(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
2 July 2009 (02.07.2009)

PCT

(10) International Publication Number
WO 2009/082601 A1

(51) International Patent Classification:
G02B 5/126 (2006.01) *B29D 11/00* (2006.01)
G02B 5/128 (2006.01)

(21) International Application Number: PCT/US2008/085340

(22) International Filing Date: 3 December 2008 (03.12.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/016,224 21 December 2007 (21.12.2007) US

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(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, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, 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,

[Continued on next page]

(54) **Title:** RETROREFLECTIVE ARTCLES IN THE FORM OF GARMENTS, FIBERS AND FILAMENTS

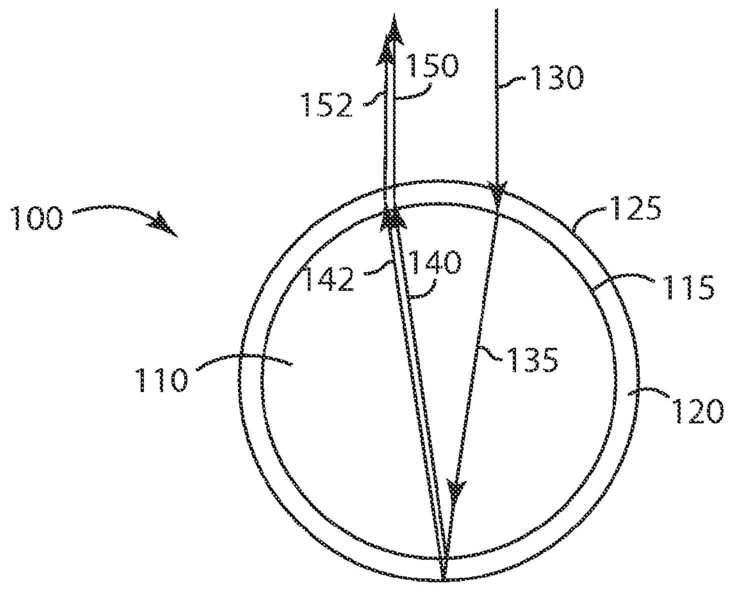

FIG. 1

(57) Abstract: Retroreflective articles are provided in the form of garments, fibers and filaments made with retroreflective elements that each include a solid spherical core (110) with an outer core surface, the outer core surface (115). providing a first interface; a first complete concentric optical interference layer (120) having an inner surface overlying the outer core surface (115) and an outer surface (125), the outer surface of the first complete concentric optical interference layer providing a second interface. In some embodiments, the retroreflective elements each include a second complete concentric optical interference layer having an inner surface overlying the outer surface of the first complete concentric optical interference layer and an outer surface, the outer surface of the second complete concentric optical interference layer providing a third interface. In other embodiments, the retroreflective elements each further include a third complete concentric optical interference layer having an inner surface overlying the outer surface of the second complete concentric optical interference layer and an outer surface, the outer surface of the third complete concentric optical interference layer providing a fourth interface. The garments include a surface having a plurality of the foregoing retroreflective elements disposed on the surface. The fibers include an elongate fibrous body having a plurality of the retroreflective elements adhered to the fibrous body. The retroreflective filaments each include a hollow, transparent, tubular member having a plurality of the retroreflective elements contained within the tubular member.

WO 2009/082601 A1

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

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *with international search report*

RETROREFLECTIVE ARTCLES IN THE FORM OF GARMENTS, FIBERS AND FILAMENTS

The present invention relates to retroreflective articles. More specifically, the invention relates to retroreflective garments, fibers and filament comprising retroreflective elements comprised of a solid spherical core with one or more complete concentric optical interference layers disposed over the core.

Background

"Retroreflectivity" refers to the ability of an article, if engaged by a beam of light, to reflect that light substantially back in the direction of the light source. Beaded retroreflective articles generally include a plurality of transparent spherically shaped beads or retroreflective elements affixed to at least one major surface of a substrate. The retroreflective elements may be unnoticeable when the article is viewed under diffuse lighting conditions. But, features that are unseen in diffuse lighting, sometimes referred to as 'covert' features, are highly reflective when illuminated with a directed beam of light (e.g., from an automobile headlight). Covert features can include any of a variety of designs including a trademark or company logo, for example.

Articles that can be manufactured to have retroreflective properties include fibers, fabrics, materials and garments made from the foregoing. Accessory items and security articles can also be made to include retroreflective properties. Retroreflective garments may be made to include film-like coatings that comprise retroreflective elements embedded in a binder to enhance the visibility of the garment and the individual wearing it, especially at night. With enhanced visibility, retroreflective garments provide a higher level of safety near areas with significant automobile traffic, for example. Construction workers, road maintenance crews, pedestrians, runners and bikers can all benefit from garments providing such improved safety. In addition to traditional safety garments, accessory items can also be provided with retroreflective properties.

In addition to improvements in safety, retroreflective components can improve the decorative appearance of a garment, material or the like. In garments, for example, the retroreflective components can be applied in a decorative pattern using any of a variety of coating techniques.

Summary

It is desirable to improve the reflective features and/or the appearance of certain fibers, filaments and garments by the use of certain retroreflective elements, as further described herein.

In embodiments of the invention, a garment is provided, the garment comprising:

A garment surface having a plurality of retroreflective elements disposed thereon, the retroreflective elements each comprising:

A solid spherical core comprising an outer core surface, the outer core surface providing a first interface;

At least a first complete concentric optical interference layer having an inner surface overlying the outer core surface and an outer surface, the outer surface of the first complete concentric optical interference layer providing a second interface.

In other embodiments, the invention provides a retroreflective fiber comprising:

An elongate fibrous body having a plurality of retroreflective elements adhered thereto, the retroreflective elements each comprising:

A solid spherical core comprising an outer core surface, the outer core surface providing a first interface;

At least a first complete concentric optical interference layer having an inner surface overlying outer core surface and an outer surface, the outer surface of the first complete concentric optical interference layer providing a second interface.

In still other embodiments, the invention provides a retroreflective filament comprising:

A hollow, transparent, tubular member having a plurality of retroreflective elements contained therewithin, the retroreflective elements each comprising:

A solid spherical core comprising an outer core surface, the outer core surface providing a first interface;

At least a first complete concentric optical interference layer having an inner surface overlying outer core surface and an outer surface, the outer surface of the first complete concentric optical interference layer providing a second interface.

In any of the foregoing embodiments, the retroreflective elements may further comprise:

A second complete concentric optical interference layer having an inner surface overlying the outer surface of the first complete concentric optical interference layer and an outer surface, the outer surface of the second complete concentric optical interference layer providing a third interface.

In any of the foregoing embodiments, the retroreflective elements may further comprise:

A third complete concentric optical interference layer having an inner surface overlying the outer surface of the second complete concentric optical interference layer and an outer surface, the outer surface of the third complete concentric optical interference layer providing a fourth interface.

Unless otherwise indicated, the terminology used to describe the embodiments of the invention is to be construed in a manner consistent with the understanding of those skilled in the art. For the sake of clarity, the following terms are to be understood as having the meanings set forth herein:

"Light" refers to electromagnetic radiation having one or more wavelengths in the visible (i.e., from about 380 nm to about 780 nm), ultraviolet (i.e., from about 200 nm to about 380 nm), and/or infrared (i.e., from about 780 nm to about 100 micrometers) regions of the electromagnetic spectrum.

"Refractive index" refers to the index of refraction at a wavelength of 589.3 nm corresponding to the sodium yellow d-line, and a temperature of 20°C, unless otherwise specified. The term “refractive index” and its abbreviation “RI” are used interchangeably herein.

“Retroreflective mode” refers to a particular geometry of illumination and viewing that includes engaging an article with a beam of light and viewing the illuminated article from substantially the same direction, for example within 5 degrees, 4 degrees, 3, degrees, 2 degrees, or 1 degree of the illumination direction. Retroreflective mode can describe the geometry in which a person views an article or the geometry in which an instrument measures the reflectivity of an article.

"Retroreflective brightness" refers to the effectiveness with which an object or ensemble of objects, for example a retroreflective element or an ensemble of elements, or for example an article comprising one or more retroreflective elements, returns incident light back in the direction (or nearly in the direction) from which it came. Retroreflective brightness relates to the intensity of light that is retroreflected from an object, versus the intensity of light that is incident on the object.

“Coefficient of Retroreflection” (Ra) is a standard measure of the retroreflective brightness of an object, and can be expressed in units of candelas per square meter per lux, or $Cd/lux/m^2$, or Cpl. These units and measurement instruments that report the coefficient of retroreflection in such units, weight the retroreflective brightness with the luminosity function. The luminosity function describes the dependence of human eye sensitivity on the wavelength of light and is non-zero for wavelengths between approximately 380 nanometers and 780 nanometers, thus defining the visible region of the electromagnetic spectrum.

“Complete concentric optical interference layer” or “optical interference layer” refers to a translucent or transparent coating surrounding and directly adjacent to essentially the entire surface (i.e., not only a selected portion of the surface, for example only the back surface) of a bead core or surrounding and directly adjacent to the outside surface of another, inner complete concentric optical interference layer, the complete concentric optical interference layer being of essentially uniform thickness.

“Reflector” refers to a specular or diffuse reflective material that is placed in a retroreflective article at or near the focal position behind a retroreflective element in a retroreflective article. The reflective material can be a diffuse light-scattering or metallic material, or one or more layers of transparent material components that creates one or more reflective interfaces.

For clarity, in embodiments where more than one reflector is present at or near the focal position behind a spherical bead core in a retroreflective article, the material in contact with or closest to the outer surface of the bead is designated the “primary reflector.” Additional reflectors farther from the back surface of the bead are designated as “auxiliary reflectors”. A stack of directly adjacent dielectric layers is considered to be a single “reflector” for the purpose of designating primary and auxiliary reflectors. For example, an article comprising a bead having two or more complete concentric optical interference layers with back surface embedded in a pigmented binder has complete concentric optical interference layers as a primary reflector and a pigmented binder as an auxiliary reflector.

“Region” refers to a continuous portion of an article. A region typically has a boundary or general extent that is discernible to a viewer.

Those skilled in the art will more fully appreciate the scope of the present invention upon consideration of the remainder of the disclosure including the Detailed Description, the drawings and the appended claims.

Brief Description Of The Drawings

The various Figures herein are not to scale but are provided as an aid in the description of the embodiments. In describing embodiments of the invention, reference is made to the Figures in which features of the embodiments are indicated with reference numerals, with like reference numerals indicating like features, and wherein:

Figure 1 is a cross-sectional view of an embodiment of a retroreflective element for use in the articles of the invention;

Figure 2 is a cross-sectional view of another embodiment of a retroreflective element for use in the articles of the invention;

Figure 3 is a cross-sectional view of still another embodiment of a retroreflective element for use in the articles of the invention; and

Figure 4 is a flow diagram of an exemplary process for making retroreflective elements useful in the articles of the invention.

Detailed Description

The present invention provides fibers, filaments and garments comprising retroflective elements. Retroreflective elements, as described herein, can be included in fibers, filaments and garments for use in safety clothing including reflective garments and accessory items, for example. The retroreflective elements may also be included in fibers, filaments and garments to provide and/or enhance the decorative appearance thereof. In some embodiments, the retroreflective elements described herein may provide retroreflective color in that they display certain colors (e.g., “covert colors”) when viewed in a retroreflective mode. In some embodiments, the retroreflective elements described herein display enhanced retroreflective brightness with no color change.

Retroreflective brightness can be measured for various angles between the incident and reflected light (the observation angle) but is not limited to a particular range of angles. For some applications, effective retroreflectivity is desired at a return angle of zero degrees (anti-parallel to the incident light). For other applications, effective retroreflectivity is desired over a range of return angles such as from 0.1 degree to 1.5 degrees. Where visible light is used to illuminate an object, retroreflective brightness is typically described using the coefficient of retroreflection (Ra).

Retroreflective elements useful in the articles of the present invention each include a solid spherical core with one or more coated layers applied to the core, the one or more coated layers each forming a complete concentric optical interference layer surrounding the core. The first or innermost optical interference layer covers the outer surface of the spherical core. In some embodiments, a second complete concentric optical interference layer covers and is adjacent to the outer surface of the first or innermost complete concentric optical interference layer. In other embodiments, a third complete concentric optical interference layer covers and is adjacent to the outer surface of the second complete concentric optical interference layer. While the complete concentric optical interference layers typically cover the entire surface of the spherical core, optical interference layers may include small pinholes or small chip defects that penetrate the layer without impairing the optical properties of the retroreflective element.

In some embodiments, retroreflective elements may comprise additional complete concentric optical interference layers with each successive optical layer covering a previously deposited layer (e.g., a fourth concentric optical interference layer covers the third concentric optical interference layer; a fifth layer covers the fourth layer, etc.). By "concentric," what is meant is that each such optical interference layer coated over a given spherical core is a spherically shaped shell that shares its center with the center of the core.

It is within the scope of the present invention to include a variety of retroreflective elements as components of retroreflective articles. Some of the retroreflective elements incorporated into such articles will comprise the retroreflective elements having one or more complete concentric optical interference layers, as described herein. Other retroreflective elements may be included in such articles such as retroreflective elements having no optical interference layers. In some embodiments, articles comprising a mix of retroreflective elements having one or more complete concentric optical interference layers wherein the construction, thickness and/or materials are different from one retroreflective element to another or from one group of retroreflective elements to another group. For example, the first or innermost optical interference layer may vary in thickness from one retroreflective element to another by more than twenty five percent. In some embodiments, the retroreflective elements may include one concentric optical interference layer, in some embodiments two optical interferences layers, in some embodiments three optical interference layers, in some embodiments more than three optical interference layers and in some embodiments combinations of retroreflective elements having one, two, three or more optical interference layers. In some embodiments, the forgoing retroreflective elements may be combined in an article with retroreflective elements having no optical interference layers and/or with auxiliary reflectors and the like.

Complete concentric optical interference layers are applied to a spherical core to provide a retroreflective element capable of providing enhanced retroreflective brightness. When placed in an article, the retroreflective elements provide a retroreflective brightness that is greater than retroreflective brightness of identical articles comprising other forms of retroreflective elements or the like. In some embodiments, the color of the retroreflected light is the same or similar to that of the incident light. For example, the retroreflected light exhibits little or no color change from white incident light. In still other embodiments, the optical interference layers are applied to the core so that, when placed in an article, the retroreflective elements provide a retroreflected color. In some embodiments, the retroreflective elements are arranged in an article to provide a discernable pattern on the surface of the article or substrate wherein the pattern is not visible under diffuse lighting but becomes visible when viewed in the retroreflective mode. In some embodiments, the retroreflective elements may also be used to enhance the color of an article where, for example, the retroreflective elements provide retroreflected color that matches and possibly intensifies the color of the article as it normally appears in diffuse lighting.

