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(71) Applicant: **PPG INDUSTRIES OHIO, INC.** [US/US]; 3800 West 143rd Street, Cleveland, Ohio 44111 (US).

(72) Inventors: **SCHWENDEMAN, Irina G.**; 238 Courtney Place, Wexford, Pennsylvania 15090 (US). **RETSCH, Jr., William H.**; 3810 Lyndell Street, Castle Shannon, Pennsylvania 15234 (US). **REARICK, Brian K.**; 1335 Parkview Drive, Allison Park, Pennsylvania 15101 (US). **CONLEY, Carole A.**; 260 Brewer Road, Saxonburg, Pennsylvania 16056 (US).

(74) Agents: **TREBILCOCK, Christine W.** et al.; PPG Industries, Inc., One PPG Place, 39th Floor, Pittsburgh, Pennsylvania 15272 (US).

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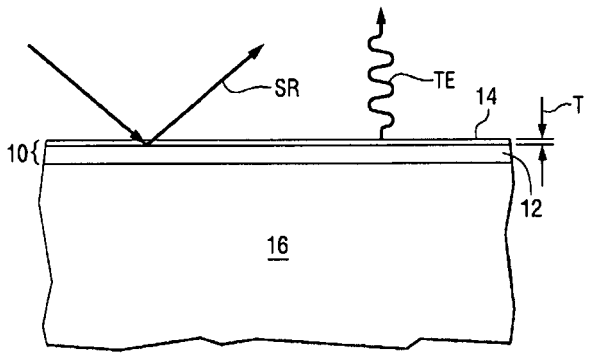


FIG. 1

(57) Abstract: Coated sheet materials having high solar reflective index and corrosion resistance, and methods of making such coated sheet materials, are disclosed. In certain embodiments, the sheet materials comprise metal such as galvanized steel roofing sheets, and the coating is deposited from a latex resin.

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COATED SHEET MATERIALS HAVING HIGH SOLAR REFLECTIVE INDEX AND CORROSION RESISTANCE, AND METHODS OF MAKING SAME

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Patent Application Serial No. 61/661,532 filed June 19, 2012, which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to coated sheet materials having high solar reflective index and corrosion resistance, and methods of making such coated sheet materials.

BACKGROUND OF THE INVENTION

[0003] Sheet materials used in architectural and other applications often require corrosion resistant properties. For example, steel and other types of metal roofing sheet materials must withstand exposure to environmental conditions for extended periods of time. Galvanized steel roofing sheets have conventionally been pre-treated with chromium-containing compositions to increase corrosion resistance. Such pretreatments may be conducted on long strips of the steel, which are then coiled into rolls for subsequent use.

[0004] Galvanized steel and other types of metal roofing materials may have high solar reflectance properties, but they tend to heat up when exposed to sunlight due to their low thermal emittance properties. As a result of such solar heating, the underlying structures can require significant amounts of energy to cool, e.g., by air conditioning.

[0005] Several recent US and state government regulations require metal roofing to meet certain solar reflective index values to avoid overheating. Solar reflective index (SRI) is calculated based upon the combination of solar reflectance and thermal emittance, with an SRI value of 65, 70 or higher being required to meet certain government regulations. Solar reflectance is measured as a percentage of solar radiation in the visible, infrared and ultraviolet regions of the electromagnetic spectrum

that is reflected from a surface, with a value of 0 or 0% corresponding to zero reflectance and a value of 1 or 100% corresponding to total reflectance. Thermal emittance is measured as the ability of a surface to shed heat, with a value of 0 or 0% corresponding to zero thermal emittance and a value of 1 or 100% corresponding to total thermal emittance. In order to reduce overheating, metal roofing with both relatively high solar reflectance and thermal emittance is desired.

[0006] Conventional metal roofing fails to meet certain government energy regulations, and the use of conventional pretreatments decreases the solar reflective index below that of the untreated metal.

SUMMARY OF THE INVENTION

[0007] An aspect of the invention provides a coated metal sheet comprising a metal substrate, and a cured coating covering at least a portion of the metal substrate, wherein: (a) the cured coating: (i) is deposited from a composition comprising a latex resin, (ii) is substantially clear, (iii) is substantially free of reflective pigments, and (iv) has a dry film thickness of at least 1 micron; and (b) the coated metal sheet has a solar reflective index of at least 65 and a corrosion resistance of at least 500h with no corrosion spots when subjected to an ASTMB117 salt spray test.

[0008] Another aspect of the invention provides a coated roof sheeting material comprising a sheet metal substrate, and a coating covering at least a portion of the sheet metal substrate, wherein the coating consists essentially of a cured latex resin, and wherein the coated roof sheeting material has a solar reflectance of at least 65 percent, a thermal emittance of at least 40 percent, and a corrosion resistance of at least 500h with no corrosion spots when subjected to an ASTMB117 salt spray test.

[0009] A further aspect of the invention provides a method of coating a sheet metal substrate comprising applying a coating composition comprising a latex resin that is substantially free of reflective pigments to the sheet metal substrate at a wet film thickness of at least 1 micron, and curing the coating composition to produce a coated metal sheet having a solar reflective index of at least 65 and a corrosion resistance of at least 500h with no corrosion spots when subjected to an ASTMB117 salt spray test.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Fig. 1 is a partially schematic side view of a coated roof sheeting material in accordance with an embodiment of the present invention, illustrating solar reflectance and thermal emittance properties.

[0011] Fig. 2 is a partially schematic side view illustrating a method of coating and coiling metal sheets in rolling mill, including the use of a roll coater for applying a coating composition to the sheets in accordance with an embodiment of the present invention.

[0012] Fig. 3 is a graph of total solar reflectance (TSR) vs. dry film thickness (DFT) for coated metal sheets in accordance with embodiments of the present invention.

[0013] Fig. 4 is a graph of thermal emittance (TE) vs. DFT for coated metal sheets in accordance with embodiments of the present invention.

[0014] Fig. 5 is a graph of solar reflective index (SRI) vs. DFT for coated metal sheets in accordance with embodiments of the present invention.

[0015] Fig. 6 is a graph of TSR vs. DFT for coated metal sheets in accordance with embodiments of the present invention.

[0016] Fig. 7 is a graph of TE vs. DFT for coated metal sheets in accordance with embodiments of the present invention.

[0017] Fig. 8 is a graph of SRI vs. DFT for coated metal sheets in accordance with embodiments of the present invention.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[0018] Fig. 1 schematically illustrates a coated sheet material 10 in accordance with an embodiment of the present invention including a substrate sheet 12 and a coating layer 14. In certain embodiments, the coated sheet 10 may be used in architectural applications, such as roof sheeting material for a building 16 or other structure. The coating 14 has a dry film thickness T typically greater than 1 micron, for example, greater than 2 or 3 microns. In certain embodiments, the dry film thickness T of the coating 14 may be from 3 to 10 or 20 microns. The substrate sheet 12 may be of any desired thickness, such as from 0.5 to 3 mm. For example, the thickness of galvanized steel roof sheeting materials may range from 0.5 to 2 mm in

certain embodiments. Although the sheet 12 shown in Fig. 1 is flat, any other shape may be provided, such as corrugated, ribbed, and the like.

[0019] As illustrated in Fig. 1, a portion of solar radiation incident on the coated sheet 10 is reflected from its surface with a total solar reflectance TSR value. As used herein, the term "total solar reflectance" means a measure of the ability of a surface material to reflect sunlight – including the visible, infrared, and ultraviolet wavelengths – on a scale of 0% to 100%. In certain embodiments, the total solar reflectance TSR of the coated sheet 10 is at least 60%, for example, at least 62% or 65%.

[0020] As further illustrated in Fig. 1, the coated sheet 10 has thermal emittance TE properties. As used herein, the term "thermal emittance" refers to the ability of a material to release absorbed heat. A number between 0 and 1, or 0% and 100%, is used to express emittance. In certain embodiments, the thermal emittance TE of the coated sheet 10 is at least 0.3 (30%), for example, at least 0.4 (40%) or 0.5 (50%).

[0021] The total solar reflectance TSR and emittance TE properties, as schematically illustrated in Fig. 1, may be combined to yield a solar reflective index ("SRI"). As used herein, the term "solar reflective index" is a value that incorporates both solar reflectance and emittance in a single value to represent a material's temperature in the sun. SRI quantifies how hot a surface would get relative to standard black and standard white surfaces. It is calculated using equations based on previously measured values of solar reflectance and emittance as laid out in the American Society for Testing and Materials Standard E 1980. In accordance with ASTM Standard E 1980, values of TSR and TE are input into a standard equation to calculate the SRI value. In certain embodiments, the solar reflective index SRI is at least 65, for example, at least 70 or 75.

