO}:\text{Al}$), indium oxide (In_2O_3) and tin oxide (SnO_2) are preferred. In a most preferred embodiment, the

electrically conductive and optically transparent layer is a tin-indium oxide layer, noted ITO layer or a tin oxide layer.

Generally, the electrically conductive layer contributes, within the stack, but in a limited manner because of its low thickness, to obtaining interferential properties and typically represents a layer with a high refractive index in said coating. This is the case for those layers made from an electrically conductive and highly transparent material such as ITO or SnO₂ layers. Accordingly, when it is present, the electrically conductive layer is preferably the outermost high refractive index layer of the interferential coating, or one of the outermost high refractive index layers of the interferential coating when it is adjacent to one or more high refractive index layers.

The electrically conductive layer may be deposited according to any suitable method, for example by vacuum evaporation deposition, preferably ion-beam-assisted (IAD, described below) to increase its transparence, or by means of cathode sputtering.

The electrically conductive layer may also be a very thin layer of a noble metal (Ag, Au, Pt, etc.) typically smaller than 1 nm in thickness and preferably less than 0.5 nm in thickness.

The various layers of the interferential coating, the sub-layer, and the optional impedance layers are preferably deposited by vapor phase deposition, under vacuum, according to any of the following methods: i) by evaporation, optionally under ion beam assistance; ii) by ion-beam spraying; 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 evaporation under vacuum. Preferably, the deposition of each of the above-mentioned layers is conducted by evaporation under vacuum. Such a process does advantageously avoid heating the substrate, which is particularly interesting for coating heat-sensitive substrates such as organic glasses.

A treatment step with energetic species such as previously defined may also be carried out, simultaneously whilst depositing one or more of the various layers of the interference coating, sub-layer, or optional impedance layers. In particular, working under ion assistance enables to pack said layers while they are being formed, and increases their compression and refractive index. The use of ion assistance during the deposition of a layer produces a layer that is structurally different from a layer deposited without ion assistance.

The ion assisted deposition method or IAD is notably described in US patent application 2006/017011 and in US patent 5,268,781. Vapor phase deposition under ion assistance comprises depositing onto a substrate a layer of material by simultaneously bombarding by means of an ion beam said layer while it is being formed, and preferably under ion bombardment achieved by means of an ion gun. The ion bombardment leads to an atomic rearrangement in the coating being formed, which increases its density. The IAD not only allows an improvement of the deposited layer adhesion, but also an increase in their refractive index. The IAD operation may be performed by means of an ion gun, where ions are particles composed of gas atoms from which one or more electron(s) is or are extracted. It does

preferably consist of bombarding the surface to be treated with oxygen ions. Other ionized gases may be used, either combined with oxygen, or not, 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.

In a preferred embodiment of the present invention, the deposition of the high refractive index layer of the interferential coating having a refractive index higher than 1.55 and a thickness higher than or equal to 15 nm (preferably higher than or equal to 20 nm, more preferably higher than or equal to 25 nm) that is the furthest from the substrate has been carried out under ionic assistance, i.e., by bombarding by means of an ion beam said high refractive index layer while it is being formed, and preferably under ion bombardment achieved by means of an ion gun. This is the second alternative means according to the invention that has been found by the present inventors to obtain an article having an improved abrasion resistance.

According to this embodiment, the antireflection coating comprises at least one high refractive index layer having a refractive index higher than 1.55 and a thickness higher than or equal to 15 nm, and the one that is the furthest from the substrate is deposited under ionic assistance. In other words, according to this embodiment, the high refractive index layer of the interferential coating that is the furthest from the substrate, when it has a thickness higher than or equal to 15 nm, is deposited under ionic assistance. According to this embodiment, when the high refractive index layer of the interferential coating that is the furthest from the substrate has a thickness lower than 15 nm, for example when the high refractive index layer that is the furthest from the substrate is a thin electrically conductive layer, the layer that is deposited under ionic assistance is the first (closest) high refractive index layer of the interferential coating having a thickness higher than or equal to 15 nm that is present under said high refractive index layer of the interferential coating having a thickness lower than 15 nm that is the furthest from the substrate.

In one embodiment of the present invention, the high refractive index layer of the interferential coating having a refractive index higher than 1.55 that is the furthest from the substrate is an electrically conductive layer having a thickness lower than 15 nm. In another embodiment, the high refractive index layer of the interferential coating having a refractive index higher than 1.55 and a thickness higher than or equal to 15 nm that is the furthest from the substrate is a ZrO_2 or Ta_2O_5 layer, preferable a ZrO_2 layer, and such layer is preferably deposited under ionic assistance.

In a preferred embodiment, the first and second alternative means according to the invention to obtain an article having an improved abrasion resistance are combined to obtain an optimal abrasion resistance improvement. In this embodiment, the optical article has a) a ratio R_D is higher than or equal to 1.5, and b) the deposition of the high refractive index layer of the interferential coating having a refractive index higher than 1.55 and a thickness higher than or equal to 15 nm (preferably ≥ 20 nm, more preferably ≤ 25 nm) that is the furthest from the substrate is carried out under ionic assistance by bombarding by means of an ion beam said high refractive index layer while it is being formed.

According to an embodiment of the present invention, the deposition of all the high refractive index layers of the interferential coating having a refractive index higher than 1.55 has been carried out under ionic assistance, i.e., those layers have been deposited under the assistance of a source of ions during the formation of those layers.

5 The outermost low refractive index layer(s) of the interferential coating is (are) preferably deposited without ionic assistance, preferably without concomitant treatment with energetic species. In another embodiment, the low refractive index layers of the interferential coating and/or the sub-layer are (is) deposited without ionic assistance, preferably without concomitant treatment with energetic species.

10 In one embodiment, no layer of the interferential coating is deposited under ion assistance (preferably no layer of the interferential coating is deposited under concomitant treatment with energetic species), except the electrically conductive layer(s), if present in the interferential coating.

15 In a further embodiment, no layer of the interferential coating is deposited under ion assistance (preferably no layer of the interferential coating is deposited under concomitant treatment with energetic species), except the electrically conductive layer(s), if present in the interferential coating, and an outermost high refractive index layer of the interferential coating having a refractive index higher than 1.55 and a thickness higher than or equal to 15 nm that is the furthest from the substrate.

