STRUCTURALLY-COLORED ARTICLES AND METHODS OF MAKING AND USING STRUCTURALLY-COLORED ARTICLES

BACKGROUND

Structural color is caused by the physical interaction of light with the micro- or nano-features of a surface and the bulk material as compared to color derived from the presence of dyes or pigments that absorb or reflect specific wavelengths of light based on the chemical properties of the dyes or pigments. Color from dyes and pigments can be problematic in a number of ways. For example, dyes and pigments and their associated chemistries for fabrication and incorporation into finished goods may not be environmentally friendly.

BRIEF DESCRIPTION OF THE DRAWINGS

Further embodiments of the present disclosure will be more readily appreciated upon review of the detailed description of its various embodiments, described below, when taken in conjunction with the accompanying drawings.

Figures 1A-1M illustrate footwear, apparel, athletic equipment, containers, electronic equipment, and vision wear that include the optical element of the present disclosure.

Figures 2A-2B illustrate side views of an exemplary optical element of the present disclosure.

DESCRIPTION

The present disclosure provides for articles that exhibit structural colors through the use of optical elements, where structural colors are visible colors produced, at least in part, through optical effects (e.g., through scattering, refraction, reflection, interference, and/or diffraction of visible wavelengths of light). The structural color imparts an aesthetically appealing color to the article without requiring the use of inks or pigments and the environmental impact associated with their use.

An exemplary article includes a film that forms an externally-facing or internally-facing portion of a component of the article, such as an article of footwear or an article of sports equipment. An optical element is disposed on a surface of the film, or within the film, where the optical element alone or in combination with an optional textured surface (e.g., a textured surface or textured structure or textured layer), or optionally in combination with a primer layer, or optionally in combination with both a textured surface and a primer layer, imparts a structural color to the component. The optional textured surface and optional primer layer can be part of the optical element, or can be separate from the optical element, but, when used with the optical element,

combine to impart the structural color. In other words, while the optical element alone can impart a first structural color, the combination of the optical element with the optional textured structure or primer layer or both can impart a second structural color, which differs from the first structural color based on a color parameter such as hue, lightness, and/or iridescence type. In such cases, the combination of the optical element and the textured surface and/or the primer layer can impart the structural color to the component.

After disposing the film and the optical element on the component, the component appears to be structurally colored (i.e., to have a new, different color than the component would have without the film and optical element), without the application of additional pigments or dyes to the article. For example, the structural color can differ from the color of the underlying surface of the component based on a color parameter such as hue, lightness, iridescence type, or any combination thereof. In particular examples, the structural color and the color of the underlying surface of the article differ both in hue and iridescence type, where the structural color is iridescent (e.g., exhibits two or more different hues when viewed from at least two different angles 15 degrees apart), and the color of the underlying surface is not iridescent. The optical element can be disposed (*e.g.*, affixed, attached, adhered, bonded, joined) to an interior or exterior-facing surface of the component. The component can then be incorporated into an article, such as a sole or an upper for an article of footwear. The sole and/or upper can be designed so that the structural color is visible in the finished article.

The present disclosure provides for an article having a film forming at least a portion of a component, the film having a first film surface, a second film surface opposing the first film surface, and a film core between the first film surface and the second film surface, wherein the first film surface or the second film surface or the film core or any combination thereof include a film polymeric material, wherein the first film surface forms the externally-facing surface of the component or the internally-facing surface of the component; and an optical element disposed on the first film surface, on the second film surface, or within the film core, wherein the optical element has a first side and a second side opposing the first side, wherein the first side of the optical element, the second side of the optical element, or both, impart a structural color to the component.

In some aspects, the film can form an exterior-facing surface of the component, with the first film surface facing the exterior of the article. The optical element as disposed on the component, imparts a structural color to externally-facing surface of the component. In some aspects, such as when the component is substantially transparent (e.g., about 70% or more, about 80% or more, about 90% or more, about 95% or more, about 99% or more), the film and optical element can be disposed on an internally-facing surface of the component, and the structural color imparted by the optical element can be visible or perceivable from the exterior of the component.

While in many examples of this disclosure, a highly iridescent structural color (e.g., a color which shifts over a wide range of hues when viewed from different angles) can be obtained, in other examples a structural color which does not shift over a wide range of hues when viewed from different angles (e.g., a structural color which does not shift hues, or which shifts over a limited number of hues depending upon the viewing angle) also can be obtained.

In one example, the present disclosure provides for an article having an optical element that, when measured according to the CIE 1976 color space under a given illumination condition at three observation angles between -15 degrees and +60 degrees, has a first color measurement at a first angle of observation having coordinates L_1^* and a_1^* and b_1^*, and a second color measurement at a second angle of observation having coordinates L_2^* and a_2^* and b_2^*, and a third color measurement at a third angle of observation having coordinates L_3^* and a_3^* and b_3^*, wherein the L_1^*, L_2^*, and L_3^* values may be the same or different, wherein the a_1^*, a_2^*, and a_3^* coordinate values may be the same or different, wherein the b_1^*, b_2^*, and b_3^* coordinate values may be the same or different, and wherein the range of the combined a_1^*, a_2^* and a_3^* values is less than about 40% of the overall scale of possible a* values.

In another example, the present disclosure provides for an article having an optical element that, when measured according to the CIE 1976 color space under a given illumination condition at two observation angles between -15 degrees and +60 degrees, has a first color measurement at a first angle of observation having coordinates L_1^* and a_1^* and b_1^*, and a second color measurement at a second angle of observation having coordinates L_2^* and a_2^* and b_2^*, wherein the L_1^* and L_2^* values may be the same or different, wherein the a_1^* and a_2^* coordinate values may be the same or different, wherein the b_1^* and b_2^* coordinate values may be the same or different, and wherein the ΔE^*_{ab} between the first color measurement and the second color measurement is less than or equal to about 100, where $\Delta E^*_{ab} = [(L_1^*-L_2^*)^2 + (a_1^*-a_2^*)^2 + (b_1^*-b_2^*)^2]^{1/2}$.

In yet another example, the present disclosure provides for an article having an optical element that, when measured according to the CIELCH color space under a given illumination condition at three observation angles between -15 degrees and +60 degrees, has a first color measurement at a first angle of observation having coordinates L_1^* and C_1^* and $h_1°$, and a second color measurement at a second angle of observation having coordinates L_2^* and C_2^* and $h_2°$, and a third color measurement at a third angle of observation having coordinates L_3^* and C_3^* and $h_3°$, wherein the L_1^*, L_2^*, and L_3^* values may be the same or different, wherein the C_1^*, C_2^*, and C_3^* coordinate values may be the same or different, wherein the $h_1°$, $h_2°$ and $h_3°$ coordinate values may be the same or different, and wherein the range of the combined $h_1°$, $h_2°$ and $h_3°$ values is less than about 60 degrees.

The present disclosure also provides a method of making a component, comprising disposing a first film surface to an externally-facing surface of a component, wherein the film comprises a film polymeric material and the film has a second film surface opposed to the first film surface and a film core between the first film surface and the second film surface; and wherein the first film surface or the second film surface includes an optical element having a first side and a second opposed to the first side, and the first side of the optical element or the second side of the optical element, or both, impart a structural color to the component. Optionally, the method can further include disposing the optical element on the film, such as on the first film surface or the second film surface, before or after disposing the film to the component.

Now having described embodiments of the present disclosure generally, additional discussion regarding embodiments will be described in greater details.

This disclosure is not limited to particular embodiments described, and as such may, of course, vary. The terminology used herein serves the purpose of describing particular embodiments only, and is not intended to be limiting, since the scope of the present disclosure will be limited only by the appended claims.

Where a range of values is provided, each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limit of that range and any other stated or intervening value in that stated range, is encompassed within the disclosure. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges and are also encompassed within the disclosure, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the disclosure.

As will be apparent to those of skill in the art upon reading this disclosure, each of the individual embodiments described and illustrated herein has discrete components and features which may be readily separated from or combined with the features of any of the other several embodiments without departing from the scope or spirit of the present disclosure. Any recited method may be carried out in the order of events recited or in any other order that is logically possible.

Embodiments of the present disclosure will employ, unless otherwise indicated, techniques of material science, chemistry, textiles, polymer chemistry, and the like, which are within the skill of the art. Such techniques are explained fully in the literature.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art of material science,

chemistry, textiles, polymer chemistry, and the like. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present disclosure, suitable methods and materials are described herein.

As used in the specification and the appended claims, the singular forms “a,” “an,” and “the” may include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a support” includes a plurality of supports. In this specification and in the claims that follow, reference will be made to a number of terms that shall be defined to have the following meanings unless a contrary intention is apparent.

The present disclosure provides for components that have structural color. The component can be incorporated into a number of different types of articles of manufacture, such as articles of footwear, components of footwear, articles of apparel, components of apparel, articles of sporting equipment, and components of sporting equipment. In particular, the articles of manufacture can include footwear (*e.g.*, dress shoes, athletic footwear, hiking boots, work boots, or the like), skates (*e.g.*, hockey skates, figure skates, in-line skates, roller skates, or the like), apparel (*e.g.*, shirts, jerseys, pants, shorts, gloves, glasses, socks, hats, caps, jackets, undergarments) or components thereof, containers (*e.g.*, backpacks, bags), and upholstery for furniture (*e.g.*, chairs, couches, car seats), bed coverings (*e.g.*, sheets, blankets), table coverings, towels, flags, tents, sails, and parachutes. In addition, the bladder can be used to produce articles or other items that are disposed on the article, where the article can be striking devices (*e.g.*, bats, rackets, sticks, mallets, golf clubs, paddles, etc.), athletic equipment (*e.g.*, golf bags, baseball and football gloves, soccer ball restriction structures), protective equipment (*e.g.*, pads, helmets, guards, visors, masks, goggles, etc.), locomotive equipment (*e.g.*, bicycles, motorcycles, skateboards, cars, trucks, boats, surfboards, skis, snowboards, etc.), balls or pucks for use in various sports, fishing or hunting equipment, furniture, electronic equipment, construction materials, eyewear, timepieces, jewelry, and the like.

The article can be an article of footwear. The article of footwear can be designed for a variety of uses, such as sporting, athletic, military, work-related, recreational, or casual use. Primarily, the article of footwear is intended for outdoor use on unpaved surfaces (in part or in whole), such as on a ground surface including one or more of grass, turf, gravel, sand, dirt, clay, mud, and the like, whether as an athletic performance surface or as a general outdoor surface. However, the article of footwear may also be desirable for indoor applications, such as indoor sports including dirt playing surfaces for example (e.g., indoor baseball fields with dirt infields).

The article of footwear is designed for use in outdoor sporting activities, such as global football/soccer, golf, American football, rugby, baseball, running, track and field, cycling (e.g., road

cycling and mountain biking), and the like. The article of footwear can optionally include traction elements (e.g., lugs, cleats, studs, and spikes as well as tread patterns) to provide traction on soft and slippery surfaces, where components of the present disclosure can be used or applied between or among the traction elements and optionally on the sides of the traction elements but on the surface of the traction element that contacts the ground or surface. Cleats, studs and spikes are commonly included in footwear designed for use in sports such as global football/soccer, golf, American football, rugby, baseball, and the like, which are frequently played on unpaved surfaces. Lugs and/or exaggerated tread patterns are commonly included in footwear including boots design for use under rugged outdoor conditions, such as trail running, hiking, and military use.

Referring to FIGS. 1A-1M, the optical element of the present disclosure may be disclosed on many types of articles, including footwear, apparel, athletic equipment, container, electronic equipment, and vision wear. The optical element is represented by hashed areas 12A'/12M'-12A"/12M". The location of the optical element is provided only to indicate one possible area that the optical element can be located. Also, two locations are illustrated in the figures, but this is done only for illustration purposes as the articles can include one or a plurality of optical elements, where the size and location can be determined based on the item. The optical element(s) located on each item can represent a number, letter, symbol, design, emblem, graphic mark, icon, logo, or the like.

The article of manufacture can be an article of apparel (i.e., a garment). The article of apparel can be an article of apparel designed for athletic or leisure activities. The article of apparel can be an article of apparel designed to provide protection from the elements (e.g., wind and/or rain), or from impacts.

The article of manufacture can be an article of sporting equipment. The article of sporting equipment can be designed for use in indoor or outdoor sporting activities, such as global football/soccer, golf, American football, rugby, baseball, running, track and field, cycling (*e.g.*, road cycling and mountain biking), and the like.

Articles of the present disclosure include the optical element that has the characteristic of producing optical effects such as structural color. The optical element includes at least one optical layer (*e.g.*, a multilayer reflector or a multilayer filter) optionally in combination with a textured surface (*e.g.*, integral to the optical element or as part of the surface of the article), optionally with a primer layer, optionally with a protective layer, or optionally with any combination of the textured surface, the primer layer, and the protective layer. The optical element or the combination of the optical element optionally with the textured surface and/or primer layer impart structural color (*e.g.*, single color, multicolor, iridescent), to the article.

Following disposing of the optical element on the article, the article appears to be colored (i.e., to have a new, different color (*e.g.*, in hue or otherwise defined herein) than the surface of the article had prior to the disposing) without the application of pigments or dyes to the article. However, pigments and/or dyes can be used in conjunction with the structural color structure to produce aesthetically pleasing effects.

As has been described herein, the structural color can include one of a number of colors. The "color" of an article as perceived by a viewer can differ from the actual color of the article, as the color perceived by a viewer is determined by the actual color of the article by the presence of optical elements which may absorb, refract, interfere with, or otherwise alter light reflected by the article, by the viewer's ability to detect the wavelengths of light reflected by the article, by the wavelengths of light used to illuminate the article, as well as other factors such as the coloration of the environment of the article, and the type of incident light (e.g., sunlight, fluorescent light, and the like). As a result, the color of an object as perceived by a viewer can differ from the actual color of the article.

Conventionally, color is imparted to man-made objects by applying colored pigments or dyes to the object. More recently, methods of imparting "structural color" to man-made objects have been developed. Structural color is color which is produced, at least in part, by microscopically structured surfaces that interfere with visible light contacting the surface. The structural color is color caused by physical phenomena including the scattering, refraction, reflection, interference, and/or diffraction of light, unlike color caused by the absorption or emission of visible light through coloring matters. For example, optical phenomena which impart structural color can include multilayer interference, thin-film interference, refraction, dispersion, light scattering, Mie scattering, diffraction, and diffraction grating. In various aspects described herein, structural color imparted to an article can be visible to a viewer having 20/20 visual acuity and normal color vision from a distance of about 1 meter from the article.

As described herein, structural color is produced, at least in part, by the optical element, as opposed to the color being produced solely by pigments and/or dyes. The coloration of a structurally-colored article can be due solely to structural color (i.e., the article, a colored portion of the article, or a colored outer layer of the article can be substantially free of pigments and/or dyes). Structural color can also be used in combination with pigments and/or dyes, for example, to alter all or a portion of a structural color.

"Hue" is commonly used to describe the property of color which is discernible based on a dominant wavelength of visible light, and is often described using terms such as magenta, red, orange, yellow, green, cyan, blue, indigo, violet, etc. or can be described in relation (*e.g.*, as

similar or dissimilar) to one of these. The hue of a color is generally considered to be independent of the intensity or lightness of the color. For example, in the Munsell color system, the properties of color include hue, value (lightness) and chroma (color purity). Particular hues are commonly associated with particular ranges of wavelengths in the visible spectrum: wavelengths in the range of about 700 to 635 nanometers are associated with red, the range of about 635 to 590 nanometers is associated with orange, the range of about 590 to 560 nanometers is associated with yellow, the range of about 560 to 520 nanometers is associated with green, the range of about 520 to 490 nanometers is associated with cyan, the range of about 490 nanometers to 450 nanometers is associated with blue, and the range of about 450 to 400 nanometers is associated with violet.

The color (including the hue) of an article as perceived by a viewer can differ from the actual color of the article. The color as perceived by a viewer depends not only on the physics of the article, but also its environment, and the characteristics of the perceiving eye and brain. For example, as the color perceived by a viewer is determined by the actual color of the article (*e.g.*, the color of the light leaving the surface of the article), by the viewer's ability to detect the wavelengths of light reflected or emitted by the article, by the wavelengths of light used to illuminate the article, as well as other factors such as the coloration of the environment of the article, and the type of incident light (*e.g.*, sunlight, fluorescent light, and the like). As a result, the color of an object as perceived by a viewer can differ from the actual color of the article.

When used in the context of structural color, one can characterize the hue of a structurally-colored article, i.e., an article that has been structurally colored by incorporating an optical element into the article, based on the wavelengths of light the structurally-colored portion of the article absorbs and reflects (*e.g.*, linearly and non-linearly). While the optical element may impart a first structural color, the presence of an optional textured surface and/or primer layer can alter the structural color. Other factors such as coatings or transparent elements may further alter the perceived structural color. The hue of the structurally colored article can include any of the hues described herein as well as any other hues or combination of hues. The structural color can be referred to as a "single hue" (i.e., the hue remains substantially the same, regardless of the angle of observation and/or illumination), or "multihued" (i.e., the hue varies depending upon the angle of observation and/or illumination). The multihued structural color can be iridescent (i.e., the hue changes gradually over two or more hues as the angle of observation or illumination changes). The hue of an iridescent multihued structural color can change gradually across all the hues in the visible spectrum (*e.g.*, like a "rainbow") as the angle of observation or illumination changes. The hue of an iridescent multihued structural color can

change gradually across a limited number of hues in the visible spectrum as the angle of observation or illumination changes, in other words, one or more hues in the visible spectrum (*e.g.*, red, orange, yellow, etc.) are not observed in the structural color as the angle of observation or illumination changes. Only one hue, or substantially one hue, in the visible spectrum may be present for a single-hued structural color. The hue of a multihued structural color can change more abruptly between a limited number of hues (*e.g.*, between 2-8 hues, or between 2-4 hues, or between 2 hues) as the angle of observation or illumination changes.

The structural color can be a multi-hued structural color in which two or more hues are imparted by the structural color.

The structural color can be iridescent multi-hued structural color in which the hue of the structural color varies over a wide number of hues (e.g., 4, 5, 6, 7, 8 or more hues) when viewed at a single viewing angle, or when viewed from two or more different viewing angles that are at least 15 degrees apart from each other.

The structural color can be limited iridescent multi-hue structural color in which the hue of the structural color varies, or varies substantially (*e.g.*, about 90 percent, about 95 percent, or about 99 percent) over a limited number of hues (e.g., 2 hues, or 3 hues) when viewed from two or more different viewing angles that are at least 15 degrees apart from each other. In some aspects, a structural color having limited iridescence is limited to two, three or four hues selected from the RYB primary colors of red, yellow and blue, optionally the RYB primary and secondary colors of red, yellow, blue, green, orange and purple, or optionally the RYB primary, secondary and tertiary colors of red, yellow, blue, green, orange purple, green-yellow, yellow-orange, orange-red, red-purple, purple-blue, and blue-green.

The structural color can be single-hue angle-independent structural color in which the hue, the hue and value, or the hue, value and chroma of the structural color is independent of or substantially (*e.g.*, about 90 percent, about 95 percent, or about 99 percent) independent of the angle of observation. For example, the single-hue angle-independent structural color can display the same hue or substantially the same hue when viewed from at least 3 different angles that are at least 15 degrees apart from each other (*e.g.*, single-hue structural color).

The structural color imparted can be a structural color having limited iridescence such that, when each color observed at each possible angle of observation is assigned to a single hue selected from the group consisting of the primary, secondary and tertiary colors on the red yellow blue (RYB) color wheel, for a single structural color, all of the assigned hues fall into a single hue group, wherein the single hue group is one of a) green-yellow, yellow, and yellow-orange; b) yellow, yellow-orange and orange; c) yellow-orange, orange, and orange-red; d)

orange-red, and red-purple; e) red, red-purple, and purple; f) red-purple, purple, and purple-blue; g) purple, purple-blue, and blue; h) purple-blue, blue, and blue-green; i) blue, blue-green and green; and j) blue-green, green, and green-yellow. In other words, in this example of limited iridescence, the hue (or the hue and the value, or the hue, value and chroma) imparted by the structural color varies depending upon the angle at which the structural color is observed, but the hues of each of the different colors viewed at the various angles of observations varies over a limited number of possible hues. The hue visible at each angle of observation can be assigned to a single primary, secondary or tertiary hue on the red yellow blue (RYB) color wheel (i.e., the group of hues consisting of red, yellow, blue, green, orange purple, green-yellow, yellow-orange, orange-red, red-purple, purple-blue, and blue-green). For example, while a plurality of different colors are observed as the angle of observation is shifted, when each observed hue is classified as one of red, yellow, blue, green, orange purple, green-yellow, yellow-orange, orange-red, red-purple, purple-blue, and blue-green, the list of assigned hues includes no more than one, two, or three hues selected from the list of RYB primary, secondary and tertiary hues. In some examples of limited iridescence, all of the assigned hues fall into a single hue group selected from hue groups a)-j), each of which include three adjacent hues on the RYB primary, secondary and tertiary color wheel. For example, all of the assigned hues can be a single hue within hue group h) (e.g., blue), or some of the assigned hues can represent two hues in hue group h) (e.g., purple-blue and blue), or can represent three hues in hue group h) (e.g., purple-blue, blue, and blue-green).

Similarly, other properties of the structural color, such as the lightness of the color, the saturation of the color, and the purity of the color, among others, can be substantially the same regardless of the angle of observation or illumination, or can vary depending upon the angle of observation or illumination. The structural color can have a matte appearance, a glossy appearance, or a metallic appearance, or a combination thereof.

As discussed above, the color (including hue) of a structurally-colored article can vary depending upon the angle at which the structurally-colored article is observed or illuminated. The hue or hues of an article can be determined by observing the article, or illuminating the article, at a variety of angles using constant lighting conditions. As used herein, the “angle” of illumination or viewing is the angle measured from an axis or plane that is orthogonal to the surface. The viewing or illuminating angles can be set between about 0 and 180 degrees. The viewing or illuminating angles can be set at 0 degrees, 15 degrees, 30 degrees, 45 degrees, 60 degrees, and -15 degrees and the color can be measured using a colorimeter or spectrophotometer (*e.g.*, Konica Minolta), which focuses on a particular area of the article to

measure the color. The viewing or illuminating angles can be set at 0 degrees, 15 degrees, 30 degrees, 45 degrees, 60 degrees, 75 degrees, 90 degrees, 105 degrees, 120 degrees, 135 degrees, 150 degrees, 165 degrees, 180 degrees, 195 degrees, 210 degrees, 225 degrees, 240 degrees, 255 degrees, 270 degrees, 285 degrees, 300 degrees, 315 degrees, 330 degrees, and 345 degrees and the color can be measured using a colorimeter or spectrophotometer. In a particular example of a multihued article colored using only structural color, when measured at 0 degrees, 15 degrees, 30 degrees, 45 degrees, 60 degrees, and -15 degrees, the hues measured for article consisted of “blue” at three of the measurement angles, “blue-green” at 2 of the measurement angles and “purple” at one of the measurement angles.

In other embodiments, the color (including hue, value and/or chroma) of a structurally-colored article does not change substantially, if at all, depending upon the angle at which the article is observed or illuminated. In instances such as this the structural color can be an angle-independent structural color in that the hue, the hue and value, or the hue, value and chroma observed is substantially independent or is independent of the angle of observation.

Various methodologies for defining color coordinate systems exist. One example is L*a*b* color space, where, for a given illumination condition, L* is a value for lightness, and a* and b* are values for color-opponent dimensions based on the CIE coordinates (CIE 1976 color space or CIELAB). In an embodiment, a structurally-colored article having structural color can be considered as having a “single” color when the change in color measured for the article is within about 10% or within about 5% of the total scale of the a* or b* coordinate of the L*a*b* scale (CIE 1976 color space) at three or more measured observation or illumination angles selected from measured at observation or illumination angles of 0 degrees, 15 degrees, 30 degrees, 45 degrees, 60 degrees, and -15 degrees. In certain embodiments, colors which, when measured and assigned values in the L*a*b* system that differ by at least 5 percent of the scale of the a* and b* coordinates, or by at least 10 percent of the scale of the a* and b* coordinates, are considered to be different colors. The structurally-colored article can have a change of less than about 40%, or less than about 30%, or less than about 20%, or less than about 10%, of the total scale of the a* coordinate or b* coordinate of the L*a*b* scale (CIE 1976 color space) at three or more measured observation or illumination angles.

A change in color between two measurements in the CIELAB space can be determined mathematically. For example, a first measurement has coordinates L_1^*, a_1^* and b_1^*, and a second measurement has coordinates L_2^*, a_2^* and b_2^*. The total difference between these two measurements on the CIELAB scale can be expressed as ΔE^*_{ab}, which is calculated as follows: $\Delta E^*_{ab} = [(L_1^*-L_2^*)^2 + (a_1^*-a_2^*)^2 + (b_1^*-b_2^*)^2]^{1/2}$. Generally speaking, if two colors have a ΔE^*_{ab} of

less than or equal to 1, the difference in color is not perceptible to human eyes, and if two colors have a ΔE^*_{ab} of greater than 100 the colors are considered to be opposite colors, while a ΔE^*_{ab} of about 2-3 is considered the threshold for perceivable color difference. In certain embodiments, a structurally colored article having structural color can be considered as having a "single" color when the ΔE^*_{ab} is less than 60, or less than 50, or less than 40, or less than 30, between three or more measured observation or illumination angles selected from measured at observation or illumination angles of 0 degrees, 15 degrees, 30 degrees, 45 degrees, 60 degrees, and -15 degrees. The structurally-colored article can have a ΔE*ab that is less than about 100, or less than about 80, or less than about 60, between two or more measured observation or illumination angles.

Another example of a color scale is the CIELCH color space, where, for a given illumination condition, L* is a value for lightness, C* is a value for chroma, and h° denotes a hue as an angular measurement. In an embodiment, a structurally-colored article having structural color can be considered as having a "single" color when the color measured for the article is less than 10 degrees different or less than 5 degrees different at the h° angular coordinate of the CIELCH color space, at three or more measured observation or illumination angles selected from measured at observation or illumination angles of 0 degrees, 15 degrees, 30 degrees, 45 degrees, 60 degrees, and -15 degrees. In certain embodiments, colors which, when measured and assigned values in the CIELCH system that vary by at least 45 degrees in the h° measurements, are considered to be different colors The structurally-colored article can have a change of less than about 60 degrees, or less than about 50 degrees, or less than about 40 degrees, or less than about 30 degrees, or less than about 20 degrees, or less than about 10 degrees, in the h° measurements of the CIELCH system at three or more measured observation or illumination angles.

Another system for characterizing color includes the "PANTONE" Matching System (Pantone LLC, Carlstadt, New Jersey, USA), which provides a visual color standard system to provide an accurate method for selecting, specifying, broadcasting, and matching colors through any medium. In an example, a structurally-colored article having a structural color can be considered as having a "single" color when the color measured for the article is within a certain number of adjacent standards, *e.g.*, within 20 adjacent PANTONE standards, at three or more measured observation or illumination angles selected from 0 degrees, 15 degrees, 30 degrees, 45 degrees, 60 degrees, and -15 degrees

Now having described color, additional details regarding the optical element are provided. As described herein, the article includes the optical element. The optical element

includes at least one optical layer. The optical element that can be or include a single or multilayer reflector or a multilayer filter. The optical element can function to modify the light that impinges thereupon so that structural color is imparted to the article. The optical element can include at least one optical layer and optionally one or more additional layers (e.g., a protective layer, the textured layer, the primer layer, a polymer layer, and the like).