[0022] In accordance with embodiments of the invention, the coating composition comprises a latex resin. The latex resin may, or may not, be self-crosslinking. The latex resin typically comprises from 20 to 60 weight percent of the coating composition, for example, from about 30 to about 50 weight percent. In certain embodiments, suitable monomers used for preparing the latex resins may include vinyl aromatic monomers such as styrene, cycloaliphatic monomers such as

cyclohexyl methacrylate, and long-chain aliphatic monomers such as 2-ethylhexyl acrylate, MMA and/or 2-ethylhexyl methacrylate. Other types of monomers include cyclohexene, 2-ethyl-1-hexene, cyclohexanol, alpha-methylstyrene, 2-ethylhexanol, 2-ethylhexyl acetate, methyl-4-phenyl butyrate, methyl myristate and/or methyl palmitate.

[0023] In certain embodiments, the monomers used in the latex resin comprise a vinyl aromatic compound, such as a vinyl aromatic monomer, which, in certain embodiments, comprises a compound that has a calculated Tg of least 100°C. Specific examples of vinyl aromatic compounds are styrene (which has a calculated Tg of 100°C), α-methylstyrene (which has a calculated Tg of 168°C), vinyltoluene, p-methylstyrene, ethylvinylbenzene, vinylnaphthalene, vinylxylenes, α-methylstyrene dimer (meth)acrylate, penta fluoro styrene, and the like. In certain embodiments, styrene or another vinyl aromatic monomer may comprise the most predominant monomer of the resin on a weight percent basis.

[0024] In certain embodiments, the monomers of the latex resin include cycloaliphatic (meth)acrylate monomers, such as trimethylcyclohexyl acrylate, t-butyl cyclohexyl acrylate, dicyclopentadiene (meth)acrylate, trimethylcyclohexyl methacrylate (calculated Tg of 98°C), cyclohexyl methacrylate (calculated Tg of 83°C), isobornyl methacrylate (calculated Tg of 110°C), 2-ethylhexyl methacrylate, tetrahydrofurfuryl methacrylate, 3,3,5-trimethylcyclohexyl methacrylate (calculated Tg of 125°C), and/or 4-t-butylcyclohexyl methacylate, and the like.

[0025] In certain embodiments, the monomers of the latex resin include an alkyl(meth)acrylate, which, in certain embodiments, comprises a compound that has a calculated Tg of least 100°C. Specific examples of alkyl(meth)acrylates are C_1-C^{24} alkyl(meth)acrylates, such as methyl(meth)acrylate (which has a calculated Tg of 105°C), propyl(meth)acrylate, butyl(meth)acrylate, isobutyl(meth)acrylate, hexyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, octyl(meth)acrylate, decyl(meth)acrylate, dodecyl(meth)acrylate, pentadecyl(meth)acrylate, hexadecyl(meth)acrylate, octadecyl(meth)acrylate, and nonadecyl(meth)acrylate, and mixtures thereof. Other monomers include, for example, nitriles, such as acrylonitrile and/or methacrylonitrile.

[0026] Some non-limiting examples of latex resins that may be used in the coating compositions of the present invention are commercially available from Nuplex,

Lubrizol, Rohm and Haas, Alberdingk Boley Company, Omnova and DSM Neoresins, such as Joncryl 1982, Caroboset CR-781, Alberdingk AC 2403, Alberdingk 2360, Neocryl XK-98 and the like.

[0027] The latex resin may have an average particle size of from 50 nm to 300 nm, for example from 60 nm to 100 or 150 nm; a glass transition temperature (T_G) of from -20 to 100°C, typically from zero to 20 or 50°C; and an acid number of from 0 to 20, typically from 2 to 10.

[0028] The coating compositions of the present invention may be waterborne. In certain embodiments, water may comprise from 20 to 80 weight percent of the coating compositions, for example, from 50 to 65 weight percent. In certain embodiments, the coating compositions comprise less than 10 weight percent organic solvents, for example, less than 7 or 4 weight percent, based on the total weight of the composition. The resin solids content of the coating compositions may be relatively high, for example, greater than 35 or 40 weight percent, based on the total weight of the composition.

[0029] The coating compositions may have little or no volatile organic content (VOC). For example, the coating compositions may comprise less than 1.5 weight percent VOCs, for example, less than 1 or 0.5 weight percent VOCs, based on the total weight of the composition. In certain embodiments, the coating compositions are substantially free of VOCs.

[0030] The coating compositions may further comprise at least one coalescing agent in an amount of up to 10 weight percent, for example, in an amount of from 2 to 3 weight percent, based on the total weight of the coating composition. Examples of suitable coalescing agents include butyl carbitol commercially available from Dow Chemical Company, Dowanol DPM, Dowanol DPnB, Dowanol PPh, butyl cellosolve or Dowanol DPnP. In accordance with embodiments of the present invention, the coalescing agents form a thin film around the latex resin particles, which helps them coalesce. Improved coalescence of the latex resin particles results in very fine particle sizes and a uniform microstructure, which provides improved corrosion protection in comparison with other types of coatings having larger resin particle sizes. For example, in accordance with certain embodiments of the present invention, the average

resin particle size may be less than 150 nanometers, for example, less than 100 or 80 nanometers.

[0031] In certain embodiments, wax may be added to the coating compositions in amounts up to 10 weight percent, for example, from 0.5 to 3 weight percent, based on the total weight of the coating composition. Suitable types of wax include Ceraflour 913, Worleeadd 352, Aquamat 272, Aquamat 270, Aquacer 539, and combinations thereof. For example, wax sold under the designation Aquamat 272 by BYK Chemie may be used. The type and amount of wax may be controlled in order to improve scratch resistance of the coated sheet materials. For example, when the coated sheets are formed into coils, the use of wax additives may reduce or prevent scratching during the coiling an uncoiling processes, as well as during subsequent installation and use of the coated sheet materials. In certain embodiments, the amount of wax added to the coating composition is limited in order to avoid unwanted slippage when the coated sheets are coiled, e.g., to prevent unwanted "telescoping" of the coils due to low friction between the adjacent coil layers.

[0032] Various other additives may optionally be added to the coating compositions in accordance with certain embodiments of the invention. For example, suitable additives include thickeners, defoamers, surfactants, rust inhibitors, pH control agents, silica, and tints.

[0033] Suitable thickeners include Acrysol ASE-60, Aquatix 8421, DSX-1550, and Laponite RD. When used, such thickening agents may be present in amounts up to 7 weight percent, for example, from 0.5 to 4 weight percent, based on the total weight of the coating composition.

[0034] Suitable defoamers include BYK-011, BYK-20, BYK-32, BYK 34 and Drewplus L-419 available from Ashland in amounts up to 2 weight percent, for example, from 0.1 to 0.5 weight percent, based on the total weight of the coating composition.

[0035] Suitable surfactants include Zonyl FSP available from DuPont, Surfynol 104E available from Air Products, BYK 346, and BYK348 in amounts up to 2 weight percent, for example, from 0.1 to 0.5 weight percent, based on the total weight of the coating composition.

[0036] Suitable rust inhibitors include Halox 550, Halox Flash X-150, 330, Halox SZP-391, ammonium benzoate, and sodium nitrite in typical amounts up to 1 weight percent, for example, from 0.4 to 0.6 weight percent, based on the total weight of the coating composition.

[0037] In certain embodiments, the coating compositions are substantially free of certain metal salts such as metal phosphates, phosphocarbonates and phosphosilicates. For example, the compositions may be substantially free of zinc phosphate, calcium phosphate, calcium phosphosilicate and/or calcium-enriched silica.

[0038] Suitable pH control agents include any water soluble amine such as dimethylethanol amine (DMEA) available from Avecia in typical amounts up to 1 weight percent, for example, from 0.01 to 0.2 weight percent, based on the total weight of the coating composition.

[0039] In accordance with certain embodiments of the invention, the coatings are substantially free of chrome. In such embodiments, chrome is not purposely added to the coating compositions and is only present in trace levels or as an impurity.