20 Optionally, the deposition of one or more of said layers is performed by supplying (a supplementary) gas during the deposition step of the layer in a vacuum chamber, such as disclosed in US 2008/206470. Concretely, an additional gas such as a rare gas, for example argon, krypton, xenon, neon; a gas such as oxygen, nitrogen, or mixtures of two gases or more amongst these, is or are introduced into the vacuum deposition chamber while the layer is being
25 deposited. The gas employed during this deposition step is not an ionized gas, more preferably not an activated gas.

This gas supply makes it possible to regulate the pressure and differs from an ionic bombardment treatment, such as ion assistance. It generally enables the limitation of stress in the interferential coating and to reinforce the adhesion of the layers. When such deposition
30 method is used, which is called deposition under gas pressure regulation, it is preferred to work under an oxygen atmosphere (so called "passive oxygen"). The use of an additional gas supply during the deposition of a layer produces a layer that is structurally different from a layer deposited without additional gas supply.

35 In an embodiment of the invention, the deposition of the sub-layer is performed in a vacuum chamber under a pressure lower than any one of the following values: 1.6×10^{-4} mBar, 1.5×10^{-4} mBar, 1.4×10^{-4} mBar, 1.3×10^{-4} mBar, 1.2×10^{-4} mBar, 1.1×10^{-4} mBar, preferably lower than 10^{-4} mBar, more preferably lower than $8 \cdot 10^{-5}$ mBar and even better lower than any one of the following values $7 \cdot 10^{-5}$ mBar, $6 \cdot 10^{-5}$ mBar, $5 \cdot 10^{-5}$ mBar, $4 \cdot 10^{-5}$ mBar, $3 \cdot 10^{-5}$ mBar. Typically, in this preferred embodiment, the pressure is around 1.6×10^{-5} mBar.

In a preferred embodiment of the invention, the deposition of the sub-layer is performed in a vacuum chamber in which no supplementary gas is supplied during said deposition. It has been found that depositing the sub-layer under a low pressure, and ideally without gas supply to obtain a still lower pressure, leads to a sub-layer with a lower porosity, a higher compression and density, and an increase of the abrasion resistance of the optical article.

In another embodiment, the outermost high refractive index layer(s) of the interferential coating, except the electrically conductive layers, if present in outermost position, is (are) deposited in a vacuum chamber in which at least one supplementary gas is supplied during said deposition. In another embodiment, the high refractive index layer(s) of the interferential coating, except the electrically conductive layer(s), if present in outermost position, is (are) deposited in a vacuum chamber in which at least one supplementary gas is supplied during said deposition.

According to a particularly preferred embodiment, the optical article comprises, starting from the surface of the substrate optionally coated with one or more functional coatings such as a primer coating and/or a hard coat, preferably a low refractive index impedance coating having a thickness ranging from 4 to 50 nm, preferably from 20 to 40 nm, preferably of silica, preferably a high refractive index impedance coating having a thickness ranging from 3 to 12 nm, more preferably from 4 to 10 nm, preferably of zirconia, a sub-layer having a thickness of from 250 to 450 nm, more preferably from 275 to 425 nm, even more preferably from 300 to 400 nm, preferably a silica-based sub-layer, and an interferential coating, preferably an anti-reflective coating, containing in the following order, a high refractive index layer with a thickness of from 8 to 35 nm, preferably of from 10 to 30 nm, preferably of zirconia, a layer with a low refractive index with a thickness of from 8 to 50 nm, preferably of from 10 to 45 nm, preferably of silica, a layer with a high refractive index with a thickness of from 20 to 110 nm, preferably of from 25 to 100 nm, preferably of zirconia, optionally an electrically conductive layer with a thickness of from 3 to 15 nm, preferably of from 4 to 8 nm, preferably made of tin oxide, and a layer with a low refractive index with a thickness of from 70 to 150 nm, preferably of from 75 to 140 nm, preferably of silica.

The interferential coating / sub-layer / optional impedance layer(s) system may be deposited directly onto a bare substrate. In some applications, it is preferred that the main surface of the substrate be coated with one or more functional coatings improving its optical and/or mechanical properties, prior to depositing the interferential coating of the invention. These functional coatings traditionally used in optics may be, without limitation, an impact-resistant primer layer, an abrasion- and/or scratch-resistant coating (hard coat), a polarized coating, an antistatic coating, a photochromic coating, a tinted coating or a stack made of two or more of such coatings.

The impact-resistant primer coating which may be used in the present invention can be any coating typically used for improving impact resistance of a finished optical article. By definition, an impact-resistant primer coating is a coating which improves the impact resistance

of the finished optical article as compared with the same optical article but without the impact-resistant primer coating.

Typical impact-resistant primer coatings are (meth)acrylic based coatings and polyurethane based coatings. In particular, the impact-resistant primer coating according to the invention can be made from a latex composition such as a poly(meth)acrylic latex, a polyurethane latex or a polyester latex.

Preferred primer compositions include compositions based on thermoplastic polyurethanes, such as those described in the patents JP 63-141001 and JP 63-87223, poly(meth)acrylic primer compositions, such as those described in the patents US 5,015,523 and US 6,503,631, compositions based on thermosetting polyurethanes, such as those described in the patent EP 0404111 and compositions based on poly(meth)acrylic latexes or polyurethane latexes, such as those described in the patents US 5,316,791 and EP 0680492. Preferred primer compositions are compositions based on polyurethanes and compositions based on latexes, in particular polyurethane latexes, poly(meth)acrylic latexes and polyester latexes, as well as their combinations. In one embodiment, the impact-resistant primer comprises colloidal fillers.

Poly(meth)acrylic latexes are latexes based on copolymers essentially made of a (meth)acrylate, such as for example ethyl (meth)acrylate, butyl (meth)acrylate, methoxyethyl (meth)acrylate or ethoxyethyl (meth)acrylate, with at least one other co-monomer in a typically lower amount, such as for example styrene.

Commercially available primer compositions suitable for use in the invention include the Witcobond® 232, Witcobond® 234, Witcobond® 240, Witcobond® 242 compositions (marketed by BAXENDEN CHEMICALS), Neorez® R-962, Neorez® R-972, Neorez® R-986 and Neorez® R-9603 (marketed by ZENECA RESINS), and Neocryl® A-639 (marketed by DSM coating resins).

The thickness of the impact-resistant primer coating, after curing, typically ranges from 0.05 to 30 µm, preferably 0.2 to 20 µm and more particularly from 0.5 to 10 µm, and even better 0.6 to 5 µm or 0.6 to 3 µm, and most preferably 0.8 to 1.5 microns.

