

TITANIUM DIOXIDE

FIELD OF THE INVENTION

[0001] This disclosure, in general, relates to improved colored solar reflective systems, colored compositions containing the colored solar reflective systems, and to various uses of such colored compositions.

BACKGROUND

[0002] New technologies are continuously being developed to improve energy efficiency. One such technology is the use of infrared reflective pigments in coatings positioned on a building's (or other object's) exterior. As one is aware, the sun emits about 50% of its energy as near-infrared radiation. When this near-infrared radiation is absorbed, it is physically converted into heat. Coatings containing infrared reflective pigments work by reflecting away sunlight and by blocking the transfer of heat thereby reducing the heat load to the building. For example, white pigments, such as titanium oxide, have been used in coatings to reflect a majority of the sun's energy. Oftentimes, it is desirable to provide a colored coating in place of white for aesthetic reasons. However, the selection of non-white pigments that are available for use is limited since they tend to absorb more of the sun's energy than is desired leading to a marked reduction in the above-described effect. Thus, various systems have been and continue to be developed to provide colored coatings having improved solar reflectance.

[0003] For example, U.S. Pat. No. 5,540,998 describes a system in which two or more non-white pigments having particle diameters of 50 μm or less are combined to yield a color of low lightness, and in particular, achromatic black. U.S. Pat. No. 5,962,143 further describes a dark colored coating that contains one or more black pigments, one or more non-white pigments and silicic acid.

[0004] In U.S. Pat. No. 6,174,360, the use of complex inorganic colored pigments (CICP's) in coatings is taught to exhibit dark drab colors in the visible portion along with reflectivity in the near-infrared portion of the electromagnetic spectrum.

[0005] U.S. Pat. No. 6,336,397 describes an infrared reflective system containing two or more layers with one layer containing a resin and pigment which provides the desired color and another layer containing a pigment which provides infrared reflectance. U.S. Pat. Publ. No. 2009/0268278 also discloses a two layer sheet-like infrared reflective system having a top layer consisting of a synthetic resin and an organic pigment and a bottom layer consisting of a synthetic resin and a titanium oxide-based white pigment.

[0006] In addition, U.S. Pat. No. 6,521,038 teaches a near-infrared reflecting composite pigment containing a near-infrared non-absorbing colorant and a white pigment that is coated with such a colorant. The composite pigment may then be used as a coloring agent in coatings.

[0007] Finally, WO 2009/136141 describes the use of near-infrared-scattering particulate material which provides high reflection of near-infrared radiation and diminished reflectance of visible light in combination with various non-white colorants.

[0008] Although each provide solar reflectance, some of the disadvantages in using these currently available systems include: they provide relatively pale coloring since a high level of conventional titanium dioxide is needed to give the desired level of solar reflection; application of two or more layers is both time consuming and costly and can result in coatings having a patchy or non-uniform appearance that tends to lighten over time; and impurities contained within the systems can lead to absorptions in the near-infrared part of the spectrum resulting in a reduction of solar reflectance. As such, alternative systems which exhibit enhanced solar reflectivity in a wide range of dark or more intense uniform colors than is otherwise achievable is still highly desirable.

SUMMARY

[0009] The present invention provides a colored solar reflective system including a particulate material having a large average particle size and an organic pigment which is chosen based on the following properties: (i) it must strongly absorb in the visible light region; (ii) it must negligibly absorb in the near-infrared light region; and (iii) it must negligibly scatter light in the visible light region. The solar reflective system, which may

be used in a coating composition or as a composition from which articles can be formed, exhibits a dark, intense color while also providing enhanced total solar reflectance.

[0010] In one aspect, the present disclosure provides a colored solar reflective system containing (1) a particulate material having a substantially rutile crystal habit and having an average particle size of between about 0.5 μm and about 2.0 μm and (2) an organic pigment having a maximum absorption coefficient of about 5,000 mm^{-1} or greater in the visible light region, a maximum scattering coefficient of about 500 mm^{-1} or less in the visible light region, and an average absorption coefficient of about 50 mm^{-1} or less in the near-infrared light region. In some embodiments, the organic pigment having the above properties may be a single organic pigment or it may be a mixture of organic pigments where each pigment has the above properties.

[0011] In another aspect, the colored solar reflective system may be dispersed within a vehicle to form a colored composition. The colored composition may then be used as a one layer coating or as a composition from which articles can be formed.

BRIEF DESCRIPTION OF FIGURES

[0012] For a detailed understanding and better appreciation of the present invention, reference should be made to the following detailed description of the invention, taken in conjunction with the accompanying figure.

[0013] Figure 1 is a graph depicting the reflectance for ral 8007 (fawn brown) at various wavelengths. It shows reflectance against wavelength for ral 8007 (fawn brown) for a comparative system and an inventive reflective system.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

[0014] In this specification and in the claims which follow, reference will be made to a number of terms which shall be understood to have the following meanings.

[0015] The term "visible light" refers to electromagnetic radiation having a wavelength in the range of 400 nm to 760 nm of the electromagnetic spectrum.

[0016] The term "near-infrared light" refers to electromagnetic radiation having a wavelength within the range of 760 nm to about 2500 nm of the electromagnetic spectrum.