When placed within an article, a retroreflective element having a complete concentric optical interference layer on a solid spherical core creates two light-reflective interfaces at the back of a retroreflective element. The thickness of the coating provides an optical thickness that results in a constructive or destructive interference condition for one or more wavelengths that fall within the wavelength range corresponding to visible light (approximately 380 nanometers to approximately 780 nanometers). "Optical thickness" refers to the physical thickness of a coating multiplied by its index of refraction. Such constructive or destructive interference conditions are periodic with increasing optical thickness for the optical interference coating, up to the coherence length of the illumination. With increasing coating thicknesses, constructive interference for a given wavelength will occur first when the optical path through the coating and back again, combined with any phase inversions caused by the sign of refractive index change at either or both interfaces, leads to a phase difference of 2π radians for the two components of light that reflect from the two interfaces. With further increase in thickness, the same constructive interference condition will be achieved again when the phase difference is equal to 4π radians. Similar behavior will occur for further increases in thickness.

The thickness period that separates successive occurrences of the constructive interference condition (that is, the increment in thickness for the coating which leads to repetition of nominally the same interference condition for a given wavelength (*in vacuo*) of light that is reflected from the two surfaces of the coating) is given by one half of the wavelength *in vacuo* divided by the index of refraction of the coating. Each occurrence of a given interference condition with increasing coating thickness from zero nanometers can be assigned a period number (e.g., n = 1,2,3…). When retroreflective elements comprising an optical interference layer are illuminated with broadband light (light comprising many wavelengths, for example white light), a range of interference effects characterize the retroreflective behavior for the different wavelengths. These optical phenomena become more complex when more than one optical interference layer is applied to the spherical core.

It has been found that the retroreflected color and brightness of retroreflective articles comprising retroreflective elements having two or more complete concentric optical interference layers exhibit periodic behaviors and interdependencies with increasing coating layer thicknesses. Retroreflective elements made with multiple complete concentric optical interference layers, or articles comprising such retroreflective elements, exhibit oscillations of magnitude (e.g., peaks and valleys) in the coefficient of retroreflection (Ra) as one or more of the interference layers increases in thickness. In some embodiments, high coefficient of retroreflection is achieved for white light illumination without the generation of color for the retroreflected light. In other embodiments, high coefficient of retroreflection is generated for white light illumination accompanied by the generation of retroreflected light of color. In some embodiments, the articles can include regions of retroreflective elements that provide any of a variety of displays or designs having a distinctive appearance and/or color under diffuse lighting, as well as a retroreflected color or lack of retroreflected color with a high coefficient of retroreflection under white light illumination when viewed in a retroreflective viewing mode.

The coherence length for non-laser light (for example light produced by an incandescent lamp, a gas discharge lamp, or a light-emitting diode) limits the values of n (and hence the total coating thickness) for which strong interference effects are observed. For non-laser light, interference effects tend to vanish for thicknesses corresponding to n = 10 or more, and are greatly diminished at about half of that thickness. For retroreflective elements partially embedded in adhesive with an index of refraction of approximately 1.55, illuminated on their air-exposed side, and comprising a single complete concentric optical interference coating with refractive index of about 2.4, five peaks in photopically weighted retroreflective brightness are established by interference coatings of thicknesses ranging from zero nanometers up to approximately 600 nanometers. These physical thickness values correspond to an optical thickness of up to about 1500 nm. For articles comprising retroreflective elements with a single complete concentric optical interference coating having a refractive index of about 1.4, five peaks in photopically weighted retroreflective brightness are established by interference coatings of thicknesses ranging from zero nanometers up to approximately 1200 nanometers, corresponding to an optical thickness of less than 1700 nm. In some embodiments, a visible light interference layer comprises a coating with an optical thickness less than about 1500 nm.

The retroreflective elements may be included in the construction of any of articles such as the garments described herein. Within the construction of such articles, retroreflective elements having one or more complete concentric optical interference layers may be combined with other reflective and/or retroflective materials including for example uncoated retroreflective glass beads having a high index of refraction. Retroreflective articles according to the present invention may optionally include one or more auxiliary reflectors wherein the retroreflective elements and the auxiliary reflector act collectively to return fractions of incident light back in the direction of the source. In some embodiments, a suitable auxiliary reflector is a diffuse light-scattering pigmented binder into which retroreflective elements are partially embedded. A pigmented binder is an auxiliary reflector when the pigment type and loading are selected to create a diffuse-scattering material (for example, greater than 75% diffuse reflection), as opposed to when the selection of pigment and loading are done simply to color a the binder. Examples of pigments that lead to diffuse scattering include titanium dioxide particles and calcium carbonate particles.

In other embodiments, a suitable auxiliary reflector comprises a specular-pigmented binder into which retroreflective elements are partially embedded. Examples of specular pigments include mica flakes, titanated mica flakes, pearlescent pigments, and nacreous pigments.

In still other embodiments, a suitable auxiliary reflector is a metal thin film that is selectively placed behind the retroreflective element in a retroreflective article.

In still another embodiment, a suitable auxiliary reflector is a dielectric stack of thin films selectively placed behind the retroreflective element in a retroreflective article.

In the case of a retroreflective article wherein the index of refraction of the retroreflective element is between 1.5 and 2.1 and the front surface of the retroreflective element is exposed to air, auxiliary reflectors can be placed adjacent to the back side of the retroreflective elements. In the case of a retroreflective article wherein the retroreflective element is enclosed on its front surface with a transparent material that contacts its front surface or is covered on its front surface by water when in use, auxiliary reflectors may be spaced behind the back surface of the retroreflective elements.

In some embodiments, the present invention provides retroreflective articles for which the need for auxiliary reflectors is optional. Consequently, use of the retroreflective elements having one or more complete concentric optical interference layers can provide enhanced retroreflective brightness as well as reduced manufacturing costs as compared with the cost of manufacturing similar articles that require auxiliary reflectors or alternative primary reflectors. Moreover, the elimination of alternative or auxiliary reflectors can improve the ambient-lit appearance and durability of retroreflective articles made with retroreflective elements having one or more complete concentric optical interference layers.

Retroreflective articles without auxiliary reflectors typically include a plurality of retroreflective elements partially embedded in a transparent (colored or non-colored), non-light-scattering, non-reflective binder (for example a clear, colorless, polymeric binder), and wherein the focal position for light incident on the retroreflective elements is within the binder or at the interface between the retroreflective element and the binder. In some constructions, retroreflective elements include spherical cores in the form of microspheres having an index of refraction of about 1.9. The retroreflective elements are partially embedded in a clear, colorless binder and their front surfaces are exposed to air, providing focal positions near the interface between the back side of the retroreflective elements and the binder. It has been noted that one or more complete concentric optical interference layers can increase the coefficient of retroreflection (Ra).

Articles comprising solid microspheres with an index of refraction of about 1.9 but without concentric optical interference layers, embedded in a clear acrylate adhesive, typically exhibit an Ra of approximately 8 Cd/lux/m^2 at – 4 degrees entrance angle and 0.2 degrees observation angle. The application of a single complete concentric optical interference layer of low index of refraction (for example 1.4) or high index of refraction (e.g., 2.2) to the microspheres increases the Ra to as high as 18 Cd/lux/m^2 and as high as 30 Cd/lux/m^2, respectively. The use of two complete concentric optical interference layers over the microsphere core, when placed in an article as described above, provide an increase in the Ra to greater than about 50 Cd/lux/m^2 and as high as about 59 Cd/lux/m^2. When articles have been made comprising microspheres having three complete concentric optical interference layers, the Ra has increased to greater than 100 Cd/lux/m^2 and to as high as 113 Cd/lux/m^2. Thus, the retroreflective elements of the invention and articles made with such retroreflective elements exhibit useful levels of retroreflection in the absence of auxiliary reflectors.

Retroreflective elements having complete concentric optical interference layers are incorporated into any of a variety of articles such as fibers, filaments, garments and the like. The use of such retroreflective elements in garments serves a safety function by enhancing the reflectivity of the article and the visibility of the wearer of the garment. In some embodiments, the retroreflective elements provide a decorative function in that they are placed in a garment or the like for the purpose of providing a decorative design. In some embodiments, the retroreflective elements provide both decorative and safety features.

Referring to the drawings, Figure 1 illustrates, in cross-section, a first embodiment of a retroreflective element 100 useful in the present invention. The retroreflective element 100 includes a transparent, substantially spherical, solid core 110 having an outer surface 115 that provides a first interface. A first concentric optical interference layer 120 includes an inner surface that overlays the surface 115 of the core 110. Concentric optical interference layer 120 forms a substantially uniform and complete layer over the entire surface 115 of spherical core 110, and the outer surface 125 of layer 120 provides a second interface. Minor imperfections in the layer 120 (e.g., pinholes and/or minor thickness fluctuations) may be tolerated provided such imperfections are not of sufficient size or amount to render the element not retroreflective.

Light is reflected at interfaces between materials having differing refractive indices (e.g., having a difference in refractive indices of at least 0.1). Differences in the refractive indices of the core 110 and the substantially transparent first optical interference layer 120 gives rise to a first reflection at first interface 115. Differences in the refractive indices of the first optical interference layer 120 and any background medium (e.g., vacuum, gas, liquid, solid) contacting first optical interference layer 120 gives rise to a second reflection at second interface 125. Selection of the thickness and the refractive index of the first optical interference layer 120 can result in the two reflections optically interfering with each other to provide a retroreflected color (e.g., a covert color) different from what would otherwise be observed in the absence of such interference. Adjustments to the thickness and refractive index of the first optical interference layer 120 can avoid the destructive interference of the two reflections, providing constructive interference so that a retroreflected light is not of a different color. Moreover, adjusting the thickness of the optical interference layer and the refractive index thereof provides a constructive interference of the reflections from the outer surface 125 of first optical interference layer 120 and surface 115 of solid core 110, resulting in a brighter reflected intensity and enhanced visibility of the article associated with the retroreflective element.

In some embodiments, retroreflected color may be desired to provide retroreflected light in a color that enhances the design and/or the overall visibility of an article that comprises a plurality of retroreflective elements like the element 100.

Incident beam of light, represented by line 130 in Figure 1, is directed at retroreflective element 100. Light is largely transmitted through first optical interference layer 120, and enters core 110. A portion of the incident light 130 may be reflected at second interface 125 or at first interface 115. Retroreflection may result from the portion of light 130 which enters core 110 and is at least partially focused by refraction onto the back of core 110. As refracted light 135 encounters first interface 115 at the back of core 110, some of refracted light 135 is reflected back as reflected light 140 which ultimately emerges from the retroreflective element 100 as retroreflected light 150, observable in a direction that is substantially anti-parallel to incident light 130. Similarly, another portion of the focused light passes through first optical interference layer 120 and is reflected back at second interface 125 as reflected light 142. The exterior surface 125 of the retroreflective element 100 forms second interface which is directly exposed to the medium in which the retroreflective element 100 is disposed (e.g., gas, liquid, solid, or vacuum). Reflected light 142 emerges from the element as retroreflected light 152, observable in a direction that is substantially anti-parallel to incident light 130. Remaining light that is not reflected passes entirely through the retroreflective element 100. Destructive Interference between reflected light 140 and reflected light 142, and in turn retroreflected light 150 and retroreflected light 152, may give rise to a change in the observed color of the retroreflective element when viewed in a retroreflective mode. For example, destructive interference or subtraction of wavelengths from the center of the spectrum of incident white light results in retroreflected light with a red-violet hue (i.e., retrochromism).

Slightly thicker optical interference layers subtract longer wavelengths, resulting in, for example, green or blue-green hues. In some embodiments, the thickness of the optical interference layer is optimized to subtract longer wavelengths and to provide retroreflected light that enhances the color of a substrate or that reveals a covert design or pattern. In some embodiments, the thickness of the optical interference layer is selected so that the color of the retroreflected light is the same as the color of the garment.

Reflection of light at an interface between materials is dependent on the difference in the refractive indexes of the two materials. Materials for the cores and the optical interference layers may be selected from any of a variety of materials, as described herein. The selected materials may comprise either high or low refractive index materials, as long as sufficient differences in refractive indexes are maintained between that of core 110 and first optical interference layer 120, and between the first optical interference layer 120 and the medium in which the retrochromic bead is intended to be used. Each of these differences should be at least about 0.1. In some embodiments, the difference is at least about 0.2. In other embodiments, the difference is at least about 0.3, and in still other embodiments, the difference is at least about 0.5. The refractive index of first optical interference layer 120 may be either greater than or less than the refractive index of core 110. Generally, the choice of refractive index, and the corresponding choice of materials used, will be influenced by the choice of the medium that contacts the exterior surface 125 in the region where reflection is intended to occur.

The refractive indices of core 110, first concentric optical interference layer 120, and the medium in which the retroreflective element 100 is intended to be used are selected to control the focal power of the retroreflective element and the strength of reflections from interfaces 115 and 125. The brightness of retroreflected color can be maximized if balanced index of refraction differences are as large as possible.

To obtain a high level of retroreflectivity, the core 110 may be selected to have an index of refraction suitable for use where the entry medium (the medium adjacent the front surfaces of the retroreflective elements) is air. In some embodiments, when the entry medium is air, the index of refraction of the core 110 is between about 1.5 and 2.1. In some embodiments, the index of refraction of the core 110 is between about 1.8 and 1.95. In still other embodiments, the index of refraction of the core 110 is between about 1.9 and 1.94. In some embodiments, the retroreflective elements 100 are used in articles having high retroreflectivity in an exposed-lens construction under wet conditions. In such embodiments, the core 110 may be selected to have an index of refraction typically between about 2.0 and about 2.6. In other embodiments, the index of refraction of the core is between 2.3 and 2.6. In still other embodiments, the index of refraction of the core is between 2.4 and 2.55. In some embodiments, the binder may include an auxiliary reflector in the form of one or more pigments such as a diffuse-scattering or specular pigment that enhances the retroreflectivity of the article.

Upon selection of a suitable core 110, the core may then be first coated with a refractive index material to form first complete concentric optical interference layer 120. In some embodiments, as described herein, first layer 120 is first formed over to concentrically coat core 110 and is subsequently further coated with other materials of different refractive indexes to provide second, third, or more complete concentric optical interference layers, as described further herein. Retroreflective element 100 may be used as a component in a reflective article by affixing the retroreflective element to a substrate or backing by, for example, embedding the retroreflective element in a polymeric binder or adhesive to provide a beaded substrate which can be affixed to another article such as a garment, for example. In some embodiments, an auxiliary reflector may be included in the construction of the article.

In some embodiments, the solid spherical cores have a diameter within the range from about 25 microns to about 500 microns In some embodiments, the cores can have a diameter greater than about 500 micrometers. In still other embodiments, the core diameter may be greater than 1 millimeter.