[0040] In certain embodiments, chromate-containing materials may be added to the coating compositions. Such chromate-containing coating compositions may be particularly useful as primer coatings. For example, strontium chromate may be added in amounts up to 12 weight percent, for example, from 0.2 to 1 weight percent, based on the total weight of the coating composition. Such strontium chromate-containing additives may provide improved corrosion resistance properties. When used as primer coatings, the coating compositions may further include colorants and tints typically used in primers, such as titanium dioxide and the like.

[0041] In certain embodiments, silica may be added to the coating compositions, for example, in amounts from 0.1 to 2 or 3 weight percent or more. Some examples of silica include Lo-Vel 275 silica from PPG Industries and Aerosil 200 silica from Air Products.

[0042] In certain embodiments, the coating compositions and cured coatings are substantially free of reflective pigments. As used herein, the term "reflective pigment" means plate-like or sheet-like interference pigments such as mica, silicates, silicon dioxide and aluminum oxide. Solarflair 9870 from Eckart is an example of a reflective pigment. As used herein, the term "substantially free of reflective pigments"

means that the coatings have zero or minimal amounts of reflective pigments while achieving the desired level of solar reflectance and/or solar reflective index. For example, the cured coatings may have less than 2 or 1 weight percent reflective pigment. Although the coatings may be substantially free of reflective pigments, they still maintain sufficient solar reflectance properties and solar reflective index values, e.g., SRIs of 65 or greater. The cost of reflective pigment additives may thus be avoided, while still providing a desired level of solar reflectance.

[0043] In certain embodiments, at least one colored pigment or tint may be added to the coating compositions. Colored pigments and tints are different from reflective interference pigments and include standard inorganic and organic pigments, such as those found in conventional paints and primers. For example, various colored pigments are listed in the Dry Color Manufacturers Association (DCMA) classifications. Such colored pigments and tints typically comprise particles having substantially equiaxed morphologies, e.g., aspect ratios of about 1:1, in comparison with plate-like and sheet-like reflective interference pigments having relatively high aspect ratios. One suitable type of colored pigment includes TiO_2 in an amount up to 35 weight percent, for example, from 1 to 25 weight percent, based on the total weight of the coating composition. Aquext white tint commercially available from PPG Industries and Corrosperse 176E chrome tint commercially available from Wayne Pigments are examples of suitable tints.

[0044] In certain embodiments, the coating is substantially free of colored pigments and tints. For example, the coatings may be substantially clear and colorless.

[0045] In certain embodiments, conductive particles such as graphenic carbon particles may be added to the coating compositions in amounts of to 5 weight percent, for example, from 1 to 2 weight percent, based on the total weight of the coating composition. Such graphenic carbon particles may provide improved thermal emissivity properties. The graphenic carbon particles may be obtained from commercial sources, or may be made in accordance with the methods and apparatus described in U.S. Application Serial Nos. 13/249,315 and 13/309,894, which are incorporated herein by reference. Exemplary commercially available graphenic carbon particles are available from Angstron and XG Sciences.

[0046] As used herein, the term "graphenic carbon particles" means carbon particles having structures comprising one or more layers of one-atom-thick planar sheets of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. The average number of stacked layers may be less than 100, for example, less than 50. In certain embodiments, the average number of stacked layers is 30 or less, such as 20 or less, 10 or less, or, in some cases, 5 or less. The graphenic carbon particles may be substantially flat, however, at least a portion of the planar sheets may be substantially curved, curled, creased or buckled. The particles typically do not have a spheroidal or equiaxed morphology.

[0047] In certain embodiments, the graphenic carbon particles present in the compositions of the present invention have a thickness, measured in a direction perpendicular to the carbon atom layers, of no more than 10 nanometers, no more than 5 nanometers, or, in certain embodiments, no more than 4 or 3 or 2 or 1 nanometers, such as no more than 3.6 nanometers. In certain embodiments, the graphenic carbon particles may be from 1 atom layer up to 3, 6, 9, 12, 20 or 30 atom layers thick, or more. In certain embodiments, the graphenic carbon particles present in the compositions of the present invention have a width and length, measured in a direction parallel to the carbon atoms layers, of at least 50 nanometers, such as more than 100 nanometers, in some cases more than 100 nanometers up to 500 nanometers, or more than 100 nanometers up to 200 nanometers. The graphenic carbon particles may be provided in the form of ultrathin flakes, platelets or sheets having relatively high aspect ratios (aspect ratio being defined as the ratio of the longest dimension of a particle to the shortest dimension of the particle) of greater than 3:1, such as greater than 10:1.

[0048] In certain embodiments, the graphenic carbon particles used in the compositions of the present invention have relatively low oxygen content. For example, the graphenic carbon particles used in certain embodiments of the compositions of the present invention may, even when having a thickness of no more than 5 or no more than 2 nanometers, have an oxygen content of no more than 2 atomic weight percent, such as no more than 1.5 or 1 atomic weight percent, or no more than 0.6 atomic weight, such as about 0.5 atomic weight percent. The oxygen content of the graphenic carbon particles can be determined using X-ray Photoelectron

Spectroscopy, such as is described in D. R. Dreyer et al., Chem. Soc. Rev. 39, 228-240 (2010).

[0049] In certain embodiments, the graphenic carbon particles used in the compositions of the present invention have a B.E.T. specific surface area of at least 50 square meters per gram, such as 70 to 1000 square meters per gram, or, in some cases, 200 to 1000 square meters per grams or 200 to 400 square meters per gram. As used herein, the term "B.E.T. specific surface area" refers to a specific surface area determined by nitrogen adsorption according to the ASTMD 3663-78 standard based on the Brunauer-Emmett-Teller method described in the periodical "The Journal of the American Chemical Society", 60, 309 (1938).

[0050] In certain embodiments, the graphenic carbon particles used in the compositions of the present invention have a Raman spectroscopy 2D/G peak ratio of at least 1.1, for example, at least 1.2 or 1.3. As used herein, the term "2D/G peak ratio" refers to the ratio of the intensity of the 2D peak at 2692 cm^{-1} to the intensity of the G peak at 1,580 cm^{-1}.

[0051] In certain embodiments, the graphenic carbon particles used in the compositions of the present invention have a relatively low bulk density. For example, the graphenic carbon particles used in certain embodiments of the present invention are characterized by having a bulk density (tap density) of less than 0.2 g/cm^3, such as no more than 0.1 g/cm^3. For the purposes of the present invention, the bulk density of the graphenic carbon particles is determined by placing 0.4 grams of the graphenic carbon particles in a glass measuring cylinder having a readable scale. The cylinder is raised approximately one-inch and tapped 100 times, by striking the base of the cylinder onto a hard surface, to allow the graphenic carbon particles to settle within the cylinder. The volume of the particles is then measured, and the bulk density is calculated by dividing 0.4 grams by the measured volume, wherein the bulk density is expressed in terms of g/cm^3.

[0052] In certain embodiments, the graphenic carbon particles used in the compositions of the present invention have a compressed density and a percent densification that is less than the compressed density and percent densification of graphite powder and certain types of substantially flat graphenic carbon particles. Lower compressed density and lower percent densification are each currently believed

to contribute to better dispersion and/or rheological properties than graphenic carbon particles exhibiting higher compressed density and higher percent densification. In certain embodiments, the compressed density of the graphenic carbon particles is 0.9 or less, such as less than 0.8, less than 0.7, such as from 0.6 to 0.7. In certain embodiments, the percent densification of the graphenic carbon particles is less than 40%, such as less than 30%, such as from 25 to 30%.

[0053] For purposes of the present invention, the compressed density of graphenic carbon particles is calculated from a measured thickness of a given mass of the particles after compression. Specifically, the measured thickness is determined by subjecting 0.1 grams of the graphenic carbon particles to cold press under 15,000 pound of force in a 1.3 centimeter die for 45 minutes, wherein the contact pressure is 500 MPa. The compressed density of the graphenic carbon particles is then calculated from this measured thickness according to the following equation:

$$\text{Compressed Density } (g/cm^3) = \frac{0.1 \text{ grams}}{\Pi^*(1.3cm/2)^2*(\text{measured thickness in cm})}$$

[0054] The percent densification of the graphenic carbon particles is then determined as the ratio of the calculated compressed density of the graphenic carbon particles, as determined above, to 2.2 g/cm^3, which is the density of graphite.