[0017] The term "total solar reflectance" or "TSR" refers to the fraction of the incident solar energy (~360 nm-2500 nm) that is reflected by a surface in question. It is a ratio of energies of the reflected wave to that of the incident wave. For example, a reflectance of 0.8 equals a reflectance of 80% of the incident wave. The total solar reflectance may be determined as specified in standard test method ASTM E903, the entire contents of which are incorporated herein by reference.

[0018] The term "organic pigment" refers to an organic particle(s) substantially insoluble in the application medium in which it's dispersed and which imparts color.

[0019] The term "energy consumption" refers to the usage or consumption of conventional forms of energy, for example, electricity, gas, etc. Thus, the reduction of energy consumption in a structure pertains to lower usage of, for example, electricity in the structure.

[0020] The term "structure" refers to any object which may be exposed to the sun, for example, a building, an automobile, a train, a container, a vessel, piping, a road, flooring, a driveway, a parking lot, sidewalk, a swimming pool, a deck, a textile, an airplane, a ship, a submarine, a window profile, siding, roofing granules, roofing shingles, an agricultural film, or a glass product. The material of the structure is not limited; therefore, it may comprise metal, glass, ceramic, plastic, concrete, asphalt, wood, tile, natural or artificial fibers, rubber, etc.

[0021] The present disclosure in general relates to colored solar reflective systems. It has been surprisingly found that the colored solar reflective systems of the present invention allow color to be decoupled from near-infrared reflection properties, that is, the near-infrared reflectance and photocatalytic properties of the colored systems may be varied

independently from color. Thus, once a desired color has been achieved with certain organic pigments, the desired solar reflectance properties, which are dependant on the particulate concentration, may then be independently attained.

[0022] The colored solar reflective systems also provide improved infrared reflectivity in structures made with or covered by these systems while also providing previously inaccessible colors and tones, including, but not limited to, the blue part of the color spectrum. For example, application of the present colored solar reflective system to an exterior surface of a structure, such as a wall or roof, allows the structure to exhibit increased total solar reflectance. This, in turn, results in a lower surface temperature and heat transfer through the coated structure. Therefore, the interior temperature of the structure is cooler and accordingly, less energy is needed to cool the interior of the structure. In addition, the potential loss by evaporation of any volatile components contained within the structure is reduced. Furthermore, structural integrity is improved since damage caused by heat, such as cracks and thermal warping, is significantly diminished. Finally, the colored solar reflective system may be applied in a single layer coating reducing time and cost while providing a consistent coloring throughout the applied coating.

[0023] According to an embodiment, the colored solar reflective system includes (1) a particulate material having a substantially rutile crystal habit and having an average particle size of between about 0.5 μm and about 2.0 μm , preferably between about 0.6 μm and about 1.7 μm , and even more preferably between about 0.7 μm and about 1.4 μm and (2) an organic pigment having a maximum absorption coefficient of about 5,000 mm^{-1} or greater, preferably about 10,000 mm^{-1} or greater, and more preferably about 15,000 mm^{-1} or greater in the visible light region, a maximum scattering coefficient of about 500 mm^{-1} or less, preferably about 250 mm^{-1} or less, and more preferably about 100 mm^{-1} or less in the visible light region, and an average absorption coefficient of about 50 mm^{-1} or less, preferably about 30 mm^{-1} or less, and more preferably about 10 mm^{-1} or less in the near-infrared light region.

[0024] In one embodiment, the particulate material is selected from titanium dioxide, doped titanium dioxide, and a mixture thereof.

[0025] The titanium dioxide useful in the present invention is one capable of scattering near-infrared light while also providing low scattering and low absorbance of visible light. Such properties may be obtained when the titanium dioxide has an average particle size of between about 0.5 μm and about 2.0 μm . In still another embodiment, the titanium dioxide has an average particle size of between about 0.6 μm and about 1.7 μm , and more preferably between about 0.7 μm and about 1.4 μm . It has been surprisingly found that such titanium dioxide reflects near-infrared light at an unusually high level while also exhibiting noticeably diminished reflectance of visible light when compared to conventional titanium dioxide pigment. Furthermore, in contrast to conventional titanium dioxide, which is very reflective of visible light making the color of conventional colored systems in which it is used pale, the titanium dioxide of the present invention blends with the organic pigment without unduly affecting the color of the system to provide a more widely available pallet of dark, or more intensely colored systems.

[0026] As one skilled in the art is aware, crystal size is distinct from particle size. Crystal size relates to the size of the fundamental crystals which make up the particulate material. These crystals may then aggregate to some degree to form larger particles. For example, conventional titanium dioxide in the rutile crystal habit has a crystal size of about 0.17 μm - 0.29 μm and a particle size of about 0.25 μm - 0.40 μm while conventional titanium dioxide in the anatase crystal form has a crystal size of about 0.10 μm - 0.25 μm and a particle size of about 0.20 μm - 0.40 μm . The particle size is thus affected by factors such as the crystal size as well as milling techniques used during production, such as dry, wet or incorporative milling. Accordingly, in some embodiments, the particle size of the titanium dioxide is greater than the crystal size. In still other embodiments, the particle size of the titanium dioxide is about equal to the crystal size.

[0027] The crystal size and particle size of the titanium dioxide may be determined by methods well known to those skilled in the art. For example, the crystal size may be

determined by transmission electron microscopy on a rubbed out sample with image analysis of the resulting photograph. The results of the crystal size may further be validated by reference using latex NANOSHPERE™ Size Standards (available from Thermo Scientific). A method which may be used for determining the particle size of the titanium dioxide includes X-ray sedimentation.