The method of making the structurally colored article can include disposing (e.g., affixing, attaching, bonding, fastening, joining, appending, connecting, binding and including operably disposing etc.) the optical element onto an article (e.g., an article of footwear, an article of apparel, an article of sporting equipment, etc.). The article includes a component, and the component has a surface upon which the optical element can be disposed. The surface of the article can be made of a material such as a thermoplastic material or thermoset material, as described herein. For example, the article has a surface including a thermoplastic material (i.e., a first thermoplastic material), for example an externally-facing surface of the component or an internally-facing surface of the component (e.g., an externally-facing surface or an internally-facing surface a bladder). The optical element can be disposed onto the thermoplastic material, for example.

In an aspect, the temperature of at least a portion of the first surface of the article including the thermoplastic material is increased to a temperature at or above creep relaxation temperature (T_{cr}), Vicat softening temperature (T_{vs}), heat deflection temperature (T_{hd}), and/or melting temperature (T_m) of the thermoplastic material, for example to soften or melt the thermoplastic material. The temperature can be increased to a temperature at or above the creep relaxation temperature. The temperature can be increased to a temperature at or above the Vicat softening temperature. The temperature can be increased to a temperature at or above the heat deflection temperature. The temperature can be increased to a temperature at or above the melting temperature. While the temperature of the at least a portion of the first surface of the article is at or above the increased temperature (e.g., at or above the creep relaxation temperature, the heat deflection temperature, the Vicat softening temperature, or the melting temperature of the thermoplastic material), the optical element is disposed on (e.g., affixed to) the thermoplastic material within the at least a portion of the first surface of the article. Following the disposing, the temperature of the thermoplastic material is decreased to a temperature below its creep relaxation temperature to at least partially re-solidify the thermoplastic material. The thermoplastic material can be actively cooled (*e.g.*, removing the source that increases the temperature and actively (*e.g.*, flowing cooler gas adjacent the article

reducing the temperature of the thermoplastic material) or passively cooled (*e.g.*, removing the source that increases the temperature and allowing the thermoplastic layer to cool on its own).

The method of making the structurally-colored article can include disposing (e.g., affixing, attaching, bonding, fastening, joining, appending, connecting, binding) the optical element onto an article (e.g., an article of footwear, an article of apparel, an article of sporting equipment, etc.). The article includes a component, and the component has a surface upon which the optical element can be disposed. The surface of the article can be made of a material such as a thermoplastic material or thermoset material, as described herein. For example, the article has a surface including a thermoplastic material (i.e., a first thermoplastic material), for example an externally-facing surface of the component or an internally-facing surface of the component (e.g., an externally-facing surface or an internally-facing surface a bladder). The optical element can be disposed onto the thermoplastic material, for example.

The optical element has a first side (including the outer surface) and a second side opposing the first side (including the opposing outer surface), where the first side or the second side is adjacent the article. For example, when the optical element is used in conjunction with a component having internally-facing and externally-facing surfaces, such as a film or a bladder, the first side of the optical element can be disposed on the internally-facing surface of the component, such as in the following order: second side of the optical element/core of the optical element/first side of the optical element/internally-facing surface of the component/core of the component/externally-facing surface of the component. Alternatively, the second side the optical element can be disposed on the internally-facing surface of the component, such as in the following order: first side of the optical element/core of the optical element/second side of the optical element/internally-facing surface of the component/core of the component wall/externally-facing surface of the component. In another example, the first side of the optical element can be disposed on the externally-facing surface of the component, such as in the following order: internally-facing surface of the component/core of the component/externally-facing surface of the component/first side of the optical element/core of the optical element/second side of the optical element. Similarly, the second side of the optical element can be disposed on the externally-facing surface of the component, such as in the following order: internally-facing surface of the component/core of the component/externally-facing surface of the component/second side of the optical element/core of the optical element/first side of the optical element. In examples where the optional textured surface, the optional primer layer, or both are present, the textured surface and/or the primer layer can be located at the interface between the surface of the component and a side of the optical element.

The optical element or layers or portions thereof (*e.g.*, optical layer) can be formed using known techniques such as physical vapor deposition, electron beam deposition, atomic layer deposition, molecular beam epitaxy, cathodic arc deposition, pulsed laser deposition, sputtering deposition (*e.g.*, radio frequency, direct current, reactive, non-reactive), chemical vapor deposition, plasma-enhanced chemical vapor deposition, low pressure chemical vapor deposition and wet chemistry techniques such as layer-by-layer deposition, sol-gel deposition, Langmuir blodgett, and the like. The temperature of the first side can be adjusted using the technique to form the optical element and/or a separate system to adjust the temperature. Additional details are provided herein.

The optical layer(s) of the optical element can comprise a multilayer reflector. The multilayer reflector can be configured to have a certain reflectivity at a given wavelength of light (or range of wavelengths) depending, at least in part, on the material selection, thickness and number of the layers of the multilayer reflector. In other words, one can carefully select the materials, thicknesses, and numbers of the layers of a multilayer reflector and optionally its interaction with one or more other layers, so that it can reflect a certain wavelength of light (or range of wavelengths), to produce a desired structural color. The optical layer can include at least two adjacent layers, where the adjacent layers have different refractive indices. The difference in the index of refraction of adjacent layers of the optical layer can be about 0.0001 to 50 percent, about 0.1 to 40 percent, about 0.1 to 30 percent, about 0.1 to 20 percent, about 0.1 to 10 percent (and other ranges there between (*e.g.*, the ranges can be in increments of 0.0001 to 5 percent)). The index of refraction depends at least in part upon the material of the optical layer and can range from 1.3 to 2.6.

The optical layer can include 2 to 20 layers, 2 to 10 layer, 2 to 6 layers, or 2 to 4 layers. Each layer of the optical layer can have a thickness that is about one-fourth of the wavelength of light to be reflected to produce the desired structural color. Each layer of the optical layer can have a thickness of about 10 to 500 nanometers or about 90 to 200 nanometers. The optical layer can have at least two layers, where adjacent layers have different thicknesses and optionally the same or different refractive indices.

The optical element can comprise a multilayer filter. The multilayer filter destructively interferes with light that impinges upon the structure or article, where the destructive interference of the light and optionally interaction with one or more other layers or structures (*e.g.*, a multilayer reflector, a textured structure) impart the structural color. In this regard, the layers of the multilayer filter can be designed (*e.g.*, material selection, thickness, number of layer, and the like) so that a single wavelength of light, or a particular range of wavelengths of

light, make up the structural color. For example, the range of wavelengths of light can be limited to a range within plus or minus 30 percent or a single wavelength, or within plus or minus 20 percent of a single wavelength, or within plus or minus 10 percent of a single wavelength, or within plus or minus 5 percent or a single wavelength. The range of wavelengths can be broader to produce a more iridescent structural color.

The optical layer(s) can include multiple layers where each layer independently comprises a material selected from: the transition metals, the metalloids, the lanthanides, and the actinides, as well as nitrides, oxynitrides, sulfides, sulfates, selenides, and tellurides of these. The material can be selected to provide an index of refraction that when optionally combined with the other layers of the optical element achieves the desired result. One or more layers of the optical layer can be made of liquid crystals. Each layer of the optical layer can be made of liquid crystals. One or more layers of the optical layer can be made of a material such as: silicon dioxide, titanium dioxide, zinc sulfide, magnesium fluoride, tantalum pentoxide, aluminum oxide, or a combination thereof. Each layer of the optical layer can be made of a material such as: silicon dioxide, titanium dioxide, zinc sulfide, magnesium fluoride, tantalum pentoxide, aluminum oxide, or a combination thereof.

The optical element can be uncolored (*e.g.*, no pigments or dyes added to the structure or its layers), colored (*e.g.*, pigments and/or dyes are added to the structure or its layers (*e.g.*, dark or black color)), reflective, and/or transparent (*e.g.*, percent transmittance of 75 percent or more). The surface of the component upon which the optical element is disposed can be uncolored (*e.g.*, no pigments or dyes added to the material), colored (*e.g.*, pigments and/or dyes are added to the material (*e.g.*, dark or black color)), reflective, and/or transparent (*e.g.*, percent transmittance of 75 percent or more).

As used herein, in a transparent material, light passes through the material in straight lines and passes out of the material and one can see clearly through the material. For an opaque material, light does not pass through the material and one cannot see through the material at all. Translucent material is a material that falls between a transparent material and an opaque material, in that light passes through a translucent material but some of the light is scattered so that one cannot see clearly through the material.

The optical layer(s) can be formed in a layer-by-layer manner, where each layer has a different index of refraction. Each layer of the optical layer can be formed using known techniques such as physical vapor deposition including: chemical vapor deposition, pulsed laser deposition, evaporative deposition, sputtering deposition (*e.g.*, radio frequency, direct current, reactive, non-reactive), plasma enhanced chemical vapor deposition, electron beam deposition,

atomic layer deposition, molecular beam epitaxy, cathodic arc deposition, low pressure chemical vapor deposition and wet chemistry techniques such as layer by layer deposition, sol-gel deposition, Langmuir blodgett and the like.

As mentioned above, the optical element can include one or more layers in addition to the optical layer(s). The optical element has a first side (e.g, the side having a surface) and a second side (e.g., the side having a surface), where the first side or the second side is adjacent the surface of the component. The one or more other layers of the optical element can be on the first side and/or the second side of the optical element. For example, the optical element can include a protective layer and/or a polymeric layer such as a thermoplastic polymeric layer, where the protective layer and/or the polymeric layer can be on one or both of the first side and the second side of the optical element. In another example, the optical element can include a primer layer as described herein. One or more of the optional other layers can include a textured surface. Alternatively or in addition, one or more optical layers of the optical element can include a textured surface.

A protective layer can be disposed on the first and/or second side of the optical layer to protect the optical layer. The protective layer is more durable or more abrasion resistant than the optical layer. The protective layer is optically transparent to visible light. The protective layer can be on the first side of the optical element to protect the optical layer. All or a portion of the protective layer can include a dye or pigment in order to alter an appearance of the structural color. The protective layer can include silicon dioxide, glass, combinations of metal oxides, or mixtures of polymers. The protective layer can have a thickness of about 3 nanometers to 1 millimeter.

The protective layer can be formed using physical vapor deposition, chemical vapor deposition, pulsed laser deposition, evaporative deposition, sputtering deposition (*e.g.*, radio frequency, direct current, reactive, non-reactive), plasma enhanced chemical vapor deposition, electron beam deposition, cathodic arc deposition, low pressure chemical vapor deposition and wet chemistry techniques such as layer by layer deposition, sol-gel deposition, Langmuir blodgett, and the like. Alternatively or in addition, the protective layer can be applied by spray coating, dip coating, brushing, spin coating, doctor blade coating, and the like.

A polymeric layer can be disposed on the first and/or the second side of the optical element. The polymeric layer can be used to dispose the optical element onto an article, such as, for example, when the article does not include a thermoplastic material to adhere the optical element. The polymeric layer can comprise a polymeric adhesive material, such as a hot melt adhesive. The polymeric layer can be a thermoplastic material and can include one or more

layers. The thermoplastic material can be any one of the thermoplastic material described herein. The polymeric layer can be applied using various methodologies, such as spin coating, dip coating, doctor blade coating, and so on. The polymeric layer can have a thickness of about 3 nanometer to 1 millimeter.

As described above, one or more embodiments of the present disclosure provide articles that incorporate the optical element (*e.g.*, single or multilayer structures) on a side of a component of the article to impart structural color. The optical element can be disposed onto the thermoplastic material of the side of the article, and the side of the article can include a textile, including a textile comprising the thermoplastic material.

According to various aspects of the disclosure, an article having structural color comprises a film that forms at least a portion of a component of the article. The film has a first film surface (or side), a second film surface (side) opposing the first film surface, and a film core between the first film surface and the second film surface. The first film surface can form an externally-facing surface (or side) of the component or an internally-facing surface (or side) of the component. The film (e.g., the first film surface, the second film surface, or the film core) comprises a film polymeric material. An optical element is disposed on the first film surface, on the second film surface, or within the film core. The optical element has a first side and a second side opposing the first side, and the first side of the optical element, the second side of the optical element, or both, impart a structural color to the component.

According to an aspect, the structural color imparted by the optical element, as disposed on the component, is visible or perceivable to a viewer observing the article. For example, a structural color is visible or perceivable from an exterior of an article, if the structural color can be visible or perceivable to a viewer having 20/20 visual acuity and normal color vision from a distance of about 1 meter from the article.

According to the various aspects, the optical element, the film and the component can be arranged to impart a structural color in a desired location. In some aspects, the film can form an exterior-facing surface of the component, with the first film surface facing the exterior of the article. The optical element can be disposed on the first film surface (on the exterior-facing surface of the component). For example, the first side of the optical element can be disposed on the first film surface, so that the second side of the optical element is facing the exterior of the article, and the second side of the optical element imparts the structural color. In some embodiments, a primer layer can be disposed on the first side of the optical element, on the film, or between the first side of the optical element and the film. In aspects, a combination of the primer layer and the optical element imparts the structural color.

In some aspects, the film or its components (e.g., first film surface, film core, and/or second film surface) can be colored or colorless. In some embodiments, the film can have a color that is the same as or different from the structural color. In some aspects, the film has a color selected from the group consisting of: black, dark brown, dark red, dark orange, dark yellow, dark green, dark cyan, dark blue, dark violet, grey, dark magenta, dark indigo, tones thereof, tints thereof, shades thereof, and a combination thereof. In some aspects, the film has a color that is different from the structural color when measured according to one of: CIE 1976 color space (L*a*b* coordinates), the CIE LCH color space (L*C*h° coordinates), or the PANTONE color matching system, as described herein. In some aspects, the combination of the film and the optical element impart the structural color. In some aspects, the combination of the film, the optical element and the optional primer layer impart the structural color.

In some aspects, the film can form an exterior-facing surface of the component, with the first film surface facing the exterior of the article, and the optical element can be disposed on the film core (e.g., so the first film surface is disposed between the optical element and the exterior-facing surface of the component). For example, the optical element can be disposed on the film core so that the first side of the optical element is facing the exterior of the article. In this aspect, the first film surface can be transparent or translucent so that the first side of the optical element imparts the structural color, which is visible or perceivable through the first film surface. In some embodiments, a primer layer can be disposed on or adjacent to the second side of the optical element. In aspects, a combination of the primer layer and the optical element imparts the structural color.

In some aspects, the film can form an exterior-facing surface of the component, with the first film surface facing the exterior of the article, and the optical element can be disposed on the second film surface (e.g., so the film is disposed between the optical element and the exterior-facing surface of the component). For example, the first side of the optical element can be disposed on the second film surface, so that the first side of the optical element is facing the exterior of the article. In this aspect, the film can be transparent or translucent so that the first side of the optical element imparts the structural color, which is visible or perceivable through the film. In some embodiments, a primer layer can be disposed on or adjacent to the second side of the optical element. In aspects, a combination of the primer layer and the optical element imparts the structural color.

According to some aspects, the component is transparent, such as a transparent plate, such that an optical element disposed on an externally-facing surface or an internally-facing surface of the component is visible or perceivable from the exterior of the article. For example,

in some aspects, the film can form an interior-facing surface of the component, with the first film surface disposed on the interior-facing surface of the component, but facing or oriented toward the exterior of the article. The optical element can be disposed on the first film surface, e.g., between the first film surface and the component, or it can be disposed on the film core, or it can be disposed on the second film surface. For example, the optical element can be disposed so that the second side of the optical element is facing the exterior of the article, and the second side of the optical element imparts the structural color. In some embodiments, a primer layer can be disposed on the first side of the optical element. In aspects, a combination of the primer layer and the optical element imparts the structural color.

In several of the aspects, a textured surface can be disposed on the film, or the optical layer, for example on the first film surface, the film core, the second film surface, the first side of the optical layer, the second side of the optical layer, the component, or a combination thereof. In some aspects, a textured surface can be provided as part of a textured structure or textured layer included in or between the film, the optical element, and/or the component. In aspects the combination of the textured surface, with the optical element, and optionally the primer layer imparts the structural color.

According to various aspects of the disclosure, an article having structural color comprises a plate that forms at least a portion of a component of the article. The plate has a first plate surface (or side), a second plate surface (or side) opposing the first plate surface. The first plate surface can form an externally-facing surface of the component when the plate is included in a finished article. The article further comprise an optical element having a first side and a second side opposing the first side, wherein the first side of the optical element, the second side of the optical element, or both, impart a structural color to the component. In some aspects, the structural color imparted by the optical element is visible or perceivable to a viewer observing the article.

In some aspects, the plate can form an exterior-facing surface of the component, with the first plate surface facing the exterior of the article. The optical element can be disposed on the first plate surface (on the exterior-facing surface of the component). For example, the first side of the optical element can be disposed on the first plate surface, so that the second side of the optical element is facing the exterior of the article, and the second side of the optical element imparts the structural color. In some embodiments, a primer layer can be disposed on the first side of the optical element, on the plate, or between the first side of the optical element and the plate. In aspects, a combination of the primer layer and the optical element imparts the structural color.

In some aspects, the plate or its components (e.g., first plate surface, and/or second plate surface) can be colored or colorless. In some embodiments, the plate can have a color that is the same as or different from the structural color. In some aspects, the plate has a color selected from the group consisting of: black, dark brown, dark red, dark orange, dark yellow, dark green, dark cyan, dark blue, dark violet, grey, dark magenta, dark indigo, tones thereof, tints thereof, shades thereof, and a combination thereof. In some aspects, the plate has a color that is different from the structural color when measured according to one of: CIE 1976 color space (L*a*b* coordinates), the CIE LCH color space (L*C*h° coordinates), or the PANTONE color matching system, as described herein. In some aspects, the combination of the plate and the optical element impart the structural color. In some aspects, the combination of the plate, the optical element and the optional primer layer impart the structural color.

In some aspects, the plate can form an exterior-facing surface of the component, with the first plate surface facing the exterior of the article, and the optical element can be disposed on the second plate surface (e.g., so the plate is disposed between the optical element and the exterior-facing surface of the component). For example, the first side of the optical element can be disposed on the second plate surface, so that the first side of the optical element is facing the exterior of the article. In this aspect, the plate can be transparent or translucent so that the first side of the optical element imparts the structural color, which is visible or perceivable through the plate. In some embodiments, a primer layer can be disposed on or adjacent to the second side of the optical element. In aspects, a combination of the primer layer and the optical element imparts the structural color.

According to some aspects, the component is transparent, such as a transparent plate, such that an optical element disposed on an externally-facing surface or an internally-facing surface of the component is visible or perceivable from the exterior of the article. For example, in some aspects, the plate can form an interior-facing surface of the component, with the first plate surface disposed on the interior-facing surface of the component, but facing or oriented toward the exterior of the article. The optical element can be disposed on the first plate surface, e.g., between the first plate surface and the component, or it can be disposed on the second plate surface. For example, the optical element can be disposed so that the second side of the optical element is facing the exterior of the article, and the second side of the optical element imparts the structural color. In some embodiments, a primer layer can be disposed on the first side of the optical element. In aspects, a combination of the primer layer and the optical element imparts the structural color.

In several of the aspects, a textured surface can be disposed on the plate, or the optical layer, for example on the first plate surface, the second plate surface, the first side of the optical layer, the second side of the optical layer, the component, or a combination thereof. In some aspects, a textured surface can be provided as part of a textured structure or textured layer included in or between the plate, the optical element, and/or the component. In aspects the combination of the textured surface, with the optical element, and optionally the primer layer imparts the structural color.

Additional details will now be described for the optional textured surface. As described herein, the component includes the optical element and the optical element can include at least one optical layer and optionally a textured surface. The textured surface can be a surface of a textured structure or a textured layer. The textured surface may be provided as part of the optical element. For example, the optical element may comprise a textured layer or a textured structure that comprises the textured surface. The textured surface may be formed on the first or second side of the optical element. For example, a side of the optical layer may be formed or modified to provide a textured surface, or a textured layer or textured structure can be disposed on (e.g., affixed to) the first or second side of the optical element. The textured surface may be provided as part of the component to which the optical element is disposed. For example, the optical element may be disposed onto the surface of the component where the surface of the component is a textured surface, or the surface of the component includes a textured structure or a textured layer.

The textured surface (or a textured structure or textured layer including the textured surface) may be provided as a feature on or part of another medium, such as a transfer medium, and imparted to a side or layer of the optical element or to the surface of the component. For example, a mirror image or relief form of the textured surface may be provided on the side of a transfer medium, and the transfer medium contacts a side of the optical element or the surface of the component in a way that imparts the textured surface to the optical element or article. While the various embodiments herein may be described with respect to a textured surface of the optical element, it will be understood that the features of the textured surface, or a textured structure or textured layer, may be imparted in any of these ways.

The textured surface can contribute to the structural color resulting from the optical element. As described herein, structural coloration is imparted, at least in part, due to optical effects resulting from physical phenomena such as scattering, diffraction, reflection, interference or unequal refraction of light rays from an optical element. The textured surface (or its mirror image or relief) can include a plurality of profile features and flat or planar areas. The plurality of

profile features included in the textured surface, including their size, shape, orientation, spatial arrangement, etc., can affect the light scattering, diffraction, reflection, interference and/or refraction resulting from the optical element. The flat or planar areas included in the textured surface, including their size, shape, orientation, spatial arrangement, etc., can affect the light scattering, diffraction, reflection, interference and/or refraction resulting from the optical element. The desired structural color can be designed, at least in part, by adjusting one or more of properties of the profile features and/or flat or planar areas of the textured surface.

The profile features can extend from a side of the flat areas, so as to provide the appearance of projections and/or depressions therein. In an aspect, the flat areas can be flat planar areas. A profile feature may include various combinations of projections and depressions. For example, a profile feature may include a projection with one or more depressions therein, a depression with one or more projections therein, a projection with one or more further projections thereon, a depression with one or more further depressions therein, and the like. The flat areas do not have to be completely flat and can include texture, roughness, and the like. The texture of the flat areas may not contribute much, if any, to the imparted structural color. The texture of the flat areas typically contributes to the imparted structural color. For clarity, the profile features and flat areas are described in reference to the profile features extending above the flat areas, but the inverse (*e.g.*, dimensions, shapes, and the like) can apply when the profile features are depressions in the textured surface.

The textured surface can comprise a thermoplastic material. The profile features and the flat areas can be formed using a thermoplastic material. For example, when the thermoplastic material is heated above its softening temperature a textured surface can be formed in the thermoplastic material such as by molding, stamping, printing, compressing, cutting, etching, vacuum forming, etc., the thermoplastic material to form profile features and flat areas therein. The textured surface can be imparted on a side of a thermoplastic material. The textured surface can be formed in a layer of thermoplastic material. The profile features and the flat areas can be made of the same thermoplastic material or a different thermoplastic material.

The textured surface generally has a length dimension extending along an x-axis, and a width dimension extending along a z-axis, and a thickness dimension extending along a y-axis. The textured surface has a generally planar portion extending in a first plane that extends along the x-axis and the z-axis. A profile feature can extend outward from the first plane, so as to extend above or below the plane x. A profile feature may extend generally orthogonal to the first plane, or at an angle greater to or less than 90 degrees to the first plane.

The dimension (*e.g.*, length, width, height, diameter, depending upon the shape of the profile feature) of each profile feature can be within the nanometer to micrometer range. A textured surface can have a profile feature and/or flat area with a dimension of about 10 nanometers to about 500 micrometers. The profile feature can have dimensions in the nanometer range, *e.g.*, from about 10 nanometers to about 1000 nanometers. All of the dimensions of the profile feature (*e.g.*, length, width, height, diameter, depending on the geometry) can be in the nanometer range, *e.g.*, from about 10 nanometers to about 1000 nanometers. The textured surface can have a plurality of profile features having dimensions that are 1 micrometer or less. In this context, the phrase “plurality of the profile features” is meant to mean that about 50 percent or more, about 60 percent or more, about 70 percent or more, about 80 percent or more, about 90 percent or more, or about 99 percent or more of the profile features have a dimension in this range. The profile features can have a ratio of width:height and/or length:height dimensions of about 1:2 and 1:100, or 1:5 and 1:50, or 1:5 and 1:10.

The textured surface can have a profile feature and/or flat area with a dimension within the micrometer range of dimensions. A textured surface can have a profile feature and/or flat area with a dimension of about 1 micrometer to about 500 micrometers. All of the dimensions of the profile feature (*e.g.*, length, width, height, diameter, depending on the geometry) can be in the micrometer range, *e.g.*, from about 1 micrometer to about 500 micrometers. The textured surface can have a plurality of profile features having dimensions that are from about 1 micrometer to about 500 micrometer. In this context, the phrase “plurality of the profile features” is meant to mean that about 50 percent or more, about 60 percent or more, about 70 percent or more, about 80 percent or more, about 90 percent or more, or about 99 percent or more of the profile features have a dimension in this range. The height of the profile features (or depth if depressions) can be about 0.1 and 50 micrometers, about 1 to 5 micrometers, or 2 to 3 micrometers. The profile features can have a ratio of width:height and/or length:height dimensions of about 1:2 and 1:100, or 1:5 and 1:50, or 1:5 and 1:10.

A textured surface can have a plurality of profile features having a mixture of size dimensions within the nanometer to micrometer range (*e.g.*, a portion of the profile features are on the nanometer scale and a portion of the profile features are on the micrometer scale). A textured surface can have a plurality of profile features having a mixture of dimensional ratios. The textured surface can have a profile feature having one or more nanometer-scale projections or depressions on a micrometer-scale projection or depression.

The profile feature can have height and width dimensions that are within a factor of three of each other ($0.33w \leq h \leq 3w$ where w is the width and h is the height of the profile feature) and/or height and length dimensions that are within a factor of three of each other ($0.33l \leq h \leq 3l$ where l is the length and h is the height of the profile feature). The profile feature can have a ratio of length:width that is from about 1:3 to about 3:1, or about 1:2 to about 2:1, or about 1:1.5 to about 1.5:1, or about 1:1.2 to about 1.2:1, or about 1:1. The width and length of the profile features can be substantially the same or different.

The profile features can have a certain spatial arrangement. The spatial arrangement of the profile features may be uniform, such as spaced evenly apart or forming a pattern. The spatial arrangement can be random. Adjacent profile features can be about 1 to 100 micrometers apart or about 5 to 100 micrometers apart. The desired spacing can depend, at least in part, on the size and/or shape of the profile structures and the desired structural color effect.

The profile features can have a certain cross-sectional shape (with respect to a plane parallel the first plane). The textured surface can have a plurality of profile features having the same or similar cross-sectional shape. The textured surface has a plurality of profile features having a mixture of different cross-sectional shapes. The cross-sectional shapes of the profile features can include polygonal (*e.g.*, square or triangle or rectangle cross section), circular, semi-circular, tubular, oval, random, high and low aspect ratios, overlapping profile features, and the like.

The profile feature (*e.g.*, about 10 nanometers to 500 micrometers) can include an upper, convexly curved surface. The curved surface may extend symmetrically either side of an uppermost point.

The profile feature can include protrusions from the textured surface. The profile feature can include indents (hollow areas) formed in the textured surface. The profile feature can have a smooth, curved shape (*e.g.*, a polygonal cross-section with curved corners).

The profile features (whether protrusions or depressions) can be approximately conical or frusto-conical (*i.e.* the projections or indents may have horizontally or diagonally flattened tops) or have an approximately part-spherical surface (*e.g.*, a convex or concave surface respectively having a substantially even radius of curvature).

The profile features may have one or more sides or edges that extend in a direction that forms an angle to the first plane of the textured surface. The angle between the first plane and a side or edge of the profile feature is about 45 degrees or less, about 30 degrees or less, about 25 degrees or less, or about 20 degrees or less. The one or more sides or edges may extend in

a linear or planar orientation, or may be curved so that the angle changes as a function of distance from the first plane. The profile features may have one or more sides that include step(s) and/or flat side(s). The profile feature can have one or more sides (or portions thereof) that can be orthogonal or perpendicular to the first plane of the textured surface, or extend at an angle of about 10 degrees to 89 degrees to the first plane (90 degrees being perpendicular or orthogonal to the first plane)). The profile feature can have a side with a stepped configuration, where portions of the side can be parallel to the first plane of the textured surface or have an angle of about 1 degrees to 179 degrees (0 degrees being parallel to the first plane)).