Light that is reflected at an interface may be reflected with or without a phase inversion. Light that passes through a medium having a higher index of refraction and encounters an interface with a medium having a lower index of refraction will be reflected without phase inversion. In contrast, light that passes through a medium having a lower index of refraction and encounters an interface with a medium having a higher index of refraction will be reflected with phase inversion. Consequently, the thickness of the optical interference layer 120 is selected by due consideration of the refractive index of core 110, the refractive index of the first concentric optical interference layer 120, and the refractive index of the medium in which the bead 100 is disposed. In any case, the thickness should be selected such that the reflected light from exterior surface 125 is π radians (i.e., 180°) out of phase with light of the same wavelength reflected from interface 115.

In other embodiments, retroreflective elements comprising more than one complete concentric optical interference layer are provided. Referring to Figure 2, another embodiment of a retroreflective element 200 is shown and will now be described. The retroreflective element 200 includes a transparent substantially spherical solid core 210 having thereon a first optical interference layer 212. Core 210 contacts first optical interference layer 212 at first interface 216 which coincides with the outer surface of the core 210. Second concentric optical interference layer 222 overlies the first concentric optical interference layer 212 at second interface 226. Layer 222 has an exterior surface 224 that provides the outermost surface of the retroreflective element 200. The first and second optical interference layers 212 and 222 are substantially uniform in thickness and concentric with the spherical core 210.

Light is reflected at the interfaces between the materials used in the retroreflective element 200, provided that the different materials have sufficiently different refractive indexes (e.g., having a difference in refractive indexes of at least about 0.1). A sufficient difference in the refractive indexes of the core 210 and first optical interference layer 212 gives rise to a first reflection at first interface 216. Similarly, a sufficient difference in the refractive indexes of first optical interference layer 212 and second optical interference layer 222 gives rise to a second reflection at second interface 226. A sufficient difference in the refractive indexes of second optical interference layer 222 and any background medium (e.g., vacuum, gas, liquid, solid) contacting the layer 222 gives rise to a third reflection at third interface 224 of the retroreflective element 200. Selection of the thicknesses and refractive indexes of the optical interference layers 212 and 222 provide a retroreflected light.

When a plurality of retroreflective elements 200 are combined in an article, the article displays enhanced retroreflective brightness. In some embodiments, under white light illumination, the retroreflected light may destructively interfere with each other for certain wavelengths, resulting in retroreflected color that is of a different color from that which would otherwise be observed in the absence of such interference.

Referring again to Figure 2, an incident beam of light is represented by line 230 which is shown as directed at retroreflective element 200. Light 230 is largely transmitted through second optical interference layer 222 and first optical interference layer 212 before it enters core 210. However, portions of the incident light 230 may be reflected at at third interface 224, at second interface 226 or at first interface 216. The portion of the light 230 that enters core 210, is focused by refraction onto the opposite side of the core 210. The refracted light 235 encounters first interface 216 at the back of core 210, some of refracted light 235 is reflected back as reflected light 240 towards the front of the retroreflective element 200 where it emerges from the retroreflective element as retroreflected light 250 in a direction that is substantially anti-parallel to incident light 230. Another portion of the focused light passes through optical interference layer 212 and is reflected back at second interface 226 as reflected light 242. Reflected light 242 emerges from the retroreflective element as retroreflected light 252 which travels in a direction that is substantially anti-parallel to incident light 230. Still another portion of the focused light passes through first and second optical interference layers 212 and 222 and is reflected back at third interface 224 as reflected light 244 which emerges from the retroreflective element 200 as retroreflected light 254. The exterior surface of optical interference layer 224 forms a third interface with the medium in which the retroreflective element 200 is disposed (e.g., gas, liquid, solid, or vacuum). A portion of incident light is not reflected but passes entirely through the retroreflective element 200.

Interference between reflected light 240, 242, 244 and in turn retroreflected light 250, 252, 254 may give rise to a change in color of the retroreflected light, with respect to the incident light (for example incident white light). For example, subtraction of wavelengths from the center of the spectrum of incident white light results in retroreflected light with a red-violet hue (i.e., retrochromism). Slightly thicker optical interference layers subtract longer wavelengths, resulting in, for example, green or blue-green hues. When incorporated in an article, a plurality of retroreflective elements 200 can provide retroreflective color that enhance the appearance of the article by providing a covert color, design, message or the like. A retroreflective color effect can be obtained by manufacturing the retroreflective element 200 with optical interference layers 212 and 222 of different materials and by selecting the thicknesses and refractive indexes of those materials so that the aforementioned retroreflected light 250, 252, 254 destructively interferes with each other. As a result, the retroreflective element 200, when viewed in a retroreflective mode, provides retroreflected light of a different color from that which would otherwise be observed in the of absence destructive interference.

In other embodiments, the proper selection of materials, thicknesses and refractive indexes for the optical interference layers 212, 222, a retroreflective element 200 can provide retroreflected light 250, 252, 254 that is brighter (e.g., has a higher coefficient of retroreflection (Ra)) than retroreflected light from uncoated retroreflective elements, for example. When incorporated in an article, a plurality of retroreflective elements 200 provide retroreflective properties that enhance the visibility of the article. Constructive interference between reflected light 240, 242, 244 and in turn retroreflected light 250, 252, 254 gives rise to unexpected increases in the brightness or intensity of the retroreflected light. In some embodiments, coating thicknesses for the two optical interference layers can be optimized to provide maximum retroreflectivity when the layers are alternating layers of silica/titania and the core comprises a glass bead having a diameter of measuring from about 30μm to about 90μm and index of refraction of approximately 1.93. In such embodiments, a first optical interference layer 212 of silica having a thickness between about 95 nm and 120 nm, and typically about 110 nm, a second optical interference layer 222 of titania having a thickness between about 45 nm and 80 nm and typically about 60 nm, has provided significantly enhanced coefficient of retroreflection (Ra) when the retroreflective elements are partially embedded as a monolayer in acrylate adhesive.

Reflection at an interface between materials is dependent on the difference in the refractive indexes of the two materials. Materials for the cores and the optical interference layers may be selected from any of a variety of materials, as described herein. The selected materials may comprise either high or low refractive index materials, as long as a sufficient difference in the refractive indexes is maintained between adjacent materials (e.g., core/layer 212; layer 212/layer 222) and as long as the core provides the desired refraction. The difference in refractive indexes of core 210 and first optical interference layer 212, and the difference in refractive indexes of first optical interference layer 212 and second optical interference layer 222, and the difference between the refractive indexes of second optical interference layer 222 and the medium against which the back side of retroreflective element 200 is intended to be placed should each be at least about 0.1. In some embodiments, each of the differences between the adjacent layers is at least about 0.2. In other embodiments, the differences are at least about 0.3, and in still other embodiments, the differences are at least about 0.5. The refractive index of optical interference layer 212 may be either greater than or less than the refractive index of core 210. In some embodiments, the choice of refractive index, and the corresponding choice of materials used, will be determined by the choice of the medium that contacts the exterior surface of the retroreflective element 200 to form third interface 224 where reflection is intended to occur.

As described above, for completely concentrically coated retroreflective elements with a front surface surrounded by air and a rear surface surrounded by (e.g., embedded in) a medium having a refractive index of about 1.55, such as a polymer binder, and illuminated with white light, the photopically weighted net intensity of reflected light, to the extent that it is determined by the sequence of transmission and reflection events for exactly antiparallel rays of retroreflected light as they enter and leave the retroreflective element, can vary dramatically with coating thickness or thicknesses, for a given desirable set of coating materials and refractive index values. The photopically weighted net intensity of reflected light produced by the three interfaces established by two coating layers (for example, of amorphous silica, followed by amorphous titania, on a 1.93 refractive index bead core) can vary by a factor of at least four. For some choices of coatings and thicknesses, the photopically weighted net intensity of reflected light can be significantly reduced versus a retroreflective element in the form of an uncoated bead.

In other embodiments, retroreflective elements comprising more than two optical interference layers may be provided. Referring to Figure 3, another embodiment of a retroreflective element in the form of a retroreflective element 300 is shown and will now be described. The retroreflective element 300 includes a transparent substantially spherical solid core 310 having thereon a first optical interference layer 312. Core 310 contacts first optical interference layer 312 at first interface 316. Second concentric optical interference layer 322 overlies the first concentric optical interference layer 312. Layer 322 has an interior surface that contacts the exterior or outermost surface 326 of first layer 312, forming a second interface. The retroreflective element 300 includes a third optical interference layer 327 which contacts the outermost surface 324 of the second optical interference layer 322 to provide a third interface. The third optical interference layer 327 includes an exterior surface 328 which forms the outermost surface of the retroreflective element 300 and provides a fourth interface. The first, second and third optical interference layers 312, 322 and 327 are substantially uniform in thickness and concentric with the spherical core 310.

Light is reflected at the interfaces between the materials used in the retroreflective element 300, provided that the different materials have sufficiently different refractive indexes (e.g., having a difference in refractive indexes of at least about 0.1). A sufficient difference in the refractive indexes of the core 310 and first optical interference layer 312 gives rise to a first reflection at first interface 316. Similarly, a sufficient difference in the refractive indexes of first optical interference layer 312 and second optical interference layer 322 gives rise to a second reflection at second interface 326. A sufficient difference in the refractive indexes of second optical interference layer 322 and third optical interference layer 327 gives rise to a third reflection at third interface 324. A sufficient difference in the refractive indexes of third optical interference layer 327 and any background medium (e.g., vacuum, gas, liquid, solid) contacting third optical interference layer 327 gives rise to a fourth reflection at fourth interface 328 of the retroreflective element 300. Selection of the thicknesses and refractive indexes of the optical interference layers 312, 322 and 327 the four reflections provide a retroreflected light that enhances the visibility of an article that includes the retroreflective element 300 as a part thereof. In some embodiments, under white light illumination, the four reflections may destructively interfere with each other for certain wavelengths, resulting in retrochromism wherein the retroreflected light is of a different color from that which would otherwise be observed in the absence of such interference.

Referring again to Figure 3, an incident beam of light 330 is shown as being directed at retroreflective element 300. Light 330 is shown as being largely transmitted through third optical interference layer 327, second optical interference layer 322 and first optical interference layer 312 before it enters core 310. However, portions of the incident light 330 may be reflected at fourth interface 328, at third interface 324, at second interface 326 or at first interface 316. The portion of the light 330 that enters core 310, is focused by refraction onto the opposite side of the core 310. The refracted light 335 encounters first interface 316 at the back of core 310, some of refracted light 335 is reflected back as reflected light 340 towards the front of the retroreflective element 300 where it emerges from the retroreflective element as retroreflected light 350 in a direction that is substantially anti-parallel to incident light 330. Another portion of the focused light passes through optical interference layer 312 and is reflected back at second interface 326 as reflected light 342. Reflected light 342 emerges from the retroreflective element as retroreflected light 352 which travels in a direction that is substantially anti-parallel to incident light 330. Still another portion of the focused light passes through first and second optical interference layers 312 and 322 and is reflected back at third interface 324 as reflected light 344 which emerges from the retroreflective element 300 as retroreflected light 354. Still another portion of the focused light passes through first, second and third optical interference layers 312, 322 and 327 and is reflected back at fourth interface 328 as reflected light 346 which emerges from the retroreflective element 300 as retroreflected light 356. The exterior surface of optical interference layer 327 forms a fourth interface 328 with the medium in which the retroreflective element 300 is disposed (e.g., gas, liquid, solid, or vacuum). A portion of incident light is not reflected but passes entirely through the retroreflective element 300.

Interference between reflected light 340, 342, 344, 346 and in turn retroreflected light 350, 352, 354, 356 may give rise to a change in color of the retroreflected light, with respect to the incident light (for example incident white light). For example, subtraction of wavelengths from the center of the spectrum of incident white light results in retroreflected light with a red-violet hue (i.e., retrochromism). Slightly thicker optical interference layers subtract longer wavelengths, resulting in, for example, green or blue-green hues. When incorporated in an article, a plurality of retroreflective elements 300 can provide retrochromic properties that enhance the appearance of the article by providing a covert color, design, message or the like. A retrochromic effect can be obtained by manufacturing the retroreflective element 300 with optical interference layers 312, 322 and 327 of different materials and by selecting the thicknesses and refractive indexes of those materials so that the aforementioned retroreflected light 350, 352, 354, 356 destructively interfere with each other. As a result, the retroreflective element 300, when viewed in a retroreflective mode, provides retroreflected light of a different color from that which would otherwise be observed in the absence of destructive interference.

In other embodiments, the proper selection of materials, thicknesses and refractive indexes for the optical interference layers 312, 322, 327, retroreflective element 300 can provide retroreflected light 350, 352, 354, 356 that is brighter (e.g., has a higher coefficient of retroreflection (Ra)) than retroreflected light from uncoated retroreflective elements, for example. When incorporated in an article, a plurality of retroreflective elements 300 provide retroreflective properties that enhance the visibility of the article. Constructive interference between reflected light 340, 342, 344, 346 and in turn retroreflected light 350, 352, 354, 356 gives rise to unexpected increases in the brightness or intensity of the retroreflected light. In some embodiments, coating thicknesses for the three optical interference layers can be optimized to provide maximum retroreflectivity when the layers are alternating layers of silica/titania/silica and the core comprises a solid glass bead having a diameter of measuring from about 30μm to about 90μm and index of refraction of approximately 1.93. In such embodiments, a first optical interference layer 312 of silica having a thickness between about 95 nm and 120 nm, and typically about 110 nm, a second optical interference layer 322 of titania having a thickness between about 45 nm and 80 nm and typically about 60 nm, and a third optical interference layer 327 of silica having a thickness between about 70 nm and 115 nm, and typically about 100 nm, has provided significantly enhanced coefficient of retroreflection (Ra) when the retroreflective elements are partially embedded as a monolayer in acrylate adhesive.

Reflection at an interface between materials is dependent on the difference in the refractive indexes of the two materials. Materials for the cores and the optical interference layers may be selected from any of a variety of materials, as described herein. The selected materials may comprise either high or low refractive index materials, as long as a sufficient difference in the refractive indexes is maintained between adjacent materials (e.g., core 310/layer 312; layer 312/layer 322; layer 322/layer 327) and as long as the core provides the desired refraction. The difference in refractive indexes of core 310 and first optical interference layer 312, and the difference in refractive indexes of first optical interference layer 312 and second optical interference layer 322, and the difference between the refractive indexes of second optical interference layer 322 and third optical interference layer 327, and the difference between the refractive indexes of third optical interference layer 327 and the medium against which the back side of retroreflective element 300 is intended to be placed should each be at least about 0.1. In some embodiments, each of the differences between the adjacent layers is at least about 0.2. In other embodiments, the differences are at least about 0.3, and in still other embodiments, the differences are at least about 0.5. The refractive index of optical interference layer 312 may be either greater than or less than the refractive index of core 310. In some embodiments, the choice of refractive index, and the corresponding choice of materials used, will be determined by the choice of the medium that contacts the exterior surface of the retroreflective element 300 to form third interface 324 where reflection is intended to occur.