The impact-resistant primer coating is preferably in direct contact with an abrasion- and/or scratch-resistant coating.

The abrasion- and/or scratch-resistant coating may be any layer traditionally used as an anti-abrasion and/or anti-scratch coating in the field of optical lenses.

The abrasion- and/or scratch-resistant coatings are preferably hard coatings based on poly(meth)acrylates or silanes, generally comprising one or more mineral fillers intended to increase the hardness and/or the refractive index of the coating once cured.

Abrasion- and/or scratch-resistant coatings are preferably prepared from compositions comprising at least one alkoxysilane and/or a hydrolyzate thereof, obtained for example through hydrolysis with a hydrochloric acid solution and optionally condensation and/or curing catalysts.

Suitable coatings that are recommended for the present invention include coatings based on epoxysilane hydrolyzates such as those described in the patents EP 0614957, US 4211823 and US 5015523.

A preferred abrasion- and/or scratch-resistant coating composition is the one disclosed in the patent EP 0614957, in the name of the applicant. It comprises a hydrolyzate of epoxy trialkoxysilane and dialkyl dialkoxysilane, colloidal silica and a catalytic amount of an aluminum-based curing catalyst such as aluminum acetylacetonate, the rest being essentially composed of solvents traditionally used for formulating such compositions. Preferably, the hydrolyzate used is a hydrolyzate of γ -glycidoxypyrtrimethoxysilane (GLYMO) and dimethyldiethoxysilane (DMDES).

The abrasion- and/or scratch-resistant coating composition may be deposited by known methods and is then cured, preferably using heat or ultraviolet radiation. The thickness of the (cured) abrasion- and/or scratch-resistant coating does generally vary from 2 to 10 μm , preferably from 3 to 5 μm .

The optical article according to the invention may also comprise coatings formed on the interferential coating and capable of modifying the surface properties thereof, such as a hydrophobic and/or oleophobic coating (antifouling top coat). These coatings are preferably deposited onto the outer layer of the interferential coating. Generally, their thickness is lower than or equal to 10 nm, does preferably range from 1 to 10 nm, more preferably from 1 to 5 nm. Antifouling top coats are generally coatings of the fluorosilane or fluorosilazane type, preferably comprising fluoropolyether moieties and more preferably perfluoropolyether moieties. More detailed information on these coatings is disclosed in WO 2012076714.

Instead of a hydrophobic coating, a hydrophilic coating may be used which provides anti-fog properties (anti-fog coating), or a precursor of an anti-fog coating which provides anti-fog properties when associated with a surfactant. Examples of such anti-fog precursor coatings are described in the patent application WO 2011/080472.

The additional coatings such as primers, hard coats and antifouling top coats may be deposited onto a main face of the substrate using methods known in the art, including spin-coating, dip-coating, spray-coating, evaporation, sputtering, chemical vapor deposition and lamination.

Typically, an optical article according to the invention comprises a substrate that is successively coated with an impact-resistant primer layer, an anti-abrasion and/or scratch-resistant layer, 1, 2 or 3 impedance layers, a sub-layer and an interferential coating according to the invention, and a hydrophobic and/or oleophobic coating, or a hydrophilic coating which provides anti-fog properties, or an anti-fog precursor coating.

Due to the presence of the sub-layer and interferential coating according to the invention (as an example an antireflective coating), the optical articles of the invention exhibit a high value of abrasion resistance measured according to the Bayer ASTM (Bayer sand) operating protocol described hereafter, i.e., in accordance with the ASTM F735-81 standard.

According to the present invention, the optical article, the main face of which, preferably the front face, is covered by the interferential stack of the invention, exhibits a Bayer value measured in accordance with the ASTM F735-81 standard (sand Bayer value) higher than 7, preferably higher than any one of the following value: 7.5, 8, 8.5, 9, 9.5, 10, 11. Thus, the

present invention provides optical articles with a high abrasion resistance, since typical sand
Bayer values for optical articles are around 5. Such values can be obtained by controlling the
thickness of the sub-layer, the R_D ratio, and/or the deposition parameters, in particular the
pressure during the deposition of the sub-layer and/or the ion assistance during the deposition
of the high refractive index layer of the interferential coating having a thickness higher than or
equal to 15 nm that is the furthest from the substrate.

In an embodiment, the optical article is a lens and the interferential coating and sub-layer
are applied on the front main face of the lens.

In a preferred embodiment, the front main face of the ophthalmic lens according to the
invention as defined before exhibits a Bayer value V1 and the back (concave) main face of said
lens is coated by an interferential coating, preferably an antireflective coating, different from that
of the front main face and that exhibits a Bayer value V2, V1 and V2 satisfying the following
relationship:

V1-V2 is higher than 0.5, preferably higher than 1, more preferably higher than 1.5, even
better higher than at least one of the following values: 2; 2.5; 3; 3.5; 4, and V1 is higher than or
equal to 7, more preferably higher than or equal to 8. V1 and V2 are measured in accordance
with the ASTM F735-81 standard.

The Bayer values being measurable only on a convex surface, the interferential coating
on the back main face has to be reproduced on a convex surface on a separate lens, and its
Bayer value measured according to the same protocol as the front face in order to obtain the V2
value. The back main face may also comprise a sub-layer and/or impedance layers, as defined
previously.

In another embodiment, V1-V2 is higher than 0.5, preferably higher than 1, more
preferably higher than 1.5, even better higher than at least one of the following values: 2; 2.5; 3;
3.5; 4, and the front main face exhibits a R_{uv} value at an angle of incidence of 15° higher than
5% and the back main face exhibits a R_{uv} value at an angle of incidence of 35° lower than 5%,
preferably lower than or equal to 4.5%, more preferably lower than or equal to 4% and even
better lower than or equal to 3.5%, with the proviso that the reflection on the front main face at
an angle of incidence of 15° , noted $R(15^\circ)$, and/or $R_m(15^\circ)$ (defined hereunder) and/or the
average reflectance of the front main face coated with the interferential coating of the invention,
between 350 nm and a wavelength comprised between 380 nm and 400 nm, preferably
between 350 nm and 380 nm, weighted by the function $W(\lambda)$, do(es) not exceed the values
defined later in this application.

R_{uv} is the mean reflection factor of a face of an optical article between 280 nm and 380
nm, weighted by the function $W(\lambda)$ defined in the ISO 13666:1998 standard, measured in the
present application at an angle of incidence of 35° for the back main face and at an angle of
incidence of 15° for the front main face. Definition of $W(\lambda)$ and calculation examples for angles
of incidence at 30° and 45° are specified in WO 2012/076714. The person skilled in the art can
easily implement calculation based on reflection values measured on the respective faces at the
wished incidence angle (15° , 35°).