The textured surface can have profile features with varying shapes (*e.g.*, the profile features can vary in shape, height, width and length among the profile features) or profile features with substantially uniform shapes and/or dimensions. The structural color produced by the textured surface can be determined, at least in part, by the shape, dimensions, spacing, and the like, of the profile features.

The profile features can be shaped so as to result in a portion of the surface (*e.g.*, about 25 to 50 percent or more) being about normal to the incoming light when the light is incident at the normal to the first plane of the textured surface. The profile features can be shaped so as to result in a portion of the surface (*e.g.*, about 25 to 50 percent or more) being about normal to the incoming light when the light is incident at an angle of up to 45 degrees to the first plane of the textured surface.

The spatial orientation of the profile features on the textured surface is set to reduce distortion effects, *e.g.*, resulting from the interference of one profile feature with another in regard to the structural color of the structure. Since the shape, dimension, relative orientation of the profile features can vary considerably across the textured surface, the desired spacing and/or relative positioning for a particular area (*e.g.*, in the micrometer range or about 1 to 10 square micrometers) having profile features can be appropriately determined. As discussed herein, the shape, dimension, relative orientation of the profile features affect the contours of the optical layer, so the dimensions (*e.g.*, thickness), index of refraction, number of layers in the optical element are considered when designing the textured side of the texture layer.

The profile features are located in nearly random positions relative to one another across a specific area of the textured surface (*e.g.*, in the micrometer range or about 1 to 10 square micrometers to centimeter range or about 0.5 to 5 square centimeters, and all range increments therein), where the randomness does not defeat the purpose of producing the structural color. In other words, the randomness is consistent with the spacing, shape, dimension, and relative

orientation of the profile features, the dimensions (*e.g.*, thickness), index of refraction, and number of layers in the optical layer, and the like, with the goal to achieve the structural color.

The profile features are positioned in a set manner relative to one another across a specific area of the textured surface to achieve the purpose of producing the structural color. The relative positions of the profile features do not necessarily follow a pattern, but can follow a pattern consistent with the desired structural color. As mentioned above and herein, various parameters related to the profile features, flat areas, and optical element (e.g., optical layer) can be used to position the profile features in a set manner relative to one another.

The textured surface can include micro and/or nanoscale profile features that can form gratings (*e.g.*, a diffractive grating), photonic crystal structure, a selective mirror structure, crystal fiber structures, deformed matrix structures, spiraled coiled structures, surface grating structures, and combinations thereof. The textured surface can include micro and/or nanoscale profile features that form a grating having a periodic or non-periodic design structure to impart the structural color. The micro and/or nanoscale profile features can have a peak-valley pattern of profile features and/or flat areas to produce the desired structural color. The grading can be an Echelette grating.

The profile features and the flat areas of the textured surface in the optical element can appear as topographical undulations in each layer of the optical layer. For example, referring to FIGS. 2A and 2B, an optical element 200 includes a textured structure 220 having a plurality of profile features 222 and flat areas 224. As described herein, one or more of the profile features 222 can be projections from a surface of the textured structure 220 (as shown in FIG. 2A), and/or one or more of the profile features 222 can be depressions in a surface of the textured structure 220 (as shown in FIG. 2B). One or more optical layers 240 are disposed on the side or surface of the textured structure 220 having the profile features 222 and flat areas 224. In some embodiments, the resulting topography of the one or more optical layers 240 is not identical to the topography of the textured structure 220, but rather, the one or more optical layers 240 can have elevated or depressed regions 242 which are either elevated or depressed relative to the height of the planar regions 244 and which roughly correspond to the location of the profile features 222 of the textured structure 220. The one or more optical layers 240 also have planar regions 244 that roughly correspond to the location of the flat areas 224 of the textured structure 220. Due to the presence of the elevated or depressed regions 242 and the planar regions 244, the resultant overall topography of the optical layer 240 can be that of an undulating or wave-like structure. The dimension, shape, and spacing of the profile features along with the number of layers of the optical layer, the thickness of each of the layers,

refractive index of each layer, and the type of material, can be used to produce an optical element which results in a particular structural color.

Now having described the optical element and the textured surface, additional details will be provided for the optionally present primer layer. The optical element is used to impart the structural color, where the optical element can include (e.g., as part of the optical element) or use the primer layer to produce the structural color. As described herein, the optical element can also include (e.g., as part of optical element) the optional textured surface, such as a texture layer and/or a textured structure. The combination of the optical element and the optional texture layer and the optional primer layer can form a structural color structure having one of the following designs: texture layer/primer layer/optical element or primer layer/texture layer/optical element. The primer layer can have a thickness of about 3 nanometers to 200 micrometers, or about 1 to about 200 micrometers, or about 10 to about 100 micrometers, or about 10 to about 80 micrometers. The structural color structure can include the combination of the primer layer, the optical element, and (optionally) textured surface. Selection of variables associated with the primer layer, texture layer, and the optical element, can be used to control and select the desired structural color.

The structural color structure can include the primer layer, the textured surface (optionally), and the optical element (e.g., optical layer), where the optical element is disposed on the textured surface or the primer layer, depending upon the design. The combination of the primer layer, the textured surface, and the optical element imparts structural color, to the article, where the structural color is different than the primer color, optionally with or without the application of pigments or dyes to the article. The optical element can be disposed onto the primer layer and/or the textured surface. The primer layer can include the textured surface as described herein. For example, the primer layer can be formed in a way so that it has the textured surface.

The primer layer can include a paint layer (e.g., dyes, pigments, and a combination thereof), an ink layer, a reground layer, an at least partially degraded polymer layer, a metal layer, an oxide layer, or a combination thereof. The primer layer can have a light or dark color. The primer layer can have a dark color. For example the dark color can be selected from: black, shades of black, brown, dark shades of brown, dark shades of red, dark shades of orange, dark shades of yellow, dark shades of green, dark shades of cyan, dark shades of blue, dark shades of violet, grey, dark shades of gray, dark shades of magenta, dark shades of indigo, tones, tints, shades, or hues of any of these, and a combination thereof. The color can be defined using the L*a*b system, where the value of L* can be about 70 or less, about 60 or

less, about 50 or less, about 40 or less, or about 30 or less and a* and b* coordinate values can vary across the positive and negative value scales.

The primer layer can be formed using digital printing, inkjet printing, offset printing, pad printing, screen printing, flexographic printing, heat transfer printing, physical vapor deposition including: chemical vapor deposition, pulsed laser deposition, evaporative deposition, sputtering deposition (radio frequency, direct current, reactive, non-reactive), plasma enhanced chemical vapor deposition, electron beam deposition, cathodic arc deposition, low pressure chemical vapor deposition and wet chemistry techniques such as layer by layer deposition, sol-gel deposition, or Langmuir blodgett. Alternatively or in addition, the primer layer can be applied by spray coating, dip coating, brushing, spin coating, doctor blade coating, and the like.

The primer layer can have a percent transmittance of about 40% or less, about 30% or less, about 20% or less, about 15% or less, about 10% or less, about 5% or less, or about 1% or less, where “less” can include about 0% (e.g., 0 to 0.01 or 0 to 0.1), about 1%, about 2.5%, or about 5%.

The primer layer can include a paint composition that, upon applying to the structure, forms a thin layer. The thin layer can be a solid film having a dark color, such as those described above. The paint composition can include known paint compositions that can comprise one or more of the following components: one or more paint resin, one or more polymers, one or more dyes, and one or more pigments as well as water, film-forming solvents, drying agents, thickeners, surfactants, anti-skinning agents, plasticizers, mildewcides, mar-resistant agents, anti-flooding agents, and combinations thereof.

The primer layer can comprise a reground, and at least partially degraded, polymer layer. The reground, and at least partially degraded, polymer layer can have a dark color, such as those described above.

The primer layer can include a metal layer or the oxide layer. The metal layer or the oxide layer can have a dark color, such as those described above. The oxide layer can be a metal oxide, a doped metal oxide, or a combination thereof. The metal layer, the metal oxide or the doped metal oxide can include the following: the transition metals, the metalloids, the lanthanides, and the actinides, as well as nitrides, oxynitrides, sulfides, sulfates, selenides, tellurides and a combination of these. The metal oxide can include titanium oxide, aluminum oxide, silicon dioxide, tin dioxide, chromia, iron oxide, nickel oxide, silver oxide, cobalt oxide, zinc oxide, platinum oxide, palladium oxide, vanadium oxide, molybdenum oxide, lead oxide, and combinations thereof as well as doped versions of each. In some aspects, the primer layer can consist essentially of a metal oxide. In some aspects, the primer layer can consist

essentially of titanium dioxide or silicon dioxide. In some aspects, the primer layer can consist essentially of titanium dioxide. The metal oxide can be doped with water, inert gasses (e.g., argon), reactive gasses (e.g., oxygen or nitrogen), metals, small molecules, and a combination thereof. In some aspects, the primer layer can consist essentially of a doped metal oxide or a doped metal oxynitride or both.

The primer layer can be a coating on the surface of the article. The coating can be chemically bonded (e.g., covalently bonded, ionically bonded, hydrogen bonded, and the like) to the surface of the article. The coating has been found to bond well to a surface made of a polymeric material. In an example, the surface of the article can be made of a polymeric material such as a polyurethane, including a thermoplastic polyurethane (TPU), as those described herein.

The coating can be a crosslinked coating that includes one or more colorants such as solid pigment particles or dye. The crosslinked coating can be a matrix of crosslinked polymers (e.g., a crosslinked polyester polyurethane polymer or copolymer). The colorants can be entrapped in the coating, including entrapped in the matrix of crosslinked polymers. The solid pigment particles or dye can be physically entrapped in the crosslinked polymer matrix, can be chemically bonded (e.g., covalently bonded, ionically bonded, hydrogen bonded, and the like, with the coating including the polymeric matrix or with the material forming the surface of the article to which the coating is applied), or a combination of physically bonded and chemically bonded with the coating or article. The crosslinked coating can have a thickness of about 0.01 micrometers to 1000 micrometers.

The coating can be a product (or also referred to as “crosslinked product”) of crosslinking a polymeric coating composition. The polymeric coating composition can include one or more colorants (e.g., solid pigment particles or dye) in a dispersion of polymers. The dispersion of polymers can include a water-borne dispersion of polymers such as a water-borne dispersion of polyurethane polymers, including polyester polyurethane copolymers). The water-borne dispersion of polymers can be crosslinked to entrap the colorants. The colorants can be physically entrapped in the crosslinked product, can be chemically bonded (e.g., covalently bonded, ionically bonded, hydrogen bonded, and the like, with the crosslinked copolymer matrix), or can be both physically bonded and chemically bonded with the crosslinked product. The product can be formed by crosslinking the polymeric coating composition. The product can have a thickness of about 0.01 micrometer to 1000 micrometers.

The coating can include colorants such a pigment (e.g., a solid pigment particle) or a dye. The solid pigment particles can include inorganic pigments such as metal and metal

oxides such as homogeneous inorganic pigments, core-shell pigments and the like, as well as carbon pigments (e.g., carbon black), clay earth pigments, and ultramarine pigments. The solid pigment particles can be biological or organic pigments. The solid pigment particles can be of a type known in the art as an extender pigment, which include, but are not limited to, calcium carbonate, calcium silicate, mica, clay, silica, barium sulfate and the like. The amount of the solid pigment particles sufficient to achieve the desired color intensity, shade, and opacity, can be in amounts up to about 5 percent to 25 percent or more by weight of the coating. The pigments can include those sold by KP Pigments such as pearl pigments, color shift pigments (e.g., CALYPSO, JEDI, VERO, BLACKHOLE, LYNX, ROSE GOLD, and the like), hypershift pigments, interference pigments and the like.

The colorant can be a dye such as an anionic dye, a cationic dye, a direct dye, a metal complex dye, a basic dye, a disperse dye, a solvent dye, a polymeric dye, a polymeric dye colorant, or a nonionic dye, where the coating can include one or more dyes and/or types of dyes. The dye can be a water-miscible dye. The dye can be a solubilized dye. The anionic dye can be an acid dye. The dye can be applied separately from the coating (e.g., either before or after the coating is applied and/or cured).

Acid dyes are water-soluble anionic dyes. Acid dyes are available in a wide variety, from dull tones to brilliant shades. Chemically, acid dyes include azo, anthraquinone and triarylmethane compounds. The “Color Index” (C.I.), published jointly by the Society of Dyers and Colourists (UK) and by the American Association of Textile Chemists and Colorists (USA), is the most extensive compendium of dyes and pigments for large scale coloration purposes, including 12000 products under 2000 C.I. generic names. In the C.I. each compound is presented with two numbers referring to the coloristic and chemical classification. The “generic name” refers to the field of application and/or method of coloration, while the other number is the “constitution number.” Examples of acid dyes include Acid Yellow 1, 17, 23, 25, 34, 42, 44, 49, 61, 79, 99, 110, 116, 127, 151, 158:1, 159, 166, 169, 194, 199, 204, 220, 232, 241, 246, and 250; Acid Red, 1, 14, 17, 18, 42, 57, 88, 97, 118, 119, 151, 183, 184, 186, 194, 195, 198, 211, 225, 226, 249, 251, 257, 260, 266, 278, 283, 315, 336, 337, 357, 359, 361, 362, 374, 405, 407, 414, 418, 419, and 447; Acid Violet 3, 5, 7, 17, 54, 90, and 92; Acid Brown 4, 14, 15, 45, 50, 58, 75, 97, 98, 147, 160:1, 161, 165, 191, 235, 239, 248, 282, 283, 289, 298, 322, 343, 349, 354, 355, 357, 365, 384, 392, 402, 414, 420, 422, 425, 432, and 434; Acid Orange 3, 7, 10, 19, 33, 56, 60, 61, 67, 74, 80, 86, 94, 139, 142, 144, 154, and 162; Acid Blue 1, 7, 9, 15, 92, 133, 158, 185, 193, 277, 277:1, 314, 324, 335, and 342; Acid Green 1, 12, 68:1, 73, 80, 104, 114, and 119; Acid Black 1, 26, 52, 58, 60, 64, 65, 71, 82, 84, 107, 164, 172, 187, 194, 207, 210, 234,

235, and combinations of these. The acid dyes may be used singly or in any combination in the ink composition.

Acid dyes and nonionic disperse dyes are commercially available from many sources, including Dystar L.P., Charlotte, NC under the tradename TELON , Huntsman Corporation, Woodlands, TX, USA under the tradename ERIONYL and TECTILON, BASF SE, Ludwigshafen, Germany under the tradename BASACID, and Bezema AG, Montlingen, Switzerland under the tradename Bemacid.

The colorant can include the dye and a quaternary (tetraalkyl) ammonium salt, in particular when the dye is acidic dye. The quaternary (tetraalkyl) ammonium salt can react with the dye (e.g., acid dye) to form a complexed dye that can be used in the coating. The “alkyl” group can include C1 to C10 alkyl groups. The quaternary (tetraalkyl) ammonium salt can be selected from soluble tetrabutylammonium compounds and tetrahexylammonium compounds. The counterion of the quaternary ammonium salt should be selected so that the quaternary ammonium salt forms a stable solution with the dye (e.g., anionic dye). The quaternary ammonium compound may be, for example, a halide (such as chloride, bromide or iodide), hydroxide, sulfate, sulfite, carbonate, perchlorate, chlorate, bromate, iodate, nitrate, nitrite, phosphate, phosphite, hexfluorophosphite, borate, tetrafluoroborate, cyanide, isocyanide, azide, thiosulfate, thiocyanate, or carboxylate (such as acetate or oxalate). The tetraalkylammonium compound can be or include a tetrabutylammonium halide or tetrahexylammonium halide, particularly a tetrabutylammonium bromide or chloride or a tetrahexylammonium bromide or chloride. The coating (e.g., coating, polymeric coating composition (prior to curing) can include about 1 to 15 weight percent of the quaternary ammonium salt. The molar ratio of the acid dye to the quaternary ammonium compound can range from about 3:1 to 1:3 or about 1.5:1 to 1:1.5.

The coating (e.g., coating, polymeric coating composition (prior to curing), monomers and/or polymers of the matrix of crosslinked polymers, or precursors of the coating) can include a cross-linker, which functions to crosslink the polymeric components of the coating. The cross-linker can be a water-borne cross-linker. The cross-linker can include one or more of the following: a polycarboxylic acid crosslinking agent, an aldehyde crosslinking agent, a polyisocyanate crosslinking agent, or a combination thereof. The polycarboxylic acid crosslinking agent can be a polycarboxylic acid having from 2 to 9 carbon atoms. For example, the cross-linker can include a polyacrylic acid, a polymaleic acid, a copolymer of acid, a copolymer of maleic acid, fumaric acid, or 1, 2, 3, 4-butanetetracarboxylic acid. The concentration of the cross-linker can be about 0.01 to 5 weight percent or 1 to 3 weight percent of the coating.

The coating (e.g., coating, polymeric coating composition (prior to curing), monomers and/or polymers of the matrix of crosslinked polymers, or precursors of the coating) can include a solvent. The solvent can be an organic solvent. The organic solvent can be a water-miscible organic solvent. The coating may not include water, or may be essentially free of water. For example, the solvent can be or includes acetone, ethanol, 2-propanol, ethyl acetate, isopropyl acetate, methanol, methyl ethyl ketone, 1-butanol, t-butanol, or any mixture thereof.

Additional details are provided regarding the polymeric materials referenced herein for example, the polymers described in reference to the article, components of the article, structures, layers, plates, films, bladders, foams, primer layer, coating, and the like. The polymer can be a thermoset polymer or a thermoplastic polymer. The polymer can be an elastomeric polymer, including an elastomeric thermoset polymer or an elastomeric thermoplastic polymer. The polymer can be selected from: polyurethanes (including elastomeric polyurethanes, thermoplastic polyurethanes (TPUs), and elastomeric TPUs), polyesters, polyethers, polyamides, vinyl polymers (*e.g.*, copolymers of vinyl alcohol, vinyl esters, ethylene, acrylates, methacrylates, styrene, and so on), polyacrylonitriles, polyphenylene ethers, polycarbonates, polyureas, polystyrenes, co-polymers thereof (including polyester-polyurethanes, polyether-polyurethanes, polycarbonate-polyurethanes, polyether block polyamides (PEBAs), and styrene block copolymers) , and any combination thereof, as described herein. The polymer can include one or more polymers selected from the group consisting of polyesters, polyethers, polyamides, polyurethanes, polyolefins copolymers of each, and combinations thereof.

The term “polymer” refers to a chemical compound formed of a plurality of repeating structural units referred to as monomers. Polymers often are formed by a polymerization reaction in which the plurality of structural units become covalently bonded together. When the monomer units forming the polymer all have the same chemical structure, the polymer is a homopolymer. When the polymer includes two or more monomer units having different chemical structures, the polymer is a copolymer. One example of a type of copolymer is a terpolymer, which includes three different types of monomer units. The co-polymer can include two or more different monomers randomly distributed in the polymer (*e.g.*, a random co-polymer). Alternatively, one or more blocks containing a plurality of a first type of monomer can be bonded to one or more blocks containing a plurality of a second type of monomer, forming a block copolymer. A single monomer unit can include one or more different chemical functional groups.

Polymers having repeating units which include two or more types of chemical functional groups can be referred to as having two or more segments. For example, a polymer having

repeating units of the same chemical structure can be referred to as having repeating segments. Segments are commonly described as being relatively harder or softer based on their chemical structures, and it is common for polymers to include relatively harder segments and relatively softer segments bonded to each other in a single monomeric unit or in different monomeric units. When the polymer includes repeating segments, physical interactions or chemical bonds can be present within the segments or between the segments or both within and between the segments. Examples of segments often referred to as hard segments include segments including a urethane linkage, which can be formed from reacting an isocyanate with a polyol to form a polyurethane. Examples of segments often referred to as soft segments include segments including an alkoxy functional group, such as segments including ether or ester functional groups, and polyester segments. Segments can be referred to based on the name of the functional group present in the segment (*e.g.*, a polyether segment, a polyester segment), as well as based on the name of the chemical structure which was reacted in order to form the segment (*e.g.*, a polyol-derived segment, an isocyanate-derived segment). When referring to segments of a particular functional group or of a particular chemical structure from which the segment was derived, it is understood that the polymer can contain up to 10 mole percent of segments of other functional groups or derived from other chemical structures. For example, as used herein, a polyether segment is understood to include up to 10 mole percent of non-polyether segments.

As previously described, the polymer can be a thermoplastic polymer. In general, a thermoplastic polymer softens or melts when heated and returns to a solid state when cooled. The thermoplastic polymer transitions from a solid state to a softened state when its temperature is increased to a temperature at or above its softening temperature, and a liquid state when its temperature is increased to a temperature at or above its melting temperature. When sufficiently cooled, the thermoplastic polymer transitions from the softened or liquid state to the solid state. As such, the thermoplastic polymer may be softened or melted, molded, cooled, re-softened or re-melted, re-molded, and cooled again through multiple cycles. For amorphous thermoplastic polymers, the solid state is understood to be the “rubbery” state above the glass transition temperature of the polymer. The thermoplastic polymer can have a melting temperature from about 90 degrees C to about 190 degrees C when determined in accordance with ASTM D3418-97 as described herein below, and includes all subranges therein in increments of 1 degree. The thermoplastic polymer can have a melting temperature from about 93 degrees C to about 99 degrees C when determined in accordance with ASTM D3418-97 as described herein below. The thermoplastic polymer can have a melting temperature from about

112 degrees C to about 118 degrees C when determined in accordance with ASTM D3418-97 as described herein below.

The glass transition temperature is the temperature at which an amorphous polymer transitions from a relatively brittle “glassy” state to a relatively more flexible “rubbery” state. The thermoplastic polymer can have a glass transition temperature from about -20 degrees C to about 30 degrees C when determined in accordance with ASTM D3418-97 as described herein below. The thermoplastic polymer can have a glass transition temperature (from about -13 degree C to about -7 degrees C when determined in accordance with ASTM D3418-97 as described herein below. The thermoplastic polymer can have a glass transition temperature from about 17 degrees C to about 23 degrees C when determined in accordance with ASTM D3418-97 as described herein below.

The thermoplastic polymer can have a melt flow index from about 10 to about 30 cubic centimeters per 10 minutes (cm^3/10 min) when tested in accordance with ASTM D1238-13 as described herein below at 160 degrees C using a weight of 2.16 kilograms (kg). The thermoplastic polymer can have a melt flow index from about 22 cm^3/10 min to about 28 cm^3/10 min when tested in accordance with ASTM D1238-13 as described herein below at 160 degrees C using a weight of 2.16 kg.

The thermoplastic polymer can have a cold Ross flex test result of about 120,000 to about 180,000 cycles without cracking or whitening when tested on a thermoformed plaque of the thermoplastic polymer in accordance with the cold Ross flex test as described herein below. The thermoplastic polymer can have a cold Ross flex test result of about 140,000 to about 160,000 cycles without cracking or whitening when tested on a thermoformed plaque of the thermoplastic polymer in accordance with the cold Ross flex test as described herein below.

The thermoplastic polymer can have a modulus from about 5 megaPascals (MPa) to about 100 MPa when determined on a thermoformed plaque in accordance with ASTM D412-98 Standard Test Methods for Vulcanized Rubber and Thermoplastic Rubbers and Thermoplastic Elastomers-Tension with modifications described herein below. The thermoplastic polymer can have a modulus from about 20 MPa to about 80 MPa when determined on a thermoformed plaque in accordance with ASTM D412-98 Standard Test Methods for Vulcanized Rubber and Thermoplastic Rubbers and Thermoplastic Elastomers-Tension with modifications described herein below.

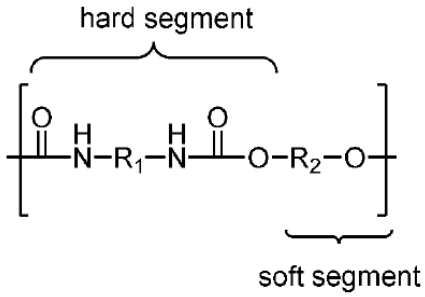
The polymer can be a thermoset polymer. As used herein, a “thermoset polymer” is understood to refer to a polymer which cannot be heated and melted, as its melting temperature is at or above its decomposition temperature. A “thermoset material” refers to a material which

comprises at least one thermoset polymer. The thermoset polymer and/or thermoset material can be prepared from a precursor (*e.g.*, an uncured or partially cured polymer or material) using thermal energy and/or actinic radiation (*e.g.*, ultraviolet radiation, visible radiation, high energy radiation, infrared radiation) to form a partially cured or fully cured polymer or material which no longer remains fully thermoplastic. In some cases, the cured or partially cured polymer or material may remain thermoelastic properties, in that it is possible to partially soften and mold the polymer or material at elevated temperatures and/or pressures, but it is not possible to melt the polymer or material. The curing can be promoted, for example, with the use of high pressure and/or a catalyst. In many examples, the curing process is irreversible since it results in cross-linking and/or polymerization reactions of the precursors. The uncured or partially cured polymers or materials can be malleable or liquid prior to curing. In some cases, the uncured or partially cured polymers or materials can be molded into their final shape, or used as adhesives. Once hardened, a thermoset polymer or material cannot be re-melted in order to be reshaped. The textured surface can be formed by partially or fully curing an uncured precursor material to lock in the textured surface..

Polyurethane

The polymer can be a polyurethane, such as a thermoplastic polyurethane (also referred to as “TPU”). Alternatively, the polymer can be a thermoset polyurethane. Additionally, polyurethane can be an elastomeric polyurethane, including an elastomeric TPU or an elastomeric thermoset polyurethane. The elastomeric polyurethane can include hard and soft segments. The hard segments can comprise or consist of urethane segments (*e.g.*, isocyanate-derived segments). The soft segments can comprise or consist of alkoxy segments (*e.g.*, polyol-derived segments including polyether segments, or polyester segments, or a combination of polyether segments and polyester segments). The polyurethane can comprise or consist essentially of an elastomeric polyurethane having repeating hard segments and repeating soft segments.

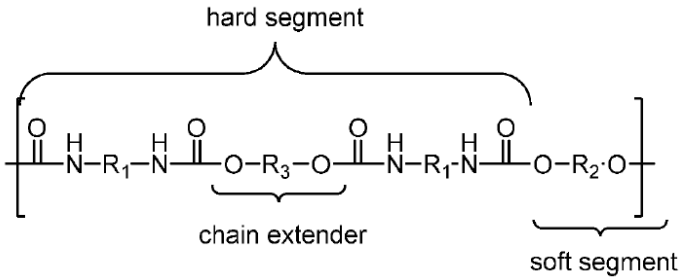
One or more of the polyurethanes can be produced by polymerizing one or more isocyanates with one or more polyols to produce polymer chains having carbamate linkages (-N(CO)O—) as illustrated below in Formula 1, where the isocyanate(s) each preferably include two or more isocyanate (—NCO) groups per molecule, such as 2, 3, or 4 isocyanate groups per molecule (although, mono-functional isocyanates can also be optionally included, *e.g.*, as chain terminating units).



(Formula 1)

Each R_1 group and R_2 group independently is an aliphatic or aromatic group. Optionally, each R_2 can be a relatively hydrophilic group, including a group having one or more hydroxyl groups.

Additionally, the isocyanates can also be chain extended with one or more chain extenders to bridge two or more isocyanates, increasing the length of the hard segment. This can produce polyurethane polymer chains as illustrated below in Formula 2, where R_3 includes the chain extender. As with each R_1 and R_2, each R_3 independently is an aliphatic or aromatic functional group..