As described above, for completely concentrically coated retroreflective elements with a front surface surrounded by air and a rear surface surrounded by (e.g., embedded in) a medium having a refractive index of about 1.55, such as a polymer binder, and illuminated with white light, the photopically weighted net intensity of reflected light, to the extent that it is determined by the sequence of transmission and reflection events for exactly antiparallel rays of retroreflected light as they enter and leave the retroreflective element, can vary dramatically with coating thickness or thicknesses, for a given desirable set of coating materials and refractive index values. The photopically weighted net intensity of reflected light produced by the four interfaces established by three coating layers (for example, of amorphous silica, followed by amorphous titania, followed by amorphous silica, on a 1.93 refractive index bead core) can vary by a factor of at least four. For some choices of coatings and thicknesses, the photopically weighted net intensity of reflected light can be significantly reduced versus a retroreflective element in the form of an uncoated bead.

Suitable materials to use as coatings for the foregoing optical interference layers include inorganic materials that provide transparent coatings. Such coatings tend to make bright, highly retroreflective articles. Included within the foregoing inorganic materials are inorganic oxides such as TiO_2 (refractive index of 2.2-2.7) and SiO_2 (refractive index of 1.4 – 1.5) and inorganic sulfides such as ZnS (refractive index of 2.2). The foregoing materials can be applied using any of a variety of techniques. Other suitable materials having a relatively high refractive index include CdS, CeO_2, ZrO_2, Bi_2O_3, ZnSe, WO_3, PbO, ZnO, Ta_2O_5, and others known to those skilled in the art. Other low refractive index materials suitable for use in the present invention include Al_2O_3, B_2O_3, AlF_3, MgO, CaF_2, CeF_3, LiF, MgF_2 and Na_3AlF_6.

Where the coated retroreflective elements of the invention are to be used in an environment where water insolubility is not needed, other materials may be used such as, for example, sodium chloride (NaCl). Additionally, it is within the scope of the invention to concentrically coat the bead cores with multiple layers wherein at least one of the layers is an organic coating. In some embodiments, the use of one or more organic coatings is preferred when the organic coating, and other coatings supported on it, are to be preferentially removed from the front surface of the coated retroreflective elements. The selective removal of front surface coatings might be desired to provide a coating design with high reflectivity for its collection of interfaces when intact and adjacent to a background polymeric binder, but to lower reflectivity for the front-face when the those front-face coatings were removed.

In some embodiments, portions of one or more of the optical interference layers can be removed to expose underlying optical interference layer(s) or to expose at least a portion of the core. Removal of portions of one or more optical interference layer(s) can occur during the initial manufacture of the retroreflective elements, prior to release of a product into the field or at a later time after product comprising the retroreflective elements has already been released and applied in an end use (e.g., removal by wear).

In some embodiments, the retroreflective elements 300 are used in articles having high retroreflectivity in an exposed-lens construction under dry conditions. In such embodiments, the solid spherical core 310 of the retroreflective element 300 has an index of refraction typically between about 1.5 and about 2.1. Typically, when the entry medium is air, the index of refraction of the core 310 is between about 1.5 and 2.1. In other embodiments, the index of refraction of the core 310 is between about 1.7 and about 2.0. In other embodiments, the index of refraction of the core 310 is between 1.8 and 1.95. In other embodiments, the index of refraction of the core 310 is between 1.9 and 1.94.

In order to obtain a desired level of retroreflectivity, the solid spherical core 310 may be selected to have a relatively high index of refraction. In some embodiments, the index of refraction of the core is greater than about 1.5. In other embodiments, the index of refraction of the core is between about 1.55 and about 2.0. In some embodiments, the core 310 may be first coated with low refractive index material (e.g., 1.4-1.7) to form first optical interference layer 312, followed by coating with a high refractive index material (e.g., 2.0-2.6) to form the second optical interference layer 322. Thereafter, the third optical interference layer 327 may be coated over the second optical interference layer using a low refractive index material (e.g., 1.4-1.7). The retroreflective element 300 may be used as a component in a reflective article by affixing the retroreflective element to a substrate or backing. In such a construction, third optical interference layer 327 is affixed to the substrate by, for example, a polymeric adhesive or binder. In some embodiments of the aforementioned articles, an auxiliary reflector may be provided by, for example, use of a pigmented binder that includes diffuse-scattering or specular pigment to enhance the reflective properties and the retroreflectivity of the article.

In other embodiments, the solid spherical core 310 is selected to have a relatively high index of refraction (e.g., greater than about 1.5). In such embodiments, the solid core 310 is first coated with high refractive index material (e.g., 2.0-2.6) to form the first optical interference layer 312, and is then coated with a low refractive index material (e.g., 1.4-1.7) to provide a second optical interference layer 322. Thereafter, the third optical interference layer 327 may be coated over the second optical interference layer using a high refractive index material (e.g., 2.0-2.6). The resulting retroreflective element 300 may be used as a component of a reflective article with the retroreflective element 300 affixed to a substrate or backing. In such a construction, the retroreflective element is affixed to the substrate with third optical interference layer 327 embedded, for example, in a polymeric binder. In some embodiments, the binder itself may be pigmented with diffuse-scattering or specular pigment that enhances the retroreflectivity of the article.

Articles comprising the retroreflective elements described herein can be made to provide patterns when viewed in a retroreflective mode. As used herein, a "pattern" is defined by and composed of a plurality of regions. In some embodiments of the invention, the coated retroreflective elements are arranged in regions which are each discernible if viewed in both retroreflective and other modes. Retrochromic patterns can comprise one or more retrochromic regions that are discernible only when viewed in retroreflective mode. Such retrochromic patterns are referred to as being "covert" patterns.

Retroreflective patterns, including those that are retrochromic, may be of any size and/or shape (e.g., substantially one, two, or three dimensional) and may be provided in geometric shapes such as, for example, circle(s), line(s) (e.g., wavy, straight or curved), polygon(s) (e.g., triangle(s), square(s), rectangle(s)), polyhedron(s) (e.g., cube, tetrahedron, pyramid, sphere), or other indicia such as one or more alphanumeric character(s) (e.g., letter(s), number(s), trademark(s), logo(s), official seal(s)), and/or graphics. In some embodiments, retroreflective and/or retrochromic patterns are provided that are microscopic in size in that the patterns require magnification or other viewing aids to discern them. Larger retroreflective and/or retrochromic patterns are also useful, and it is within the scope of the present invention to provide microscopic retroreflective and/or retrochromic patterns within larger retroreflective and/or retrochromic patterns.

Retroreflective and/or retrochromic patterns are formed utilizing the coated retroreflective elements described herein, and optionally including other retroreflective and/or retrochromic retroreflective elements such as, for example, those described in U.S. Patent No. 7,036,944 (Budd et al.); and/or with retroreflective non-retrochromic retroreflective elements as described in, for example, U.S. Patent Nos. 2,326,634 (Gebhard et al.), and 5,620,775 (LaPerre), the entire disclosures of which are incorporated herein by reference thereto.

When the retroreflective elements of the invention are incorporated into an article, the construction of the retroreflective elements can influence whether the article is highly retroreflective as well as whether the article, when viewed in the retroreflective mode, also exhibits covert color. For retroreflective elements coated with silica and/or titania, coating thicknesses of the metal oxide layers can influence the retroreflective characteristics of the finished article. For example, retroreflective elements comprising two complete concentric optical interference layers coated on a 1.9 RI glass core with the first optical interference layer being silica of a thickness of about 110 nm and the second optical interference layer being titania, can produce significant covert color when the second optical interference layer of titania is at a coated thickness within the range from 100 nm to 215 nm. Where the titania layer is less than 100 nm, little or no color is observed. These observations apply whether the retroreflective elements are adhered to a polymer backing or whether they are observed in a glass vial with “air” adjacent the entire retroreflective element outer surface. Retroreflective elements comprising three complete concentric optical interference layers coated on a 1.9 RI glass core with the first optical interference layer being silica of a thickness of about 110 nm and the second optical interference layer being titania of a thickness of about 60 nm, and the third optical interference layer being silica can produce significant covert color when the third optical interference layer of silica is coated to have a thickness within the range from 50 nm to 75 nm as well as from 95nm to 120 nm when the retroreflective elements are observed in a glass vial. Little or no color is observed for coating thicknesses within the rage from 0-50 or 75-95 nm. When the retroreflective elements are adhered to a polymer backing, color is observed for retroreflective elements having a third optical interference layer of silica at within the range from 30 nm to 120 nm.

Retroreflective elements having complete concentric optical interference layers of silica, titania, and silica that exhibit a retroreflected color and are retrochromic can exhibit one retroreflected color when the back of the retroreflective element is surrounded by air and a different retroreflected color when the back of the retroreflective element is embedded in a polymer. A color shifting retroreflective article can comprise retroreflective elements that are partially sunken into a polymer layer or substrate. In such embodiments, if the retroreflective elements comprise sufficient exposed area, the focal region for incident light can be configured by the viewer to be near an area on the surface of the element that is embedded in the polymer, or to be near an area of the surface of the retroreflective element that is above (e.g., not sunken into) the polymer layer or substrate by, for example, tilting the article. The retroreflected color associated with a polymer encased rear surface will be exhibited for a range of illumination incidence angles ranging from normal to the surface (i.e., zero degrees) to some critical angle. The retroreflected color associated with an air encased rear surface will be exhibited for illumination incidence angles greater than the critical angle as measured from the normal to the surface (i.e., 90 degrees would correspond to incident light parallel to the surface). It will be appreciated that other materials and constructions of retroreflective elements and articles comprising such retroreflective elements will also provide retroreflective color or enhanced retroreflective brightness in addition to the foregoing constructions. All such embodiments are considered within the scope of the invention.

Manufacture of Retroreflective elements

Retroreflective elements may be conveniently and economically prepared using a fluidized bed of transparent beads and vapor deposition techniques. In general, the processes of depositing vapor phase materials onto a fluidized (i.e., agitated) bed of a plurality of beads, as used herein, can be collectively referred to as "vapor deposition processes" in which a concentric layer is deposited on the surface of respective transparent beads from a vapor form. In some embodiments, vapor phase precursor materials are mixed in proximity to the transparent beads and chemically react in situ to deposit a layer of material on the respective surfaces of the transparent beads. In other embodiments, material is presented in vapor form and deposits as a layer on the respective surfaces of the transparent beads with essentially no chemical reaction.

Depending upon the deposition process being used, precursor material(s) (in the case of a reaction-based deposition process) or layer material(s) (in the case of a non-reaction-based process), typically in vapor phase, is or are placed in a reactor with transparent beads. The present invention desirably utilizes a vapor phase hydrolysis reaction to deposit a concentric optical interference layer (e.g., a layer of metal oxide) onto the surface of a respective core. Such process is sometimes referred to as a chemical vapor deposition ("CVD") reaction.

Desirably, a low temperature, atmospheric pressure chemical vapor deposition ("APCVD") process is used. Such processes do not require vacuum systems and can provide high coating rates. Hydrolysis-based APCVD (i.e., APCVD wherein water reacts with a reactive precursor) is most desired because of the ability to obtain highly uniform layers at low temperatures, e.g., typically well below 300°C.

The following is an illustrative vapor phase hydrolysis-based reaction:

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$$

In the illustrative reaction, water vapor and titanium tetrachloride, taken together, are considered metal oxide precursor materials.

Useful fluidized bed vapor deposition techniques are described, for example, in U.S. Pat. No. 5,673,148 (Morris et al.), the disclosure of which is incorporated herein by reference.

A well-fluidized bed can ensure that uniform layers are formed both for a given particle and for the entire population of particles. In order to form substantially continuous layers covering essentially the entire surfaces of the transparent beads, the transparent beads are suspended in a fluidized bed reactor. Fluidizing typically tends to effectively prevent agglomeration of the transparent beads, achieve uniform mixing of the transparent beads and reaction precursor materials, and provide more uniform reaction conditions, thereby resulting in highly uniform concentric optical interference layers. By agitating the transparent beads, essentially the entire surface of each assembly is exposed during the deposition, and the assembly and reaction precursors or layer material may be well intermixed, so that substantially uniform and complete coating of each bead is achieved.

If using transparent beads that tend to agglomerate, it is desirable to coat the transparent beads with fluidizing aids, e.g., small amounts of fumed silica, precipitated silica, methacrylato chromic chloride having the trade designation "VOLAN" (available from Zaclon, Inc., Cleveland, Ohio). Selection of such aids and of useful amounts thereof may be readily determined by those with ordinary skill in the art.

One technique for getting precursor materials into the vapor phase and adding them to the reactor is to bubble a stream of gas, desirably a non-reactive gas, referred to herein as a carrier gas, through a solution or neat liquid of the precursor material and then into the reactor. Exemplary carrier gases include argon, nitrogen, oxygen, and/or dry air.

Optimum flow rates of carrier gas(es) for a particular application typically depend, at least in part, upon the temperature within the reactor, the temperature of the precursor streams, the degree of assembly agitation within the reactor, and the particular precursors being used, but useful flow rates may be readily determined by routine optimization techniques. Desirably, the flow rate of carrier gas used to transport the precursor materials to the reactor is sufficient to both agitate the transparent beads and transport optimal quantities of precursor materials to the reactor.

Referring to Figure 4, an exemplary process for the manufacture of retroreflective elements is schematically shown. A carrier gas is fed through line 402a, and the gas is bubbled through water bubbler 404, to produce water vapor-containing precursor stream which is directed through steam line 408. A second stream of carrier gas is fed through line 402b and is bubbled through titanium tetrachloride bubbler 406, to produce titanium tetrachloride-containing precursor stream which is directed through line 430. Precursor streams within lines 408 and 430 are transported into reactor 420. Cores are introduced into reactor 420 through inlet 410, and outlet 400 is provided for the removal of retroreflective elements 400 from the reactor 420.

Precursor flow rates are adjusted to provide an adequate deposition rate onto the uncoated beads and to provide a metal oxide layer of a desired quality and character. Desirably, flow rates are adjusted such that the ratios of precursor materials present in the reactor chamber promote metal oxide deposition at the surface of the transparent beads with minimal formation of discrete, i.e., free floating, metal oxide particles, elsewhere in the chamber. For example, if depositing layers of titania from titanium tetrachloride and water, a ratio of between about eight water molecules per each titanium tetrachloride molecule to one water molecule per two titanium tetrachloride molecule is generally suitable, with about two water molecules of water per titanium tetrachloride molecule being preferred. Under these conditions there is sufficient water to react with most of the titanium tetrachloride and most of the water is adsorbed onto the surface of the retroreflective element. Much higher ratios tend to yield substantial quantities of unadsorbed water that might result in formation of oxide particulates rather than the desired oxide layers.