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 relative light transmission factor in the visible spectrum T_v is higher than or equal to any one of the following values: 87 %, 88 %, 89 %, 90 %, 92 %, 95 %, 96 %, 97 %, 98 %. Said T_v factor preferably ranges from 87 % to 98.5 %, more preferably from 87 % to 97 %, even better from 87 % to 96 %. In another embodiment, T_v ranges from 89 % to 98 %, preferably from 90 % to 98 %, better 95 % to 97 %.

The T_v factor, also called "luminous transmission" of the system, is such as defined in ISO standard 13666:1998 and is measured accordingly to standard ISO 8980-3. It is defined as the 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).

The "mean light reflection factor," noted R_v , also called "luminous reflection", is such as defined in the ISO 13666:1998 Standard, and measured in accordance with the ISO 8980-4 Standard (for an angle of incidence lower than 17° , typically of 15°), i.e. this is the weighted spectral reflection average over the whole visible spectrum between 380 and 780 nm.

The mean light reflection factor R_v of the face of the lens coated by an anti-reflection coating according to the invention is preferably lower than 2.5 % (per face), preferably lower than 2 %, more preferably lower than 1 %, even more preferably ≤ 0.85 %, per face of the article.

According to an embodiment of the invention, the reflection $R(15^\circ)$ (measured at an incidence angle of 15°) of the main face of the optical article coated according to the invention is lower than 50 % for at least one wavelength in the wavelength range 300-350 nm.

According to another embodiment of the invention, the reflection $R(15^\circ)$ of the main face of the optical article coated according to the invention is lower than 50 % at the wavelength 320 nm.

According to an embodiment of the invention, the mean reflection coefficient $R_m(15^\circ)$ (non weighted average reflection) in the wavelength range 300-350 nm of the main face of the optical article coated according to the invention is lower than 50 %, preferably lower than or equal to 45 %.

The average reflectance of the coated front main face of the interferential coating of the invention, between 350 nm and a wavelength comprised between 380 nm and 400 nm, preferably between 350 nm and 380 nm, weighted by the function $W(\lambda)$, is generally lower than 35 %, preferably lower than or equal to 32 %, more preferably lower than or equal to 30 % and even better in certain cases lower than or equal to 25 % or 20 %, for at least one angle of incidence comprised between 0° and 17° .

In each of these embodiments, the total number of layers in the interferential coating, preferably an antireflection coating, is preferably higher than or equal to 3, preferably lower than or equal to 5, and/or the total thickness of the interferential coating (preferably an antireflective coating) plus the thickness of the sub-layer plus the thickness of the impedance layer(s) if

present is preferably lower than 1 micrometer, more preferably lower than or equal to 800 nm or 500 nm.

The definition of the average reflectance and function $W(\lambda)$ is described in WO 2016/102857. $W(\lambda)$ is also described in WO 2012/076714.

5 The colorimetric coefficients C^* and h of the optical article of the invention in the international colorimetric CIE $L^*a^*b^*$ are calculated between 380 and 780 nm, taking the standard illuminant D65 and the observer into account (angle of incidence: 15°). The observer is a "standard observer" (10°) as defined in the international colorimetric system CIE $L^*a^*b^*$.

10 The colorimetric coefficients of the lenses of the invention have a good robustness. The robustness σh of the optical article, defined in WO 2015/000534, is satisfactory, and preferably lower than or equal to 8° , more preferably lower than or equal to 7.5° , for a hue angle h corresponding to green.

It is possible to prepare interferential coatings without limitation as regards their hue angle (h), which relates to the residual color displayed by said interferential coating, and preferably ranges from 40° to 300° , more preferably from 50° to 290° . In some embodiments, 15 the optical article has a hue angle (h) ranging from 240° to 300° , preferably from 250° to 290° , more preferably from 260° to 280° , thus resulting in a perceived residual reflected color blue to violet, preferably close to violet. In another embodiment, the optical article has a hue angle (h) higher than or equal to 135° , more preferably higher than or equal to 140° and better ranging 20 from 140° to 160° , thus resulting in an interferential coating having a green reflection. In another embodiment, the optical article has a hue angle (h) ranging from 40° to 90° , preferably 50° to 90° , better 50° to 70° , thus resulting in an interferential coating having a gold reflection.

In some aspects of the invention, the interferential coating has a chroma (C^*) that is lower than 15 (for an angle of incidence of 15°), more preferably lower than 13. Obtaining low 25 residual color intensity (chroma) articles is preferable with respect to wearer's comfort viewpoint, in the cases of lenses.

The invention further relates to a method of manufacturing an optical article such as described hereabove, comprising:

- providing an optical article comprising a substrate having at least one main face,
- 30 - depositing onto a main surface of the substrate a monolayer sub-layer having an exposed surface and a thickness higher than or equal to 250 nm,
- depositing onto said exposed surface of the sub-layer a multilayer interferential coating comprising at least one high refractive index layer having a refractive index higher than 1.55 and at least one low refractive index layer having a refractive index of 1.55 or less, thereby 35 obtaining a coated optical article, having a Bayer value determined in accordance with the ASTM F735-81 standard higher than or equal to 7, and

a) the ratio:

$$R_D = \frac{\text{thickness of the outermost low refractive index layer(s) of the int erferential coating}}{\text{thickness of the outermost high refractive index layer(s) of the int erferential coating}}$$

is higher than or equal to 1.5, and/or

b) the deposition of the high refractive index layer of the interferential coating having a refractive index higher than 1.55 and a thickness higher than or equal to 15 nm that is the furthest from the substrate is carried out under ionic assistance by bombarding by means of an ion beam said high refractive index layer while it is being formed.

5 In preferred embodiments, the exposed surface of the sub-layer has been submitted to an ionic bombardment treatment prior to depositing said multilayer interferential coating, and/or the deposition of the sub-layer is conducted in a vacuum chamber in which no supplementary gas is supplied during said deposition.

10 In another embodiment, the exposed surface of at least one layer of the multilayer interferential coating has been submitted to an ionic bombardment treatment prior to depositing the subsequent layer of said multilayer interferential coating.