[0055] In certain embodiments, the graphenic carbon particles have a measured bulk liquid conductivity of at least 100 microSiemens, such as at least 120 microSiemens, such as at least 140 microSiemens immediately after mixing and at later points in time, such as at 10 minutes, or 20 minutes, or 30 minutes, or 40 minutes. For the purposes of the present invention, the bulk liquid conductivity of the graphenic carbon particles is determined as follows. First, a sample comprising a 0.5% solution of graphenic carbon particles in butyl cellosolve is sonicated for 30 minutes with a bath sonicator. Immediately following sonication, the sample is placed in a standard calibrated electrolytic conductivity cell (K=1). A Fisher Scientific AB 30 conductivity meter is introduced to the sample to measure the conductivity of the sample. The conductivity is plotted over the course of about 40 minutes.

[0056] In accordance with certain embodiments, percolation, defined as long range interconnectivity, occurs between the conductive graphenic carbon particles.

Such percolation may reduce the resistivity of the coating compositions. The conductive graphenic particles may occupy a minimum volume within the coating such that the particles form a continuous, or nearly continuous, network. In such a case, the aspect ratios of the graphenic carbon particles may affect the minimum volume required for percolation. Furthermore, the surface energy of the graphenic carbon particles may be the same or similar to the surface energy of the elastomeric rubber. Otherwise, the particles may tend to flocculate or demix as they are processed.

[0057] The graphenic carbon particles utilized in the compositions of the present invention can be made, for example, by thermal processes. In accordance with embodiments of the invention, the graphenic carbon particles are produced from carbon-containing precursor materials that are heated to high temperatures in a thermal zone. For example, the graphenic carbon particles may be produced by the systems and methods disclosed in United States Patent Application Serial Nos. 13/249,315 and 13/309,894.

[0058] In certain embodiments, the graphenic carbon particles may be made by using the apparatus and method described in United States Patent Application Serial No. 13/249,315 at [0022] to [0048] in which (i) one or more hydrocarbon precursor materials capable of forming a two-carbon fragment species (such as n-propanol, ethane, ethylene, acetylene, vinyl chloride, 1,2-dichloroethane, allyl alcohol, propionaldehyde, and/or vinyl bromide) is introduced into a thermal zone (such as a plasma); and (ii) the hydrocarbon is heated in the thermal zone to a temperature of at least 1,000°C to form the graphenic carbon particles. In other embodiments, the graphenic carbon particles may be made by using the apparatus and method described in United States Patent Application Serial No. 13/309,894 at [0015] to [0042] in which (i) a methane precursor material (such as a material comprising at least 50 percent methane, or, in some cases, gaseous or liquid methane of at least 95 or 99 percent purity or higher) is introduced into a thermal zone (such as a plasma); and (ii) the methane precursor is heated in the thermal zone to form the graphenic carbon particles. Such methods can produce graphenic carbon particles having at least some, in some cases all, of the characteristics described above.

[0059] During production of the graphenic carbon particles by the methods described above, a carbon-containing precursor is provided as a feed material that may

be contacted with an inert carrier gas. The carbon-containing precursor material may be heated in a thermal zone, for example, by a plasma system. In certain embodiments, the precursor material is heated to a temperature ranging from 1,000°C to 20,000°C, such as 1,200°C to 10,000°C. For example, the temperature of the thermal zone may range from 1,500 to 8,000°C, such as from 2,000 to 5,000°C. Although the thermal zone may be generated by a plasma system, it is to be understood that any other suitable heating system may be used to create the thermal zone, such as various types of furnaces including electrically heated tube furnaces and the like.

[0060] The gaseous stream may be contacted with one or more quench streams that are injected into the plasma chamber through at least one quench stream injection port. The quench stream may cool the gaseous stream to facilitate the formation or control the particle size or morphology of the graphenic carbon particles. In certain embodiments of the invention, after contacting the gaseous product stream with the quench streams, the ultrafine particles may be passed through a converging member. After the graphenic carbon particles exit the plasma system, they may be collected. Any suitable means may be used to separate the graphenic carbon particles from the gas flow, such as, for example, a bag filter, cyclone separator or deposition on a substrate.

[0061] Without being bound by any theory, it is currently believed that the foregoing methods of manufacturing graphenic carbon particles are particularly suitable for producing graphenic carbon particles having relatively low thickness and relatively high aspect ratio in combination with relatively low oxygen content, as described above. Moreover, such methods are currently believed to produce a substantial amount of graphenic carbon particles having a substantially curved, curled, creased or buckled morphology (referred to herein as a "3D" morphology), as opposed to producing predominantly particles having a substantially two-dimensional (or flat) morphology. This characteristic is believed to be reflected in the previously described compressed density characteristics and is believed to be beneficial in the present invention because, it is currently believed, when a significant portion of the graphenic carbon particles have a 3D morphology, "edge to edge" and "edge-to-face" contact between graphenic carbon particles within the composition may be promoted. This is thought to be because particles having a 3D morphology are less likely to be

aggregated in the composition (due to lower Van der Waals forces) than particles having a two-dimensional morphology. Moreover, it is currently believed that even in the case of "face to face" contact between the particles having a 3D morphology, since the particles may have more than one facial plane, the entire particle surface is not engaged in a single "face to face" interaction with another single particle, but instead can participate in interactions with other particles, including other "face to face" interactions, in other planes. As a result, graphenic carbon particles having a 3D morphology are currently thought to provide the best conductive pathway in the present compositions and are currently thought to be useful for obtaining electrical conductivity characteristics sought by the present invention, particularly when the graphenic carbon particles are present in the composition in relatively low amounts.

[0062] Fig. 2 schematically illustrates a roll coating method for applying coating compositions onto sheet materials in accordance with an embodiment of the present invention. In the embodiment shown, the coating operation may be conducted in a conventional rolling mill. Metal sheet material, such as galvanized steel or the like, is provided in a long strip 5 that passes under oppositely-rotating coating rollers 20 and 22, which are fed with a supply of a coating composition 24. The uncoated strip 5 passes under the coating rollers 20 and 22, where a layer of the coating composition 24 is deposited on the upper surface of the sheet material. The coated sheet material 10 may be formed into a coil 26 for storage and transportation for use in various applications, such as galvanized steel roof sheeting.

[0063] During the roll coating process, the coating composition is typically applied to the sheet material 5 with a wet film thickness of at least 1 micron, typically at least 1 or 5 microns. In certain embodiments, the wet film thickness of the coating material is from 5 to 15 or 20 microns. In certain embodiments, the deposition rate of the coating composition may be at least 200 ft/min, typically at least 300 ft/min or 350 ft/min.

[0064] After application, the coating compositions typically dry and cure quickly with minimal VOC emissions. Curing times are typically in less than 1 minute, for example, less than 10 or 5 seconds. Typical curing temperatures are below 300°F, for example, below 275° or 250°F. In certain embodiments, curing times may be less than 3 or 2 seconds at temperatures of 225°F or 200°F, or less.

[0065] The dry film thickness of the cured coating is typically at least 1 micron up to 15 or 20 microns. For example, the dry film thickness may be from 5 to 10 microns. In accordance with the present invention, such relatively thin coating layers have been found to significantly increase the solar reflective index of metal roof sheeting materials.

[0066] The following examples illustrate various aspects of the present invention, but are not intended to limit the scope of the invention.

EXAMPLES

[0067] Coating compositions were prepared and tested as described in Tables 1-4 below.

Table 1

Coating Composition Nos. 1-3

Components	Sample No. 1	Sample No. 2	Sample No. 3
Acrylic Latex Resin	198.10	199.18	165.41
Deionized Water	15.23	17.84	85.30
Defoamer	0.48	0.48	0.51
Surfynol Surfactant	1.04	1.04	1.06
Surfactant	1.04	1.04	1.06
Coalescing Agent	10.01	10.01	10.15
Chrome Tint	5.98	–	5.98
White Tint	–	–	154.63
Rust Inhibitor	2.41	2.43	2.46
Thickener	3.55	3.55	5.36
Deionized Water	3.55	3.55	0.54
pH Control Agent	0.53	0.53	0.54
Deionized Water	0.53	0.53	0.54
Wax	3.64	3.64	10.52
Total Weight in Grams	246.09	243.82	444.06

Table 2

Coating Composition No. 4

Components	Sample No. 4
Latex Resin	201.14
UC Intermediate[1]	22.27
Deionized Water	3.70
Defoamer	0.13
Rust Inhibitor Pigment	8.05
Surfactant	0.24
Silica	1.08
Deionized Water	0.10
Total Weight in Grams	236.62

[1] Acrylic Emulsion Joncryl 538 (98.88); Defoamer (0.74); Deionized Water (5.0); Silica (25.11); Corrosion Pigment (49.78); Reflective Pigment (25.11); and Defoamer (0.26).