In some embodiments, precursor materials have sufficiently high vapor pressures that sufficient quantities of precursor material will be transported to the reactor for both the hydrolysis reaction and the layer deposition process to proceed at a convenient rate. For instance, precursor materials having relatively higher vapor pressures typically provide faster deposition rates than precursor materials having relatively lower vapor pressures, thereby enabling the use of shorter deposition times. Precursor sources may be cooled to reduce vapor pressure or heated to increase vapor pressure of the material. The latter may necessitate heating of tubing or other means used to transport the precursor material to the reactor, to prevent condensation between the source and the reactor. In many instances, precursor materials will be in the form of neat liquids at room temperature. In some instances, precursor materials may be available as sublimable solids.

In some embodiments, the coating of glass beads utilizes precursor materials capable of forming dense metal oxide coatings via hydrolysis reactions at temperatures below about

300°C, and typically below about 200°C. In some embodiments, titanium tetrachloride and/or silicon tetrachloride, and water are used as precursor materials. In addition to volatile metal chlorides, some embodiments of the invention utilize other precursor materials such as, for example, mixtures of water and at least one of: metal alkoxide(s) (e.g., titanium isopropoxide, silicon ethoxide, zirconium n-propoxide), metal alkyl(s) (e.g., trimethylaluminum, diethylzinc). It may be desirable to utilize several precursors simultaneously in a coating process.

Desirably, mutually reactive precursor materials, e.g., $TiCl_4$ and H_2O, are not mixed prior to being added to the reactor in order to prevent premature reaction within the transport system. Accordingly, multiple gas streams into the reaction chamber can be provided.

Vapor deposition processes include hydrolysis based CVD and/or other processes. In such processes, the beads are typically maintained at a temperature suitable to promote effective deposition and formation of the concentric optical interference layer with desired properties on the beads. Increasing the temperature at which the vapor deposition process is conducted typically yields a resultant concentric layer that is denser and retains fewer fugitive unreacted precursors. Sputtering or plasma-assisted chemical vapor deposition processes, if utilized, often require minimal heating of the article being coated, but typically require vacuum systems, and can be difficult to use if coating particulate materials such as small glass beads.

Typically, a deposition process that operates at a temperature low enough not to undesirably degrade the transparent beads should be selected. Thus, deposition of the optical interference layer is desirably achieved using a hydrolysis-based APCVD process at temperatures below about 300°C, more typically below about 200°C.

Titania and titania-silica layers deposited from tetrachlorides are particularly desired, and are easily deposited by APCVD at low temperatures, e.g., between about 120°C and about 160°C.

Any dimensionally stable, substantially spherical, transparent bead may be used as a core for the concentrically coated retroreflective elements used in the present invention. Cores may be inorganic, polymeric or other provided that they are substantially transparent to one or more wavelengths, typically all wavelengths, of visible light. In some embodiments, cores have a diameter from about 20 to about 500 micrometers. In other embodiments, cores have a diameter from about 50 to about 100 micrometers. Other diameters may also be used.

Cores suitable for use in the invention comprise a material, desirably an inorganic glass comprising silica, having a refractive index from about 1.5 to about 2.5 or higher. In some embodiments, the cores have a refractive index from about 1.7 to about 1.9. Cores may also have a lower refractive index value depending on the particular intended application, and the composition of the concentric optical interference layer. For example, a silica glass retroreflective element with refractive index as low as about 1.50 may be desirably used as a core because of the low cost and high availability of soda-lime-silica (i.e., window glass). Optionally, cores may further comprise a colorant.

Exemplary materials that may be utilized as a core include any of a variety of glasses (e.g., mixtures of metal oxides such as SiO_2, B_2O_3, TiO_2, ZrO_2, Al_2O_3, BaO, SrO, CaO, MgO, K_2O, Na_2O). In other embodiments, the cores may comprise solid, transparent, non-vitreous, ceramic particles such as those as described in, for example, U.S. Pat. Nos. 4,564,556 (Lange) and 4,758,469 (Lange), the disclosures of which are incorporated in their entireties herein by reference thereto. Commercially available glass retroreflective elements suitable for use as cores herein include those available from Flex-O-Lite, Inc. of Chesterfield, Mo.

Exemplary useful colorants include transition metals, dyes, and/or pigments, and are typically selected according to compatibility with the chemical composition of the core, and the processing conditions utilized.

The concentric optical interference layer employed in practice according to the present invention may be of any transparent material having a different refractive index than the core supporting the layer. In some embodiments, the concentric optical interference layer(s) should be sufficiently smooth so as to be optically clear while also being tough in that the optical interference layer(s) is not easily chipped or flaked.

In embodiments, the concentric optical interference layer(s) comprise metal oxide. Exemplary metal oxides useful for the concentric optical interference layer include titania, alumina, silica, tin oxide, zirconia, antimony oxide, and mixed oxides thereof. Desirably, the optical interference layer comprises one of the following: titanium dioxide, silicon dioxide, aluminum oxide, or a combination thereof. In some embodiments, titania and titania/silica layers are used because they are readily deposited to form durable layers.

Portions of retroreflective elements having various optical interference layer thicknesses and retroreflective colors can be removed from a reactor sequentially. One, two, three, or more pluralities of retroreflective elements, each plurality having a different retroreflective color and collectively comprising a retrochromic color palette, may thus be easily obtained by charging a reactor with a large quantity of beads and sequentially removing portions of retroreflective elements during a continuing coating run.

In one embodiment, the progress of layer deposition may be monitored by viewing the beads in retroreflective mode, for example, by using a retroviewer (e.g., as described in U.S. Pat. Nos. 3,767,291 (Johnson) and 3,832,038 (Johnson), the disclosures of which are incorporated herein by reference) either in situ using a glass-walled reactor or by removal from the reactor. Retroviewers useful for viewing intrinsically retrochromic beads and articles containing them are also readily commercially available, for example, under the trade designation “3M VIEWER” from 3M Company, St. Paul, MN.

<u>Materials and Article</u>

The above described retroreflective elements may be applied to or incorporated in any of a variety of articles such as fibers, filaments and garments with enhanced retroreflective properties. In some embodiments, the articles provide retroreflective color.

Non-limiting examples of garments include safety vests (e.g. for construction workers), jackets, shirts, hard hats, pants, shoes, running apparel, biking apparel, athletic shoes (e.g., running shoes), other sportswear and the like. A plurality of retroreflective elements may be arranged on a surface of a garment ("garment surface") in one or more regions, for example, with each region providing a pattern or design (or a portion of a pattern or design) that becomes visible when viewed in a retroreflective mode. In some embodiments, retroreflective safety garments are provided comprising a plurality of retroreflective elements affixed to a garment surface and providing a safety function in that incident light (e.g., light from an automobile headlight) is retroreflected by the retroreflective elements in the pattern or design to enhance the visibility of the person wearing the garment. In some embodiments, garment surfaces are provided comprising retroflective elements arranged in a design or pattern that may be considered aesthetically appealing while also exhibiting enhanced retroreflective brightness when viewed in a retroreflective mode. Because of the enhanced retroreflective brightness, such designs or patterns also serve at least a secondary safety function.

In embodiments of the invention, retroreflective elements having one or more complete concentric optical interference layers are first affixed to and supported on a backing or substrate to provide a retroreflective sheet which, in turn, can be affixed to a garment surface. In some embodiments, the retroreflective elements are arranged on a substrate in a pattern or design comprising one or more regions with the retroreflective elements within each region providing distinct retroreflective properties. For example, retroreflective elements may be applied to a substrate to provide a striped pattern that is brightly retroreflective and optionally provides retroreflective color. Depending on the intended application, the pattern is provided to be large enough to be discernible at a distance.

When a retroreflective sheet is affixed to a garment surface to provide a safety vest or similar safety clothing, the striped pattern is brightly retroreflective and is visible from a significant distance when illuminated by, for example, an automobile headlight. A retroreflective pattern or design can comprise a combination of retroreflective components (e.g., retroreflective elements) and non-retroreflective components so that the pattern or design has an initial appearance when seen in ambient or diffuse lighting and a second appearance when viewed in a retroreflective mode. In some embodiments, the retroreflective elements may provide retroreflective color. As will be appreciated by those skilled in the art, non-retroreflective components may also be added to the backing or substrate and can include, for example, conventional colorants such as dyes, pigments or the like to color at least a portion of the design or pattern when viewed under ambient or diffuse lighting.

Substrates for retroreflective elements can be made from any of a variety of suitable materials so long as the substrate material is suitable for inclusion in a garment. Suitable materials include metallic films, polymeric films, woven materials, knitted materials, nonwoven materials and the like. In some embodiments, retroreflective elements are bonded to at least one major surface of a film such as a polymeric film. In some embodiment, the retroreflective elements may be adhered to the substrate with an adhesive. In some embodiments, the retroreflective elements are at least partially embedded in, and thereby affixed to, one of the major surfaces of a polymeric film to thereby affixed the elements to the substrate with a portion of each retroreflective element extending above the major surface of the substrate. In some embodiments, the substrate is a film comprising one or more thermoplastic polymers. In some embodiments, the substrate comprises another material coated with a polymer. In the foregoing embodiments, the material may be a non-polymer. In one embodiment, a suitable substrate comprises a sheet of polyethylene coated paper. In some embodiments, the substrate comprises a thermosetting polymer which is at last partially crosslinked.

In embodiments where the retroreflective elements may be directly affixed to a garment surface using a chemical binder or adhesive, suitable binders or adhesives may comprise one or more polymers, monomers, oligomers and the like. Suitable polymers for use as binder can include, but are not limited to, organic solvent-soluble polymers, water-based polymer dispersions, radiation curable polymers, and combinations thereof.

Organic solvent-soluble polymers can include polyurethanes, acrylic polymers, polyamides, copolymers thereof, and combinations thereof. Commercially available solvent-based polyurethanes can include those available under the trade designation PERMUTHANE from Stahl USA, Peabody, MA, such as SU26-248, an aliphatic polyurethane in toluene. Other suitable polyurethanes can include Estanes available from B.F. Goodrich (Cleveland, OH), such as Estane 5715 and 5778, and Morthanes available from Huntsman polyurethanes (Ringwood, Il), such as CA118 and CA237, both of which are polyester polyurethanes. Other suitable polymers can include those available from NeoResins DSM under the trade designation U-371.

Examples of water-based polymer dispersions can include polyurethanes, polyureas, polyacrylics, polyethers, polyester, and copolymers thereof and combinations thereof. Suitable aqueous dispersions can include urethanes such as those available under the trade designation NEOREZ from DSM NeoResins, Wilmington, MA, particularly NEOREZ R-960 and NEOREZ R-9699; acrylics such as those available under the trade designation NEOCRYL from DSM NeoResins, such as NEOCRYL XK-90, NEOCRLYL XK-96 and NEOCRYL XK-95; and, acrylic urethane copolymers, such as those available under the trade designation NEOPAC from DSM NeoResins. Other water-based urethanes can include RU-077 and RU-075 available from Stahl USA, Peabody, MA.

The above-listed polymers may also be partially or fully cross-linked to improve wash durability of such materials. To initiate the cross-linking, the polymeric binder material can include chain extension agents and chemical cross-linking agents. Examples of cross-linking agents can include isocyanates such as those available under the trade designation DESMODUR from Bayer AG (Pittsburg, PA), aziridine crosslinkers such as those available under the trade designation CX-100 from DSM NeoResins and those available under the trade designation XR-2500 from Stahl USA. Suitable chain extension agents can include carbodiimides, such as those available under the trade designation EX62-944, and melamines such as those available under the trade designation XR-9174, both available from Stahl USA.

Examples of suitable cross-linkable polymer compositions include self cross-linking polymer dispersions, where the deposited coating self cross-links upon drying to form a durable coating layer. Self cross-linking polymer dispersions typically contain side groups that react to form chemical bonds via condensation polymerizations, which take place upon evaporation of water. Self cross-linking polymer dispersions offer the advantage of forming a durable binder material that is solvent resistant without requiring cross-linking agents. Examples of self cross-linking urethane dispersions can include polyester-urethanes that are terminated by hydrolysable silyl groups and contain solubilizing sulfonic acid functional groups. Such polyester-urethanes are described in Krepski, et al., U.S. Patent No. 5,929,160, which is incorporated by reference in its entirety. Additional examples of suitable self cross-linking urethane dispersions can include polyurethane water-based dispersions containing hydroxyl groups to accomplish the self cross-linking function. Suitable hydroxyl group-based polyurethanes can include those prepared pursuant to the process described in Mazanek et al., U.S. Patent Publication No. 2003/0199632, which is incorporated by reference in its entirety. Even further additional examples of suitable self cross-linking urethane dispersions can include polyurethane polymer hybrid dispersions based on oxidatively drying polyols, such as those disclosed in Ingrisch et al., U.S. Patent No. 6,462,127, which is incorporated by reference in its entirety.

Examples of commercially available self cross-linking polymers include dispersions sold under the trade designations "RHEOPLEX" and "ROVACE," available from Rohm and Haas Company, Philadelphia, PA, which are typically used as binders for textile and non-woven substrates for the protection of color dyes applied to the substrates. Exemplary compositions include the trade designated "RHEOPLEX HA-12" (non-ionic dispersion with glass transition temperature of about 19°C) and "RHEOPLEX TR-407" (anionic dispersion with glass transition temperature of 34°C), both of which exhibit good wash durability and chemical resistance. Additional examples of commercially available self cross-linking polymers can include the trade designated "NEOREZ R-551" polyether-based polymers and "NEOCRYL XK-98" acrylic emulsion polymers, both of which are available from DSM NeoResins, Wilmington, MA.

Examples of radiation curable polymers can include those described in Ylitalo et al., PCT Publication No. WO 2007/070650, which is incorporated herein by reference in its entirety.

Examples of suitable adhesives that can by used to bond the retroreflective element to the substrate or garment include one or more adhesives based on acrylates, urethanes, silicones, epoxies, rubber based adhesives (including natural rubber, polyisoprene, polyisobutylene, and butyl rubber, block copolymers, and thermoplastic rubbers), and combinations thereof.

Examples of suitable acrylates include polymers of alkyl acrylate monomers such as methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, methyl acrylate, ethyl acrylate, n-butyl acrylate, iso-octyl acrylate, iso-nonyl acrylate, 2-ethyl-hexyl acrylate, decyl acrylate, dodecyl acrylate, n-butyl acrylate, hexyl acrylate, and combinations thereof. Examples of commercially available block copolymers include those available under the trade designation "KRATON G-1657" from Kraton Polymers, Westhollow, TX.