[0028] Because of higher refractive index, the particulate material contains titanium dioxide substantially in a rutile crystal habit. Thus, according to another embodiment, greater than 90% by weight of the titanium dioxide, preferably greater than 95% by weight of the titanium dioxide, and even more preferably greater than 99% by weight of the titanium dioxide, based on the total weight of the particulate material, is in the rutile crystal habit. In still another embodiment, the particulate material may further contain titanium dioxide which is in an anatase crystal form.

[0029] Known processes which may be used to prepare the titanium dioxide include, but are not limited to, the sulfate process, chloride process, fluoride process, hydrothermal process, aerosol process and leaching process; however, each such known process is modified by one or more of the following conditions:

- (a) treating at a higher temperature, for example, 900°C or higher;
- (b) treating for a longer period of time, for example, 5 hours or more;
- (c) increasing or reducing typical levels of growth moderators present during the process; and
- (d) reducing the typical level of rutile seeds.

Thus, for example, the titanium dioxide may be prepared by the sulfate process which generally includes:

- (i) reacting a titaniferous feedstock with sulfuric acid to form a solid, water soluble reaction cake;

- (ii) dissolving the reaction cake in water and/or weak acid to produce a titanium sulfate solution;
- (iii) hydrolyzing the titanium sulfate solution to convert titanium sulfate to titanium dioxide hydrate; and
- (iv) separating the precipitated titanium dioxide hydrate from the solution and calcining to obtain titanium dioxide

wherein the process is modified by one or more of the conditions (a) – (d) described above. In one embodiment the process is modified by condition (a); in another the process is modified by condition (b); in another the process is modified by condition (c); and in another the process is modified by condition (d).

[0030] The titanium dioxide of the present disclosure may be white or translucent or it may be colored. Preferably, the titanium dioxide is white. Thus, in one embodiment, the titanium dioxide has a lightness value L^* (CIE $L^*a^*b^*$ color space) greater than 95, an a^* value less than 5 and a b^* value less than 5.

[0031] Preferably, the particulate material contains greater than 70% by weight of titanium dioxide, based on the total weight of the particulate material. In another embodiment, the particulate material contains greater than 80% by weight, preferably greater than 90% by weight, more preferably greater than 95% by weight and even more preferably greater than 99.5% by weight of titanium dioxide, based on the total weight of the particulate material.

[0032] In another embodiment, the particulate material is a doped titanium dioxide. As used herein, “doped titanium dioxide” refers to the titanium dioxide of the present disclosure but further including one or more dopants which have been incorporated during preparation of the titanium dioxide. The dopants, which may be incorporated by known processes, may include, but are not limited to, calcium, magnesium, sodium, vanadium, chromium, manganese, iron, nickel, aluminum, antimony, phosphorus, niobium or cesium. The dopant may be incorporated in an amount of no more than 30% by weight, preferably no more than 15% by weight, and more preferably no more than

5% by weight, based on the total weight of the titanium dioxide. For example the dopant may be incorporated in an amount of from 0.1 to 30% by weight, or 0.5 to 15% by weight, or 1 to 5% by weight, relative to the total weight of the titanium dioxide. Because of its higher refractive index, such doped titanium dioxide may be recognized by being substantially in a rutile crystal habit. In other embodiments, the particulate material may further contain doped titanium dioxide in an anatase crystal form.

[0033] In still another embodiment, the particulate material may further be treated as known in the art with a coating agent to form coated titanium dioxide or coated doped titanium dioxide. For example, the particulate material may be dispersed in water along with the coating agent. The pH of the solution may then be adjusted to precipitate the desired hydrated oxide to form a coating on the surface of the particulate material. After coating, the particulate material may be washed and dried before being ground, for example, in a fluid energy mill or micronizer, to separate particles stuck together by the coating. At this milling stage, an organic surface treatment, may also be applied if desired.

[0034] Coating agents suitable for use include those commonly used to coat an inorganic oxide or hydrous oxide onto the surface of particles. Typical inorganic oxides and hydrous oxides include one or more oxides and/or hydrous oxides of silicon, aluminum, titanium, zirconium, magnesium, zinc, cerium, phosphorus, or tin, for example, Al_2O_3 , SiO_2 , ZrO_2 , CeO_2 , P_2O_5 , sodium silicate, potassium silicate, sodium aluminate, aluminum chloride, aluminum sulphate, or a mixture thereof. The amount of coating coated onto the surface of the titanium dioxide or doped titanium dioxide may range from about 0.1% by weight to about 20% by weight of the inorganic oxide and/or hydrous oxide relative to the total weight of the titanium dioxide or doped titanium dioxide.

[0035] Organic surface treatments suitable for application at the milling stage include polyols, amines, alkyl phosphonic acids and silicone derivatives. For example, the organic surface treatment may be trimethylolpropane, pentaerythritol, triethanolamine, n-octyl phosphonic acid or trimethylolethane.