(Formula 2)

Each R_1 group in Formulas 1 and 2 can independently include a linear or branched group having from 3 to 30 carbon atoms, based on the particular isocyanate(s) used, and can be aliphatic, aromatic, or include a combination of aliphatic portions(s) and aromatic portion(s). The term “aliphatic” refers to a saturated or unsaturated organic molecule or portion of a molecule that does not include a cyclically conjugated ring system having delocalized pi electrons. In comparison, the term “aromatic” refers to an organic molecule or portion of a molecule having a cyclically conjugated ring system with delocalized pi electrons, which exhibits greater stability than a hypothetical ring system having localized pi electrons.

Each R_1 group can be present in an amount of about 5 percent to about 85 percent by weight, from about 5 percent to about 70 percent by weight, or from about 10 percent to about 50 percent by weight, based on the total weight of the reactant compounds or monomers which form the polymer.

In aliphatic embodiments (from aliphatic isocyanate(s)), each R_1 group can include a linear aliphatic group, a branched aliphatic group, a cycloaliphatic group, or combinations thereof. For instance, each R_1 group can include a linear or branched alkylene group having from 3 to 20 carbon atoms (*e.g.*, an alkylene having from 4 to 15 carbon atoms, or an alkylene having from 6 to 10 carbon atoms), one or more cycloalkylene groups having from 3 to 8 carbon atoms (*e.g.*, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, or cyclooctyl), and combinations thereof. The term "alkene" or "alkylene" as used herein refers to a bivalent hydrocarbon. When used in association with the term C_n it means the alkene or alkylene group has "n" carbon atoms. For example, C_{1-6} alkylene refers to an alkylene group having, *e.g.*, 1, 2, 3, 4, 5, or 6 carbon atoms.

Examples of suitable aliphatic diisocyanates for producing the polyurethane polymer chains include hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), butylenediisocyanate (BDI), bisisocyanatocyclohexylmethane (HMDI), 2,2,4–trimethylhexamethylene diisocyanate (TMDI), bisisocyanatomethylcyclohexane, bisisocyanatomethyltricyclodecane, norbornane diisocyanate (NDI), cyclohexane diisocyanate (CHDI), 4,4'-dicyclohexylmethane diisocyanate (H12MDI), diisocyanatododecane, lysine diisocyanate, and combinations thereof.

The isocyanate-derived segments can include segments derived from aliphatic diisocyanate. A majority of the isocyanate-derived segments can comprise segments derived from aliphatic diisocyanates. At least 90% of the isocyanate-derived segments are derived from aliphatic diisocyanates. The isocyanate-derived segments can consist essentially of segments derived from aliphatic diisocyanates. The aliphatic diisocyanate-derived segments can be derived substantially (*e.g.*, about 50 percent or more, about 60 percent or more, about 70 percent or more, about 80 percent or more, about 90 percent or more) from linear aliphatic diisocyanates. At least 80% of the aliphatic diisocyanate-derived segments can be derived from aliphatic diisocyanates that are free of side chains. The segments derived from aliphatic diisocyanates can include linear aliphatic diisocyanates having from 2 to 10 carbon atoms.

When the isocyanate-derived segments are derived from aromatic isocyanate(s)), each R_1 group can include one or more aromatic groups, such as phenyl, naphthyl, tetrahydronaphthyl, phenanthrenyl, biphenylenyl, indanyl, indenyl, anthracenyl, and fluorenyl. Unless otherwise indicated, an aromatic group can be an unsubstituted aromatic group or a substituted aromatic group, and can also include heteroaromatic groups. "Heteroaromatic" refers to monocyclic or polycyclic (*e.g.*, fused bicyclic and fused tricyclic) aromatic ring systems, where one to four ring atoms are selected from oxygen, nitrogen, or sulfur, and the remaining

ring atoms are carbon, and where the ring system is joined to the remainder of the molecule by any of the ring atoms. Examples of suitable heteroaryl groups include pyridyl, pyrazinyl, pyrimidinyl, pyrrolyl, pyrazolyl, imidazolyl, thiazolyl, tetrazolyl, oxazolyl, isooxazolyl, thiadiazolyl, oxadiazolyl, furanyl, quinolinyl, isoquinolinyl, benzoxazolyl, benzimidazolyl, and benzothiazolyl groups.

Examples of suitable aromatic diisocyanates for producing the polyurethane polymer chains include toluene diisocyanate (TDI), TDI adducts with trimethyloylpropane (TMP), methylene diphenyl diisocyanate (MDI), xylene diisocyanate (XDI), tetramethylxylylene diisocyanate (TMXDI), hydrogenated xylene diisocyanate (HXDI), naphthalene 1,5-diisocyanate (NDI), 1,5-tetrahydronaphthalene diisocyanate, para-phenylene diisocyanate (PPDI), 3,3' –dimethyldipheny1-4, 4' –diisocyanate (DDDI), 4,4 '-dibenzyl diisocyanate (DBDI), 4-chloro-1,3-phenylene diisocyanate, and combinations thereof. The polymer chains can be substantially free of aromatic groups.

The polyurethane polymer chains can be produced from diisocyanates including HMDI, TDI, MDI, H_{12} aliphatics, and combinations thereof. For example, the polyurethane can comprise one or more polyurethane polymer chains produced from diisocyanates including HMDI, TDI, MDI, H_{12} aliphatics, and combinations thereof.

Polyurethane chains which are at least partially crosslinked or which can be crosslinked, can be used in accordance with the present disclosure. It is possible to produce crosslinked or crosslinkable polyurethane chains by reacting multi-functional isocyanates to form the polyurethane. Examples of suitable triisocyanates for producing the polyurethane chains include TDI, HDI, and IPDI adducts with trimethyloylpropane (TMP), uretdiones (i.e., dimerized isocyanates), polymeric MDI, and combinations thereof.

The R_3 group in Formula 2 can include a linear or branched group having from 2 to 10 carbon atoms, based on the particular chain extender polyol used, and can be, for example, aliphatic, aromatic, or an ether or polyether. Examples of suitable chain extender polyols for producing the polyurethane include ethylene glycol, lower oligomers of ethylene glycol (*e.g.*, diethylene glycol, triethylene glycol, and tetraethylene glycol), 1,2-propylene glycol, 1,3-propylene glycol, lower oligomers of propylene glycol (*e.g.*, dipropylene glycol, tripropylene glycol, and tetrapropylene glycol), 1,4-butylene glycol, 2,3-butylene glycol, 1,6-hexanediol, 1,8-octanediol, neopentyl glycol, 1 ,4-cyclohexanedimethanol, 2-ethyl-1,6-hexanediol, 1-methyl-1,3-propanediol, 2-methyl-1,3-propanediol, dihydroxyalkylated aromatic compounds (*e.g.*, bis(2-hydroxyethyl) ethers of hydroquinone and resorcinol, xylene-a,a-diols, bis(2-hydroxyethyl) ethers of xylene-a,a-diols, and combinations thereof.

The R_2 group in Formula 1 and 2 can include a polyether group, a polyester group, a polycarbonate group, an aliphatic group, or an aromatic group. Each R_2 group can be present in an amount of about 5 percent to about 85 percent by weight, from about 5 percent to about 70 percent by weight, or from about 10 percent to about 50 percent by weight, based on the total weight of the reactant monomers.

At least one R_2 group of the polyurethane includes a polyether segment (i.e., a segment having one or more ether groups). Suitable polyether groups include, but are not limited to, polyethylene oxide (PEO), polypropylene oxide (PPO), polytetrahydrofuran (PTHF), polytetramethylene oxide (PTMO), and combinations thereof. The term “alkyl” as used herein refers to straight chained and branched saturated hydrocarbon groups containing one to thirty carbon atoms, for example, one to twenty carbon atoms, or one to ten carbon atoms. When used in association with the term C_n it means the alkyl group has “n” carbon atoms. For example, C_4 alkyl refers to an alkyl group that has 4 carbon atoms. C_{1-7} alkyl refers to an alkyl group having a number of carbon atoms encompassing the entire range (i.e., 1 to 7 carbon atoms), as well as all subgroups (*e.g.*, 1-6, 2-7, 1-5, 3-6, 1, 2, 3, 4, 5, 6, and 7 carbon atoms). Non-limiting examples of alkyl groups include, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl (2-methylpropyl), t-butyl (1,1- dimethylethyl), 3,3-dimethylpentyl, and 2-ethylhexyl. Unless otherwise indicated, an alkyl group can be an unsubstituted alkyl group or a substituted alkyl group.

In some examples of the polyurethane, the at least one R_2 group includes a polyester group. The polyester group can be derived from the polyesterification of one or more dihydric alcohols (*e.g.*, ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 1,4-butanediol, 1,3-butanediol, 2-methylpentanediol, 1,5,diethylene glycol,1,5-pentanediol, 1,5-hexanediol, 1,2-dodecanediol, cyclohexanedimethanol, and combinations thereof) with one or more dicarboxylic acids (*e.g.*, adipic acid, succinic acid, sebacic acid, suberic acid, methyladipic acid, glutaric acid, pimelic acid, azelaic acid, thiodipropionic acid and citraconic acid and combinations thereof). The polyester group also can be derived from polycarbonate prepolymers, such as poly(hexamethylene carbonate) glycol, poly(propylene carbonate) glycol, poly(tetramethylene carbonate)glycol, and poly(nonanemethylene carbonate) glycol. Suitable polyesters can include, for example, polyethylene adipate (PEA), poly(1,4-butylene adipate), poly(tetramethylene adipate), poly(hexamethylene adipate), polycaprolactone, polyhexamethylene carbonate, poly(propylene carbonate), poly(tetramethylene carbonate), poly(nonanemethylene carbonate), and combinations thereof.

At least one R_2 group can include a polycarbonate group. The polycarbonate group can be derived from the reaction of one or more dihydric alcohols (*e.g.*, ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 1,4-butanediol, 1,3-butanediol, 2-methylpentanediol, 1,5, diethylene glycol, 1,5-pentanediol, 1,5-hexanediol, 1,2-dodecanediol, cyclohexanedimethanol, and combinations thereof) with ethylene carbonate.

The aliphatic group can be linear and can include, for example, an alkylene chain having from 1 to 20 carbon atoms or an alkenylene chain having from 1 to 20 carbon atoms (*e.g.*, methylene, ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, tridecylene, ethenylene, propenylene, butenylene, pentenylene, hexenylene, heptenylene, octenylene, nonenylene, decenylene, undecenylene, dodecenylene, tridecenylene). The term “alkene” or “alkylene” refers to a bivalent hydrocarbon. The term “alkenylene” refers to a bivalent hydrocarbon molecule or portion of a molecule having at least one double bond.

The aliphatic and aromatic groups can be substituted with one or more pendant relatively hydrophilic and/or charged groups. The pendant hydrophilic group can include one or more (*e.g.*, 2, 3, 4, 5, 6, 7, 8, 9, 10 or more) hydroxyl groups. The pendant hydrophilic group includes one or more (*e.g.*, 2, 3, 4, 5, 6, 7, 8, 9, 10 or more) amino groups. In some cases, the pendant hydrophilic group includes one or more (*e.g.*, 2, 3, 4, 5, 6, 7, 8, 9, 10 or more) carboxylate groups. For example, the aliphatic group can include one or more polyacrylic acid group. In some cases, the pendant hydrophilic group includes one or more (*e.g.*, 2, 3, 4, 5, 6, 7, 8, 9, 10 or more) sulfonate groups. In some cases, the pendant hydrophilic group includes one or more (*e.g.*, 2, 3, 4, 5, 6, 7, 8, 9, 10 or more) phosphate groups. In some examples, the pendant hydrophilic group includes one or more ammonium groups (e.g., tertiary and/or quaternary ammonium). In other examples, the pendant hydrophilic group includes one or more zwitterionic groups (*e.g.*, a betaine, such as poly(carboxybetaine (pCB) and ammonium phosphonate groups such as a phosphatidylcholine group).

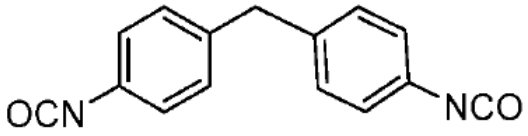
The R_2 group can include charged groups that are capable of binding to a counterion to ionically crosslink the polymer and form ionomers. For example, R_2 is an aliphatic or aromatic group having pendant amino, carboxylate, sulfonate, phosphate, ammonium, or zwitterionic groups, or combinations thereof.

When a pendant hydrophilic group is present, the pendant hydrophilic group can be at least one polyether group, such as two polyether groups. In other cases, the pendant hydrophilic group is at least one polyester. The pendant hydrophilic group can be a polylactone group (*e.g.*, polyvinylpyrrolidone). Each carbon atom of the pendant hydrophilic group can

optionally be substituted with, *e.g.*, an alkyl group having from 1 to 6 carbon atoms. The aliphatic and aromatic groups can be graft polymeric groups, wherein the pendant groups are homopolymeric groups (*e.g.*, polyether groups, polyester groups, polyvinylpyrrolidone groups).

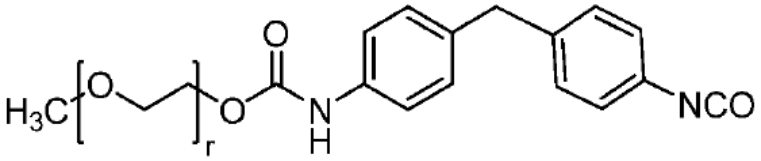
The pendant hydrophilic group can be a polyether group (*e.g.*, a polyethylene oxide (PEO) group, a polyethylene glycol (PEG) group), a polyvinylpyrrolidone group, a polyacrylic acid group, or combinations thereof.

The pendant hydrophilic group can be bonded to the aliphatic group or aromatic group through a linker. The linker can be any bifunctional small molecule (*e.g.*, one having from 1 to 20 carbon atoms) capable of linking the pendant hydrophilic group to the aliphatic or aromatic group. For example, the linker can include a diisocyanate group, as previously described herein, which when linked to the pendant hydrophilic group and to the aliphatic or aromatic group forms a carbamate bond. The linker can be 4,4'-diphenylmethane diisocyanate (MDI), as shown below.



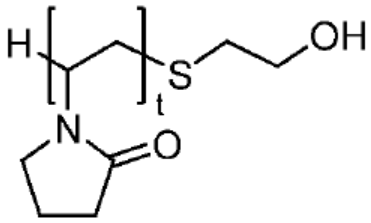
(Formula 3)

The pendant hydrophilic group can be a polyethylene oxide group and the linking group can be MDI, as shown below.



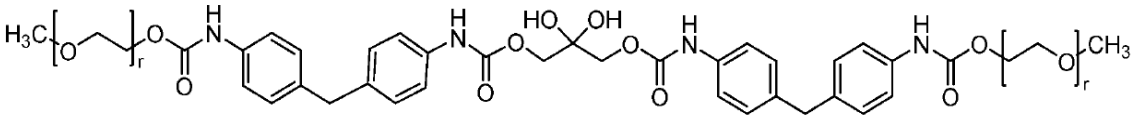
(Formula 4)

The pendant hydrophilic group can be functionalized to enable it to bond to the aliphatic or aromatic group, optionally through the linker. For example, when the pendant hydrophilic group includes an alkene group, which can undergo a Michael addition with a sulfhydryl-containing bifunctional molecule (i.e., a molecule having a second reactive group, such as a hydroxyl group or amino group), resulting in a hydrophilic group that can react with the polymer backbone, optionally through the linker, using the second reactive group. For example, when the pendant hydrophilic group is a polyvinylpyrrolidone group, it can react with the sulfhydryl group on mercaptoethanol to result in hydroxyl-functionalized polyvinylpyrrolidone, as shown below.

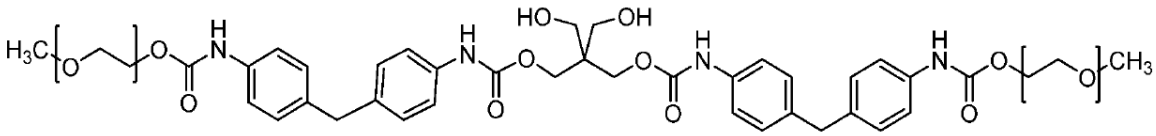


(Formula 5)

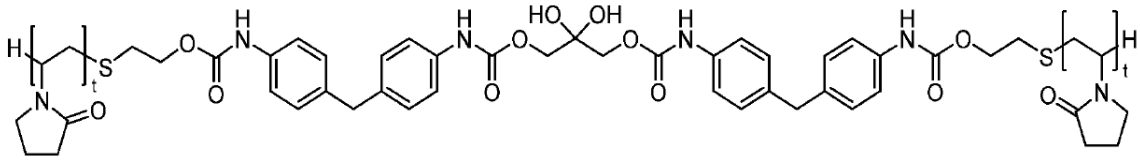
At least one R_2 group in the polyurethane can include a polytetramethylene oxide group. At least one R_2 group of the polyurethane can include an aliphatic polyol group functionalized with a polyethylene oxide group or polyvinylpyrrolidone group, such as the polyols described in E.P. Patent No. 2 462 908, which is hereby incorporated by reference. For example, the R_2 group can be derived from the reaction product of a polyol (*e.g.*, pentaerythritol or 2,2,3-trihydroxypropanol) and either MDI-derivatized methoxypolyethylene glycol (to obtain compounds as shown in Formulas 6 or 7) or with MDI-derivatized polyvinylpyrrolidone (to obtain compounds as shown in Formulas 8 or 9) that had been previously been reacted with mercaptoethanol, as shown below.



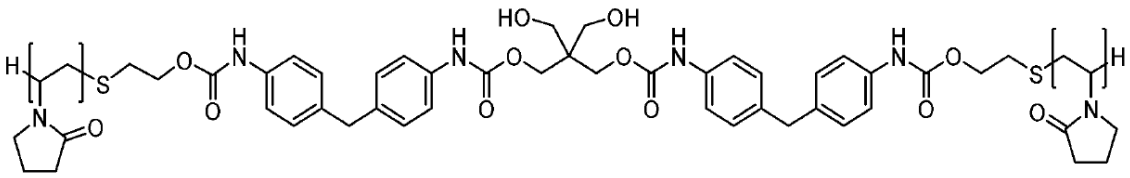
(Formula 6)



(Formula 7)

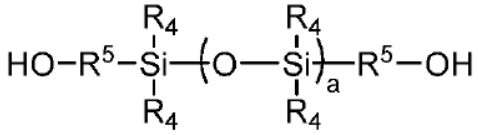


(Formula 8)



(Formula 9)

At least one R_2 of the polyurethane can be a polysiloxane, In these cases, the R_2 group can be derived from a silicone monomer of Formula 10, such as a silicone monomer disclosed in U.S. Pat. No. 5,969,076, which is hereby incorporated by reference:



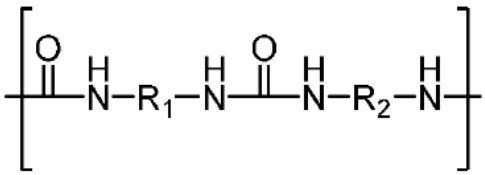
(Formula 10)

wherein: a is 1 to 10 or larger (*e.g.*, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10); each R_4 independently is hydrogen, an alkyl group having from 1 to 18 carbon atoms, an alkenyl group having from 2 to 18 carbon atoms, aryl, or polyether; and each R_5 independently is an alkylene group having from 1 to 10 carbon atoms, polyether, or polyurethane.

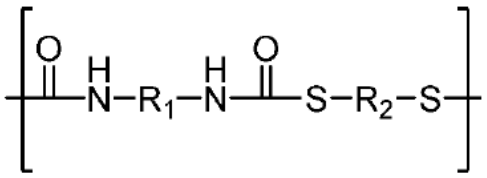
Each R_4 group can independently be a H, an alkyl group having from 1 to 10 carbon atoms, an alkenyl group having from 2 to 10 carbon atoms, an aryl group having from 1 to 6 carbon atoms, polyethylene, polypropylene, or polybutylene group. Each R_4 group can independently be selected from the group consisting of methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, s-butyl, t-butyl, ethenyl, propenyl, phenyl, and polyethylene groups.

Each R_5 group can independently include an alkylene group having from 1 to 10 carbon atoms (*e.g.*, a methylene, ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, or decylene group). Each R_5 group can be a polyether group (*e.g.*, a polyethylene, polypropylene, or polybutylene group). Each R_5 group can be a polyurethane group.

Optionally, the polyurethane can include an at least partially crosslinked polymeric network that includes polymer chains that are derivatives of polyurethane. The level of crosslinking can be such that the polyurethane retains thermoplastic properties (i.e., the crosslinked thermoplastic polyurethane can be melted and re-solidified under the processing conditions described herein). The crosslinked polyurethane can be a thermoset polymer. This crosslinked polymeric network can be produced by polymerizing one or more isocyanates with one or more polyamino compounds, polysulfhydryl compounds, or combinations thereof, as shown in Formulas 11 and 12, below:



(Formula 11)



(Formula 12)

wherein the variables are as described above. Additionally, the isocyanates can also be chain extended with one or more polyamino or polythiol chain extenders to bridge two or more isocyanates, such as previously described for the polyurethanes of Formula 2.

The polyurethane chain can be physically crosslinked to another polyurethane chain through *e.g.*, nonpolar or polar interactions between the urethane or carbamate groups of the polymers (the hard segments). The R_1 group in Formula 1, and the R_1 and R_3 groups in Formula 2, form the portion of the polymer often referred to as the “hard segment”, and the R_2 group forms the portion of the polymer often referred to as the “soft segment”. The soft segment is covalently bonded to the hard segment. The polyurethane having physically crosslinked hard and soft segments can be a hydrophilic polyurethane (i.e., a polyurethane, including a thermoplastic polyurethane, including hydrophilic groups as disclosed herein).

The polyurethane can be a thermoplastic polyurethane composed of MDI, PTMO, and 1,4-butylene glycol, as described in U.S. Patent No. 4,523,005. Commercially available polyurethanes suitable for the present use include, but are not limited to those under the tradename “SANCURE” (*e.g.*, the “SANCURE” series of polymer such as “SANCURE” 20025F) or "TECOPHILIC" (*e.g.*, TG-500, TG-2000, SP-80A-150, SP-93A-100, SP-60D-60) (Lubrizol, Countryside, IL, USA), “PELLETHANE“ 2355-85ATP and 2355-95AE (Dow Chemical Company of Midland, MI, USA.), "ESTANE" (*e.g.*, ALR G 500, or 58213; Lubrizol, Countryside, IL, USA).

One or more of the polyurethanes (*e.g.*, those used in the primer as the coating (*e.g.*, water-dispersible polyurethane)) can be produced by polymerizing one or more isocyanates with one or more polyols to produce copolymer chains having carbamate linkages (-N(C=O)O-) and one or more water-dispersible enhancing moieties, where the polymer chain includes one or more water-dispersible enhancing moieties (*e.g.*, a monomer in polymer chain). The water-dispersible polyurethane can also be referred to as “a water-borne polyurethane polymer dispersion.” The water-dispersible enhancing moiety can be added to the chain of Formula 1 or 2 (*e.g.*, within the chain and/or onto the chain as a side chain). Inclusion of the water-dispersible enhancing moiety enables the formation of a water-borne polyurethane dispersion. The term "water-borne" herein means the continuous phase of the dispersion or formulation of about 50 weight percent to 100 weight percent water, about 60 weight percent to 100 weight

percent water, about 70 weight percent to 100 weight percent water, or about 100 weight percent water. The term “water-borne dispersion” refers to a dispersion of a component (*e.g.*, polymer, cross-linker, and the like) in water without co-solvents. The co-solvent can be used in the water-borne dispersion and the co-solvent can be an organic solvent. Additional detail regarding the polymers, polyurethanes, isocyantes and the polyols are provided below.

The polyurethane (*e.g.*, a water-borne polyurethane polymer dispersion) can include one or more water-dispersible enhancing moieties. The water-dispersible enhancing moiety can have at least one hydrophilic (*e.g.*, poly(ethylene oxide)), ionic or potentially ionic group to assist dispersion of the polyurethane, thereby enhancing the stability of the dispersions. A water-dispersible polyurethane can be formed by incorporating a moiety bearing at least one hydrophilic group or a group that can be made hydrophilic (*e.g.*, by chemical modifications such as neutralization) into the polymer chain. For example, these compounds can be nonionic, anionic, cationic or zwitterionic or the combination thereof. In one example, anionic groups such as carboxylic acid groups can be incorporated into the chain in an inactive form and subsequently activated by a salt-forming compound, such as a tertiary amine. Other water-dispersible enhancing moieties can also be reacted into the backbone through urethane linkages or urea linkages, including lateral or terminal hydrophilic ethylene oxide or ureido units.

The water-dispersible enhancing moiety can be a one that includes carboxyl groups. Water-dispersible enhancing moiety that include a carboxyl group can be formed from hydroxy-carboxylic acids having the general formula $(HO)_xQ(COOH)_y$, where Q can be a straight or branched bivalent hydrocarbon radical containing 1 to 12 carbon atoms, and x and y can each independently be 1 to 3. Illustrative examples include dimethylolpropanoic acid (DMPA), dimethylol butanoic acid (DMBA), citric acid, tartaric acid, glycolic acid, lactic acid, malic acid, dihydroxymalic acid, dihydroxytartaric acid, and the like, and mixtures thereof.

The water-dispersible enhancing moiety can include reactive polymeric polyol components that contain pendant anionic groups that can be polymerized into the backbone to impart water dispersible characteristics to the polyurethane. Anionic functional polymeric polyols can include anionic polyester polyols, anionic polyether polyols, and anionic polycarbonate polyols, where additional detail is provided in U.S. Pat. No. 5,334,690.

The water-dispersible enhancing moiety can include a side chain hydrophilic monomer. For example, the water-dispersible enhancing moiety including the side chain hydrophilic monomer can include alkylene oxide polymers and copolymers in which the alkylene oxide groups have from 2-10 carbon atoms as shown in U.S. Patent 6,897,281. Additional types of water-dispersible enhancing moieties can include thioglycolic acid, 2,6-dihydroxybenzoic acid,

sulfoisophthalic acid, polyethylene glycol, and the like, and mixtures thereof. Additional details regarding water-dispersible enhancing moieties can be found in U.S. Patent 7,476,705.

Polyamides

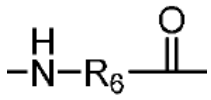
The polymer can comprise a polyamide, such as a thermoplastic polyamide, or a thermoset polyamide. The polyamide can be an elastomeric polyamide, including an elastomeric thermoplastic polyamide or an elastomeric thermoset polyamide. The polyamide can be a polyamide homopolymer having repeating polyamide segments of the same chemical structure. Alternatively, the polyamide can comprise a number of polyamide segments having different polyamide chemical structures (*e.g.*, polyamide 6 segments, polyamide 11 segments, polyamide 12 segments, polyamide 66 segments, etc.). The polyamide segments having different chemical structure can be arranged randomly, or can be arranged as repeating blocks.

The polyamide can be a co-polyamide (i.e., a co-polymer including polyamide segments and non-polyamide segments). The polyamide segments of the co-polyamide can comprise or consist of polyamide 6 segments, polyamide 11 segments, polyamide 12 segments, polyamide 66 segments, or any combination thereof. The polyamide segments of the co-polyamide can be arranged randomly, or can be arranged as repeating segments. The polyamide segments can comprise or consist of polyamide 6 segments, or polyamide 12 segments, or both polyamide 6 segment and polyamide 12 segments. In the example where the polyamide segments of the co-polyamide include of polyamide 6 segments and polyamide 12 segments, the segments can be arranged randomly. The non-polyamide segments of the co-polyamide can comprise or consist of polyether segments, polyester segments, or both polyether segments and polyester segments. The co-polyamide can be a block co-polyamide, or can be a random co-polyamide. The copolyamide can be formed from the polycondensation of a polyamide oligomer or prepolymer with a second oligomer prepolymer to form a copolyamide (i.e., a co-polymer including polyamide segments. Optionally, the second prepolymer can be a hydrophilic prepolymer.