Additional examples of suitable adhesive materials include those described in Draheim et al., U.S. Patent Application Publication No. 2003/0012936. Several of such adhesive materials are commercially available under the trade designations "8141", "8142", and "8161" adhesives from 3M Company, St. Paul, MN.

In some embodiments, the adhesive or binder may comprise a polymeric matrix with or without optional filler particles such as titanium dioxide, talc, calcium carbonate and combinations of the foregoing. In some embodiments, filler particles can be used that provide reflective properties and which may function as auxiliary reflectors such as nacreous, pearlescent, and specular pigments. An example of specular pigments includes titanated mica particles. The inclusion of reflective pigments in a binder may be desired to enhance the reflective properties of an article and further enhance the retroreflected brightness provided by the retroreflective elements described herein. In aspects of the foregoing embodiments, the use of a colored adhesive, pigment, dye, or ink can enhance the reflective properties of the article or garment to which the retroreflective elements are applied. In some embodiments, fluorescent bonding materials may be used to secure the retroreflective elements to a garment surface to provide a surface that is brightly reflective in diffuse lighting as well as being highly retroreflective.

In some embodiments, an adhesive or bonding agent is prepared with a photochromic dye dissolved in an appropriate solvent. The resulting bonding agent is coated onto a substrate to provide a tacky layer of suitable thickness (e.g., 10 – 100 microns). Retroreflective elements are sprinkled onto the layer of bonding agent and are pressed into the layer to ensure a firm bond. Excess retroreflective elements can be gently brushed off of the surface of the bonding agent which is then dried or cured (e.g., by heating). In the resulting article, retroreflective elements are bonded to a garment surface or the like in a manner that provides a photochromic effect, i.e., when the resulting retroreflective article is exposed to light of certain wavelengths, the photochromic dye will change color during the exposure period but will return to its original color (or its lack of color) when the light source is removed. With retroreflective elements embedded in the bonding agent, the associated article will also be retroreflective, and in some embodiments will also display retroreflective color.

In embodiments where the adhesive provides color to the garment surface, retroreflective elements are mixed with a coloring agent such as a colored adhesive comprising a pigment, a dye, an ink, or the like. The mixture of retroreflective elements and colorant is applied to a substrate in a single step, and in some embodiments, the mixture is used to create a specific image such as a company name, symbol or logo, for example, on a garment surface, by applying (e.g., by printing) the colored mixture to the surface. The colorant may be selected to provide a final image that is highly visible under diffuse or ambient lighting, but the presence of the retroreflective elements alters the image when viewed in a retroreflective mode. In some embodiments, the retroreflective elements provide for no change in the overall color or shape of the image but provide enhanced retroreflective brightness. In other embodiments, the retroreflective elements provide retroreflective color when viewed in a retroreflective mode.

While different methods have been briefly discussed, the present invention is not limited to any particular method of applying retroreflective elements to a substrate, garment surface or the like. Concentrically coated retroreflective elements may be applied to a substrate using any of a variety of methods. In some embodiments, a two step process may be used in which adhesive is first applied to a substrate using a conventional coating method such as knife coating, or any pattern printing methods such as screen printing, flex printing, gravure printing, or inkjet printing. Thereafter, concentrically coated retroreflective elements may be applied to the adhesive by flood coating or by area sprinkling of the beads. Alternatively, a one step coating process may be used where the concentrically coated retroreflective elements are mixed with an adhesive and thereafter applied to a substrate in a single coating step using a suitable coating method such as roll coating, knife coating, gravure coating or the like.

Retroreflective elements may be positioned in or on a substrate to provide a retroreflective sheet which can be applied to a garment surface, as previously described. In addition to the retroreflective elements, a retroreflective sheet may incorporate one or more auxiliary reflectors such as a thin film metal reflector, for example, to provide a garment surface with a metallic appearance when viewed in ambient or diffuse lighting and under non-retroreflective geometries. Such an auxiliary reflector is positioned on the substrate so that it is behind the retroreflective elements (e.g., between the surface of the substrate and the retroreflective elements) so that light reflects back from the surface of the retroreflective sheet. Other constructions utilizing auxiliary reflectors are contemplated within the scope of the invention.

In some embodiments of the invention, retroreflective elements comprising one or more completely concentrically coated optical interference layers may first be incorporated into components of a garment. In turn, the components may be included in a garment surface. In some embodiments, individual fibers are provided that include a plurality of retroreflective elements with one or more concentrically coated optical interference layers affixed along at least a portion of the length of an elongate fibrous body to thereby provide a retroreflective fiber. Retroreflective fibers may be prepared by coating or applying an adhesive material along at least a portion of the length of a conventional fiber and thereafter applying retroreflective elements to the adhesive coated fiber to provide a retroreflective fiber suitable for inclusion into a garment surface or a fabric (e.g., nonwoven materials, woven materials, knitted materials and the like) or in any of a variety of accessory items such as earrings, shoe laces, neck and wrist chains, for example. In some embodiments of the foregoing fiber, the adhesive is an acrylic pressure sensitive adhesive and the fiber is a polyester thread.

In other embodiments, retroreflective elements comprising one or more complete concentric optical interference layers are incorporated into filament-like constructions (“filaments”) comprised of a hollow transparent tubular member providing an interior space within the member with sufficient internal volume capacity to hold a plurality of retroreflective elements therewithin. The tubular member may be of any desired length and has a sufficient width to accommodate the width of single retroreflective elements. In some embodiments, the width of the tubular member is approximately the same as or just slightly wider that the width of a single retroreflective element so that the retroreflective elements within the tubular member are stacked in column of single elements, one on top of another. In some embodiments, the internal width of the tubular member is a multiple of the width of the individual retroreflective elements to accommodate a tubular column of retroreflective elements having a width that is at least twice the width of a single retroreflective element, in some embodiments more than five retroreflective elements wide, in some embodiments more than 10 retroreflective elements wide, in some embodiments more than 20 retroreflective elements wide and in some embodiments more than 30 retroreflective elements wide. In some embodiments, the internal diameter of the tubular member is between about 45 and about 70 microns, and the outer diameter is between about 65 and about 100 microns. The finished filament will show enhanced retroreflective light intensity. In some embodiments, the concentrically coated retroreflective elements will provide one or more retroreflected colors when the filament is viewed in a retroreflective mode. The foregoing retroreflective filaments are suitable for inclusion in a garment surface or a fabric (e.g., nonwoven materials, woven materials, knitted materials and the like) or in any of a variety of accessory items such as earrings, shoe laces, neck and wrist chains, for example.

The following non-limiting examples illustrate specific embodiments of the present invention.

EXAMPLES

The following standard procedures were employed.

Procedure A: Preparation of Retroreflective elements

Retroreflective elements with complete concentric optical interference layers were formed by depositing metal oxide (titania or silica) coatings onto transparent bead cores using an atmospheric pressure chemical vapor deposition process (APCVD) similar to that described in U.S. Pat. No. 5,673,148 (Morris et al.), the disclosure of which is incorporated herein by reference thereto. The reactor had an internal diameter of 30 mm. The initial charge of transparent bead cores weighed 60g. For silica coatings, the reaction temperature was set at 40°C while titania coatings were deposited using a reaction temperature of 140°C. The desired reaction temperature was controlled by immersing the reactor in a heated oil bath maintained at a constant temperature. The bed of beads was fluidized with a stream of nitrogen gas introduced into the reactor through a glass frit reactor base. Once satisfactory fluidization was achieved, water vapor was introduced into the reactor through the base glass frit using a stream of nitrogen carrier gas passed through a water bubbler. The metal oxide precursor compounds (either $SiCl_4$ or $TiCl_4$) were vaporized by passing nitrogen carrier gas through a bubbler containing the neat liquid precursor and introducing the vaporized compounds into the reactor through a glass tube extending downward into the fluidized bead bed.

For retroreflective elements having multiple coatings, the additional layers were deposited by repeating the procedure for each additional complete concentric optical interference layer.

Flow rates of the reactant-laden carrier gases and reaction temperatures for silica and titania coatings are reported in Table 1.

Table 1

Type of coating	Reaction Temp (°C)	Precursor	Precursor bubbler flow rate (cc/min)	Water bubbler flow rate (cc/min)	Extra Nitrogen flow rate (cc/min)
SiO_2	40	$SiCl_4$	40	600	500
TiO_2	140	$TiCl_4$	600	600	500

In some instances, samples of different coating thicknesses were made by varying the coating times. This was accomplished by removing a small volume of retroreflective elements from the reactor at different times. Coating rates were determined by fracturing certain concentrically coated glass retroreflective elements that had been sampled from the reactor at known coating deposition times and examining the fracture pieces with a scanning electron microscope to directly measure the coating thicknesses. Thereafter, the thicknesses of the concentric coatings were calculated from known coating times and coating rates. A coating rate of ~2 nm/min was typical for the silica coatings, and a coating rate of ~5 nm/min was typical for the titania coatings.

<u>Procedure B: Patch Brightness</u>

Measurements of retroreflected brightness include "patch brightness" measurements of the coefficient of retroreflection (Ra) of a layer of retroreflective elements. Clear Patch Brightness as well as White Patch Brightness measurements were made. Clear Patch Brightness results are designated herein as "Ra (CP)" and White Patch Brightness results are designated as "Ra (WP)." In either case, layers of retroreflective elements were made by sprinkling retroreflective elements onto an adhesive tape and placing the construction under a retroluminometer. For Clear Patch Brightness, sample constructions were prepared by partially embedding the retroreflective elements in the adhesive of a transparent tape (3M Scotch 375 Clear Tape) and placing the tape on top of a sheet of paper having a dark (black) background. White Patch Brightness sample constructions were prepared by partially embedding the retroreflective elements in the adhesive of a tape in which the adhesive was pigmented with titanium dioxide to impart a white color. Retroreflective elements were typically embedded so that < 50% of the retroreflective element diameter was sunk in the adhesive. For each of the Patch Brightness constructions, the Ra in Cd/m^2/lux was determined according to the procedure established in Procedure B of ASTM Standard E 809-94a, measured at an entrance angle of -4.0 degrees and an observation angle of 0.2 degrees. The photometer used for those measurements is described in U.S. Defensive Publication No. T987,003.

<u>Procedure C: Color Measurements</u>

The retroreflective color or retrochromic effects were quantified by measuring color coordinates using an optical spectrometer (MultiSpec Series System with an MCS UV-NIR spectrometer and 50 watt halogen light source and bifurcated optical fiber probe, commercially available from Tec5 AG, Oberursol, Germany). Concentrically coated retroreflective elements were partially embedded in the adhesive of a commercially available tape (3M Scotch 375 Clear Tape). The embedded retroreflective elements were placed under a fiber optic probe at a distance of ~5mm, and spectral measurements were made in the wavelength range 300 nm – 1050 nm using a black background. A front surface mirror was used as the reference, and all measurements were normalized. Chromaticity coordinates were calculated from the reflectance spectra using (MultiSpec® Pro software with color module, commercially available from Tec5 AG, Oberursol, Germany). Color coordinates were measured for retroreflective elements made according to certain Comparative Examples and certain Examples, as specified herein. A CIE chromaticity diagram (1931 version) was referenced as well as a standard black body curve. The black body curve passes through white between approximately 4800K and 7500K. The corresponding color coordinates at these temperatures are (0.353, 0.363) and (0.299, 0.317). Measurements made from retroreflective elements showing little or no visible color in retroreflection lay within 0.01 of the black body radiation curve between 4800K and 7500K. It should be noted that the (x, y) coordinates correspond to the 1964 10 degree field of view modification to the original 1931 coordinates. The CIE chart and black body radiation curves are described in Zukauskas et al., *Introduction to Solid State Lighting*, John Wiley and Sons (2002); Chapter 2 (Vision, Photometry, and Colorimetry), pp. 7 - 15.

Comparative Example 1 and Examples 2 – 44

The bead cores used in the preparation of Comparative Example 1 and Examples 2 - 44 are referred to herein as Type I bead cores which were transparent glass beads having a refractive index of about 1.93, an average diameter of about 60 µm, and an approximate composition of 42.5% TiO_2, 29.4% BaO, 14.9% SiO_2, 8.5% Na_2O, 3.3% B_2O_3, and 1.4% K_2O by weight. Comparative Example 1 was an uncoated Type I bead core. Examples 2 – 44 were prepared according to the above Procedure A to have a single complete concentric interference layer. For Examples 2 – 25, the single complete concentric interference layer was silica while Examples 26 – 44 had a single complete concentric interference layer of titania. Coating times, calculated coating thicknesses, and retroreflected brightness (Ra) of Clear Patch constructions made with the bead cores are reported in Table 2.

Table 2

Sample	Coating material	Coating time (min)	Estimated coating thickness (nm)	Ra (CP)
C. Ex. 1	none	uncoated	uncoated	7.7
Ex. 2	SiO_2	18	36	9.76
Ex. 3	SiO_2	22	44	10.5
Ex. 4	SiO_2	26	52	11.7
Ex. 5	SiO_2	31	62	12.8
Ex. 6	SiO_2	34	68	13.5
Ex. 7	SiO_2	37	74	14.4
Ex. 8	SiO_2	40	80	15.1
Ex. 9	SiO_2	44	88	16.1
Ex. 10	SiO_2	48	96	17
Ex. 11	SiO_2	52	104	17.5
Ex. 12	SiO_2	55	110	17.1
Ex. 13	SiO_2	58	116	17
Ex. 14	SiO_2	61	122	15.3
Ex. 15	SiO_2	63	126	14.7
Ex. 16	SiO_2	65	130	13.2
Ex. 17	SiO_2	67	134	12.3
Ex. 18	SiO_2	69	138	11.1
Ex. 19	SiO_2	71	142	10.2
Ex. 20	SiO_2	73	146	9.3
Ex. 21	SiO_2	76	152	8.6
Ex. 22	SiO_2	78	156	8.2

Sample	Coating material	Coating time (min)	Estimated coating thickness (nm)	Ra (CP)
Ex. 23	SiO_2	81	162	8.16
Ex. 24	SiO_2	84	168	8.55
Ex. 25	SiO_2	88	176	9.3
Ex. 26	TiO_2	6	30	18.5
Ex. 27	TiO_2	10	50	26.7
Ex. 28	TiO_2	13	65	30.1
Ex. 29	TiO_2	19	95	27.9
Ex. 30	TiO_2	22	110	22.7
Ex. 31	TiO_2	26	130	13.9
Ex. 32	TiO_2	30	150	16.1
Ex. 33	TiO_2	32	160	17.5
Ex. 34	TiO_2	38	190	21.3
Ex. 35	TiO_2	40	200	21.1
Ex. 36	TiO_2	42	210	17.9
Ex. 37	TiO_2	45	225	17.7
Ex. 38	TiO_2	48	240	17.8
Ex. 39	TiO_2	50	250	18.1
Ex. 40	TiO_2	53	265	17.7
Ex. 41	TiO_2	55	275	18.4
Ex. 42	TiO_2	58	290	17.6
Ex. 43	TiO_2	60	300	18.6
Ex. 44	TiO_2	65	325	18.6

Retroreflective color was assessed for Comparative Example 1 and Example 6, 9, 11 and 13 according to Procedure C. Table 2A lists the color coordinates, observed color, distance from black body radiation curve between 4800K and 7500K and the coordinates for the closest point on the black body radiation curve between 4800K and 7500K. The designation “L/N” indicates little or no color was observed.