[0036] In addition to the particulate material described above, the colored solar reflective system also includes an organic pigment. According to various embodiments, the organic pigment may be selected from a black, brown, blue, cyan, green, violet, magenta, red, orange, yellow pigment and a mixture thereof. The selection will depend on the necessary organic pigments needed to achieve the desired color, for example, vibrant blues, reds, browns and greens. The organic pigment may be obtained from commercial sources and is chosen based on the following properties: (i) it must strongly absorb in the visible light region; (ii) it must negligibly absorb in the near-infrared light region; and (iii) it must negligibly scatter light in the visible light region. By “strongly absorb in the visible light region”, the organic pigment must have a maximum absorption coefficient of at least about $5,000 \text{ mm}^{-1}$, preferably at least about $10,000 \text{ mm}^{-1}$, and more preferably at least about $15,000 \text{ mm}^{-1}$ in the visible light region. By “negligibly absorb in the near-infrared light region”, the organic pigment must have an average absorption coefficient of less than about 50 mm^{-1} , preferably less than about 30 mm^{-1} , more preferably less than about 15 mm^{-1} , and even more preferably less than about 10 mm^{-1} in the near-infrared light region. By “negligibly scatter light in the visible light region”, the organic pigment must have a maximum scattering coefficient of less than about 500 mm^{-1} , preferably less than about 250 mm^{-1} , and more preferably less than about 100 mm^{-1} in the visible light region. The absorption and scattering coefficients may be determined by methods well known to those skilled in the art, for example, such as those described in “Solar Spectral Optical Properties of Pigments – Part I: Model for Deriving Scattering and Absorption Coefficients From Transmittance and Reflectance Measurements”, R. Levinson et al., *Solar Energy Materials and Solar Cells* 89 (2005) 319-349, the entire contents of which is incorporated herein by reference.

[0037] In some embodiments, the organic pigment is one organic pigment having the above described properties (i), (ii) and (iii). In other embodiments, the organic pigment is a mixture of more than one organic pigment, each having the above described properties (i), (ii), and (iii). In yet other embodiments, the colored solar reflective system is characterized by further containing less than about 5% by weight, based on the total weight of the colored solar reflective system, of one or more organic pigments which do not have the above described properties (i), (ii) and (iii). In still another embodiment, the

colored solar reflective system is characterized by further containing less than about 2.5 % by weight, preferably less than about 1% by weight, based on the total weight of the colored solar reflective system, of one or more organic pigments which do not have the above described properties (i), (ii) and (iii). In one embodiment, the colored solar reflective system is contains from 0 to 2.5 % by weight, such as from 0.1 to 1% by weight, based on the total weight of the colored solar reflective system, of one or more organic pigments which do not have the above described properties (i), (ii) and (iii).

[0038] According to one embodiment, the (or each) organic pigment may be an azo, anthraquinone, phthalocyanine, perinone/perylene, indigo/thioindigo, dioxazine, quinacridone, isoindolinone, isoindoline, diketopyrrolopyrrole, azomethine or azomethine-azo pigment.

[0039] The colored solar reflective system may be formed by combining the particulate material and organic pigment. Thus, in one embodiment, the colored solar reflective system may be prepared by a method comprising mixing the particulate material with the organic pigment. Mixing may occur by any known means.

[0040] In still another embodiment, the present disclosure provides a colored composition containing the colored solar reflective system dispersed within a vehicle. The vehicle may be any component or combination of components within which the colored solar reflective system can be dispersed. The amount of colored solar reflective system included in the colored composition is an amount sufficient to provide about 0.1% by volume to about 20% by volume of organic pigment, based on the total volume of the colored composition, and about 0.5% by volume to about 40% by volume of particulate material, based on the total volume of the colored composition. Thus, in one embodiment, the colored composition comprises about 0.1% by volume to about 20% by volume of organic pigment and about 0.5% by volume to about 40% by volume of particulate material, based on the total volume of the colored composition, dispersed within a vehicle.

[0041] According to one embodiment, the vehicle is a synthetic or natural resin. The resin may be, but is not limited to, a polyolefin resin, polyvinyl chloride resin, ABS resin,

polystyrene resin, methacrylic resin, polycarbonate resin, polyethylene terephthalate resin, polyamide resin, alkyd resin, acrylic resin, polyurethane resin, polyester resin, melamine resin, fluoropolymer, or epoxy resin.

[0042] In another embodiment, the vehicle is a carrier. The carrier may be, but is not limited to, an aqueous solvent, for example, water. The carrier may also be a non-aqueous solvent, for example, an organic solvent such as a petroleum distillate, alcohol, ketone, ester, glycol ether and the like.

[0043] In yet another embodiment, the vehicle is a binder. The binder may be, but is not limited to, a metal silicate binder, for example an aluminosilicate binder. The binder may also be a polymeric binder, for example, an acrylic polymer or copolymer binder.

[0044] The colored composition may further include one or more customary additives. Additives suitable for use include, but are not limited to, thickeners, stabilizers, emulsifiers, texturizers, adhesion promoters, UV stabilizers, de-glossing agents, dispersants, antifoaming agents, wetting agents, coalescing agents, and biocides/fungicides.

[0045] The colored composition may also include one or more spacer particles useful in spacing out or supporting material contained within the composition. The spacer particles may be silica, silicates, aluminates, sulphates, carbonates, clays, or polymeric particles in the form of hollow beads or in the form of microspheres.

[0046] The colored composition may be used as a coating composition, for example, as a paint, ink, liquid coating, powder coating, etc., or it may be used as a composition, for example, as a plastic or polymer molding composition, from which articles can be formed by molding, extrusion or other known processes.