The polyamide can be a polyamide-containing block co-polymer. For example, the block co-polymer can have repeating hard segments, and repeating soft segments. The hard segments can comprise polyamide segments, and the soft segments can comprise non-polyamide segments. The polyamide-containing block co-polymer can be an elastomeric co-polyamide comprising or consisting of polyamide-containing block co-polymers having repeating hard segments and repeating soft segments. In block co-polymers, including block co-polymers having repeating hard segments and soft segments, physical crosslinks can be present within the segments or between the segments or both within and between the segments.

The polyamide itself, or the polyamide segment of the polyamide-containing block co-polymer can be derived from the condensation of polyamide prepolymers, such as lactams, amino acids, and/or diamino compounds with dicarboxylic acids, or activated forms thereof. The resulting polyamide segments include amide linkages (—(CO)NH—). The term “amino acid” refers to a molecule having at least one amino group and at least one carboxyl group. Each polyamide segment of the polyamide can be the same or different.

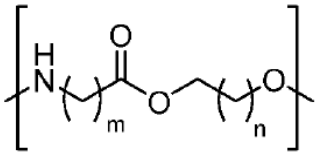
The polyamide or the polyamide segment of the polyamide-containing block co-polymer can be derived from the polycondensation of lactams and/or amino acids, and can include an amide segment having a structure shown in Formula 13, below, wherein R_6 group represents the portion of the polyamide derived from the lactam or amino acid.



(Formula 13)

The R_6 group can be derived from a lactam. The R_6 group can be derived from a lactam group having from 3 to 20 carbon atoms, or a lactam group having from 4 to 15 carbon atoms, or a lactam group having from 6 to 12 carbon atoms. The R_6 group can be derived from caprolactam or laurolactam. The R_6 group can be derived from one or more amino acids. The R_6 group can be derived from an amino acid group having from 4 to 25 carbon atoms, or an amino acid group having from 5 to 20 carbon atoms, or an amino acid group having from 8 to 15 carbon atoms. The R_6 group can be derived from 12-aminolauric acid or 11-aminoundecanoic acid.

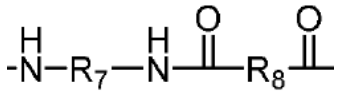
Optionally, in order to increase the relative degree of hydrophilicity of the polyamide-containing block co-polymer, Formula 13 can include a polyamide-polyether block copolymer segment, as shown below:



(Formula 14)

wherein m is 3-20, and n is 1-8. Optionally, m is 4-15, or 6-12 (*e.g.*, 6, 7, 8, 9, 10, 11, or 12), and n is 1, 2, or 3. For example, m can be 11 or 12, and n can be 1 or 3. The polyamide or the polyamide segment of the polyamide-containing block co-polymer can be derived from the condensation of diamino compounds with dicarboxylic acids, or activated forms thereof, and can

include an amide segment having a structure shown in Formula 15, below, wherein the R_7 group represents the portion of the polyamide derived from the diamino compound, and the R_8 group represents the portion derived from the dicarboxylic acid compound:

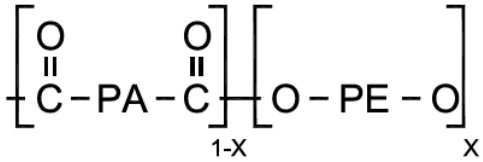


(Formula 15)

The R_7 group can be derived from a diamino compound that includes an aliphatic group having from 4 to 15 carbon atoms, or from 5 to 10 carbon atoms, or from 6 to 9 carbon atoms. The diamino compound can include an aromatic group, such as phenyl, naphthyl, xylyl, and tolyl. Suitable diamino compounds from which the R_7 group can be derived include, but are not limited to, hexamethylene diamine (HMD), tetramethylene diamine, trimethyl hexamethylene diamine (TMD),m-xylylene diamine (MXD), and 1,5-pentamine diamine. The R_8 group can be derived from a dicarboxylic acid or activated form thereof, including an aliphatic group having from 4 to 15 carbon atoms, or from 5 to 12 carbon atoms, or from 6 to 10 carbon atoms. The dicarboxylic acid or activated form thereof from which R_8 can be derived includes an aromatic group, such as phenyl, naphthyl, xylyl, and tolyl groups. Suitable carboxylic acids or activated forms thereof from which R_8 can be derived include adipic acid, sebacic acid, terephthalic acid, and isophthalic acid. The polyamide chain can be substantially free of aromatic groups.

Each polyamide segment of the polyamide (including the polyamide-containing block co-polymer) can be independently derived from a polyamide prepolymer selected from the group consisting of 12-aminolauric acid, caprolactam, hexamethylene diamine and adipic acid.

The polyamide can comprise or consist essentially of a poly(ether-block-amide). The poly(ether-block-amide) can be formed from the polycondensation of a carboxylic acid terminated polyamide prepolymer and a hydroxyl terminated polyether prepolymer to form a poly(ether-block-amide), as shown in Formula 16:



(Formula 16)

The poly(ether block amide) polymer can be prepared by polycondensation of polyamide blocks containing reactive ends with polyether blocks containing reactive ends. Examples include: 1) polyamide blocks containing diamine chain ends with polyoxyalkylene blocks

containing carboxylic chain ends; 2) polyamide blocks containing dicarboxylic chain ends with polyoxyalkylene blocks containing diamine chain ends obtained by cyanoethylation and hydrogenation of aliphatic dihydroxylated alpha-omega polyoxyalkylenes known as polyether diols; 3) polyamide blocks containing dicarboxylic chain ends with polyether diols, the products obtained in this particular case being polyetheresteramides. The polyamide block of the poly(ether-block-amide) can be derived from lactams, amino acids, and/or diamino compounds with dicarboxylic acids as previously described. The polyether block can be derived from one or more polyethers selected from the group consisting of polyethylene oxide (PEO), polypropylene oxide (PPO), polytetrahydrofuran (PTHF), polytetramethylene oxide (PTMO), and combinations thereof.

The poly(ether block amide) polymers can include those comprising polyamide blocks comprising dicarboxylic chain ends derived from the condensation of α, ω-aminocarboxylic acids, of lactams or of dicarboxylic acids and diamines in the presence of a chain-limiting dicarboxylic acid. In poly(ether block amide) polymers of this type, a α, ω-aminocarboxylic acid such as aminoundecanoic acid can be used; a lactam such as caprolactam or lauryllactam can be used; a dicarboxylic acid such as adipic acid, decanedioic acid or dodecanedioic acid can be used; and a diamine such as hexamethylenediamine can be used; or various combinations of any of the foregoing. The copolymer can comprise polyamide blocks comprising polyamide 12 or of polyamide 6.

The poly(ether block amide) polymers can include those comprising polyamide blocks derived from the condensation of one or more α, ω-aminocarboxylic acids and/or of one or more lactams containing from 6 to 12 carbon atoms in the presence of a dicarboxylic acid containing from 4 to 12 carbon atoms, and are of low mass, i.e., they have a number-average molecular weight of from 400 to 1000. In poly(ether block amide) polymers of this type, an α, ω-aminocarboxylic acid such as aminoundecanoic acid or aminododecanoic acid can be used; a dicarboxylic acid such as adipic acid, sebacic acid, isophthalic acid, butanedioic acid, 1,4-cyclohexyldicarboxylic acid, terephthalic acid, the sodium or lithium salt of sulphoisophthalic acid, dimerized fatty acids (these dimerized fatty acids have a dimer content of at least 98 weight percent and are preferably hydrogenated) and dodecanedioic acid HOOC—$(CH_2)_{10}$—COOH can be used; and a lactam such as caprolactam and lauryllactam can be used; or various combinations of any of the foregoing. The copolymer can comprise polyamide blocks obtained by condensation of lauryllactam in the presence of adipic acid or dodecanedioic acid and with a number average molecular weight of at least 750 have a melting temperature of from about 127 to about 130 degrees C. The various constituents of the polyamide block and their

proportion can be chosen in order to obtain a melting point of less than 150 degrees C, or from about 90 degrees C to about 135 degrees C.

The poly(ether block amide) polymers can include those comprising polyamide blocks derived from the condensation of at least one α, ω-aminocarboxylic acid (or a lactam), at least one diamine and at least one dicarboxylic acid. In copolymers of this type, a α,ω-aminocarboxylic acid, the lactam and the dicarboxylic acid can be chosen from those described herein above and the diamine that can be used can include an aliphatic diamine containing from 6 to 12 atoms and can be acyclic and/or saturated cyclic such as, but not limited to, hexamethylenediamine, piperazine, 1-aminoethylpiperazine, bisaminopropylpiperazine, tetramethylenediamine, octamethylene-diamine, decamethylenediamine, dodecamethylenediamine, 1,5-diaminohexane, 2,2,4-trimethyl-1,6-diaminohexane, diamine polyols, isophoronediamine (IPD), methylpentamethylenediamine (MPDM), bis(aminocyclohexyl)methane (BACM) and bis(3-methyl-4-aminocyclohexyl)methane (BMACM).

The polyamide can be a thermoplastic polyamide and the constituents of the polyamide block and their proportion can be chosen in order to obtain a melting temperature of less than 150 degrees C, such as a melting point of from about 90 degrees C to about 135 degrees C. The various constituents of the thermoplastic polyamide block and their proportion can be chosen in order to obtain a melting point of less than 150 degrees C, such as from about and 90 degrees C to about 135 degrees C.

The number average molar mass of the polyamide blocks can be from about 300 grams per mole to about 15,000 grams per mole, from about 500 grams per mole to about 10,000 grams per mole, from about 500 grams per mole to about 6,000 grams per mole, from about 500 grams per mole to about 5,000 grams per mole, or from about 600 grams per mole to about 5,000 grams per mole. The number average molecular weight of the polyether block can range from about 100 to about 6,000, from about 400 to about 3000, or from about 200 to about 3,000. The polyether (PE) content (x) of the poly(ether block amide) polymer can be from about 0.05 to about 0.8 (i.e., from about 5 mole percent to about 80 mole percent). The polyether blocks can be present in the polyamide in an amount of from about 10 weight percent to about 50 weight percent, from about 20 weight percent to about 40 weight percent, or from about 30 weight percent to about 40 weight percent. The polyamide blocks can be present in the polyamide in an amount of from about 50 weight percent to about 90 weight percent, from about 60 weight percent to about 80 weight percent, or from about 70 weight percent to about 90 weight percent.

The polyether blocks can contain units other than ethylene oxide units, such as, for example, propylene oxide or polytetrahydrofuran (which leads to polytetramethylene glycol

sequences). It is also possible to use simultaneously PEG blocks, i.e., those consisting of ethylene oxide units, polypropylene glycol (PPG) blocks, i.e. those consisting of propylene oxide units, and poly(tetramethylene ether)glycol (PTMG) blocks, i.e. those consisting of tetramethylene glycol units, also known as polytetrahydrofuran. PPG or PTMG blocks are advantageously used. The amount of polyether blocks in these copolymers containing polyamide and polyether blocks can be from about 10 weight percent to about 50 weight percent of the copolymer, or from about 35 weight percent to about 50 weight percent.

The copolymers containing polyamide blocks and polyether blocks can be prepared by any means for attaching the polyamide blocks and the polyether blocks. In practice, two processes are essentially used, one being a 2-step process and the other a one-step process.

In the two-step process, the polyamide blocks having dicarboxylic chain ends are prepared first, and then, in a second step, these polyamide blocks are linked to the polyether blocks. The polyamide blocks having dicarboxylic chain ends are derived from the condensation of polyamide precursors in the presence of a chain-stopper dicarboxylic acid. If the polyamide precursors are only lactams or α,ω-aminocarboxylic acids, a dicarboxylic acid is added. If the precursors already comprise a dicarboxylic acid, this is used in excess with respect to the stoichiometry of the diamines. The reaction usually takes place from about 180 to about 300 degrees C, such as from about 200 degrees to about 290 degrees C, and the pressure in the reactor can be set from about 5 to about 30 bar and maintained for approximately 2 to 3 hours. The pressure in the reactor is slowly reduced to atmospheric pressure and then the excess water is distilled off, for example for one or two hours.

Once the polyamide having carboxylic acid end groups has been prepared, the polyether, the polyol and a catalyst are then added. The total amount of polyether can be divided and added in one or more portions, as can the catalyst. The polyether is added first and the reaction of the OH end groups of the polyether and of the polyol with the COOH end groups of the polyamide starts, with the formation of ester linkages and the elimination of water. Water is removed as much as possible from the reaction mixture by distillation and then the catalyst is introduced in order to complete the linking of the polyamide blocks to the polyether blocks. This second step takes place with stirring, preferably under a vacuum of at least 50 millibar (5000 Pascals) at a temperature such that the reactants and the copolymers obtained are in the molten state. By way of example, this temperature can be from about 100 to about 400 degrees C, such as from about 200 to about 250 degrees C. The reaction is monitored by measuring the torque exerted by the polymer melt on the stirrer or by measuring the electric power consumed by the stirrer. The end of the reaction is determined by the value of the torque or of the target

power. The catalyst is defined as being any product which promotes the linking of the polyamide blocks to the polyether blocks by esterification. The catalyst can be a derivative of a metal (M) chosen from the group formed by titanium, zirconium and hafnium. The derivative can be prepared from a tetraalkoxides consistent with the general formula $M(OR)_4$, in which M represents titanium, zirconium or hafnium and R, which can be identical or different, represents linear or branched alkyl radicals having from 1 to 24 carbon atoms.

The catalyst can comprise a salt of the metal (M), particularly the salt of (M) and of an organic acid and the complex salts of the oxide of (M) and/or the hydroxide of (M) and an organic acid. The organic acid can be formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, caprylic acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, cyclohexanecarboxylic acid, phenylacetic acid, benzoic acid, salicylic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid, fumaric acid, phthalic acid or crotonic acid. The organic acid can be an acetic acid or a propionic acid. M can be zirconium and such salts are called zirconyl salts, *e.g.*, the commercially available product sold under the name zirconyl acetate.

The weight proportion of catalyst can vary from about 0.01 to about 5 percent of the weight of the mixture of the dicarboxylic polyamide with the polyetherdiol and the polyol. The weight proportion of catalyst can vary from about 0.05 to about 2 percent of the weight of the mixture of the dicarboxylic polyamide with the polyetherdiol and the polyol.

In the one-step process, the polyamide precursors, the chain stopper and the polyether are blended together; what is then obtained is a polymer having essentially polyether blocks and polyamide blocks of highly variable length, but also the various reactants that have reacted randomly, which are distributed randomly along the polymer chain. They are the same reactants and the same catalyst as in the two-step process described above. If the polyamide precursors are only lactams, it is advantageous to add a little water. The copolymer has essentially the same polyether blocks and the same polyamide blocks, but also a small portion of the various reactants that have reacted randomly, which are distributed randomly along the polymer chain. As in the first step of the two-step process described above, the reactor is closed and heated, with stirring. The pressure established is from about 5 to about 30 bar. When the pressure no longer changes, the reactor is put under reduced pressure while still maintaining vigorous stirring of the molten reactants. The reaction is monitored as previously in the case of the two-step process.

The proper ratio of polyamide to polyether blocks can be found in a single poly(ether block amide), or a blend of two or more different composition poly(ether block amide)s can be

used with the proper average composition. It can be useful to blend a block copolymer having a high level of polyamide groups with a block copolymer having a higher level of polyether blocks, to produce a blend having an average level of polyether blocks of about 20 to about 40 weight percent of the total blend of poly(amid-block-ether) copolymers, or about 30 to about 35 weight percent. The copolymer can comprise a blend of two different poly(ether-block-amide)s comprising at least one block copolymer having a level of polyether blocks below 35 weight percent, and a second poly(ether-block-amide) having at least 45 weight percent of polyether blocks.

Exemplary commercially available copolymers include, but are not limited to, those available under the tradenames of “VESTAMID” (Evonik Industries, Essen, Germany); “PLATAMID” (Arkema, Colombes, France), *e.g.*, product code H2694; “PEBAX” (Arkema), *e.g.*, product code “PEBAX MH1657” and “PEBAX MV1074”; “PEBAX RNEW” (Arkema); “GRILAMID” (EMS-Chemie AG, Domat-Ems, Switzerland), or also to other similar materials produced by various other suppliers.

The polyamide can be physically crosslinked through, *e.g.*, nonpolar or polar interactions between the polyamide groups of the polymers. In examples where the polyamide is a copolyamide, the copolyamide can be physically crosslinked through interactions between the polyamide groups, and optionally by interactions between the copolymer groups. When the co-polyamide is physically crosslinked through interactions between the polyamide groups, the polyamide segments can form the portion of the polymer referred to as the hard segment, and copolymer segments can form the portion of the polymer referred to as the soft segment. For example, when the copolyamide is a poly(ether-block-amide), the polyamide segments form the hard segments of the polymer, and polyether segments form the soft segments of the polymer. Therefore, in some examples, the polymer can include a physically crosslinked polymeric network having one or more polymer chains with amide linkages.

The polyamide segment of the co-polyamide can include polyamide-11 or polyamide-12 and the polyether segment can be a segment selected from the group consisting of polyethylene oxide, polypropylene oxide, and polytetramethylene oxide segments, and combinations thereof.

The polyamide can be partially or fully covalently crosslinked, as previously described herein. In some cases, the degree of crosslinking present in the polyamide is such that, when it is thermally processed, *e.g.*, in the form of a yarn or fiber to form the articles of the present disclosure, the partially covalently crosslinked thermoplastic polyamide retains sufficient thermoplastic character that the partially covalently crosslinked thermoplastic polyamide is

melted during the processing and re-solidifies. In other cases, the crosslinked polyamide is a thermoset polymer.

Polyesters

The polymers can comprise a polyester. The polyester can comprise a thermoplastic polyester, or a thermoset polyester. Additionally, the polyester can be an elastomeric polyester, including a thermoplastic polyester or a thermoset elastomeric polyester. The polyester can be formed by reaction of one or more carboxylic acids, or its ester-forming derivatives, with one or more bivalent or multivalent aliphatic, alicyclic, aromatic or araliphatic alcohols or a bisphenol. The polyester can be a polyester homopolymer having repeating polyester segments of the same chemical structure. Alternatively, the polyester can comprise a number of polyester segments having different polyester chemical structures (*e.g.*, polyglycolic acid segments, polylactic acid segments, polycaprolactone segments, polyhydroxyalkanoate segments, polyhydroxybutyrate segments, etc.). The polyester segments having different chemical structure can be arranged randomly, or can be arranged as repeating blocks.

Exemplary carboxylic acids that can be used to prepare a polyester include, but are not limited to, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, nonane dicarboxylic acid, decane dicarboxylic acid, undecane dicarboxylic acid, terephthalic acid, isophthalic acid, alkyl-substituted or halogenated terephthalic acid, alkyl-substituted or halogenated isophthalic acid, nitro-terephthalic acid, 4,4'-diphenyl ether dicarboxylic acid, 4,4'-diphenyl thioether dicarboxylic acid, 4,4'-diphenyl sulfone-dicarboxylic acid, 4,4'-diphenyl alkylenedicarboxylic acid, naphthalene-2,6-dicarboxylic acid, cyclohexane-1,4-dicarboxylic acid and cyclohexane-1,3-dicarboxylic acid. Exemplary diols or phenols suitable for the preparation of the polyester include, but are not limited to, ethylene glycol, diethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, 1,2-propanediol, 2,2-dimethyl-1,3-propanediol, 2,2,4-trimethylhexanediol, p-xylenediol, 1,4-cyclohexanediol, 1,4-cyclohexane dimethanol, and bis-phenol A.

The polyester can be a polybutylene terephthalate (PBT), a polytrimethylene terephthalate, a polyhexamethylene terephthalate, a poly-1,4-dimethylcyclohexane terephthalate, a polyethylene terephthalate (PET), a polyethylene isophthalate (PEI), a polyarylate (PAR), a polybutylene naphthalate (PBN), a liquid crystal polyester, or a blend or mixture of two or more of the foregoing.

The polyester can be a co-polyester (i.e., a co-polymer including polyester segments and non-polyester segments). The co-polyester can be an aliphatic co-polyester (i.e., a co-polyester in which both the polyester segments and the non-polyester segments are aliphatic).

Alternatively, the co-polyester can include aromatic segments. The polyester segments of the co-polyester can comprise or consist essentially of polyglycolic acid segments, polylactic acid segments, polycaprolactone segments, polyhydroxyalkanoate segments, polyhydroxybutyrate segments, or any combination thereof. The polyester segments of the co-polyester can be arranged randomly, or can be arranged as repeating blocks.

For example, the polyester can be a block co-polyester having repeating blocks of polymeric units of the same chemical structure which are relatively harder (hard segments), and repeating blocks of the same chemical structure which are relatively softer (soft segments). In block co-polyesters, including block co-polyesters having repeating hard segments and soft segments, physical crosslinks can be present within the blocks or between the blocks or both within and between the blocks. The polymer can comprise or consist essentially of an elastomeric co-polyester having repeating blocks of hard segments and repeating blocks of soft segments.

The non-polyester segments of the co-polyester can comprise or consist essentially of polyether segments, polyamide segments, or both polyether segments and polyamide segments. The co-polyester can be a block co-polyester, or can be a random co-polyester. The co-polyester can be formed from the polycondensation of a polyester oligomer or prepolymer with a second oligomer prepolymer to form a block copolyester. Optionally, the second prepolymer can be a hydrophilic prepolymer. For example, the co-polyester can be formed from the polycondensation of terephthalic acid or naphthalene dicarboxylic acid with ethylene glycol, 1,4-butanediol, or 1,3-propanediol. Examples of co-polyesters include polyethylene adipate, polybutylene succinate, poly(3-hydroxbutyrate-co-3-hydroxyvalerate), polyethylene terephthalate, polybutylene terephthalate, polytrimethylene terephthalate, polyethylene napthalate, and combinations thereof. The co-polyamide can comprise or consist of polyethylene terephthalate.

The polyester can be a block copolymer comprising segments of one or more of polybutylene terephthalate (PBT), a polytrimethylene terephthalate, a polyhexamethylene terephthalate, a poly-1,4-dimethylcyclohexane terephthalate, a polyethylene terephthalate (PET), a polyethylene isophthalate (PEI), a polyarylate (PAR), a polybutylene naphthalate (PBN), and a liquid crystal polyester. For example, a suitable polyester that is a block copolymer can be a PET/PEI copolymer, a polybutylene terephthalate/tetraethylene glycol copolymer, a polyoxyalkylenediimide diacid/polybutylene terephthalate copolymer, or a blend or mixture of any of the foregoing.

The polyester can be a biodegradable resin, for example, a copolymerized polyester in which poly(α-hydroxy acid) such as polyglycolic acid or polylactic acid is contained as principal repeating units.

The disclosed polyesters can be prepared by a variety of polycondensation methods known to the skilled artisan, such as a solvent polymerization or a melt polymerization process.

Polyolefins

The polymers can comprise or consist essentially of a polyolefin. The polyolefin can be a thermoplastic polyolefin or a thermoset polyolefin. Additionally, the polyolefin can be an elastomeric polyolefin, including a thermoplastic elastomeric polyolefin or a thermoset elastomeric polyolefin. Exemplary polyolefins can include polyethylene, polypropylene, and olefin elastomers (*e.g.*,metallocene-catalyzed block copolymers of ethylene and α-olefins having 4 to about 8 carbon atoms). The polyolefin can be a polymer comprising a polyethylene, an ethylene-α-olefin copolymer, an ethylene-propylene rubber (EPDM), a polybutene, a polyisobutylene, a poly-4-methylpent-1-ene, a polyisoprene, a polybutadiene, a ethylene-methacrylic acid copolymer, and an olefin elastomer such as a dynamically cross-linked polymer obtained from polypropylene (PP) and an ethylene-propylene rubber (EPDM), and blends or mixtures of the foregoing. Further exemplary polyolefins include polymers of cycloolefins such as cyclopentene or norbornene.

It is to be understood that polyethylene, which optionally can be crosslinked, is inclusive a variety of polyethylenes, including low density polyethylene (LDPE), linear low density polyethylene (LLDPE), (VLDPE) and (ULDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), high density and high molecular weight polyethylene (HDPE-HMW), high density and ultrahigh molecular weight polyethylene (HDPE-UHMW), and blends or mixtures of any the foregoing polyethylenes. A polyethylene can also be a polyethylene copolymer derived from monomers of monolefins and diolefins copolymerized with a vinyl, acrylic acid, methacrylic acid, ethyl acrylate, vinyl alcohol, and/or vinyl acetate. Polyolefin copolymers comprising vinyl acetate-derived units can be a high vinyl acetate content copolymer, *e.g.*, greater than about 50 weight percent vinyl acetate-derived composition.

The polyolefin can be formed through free radical, cationic, and/or anionic polymerization by methods well known to those skilled in the art (*e.g.*, using a peroxide initiator, heat, and/or light). The disclosed polyolefin can be prepared by radical polymerization under high pressure and at elevated temperature. Alternatively, the polyolefin can be prepared by catalytic polymerization using a catalyst that normally contains one or more metals from group IVb, Vb, VIb or VIII metals. The catalyst usually has one or more than one ligand, typically

oxides, halides, alcoholates, esters, ethers, amines, alkyls, alkenyls and/or aryls that can be either p- or s-coordinated complexed with the group IVb, Vb, VIb or VIII metal. The metal complexes can be in the free form or fixed on substrates, typically on activated magnesium chloride, titanium(III) chloride, alumina or silicon oxide. The metal catalysts can be soluble or insoluble in the polymerization medium. The catalysts can be used by themselves in the polymerization or further activators can be used, typically a group Ia, IIa and/or IIIa metal alkyls, metal hydrides, metal alkyl halides, metal alkyl oxides or metal alkyloxanes. The activators can be modified conveniently with further ester, ether, amine or silyl ether groups.

Suitable polyolefins can be prepared by polymerization of monomers of monolefins and diolefins as described herein. Exemplary monomers that can be used to prepare the polyolefin include, but are not limited to, ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 2-methyl-1-propene, 3-methyl-1-pentene, 4-methyl-1-pentene, 5-methyl-1-hexene and mixtures thereof.

Suitable ethylene-α-olefin copolymers can be obtained by copolymerization of ethylene with an α-olefin such as propylene, butene-1, hexene-1, octene-1,4-methyl-1-pentene or the like having carbon numbers of 3 to 12.

Suitable dynamically cross-linked polymers can be obtained by cross-linking a rubber component as a soft segment while at the same time physically dispersing a hard segment such as PP and a soft segment such as EPDM by using a kneading machine such as a Banbury mixer and a biaxial extruder.

The polyolefin can be a mixture of polyolefins, such as a mixture of two or more polyolefins disclosed herein above. For example, a suitable mixture of polyolefins can be a mixture of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) or mixtures of different types of polyethylene (for example LDPE/HDPE).

The polyolefin can be a copolymer of suitable monolefin monomers or a copolymer of a suitable monolefin monomer and a vinyl monomer. Exemplary polyolefin copolymers include ethylene/propylene copolymers, linear low density polyethylene (LLDPE) and mixtures thereof with low density polyethylene (LDPE), propylene/but-1-ene copolymers, propylene/isobutylene copolymers, ethylene/but-1-ene copolymers, ethylene/hexene copolymers, ethylene/methylpentene copolymers, ethylene/heptene copolymers, ethylene/octene copolymers, propylene/butadiene copolymers, isobutylene/isoprene copolymers, ethylene/alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate copolymers and their copolymers with carbon monoxide or ethylene/acrylic acid copolymers and their salts (ionomers) as well as terpolymers of ethylene with propylene and a diene such as hexadiene, dicyclopentadiene or ethylidene-norbornene; and mixtures of such copolymers with one another

and with polymers mentioned in 1) above, for example polypropylene/ethylene-propylene copolymers, LDPE/ethylene-vinyl acetate copolymers (EVA), LDPE/ethylene-acrylic acid copolymers (EAA), LLDPE/EVA, LLDPE/EAA and alternating or random polyalkylene/carbon monoxide copolymers and mixtures thereof with other polymers, for example polyamides.