[0068] The components listed in Tables 1 and 2 above were added together in the order described in each table under gentle stirring. The coating compositions were allowed to equilibrate overnight before panel preparation. Viscosity and pH were

checked the next day. The coating compositions were applied to galvanized steel substrates using a wire drawdown bar. The coated panels were placed in a conveyor oven set at a temperature to obtain a peak metal temperature of 190°F in two seconds dwell time (line speed). The coated panels were tested, with the results shown in Table 3 below.

Table 3

Test Results

	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4
% Weight Solids	41.82	41.62	45.0	44.03
Viscosity (Seconds) (measured using #4 Zahn Cup at room temperature)	10-15	10-15	12-20	9-25
Dry Film Thickness	0.15-0.20 (mils) 3.8-5.1 (microns)	0.15-0.20 (mils) 3.8-5.1 (microns)	0.4-0.5 (mils) 10.2-12.7 (microns)	0.15-0.25 (mils) 3.8-6.4 (microns)
Pencil Hardness	HB-F	HB-F	HB-F	B
T-Bend	1/3 np/nc	1/3 np/nc	1/3 np/nc	1/3 np/nc
Reverse Impact	Pass	Pass	Pass	Pass
X-Hatch Adhesion	Pass	Pass	Pass	Pass
Butler Immersion	No Corrosion	No Corrosion	No Corrosion	Corrosion – fail
Salt Spray	No Black Spots	No Black Spots	No Black Spots	Corrosion – fail
Wet Stack	No Pressure Mottling	No Pressure Mottling	No Pressure Mottling	Pressure mottling, black spots
TSR (%)	66.8	65	70.7	66.8
TE (%)	54	58	78	54
SRI	71	69	84	71

[0069] In accordance with the pencil hardness test, ASTM D3363, a pencil is held firmly against the coating at a 45 degree angle and pushed away from the operator in a 0.25 inch stroke. Sufficient pressure is exerted downward and forward either to cut or scratch the film. The process is repeated down the hardness scale until a pencil is found that will not cut through the film to the substrate. The scale of hardness is: 6B (very soft) up to a 6H (very hard).

[0070] In accordance with the Butler immersion test, ASTM D870, panels with cut edges are placed in a cup of covered tap water, and placed in a humidity cabinet 100F/100% humidity, for 1000 hours. The panels are then removed from the water,

and visually evaluated for any red or white rust, black spots and or blisters on the faces and edges of the panels.

[0071] In accordance with the salt spray test, ASTM B117, panels are placed with taped cut edges in a 95F/5% NaCl solution cabinet for 1000 hours. The panels are then removed from the cabinet and visually evaluated for any red or white rust, black spots and blister defects on the faces of the panels.

[0072] In accordance with the wet stack test, ASTM D7376-10A, panels are sprayed with DI-water, stacked face to face, and clipped together in a bundle to simulate a wound coil. The bundles are placed in a 100F/100% humidity cabinet for 1000 hours. The bundles are then removed and visually evaluated for dark stains or white stains (pressure mottling).

[0073] Galvanized steel panels coated with compositions similar to Sample Nos. 1 and 2 described above were tested for TSR, TE and SRI properties at various dry film thicknesses (DFT). The results are shown in the plots of Figs. 3, 4 and 5.

[0074] Galvanized steel panels coated with compositions similar to Sample Nos. 1 and 2 described above, but with additions of interference pigment available from Eckart under the designation SolarFlair in an amount of 5 weight percent based on the total weight of the coating composition, were tested for TSR, TE and SRI properties at various dry film thicknesses (DFT). The results are shown in the plots of Figs. 6, 7 and 8.

[0075] Different types of graphenic carbon were added in an amount of 1 weight percent to coating compositions similar to Sample No. 1 above. Sample No. 5 included graphenic carbon particles produced in accordance with U.S. Patent Application Serial No. 13/309,894. Sample No. 6 included commercially available graphenic carbon particles from Angstron sold under the designation N-006-010-P. Sample No. 7 included commercially available graphenic carbon particles from XG Sciences sold under the designation X-GNP-M-25. Panels were prepared by drawdown on a galvanized steel substrate at a film thickness of 5 microns. The panels were then cured at peak metal temperature of 190°F for 2 seconds using a conveyer oven. The panels were tested, with the results shown below in Table 4.

Table 4

Test Results

Sample No.	% Graphene	Graphene Type	Diameter (microns)	Thickness (nm)	SRV	TE	SRI	Salt Spray – 1000h
1	0%	NA	NA	NA	66.3	0.55	70	Excellent
5	1%	Graphenic Carbon Particles .			59.7	0.54	59	very few blisters
6	1%	Commercially available N-006-010-P graphenic carbon	<14	10-20	42.2	0.72	41	Excellent
7	1%	Commercially available X-GNP-M-25 graphenic carbon	25	6	59.5	0.56	60	dense blisters

[0076] For purposes of this detailed description, it is to be understood that the invention may assume various alternative variations and step sequences, except where expressly specified to the contrary. Moreover, other than in any operating examples, or where otherwise indicated, all numbers expressing, for example, quantities of ingredients used in the specification and claims are to be understood as being modified in all instances by the term "about". Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0077] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard variation found in their respective testing measurements.

[0078] Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of "1 to 10" is intended to include all sub-ranges between (and including) the recited minimum value of 1 and the recited maximum value of 10, that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less than 10.

[0079] In this application, the use of the singular includes the plural and plural encompasses singular, unless specifically stated otherwise. In addition, in this application, the use of "or" means "and/or" unless specifically stated otherwise, even though "and/or" may be explicitly used in certain instances.

[0080] It will be readily appreciated by those skilled in the art that modifications may be made to the invention without departing from the concepts disclosed in the foregoing description. Such modifications are to be considered as included within the following claims unless the claims, by their language, expressly state otherwise. Accordingly, the particular embodiments described in detail herein are illustrative only and are not limiting to the scope of the invention which is to be given the full breadth of the appended claims and any and all equivalents thereof.

WE CLAIM:

1. A coated metal sheet comprising:

a metal substrate; and

a cured coating covering at least a portion of the metal substrate, wherein:

(a) the cured coating:

(i) is deposited from a composition comprising a latex resin,

(ii) is substantially clear,

(iii) is substantially free of reflective pigments, and

(iv) has a dry film thickness of at least 1 micron; and

(b) the coated metal sheet has a solar reflective index of at least 65 and a corrosion resistance of at least 500h with no corrosion spots when subjected to an ASTMB117 salt spray test.

2. The metal sheet of Claim 1, wherein the latex resin is self-crosslinking.

3. The metal sheet of Claim 1, wherein the latex resin is prepared from at least one vinyl aromatic monomer.

4. The metal sheet of Claim 1, wherein the latex resin has an average particle size of from 50 to 300 nm.

5. The metal sheet of Claim 1, wherein the cured coating has a dry film thickness of at least 2 microns.

6. The metal sheet of Claim 1, wherein the cured coating has a dry film thickness of from 3 to 20 microns.

7. The metal sheet of Claim 1, wherein the cured coating further comprises a coalescing agent, wax, viscosity enhancing agent and/or a thickening agent.

8. The metal sheet of Claim 1, wherein the cured coating further comprises from 0.5 to 3 weight percent wax.

9. The metal sheet of Claim 1, wherein the cured coating is substantially free of chrome.

10. The metal sheet of Claim 1, wherein the cured coating is substantially free of metal phosphate.

11. The metal sheet of Claim 1, wherein the cured coating comprises at least one chromate.

12. The metal sheet of Claim 1, wherein the cured coating further comprises a colored pigment or a tint.

13. The metal sheet of Claim 1, wherein the cured coating further comprises up to 6 weight percent of a reflective pigment.

14. The metal sheet of Claim 1, wherein the cured coating further comprises graphenic carbon particles.

15. The rubber formulation of Claim 14, wherein the cured coating comprises up to 5 weight percent of the graphenic carbon particles.