[0047] Thus, in one embodiment, the present disclosure provides a one layer solar reflective colored coating containing the colored solar reflective system dispersed within the vehicle. In another embodiment, the one layer solar reflective colored coating has a lightness value L^* (CIE $L^*a^*b^*$ color space) of 75 or less, preferably 65 or less, more preferably 55 or less, and even more preferably 45 or less.

[0048] As mentioned above, the colored solar reflective system also provides enhanced near-infrared reflectivity. Thus, in another embodiment, the one layer solar reflective colored coating has a total solar reflectance of greater than 30%. In still another embodiment, the one layer solar reflective colored coating has a total solar reflectance of greater than 35%, preferably greater than 40%, and even more preferably greater than 45%.

[0049] Once formulated, the one layer solar reflective colored coating may be applied to one or more surfaces of a structure. Thus, in another embodiment, the present disclosure provides a structure comprising the one layer solar reflective colored coating.

[0050] In another embodiment the one layer solar reflective colored coating covers a substrate, where the substrate absorbs a proportion of near-infrared radiation. The thickness of the reflective layer is such that more than 1% of the incident near-infrared radiation reaches the substrate.

[0051] In yet still another embodiment, the present disclosure provides a method for reducing the energy consumption of a structure by applying the one layer solar reflective colored coating to one or more surfaces of the structure. The one layer solar reflective colored coating may be applied by any known means, for example, by brushing, rolling spraying, dipping, etc. Because of its enhanced near-infrared reflectivity, the one layer solar reflective colored coating causes the surface temperature of the resultant coated surface to be lowered relative to the surface temperature of a surface coated with a non-reflective coating of the same color. Thus, less energy is needed to cool the interior of the structure.

[0052] The one layer solar reflective colored coating presented herein may also be applied to the surface of a structure after one or more primers have been applied to the structure. For example, the surface of the structure may be coated with a primer before application of the one layer colored coating.

[0053] The present disclosure also provides an article comprising the colored composition. In one embodiment, the article has a lightness value L^* (CIE $L^*a^*b^*$ color

space) of 75 or less, preferably 65 or less, more preferably 55 or less, and even more preferably 45 or less.

[0054] As mentioned above, the colored solar reflective system also provides enhanced near-infrared reflectivity. Thus, in another embodiment, the article has a total solar reflectance of greater than 30%. In still another embodiment, the article has a total solar reflectance of greater than 35%, preferably greater than 40%, and even more preferably greater than 45%. Total solar reflectance may be determined according to the method described in ASTM E903.

[0055] The present invention will be further illustrated by a consideration of the following examples, which are intended to be exemplary of the invention.

Examples

[0056] Example 1A. An experimental program was undertaken to color match ral 8007 (fawn brown). The target was: $L^*=39.56$, $a^*=12.20$, and $b^*=18.01$. The organic pigments PB60 (Albion Colours Bricofor Blue 3GRP), PY154 (High Performance Colours PY1540) and PR122 (High Performance Colours PR1220), where the PB60 and PY154 were used in combination with titanium dioxide having an average particle size of 1.4 μm . This system was then compared against a system containing the inventive combination of organic pigments PY128 (Ciba 8GNP), PR122 (High Performance Colours PR1220) and PV23 (Ciba Cromophtal Violet Gt) with titanium dioxide having an average particle size of 1.4 μm

[0057] A tinter concentrate was prepared for each of the specified pigments (PB60, PY154, PR122, PY128, PV23) using an acrylic resin, a wetting and dispersing additive, a solvent and the specified tint. The quantities of each component are specified in Table 1. This tint concentrate was milled with steel ballotini.

Tinter Concentrate Component	% by weight
60% Acrylic Resin (40% solvent)	78
Solvent	4
Wetting & Dispersing Additive	9
Tint	9

Table 1: Tinter concentrate components.

[0058] A colored resin solution was then made up by taking the quantities specified in Table 2 of each of the required tinter concentrates and vigorously mixing for 2 minutes with the specified amount of additional acrylic resin.

	Comparative colored resin	Inventive colored resin
Tint conc PB60 (g)	1.6	0
Tint conc PY154 (g)	26.0	0
Tint conc PR122 (g)	5.2	1.5
Tint conc PV23 (g)	0	1.0
Tint conc PY128 (g)	0	13.7
60% Acrylic Resin (40% solvent) (g)	0.7	16.6

Table 2: Colored resin solution make up.

The titanium dioxide (quantity specified in table 3) was added to 7.5 g of the colored resin solution to create a millbase which was then vigorously mixed for 30 seconds. This tinted millbase was then let down with a further 13 g of colored resin. This millbase was then milled for an additional 2 minutes.

	Comparative colored resin	Inventive colored resin
TiO ₂ (g)	7.1	2.75
TiO ₂ volume conc. %	14.5	6

Table 3: Quantity of titanium dioxide added to colored resin solution.

[0059] The test paint was then applied to an opacity chart using a number 150 wire wound applicator; the gauge of which determined the nominal wet film thickness. The solvents were allowed to evaporate and the panel was stoved at 105°C for 30 minutes. This process was then repeated to give a second coating.

[0060] Reflectance spectra were measured using a UV/vis/NIR spectrophotometer with an integrating sphere and a wavelength range of 300 nm – 2500 nm. Total Solar Reflectance was calculated from this data, according to the method described in ASTM E903. L*, a* & b* under a D65 illuminant, were also calculated from this data.