The polyolefin can be a polypropylene homopolymer, a polypropylene copolymers, a polypropylene random copolymer, a polypropylene block copolymer, a polyethylene homopolymer, a polyethylene random copolymer, a polyethylene block copolymer, a low density polyethylene (LDPE), a linear low density polyethylene (LLDPE), a medium density polyethylene, a high density polyethylene (HDPE), or blends or mixtures of one or more of the preceding polymers.

The polyolefin can be a polypropylene. The term “polypropylene,” as used herein, is intended to encompass any polymeric composition comprising propylene monomers, either alone or in mixture or copolymer with other randomly selected and oriented polyolefins, dienes, or other monomers (such as ethylene, butylene, and the like). Such a term also encompasses any different configuration and arrangement of the constituent monomers (such as atactic, syndiotactic, isotactic, and the like). Thus, the term as applied to fibers is intended to encompass actual long strands, tapes, threads, and the like, of drawn polymer. The polypropylene can be of any standard melt flow (by testing); however, standard fiber grade polypropylene resins possess ranges of Melt Flow Indices between about 1 and 1000.

The polyolefin can be a polyethylene. The term “polyethylene,” as used herein, is intended to encompass any polymeric composition comprising ethylene monomers, either alone or in mixture or copolymer with other randomly selected and oriented polyolefins, dienes, or other monomers (such as propylene, butylene, and the like). Such a term also encompasses any different configuration and arrangement of the constituent monomers (such as atactic, syndiotactic, isotactic, and the like). Thus, the term as applied to fibers is intended to encompass actual long strands, tapes, threads, and the like, of drawn polymer. The polyethylene can be of any standard melt flow (by testing); however, standard fiber grade polyethylene resins possess ranges of Melt Flow Indices between about 1 and 1000.

The thermoplastic and/or thermosetting material can further comprise one or more processing aids. The processing aid can be a non-polymeric material. These processing aids can be independently selected from the group including, but not limited to, curing agents, initiators, plasticizers, mold release agents, lubricants, antioxidants, flame retardants, dyes, pigments, reinforcing and non-reinforcing fillers, fiber reinforcements, and light stabilizers

In aspects of the disclosure, the film polymeric material and/or the component polymeric material can comprise a thermoplastic material. For example, the thermoplastic material can be one or more of thermoplastic polyurethanes, thermoplastic polyesters, thermoplastic polyamides, thermoplastic polyolefins, or a co-polymer or combination including of any of the foregoing.

In an aspect, the thermoplastic material onto which the optical element is disposed can have a softening or melting point of about 80° C to about 140° C. In another aspect, the thermoplastic material is increased to a temperature at or above creep relaxation temperature (T_{cr}), Vicat softening temperature (T_{vs}), heat deflection temperature (T_{hd}), and/or melting temperature (T_m), and then the optical element is adhered to the thermoplastic material. In an aspect, the optical element can be disposed to or affixed to the thermoplastic material while the temperature is maintained at or above the creep relaxation temperature, the heat deflection temperature, the Vicat softening temperature, or the melting temperature, of the thermoplastic material. In another aspect, the optical element can be disposed or affixed to the thermoplastic material after the temperature is allowed to drop below the creep relaxation temperature, the heat deflection temperature, the Vicat softening temperature, or the melting temperature of the thermoplastic material, as long as the thermoplastic material only partially re-solidified and the optical element can be affixed thereto.

In general, the thermoplastic material can have a creep relaxation temperature (T_{cr}) of about 80° C to about 140° C, or from about 90° C to about 130° C, or about 100° C to about 120° C. In general, the thermoplastic material can have a Vicat softening temperature (T_{vs}) of about 80° C to about 140° C, or from about 90° C to about 130° C, or about 100° C to about 120° C. In general, the thermoplastic material can have a heat deflection temperature (T_{hd}) of about 80° C to about 140° C, or from about 90° C to about 130° C, or about 100° C to about 120° C. In general, the thermoplastic material can have a melting temperature (T_m) of about 80° C to about 140° C, or from about 90° C to about 130° C, or about 100° C to about 120° C.

In aspects of the disclosure, film polymeric material and/or the component polymeric material can comprise a thermoset material. For example, in aspects, the thermoset material can comprise a thermoset polyurethane polymer, thermoset polyurea polymer, thermoset polyamide polymer, thermoset polyolefin polymer, or thermoset silicone polymer, or a co-polymer or combination including any of the foregoing.

In aspects of the disclosure, the component polymeric material can comprise a polymeric foam material. For example, the polymeric foam material can include a polyolefin foam, polyurethane foam, an ethylene-vinyl acetate (EVA) foam, a propylene foam, or a

combination thereof. In some aspects, the polymeric foam material can include a blend with one or more additional materials to impart additional characteristics or properties to the component. In some aspects, the polymeric foam composition can include one or more other components. A foam composition can include a chemical blowing agent such as a carbonate, bicarbonate, carboxylic acid, azo compound, isocyanate, persulfate, peroxide, or a combination thereof. The foam composition can include about 1 parts per hundred resin to about 10 parts per hundred resin, or about 3 parts per hundred resin to about 7 parts per hundred resin of the chemical blowing agent. In some aspects, the chemical blowing agent has a decomposition temperature of about 130°C to about 160°C, or about 135°C to about 155°C. A foam composition can include a crosslinking agent such as an aliphatic unsaturated amide, such as methylenebisacryl- or -methacrylamide or ethylenebisacrylamide; aliphatic esters of polyols or alkoxylated polyols with ethylenically unsaturated acids, such as di(meth)acrylates or tri(meth)acrylates of butanediol or ethylene glycol, polyglycols or trimethylolpropane; di- and tri-acrylate esters of trimethylolpropane; acrylate and methacrylate esters of glycerol and pentaerythritol; allyl compounds, such as allyl (meth)acrylate, alkoxylated allyl (meth)acrylate, triallyl cyanurate, triallyl isocyanurate, maleic acid diallyl ester, poly-allyl esters, vinyl trimethoxysilane, vinyl triethoxysilane, polysiloxane comprising at least two vinyl groups, tetraallyloxyethane, tetraallyloxyethane, triallylamine, and tetraallylethylenediamine; or a mixture thereof. In some aspects, the foam composition includes about 0.1 parts per hundred resin to about 1.5 parts per hundred resin, or about 0.3 parts per hundred resin to about 0.8 parts per hundred resin of the crosslinking agent. In some aspects, a foam composition can include zinc oxide. In some aspects, the zinc oxide can be present from about 0.1 parts per hundred resin to about 5 parts per hundred resin, or about 0.7 parts per hundred resin to about 2 parts per hundred resin. In some aspects, the foam composition can include calcium carbonate. In some aspects, the calcium carbonate can be present from about 1 parts per hundred resin to about 10 parts per hundred resin, or from about 3 parts per hundred resin to about 7 parts per hundred resin. In some aspects, the foam composition can include a dye or pigment. In some aspects, the dye or pigment is present in the resin composition at a level of about 0 parts per hundred resin to about 10 parts per hundred resin, or about 0.5 parts per hundred resin to about 5 parts per hundred resin based upon the weight of the resin composition.

In aspects of the disclosure in which the component forms an article of footwear, such as a sole of an article of footwear, the film polymeric material and/or the component polymeric material can include a polymeric composition providing additional abrasion resistance and durability as necessary or desirable for use in such articles. In some aspects, the polymeric

composition can pass a flex test pursuant to the Cold Ross Flex Test as described further herein. In some aspects the polymeric composition, the polymeric composition can have suitable abrasion loss when measured pursuant to ASTM D 5963-97, as described further herein. In some aspects, the polymeric composition has an abrasion loss of about 0.07 cubic centimeters (cm^3) to about 0.1 cubic centimeters (cm^3), about 0.08 cubic centimeters (cm^3) to about 0.1 cubic centimeters (cm^3), or about 0.08 cubic centimeters (cm^3) to about 0.11 cubic centimeters (cm^3) pursuant to ASTM D 5963-97a using the Material Sampling Procedure.

In some aspects, the polymeric compositions can include a variety of polyolefin copolymers. The copolymers can be alternating copolymers or random copolymers or block copolymers or graft copolymers. In some aspects, the copolymers are random copolymers. In some aspects, the copolymer includes a plurality of repeat units, with each of the plurality of repeat units individually derived from an alkene monomer having about 1 to about 6 carbon atoms. In other aspects, the copolymer includes a plurality of repeat units, with each of the plurality of repeat units individually derived from a monomer selected from the group consisting of ethylene, propylene, 4-methyl-1-pentene, 1-butene, 1-octene, and a combination thereof.

In some aspects, the polyolefin copolymer is a random copolymer of a first plurality of repeat units and a second plurality of repeat units, and each repeat unit in the first plurality of repeat units is derived from ethylene and the each repeat unit in the second plurality of repeat units is derived from a second olefin. In some aspects, the second olefin is an alkene monomer having about 1 to about 6 carbon atoms. In other aspects, the second olefin includes propylene, 4-methyl-1-pentene, 1-butene, or other linear or branched terminal alkenes having about 3 to 12 carbon atoms. In some aspects, the polyolefin copolymer contains about 80% to about 99%, about 85% to about 99%, about 90% to about 99%, or about 95% to about 99% polyolefin repeat units by weight based upon a total weight of the polyolefin copolymer. In some aspects, the polyolefin copolymer consists essentially of polyolefin repeat units. In some aspects, polymers in the polymeric composition consist essentially of polyolefin copolymers.

In some aspects, the polyolefin copolymer can include ethylene, i.e. can include repeat units derived from ethylene. In some aspects, the polyolefin copolymer includes about 1% to about 5%, about 1% to about 3%, about 2% to about 3%, or about 2% to about 5% ethylene by weight based upon a total weight of the polyolefin copolymer.

In some aspects the polyolefin copolymer is substantially free of polyurethanes. In some aspects, the polymer chains of the polyolefin copolymer are substantially free of urethane repeat units. In some aspects, the polymeric composition is substantially free of polymer chains including urethane repeat units. In some aspects, the polyolefin copolymer is substantially free

of polyamide. In some aspects, the polymer chains of the polyolefin copolymer are substantially free of amide repeat units. In some aspects, the polymeric composition is substantially free of polymer chains including amide repeat units.

In some aspects, the polyolefin copolymer includes polypropylene or is a polypropylene copolymer. In some aspects, the polymer component of the polymeric composition (i.e., the portion of the polymeric composition that is formed by all of the polymers present in the composition) consists essentially of polypropylene copolymers. The polypropylene copolymer can include a random copolymer, e.g. a random copolymer of ethylene and propylene. The polypropylene copolymer can include about 80% to about 99%, about 85% to about 99%, about 90% to about 99%, or about 95% to about 99% propylene repeat units by weight based upon a total weight of the polypropylene copolymer. In some aspects, the polypropylene copolymer includes about 1% to about 5%, about 1% to about 3%, about 2% to about 3%, or about 2% to about 5% ethylene by weight based upon a total weight of the polypropylene copolymer. In some aspects, the polypropylene copolymer is a random copolymer including about 2% to about 3% of a first plurality of repeat units by weight and about 80% to about 99% by weight of a second plurality of repeat units based upon a total weight of the polypropylene copolymer.

In some aspects, a polymeric composition can include a resin modifier that can improved flexural durability while maintaining suitable abrasion resistance. For example, in some aspects the resulting polymer composition including the resin modifier can pass a flex test pursuant to the Cold Ross Flex Test using the Plaque Sampling Procedure, and at the same time, the polymeric composition can still have a suitable abrasion loss when measured pursuant to ASTM D 5963-97a using the Material Sampling Procedure. In some aspects, the polymeric composition including the resin modifier has no significant change in the abrasion loss as compared to an abrasion loss of a substantially similar polymeric composition without the resin modifier, when measured pursuant to ASTM D 5963-97a using the Material Sampling Procedure. A change in abrasion loss, as used herein, is said to not be significant when the change is about 30%, about 25%, about 20%, about 15%, about 10%, or less when measured pursuant to ASTM D 5963-97a using the Material Sampling Procedure.

The combination of abrasion resistance and flexural durability can be related to the overall crystallinity of the polymeric composition. In some aspects, the polymeric composition has a percent crystallization (% crystallization) of about 45%, about 40%, about 35%, about 30%, about 25% or less when measured according to the Differential Scanning Calorimeter (DSC) Test using the Material Sampling Procedure. In some aspects, the resin modifier can provide a decrease in the percent crystallinity (% crystallinity) of the polymeric composition, as

compared to a substantially similar polymeric composition without the resin modifier. In some aspects, the resin composition has a percent crystallization (% crystallization) that is at least 6, at least 5, at least 4, at least 3, or at least 2 percentage points less than a percent crystallization (% crystallization) a substantially similar polymeric composition without the resin modifier when measured according to the Differential Scanning Calorimeter (DSC) Test using the Material Sampling Procedure.

In some aspects, the effective amount of the resin modifier is about 5% to about 30%, about 5% to about 25%, about 5% to about 20%, about 5% to about 15%, about 5% to about 10%, about 10% to about 15%, about 10% to about 20%, about 10% to about 25%, or about 10% to about 30% by weight based upon a total weight of the polymeric composition. In some aspects, the effective amount of the resin modifier is about 20%, about 15%, about 10%, about 5%, or less by weight based upon a total weight of the polymeric composition.

In aspects, the resin modifier can include a variety of known resin modifiers. In some aspects, the resin modifier is a metallocene catalyzed copolymer primarily composed of isotactic propylene repeat units with about 11% by weight-15% by weight of ethylene repeat units based on a total weight of metallocene catalyzed copolymer randomly distributed along the copolymer. In some aspects, the resin modifier includes about 10% to about 15% ethylene repeat units by weight based upon a total weight of the polymeric resin modifier. In some aspects, the resin modifier is a copolymer containing isotactic propylene repeat units and ethylene repeat units.

In some aspects of the disclosure, the film and/or the component can further include a textile. For example, in some aspects the component can include a textile to provide rigidity, strength or support to the component. In some aspects, a textile can be included on the film and/or the component to provide improved bonding between the component and other components of the article, such as a sole structure or upper of an article of footwear. In some aspects, the textile can provide a desired aesthetic characteristic to the component or article. In some aspects, the optical element can be disposed on a textile, such as a textile having a thermoplastic material.

The textile can be a nonwoven textile, a synthetic leather, a knit textile, or a woven textile. The textile can comprise a first fiber or a first yarn, where the first fiber or the first yarn can include at least an outer layer formed of the first thermoplastic material. A region of the first or second surface of the structure onto which the optical element is disposed can include the first fiber or the first yarn in a non-filamentous conformation. The optical element can be disposed onto the textile or the textile can be processed so that the optical element can be disposed onto the textile. The textured surface can be made of or formed from the textile

surface. The primer layer can be disposed on the textile surface and then the optical element can be disposed onto the primer layer. The textile surface can be used to form the textured surface, and either before or after this, the primer layer can be optionally applied to the textured surface prior to disposing the optical element to the textile.

A “textile” may be defined as any material manufactured from fibers, filaments, or yarns characterized by flexibility, fineness, and a high ratio of length to thickness. Textiles generally fall into two categories. The first category includes textiles produced directly from webs of filaments or fibers by randomly interlocking to construct non-woven fabrics and felts. The second category includes textiles formed through a mechanical manipulation of yarn, thereby producing a woven fabric, a knitted fabric, a braided fabric, a crocheted fabric, and the like.

The terms “filament,” “fiber,” or “fibers” as used herein refer to materials that are in the form of discrete elongated pieces that are significantly longer than they are wide. The fiber can include natural, manmade or synthetic fibers. The fibers may be produced by conventional techniques, such as extrusion, electrospinning, interfacial polymerization, pulling, and the like. The fibers can include carbon fibers, boron fibers, silicon carbide fibers, titania fibers, alumina fibers, quartz fibers, glass fibers, such as E, A, C, ECR, R, S, D, and NE glasses and quartz, or the like. The fibers can be fibers formed from synthetic polymers capable of forming fibers such as poly(ether ketone), polyimide, polybenzoxazole, poly(phenylene sulfide), polyesters, polyolefins (*e.g.*, polyethylene, polypropylene), aromatic polyamides (*e.g.,* an aramid polymer such as para-aramid fibers and meta-aramid fibers), aromatic polyimides, polybenzimidazoles, polyetherimides, polytetrafluoroethylene, acrylic, modacrylic, poly(vinyl alcohol), polyamides, polyurethanes, and copolymers such as polyether-polyurea copolymers, polyester-polyurethanes, polyether block amide copolymers, or the like. The fibers can be natural fibers (*e.g.*, silk, wool, cashmere, vicuna, cotton, flax, hemp, jute, sisal). The fibers can be man-made fibers from regenerated natural polymers, such as rayon, lyocell, acetate, triacetate, rubber, and poly(lactic acid).

The fibers can have an indefinite length. For example, man-made and synthetic fibers are generally extruded in substantially continuous strands. Alternatively, the fibers can be staple fibers, such as, for example, cotton fibers or extruded synthetic polymer fibers can be cut to form staple fibers of relatively uniform length. The staple fiber can have a have a length of about 1 millimeter to 100 centimeters or more as well as any increment therein (*e.g.*, 1 millimeter increments).

The fiber can have any of a variety of cross-sectional shapes. Natural fibers can have a natural cross-section, or can have a modified cross-sectional shape (*e.g.*, with processes such

as mercerization). Man-made or synthetic fibers can be extruded to provide a strand having a predetermined cross-sectional shape. The cross-sectional shape of a fiber can affect its properties, such as its softness, luster, and wicking ability. The fibers can have round or essentially round cross sections. Alternatively, the fibers can have non-round cross sections, such as flat, oval, octagonal, rectangular, wedge-shaped, triangular, dog-bone, multi-lobal, multi-channel, hollow, core-shell, or other shapes.

The fiber can be processed. For example, the properties of fibers can be affected, at least in part, by processes such as drawing (stretching) the fibers, annealing (hardening) the fibers, and/or crimping or texturizing the fibers.

In some cases a fiber can be a multi-component fiber, such as one comprising two or more co-extruded polymeric materials. The two or more co-extruded polymeric materials can be extruded in a core-sheath, islands-in-the-sea, segmented-pie, striped, or side-by-side configuration. A multi-component fiber can be processed in order to form a plurality of smaller fibers (*e.g.*, microfibers) from a single fiber, for example, by remove a sacrificial material.

The fiber can be a carbon fiber such as TARIFYL produced by Formosa Plastics Corp. of Kaohsiung City, Taiwan, (*e.g.*, 12,000, 24,000, and 48,000 fiber tows, specifically fiber types TC-35 and TC-35R), carbon fiber produced by SGL Group of Wiesbaden, Germany (*e.g.*, 50,000 fiber tow), carbon fiber produced by Hyosung of Seoul, South Korea, carbon fiber produced by Toho Tenax of Tokyo, Japan, fiberglass produced by Jushi Group Co., LTD of Zhejiang, China (*e.g.*, E6, 318, silane-based sizing, filament diameters 14, 15, 17, 21,and 24 micrometers), and polyester fibers produced by Amann Group of Bonningheim, Germany (*e.g.*, SERAFILE 200/2 non-lubricated polyester filament and SERAFILE COMPHIL 200/2 lubricated polyester filament).

A plurality of fibers includes 2 to hundreds or thousands or more fibers. The plurality of fibers can be in the form of bundles of strands of fibers, referred to as tows, or in the form of relatively aligned staple fibers referred to as sliver and roving. A single type fiber can be used either alone or in combination with one or more different types of fibers by co-mingling two or more types of fibers. Examples of co-mingled fibers include polyester fibers with cotton fibers, glass fibers with carbon fibers, carbon fibers with aromatic polyimide (aramid) fibers, and aromatic polyimide fibers with glass fibers.

As used herein, the term “yarn” refers to an assembly formed of one or more fibers, wherein the strand has a substantial length and a relatively small cross-section, and is suitable for use in the production of textiles by hand or by machine, including textiles made using weaving, knitting, crocheting, braiding, sewing, embroidery, or ropemaking techniques. Thread

is a type of yarn commonly used for sewing.

Yarns can be made using fibers formed of natural, man-made and synthetic materials. Synthetic fibers are most commonly used to make spun yarns from staple fibers, and filament yarns. Spun yarn is made by arranging and twisting staple fibers together to make a cohesive strand. The process of forming a yarn from staple fibers typically includes carding and drawing the fibers to form sliver, drawing out and twisting the sliver to form roving, and spinning the roving to form a strand. Multiple strands can be plied (twisted together) to make a thicker yarn. The twist direction of the staple fibers and of the plies can affect the final properties of the yarn. A filament yarn can be formed of a single long, substantially continuous filament, which is conventionally referred to as a "monofilament yarn," or a plurality of individual filaments grouped together. A filament yarn can also be formed of two or more long, substantially continuous filaments which are grouped together by grouping the filaments together by twisting them or entangling them or both. As with staple yarns, multiple strands can be plied together to form a thicker yarn.

Once formed, the yarn can undergo further treatment such as texturizing, thermal or mechanical treating, or coating with a material such as a synthetic polymer. The fibers, yarns, or textiles, or any combination thereof, used in the disclosed articles can be sized. Sized fibers, yarns, and/or textiles are coated on at least part of their surface with a sizing composition selected to change the absorption or wear characteristics, or for compatibility with other materials. The sizing composition facilitates wet-out and wet-through of the coating or resin upon the surface and assists in attaining desired physical properties in the final article. An exemplary sizing composition can comprise, for example, epoxy polymers, urethane-modified epoxy polymers, polyester polymers, phenol polymers, polyamide polymers, polyurethane polymers, polycarbonate polymers, polyetherimide polymers, polyamideimide polymers, polystylylpyridine polymers, polyimide polymers bismaleimide polymers, polysulfone polymers, polyethersulfone polymers, epoxy-modified urethane polymers, polyvinyl alcohol polymers, polyvinyl pyrrolidone polymers, and mixtures thereof.

Two or more yarns can be combined, for example, to form composite yarns such as single- or double-covered yarns, and corespun yarns. Accordingly, yarns may have a variety of configurations that generally conform to the descriptions provided herein.

The yarn can comprise at least one thermoplastic material (*e.g.*, one or more of the fibers can be made of thermoplastic material). The yarn can be made of a thermoplastic material. The yarn can be coated with a layer of a material such as a thermoplastic material.

The linear mass density or weight per unit length of a yarn can be expressed using

various units, including denier (D) and tex. Denier is the mass in grams of 9000 meters of yarn. The linear mass density of a single filament of a fiber can also be expressed using denier per filament (DPF). Tex is the mass in grams of a 1000 meters of yarn. Decitex is another measure of linear mass, and is the mass in grams for a 10,000 meters of yarn.

As used herein, tenacity is understood to refer to the amount of force (expressed in units of weight, for example: pounds, grams, centinewtons or other units) needed to break a yarn (i.e., the breaking force or breaking point of the yarn), divided by the linear mass density of the yarn expressed, for example, in (unstrained) denier, decitex, or some other measure of weight per unit length. The breaking force of the yarn is determined by subjecting a sample of the yarn to a known amount of force, for example, using a strain gauge load cell such as an INSTRON brand testing system (Norwood, MA, USA). Yarn tenacity and yarn breaking force are distinct from burst strength or bursting strength of a textile, which is a measure of how much pressure can be applied to the surface of a textile before the surface bursts.

Generally, in order for a yarn to withstand the forces applied in an industrial knitting machine, the minimum tenacity required is approximately 1.5 grams per Denier. Most yarns formed from commodity polymeric materials generally have tenacities in the range of about 1.5 grams per Denier to about 4 grams per Denier. For example, polyester yarns commonly used in the manufacture of knit uppers for footwear have tenacities in the range of about 2.5 to about 4 grams per Denier. Yarns formed from commodity polymeric materials which are considered to have high tenacities generally have tenacities in the range of about 5 grams per Denier to about 10 grams per Denier. For example, commercially available package dyed polyethylene terephthalate yarn from National Spinning (Washington, NC, USA) has a tenacity of about 6 grams per Denier, and commercially available solution dyed polyethylene terephthalate yarn from Far Eastern New Century (Taipei, Taiwan) has a tenacity of about 7 grams per Denier. Yarns formed from high performance polymeric materials generally have tenacities of about 11 grams per Denier or greater. For example, yarns formed of aramid fiber typically have tenacities of about 20 grams per Denier, and yarns formed of ultra-high molecular weight polyethylene (UHMWPE) having tenacities greater than 30 grams per Denier are available from Dyneema (Stanley, NC, USA) and Spectra (Honeywell-Spectra, Colonial Heights, VA, USA).

Various techniques exist for mechanically manipulating yarns to form a textile. Such techniques include, for example, interweaving, intertwining and twisting, and interlooping. Interweaving is the intersection of two yarns that cross and interweave at right angles to each other. The yarns utilized in interweaving are conventionally referred to as “warp” and “weft.” A woven textile includes include a warp yarn and a weft yarn. The warp yarn extends in a first

direction, and the weft strand extends in a second direction that is substantially perpendicular to the first direction. Intertwining and twisting encompasses various procedures, such as braiding and knotting, where yarns intertwine with each other to form a textile. Interlooping involves the formation of a plurality of columns of intermeshed loops, with knitting being the most common method of interlooping. The textile may be primarily formed from one or more yarns that are mechanically-manipulated, for example, through interweaving, intertwining and twisting, and/or interlooping processes, as mentioned above.

The textile can be a nonwoven textile. Generally, a nonwoven textile or fabric is a sheet or web structure made from fibers and/or yarns that are bonded together. The bond can be a chemical and/or mechanical bond, and can be formed using heat, solvent, adhesive or a combination thereof. Exemplary nonwoven fabrics are flat or tufted porous sheets that are made directly from separate fibers, molten plastic and/or plastic film. They are not made by weaving or knitting and do not necessarily require converting the fibers to yarn, although yarns can be used as a source of the fibers. Nonwoven textiles are typically manufactured by putting small fibers together in the form of a sheet or web (similar to paper on a paper machine), and then binding them either mechanically (as in the case of felt, by interlocking them with serrated or barbed needles, or hydro-entanglement such that the inter-fiber friction results in a stronger fabric), with an adhesive, or thermally (by applying binder (in the form of powder, paste, or polymer melt) and melting the binder onto the web by increasing temperature). A nonwoven textile can be made from staple fibers (*e.g.*, from wetlaid, airlaid, carding/crosslapping processes), or extruded fibers (*e.g.*, from meltblown or spunbond processes, or a combination thereof), or a combination thereof. Bonding of the fibers in the nonwoven textile can be achieved with thermal bonding (with or without calendering), hydro-entanglement, ultrasonic bonding, needlepunching (needlefelting), chemical bonding (*e.g.*, using binders such as latex emulsions or solution polymers or binder fibers or powders), meltblown bonding (*e.g.*, fiber is bonded as air attenuated fibers intertangle during simultaneous fiber and web formation).

In accordance with some aspects, the component or article can include a cushioning element, such as a bladder. The film or the plate can be part of, disposed on, disposed in, or otherwise associated with the bladder. For example, the article can include one or more bladders and the film or plate can be part of, disposed on, or otherwise associated with the bladder, where the film or plate can include an optical element. The bladder can be unfilled, partially inflated, or fully inflated when the structural design (*e.g.*, optical element) is adhered to the bladder. The bladder is a bladder capable of including a volume of a fluid. An unfilled bladder is a fluid-fillable bladder and a filled bladder is one which has been at least partially

inflated with a fluid at a pressure equal to or greater than atmospheric pressure. When disposed onto or incorporated into an article, the bladder is generally, at that point, a fluid-filled bladder. The fluid be a gas or a liquid. The gas can include air, nitrogen gas (N_2), or other appropriate gas.