15 In another embodiment, the exposed surface of each layer of the multilayer interferential coating except the layer of said coating that is the furthest from the substrate has been submitted to an ionic bombardment treatment prior to depositing the subsequent layer of said multilayer interferential coating. This embodiment involving multiple interlayer bombardments is preferably implemented when the sub-layer is deposited under a low pressure ($< 1.6 \times 10^{-4}$ mBar or even better in a vacuum chamber without supplying any additional gas during the deposition) to get a better adhesion of the layers within the interferential stack.

20 When impedance layers are present, the exposed surface of the outermost impedance layer is preferably submitted to an ionic bombardment treatment prior to depositing the subsequent layer, which is generally the sub-layer.

25 In another embodiment, the exposed surface of the following layers is submitted to an ionic bombardment treatment prior to depositing the subsequent layer onto said layers: the outermost impedance layer (when present), the sub-layer and each layer of the multilayer interferential coating except the outermost layer of said coating.

In one embodiment, the present optical article is prepared by forming on the substrate a primer coating and/or an abrasion- and/or scratch-resistant coating in a first manufacturing site, while the other coatings are formed in a second manufacturing site.

30 The following examples illustrate the present invention in a more detailed, but non-limiting manner. Unless stated otherwise, all thicknesses disclosed in the present application relate to physical thicknesses. The percentages given in the tables are weight percentages. Unless otherwise specified, the refractive indexes referred to in the present invention are expressed at 20-25°C for a wavelength of 550 nm.

35

EXAMPLES

1. General procedures

The articles employed in the examples comprise a 65 mm-diameter polythiourethane MR8® lens substrate (from Mitsui Toatsu Chemicals Inc., refractive index = 1.59), with a power of -2.00 diopters and a thickness of 1.2 mm, coated on its convex face with the impact resistant primer coating based on a W234™ polyurethane material disclosed in the experimental part of WO 2010/109154 modified to have a refractive index of 1.6 by addition of high refractive index colloids and the abrasion- and scratch-resistant coating (hard coat) disclosed in example 3 of EP 0614957 (modified to have a refractive index of 1.6 rather than 1.5 by adding high refractive index colloids), optionally impedance layers, a sub-layer, an anti-reflection coating having a specific R_D ratio, and the antifouling coating disclosed in the experimental section of patent application WO 2010/109154, i.e., by evaporation under vacuum of the Optool DSX® compound marketed by Daikin Industries (thickness: from 2 to 5 nm).

The various layers such as the sub-layers, optical impedance layers and the layers of the antireflection coating were deposited without heating the substrates, by vacuum evaporation, optionally assisted (IAD) during the deposition by a beam of oxygen and possibly argon ions, when specified (evaporation source: electron gun), and optionally under pressure regulation by supplying (passive) O₂ gas into the chamber, where indicated.

The vacuum evaporation device that made it possible to deposit the various antireflective layers was a vacuum coater BAK from Physimex having two systems for evaporating materials, an electron gun evaporation system and a thermal evaporator (Joule-effect evaporation system), and a Mark 2+ ion gun from VEECO for use in the preliminary phase of preparation of the surface of the substrate by argon ion bombardment (IPC) and in the ion-assisted deposition (IAD) of the layers.

2. Preparation of the optical articles

The lenses were placed on a carousel provided with circular openings intended to accommodate the lenses to be treated, the concave side facing the evaporation sources and the ion gun.

The method for producing optical articles comprises introducing the lens substrate provided with the primer and abrasion-resistant coatings into a vacuum deposition chamber, conducting a pumping step until a high vacuum was created, followed by an ion gun conditioning step (IGC, such as disclosed in FR 2957454, 3.5×10^{-5} mBar as starting pressure, 140 V, 3.5 A, argon, 60 seconds), a substrate surface activation step using a bombardment with an argon ion beam (IPC) with a starting pressure of $5 \cdot 10^{-4}$ mBar (the ion gun was set to 1 A, 100 V, 60 seconds), stopping the ionic irradiation, and then successively evaporating the required number of layers (optional intermediate optical impedance layers, sub-layer, antireflection coating layers and antifouling coating) at a rate ranging from 0.4 to 3 nm/s, and lastly a ventilation step.

Forming an antireflection stack according to the present invention comprises a deposition step of a thin SiO₂ optical (impedance) layer at a rate of 2 nm/s under an O₂ pressure

of $8 \cdot 10^{-5}$ mBar, a deposition step of a thin ZrO_2 optical (impedance) layer at a rate of 1 nm/s under an O_2 pressure of $7 \cdot 10^{-5}$ mBar, a surface activation step of this ZrO_2 layer using an argon ion beam for 30 seconds (same treatment as IPC already conducted directly on the substrate), a deposition step of a SiO_2 sub-layer at a rate of 3 nm/s optionally under an O_2 atmosphere (at a pressure of $2.1 \cdot 10^{-4}$ mBar in comparative examples 3, 4 and 5 where O_2 gas was supplied, or $1.5 \cdot 10^{-5}$ mBar in the other examples where no supplementary gas supply was performed), a surface activation step of the sub-layer using an argon ion beam for 30 seconds (same treatment as IPC already conducted directly on the substrate), a deposition step of a HI layer (ZrO_2) at a rate of 2 nm/s under an O_2 pressure of $7 \cdot 10^{-5}$ mBar, a deposition step of a LI layer (SiO_2) at a rate of 2 nm/s, a deposition step of a HI layer (ZrO_2) at a rate of 2 nm/s under an O_2 pressure of $7 \cdot 10^{-5}$ mBar (with an oxygen ion assistance in examples 1, 2, 4 and comparative example 4; ion gun: 3 A, 300 V), a deposition step of an SnO_2 layer (HI, electrically conductive) at a rate of 1 nm/s with an oxygen ion assistance (ion gun: 1.2 A, 100 V), a deposition step of a LI layer (SiO_2) at a rate of 3 nm/s, and lastly a deposition step of an Optool DSX[®] layer at a rate of 0.4 nm/s.

In examples 1-5 and comparative examples 1 and 2, a surface activation step using an argon ion beam for 30 seconds (same treatment as IPC already conducted directly on the substrate) was performed on each layer of the antireflection coating except the external SiO_2 layer.

In comparative examples 1 and 2, characteristics (a) and (b) were omitted, i.e., the R_D ratio was lower than 2 and the deposition of the outermost ZrO_2 layer has been carried out without ionic assistance.

In comparative example 3, characteristic (b) was omitted, i.e., the deposition of the outermost ZrO_2 layer has been carried out without ionic assistance, and the sub-layer had a thickness lower than 250 nm.