[0061] In an attempt to reach the same % TSR in the comparative system as in the inventive system, the TiO₂ PVC had to be increased in the comparative system. Despite this increase it was still not possible to achieve the highest % TSR of the inventive system. The required color was also unachievable in the comparative system as the yellow pigment scattered significant light in the visible light region. The blue pigment displayed significant absorption in the region above 760 nm, detracting from the reflectance potential. This can clearly be seen in Figure 1 where there is much less reflectance after 760 nm in the comparative system. Despite the additional titanium dioxide in the comparative system, the % TSR is still lower than in this system as compared to the inventive system due to the absorption in the near-infrared region from the blue pigment. The % TSR for each system is provided in Table 4 below.

ral 8007	Comparative system	Inventive system
% TSR over black	43.52	44.50
% TSR over white	43.80	49.67

Table 4: % TSR for ral 8007.

[0062] Example 1B. A PVC plaque was made in color ral 8007 (fawn brown) using titanium dioxide having an average particle size of 1.4 µm. Stock solutions of PY128 (Ciba 8GNP), PR122 (High Performance Colours PR1220) and PV23 (Ciba Cromophthal Violet Gt) were prepared by mixing 40 g of each pigment with 350 g acetyltributyl citrate.

Component	grams per 100 g resin
PVC Resin	100
Stearic acid	0.5
Lankromark LZB320	2.5
DIMP	8.49
PV23 stock solution	6.5
PR122 stock solution	10.6
PY128 stock solution	39.1
TiO ₂	34.45

Table 5: PVC formulation.

[0063] The PVC plaque was prepared as follows: a dry blend was prepared using a crypto-peerless type mixer. A J.R. Dare two-roll mill (140°C front & 135°C rear roller) was then used to produce PVC. The resultant PVC was preheated for 3 minutes at 165°C then pressed for 2 minutes at 15te/in².

[0064] Reflectance spectra were measured using a UV/vis/NIR spectrophotometer with an integrating sphere and a wavelength range of 300 nm – 2500 nm. Total Solar Reflectance was calculated from this data, according to the method described in ASTM E903 and was determined to be equal to 50.87 %.

[0065] Example 2. The inventive system of titanium dioxide having an average particle size of 1.4 µm and organic pigments PY180 (Clariant Fast Yellow HG), PR122 (HPC PR1220), PV23 (Ciba Cromophthal Violet Gt), PB15:3 (HPC PB1530), PBlack 32 (BASF Paliogen Black L0086), PO71 (Ciba Irgazin DPP Cosmoray) were used in a paint system to make colored paints to match ral standards 6011, 7010, 7022 and 7034.

[0066] A tint concentrate was prepared for each of the specified pigments (PY180, PR122, PV23, PB15:3, PBlack 32, PO71) using an acrylic resin, a wetting and dispersing additive, a solvent and the specified tint. The quantities of each component are specified in Table 6. This tint concentrate was then milled with steel ballotini.

	PV23, PB 15:3, PBlack 32	PR122, PY180, PO 71
Tinter Concentrate Component	% by weight	% by weight
60% Acrylic Resin (40% solvent)	78	71
Solvent	4	4
Wetting & Dispersing Additive	9	8
Tint	9	16

Table 6: Tinter concentrate components.

A colored resin solution was made up by taking the quantities as specified in Table 7 of each of the required tinter concentrates and vigorously mixing for 2 minutes with the specified amount of additional acrylic resin.

	ral 6011 (Reseda green)	ral 7010 (Tarpaulin grey)	ral 7022 (Umbra grey)	ral 7034 (Yellow grey)
Tint conc PV23 (g)	-	1.19	7.25	-
Tint conc PR122 (g)	-	-	-	-
Tint conc PY180 (g)	3.78	-	6.48	0.61
Tint conc PO71 (g)	-	4.15	-	2.44
Tint conc PB15:3 (g)	0.53	-	-	-
Tint conc PBK32 (g)	10.49	26.85	19.23	4.57
60% Acrylic Resin (40% solvent) (g)	17.98	1.11	0.38	24.95

Table 7: Colored resin solution make up.

[0067] The titanium dioxide was added, in the quantities specified in Table 8, to 7.50 g of the colored resin solution to create a millbase which was then vigorously mixed for 30 seconds. This tinted millbase was then let down with a further quantity of 13.00 g colored resin. This millbase was then milled for an additional 2 minutes.

	ral 6011 (Reseda green)	ral 7010 (Tarpaulin grey)	ral 7022 (Umbra grey)	ral 7034 (Yellow grey)
TiO ₂ (g)	27.9	25.6	19.1	29.2
TiO ₂ volume conc. %	40.0	41.0	33.5	40.0

Table 8: Quantity of titanium dioxide added to colored resin solution.

[0068] The paint was drawn down over a black substrate using a number 6 wire wound applicator to give a dry film thickness of about 28 microns. The solvents were allowed to evaporate and the panel was then stoved at 105°C for 30 minutes. Reflectance spectra were measured using a UV/vis/NIR spectrophotometer with an integrating sphere and a wavelength range of 300 nm – 2500 nm. Total Solar Reflectance was calculated from this data, according to the method described in ASTM E903.