16. The metal sheet of Claim 1, wherein the metal is in the form of a coil.

17. The metal sheet of Claim 1, wherein the metal substrate comprises a metal roofing sheet.

18. The metal sheet of Claim 1, wherein the metal substrate comprises galvanized steel.

19. The metal sheet of Claim 1, wherein the coated metal sheet has a solar reflectance of at least 65.

20. The metal sheet of Claim 1, wherein the metal sheet has a thermal emittance of at least 40 percent.

21. A coated roof sheeting material comprising:

a sheet metal substrate; and

a coating covering at least a portion of the sheet metal substrate, wherein the coating consists essentially of a cured latex resin, and wherein the coated roof sheeting material has a solar reflectance of at least 65 percent, a thermal emittance of at least 40 percent, and a corrosion resistance of at least 500h with no corrosion spots when subjected to an ASTMB117 salt spray test.

22. The coated roof sheeting material of Claim 21, wherein the sheet metal substrate comprises galvanized steel.

23. The coated roof sheeting material of Claim 22, wherein the galvanized steel is in the form of a coil.

24. The coated roof sheeting material of Claim 21, wherein the coating is deposited from a composition comprising a latex resin and has a dry film thickness of at least 1 micron.

25. A method of coating a sheet metal substrate comprising:

applying a coating composition comprising a latex resin that is substantially free of reflective pigments to the sheet metal substrate at a wet film thickness of at least 1 micron; and

curing the coating composition to produce a coated metal sheet having a solar reflective index of at least 65 and a corrosion resistance of at least 500h with no corrosion spots when subjected to an ASTMB117 salt spray test.

26. The method of Claim 25, wherein the coating composition is waterborne.

27. The method of Claim 25, wherein the coating composition further comprises a coalescing agent, wax, viscosity enhancing agent and/or thickening agent.

28. The method of Claim 25, wherein the coating composition has a viscosity of at least 10 seconds measured by a No. 4 Zahn cup at room temperature.

29. The method of Claim 25, wherein the latex resin has a glass transition temperature of less than 50°C.

30. The method of Claim 25, wherein the coating composition comprises less than 5 weight percent volatile organic solvent.

31. The method of Claim 25, wherein the coating composition has a VOC of less than 1.5.

32. The method of Claim 25, wherein the coating composition is hydrophobic.

33. The method of Claim 25, wherein the coating composition is substantially free of chrome and metal phosphate.

34. The method of Claim 25, wherein the coating composition is applied by roll coating.

35. The method of Claim 34, wherein the coating composition is applied at a rate of at least 200 ft/min.

36. The method of Claim 25, wherein the coating is cured at a temperature of less than 250° for a time of less than 10 seconds.