The bladder can have a gas transmission rate for nitrogen gas, for example, where a bladder wall of a given thickness has a gas transmission rate for nitrogen that is at least about ten times lower than the gas transmission rate for nitrogen of a butyl rubber layer of substantially the same thickness as the thickness of the bladder described herein. The bladder can have a first bladder wall having a first bladder wall thickness (*e.g.*, about 0.1 to 40 mils). The bladder can have a first bladder wall that can have a gas transmission rate (GTR) for nitrogen gas of less than about 15 cm^3/m^2•atm•day, less than about 10 m^3/m^2•atm•day, less than about 5 cm^3/m^2•atm•day, less than about 1 cm^3/m^2•atm•day (*e.g.*, from about 0.001 cm^3/m^2•atm•day to about 1 cm^3/m^2•atm•day, about 0.01 cm^3/m^2•atm•day to about 1 cm^3/m^2•atm•day or about 0.1 cm^3/m^2•atm•day to about 1 cm^3/m^2•atm•day) for an average wall thickness of 20 mils. The bladder can have a first bladder wall having a first bladder wall thickness, where the first bladder wall has a gas transmission rate of 15 cm^3/m^2•atm•day or less for nitrogen for an average wall thickness of 20 mils.

In an aspect, the bladder has a bladder wall having an interior-facing side (internally-facing side) and an exterior-facing side (externally-facing side), where the interior-facing side defines at least a portion of an interior region of the bladder. In an aspect, the film or plate can be part of, disposed on, disposed in, or otherwise associated with the bladder wall. In this regard, the multi-layer optical film (optical element) having a first side and a second opposing side can be disposed on the exterior-facing side of the bladder, the interior-facing side of the bladder, or both. The exterior-facing side of the bladder, the interior-facing side of the bladder, or both can include a plurality of topographical structures (e.g., textured surface) extending from the exterior-facing side of the bladder wall, the interior-facing side of the bladder, or both, where the first side or the second side of the multi-layer optical film is disposed on the exterior-facing side of the bladder wall and covering some or all of the plurality of topographical structures, the interior-facing side of the bladder wall and covering some or all of the plurality of topographical structures, or both, and wherein the multi-layer optical film imparts a structural color to the bladder wall. The primer layer can be disposed on the exterior-facing side of the bladder, the interior-facing side of the bladder, or both, between the bladder wall and the multi-layer optical film.

In a particular aspect, the bladder can include a top wall operably secured to the footwear upper, a bottom wall opposite the top wall, and one or more sidewalls extending between the top wall and the bottom wall of the inflated bladder. The top wall, the bottom wall, and the one or more sidewalls collectively define an interior region of the inflated bladder, and wherein the one or more sidewalls each comprise an exterior-facing side. The multi-layer optical film having a first side and a second opposing side can be disposed on the exterior-facing side of the bladder, the interior-facing side of the bladder, or both. The exterior-facing side of the bladder, the interior-facing side of the bladder, or both can include a plurality of topographical structures extending from the exterior-facing side of the bladder wall, the interior-facing side of the bladder, or both, where the first side or the second side of the multi-layer optical film is disposed on the exterior-facing side of the bladder wall and covering some or all of the plurality of topographical structures, the interior-facing side of the bladder wall and covering some or all of the plurality of topographical structures, or both, and wherein the multi-layer optical film imparts a structural color to the bladder wall. The primer layer can be disposed on the exterior-facing side of the bladder, the interior-facing side of the bladder, or both, between the bladder wall and the multi-layer optical film

An accepted method for measuring the relative permeance, permeability, and diffusion of inflated bladders is ASTM D-1434-82-V. See, *e.g.*, U.S. Patent No. 6,127,026, which is incorporated by reference as if fully set forth herein. According to ASTM D-1434-82-V, permeance, permeability and diffusion are measured by the following formulae:

Permeance

(quantity of gas)/[(area)x(time)x(pressure difference)] = permeance (GTR)/(pressure difference) = cm^3/m^2•atm•day (i.e., 24 hours)

Permeability

[(quantity of gas)x(film thickness)][(area)x(time)x(pressure difference)] = permeability [(GTR)x(film thickness)]/(pressure difference) = [(cm^3)(mil)]/m^2•atm•day (i.e., 24 hours)

Diffusion at one atmosphere

(quantity of gas)/[(area)x(time)] = GTR = cm^3/m^2•day (i.e., 24 hours)

The bladder can include a bladder wall that includes a film including at least one polymeric layer or at least two or more polymeric layers. Each of the polymeric layers can be about 0.1 to 40 mils in thickness.

The polymeric layer can be formed of polymer material such as a thermoplastic material. The thermoplastic material can include an elastomeric material, such as a thermoplastic elastomeric material. The thermoplastic materials can include thermoplastic polyurethane (TPU), such as those described herein. The thermoplastic materials can include polyester-based TPU, polyether-based TPU, polycaprolactone-based TPU, polycarbonate-based TPU, polysiloxane-based TPU, or combinations thereof. Non-limiting examples of thermoplastic material that can be used include: “PELLETHANE” 2355-85ATP and 2355-95AE (Dow Chemical Company of Midland, MI., USA), “ELASTOLLAN” (BASF Corporation, Wyandotte, MI, USA) and “ESTANE” (Lubrizol, Brecksville, OH, USA), all of which are either ester or ether based. Additional thermoplastic material can include those described in U.S. Pat. Nos. 5,713,141; 5,952,065; 6,082,025; 6,127,026; 6,013,340; 6,203,868; and 6,321,465, which are incorporated herein by reference.

The polymeric layer can be formed of one or more of the following: ethylene-vinyl alcohol copolymers (EVOH), poly(vinyl chloride), polyvinylidene polymers and copolymers (*e.g.*, polyvinylidene chloride), polyamides (*e.g.*, amorphous polyamides), acrylonitrile polymers (*e.g.*, acrylonitrile-methyl acrylate copolymers), polyurethane engineering plastics, polymethylpentene resins, ethylene-carbon monoxide copolymers, liquid crystal polymers, polyethylene terephthalate, polyether imides, polyacrylic imides, and other polymeric materials known to have relatively low gas transmission rates. Blends and alloys of these materials as well as with the TPUs described herein and optionally including combinations of polyimides and crystalline polymers, are also suitable. For instance, blends of polyimides and liquid crystal polymers, blends of polyamides and polyethylene terephthalate, and blends of polyamides with styrenics are suitable.

Specific examples of polymeric materials of the polymeric layer can include acrylonitrile copolymers such as ”BAREX” resins, available from Ineos (Rolle, Switzerland); polyurethane engineering plastics such as “ISPLAST” ETPU available from Lubrizol (Brecksville, OH, USA); ethylene-vinyl alcohol copolymers marketed under the tradenames “EVAL” by Kuraray (Houston, TX, USA), “SOARNOL” by Nippon Gohsei (Hull, England), and “SELAR OH” by DuPont (Wilmington, DE, USA); polyvinylidiene chloride available from S.C. Johnson (Racine, WI, USA) under the tradename “SARAN”, and from Solvay (Brussels, Belgium) under the tradename “IXAN”; liquid crystal polymers such as “VECTRA” from Celanese (Irving, TX, USA)

and “XYDAR” from Solvay; “MDX6” nylon, and amorphous nylons such as “NOVAMID” X21 from Koninklijke DSM N.V (Heerlen, Netherlands), “SELAR PA” from DuPont; polyetherimides sold under the tradename “ULTEM” by SABIC (Riyadh, Saudi Arabia); poly(vinyl alcohol)s; and polymethylpentene resins available from Mitsui Chemicals (Tokyo, Japan) under the tradename “TPX”.

Each polymeric layer of the film can be formed of a thermoplastic material which can include a combination of thermoplastic polymers. In addition to one or more thermoplastic polymers, the thermoplastic material can optionally include a colorant, a filler, a processing aid, a free radical scavenger, an ultraviolet light absorber, and the like. Each polymeric layer of the film can be made of a different of thermoplastic material including a different type of thermoplastic polymer.

The bladder can be made by applying heat, pressure and/or vacuum to a film. The bladder (*e.g.*, one or more polymeric layers) can be formed using one or more polymeric materials, and forming the bladder using one or more processing techniques including, for example, extrusion, blow molding, injection molding, vacuum molding, rotary molding, transfer molding, pressure forming, heat sealing, casting, low-pressure casting, spin casting, reaction injection molding, radio frequency (RF) welding, and the like. The bladder can be made by co-extrusion followed by heat sealing or welding to give an inflatable bladder, which can optionally include one or more valves (*e.g.*, one way valves) that allows the bladder to be filled with the fluid (*e.g.*, gas).

In examples where the bladder includes the optical element, the optical element can be disposed onto the internally-facing surface (side) of the bladder or the externally-facing surface (side) of the bladder. The textured layer can be the internally-facing surface (side) or the externally-facing surface (side) of the bladder. The optical element can include the optical layer and optionally the primer layer and texture structure. The textured layer can be the internally-facing surface (side) or the externally-facing surface (side) of the bladder (*e.g.*, where the internally-facing or externally-facing side is made of a thermoplastic material) and the primer layer disposed thereon and the optical element disposed on the primer layer.

Having described various aspects and features of an article or component of an article, we now turn to describing various aspects of making such an article and/or component of an article. Generally speaking, a method for making an article or a component of an article includes disposing a film having an optical element to a component. In an aspect, the film comprises a film polymeric material, and has a first film surface, a second film surface opposed to the first film surface, and a film core disposed therebetween. The first film surface, the

second film surface, or both include an optical element that has a first side and a second side. In an aspect, a method includes disposing the first film surface to an externally-facing surface of a component, where the first side of the optical element, the second side of the optical element, or both impart a structural color to the component.

According to some aspects, the first side of the optical element or the second side of the optical element is disposed on the first film surface, e.g., on the surface of the film that is affixed to the component. In some aspects, the method further includes disposing the optical element on the first film surface prior to the step of disposing the first film surface to the externally-facing surface of the component.

According to some aspects, the method includes disposing the first side of the optical element or the second side of the optical element on the second film surface, e.g., on the surface of the film that is facing away from the component. In some aspects, the method further includes disposing the optical element on the second film surface prior to the step of disposing the first film surface to the externally-facing surface of the component. In other aspects, the method includes disposing the optical element on the second film surface after the step of disposing the first film surface to the externally-facing surface of the component.

In further aspects, disposing the optical element onto the first film surface or onto the second film surface includes depositing the optical element (or one or more layers thereof) onto the first film surface or the second film surface, such as by using a technique comprising: physical vapor deposition, electron beam deposition, atomic layer deposition, molecular beam epitaxy, cathodic arc deposition, pulsed laser deposition, sputtering, chemical vapor deposition, plasma-enhanced chemical vapor deposition, low pressure chemical vapor deposition, a wet chemistry technique, or combinations thereof.

While some aspects include methods for disposing the film and the optical element on an externally-facing surface of a component, other aspects include disposing the film and the optical element on a second surface of a component, where the component is substantially transparent or clear, so that the structural color imparted by the optical element is visible or perceivable to a viewer that is observing the externally-facing surface of the component. For example, in an aspect, the method includes disposing the first film surface onto a second surface of the component, and disposing the optical element on the first film surface or the second film surface, where the first side of the optical element, the second side of the optical element, or both impart a structural color to the component.

In some aspects, the component polymeric material or component polymeric precursor material can be directly injected onto the first film surface, resulting in a component with the film.

In some aspects, the film can be affixed to the component during a molding process. In some aspects, the step of disposing the first film surface onto the externally-facing surface of the component comprises providing a mold having a mold surface, inserting the film into the mold with the second film surface contacting the mold surface, pouring or injecting a component polymeric material or component polymeric precursor material into the mold with the included film, molding the component polymeric material or component precursor polymeric material to form the component and disposing the first film surface onto the externally-facing surface of the component, and then removing the component with the affixed film from the mold.

In some aspects, the method can include injection molding a component polymeric composition, such as a pelletized component polymeric composition, to form the component. In some aspects, injection molding can include the use of a non-rotating, cold plunger to force a pelletized polymeric composition through a heated cylinder wherein the polymeric composition is heated by heat conducted from the walls of the cylinder to the polymeric composition. The injection molding can include the use of a rotating screw, disposed co-axially of a heated barrel, for conveying the pelletized polymeric composition toward a first end of the screw and to heat the polymeric composition by the conduction of heat from the heated barrel to the polymeric composition. As the component polymeric composition is conveyed by the screw mechanism toward the first end, the screw is translated toward the second end so as to produce a reservoir space at the first end. When sufficient melted component polymeric composition is collected in the reservoir space, the screw mechanism can be pushed toward the first end so as to inject the material into the mold.

In some aspects, the method can further include one or more steps of making or providing the component polymeric material or component polymeric precursor polymeric material. For example, in an aspect, a method for making a component polymeric composition can include blending the components of the polymeric composition, melting the components of the polymeric composition, extruding the polymeric composition, or various combinations thereof. The methods can further include extruding the component polymeric composition to form an extruded component polymeric composition. The methods of extruding the polymeric composition can include manufacturing long products of relatively constant cross-section (rods, sheets, pipes, films, wire insulation coating). The methods of extruding the polymeric composition can include conveying a softened polymeric composition through a die with an opening. The polymeric composition can be conveyed forward by a feeding screw and forced through the die. Heating elements, placed over the barrel, can soften and melt the polymeric composition. The temperature of the material can be controlled by thermocouples. The product

leaving the die can be cooled, for example by blown air or in a water bath, to form the extruded polymeric composition. Alternatively, the product leaving the die can be pelletized with little cooling. Methods of pelletizing can include melt pelletizing (hot cut) whereby the melt coming from a die is almost immediately cut into pellets that are conveyed and cooled by liquid or gas. Methods of pelletizing can include strand pelletizing (cold cut) whereby the melt coming from the die head is converted into strands (the extruded polymeric composition) that are cut into pellets after cooling and solidification. The pellets can then be used in other steps, e.g., injection-molding.

In some aspects, the component polymeric material comprises a thermoplastic polymeric material, and disposing the film to the component polymeric material comprises (i) increasing a temperature of the component polymeric material to a first temperature above a melting or softening point of the component polymeric material, (ii) contacting the component polymeric material and the first film surface while the component polymeric material is at or above the first temperature, and (iii) keeping the component polymeric material and the first film surface in contact with each other while decreasing the temperature of the component material to a second temperature below the melting or softening point of the component polymeric material, disposing the component polymeric material and the first film surface to each other.

In some aspects, the film polymeric material comprises a thermoplastic material. In an aspect, the first film surface is defined by a film thermoplastic material, and disposing the first film surface to the component comprises (i) increasing a temperature of the film thermoplastic polymeric material to a first temperature above a melting or softening point of the film thermoplastic polymeric material, (ii) contacting the externally-facing surface of the component and the first film surface while the film thermoplastic polymeric material is at the first temperature, and (iii) keeping the externally-facing surface of the component and the first film surface in contact with each other while decreasing the temperature of the film thermoplastic polymeric material to a second temperature below the melting or softening point of the film thermoplastic polymeric material, disposing the externally-facing surface of the component and the first film surface to each other.

In some aspects, both the first film surface and the externally-facing surface of the component can include a thermoplastic material. In an aspect, the first film surface includes a film thermoplastic polymeric material and the externally-facing surface of the component is defined at least in part by a component thermoplastic material, and disposing the first film surface to the externally-facing surface of the component comprises (i) increasing a temperature of both the component thermoplastic material and the film thermoplastic polymeric material to a

first temperature, wherein the first temperature is at or above one of a melting or softening point of the component thermoplastic material and at or above one of a melting or softening point of the film thermoplastic polymeric material, (ii) contacting the externally-facing surface of the component and the first film surface while both the component thermoplastic material and the film thermoplastic polymeric material are at the first temperature, and (iii) keeping the externally-facing surface of the component and the first film surface in contact with each other while decreasing the temperature of both the component thermoplastic material and the film thermoplastic polymeric material to a second temperature below softening point of both the component thermoplastic material and the film thermoplastic polymeric material, thereby melding at least a portion of the component thermoplastic material and the film thermoplastic polymeric material with each other and forming a mechanical bond between the externally-facing surface of the component and the first film surface.

In some aspects, the component can include a thermosetting polymeric material. In an aspect, the externally-facing surface of the component includes a component polymeric precursor material, and disposing the first film surface to the externally-facing component comprises (i) contacting the component polymeric precursor material and the first film surface, and (ii) applying actinic radiation to the component polymeric precursor material to at least partially cure the component polymeric precursor material while the first film surface is in contact with the externally-facing surface of the component, thereby disposing the externally-facing surface of the component to the first film surface.

In some aspects, a second polymeric material or second polymeric precursor material can be provided between the film and the component. In some aspects, the second polymeric material or second polymeric precursor material can assist in the disposing of the film to the component, for example, providing an adhesive between the film and the component. In some aspects, the second polymeric material can be extruded or directly injected onto the first film surface or the component prior to disposing the first film surface to the component.

According to the various aspects, the method further comprises providing a textured surface to the component or article, such as, for example, where the combination of the textured surface and the optical element can impart the structural color. In some aspects, the method comprises forming a textured surface on the first film surface or the second film surface. In some aspects, the method includes forming a textured surface on the externally-facing surface of the component or on a second surface of the component. In some aspects, the method comprises forming a textured surface on the optical element, such as on the first side or the second side of the optical element. In some aspects, the method comprises providing a

textured structure comprising a textured surface, between the first film surface and the externally-facing surface of the component.

Providing or forming the textured surface can include depositing or printing a material on a surface to form a textured surface, or it can include altering a surface, such as by molding, stamping, printing, compressing, cutting, etching, vacuum forming or any combination thereof. In some aspects, a textured surface may be provided as a feature on or part of a transfer medium, and imparted to a side or layer of the optical element or to the surface of the film or component. For example, a mirror image or relief form of the textured surface may be provided on the side of a transfer medium, and the transfer medium contacts a side of the optical element or the surface of the component in a way that imparts the textured surface to the optical element or article.

According to the various aspects, the method further comprises providing a primer layer. Providing the primer layer can include providing the primer layer on or adjacent to a side of the optical element, so that the primer layer and the optical element can impart the structural color. In some aspects, the primer layer can be formed or deposited between the first film surface and the externally-facing surface of the component, or it can be formed or disposed on a second surface of the component.

According to some aspects, a method of making an article can comprise making a structurally-colored component, using one or more of the methods described herein, and combining the structurally-colored component with a second component to form an article. For example, the structurally-colored component can form a part of a sole for an article of footwear, where the method can include combining the component with another sole component, an upper, or other features of an article of footwear. In some methods, the component can be provided as a plate for an article of footwear, and the method can include adding a plurality of traction elements onto the externally-facing surface of the plate.

Now having described embodiments of the disclosure, evaluation of various properties and characteristics described herein are by various testing procedures as described herein below.

Method to Determine the Melting Temperature, and Glass Transition Temperature. The melting temperature and glass transition temperature are determined using a commercially available Differential Scanning Calorimeter (“DSC”) in accordance with ASTM D3418-97. Briefly, a 10-15 gram sample is placed into an aluminum DSC pan and then the lead was sealed with the crimper press. The DSC is configured to scan from -100 degrees C to 225 degrees C with a 20 degrees C/minute heating rate, hold at 225 degrees C for 2 minutes, and then cool down to 25 degrees C at a rate of -

10 degrees C/minute. The DSC curve created from this scan is then analyzed using standard techniques to determine the glass transition temperature and the melting temperature.

Method to Determine the Melt Flow Index. The melt flow index is determined according to the test method detailed in ASTM D1238-13 Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer, using Procedure A described therein. Briefly, the melt flow index measures the rate of extrusion of thermoplastics through an orifice at a prescribed temperature and load. In the test method, approximately 7 grams of the material is loaded into the barrel of the melt flow apparatus, which has been heated to a temperature specified for the material. A weight specified for the material is applied to a plunger and the molten material is forced through the die. A timed extrudate is collected and weighed. Melt flow rate values are calculated in grams/10 min.

Method to Determine the Creep Relation Temperature T_{cr}. The creep relation temperature T_{cr} is determined according to the exemplary techniques described in U.S. Patent No. 5,866,058. The creep relaxation temperature T_{cr} is calculated to be the temperature at which the stress relaxation modulus of the tested material is 10% relative to the stress relaxation modulus of the tested material at the solidification temperature of the material, where the stress relaxation modulus is measured according to ASTM E328-02. The solidification temperature is defined as the temperature at which there is little to no change in the stress relaxation modulus or little to no creep about 300 seconds after a stress is applied to a test material, which can be observed by plotting the stress relaxation modulus (in Pa) as a function of temperature (in °C).

Method to Determine the Vicat Softening Temperature T_{vs}. The Vicat softening temperature T_{vs} is be determined according to the test method detailed in ASTM D1525-09 Standard Test Method for Vicat Softening Temperature of Plastics, preferably using Load A and Rate A. Briefly, the Vicat softening temperature is the temperature at which a flat-ended needle penetrates the specimen to the depth of 1 mm under a specific load. The temperature reflects the point of softening expected when a material is used in an elevated temperature application. It is taken as the temperature at which the specimen is penetrated to a depth of 1 mm by a flat-ended needle with a 1 mm^2 circular or square cross-section. For the Vicat A test, a load of 10 N is used, whereas for the Vicat B test, the load is 50 N. The test involves placing a test specimen in the testing apparatus so that the penetrating needle rests on its surface at least 1 mm from the edge. A load is applied to the specimen per the requirements of the Vicat A or Vicat B test. The specimen is then lowered into an oil bath at 23 °C. The bath is raised at a rate of 50 °C or 120 °C per hour until the needle penetrates 1 mm. The test specimen must be between 3 and 6.5 mm thick and at least 10 mm in width and length. No more than three layers can be stacked to achieve minimum thickness.

Method to Determine the Heat DeflectionTemperature T_{hd}. The heat deflection temperature T_{hd} is be determined according to the test method detailed in ASTM D648-16 Standard Test Method for Deflection Temperature of Plastics Under Flexural Load in the Edgewise Position, using a 0.455 MPa applied stress. Briefly, the heat deflection temperature is the temperature at which a polymer or plastic sample deforms under a specified load. This property of a given plastic material is applied in many aspects of product design, engineering, and manufacture of products using thermoplastic components. In the test method, the bars are placed under the deflection measuring device and a load (0.455 MPa) of is placed on each specimen. The specimens are then lowered into a silicone oil bath where the temperature is raised at 2° C per minute until they deflect 0.25 mm per ASTM D648-16. ASTM uses a standard bar 5" x ½" x ¼". ISO edgewise testing uses a bar 120mm x 10mm x 4mm. ISO flatwise testing uses a bar 80mm x 10mm x 4mm.

Cold Ross Flex Test

The Cold Ross flex test is determined according the following test method. The purpose of this test is to evaluate the resistance to cracking of a sample under repeated flexing to a 60 degree angle in a cold environment. A molded plaque of the material for testing is sized to fit inside the flex tester machine. Each material is tested as five separate samples. The flex tester machine is capable of flexing samples to 60 degrees at a rate of 100 +/- 5 cycles per minute. The mandrel diameter of the machine is 10 millimeters. The flex tester machine is a Gotech GT-7006. The sample(s) are inserted into the machine according to the specific parameters of the flex machine. The machine is placed in a freezer set to -6 ºC for the test. The motor is turned on to begin flexing with the flexing cycles counted until the sample forms visible creases (e.g., whitens), or cracks. Cracking of the sample means that the surface of the material is physically split. Visible creases of lines that do not actually penetrate the surface are not cracks. The number of flex cycles the sample is exposed to is measured to a point where visible creases develop in the sample or until the sample has cracked but not yet broken in two, whichever comes first. The term “visible,” as used herein, means capable of being perceived at a distance of 12 inches by an unimpeded naked eye of a viewer having 20/20 vision under ambient light levels of 1000 foot candles. A sample which develops visible creases or cracks before completing 150,000 flex cycles is considered to fail the test, while a sample which has not developed visible creases or cracks after completing 150,000 flex cycles is considered to pass the cold Ross flex test.

Deutsches Institut für Normung (DIN) Abrasion Loss Test ASTM D 5963-97a

Abrasion loss is tested on cylindrical test pieces with a diameter of 16±0.2 mm and a minimum thickness of 6 mm cut from sheets using a ASTM standard hole drill. The abrasion loss is measured using Method B of ASTM D 5963-97a on a Gotech GT-7012-D abrasion test machine. The

tests are performed as 22°C with an abrasion path of 40 meters. The Standard Rubber #1 used in the tests has a density of 1.336 grams per cubic centimeter (g/cm^3). The smaller the abrasion loss volume, the better the abrasion resistance.

Crystallinity Determination Using Differential Scanning Calorimeter (DSC) Test

To determine percent crystallinity of a polymeric composition can be analyzed by differential scanning calorimetry (DSC) over the temperature range from -80 °C to 250°C. A heating rate of 10 °C per minute is used. The melting endotherm is measured for each sample during heating. Universal Analysis software (TA Instruments, New Castle, DE, USA) is used to calculate percent crystallinity (% crystallinity) based upon the melting endotherm for the homopolymer (e.g., 207 Joules per gram for 100% crystalline polypropylene material). Specifically, the percent crystallinity (% crystallinity) is calculated by dividing the melting endotherm measured for the copolymer or for the resin composition by the 100% crystalline homopolymer melting endotherm.

Sampling Procedures

Various properties of the polymeric compositions and components and other articles formed therefrom can be characterized using samples prepared with the following sampling procedures:

Material Sampling Procedure

A material sampling procedure can be used to obtain a neat sample of a polymeric composition or, in some instances, a sample of a material used to form a polymeric composition. The material is provided in media form, such as flakes, granules, powders, pellets, and the like. If a source of the polymeric composition is not available in a neat form, the sample can be cut from a plate or component containing the polymeric composition, thereby isolating a sample of the material.

Plaque Sampling Procedure

A polymeric composition is prepared, including the polymeric component, optional resin modifier, and other components. A portion of the polymeric composition is then be molded into a plaque sized to fit inside the Ross flexing tester used, the plaque having dimensions of about 15 centimeters (cm) by 2.5 centimeters (cm) and a thickness of about 1 millimeter (mm)to about 4 millimeter (mm) by thermoforming the resin composition in a mold. The sample is prepared by mixing the components of the polymeric composition together, melting the components, pouring or injecting the melted composition into the mold cavity, cooling the melted composition to solidify it in the mold cavity to form the plaque, and then removing the solid plaque from the mold cavity.

The present disclosure can be described in accordance with the following numbered Clauses, which should not be confused with the claims. In each of the clause sets, “disposing” can be replaced with “operably disposing.”

Clause 1. An article, comprising:

a film forming at least a portion of a component, the film having a first film surface, a second film surface opposing the first film surface, and a film core between the first film surface and the second film surface, wherein the first film surface or the second film surface or the film core or any combination thereof include a film polymeric material, wherein the first film surface forms an externally-facing surface of the component or an internally-facing surface of the component; and

an optical element disposed on the first film surface, on the second film surface, or within the film core, wherein the optical element has a first side and a second side opposing the first side, wherein the first side of the optical element, the second side of the optical element, or both, impart a structural color to the component.

Clause 2. The article of any one of the preceding clauses, wherein the first film surface forms the externally-facing surface of the component, and the first side of the optical element is disposed on the first film surface or a second side of the optical element is disposed on the second film surface.

Clause 3. The article of the preceding clause, further comprising a primer layer disposed between the first side of the optical element and the component, or on the internally-facing surface of the component, wherein the primer layer and the second side of the optical element impart a structural color to the component.

Clause 4. The article of clause 1, wherein the first film surface forms the internally-facing surface of the component, and the second side of the optical element is disposed on the first film surface, or a first side of the optical element is disposed on the second film surface.

Clause 5. The article of the preceding clause, further comprising a primer layer disposed on the first side of the optical element, wherein the primer layer and the second side of the optical element impart a structural color.