[0069] The % TSR was compared with data collated from publicly available TSR values for systems optimized using complex color inorganic pigments. The known TSR values were reported to be calculated according to ASTM E903 (weighted ordinates for 300-2500 nm), measured on topcoat and primer. The inventive system was thus not optimized since the solar reflectance was measured over a black substrate but it can be seen from Table 9 that there is still a significant increase in % TSR for the inventive system.

ral number	Color	CICP % TSR	Inventive % TSR	% TSR uplift
6011	Reseda green	35	48	13
7010	Tarpaulin grey	37	47	10
7022	Umbra grey	32	45	13
7034	Yellow grey	44	54	10

Table 9: % TSR values for various ral numbers.

[0070] Example 3. Ral 7024 (graphite grey) was made using 4 different titanium dioxide average particle sizes (0.7 micron, 1.1 micron, 1.4 micron, and 1.7 micron) and organic pigments PY180 (Clariant Fast Yellow HG), PV23 (Ciba Cromophtal Violet Gt), PBlack 32 (BASF Paliogen Black L0086). The organic pigments were made into tinter

concentrates as detailed in Table 6 above. A colored resin solution was then made up by taking the quantities as specified in Table 10 of each of the required tinter concentrates and vigorously mixing for 2 minutes with the specified amount of additional acrylic resin.

	0.7 μm TiO ₂	1.1 μm TiO ₂	1.4 μm TiO ₂	1.7 μm TiO ₂
Tint conc PV23 (g)	3.60	1.19	1.03	0.64
Tint conc PY180 (g)	0.18	0.04	0.01	0.08
Tint conc PBK32 (g)	21.42	7.76	6.86	3.54
60% Acrylic Resin (40% solvent) (g)	7.9	23.62	24.68	28.2
TiO ₂ (g)	4.64	4.92	4.80	5.00

Table 10: Colored resin solution make up and quantity of titanium dioxide added to colored resin solution.

[0071] The titanium dioxide was added to 7.50 g of the colored resin solution to create a millbase which was then vigorously mixed for 30 seconds. This tinted millbase was then let down with a further quantity of 13.00 g colored resin. This millbase was then milled for a further 2 minutes. This produced a TiO₂ volume concentration of 10% in all four paints.

[0072] The paint was drawn down over a substrate using a number 150 wire wound applicator to give a dry film thickness of about 77 microns. The solvents were allowed to evaporate and the panel was stoved at 105 °C for 30 minutes. Reflectance spectra were measured using a UV/vis/NIR spectrophotometer with an integrating sphere and a wavelength range of 300 nm – 2500 nm. Total Solar Reflectance was calculated from this data, according to the method described in ASTM E903 and the results are provided in Table 11.

ral 7024	0.7 μm TiO_2	1.1 μm TiO_2	1.4 μm TiO_2	1.7 μm TiO_2
% TSR over black substrate	47.48	42.85	42.13	35.69
% TSR over white substrate	49.87	49.67	49.65	48.50

Table 11: TSR results for ral 7024.

[0073] The 0.7 micron particle size TiO_2 gives the highest TSR value but requires a large amount of organics to be added to keep the color due to the effect of pastelisation from the TiO_2 . The 1.1 and 1.4 micron TiO_2 still give a high TSR value but use about 2/3 the amount of organics when compared to the 0.7 micron particle size TiO_2 .

[0074] The above-disclosed subject matter is to be considered illustrative, and not restrictive, and the appended claims are intended to cover all such modifications, enhancements, and other embodiments, which fall within the true scope of the present invention. Thus, to the maximum extent allowed by law, the scope of the present invention is to be determined by the broadest permissible interpretation of the following claims and their equivalents, and shall not be restricted or limited by the foregoing detailed description.

WHAT IS CLAIMED IS:

1. A colored solar reflective system comprising: (1) a particulate material having a substantially rutile crystal habit and having an average particle size of between about 0.5 μm and about 2.0 μm and (2) an organic pigment having a maximum absorption coefficient of about 5,000 mm^{-1} or greater, preferably about 10,000 mm^{-1} or greater, and more preferably about 15,000 mm^{-1} or greater in the visible light region, a maximum scattering coefficient of about 500 mm^{-1} or less, preferably about 250 mm^{-1} or less, and more preferably about 100 mm^{-1} or less in the visible light region and an average absorption coefficient of about 50 mm^{-1} or less, preferably about 30 mm^{-1} or less, and more preferably about 10 mm^{-1} or less in the infrared region.
2. The colored solar reflective system of claim 1, wherein the particulate material is selected from the group consisting of titanium dioxide, doped titanium dioxide and a mixture thereof.
3. The colored solar reflective system of claim 1 or 2, wherein the particulate material contains greater than 70% by weight of titanium dioxide, based on the total weight of the particulate material.
4. The colored solar reflective system of claim 2 or 3, wherein the doped titanium dioxide is nickel antimony titanate.
5. The colored solar reflective system of claim 2 or 3, wherein the doped titanium dioxide is chromium antimony titanate.
6. The colored solar reflective system of any one of claims 1-3, wherein the titanium dioxide has an average particle size of between about 0.7 μm and about 1.4 μm .
7. The colored solar reflective system of any one of claims 2-6, wherein the titanium dioxide and/or doped titanium dioxide are coated titanium dioxide or coated doped titanium dioxide.