In comparative example 4, characteristic (a) was omitted, i.e., the R_D ratio was lower than 2, and the sub-layer had a thickness lower than 250 nm.

In comparative example 5, characteristics (a) and (b) were omitted, i.e., the R_D ratio was lower than 2 and the deposition of the outermost ZrO_2 layer has been carried out without ionic assistance, and the sub-layer had a thickness lower than 250 nm.

3. Testing methods

The following test procedures were used to evaluate the optical articles prepared according to the present invention. Several samples for each system were prepared for measurements and the reported data were calculated with the average of the different samples.

Colorimetric measurements (in reflection) of the face coated with the stack of the invention: reflection factor R_v , hue angle h and chroma C^* in the international colorimetric CIE (L^* , a^* , b^*) space were carried out with a Zeiss spectrophotometer, taking into account the

standard illuminant D65, and the standard observer 10° (for h and C*). They are provided for an angle of incidence of 15°.

The critical temperature of the article was measured in the manner indicated in patent application WO 2008/001011. It was measured one week after production of the article, on an ORMA® lens substrate (polymer obtained by polymerization of diethylene glycol bis (allyl carbonate) from Essilor based on CR-39® monomer, refractive index = 1.5), rather than an MR8® lens substrate and with the same hard coat/primer as in the examples.

The thickness of the layers was controlled by means of a quartz microbalance.

Abrasion resistance was determined as disclosed in WO 2012/173596. Specifically, abrasion resistance was measured by means of the sand Bayer test, in accordance with the ASTM F735-81 standard, 1 week after production of the article.

The inventors noticed that the Bayer value of the article is decreasing after it has been manufactured. It is preferable to measure the value after stabilization, e.g., at least 1 week after it has been manufactured. In this application, the Bayer values for the examples have been measured 1 week after the articles have been manufactured.

The adhesion properties of the whole of the interference coating to the substrate were verified on the convex face of the lens by means of the test commonly referred to in French as the “*nx10 coups*” test (i.e. the “n×10 blows” test) described in international patent applications WO 2010/109154 and WO 99/49097. The test is performed in accordance with ISTM 02-011. Briefly, a sample to be tested is placed in a clamp and covered with a selvty cloth impregnated with isopropyl alcohol. An eraser positioned on a holder moving in translation is put in contact with the cloth. The eraser is pressed down (force = 60 Newtons) on the selvty cloth placed in contact with the lens. The test consists in the determination, for each sample, of the number of cycles required to cause a defect to appear in the antireflection coating. Therefore, the higher the value obtained in the n×10 blows test (average on 10 or 20 samples), the better the adhesion of the interference coating to the substrate. An article successfully passed the test if there is no defect after 9 cycles.

4. Results

The structural characteristics and the optical, mechanical and thermo-mechanical performances of the ophthalmic lenses obtained in the examples are detailed hereunder. The sub-layer is gray-colored. The total thickness mentioned is the thickness of the stack comprising the antireflection coating and the following additional layers: sub-layer, optical impedance layers.

Example 1	
Substrate + primer/hard coat	
SiO ₂ (b)	29 nm
ZrO ₂ (a, b)	5 nm
SiO ₂ (a)	350 nm
ZrO ₂ (a, b)	20 nm
SiO ₂ (a)	21 nm
ZrO ₂ (a, b, c)	88 nm
SnO ₂ (a, c)	6.5 nm
SiO ₂	78 nm
Top coat	
R _D	0.83
R _T	0.86
Sand Bayer	9.5
T _c	75°C
nx10 blows test	10/10 Pass
R _v	1.1-2.9 %
Total thickness	597.5 nm

Example 2	
Substrate + primer/hard coat	
SiO ₂ (b)	29 nm
ZrO ₂ (a, b)	5 nm
SiO ₂ (a)	350 nm
ZrO ₂ (a, b)	11 nm
SiO ₂ (a)	34 nm
ZrO ₂ (a, b, c)	30 nm
SnO ₂ (a, c)	6.5 nm
SiO ₂	132 nm
Top coat	
R _D	3.62
R _T	3.49
Sand Bayer	9.9
T _c	70°C
nx10 blows test	9/10 Pass
R _v	2.2-2.7 %
Total thickness	597.5 nm

Example 3	
Substrate + primer/hard coat	
SiO ₂ (b)	29 nm
ZrO ₂ (a, b)	5 nm
SiO ₂ (a)	350 nm
ZrO ₂ (a, b)	11 nm
SiO ₂ (a)	34 nm
ZrO₂ (a, b)	30 nm
SnO ₂ (a, c)	6.5 nm
SiO ₂	132 nm
Top coat	
R _D	3.62
R _T	3.49
Sand Bayer	8.2
T _c	70°C
nx10 blows test	10/10 Pass
R _v	2.7-2.8%
Total thickness	597.5 nm

Example 4	
Substrate + primer/hard coat	
SiO ₂ (b)	29 nm
ZrO ₂ (a, b)	5 nm
SiO ₂ (a)	350 nm
ZrO ₂ (a, b)	16 nm
SiO ₂ (a)	31 nm
ZrO₂ (a, b)	43 nm
SnO ₂ (a, c)	6.5 nm
SiO ₂	118 nm
Top coat	
R _D	2.38
R _T	2.27
Sand Bayer	8.3
T _c	70°C
nx10 blows test	10/10 Pass
C*	
h (°)	
σh	
R _v	1.9-2.1 %
Total thickness	598.5 nm

Example 5	
Substrate + primer/hard coat	
SiO ₂ (b)	37 nm
ZrO ₂ (a, b)	6.5 nm
SiO ₂ (a)	351 nm
ZrO ₂ (a, b)	25 nm
SiO ₂ (a)	39 nm
ZrO₂ (a, b)	40 nm
SnO ₂ (a, c)	6.5 nm
SiO ₂	98 nm
Top coat	
R _D	2.11
R _T	1.92
Sand Bayer	8.1
T _c	67°C
nx10 blows test	10/10 Pass
C*	12
h (°)	144
σh	6.7
R _v	0.83 %
Total thickness	603 nm

Comparative example 1	
Substrate + primer/hard coat	
SiO ₂ (b)	35 nm
ZrO ₂ (a, b)	5 nm
SiO ₂ (a)	370 nm
ZrO ₂ (a, b)	26 nm
SiO ₂ (a)	12.5 nm
ZrO₂ (a, b)	98.5 nm
SnO ₂ (a, c)	6.5 nm
SiO ₂	81 nm
Top coat	
R_D	0.77
R _T	0.71
Sand Bayer	6.3
T _c	66°C
nx10 blows test	10/10 Pass
C*	12
h (°)	144
σh	6.6
R _v	0.79 %
Total thickness	634.5 nm