Clause 6. The article of any one of the preceding clauses, wherein the film is a multi-layer film, having at least a first film layer defining the first film surface and a second film layer forming the film core or forming the second film surface, and the optical element is disposed between the first film layer and the second film layer.

Clause 7. The article of any one of the preceding clauses, further comprising a textured surface on the first side of optical element, on the second side of the optical element, on the first film surface, on the second film surface, on the internally-facing surface of the component, on the externally facing surface of the component, on the optional primer layer, or a combination thereof, and wherein the textured surface and the first side of the optical element, the second side of the optical element, or both, impart a structural color to the component.

Clause 8. The article of any one of the preceding clauses, further comprising a textured structure having the textured surface, wherein the textured structure is disposed within the optical element, on the first side of the optical element, on the second side of the optical element, adjacent the first film surface, on the second film surface, within the film core, on the externally-facing surface of the component, on the internally-facing surface of the core, or a combination thereof, wherein the textured surface and the first side of the optical element, the second side of the optical element, or both, impart a structural color to the component.

Clause 9. The article of any one of the preceding clauses, wherein the first side of the optical element or the second side of the optical element, with the optional primer layer, and with the optional textured surface impart a structural color to the component.

Clause 10. The article of any one of the preceding clauses, wherein a combination of the textured surface and the optical element, or a combination of the primer layer and the optical element, or a combination of the optical element, the textured surface, and the primer layer imparts the structural color.

Clause 11. The article of any one of the preceding clauses, wherein the film is substantially colorless.

Clause 12. The article of any one of the preceding clauses, wherein the component is substantially transparent.

Clause 13. The article of any one of the preceding clauses, wherein a color of the film or a color of the surface of the component without the film, or a color of an optional primer layer, or any combination thereof, differ from the color imparted by the structural color by at least one of hue, value and iridescence type.

Clause 14. The article of any one of the preceding clauses, wherein the component is at least a portion of a sole of an article of footwear, and the externally-facing surface of the component forms an externally-facing surface of the sole.

Clause 15. The article of any one of the preceding clauses, wherein the optical element includes at least one optical layer, wherein the at least one optical layer has a thickness that is about one fourth of the wavelength of visible light to be reflected by the optical element to impart the structural color.

Clause 16. The article of any one of the preceding clauses, wherein the optical element is a multilayer reflector or a multilayer filter.

Clause 17. The article of any one of the preceding clauses, wherein the multilayer reflector has at least two layers, including at least two adjacent layers having different refractive indices.

Clause 18. The article of any one of the preceding clauses, wherein at least one of the layers of the multilayer reflector has a thickness that is about one-fourth of the wavelength of visible light to be reflected by the optical layer structure to impart the structural color.

Clause 19. The article of any one of the preceding clauses, wherein at least one of the layers of the multilayer reflector comprises a material selected from the group consisting of: silicon dioxide, titanium dioxide, zinc sulfide, magnesium fluoride, tantalum pentoxide, and a combination thereof.

Clause 20. The article of any one of the preceding clauses, wherein the textured surface has a plurality of profile features and plurality of flat areas.

Clause 21. The article of any one of the preceding clauses, wherein the textured surface includes a plurality of profile features and flat planar areas, wherein the profile features extend above the flat areas of the textured surface.

Clause 22. The article of any one of the preceding clauses, wherein the dimensions of the profile features, a shape of the profile features, a spacing among the plurality of the profile features, in combination with the optical layer impart the structural color.

Clause 23. The article of any one of the preceding clauses, wherein the profile features are in random positions relative to one another over an area of the textured surface having a surface area of at least 5 square millimeters.

Clause 24. The article of any one of the preceding clauses, wherein the spacing among the profile features reduces distortion effects of the profile features produced from interfering with one another when imparting the structural color.

Clause 25. The article of any one of the preceding clauses, wherein the profile features and the flat areas result in at least one optical layer of the optical element having an undulating topography, wherein the optical layer has a planar region between neighboring depressions and/or elevations that is planar with the flat planar areas of the textured surface, and wherein the planar region has dimensions relative to the profile features to impart the structural color.

Clause 26. The article of any one of the preceding clauses, wherein the primer layer is formed from digital printing, offset printing, pad printing, screen printing, flexographic printing, or heat transfer printing.

Clause 27. The article of any one of the preceding clauses, wherein the primer layer comprises a paint or an ink.

Clause 28. The article of any one of the preceding clauses, wherein the primer layer comprises a reground, and at least partially degraded polymer.

Clause 29. The article of any one of the preceding clauses, wherein the primer layer is an oxide layer, optionally the oxide layer comprises a metal oxide or a metal oxynitride layer, wherein optionally the metal oxide or metal oxynitride is doped.

Clause 30. The article of any one of the preceding clauses wherein the primer layer consists essentially of a doped metal oxide or a doped metal oxynitride or both.

Clause 31. The article of any one of the preceding clauses, wherein the primer layer consist essentially of a metal oxide, optionally titanium dioxide or silicon dioxide, and optionally consist essentially of titanium dioxide.

Clause 32. The article of any one of the preceding clauses, wherein the primer layer is a coating, wherein the coating is a crosslinked coating including a matrix of crosslinked polymers, optionally wherein the coating comprises a plurality of solid pigment particles entrapped in the matrix of crosslinked polymers, wherein optionally the matrix of crosslinked polymers includes crosslinked elastomeric polymers, wherein optionally the crosslinked elastomeric polymers include crosslinked polyurethane homopolymers or copolymers or both, and wherein the crosslinked polyurethane copolymers include crosslinked polyester polyurethanes.

Clause 33. The article of any one of the preceding clauses, wherein the coating further comprises a dye, optionally the dye is an acid dye, and optionally the coating further comprises a quaternary ammonium compound.

Clause 34. The article of any one of the preceding clauses, wherein the matrix of crosslinked polymers of the coating include polyurethane polymers, optionally thermoplastic polyurethane polymers, optionally elastomeric polyurethane polymers, optionally the polyurethane polymers include polyester polyurethane copolymers, and optionally the polyurethane polymers consist essentially of polyester polyurethane copolymers.

Clause 35. The article of any one of the preceding clauses, wherein the primer layer has a thickness of about 1 to about 200 micrometers, or optionally of about 10 to about 100 micrometers, or optionally of about 10 to about 80 micrometers.

Clause 36. The article of any one of the preceding clauses, wherein the film polymeric material is a thermoplastic material, or an elastomeric material, or an elastomeric thermoplastic material.

Clause 37. The article of any one of the preceding clauses, wherein the thermoplastic material includes one or more thermoplastic polyurethanes, thermoplastic polyesters, thermoplastic polyamides, thermoplastic polyolefins, thermoplastic co-polymers thereof, or a combination thereof.

Clause 38. The article of any one of the preceding clauses, wherein a polymeric component of the thermoplastic material consists essentially of one or more thermoplastic polyurethanes.

Clause 39. The article of any one of the preceding clauses, wherein the film polymeric material is a thermoset material.

Clause 40. The article of any one of the preceding clauses, wherein the thermoset material comprises an elastomeric thermoset material.

Clause 41. The article of any one of the preceding clauses, wherein the thermoset material comprises thermoset polyurethane polymers, thermoset polyurea polymers, thermoset polyamide polymers, thermoset polyolefin polymers, or thermoset silicone polymers.

Clause 42. The article of any one of the preceding clauses, wherein the film has a thickness of about 3 nanometers to about 1 millimeter.

Clause 43. The article of any one of the preceding clauses, wherein the component comprises a component thermoplastic material.

Clause 44. The article of any one of the preceding clauses, wherein the component comprises a component thermoset material.

Clause 45. The article of any one of the preceding clauses, wherein the component is comprises an injection-molded component.

Clause 46. The article of any one of the preceding clauses, wherein the thermoplastic material, optionally the component thermoplastic material, includes about 70% to about 95% of a polyolefin polymer and about 5% to about 30% of a polymeric resin modifier based on a total weight of the thermoplastic material.

Clause 47. The article of any one of the preceding clauses, wherein the thermoplastic material, optionally the component thermoplastic material, has an abrasion loss of about 0.08 cubic centimeters to about 0.1 cubic centimeters pursuant to ASTM D 5963-97a using the Material Sampling Procedure.

Clause 48. The article of any one of the preceding clauses, wherein the component passes a flex test pursuant to the Cold Ross Flex Test using the Plaque Sampling Procedure

Clause 49. The article of any one of the preceding clauses, wherein the polyolefin polymer of the thermoplastic material is a random polyolefin copolymer

Clause 50. The article of any one of the preceding clauses, wherein the polyolefin polymer is a polyolefin copolymer, and the polyolefin copolymer comprises a plurality of repeat units, with each of the plurality of repeat units is individually derived from an alkene monomer having about 1 to about 6 carbon atoms

Clause 51. The article of any one of the preceding clauses, wherein the polyolefin polymer is a polyolefin copolymer and the polyolefin copolymer comprises about 2 percent to about 3 percent ethylene by weight based upon a total weight of the polyolefin copolymer.

Clause 52. The article of any one of the preceding clauses, wherein the thermoplastic material has a percent crystallization of 35 percent or less when measured according to the Differential Scanning Calorimeter (DSC) Test using the Material Sampling Procedure.

Clause 53. The article of any one of the preceding clauses, wherein the externally-facing surface of the component is defined by a polymeric foam material.

Clause 54. The article of any one of the preceding clauses, wherein the polymeric foam material is a polyurethane foam, an ethylene-vinyl acetate foam, or a combination thereof.

Clause 55. The article of any one of the preceding clauses, wherein the structural color has the appearance of a single color or multiple colors.

Clause 56. The article of any one of the preceding clauses, wherein the optical element, as disposed on the article, exhibits a color that, when measured according to the CIE 1976 color space under a given illumination condition at three observation angles between -15 degrees and +60 degrees, has a first color measurement at a first angle of observation having coordinates L_1^* and a_1^* and b_1^*, and a second color measurement at a second angle of observation having coordinates L_2^* and a_2^* and b_2^*, and a third color measurement at a third angle of observation having coordinates L_3^* and a_3^* and b_3^*, wherein the L_1^*, L_2^*, and L_3^* values may be the same or different, wherein the a_1^*, a_2^*, and a_3^* coordinate values may be the same or different, wherein the b_1^*, b_2^*, and b_3^* coordinate values may be the same or different, and wherein the range of the combined a_1^*, a_2^* and a_3^* values is less than about 40% of the overall scale of possible a* values, optionally is less than about 30% of the overall scale of possible a* values, optionally is less than about 20% of the overall scale of possible a* values, or optionally is less than about 10% of the overall scale of possible a* values.

Clause 57. The article of any one of the preceding clauses, wherein the optical element, as disposed on the article, exhibits a color that, when measured according to the CIE 1976 color space under a given illumination condition at three observation angles between -15 degrees and +60 degrees, has a first color measurement at a first angle of observation having coordinates L_1^* and a_1^* and b_1^*, and a second color measurement at a second angle of observation having coordinates L_2^* and a_2^* and b_2^*, and a third color measurement at a third angle of observation having coordinates L_3^* and a_3^* and b_3^*, wherein the L_1^*, L_2^*, and L_3^* values may be the same or different, wherein the a_1^*, a_2^*, and a_3^* coordinate values may be the same or different, wherein the b_1^*, b_2^*, and b_3^* coordinate values may be the same or different, and wherein the range of the combined b_1^*, b_2^* and b_3^* values is less than about 40% of the overall scale of possible b* values, optionally is less than about 30% of the overall scale of possible b* values, optionally is less than

about 20% of the overall scale of possible b* values, or optionally is 10% of the overall scale of possible b* values.

Clause 58. The article of any one of the preceding clauses, wherein the optical element, as disposed on the article, exhibits a color that, when measured according to the CIE 1976 color space under a given illumination condition at two observation angles between -15 degrees and +60 degrees, has a first color measurement at a first angle of observation having coordinates L_1^* and a_1^* and b_1^*, and a second color measurement at a second angle of observation having coordinates L_2^* and a_2^* and b_2^*, wherein the L_1^* and L_2^* values may be the same or different, wherein the a_1^* and a_2^* coordinate values may be the same or different, wherein the b_1^* and b_2^* coordinate values may be the same or different, and wherein the ΔE^*_{ab} between the first color measurement and the second color measurement is less than or equal to about 100, where $\Delta E^*_{ab} = [(L_1^*-L_2^*)^2 + (a_1^*-a_2^*)^2 + (b_1^*-b_2^*)^2]^{1/2}$, optionally is less than or equal to about 80, or optionally is less than or equal to about 60.

Clause 59. The article of any one of the preceding clauses, wherein the optical element, as disposed on the article, exhibits a color that, when measured according to the CIELCH color space under a given illumination condition at three observation angles between -15 degrees and +60 degrees, has a first color measurement at a first angle of observation having coordinates L_1^* and C_1^* and $h_1°$, and a second color measurement at a second angle of observation having coordinates L_2^* and C_2^* and $h_2°$, and a third color measurement at a third angle of observation having coordinates L_3^* and C_3^* and $h_3°$, wherein the L_1^*, L_2^*, and L_3^* values may be the same or different, wherein the C_1^*, C_2^*, and C_3^* coordinate values may be the same or different, wherein the $h_1°$, $h_2°$ and $h_3°$ coordinate values may be the same or different, and wherein the range of the combined $h_1°$, $h_2°$ and $h_3°$ values is less than about 60 degrees, optionally is less than about 50 degrees, optionally is less than about 40 degrees, optionally is less than about 30 degrees, or optionally is less than about 20 degrees.

Clause 60. The article of any preceding clause, wherein the structural color is visible to a viewer having 20/20 visual acuity and normal color vision from a distance of about 1 meter from the article.

Clause 61 The article of any preceding clause, wherein the structural color has a single hue.

Clause 62. The article of any preceding clause, wherein the structural color includes two or more hues.

Clause 63. The article of any preceding clause, wherein the structural color is iridescent.

Clause 64. The article of any preceding clause, wherein the structural color has limited iridescence.

Clause 65. The article of the preceding clause, wherein the structural color has limited iridescence such that, when each color visible at each possible angle of observation is assigned to a single hue selected from the group consisting of the primary, secondary and tertiary colors on the red yellow blue (RYB) color wheel, all of the assigned hues fall into a single hue group, wherein the single hue group is one of a) green-yellow, yellow, and yellow-orange; b) yellow, yellow-orange and orange; c) yellow-orange, orange, and orange-red; d) orange-red, and red-purple; e) red, red-purple, and purple; f) red-purple, purple, and purple-blue; g) purple, purple-blue, and blue; h) purple-blue, blue, and blue-green; i) blue, blue-green and green; and j) blue-green, green, and green-yellow.

Clause 66. The article of clause 98, wherein the structural color having limited iridescence is limited to two or three of the hues green-yellow, yellow, yellow-orange; or the hues purple-blue, blue, and blue-green; or the hues orange-red, red, and red-purple; or the hues blue-green, green, and green-yellow; or the hues yellow-orange, orange, and orange-red; or the hues red-purple, purple, and purple-blue.

Clause 67. The article of any preceding clause, wherein the article is an article of footwear, an article of apparel, or an article of sporting equipment.

Clause 68. The article of any preceding clause, wherein the article is an article of footwear, and the component is a sole for an article of footwear.

Clause 69. The article of any preceding clause, wherein the component is a plate for an article of footwear, and optionally the externally-facing surface of the plate includes a plurality of traction elements.

Clause 70. The article of any preceding clause, wherein the component is a plate for an article of footwear, and the externally-facing surface of the component forms a ground-facing surface of the plate.

Clause 71. The article of any preceding clause, wherein the component is a plate for an article of footwear, and optionally the second surface of the plate includes a plurality of traction elements.

Clause 72. The article of any preceding clause, wherein the component is a plate for an article of footwear, and the second surface of the component forms a ground-facing surface of the plate.

Clause 73. A method of making a component, the method comprising:

disposing a first film surface to an externally-facing surface of a component, wherein the film comprises a film polymeric material and the film has a second film surface opposed to the first film surface and a film core between the first film surface and the second film surface; and

wherein the first film surface or the second film surface includes an optical element having a first side and a second opposed to the first side, and the first side of the optical element or the second side of the optical element, or both, impart a structural color to the component.

Clause 74. The method of the preceding clause, wherein the method further comprises disposing the first side of the optical element or the second side of the optical element onto the first film surface following the step of disposing the film to the externally-facing surface of the component.

Clause 75. The method of any one of the preceding clauses, wherein the method further comprises disposing the first side of the optical element or the second side of the optical element onto the first film surface prior to the step of disposing the film to the externally-facing surface of the component.

Clause 76. The method of any one of the preceding clauses, wherein the step of disposing the first side of the optical element or the second side of the optical element onto the first film surface comprises depositing the first or second side using a technique comprising: physical vapor deposition, electron beam deposition, atomic layer deposition, molecular beam epitaxy, cathodic arc deposition, pulsed laser deposition, sputtering, chemical vapor deposition, plasma-enhanced chemical vapor deposition, low pressure chemical vapor deposition, a wet chemistry technique, or combinations thereof.

Clause 77. The method of any one of the preceding clauses, wherein disposing the first film surface onto the externally-facing side of the component comprises providing a mold; inserting the film into the mold with the second film surface contacting a mold surface; pouring or injecting a component polymeric material or a polymeric precursor material into the mold, optionally applying actinic radiation or pressure or both, molding the polymeric material or polymeric precursor material into the component, disposing the first film surface to the externally-facing surface of the component, and then removing the component with the affixed film from the mold.

Clause 78. The method of any one of the preceding clauses, wherein disposing the first film surface onto the externally-facing surface of the component comprises providing a second material comprising a polymeric material or polymeric precursor material, and disposing the first film surface to the externally-facing surface of the component with the second material between the first film surface and the externally-facing surface of the component.

Clause 79. The method of any one of the preceding clauses, wherein disposing the first film surface to the component comprises directly injecting the component polymeric material onto the first film surface.

Clause 80. The method of any one of the preceding clauses, wherein the component polymeric material is a thermoplastic polymeric material, and disposing the film to the component polymeric material comprises (i) increasing a temperature of the component polymeric material to a first

temperature above a melting or softening point of the component polymeric material, (ii) contacting the component polymeric material and the first film surface while the component polymeric material is at the first temperature, and (iii) keeping the component polymeric material and the first film surface in contact with each other while decreasing the temperature of the component material to a second temperature below the melting or softening point of the component polymeric material, disposing the component polymeric material and the first film surface to each other.

Clause 81. The method of any one of the preceding clauses, wherein the first film surface is defined by a film thermoplastic polymeric material, and disposing the film to the component comprises (i) increasing a temperature of the film thermoplastic polymeric material to a first temperature above a melting or softening point of the film thermoplastic polymeric material, (ii) contacting the externally-facing surface of the component and the first film surface while the film thermoplastic polymeric material is at the first temperature, and (iii) keeping the externally-facing surface of the component and the first film surface in contact with each other while decreasing the temperature of the film thermoplastic polymeric material to a second temperature below the melting or softening point of the film thermoplastic polymeric material, disposing the externally-facing surface of the component and the first film surface to each other.

Clause 82. The method of any one of the preceding clauses, wherein the first film surface includes a film thermoplastic polymeric material and the externally-facing surface of the component is defined by a component thermoplastic material, and disposing the first film surface to the externally-facing surface of the component comprises (i) increasing a temperature of both the component thermoplastic material and the film thermoplastic polymeric material to a first temperature, wherein the first temperature is at or above one of a melting or softening point of the component thermoplastic material and at or above one of a melting or softening point of the film thermoplastic polymeric material, (ii) contacting the externally-facing surface of the component and the first film surface while both the component thermoplastic material and the film thermoplastic polymeric material are at the first temperature, and (iii) keeping the externally-facing surface of the component and the first film surface in contact with each other while decreasing the temperature of both the component thermoplastic material and the film thermoplastic polymeric material to a second temperature below softening point of both the component thermoplastic material and the film thermoplastic polymeric material, thereby melding at least a portion of the component thermoplastic material and the film thermoplastic polymeric material with each other and forming a mechanical bond between the externally-facing surface of the component and the first film surface.

Clause 83. The method of any one of the preceding clauses, wherein the externally-facing surface of the component includes a component polymeric precursor material, and disposing the first film

surface to the externally-facing component comprises (i) contacting the component polymeric precursor material and the first film surface, and (ii) applying actinic radiation to the component polymeric precursor material to at least partially cure the component polymeric precursor material while the first film surface is in contact with the externally-facing surface of the component, thereby disposing the eternally-facing surface of the component to the first film surface.

Clause 84. The method of any one of the preceding clauses, further comprising forming a primer layer between the first film surface and the externally-facing surface of the component, or on a second surface of the component opposed to the externally-facing surface of the component.

Clause 85. The method of any one of the preceding clauses, further comprising forming a textured surface on the first film surface or the second film surface.

Clause 86. The method of any one of the preceding clauses, further comprising forming a textured surface on the externally-facing surface of the component or on the second surface of the component.

Clause 87. The method of any one of the preceding clauses, further comprising disposing a textured structure between the first film surface and the externally-facing surface of component.

Clause 88. The method of any of the preceding clauses, wherein forming a primer layer comprises forming a primer layer using a technique comprising digital printing, inkjet printing, offset printing, pad printing, screen printing, flexographic printing, heat transfer printing, physical vapor deposition including chemical vapor deposition, pulsed laser deposition, evaporative deposition, sputtering deposition, plasma enhanced chemical vapor deposition, electron beam deposition, cathodic arc deposition, low pressure chemical vapor deposition, wet chemistry techniques, spray coating, dip coating, brushing, spin coating, doctor blade coating, or combinations thereof.

Clause 89. The method of any of any one of the preceding clauses, wherein forming the textured surface on the first film surface or the externally-facing surface of the component comprises forming a textured surface on the film thermoplastic material or the component thermoplastic material or both by increasing a temperature of the film thermoplastic material or the component thermoplastic material or both above a softening temperature, and altering the first film surface or the externally-facing surface of the component by molding, stamping, printing, compressing, cutting, etching, vacuum forming or any combination thereof to form the textured surface.

Clause 90. A method of making an article, the method comprising:

making a structurally-colored component according to method of any one of the preceding method clauses; and

combining the structurally-colored component with a second component to form the article.

Clause 91. An article comprising the structurally-colored component resulting from the methods of any one of the preceding method clauses.

Clause 92. The method of making an article of any one of the preceding article clauses.

Clause 93. The method of any one of the method clauses, wherein the article is an article according to any one of the article clauses.

It should be noted that ratios, concentrations, amounts, and other numerical data may be expressed herein in a range format. It is to be understood that such a range format is used for convenience and brevity, and thus, should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. To illustrate, a concentration range of "about 0.1 percent to about 5 percent" should be interpreted to include not only the explicitly recited concentration of about 0.1 weight percent to about 5 weight percent but also include individual concentrations (*e.g.*, 1 percent, 2 percent, 3 percent, and 4 percent) and the sub-ranges (*e.g.*, 0.5 percent, 1.1 percent, 2.2 percent, 3.3 percent, and 4.4 percent) within the indicated range. The term "about" can include traditional rounding according to significant figures of the numerical value. In addition, the phrase "about 'x' to 'y'" includes "about 'x' to about 'y'".

Many variations and modifications may be made to the above-described embodiments. All such modifications and variations are intended to be included herein within the scope of this disclosure and protected by the following claims.

Claims

1. An article of footwear, apparel, or sports equipment, comprising:

a transparent or translucent film forming at least a portion of a component of the article, the film having a first film surface, a second film surface opposing the first film surface, and a film core between the first film surface and the second film surface, wherein the first film surface or the second film surface or the film core or any combination thereof include a film polymeric material, wherein the first film surface forms an externally-facing surface of the component or an internally-facing surface of the component; and

an optical element disposed on the first film surface, wherein the optical element has a first side and a second side opposing the first side, wherein the first side and the second side of the optical element impart structural color, wherein the optical element comprises 2 to 10 optical layers,

wherein the first side of the optical element imparts a first structural color to the first film surface of the article and the second side of the optical element alone imparts a second structural color to the second film surface of the article, wherein the first structural color has a first at least one hue and is visible on the first film surface and the second structural color has a second at least one hue and is visible through the opposing second film surface, and the first structural color differs from the second structural color.

2. The article of claim 1, wherein the optical element comprises 2 to 10 optical layers.

3. The article of claim 1, wherein the component is at least a portion of a sole of an article of footwear, and the externally-facing surface of the component forms an externally-facing surface of the sole.

4. The article of claim 1, wherein the component is a plate for an article of footwear, and the externally-facing surface of the plate includes a plurality of traction elements.

5. The article of claim 1, wherein the component is a plate for an article of footwear, and the externally-facing surface of the component forms a ground-facing surface of the plate.

6. The article of claim 1, wherein the component is a plate for an article of footwear, and a second surface of the plate includes a plurality of traction elements.

7. The article of claim 1, wherein the component is a plate for an article of footwear, and a second surface of the component forms a ground-facing surface of the plate.

8. The article of claim 1, wherein the optical element contains no pigments and no dyes.

9. The article of claim 1, wherein the first structural color is limited to one, two or three hues selected from a hue group, wherein the hue group is selected from the group consisting of cyan, indigo, violet, blue, blue-green, or purple green.

11. The article of claim 1, wherein the first structural color produced by optical element is a single-hued color.

12. The article of claim 1, wherein the first at least one hue is associated with a wavelength range in the visible spectrum, wherein the wavelength range is selected from: the range of about 520 to 490 nanometers, the range of about 490 nanometers to 450 nanometers, the range of about 450 to 400 nanometers, or a combination thereof.

13. The article of claim 1, wherein a first optical layer of the optical element comprises titanium dioxide, wherein a second optical layer of the optical element comprises silicon dioxide, and wherein the first layer and the second layer are adjacent one another.

14. The article of claim 1, wherein the first structural color is a multihued structural color that changes between 2-4 hues as the angle of observation or illumination changes by 15 degrees or more.

15. An article of footwear, apparel, or sports equipment, comprising:

a transparent or translucent film forming at least a portion of a component of the article, the film having a first film surface, a second film surface opposing the first film surface, and a film core between the first film surface and the second film surface, wherein the first film surface or the second film surface or the film core or any combination thereof include a film polymeric material, wherein the first film surface forms an externally-facing surface of the component or an internally-facing surface of the component; and

an optical element disposed on the first film surface, wherein the optical element has a first side and a second side opposing the first side,

wherein the optical layers of the optical element impart a first structural color from the first side of the article, wherein the optical layers the optical element alone impart a second structural color from the second side of the article, wherein the first structural color has a first at least one hue and is visible on the first film surface and the second structural color has a second at least one hue and is visible through the opposing second film surface, and the first structural color differs from the second structural color, wherein the first structural color is a multihued structural color that changes between 2-4 hues as the angle of observation or illumination changes by 15 degrees or more, wherein the second structural color is a multihued structural color that changes between 2-4 hues as the angle of observation or illumination changes by 15 degrees or more.

16. The article of claim 15, wherein each optical layer has a thickness of about 10 to 500 nanometers.

17. The article of claim 16, wherein a first optical layer of the optical element is made of a material selected from: silicon dioxide, titanium dioxide, zinc sulfide, magnesium fluoride, tantalum pentoxide, aluminum oxide, wherein a second optical layer of the optical element is made of a material selected from: silicon dioxide, titanium dioxide, zinc sulfide, magnesium fluoride, tantalum pentoxide, aluminum oxide, wherein the first layer and the second layer are made of different materials, and wherein the first layer and the second layer are adjacent one another.

18. The article of claim 15, wherein each optical layer of the optical element is made of a material selected from: silicon dioxide, titanium dioxide, zinc sulfide, magnesium fluoride, tantalum pentoxide, aluminum oxide, wherein adjacent layers are made of different materials.

19. The article of claim 15, wherein the optical element comprises 2 to 10 optical layers.

20. The article of claim 15, wherein the optical element contains no pigments and no dyes.