37. The method of Claim 25, further comprising forming the coated metal sheet into a coil.

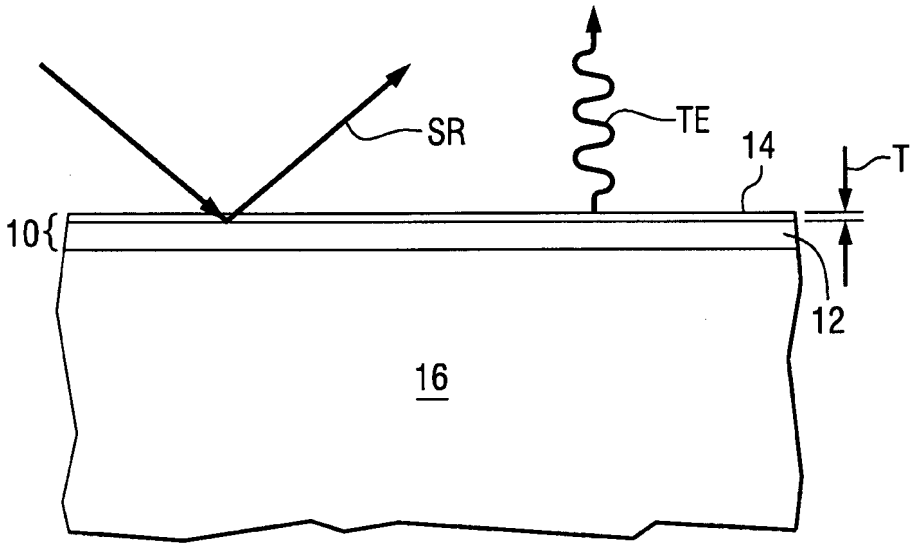


FIG. 1

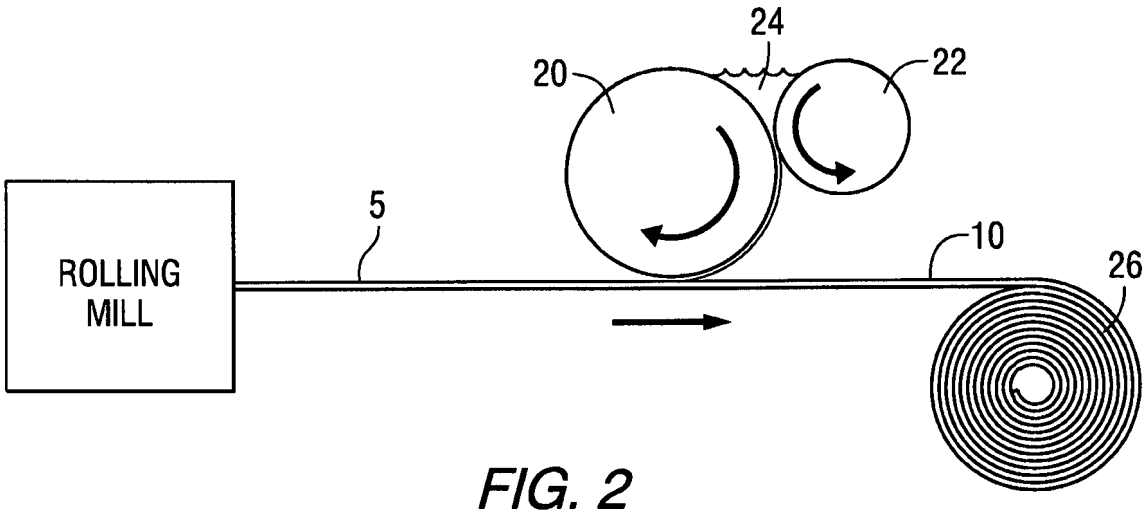


FIG. 2

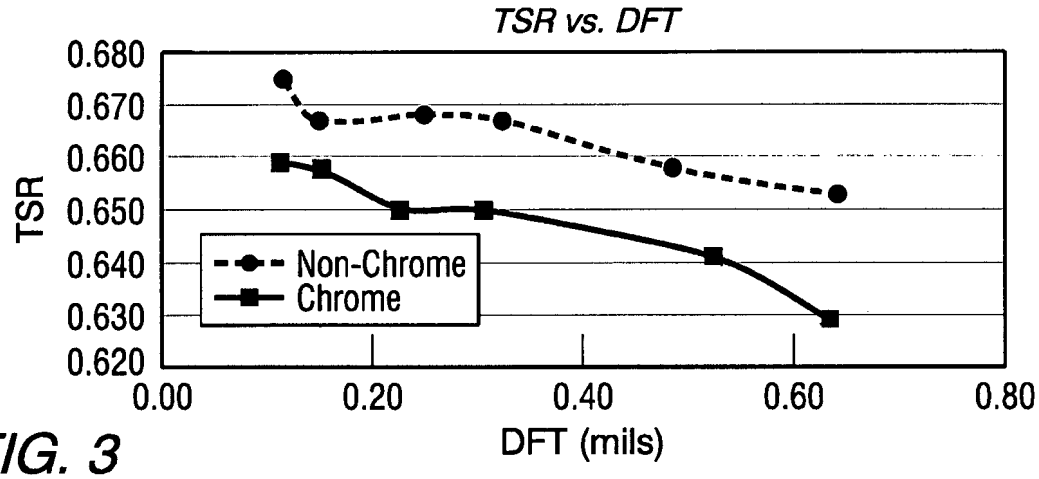


FIG. 3

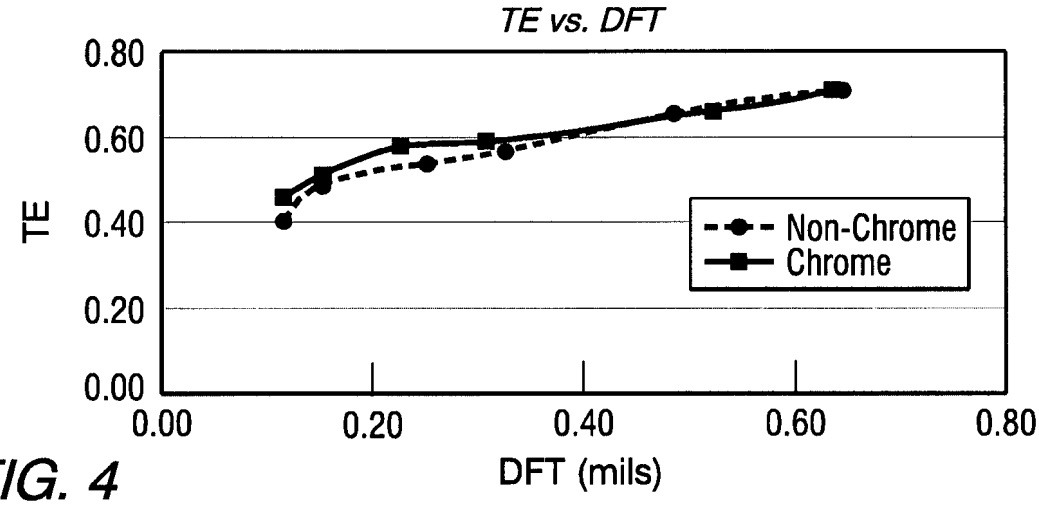


FIG. 4

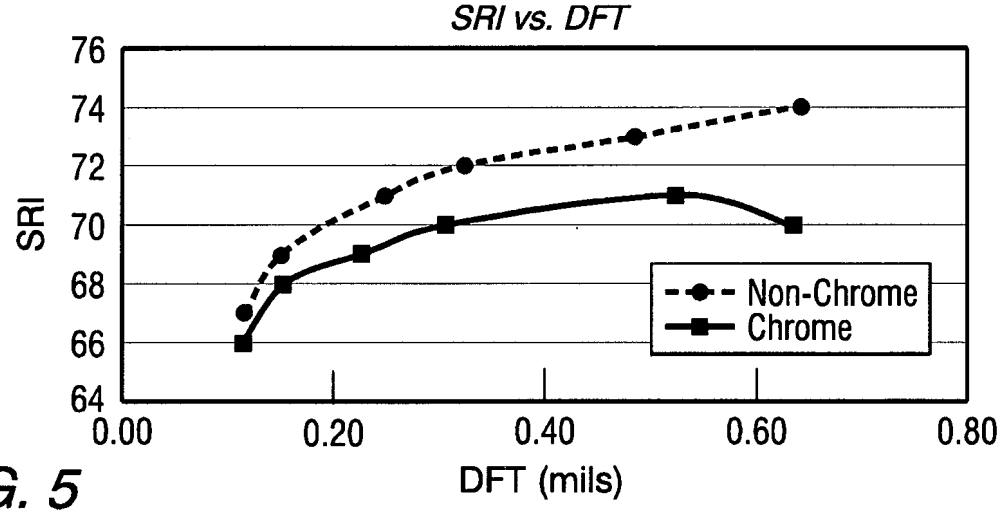


FIG. 5

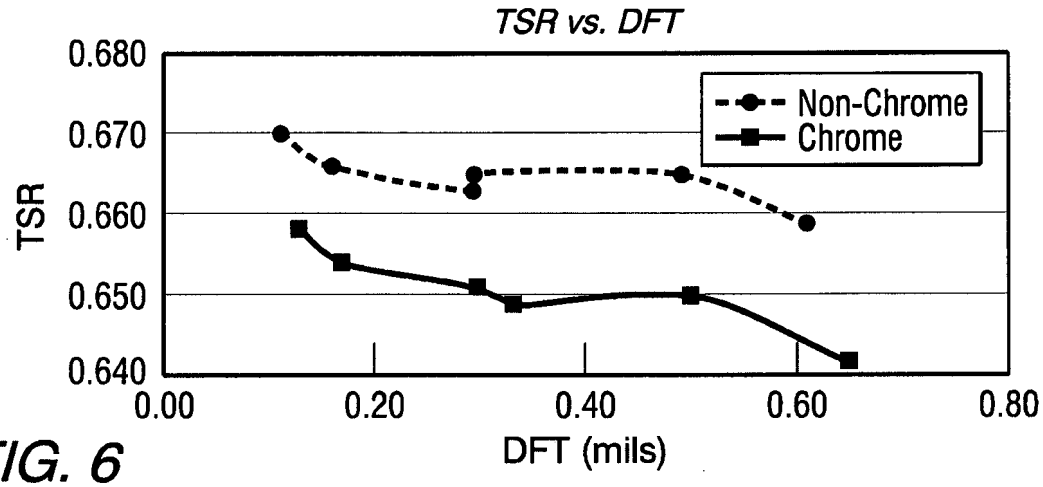


FIG. 6

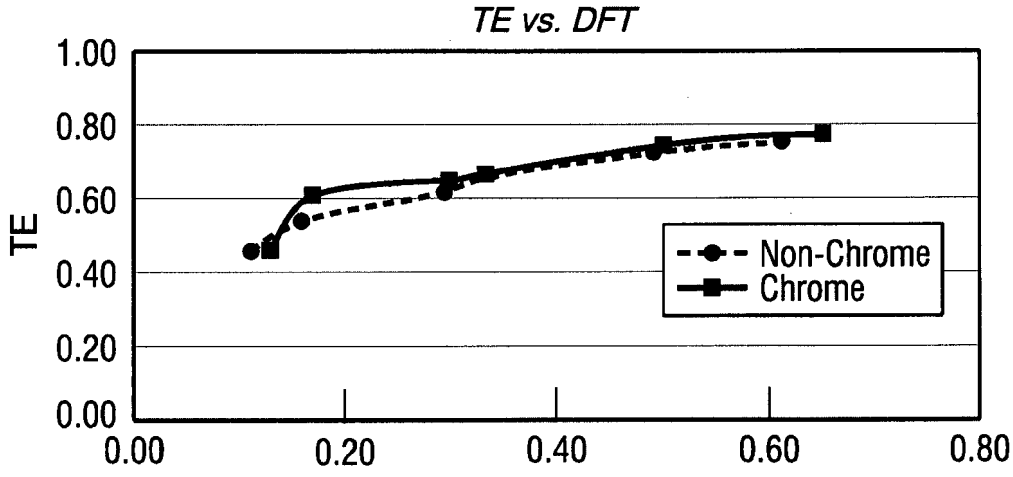


FIG. 7

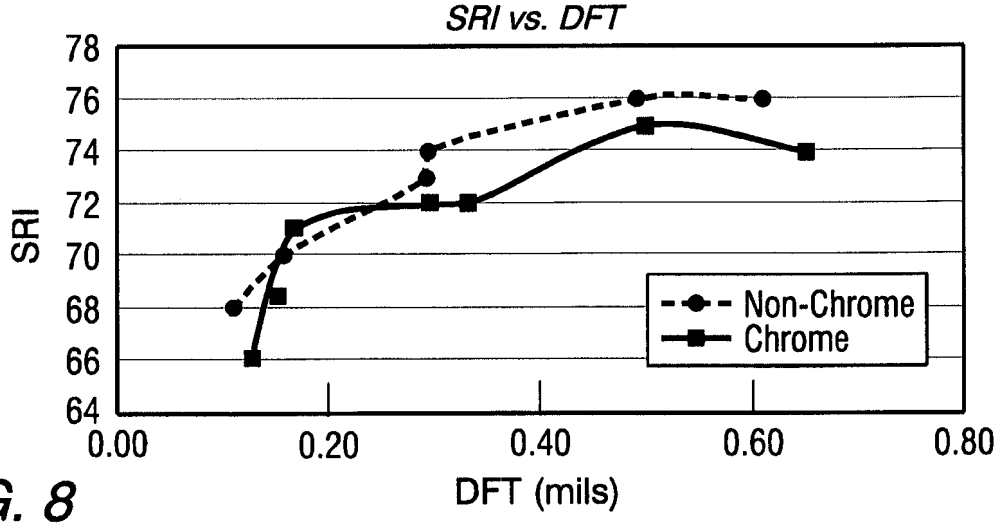


FIG. 8

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(71) Applicant: **PPG INDUSTRIES OHIO, INC.** [US/US]; 3800 West 143rd Street, Cleveland, Ohio 44111 (US).

(72) Inventors: **SCHWENDEMAN, Irina G.**; 238 Courtney Place, Wexford, Pennsylvania 15090 (US). **RETSCH, Jr., William H.**; 3810 Lyndell Street, Castle Shannon, Pennsylvania 15234 (US). **REARICK, Brian K.**; 1335 Parkview Drive, Allison Park, Pennsylvania 15101 (US). **CONLEY, Carole A.**; 260 Brewer Road, Saxonburg, Pennsylvania 16056 (US).