Comparative example 2	
Substrate + primer/hard coat	
SiO ₂ (b)	29 nm
ZrO ₂ (a, b)	5 nm
SiO ₂ (a)	350 nm
ZrO ₂ (a, b)	20 nm
SiO ₂ (a)	21 nm
ZrO ₂ (a, b)	88 nm
SnO ₂ (a, c)	6.5 nm
SiO ₂	78 nm
Top coat	
R _D	0.83
R _T	0.86
Sand Bayer	6.8
T _c	65°C
nx10 blows test	10/10 Pass
R _v	0.7 %
Total thickness	597.5 nm

Comparative example 3	
Substrate + primer/hard coat	
SiO ₂ (b)	29 nm
ZrO ₂ (a, b)	5 nm
SiO ₂ (a, b)	150 nm
ZrO ₂ (b)	16 nm
SiO ₂	31 nm
ZrO ₂ (b)	43 nm
SnO ₂ (c)	6.5 nm
SiO ₂	118 nm
Top coat	
R _D	2.38
R _T	2.27
Sand Bayer	6.2
T _c	60°C
nx10 blows test	10/10 Pass
R _v	1.8-2.1 %
Total thickness	398.5 nm

Comparative example 4	
Substrate + primer/hard coat	
SiO ₂ (b)	29 nm
ZrO ₂ (a, b)	5 nm
SiO ₂ (a, b)	150 nm
ZrO ₂ (b)	20 nm
SiO ₂	21 nm
ZrO ₂ (b, c)	88 nm
SnO ₂ (c)	6.5 nm
SiO ₂	78 nm
Top coat	
R _D	0.83
R _T	0.86
Sand Bayer	6.3
T _c	65°C
nx10 blows test	9/10 Pass
R _v	0.7-1.8 %
Total thickness	397.5 nm

Comparative example 5	
Substrate + primer/hard coat	
SiO ₂ (b)	29 nm
ZrO ₂ (a, b)	5 nm
SiO ₂ (a, b)	150 nm
ZrO ₂ (b)	20 nm
SiO ₂	21 nm
ZrO ₂ (b)	88 nm
SnO ₂ (c)	6.5 nm
SiO ₂	78 nm
Top coat	
R _D	0.83
R _T	0.86
Sand Bayer	5.2
T _c	57°C
nx10 blows test	10/10 Pass
R _v	0.85 %
Total thickness	397.5 nm

Example 6	
Substrate + primer/hard coat	
SiO ₂ (b)	35 nm
ZrO ₂ (a, b)	5 nm
SiO ₂ (a)	370 nm
ZrO ₂ (a, b)	26 nm
SiO ₂ (a)	12.5 nm
ZrO ₂ (a, b, c)	98.5 nm
SnO ₂ (a, c)	6.5 nm
SiO ₂	81 nm
Top coat	
R _D	0.77
R _T	0.71
Sand Bayer	10.3
T _c	70°C
nx10 blows test	20/20 Pass
R _v	0.79 %
Total thickness	634.5 nm
C*	12
h (°)	144

(a) Ionic bombardment treatment of the layer surface before depositing the next layer.

(b) Oxygen supply during deposition.

(c) Ion assisted deposition (IAD).

5

In all examples, there are two adjacent high refractive index layers in outermost position in the interferential coating. This means that the thicknesses of these two adjacent layers are taken into account for the calculation of the denominator of the R_D ratio.

Optical articles according to the invention, having a thick sub-layer (> 250 nm) and either a high R_D ratio (examples 3-5), or an outermost high refractive index layer of the interferential coating having a thickness ≥ 15 nm deposited under ionic assistance (example 1), or both (example 2), exhibit better abrasion resistance and better temperature resistance than comparative articles (compare example 1 with and comparative examples 2, 4, or 5 or example

10

4 with comparative example 3), while keeping a similar level of anti-reflection performance and adhesion. The Bayer values obtained are above 8, which indicates a very high level of abrasion resistance. A comparison of example 1 with comparative example 4 shows the beneficial effect on the abrasion resistance of having a thick sub-layer. A difference of more than 3 points is obtained in the Bayer values, which is highly significant. A comparison of example 4 with comparative example 2 (or comparative example 3 with comparative example 5) shows the beneficial effect on the abrasion resistance of having high R_D ratio. A difference of 1-2 points is obtained in the Bayer values, which is highly significant. Further, a comparison of example 1 with comparative example 2 (or example 2 with example 3) shows the beneficial effect on the abrasion resistance of having an outermost high refractive index layer of the interferential coating having a thickness ≥ 15 nm deposited under ionic assistance. A difference of almost 3 points is obtained in the Bayer values, which is highly significant.

In examples 1-4, the antireflection properties of the coatings were not optimized, but example 5 shows that it is possible to simultaneously obtain good mechanical, thermo-mechanical and optical properties (low reflection and high optical robustness).

CLAIMS

1. An optical article comprising a substrate having at least one main face successively coated with:

- 5 - a monolayer sub-layer having a thickness higher than or equal to 250 nm,
- a multilayer interferential coating comprising a stack of at least one high refractive index layer having a refractive index higher than 1.55 and at least one low refractive index layer having a refractive index of 1.55 or less, wherein:

the optical article has a Bayer value determined in accordance with the ASTM F735-81
10 standard higher than or equal to 7, and

a) the ratio:

$$R_D = \frac{\text{thickness of the outermost low refractive index layer(s) of the int erferential coating}}{\text{thickness of the outermost high refractive index layer(s) of the int erferential coating}}$$

is higher than or equal to 1.5, and/or

b) the interferential coating comprises at least one high refractive index layer having a
15 refractive index higher than 1.55 and a thickness higher than or equal to 15 nm, and the deposition of the high refractive index layer of the interferential coating having a refractive index higher than 1.55 and a thickness higher than or equal to 15 nm that is the furthest from the substrate has been carried out under ionic assistance by bombarding by means of an ion beam said high refractive index layer while it is being formed.

20 2. An optical article according to any one of the preceding claims, wherein the sub-layer has a thickness higher than or equal to 300 nm, preferably higher than or equal to 350 nm.