8. The colored solar reflective system of any one of claims 1-7, wherein the organic pigment is selected from the group consisting of: azo, anthraquinone, phthalocyanine, perinone/perylene, indigo/thioindigo, dioxazine, quinacridone, isoindolinone, isoindoline, diketopyrrolopyrrole, azomethine and azomethine-azo pigments.

9. A method for preparing a colored solar reflective system comprising mixing a particulate material having a substantially rutile crystal habit and having an average particle size of between about 0.5 μm and about 2.0 μm with an organic pigment having a maximum absorption coefficient of about 5,000 mm^{-1} or greater, more preferably about 10,000 mm^{-1} or greater, and even more preferably about 15,000 mm^{-1} or greater in the visible light region, a maximum scattering coefficient of about 500 mm^{-1} or less, more preferably about 250 mm^{-1} or less, and even more preferably about 100 mm^{-1} or less in the visible light region and an average absorption coefficient of about 50 mm^{-1} or less, more preferably about 30 mm^{-1} or less, and even more preferably about 10 mm^{-1} or less in the near-infrared light region.

10. A colored composition comprising a particulate material having a substantially rutile crystal habit and having an average particle size of between about 0.5 μm and about 2.0 μm , and an organic pigment having a maximum absorption coefficient of about 5,000 mm^{-1} or greater, more preferably about 10,000 mm^{-1} or greater, and even more preferably about 15,000 mm^{-1} or greater in the visible light region, a maximum scattering coefficient of about 500 mm^{-1} or less, more preferably about 250 mm^{-1} or less, and even more preferably about 100 mm^{-1} or less in the visible light region and an average absorption coefficient of about 50 mm^{-1} or less, more preferably about 30 mm^{-1} or less, and even more preferably about 10 mm^{-1} or less in the near-infrared light region, dispersed within a vehicle.

11. The colored composition of claim 10, wherein the organic pigment is present at an amount of about 0.1% by volume to about 20% by volume, based on the total weight of the colored composition, and the particulate material is present at an amount of about 0.5% by volume to about 40% by volume, based on the total weight of the colored composition.

12. The colored composition of claim 10 or 11, wherein the vehicle is a synthetic or natural resin comprising a polyolefin resin, polyvinyl chloride resin, ABS resin, polystyrene resin, methacrylic resin, polycarbonate resin, polyethylene terephthalate resin, polyamide resin, alkyd resin, acrylic resin, polyurethane resin, polyester resin, melamine resin, fluoropolymer or epoxy resin.

13. The colored composition of claim 10 or 11, wherein the vehicle is a carrier or binder.

14. The colored composition of any one of claims 10-13 which further comprises one or more thickeners, stabilizers, emulsifiers, texturizers, adhesion promoters, UV stabilizers, de-glossing agents, dispersants, antifoaming agents, wetting agents, coalescing agents, spacer particles or biocides/fungicides.

15. Use of the colored composition of any one of claims 10-14 as a paint, ink or coating or as a composition from which an article can be formed.

16. A one layer solar reflective colored coating comprising a particulate material having substantially rutile crystal habit and having an average particle size of between about 0.5 μm and about 2.0 μm . and an organic pigment having a maximum absorption coefficient of about 5,000 mm^{-1} or greater, more preferably about 10,000 mm^{-1} or greater, and even more preferably about 15,000 mm^{-1} or greater in the visible light region, a maximum scattering coefficient of about 500 mm^{-1} or less, more preferably about 250 mm^{-1} or less, and even more preferably about 100 mm^{-1} or less in the visible light region and an average absorption coefficient of about 50 mm^{-1} or less, more preferably about 30 mm^{-1} or less, and even more preferably about 10 mm^{-1} or less in the infrared region, dispersed within a vehicle.

17. The one layer solar reflective colored coating of claim 16, wherein the coating covers a substrate which absorbs a proportion of near-infrared radiation and wherein the thickness of the layer is such that more than 1% of the incident near-infrared radiation reaches the substrate.

18. The one layer solar reflective colored coating of claim 16 or 17, wherein the coating has a lightness value L^* of 75 or less, preferably 65 or less, more preferably 55 or less, and even more preferably 45 or less.

19. The one layer solar reflective colored coating of any one of claims 16-18 wherein the coating has a total solar reflectance of greater than 30%, preferably greater than 35%, even more preferably greater than 40%, and even more preferably greater than 45%.

20. A structure comprising the one layer solar reflective colored coating according to any one of claims 16-19.

21. A method for reducing the energy consumption of a structure comprising applying the one layer solar reflective colored coating of any one of claims 16-19 to one or more surfaces of the structure, wherein the one layer solar reflective colored coating causes the surface temperature of the resultant coated surface to be lowered relative to a surface temperature of a surface coated with a non-reflective coating of the same color such that less energy is needed to cool the interior of the structure.

22. An article comprising the colored composition of any one of claims 10-14 wherein the article has a lightness value L^* of 75 or less, preferably 65 or less, more preferably 55 or less, and even more preferably 45 or less.

23. The article of claim 22, wherein the article has a total solar reflectance of greater than 30%, preferably greater than 35%, more preferably greater than 40%, and even more preferably greater than 45%.

24. Use of the colored composition of any one of claims 10-14 or the coating of any one of claims 16-19 as a one layer solar reflective colored coating.

25. A structure wherein one or more surfaces of the structure are coated with the one layer solar reflective colored coating according to any one of claims 16-19.