Table 2A

Sample	Chromaticity coordinate measurements (x, y)	Observed color	Distance from black body radiation curve between 4800K and 7500K	Closest point on black body curve (x, y), between 4800K and 7500K
C.Ex.1	0.327, 0.34	L/N	0.0018	0.326, 0.341
Ex. 6	0.318, 0.334	L/N	0.0004	0.318, 0.334
Ex. 9	0.331, 0.346	L/N	0.0012	0.332, 0.347
Ex. 11	0.341, 0.355	L/N	0.001	0.342, 0.355
Ex. 13	0.344, 0.356	L/N	0.0007	0.344, 0.357

Examples 45 – 69

Examples 45 – 69 employ the Type I bead cores. The coated retroreflective elements were prepared according to Procedure A so that the coated retroreflective elements included two concentric optical interference layers. Examples 45-60 were made using Type I bead cores coated with an inner or first optical interference layer of silica and an outer or second optical interference layer of titania. Examples 61-69 were made with Type I bead cores and were coated with an inner or first optical interference layer of titania and an outer or second optical interference layer of silica. Coating materials, thicknesses, and retroreflected brightness (Ra) of clear patch constructions are reported in Table 3.

Table 3

Example	Inner layer coating material	Estimated inner layer thickness (nm)	Outer layer coating material	Estimated outer layer thickness (nm)	Ra (CP)
45	SiO_2	110	TiO_2	30	46.1
46	SiO_2	110	TiO_2	50	56.4
47	SiO_2	110	TiO_2	60	58.4
48	SiO_2	110	TiO_2	80	56.7
49	SiO_2	110	TiO_2	100	56.6
50	SiO_2	110	TiO_2	125	51
51	SiO_2	110	TiO_2	150	42
52	SiO_2	110	TiO_2	165	35.2
53	SiO_2	110	TiO_2	180	32.7
54	SiO_2	110	TiO_2	200	35.9
55	SiO_2	110	TiO_2	215	41.7
56	SiO_2	40	TiO_2	50	31.2
57	SiO_2	40	TiO_2	75	42.4
58	SiO_2	40	TiO_2	100	44.4
59	SiO_2	40	TiO_2	125	28.5
60	SiO_2	40	TiO_2	135	27.1
61	TiO_2	60	SiO_2	40	40.1
62	TiO_2	60	SiO_2	50	45.4
63	TiO_2	60	SiO_2	60	49.4
64	TiO_2	60	SiO_2	70	51.6
65	TiO_2	60	SiO_2	80	51.3
66	TiO_2	60	SiO_2	90	47.1
67	TiO_2	60	SiO_2	100	43.8
68	TiO_2	60	SiO_2	110	37.4
69	TiO_2	60	SiO_2	120	26.1

Retroreflective color was assessed for Examples 45, 47, 49, 50, 52, 54 and 55 according to Procedure C. Table 3A lists the color coordinates, observed color, distance from black body radiation curve between 4800K and 7500K and the coordinates for the closest point on the black body radiation curve between 4800K and 7500K. The designation "L/N" indicates little or no color was observed.

Table 3A

Example	Chromaticity coordinate measurements (x, y)	Observed color	Distance from black body radiation curve between 4800K and 7500K	Closest point on black body curve (x, y) between 4800K and 7500K
45	0.322, 0.347	L/N	0.0068	0.326, 0.341
47	0.343, 0.358	L/N	0.0017	0.344, 0.357
49	0.365, 0.382	light yellow	0.0225	0.353, 0.363
50	0.384, 0.393	yellow	0.0431	0.353, 0.363
52	0.34, 0.312	purple	0.0314	0.32, 0.336
54	0.292, 0.332	light blue	0.0158	0.302, 0.320
55	0.313, 0.363	light green	0.0248	0.33, 0.345

Examples 70-80

Examples 70-80 employed Type I bead cores as well as the same coating materials and used for the preparation of Examples 1– 44. The coated retroreflective elements were prepared according to Procedure A with Examples 70-80 made to include three complete concentric interference layers. Coating materials, thicknesses, and retroreflected brightness (Ra) of clear patch constructions are reported in Table 4.

Table 4

Example	Inner layer	Inner layer thickness (nm)	Second layer	Second layer thickness (nm)	Outer layer	Outer layer thickness (nm)	Ra (CP)
70	SiO_2	110	TiO_2	60	SiO_2	32	63
71	SiO_2	110	TiO_2	60	SiO_2	52	79.1
72	SiO_2	110	TiO_2	60	SiO_2	72	102
73	SiO_2	110	TiO_2	60	SiO_2	92	113
74	SiO_2	110	TiO_2	60	SiO_2	98	113
75	SiO_2	110	TiO_2	60	SiO_2	106	109
76	SiO_2	110	TiO_2	60	SiO_2	112	102

77	SiO_2	110	TiO_2	60	SiO_2	116	95.1
78	SiO_2	40	TiO_2	110	SiO_2	10	24
79	SiO_2	40	TiO_2	110	SiO_2	20	26.9
80	SiO_2	40	TiO_2	110	SiO_2	36	31.1

Retroreflective color was assessed according to Procedure C for Examples 70 and 72-75. Table 4A lists the color coordinates, observed color, distance from black body radiation curve between 4800K and 7500K and the coordinates of the closest point on the black body radiation curve between 4800K and 7500K. The designation "L/N" indicates little or no color was observed.

Table 4A

Example	Chromaticity coordinate measurements (x, y)	Observed color	Distance from black body radiation curve between 4800K and 7500K	Closest point on black body curve (x, y) between 4800K and 7500K
70	0.332, 0.352	L/N	0.0042	0.334, 0.348
72	0.341, 0.372	light yellow	0.0138	0.35, 0.362
73	0.371, 0.394	yellow	0.036	0.353, 0.363
74	0.385, 0.399	yellow-orange	0.0487	0.353, 0.363
75	0.4, 0.394	orange	0.057	0.353, 0.363

<u>Comparative Example 81 and Examples 82-104</u>

Comparative Example 81 and Examples 82-104 were prepared in the same manner as in Comparative Example 1 and Examples 2-15 and 45-53, respectively. Retroreflective color from these coated retroreflective element samples was observed and recorded. Observed retroreflective color was determined by viewing through a retroreflective viewer (available under the trade designation "3M VIEWER" from 3M Company, St. Paul, Minnesota). A layer of retroreflective elements was partially embedded in a polymer adhesive (3M Scotch 375 Clear Tape) to determine Clear Patch brightness. Table 5 summarizes the construction, observed retroreflective color and Clear Patch Brightness for the samples.

Table 5

Sample	Inner layer	Inner layer thickness (nm)	Outer layer	Outer layer thickness (nm)	Ra (CP)	Retroreflective color from clear patch constructions
C.Ex. 81	uncoated	uncoated	uncoated	uncoated	7.7	L/N
Ex. 82	SiO_2	36	none	0	9.76	L/N
Ex. 83	SiO_2	44	none	0	10.5	L/N
Ex. 84	SiO_2	52	none	0	11.7	L/N
Ex. 85	SiO_2	62	none	0	12.8	L/N
Ex. 86	SiO_2	68	none	0	13.5	L/N
Ex. 87	SiO_2	74	none	0	14.4	L/N
Ex. 88	SiO_2	80	none	0	15.1	orange
Ex. 89	SiO_2	88	none	0	16.1	rust
Ex. 90	SiO_2	96	none	0	17	purple
Ex. 91	SiO_2	104	none	0	17.5	violet
Ex. 92	SiO_2	110	none	0	17.1	bluish violet
Ex. 93	SiO_2	116	none	0	17	blue
Ex. 94	SiO_2	122	none	0	15.3	blue
Ex. 95	SiO_2	126	none	0	14.7	bluish green
Ex. 96	SiO_2	110	TiO_2	30	46.1	L/N
Ex. 97	SiO_2	110	TiO_2	50	56.4	L/N
Ex. 98	SiO_2	110	TiO_2	60	58.4	L/N
Ex. 99	SiO_2	110	TiO_2	80	56.7	L/N
Ex. 100	SiO_2	110	TiO_2	100	56.6	creamish yellow
Ex. 101	SiO_2	110	TiO_2	125	51	yellow
Ex. 102	SiO_2	110	TiO_2	165	35.2	red
Ex. 103	SiO_2	110	TiO_2	180	32.7	purple
Ex. 104	SiO_2	110	TiO_2	215	35.9	violet

* L/N – little or no color observed in retroreflection

Comparative Example 105 and Examples 106-110

White patch brightness measurements were made for several of the previously described coated retroreflective element samples. Table 6 summarizes the construction of the coated retroreflective elements as well as White Patch Brightness for these samples.

Table 6

Sample	Coated as in Example	Layer sequence	Outer layer coating material	Estimated outer layer thickness (nm)	Ra (WP)
C.Ex. 105	1	none	uncoated	uncoated	18.1
Ex. 106	11	SiO_2	SiO_2	104	23.6
Ex. 107	28	TiO_2	TiO_2	150	40.1
Ex. 108	47	SiO_2,TiO_2	TiO_2	60	67
Ex. 109	73	SiO_2,TiO_2,SiO_2	SiO_2	98	114
Ex. 110	80	SiO_2,TiO_2,SiO_2	SiO_2	36	33

<u>Comparative Example 111 and Examples 112-123</u>

Glass-ceramic bead cores were prepared according to the methods described in U.S. Patent No. 6,245,700. The Type II bead cores had a composition of ZrO_2 12.0%, Al_2O_3 29.5%, SiO_2 16.2%, TiO_2 28.0%, MgO 4.8%, CaO 9.5% (wt %), with a refractive index of ~1.89 and an average diameter about 60 um. The bead cores were coated with a single layer SiO_2 or TiO_2 according to Procedure A. The construction of the coated retroreflective elements and both Clear Patch Brightness and White Patch Brightness determinations are reported in Table 7.

Table 7

Sample	Coating material	Estimated coating thickness (nm)	Ra (CP)	Ra (WP)
C.Ex. 111	uncoated	uncoated	3.1	15.2
Ex. 112	SiO_2	20	5.6	16.8
Ex. 113	SiO_2	36	4.71	16.2
Ex. 114	SiO_2	50	5.08	16.1
Ex. 115	SiO_2	64	5.45	16.4
Ex. 116	SiO_2	78	5.6	16.3
Ex. 117	SiO_2	92	5.7	17.6
Ex. 118	SiO_2	106	6.22	16.3
Ex. 119	TiO_2	40	11	19.3
Ex. 120	TiO_2	65	14.4	21.4
Ex. 121	TiO_2	95	12.1	23
Ex. 122	TiO_2	120	6.5	17.6
Ex. 123	TiO_2	150	6.4	16.8

Comparative Example 139 and Examples 140 – 160

Bead cores designated as Type III were prepared according to the methods described in U. S. Patent 6,245,700. The Type III bead cores were made of a glass-ceramic material having a composition of TiO_2 61.3%, ZrO_2 7.6%, La_2O_3 29.1%, ZnO 2% by weight, with RI ~2.4, and an average diameter of about 60 um. The bead cores were coated with single layer coatings of SiO_2 or TiO_2 according to Procedure A. Clear Patch Brightness and White Patch Brightness measurements were recorded by covering the patch surface with water. Coating materials, coating thicknesses and the wet White Patch and wet Clear Patch Brightness measurements are summarized in Table 8.

Table 8

Sample	Coating material	Coating thickness (nm)	Wet Ra (CP)	Wet Ra (WP)
C.Ex. 139	uncoated	0	3.91	11.4
Ex. 140	SiO_2	36	4.8	11.5
Ex. 141	SiO_2	48	5.03	12.2
Ex. 142	SiO_2	60	5.3	
Ex. 143	SiO_2	72	5.83	13.6
Ex. 144	SiO_2	84	6.04	
Ex. 145	SiO_2	96	6.48	13.4
Ex. 146	SiO_2	108	6.54	13.5
Ex. 147	SiO_2	120	6.7	12.9
Ex. 148	SiO_2	132	5.7	
Ex. 149	SiO_2	144	6.09	
Ex. 150	SiO_2	156	5.44	
Ex. 151	SiO_2	168	5.1	
Ex. 152	SiO_2	180	4.5	
Ex. 153	TiO_2	30	4.12	11
Ex. 154	TiO_2	60	3.7	9.51
Ex. 155	TiO_2	90	2.73	11.7
Ex. 156	TiO_2	120	2.79	10.7
Ex. 157	TiO_2	162	3.6	11.6
Ex. 158	TiO_2	198	4.6	10.9
Ex. 159	TiO_2	240	3.75	
Ex. 160	TiO_2	288	3.1	

Example 161

Three complete concentric optical interference layers were deposited on Type III cores according to Procedure A. Table 9 summarizes the coating materials, coating thicknesses and White Patch and Clear Patch Brightness measurements. The White Patch and Clear Patch Brightness measurements were made under wet conditions as in Examples 139-160.

Table 9

Example	Inner layer coating material	Inner layer thickness (nm)	Second layer coating material	Second layer thickness (nm)	Outer layer coating material	Outer layer thickness (nm)	Wet Ra (CP)	Wet Ra (WP)
161	SiO_2	120	TiO_2	60	SiO_2	110	11.3	17.2

Embodiments of the invention have been described in some detail. Those skilled in the art will appreciate that the invention is not limited to the described embodiments, and that various changes and modifications can be made to the embodiments without departing from the spirit and scope of the invention.

What is claimed is:

1. A garment comprising:

A garment surface having a plurality of retroreflective elements disposed thereon, the retroreflective elements each comprising:

a solid spherical core comprising an outer core surface, the outer core surface providing a first interface;

at least a first complete concentric optical interference layer having an inner surface overlying outer core surface and an outer surface, the outer surface of the first complete concentric optical interference layer providing a second interface.

2. The garment according to claim 1, wherein the retroreflective elements each further comprise:

a second complete concentric optical interference layer having an inner surface overlying the outer surface of the first complete concentric optical interference layer and an outer surface, the outer surface of the second complete concentric optical interference layer providing a third interface.