3. An optical article according to any one of the preceding claims, wherein the sub-layer is a SiO₂-based layer.

4. An optical article according to any one of the preceding claims, wherein the sub-layer is
25 in direct contact with the interferential coating.

5. An optical article according to any one of the preceding claims, wherein the deposition of the sub-layer is conducted in a vacuum chamber under a pressure lower than 1.6x10⁻⁴ mBar.

6. An optical article according to any one of the preceding claims, wherein the deposition of the sub-layer is conducted in a vacuum chamber in which no supplementary gas is supplied
30 during said deposition.

7. An optical article according to any one of the preceding claims, wherein the ratio R_D is higher than or equal to 2, preferably higher than or equal to 2.1.

8. An optical article according to any one of the preceding claims, wherein the optical article has a Bayer value determined in accordance with the ASTM F735-81 standard higher than or
35 equal to 8.

9. An optical article according to any one of the preceding claims, wherein:

a) the ratio R_D is higher than or equal to 1.5, and

b) the deposition of the high refractive index layer of the interferential coating having a refractive index higher than 1.55 and a thickness higher than or equal to 15 nm that is the

furthest from the substrate is carried out under ionic assistance by bombarding by means of an ion beam said high refractive index layer while it is being formed.

10. An optical article according to any one of the preceding claims, wherein the interferential coating is an antireflection coating.

5 11. An optical article according to any one of the preceding claims, wherein the optical article is an ophthalmic lens.

12. A method of manufacturing an optical article according to any one of the preceding claims, comprising:

- providing an optical article comprising a substrate having at least one main face,
- 10 - depositing onto a main surface of the substrate a monolayer sub-layer having an exposed surface and a thickness higher than or equal to 250 nm,
- depositing onto said exposed surface of the sub-layer a multilayer interferential coating comprising at least one high refractive index layer having a refractive index higher than 1.55 and at least one low refractive index layer having a refractive index of 1.55 or less, thereby
- 15 obtaining a coated optical article, having a Bayer value determined in accordance with the ASTM F735-81 standard higher than or equal to 7, and

a) the ratio:

$$R_D = \frac{\text{thickness of the outermost low refractive index layer(s) of the int erferential coating}}{\text{thickness of the outermost high refractive index layer(s) of the int erferential coating}}$$

is higher than or equal to 1.5, and/or

20 b) the deposition of the high refractive index layer of the interferential coating having a refractive index higher than 1.55 and a thickness higher than or equal to 15 nm that is the furthest from the substrate is carried out under ionic assistance by bombarding by means of an ion beam said high refractive index layer while it is being formed.

13. A method according to claim 12, wherein the exposed surface of the sub-layer is
25 submitted to an ionic bombardment treatment prior to depositing said multilayer interferential coating, and wherein the deposition of the sub-layer is conducted in a vacuum chamber in which no supplementary gas is supplied during said deposition.

14. A method according to claim 12 or 13, wherein the exposed surface of at least one layer, preferably each layer except the one that is the furthest from the substrate, of the multilayer
30 interferential coating is submitted to an ionic bombardment treatment prior to depositing the subsequent layer of said multilayer interferential coating.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/078406

A. CLASSIFICATION OF SUBJECT MATTER
INV. G02B1/11
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

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	US 2008/002260 A1 (ARROUY FREDERIC [FR] ET AL) 3 January 2008 (2008-01-03)	1-12, 14
Y	page 14; example 6; table 1 -----	14
X	EP 2 775 341 A1 (HOYA CORP [JP]) 10 September 2014 (2014-09-10)	1-12
Y	page 16; examples 2-4 -----	13, 14
Y	EP 2 122 392 A1 (ESSILOR INT [FR]) 25 November 2009 (2009-11-25) claim 1 paragraph [0090] - paragraph [0091]; claim 42 -----	13

☐

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 February 2020

Date of mailing of the international search report

10/03/2020

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Le Masson, Nicolas

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2019/078406

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: 9(completely); 1-8, 10-14(partially)

An optical article comprising a substrate having at least one main face successively coated with:

- a monolayer sub-layer having a thickness higher than or equal to 250 nm,
- a multilayer interferential coating comprising a stack of at least one high refractive index layer having a refractive index higher than 1.55 and at least one low refractive index layer having a refractive index of 1.55 or less, wherein: the optical article has a Bayer value determined in accordance with the ASTM F735-81 standard higher than or equal to 7, and the ratio RD is higher than or equal to 1.5.

2. claims: 9(completely); 1-8, 10-14(partially)

An optical article comprising a substrate having at least one main face successively coated with:

- a monolayer sub-layer having a thickness higher than or equal to 250 nm,
- a multilayer interferential coating comprising a stack of at least one high refractive index layer having a refractive index higher than 1.55 and at least one low refractive index layer having a refractive index of 1.55 or less, wherein: the optical article has a Bayer value determined in accordance with the ASTM F735-81 standard higher than or equal to 7, and the interferential coating comprises at least one high refractive index layer having a refractive index higher than 1.55 and a thickness higher than or equal to 15 nm, and the deposition of the high refractive index layer of the interferential coating having a refractive index higher than 1.55 and a thickness higher than or equal to 15 nm that is the furthest from the substrate has been carried out under ionic assistance by bombarding by means of an ion beam said high refractive index layer while it is being formed.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/078406

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008002260 A1	03-01-2008	AU 2007264948 A1 BR PI0714043 A2 CA 2655480 A1 CN 101512389 A EP 2033019 A2 JP 2009541808 A KR 20090021188 A US 2008002260 A1 WO 2008000841 A2	03-01-2008 18-12-2012 03-01-2008 19-08-2009 11-03-2009 26-11-2009 27-02-2009 03-01-2008 03-01-2008
EP 2775341 A1	10-09-2014	EP 2775341 A1 EP 3118672 A1 EP 3561580 A1 WO 2013065715 A1	10-09-2014 18-01-2017 30-10-2019 10-05-2013
EP 2122392 A1	25-11-2009	AU 2008223906 A1 CA 2679745 A1 CN 101617248 A EP 2122392 A1 FR 2913116 A1 JP 6022743 B2 JP 6143729 B2 JP 2010519586 A JP 2015035000 A KR 20100014819 A US 2008206470 A1 WO 2008107325 A1	12-09-2008 12-09-2008 30-12-2009 25-11-2009 29-08-2008 09-11-2016 07-06-2017 03-06-2010 19-02-2015 11-02-2010 28-08-2008 12-09-2008