3. The garment according to claim 1, wherein a region of the surface having retroreflective elements includes no auxiliary reflector and has a coefficient of retroreflection, measured at -4 degrees entrance angle and 0.2 degrees observation angle, greater than 50 $Cd/lux/m^2$ and a retroreflective color with chromaticity coordinates defining a point on the CIE chromaticity diagram (1931 version) that lies within 0.01 of the line that describes black body emission between 4800K and 7500K.

4. The garment according to claim 3 wherein the first complete concentric optical interference layer and the second complete concentric optical interference layer comprise different materials, each of the materials selected from the group consisting of TiO_2, SiO_2, ZnS, CdS, CeO_2, ZrO_2, Bi_2O_3, ZnSe, WO_3, PbO, ZnO, Ta_2O_5, Al_2O_3, B_2O_3, MgO, AlF_3, CaF_2, CeF_3, LiF, MgF_2, Na_3AlF_6, and combinations of two or more of the foregoing.

5. The garment according to claim 4, wherein the retroreflective elements each further comprise:

third complete concentric optical interference layer having an inner surface overlying the outer surface of the second complete concentric optical interference layer and an outer surface, the outer surface of the third complete concentric optical interference layer providing a fourth interface.

6. The garment according to claim 5, wherein the second complete concentric optical interference layer and the third complete concentric optical interference layer comprise different materials, each of the materials selected from the group consisting of TiO_2, SiO_2, ZnS, CdS, CeO_2, ZrO_2, Bi_2O_3, ZnSe, WO_3, PbO, ZnO, Ta_2O_5, Al_2O_3, B_2O_3, MgO, AlF_3, CaF_2, CeF_3, LiF, MgF_2, Na_3AlF_6, and combinations of two or more of the foregoing.

7. The garment according to claim 1, further comprising a substrate having a first major surface and a second major surface, the plurality of retroreflective elements being retained on the first major surface of the substrate, and wherein the second major surface of the substrate is affixed to the garment surface.

8. The garment according to claim 7, wherein the substrate comprises a polymeric film, the retroreflective elements being embedded within the first major surface.

9. The garment according to claim 7, wherein the substrate comprises polyethylene coated paper, the retroreflective elements being embedded within the first major surface.

10. The garment according to claim 7, wherein the substrate comprises an adhesive that retains the retroreflective elements on the first major surface of the substrate.

11. The garment according to claim 10, wherein the adhesive comprises a diffuse light-scattering pigment and the retroreflective elements are partially embedded within the adhesive, and wherein the diffuse light-scattering pigment is selected from the group consisting of titanium dioxide particles, calcium carbonate particles, mica flakes, titanated mica flakes, pearlescent pigments, nacreous pigments and combinations of two or more of the foregoing.

12. The garment according to claim 10, further comprising an auxiliary reflector in the form of a metal film retained in the adhesive and disposed between the retroreflective elements and the first major surface of the substrate.

13. The garment according to claim 10, further comprising an auxiliary reflector in the form of a dielectric stack of thin films retained within the adhesive and disposed between the retroreflective elements and the first major surface of the substrate.

14. The garment according to claim 1 wherein, the garment is a safety vest.

15. The retroreflective article according to claim 1, wherein the article, when viewed in a retroreflective mode, exhibits enhanced retroreflective brightness.

16. The retroreflective article according to claim 1, wherein the article, when viewed in a retroreflective mode, exhibits retroreflective color.

17. A retroreflective garment according to claim 1, wherein the solid spherical core comprises a material having an index of refraction greater than about 1.5, the material selected from the group consisting of glass, glass-ceramic material and microcrystalline ceramic material.

18. A retroreflective garment according to claim 17, wherein the solid spherical core comprises a glass selected from the group consisting of silicon oxide, boron oxide, titanium oxide, zirconium oxide, aluminum oxide, barium oxide, strontium oxide, calcium oxide, magnesium oxide, potassium oxide, sodium oxide and combinations of two or more of the foregoing.

19. A retroreflective garment according to claim 1, wherein at least a portion of the retroreflective elements are adhered to individual elongate fibers.

20. A retroreflective garment according to claim 1, wherein at least a portion of the retroreflective elements are contained in filaments, each filament comprising a hollow tubular member with an interior space, the retroreflective elements being retained within the interior space.

21. A retroreflective fiber comprising:

An elongate fibrous body having a plurality of retroreflective elements adhered thereto, the retroreflective elements each comprising:

a solid spherical core comprising an outer core surface, the outer core surface providing a first interface;

at least a first complete concentric optical interference layer having an inner surface overlying outer core surface and an outer surface, the outer surface of the first complete concentric optical interference layer providing a second interface.

22. The retroreflective fiber according to claim 21, wherein the retroreflective elements each comprise:

a second complete concentric optical interference layer having an inner surface overlying the outer surface of the first complete concentric optical interference layer and an outer surface, the outer surface of the second complete concentric optical interference layer providing a third interface.

23. The retroreflective fiber according to claim 22 wherein the first complete concentric optical interference layer and the second complete concentric optical interference layer comprise different materials, each of the materials selected from the group consisting of TiO_2, SiO_2, ZnS, CdS, CeO_2, ZrO_2, Bi_2O_3, ZnSe, WO_3, PbO, ZnO, Ta_2O_5, Al_2O_3, B_2O_3, MgO, AlF_3, CaF_2, CeF_3, LiF, MgF_2, Na_3AlF_6, and combinations of two or more of the foregoing.

24. The retroreflective fiber according to claim 23, wherein the retroreflective elements each further comprise:

third complete concentric optical interference layer having an inner surface overlying the outer surface of the second complete concentric optical interference layer and an outer surface, the outer surface of the third complete concentric optical interference layer providing a fourth interface.

25. The retroreflective fiber according to claim 24, wherein the second complete concentric optical interference layer and the third complete concentric optical interference layer comprise different materials, each of the materials selected from the group consisting of TiO_2, SiO_2, ZnS, CdS, CeO_2, ZrO_2, Bi_2O_3, ZnSe, WO_3, PbO, ZnO, Ta_2O_5, Al_2O_3, B_2O_3, MgO, AlF_3, CaF_2, CeF_3, LiF, MgF_2, Na_3AlF_6, and combinations of two or more of the foregoing.

26. A retroreflective filament comprising:

A hollow, transparent, tubular member having a plurality of retroreflective elements contained therewithin, the retroreflective elements each comprising:

a solid spherical core comprising an outer core surface, the outer core surface providing a first interface;

at least a first complete concentric optical interference layer having an inner surface overlying outer core surface and an outer surface, the outer surface of the first complete concentric optical interference layer providing a second interface.

27. The retroreflective filament according to claim 26, wherein the retroreflective elements each comprise:

a second complete concentric optical interference layer having an inner surface overlying the outer surface of the first complete concentric optical interference layer and an outer surface, the outer surface of the second complete concentric optical interference layer providing a third interface.

28. The retroreflective filament according to claim 27 wherein the first complete concentric optical interference layer and the second complete concentric optical interference layer comprise different materials, each of the materials selected from the group consisting of TiO_2, SiO_2, ZnS, CdS, CeO_2, ZrO_2, Bi_2O_3, ZnSe, WO_3, PbO, ZnO, Ta_2O_5, Al_2O_3, B_2O_3, MgO, AlF_3, CaF_2, CeF_3, LiF, MgF_2, Na_3AlF_6, and combinations of two or more of the foregoing.

29. The retroreflective filament according to claim 28, wherein the retroreflective elements each further comprise:

third complete concentric optical interference layer having an inner surface overlying the outer surface of the second complete concentric optical interference layer and an outer surface, the outer surface of the third complete concentric optical interference layer providing a fourth interface.

30. The retroreflective filament according to claim 29, wherein the second complete concentric optical interference layer and the third complete concentric optical interference layer comprise different materials, each of the materials selected from the group consisting of TiO_2, SiO_2, ZnS, CdS, CeO_2, ZrO_2, Bi_2O_3, ZnSe, WO_3, PbO, ZnO, Ta_2O_5, Al_2O_3, B_2O_3, MgO, AlF_3, CaF_2, CeF_3, LiF, MgF_2, Na_3AlF_6, and combinations of two or more of the foregoing.

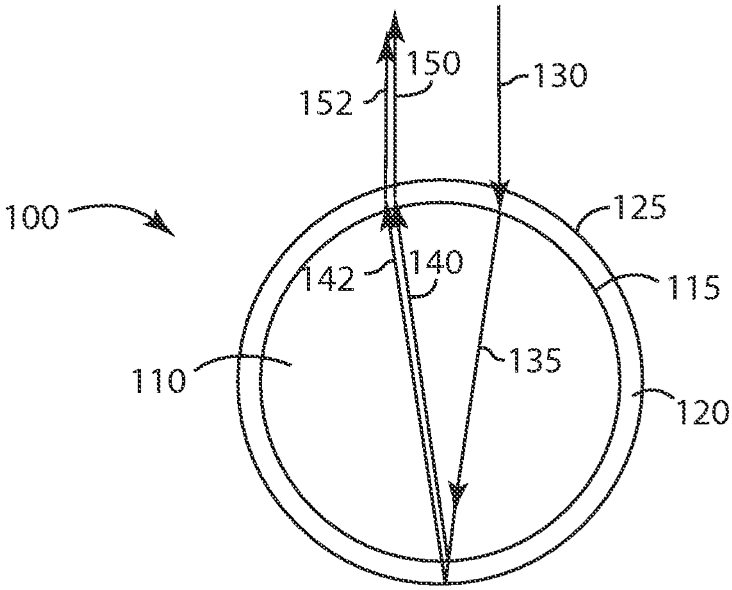
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FIG. 1

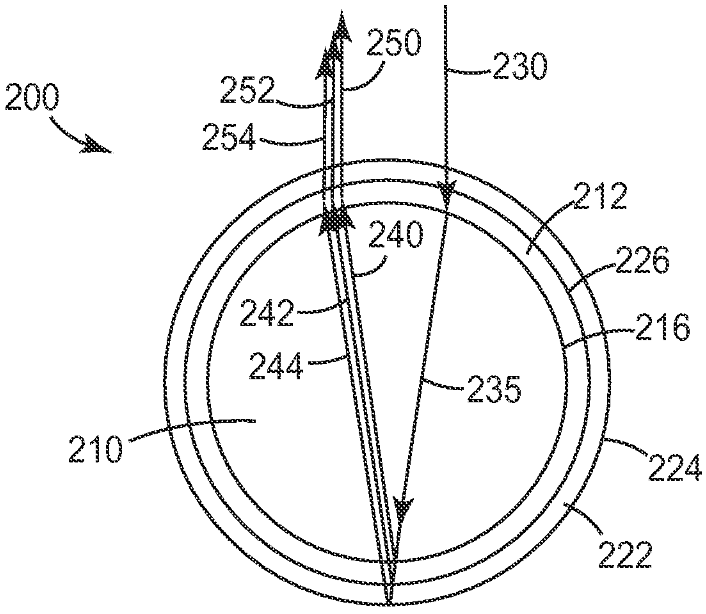
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FIG. 2

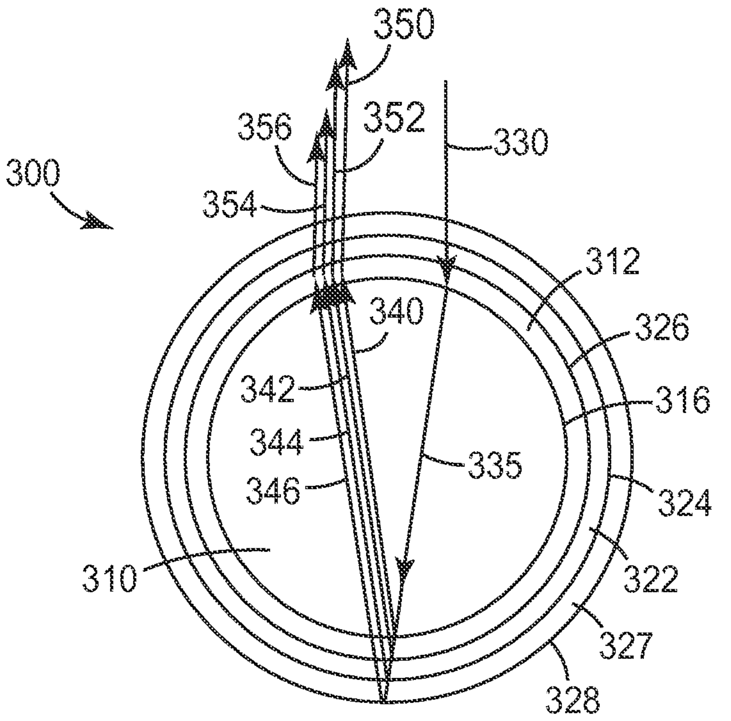
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FIG. 3

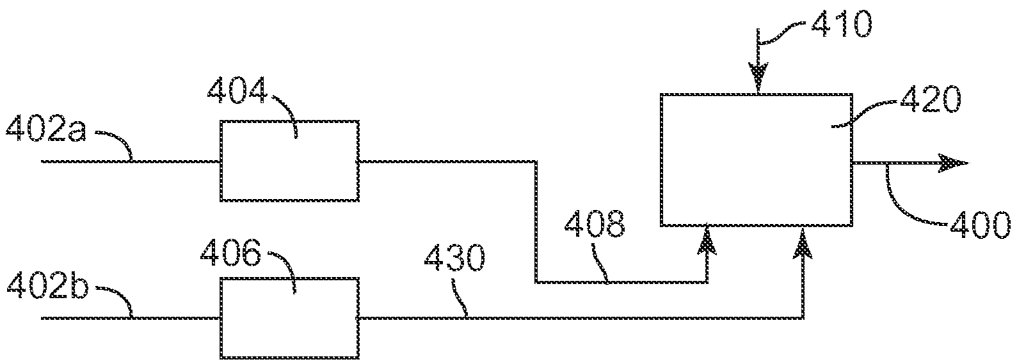
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FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2008/085340

A. CLASSIFICATION OF SUBJECT MATTER
INV. G02B5/126 G02B5/128 B29D11/00

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 B29D

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 practical, search terms used)

EPO-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 2003/193718 A1 (BUDD KENTON D [US] ET AL BUDD KENTON D [US] ET AL) 16 October 2003 (2003-10-16) the whole document	1-30
A	US 6 288 837 B1 (HUBBARD RONALD N [US]) 11 September 2001 (2001-09-11) figures 6,7	1-30
A	EP 0 949 027 A (NITTETSU MINING CO LTD [JP]; NAKATSUKA KATSUTO [JP]) 13 October 1999 (1999-10-13) paragraphs [0001], [0004], [0041]; figure 1	1-30

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

☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
20 February 2009	26/02/2009

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/US2008/085340

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