(74) Agents: **TREBILCOCK, Christine W.** et al.; PPG Industries, Inc., One PPG Place, 39th Floor, Pittsburgh, Pennsylvania 15272 (US).

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Declarations under Rule 4.17:

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

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

Published:

— *with international search report (Art. 21(3))*

[Continued on next page]

(54) Title: COATED SHEET MATERIALS HAVING HIGH SOLAR REFLECTIVE INDEX AND CORROSION RESISTANCE, AND METHODS OF MAKING SAME

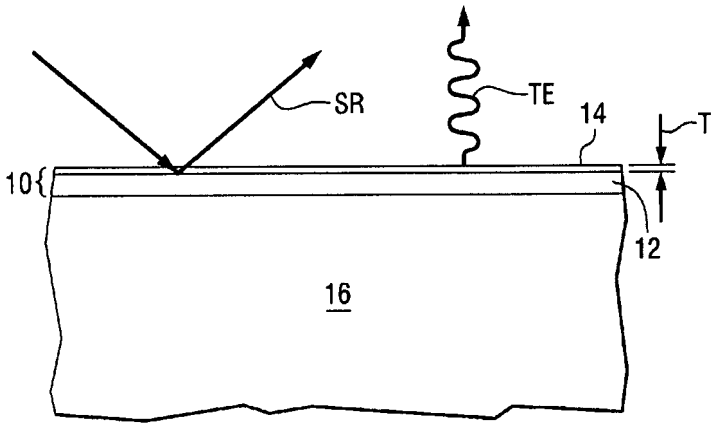


FIG. 1

(57) Abstract: Coated sheet materials having high solar reflective index and corrosion resistance, and methods of making such coated sheet materials, are disclosed. In certain embodiments, the sheet materials comprise metal such as galvanized steel roofing sheets, and the coating is deposited from a latex resin.

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— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

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International application No
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ADD. C08K3/04

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D C08K

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/045267 A1 (BASF CORP [US]; SLAWIKOWSKI MARK [US]; ALGRIM DONALD J [US]) 9 April 2009 (2009-04-09) paragraph [0016] paragraph [0024] - paragraph [0031] claims 1-5,14-20; examples 2-A ----- -/--	1,2, 5-13, 18-20

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
11 September 2013	13/02/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Matthijssen, J-J

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/046324

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of doument, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/059375 A1 (CHEMETALL GMBH [DE]; GRUSZKA CHARLES J [US]; THOMPSON AARON [US]; DEEM) 10 May 2012 (2012-05-10) page 2, line 20 - page 3, line 14 page 4, line 5 - line 8 page 6, line 5 - line 10 page 9, line 25 - line 27 page 10, line 1 page 12, line 29 - page 13, line 5 page 13, line 15 - line 27 page 14, line 13 - line 23 page 23, line 29 - line 33 page 28, line 33 - page 29, line 14 page 29, line 25 - line 28 page 33, line 8 - line 23 page 35, line 27 - line 32 page 39, line 7 - line 14 page 40, line 17 - line 24 page 55, line 22 - line 30 claims 1,5,9,11-13	1-3, 5-13, 16-20

A	US 4 239 672 A (DWORAK GERT [AT] ET AL) 16 December 1980 (1980-12-16) examples 2,5	1-20

A	Arnold Schwarzenegger: "California's Energy Efficiency Standards for Residential and Nonresidential Buildings, Title 24, Part 6, of the California Code of Regulations", , 31 December 2008 (2008-12-31), XP055017834, California USA Retrieved from the Internet: URL:http://www.energy.ca.gov/2008publications/CEC-400-2008-001/CEC-400-2008-001-CMF.PDF [retrieved on 2012-01-27] page 29 page 44 page 67 - page 69 page 93 - page 96 page 129 - page 132 page 150 - page 151 page 158 - page 159	1-20

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/046324

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

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

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-20

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

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

1. claims: 1-20

A coated metal sheet comprising:
a metal substrate; and
a cured coating covering at least a portion of the metal substrate, wherein:
(a) the cured coating:
(i) is deposited from a composition comprising a latex resin,
(ii) is substantially clear,
(iii) is substantially free of reflective pigments, and
(iv) has a dry film thickness of at least 1 micron; and
(b) the coated metal sheet has a solar reflective index of at least 65 and a corrosion resistance of at least 500h with no corrosion spots when subjected to an ASTM B117 salt spray test.

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2. claims: 21-24

A coated roof sheeting material comprising: a sheet metal substrate; and a coating covering at least a portion of the sheet metal substrate, wherein the coating consists essentially of a cured latex resin, and wherein the coated roof sheeting material has a solar reflectance of at least 65 percent, a thermal emittance of at least 40 percent, and a corrosion resistance of at least 500h with no corrosion spots when subjected to an ASTM B117 salt spray test.

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3. claims: 25-37

A method of coating a sheet metal substrate comprising: applying a coating composition comprising a latex resin that is substantially free of reflective pigments to the sheet metal substrate at a wet film thickness of at least 1 micron; and curing the coating composition to produce a coated metal sheet having a solar reflective index of at least 65 and a corrosion resistance of at least 500h with no corrosion spots when subjected to an ASTM B117 salt spray test.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2013/046324

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(71)申请人 PPG工业俄亥俄公司
地址 美国俄亥俄州
(72)发明人 I·G·施温德曼 W·H·小雷特施
B·K·里埃里克 C·A·康利
(74)专利代理机构 中国国际贸易促进委员会专利商标事务所 11038
代理人 孙悦
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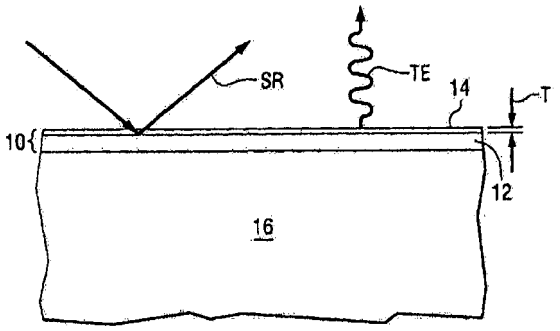
权利要求书2页 说明书12页 附图4页

(54)发明名称

具有高日光反射指数和耐腐蚀性的经涂覆的板材，及其制造方法

(57)摘要

公开了具有高日光反射指和耐腐蚀性的经涂覆的板材，和制造这种经涂覆的板材的方法。在某些实施方式中，板材包括金属例如镀锌钢材屋顶板，并且所述涂层由胶乳树脂沉积。



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1. 经涂覆的金属板，包含：

金属基材；和

覆盖该金属基材的至少一部分的固化的涂层，其中：

(a) 所述固化的涂层：

(i) 由包含胶乳树脂的组合物沉积，

(ii) 是基本上透明的，

(iii) 基本上不含反射颜料，和

(iv) 具有至少 1 微米的干膜厚度；和

(b) 所述经涂覆的金属板具有至少 65 的日光反射指数和当经受 ASTMB117 盐雾测试时至少 500 小时没有腐蚀点的耐腐蚀性。

2. 权利要求 1 所述的金属板，其中所述胶乳树脂是自交联的。

3. 权利要求 1 所述的金属板，其中所述胶乳树脂由至少一种乙烯基芳族单体制备。

4. 权利要求 1 所述的金属板，其中所述胶乳树脂具有 50-300nm 的平均粒度。

5. 权利要求 1 所述的金属板，其中所述固化的涂层具有至少 2 微米的干膜厚度。

6. 权利要求 1 所述的金属板，其中所述固化的涂层具有 3-20 微米的干膜厚度。

7. 权利要求 1 所述的金属板，其中所述固化的涂层进一步包含聚结剂、蜡、粘度增强剂和 / 或增稠剂。

8. 权利要求 1 所述的金属板，其中所述固化的涂层进一步包含 0.5-3 重量%的蜡。

9. 权利要求 1 所述的金属板，其中所述固化的涂层基本上不含铬。

10. 权利要求 1 所述的金属板，其中所述固化的涂层基本上不含金属磷酸盐。

11. 权利要求 1 所述的金属板，其中所述固化的涂层包含至少一种铬酸盐。

12. 权利要求 1 所述的金属板，其中所述固化的涂层进一步包含着色的颜料或染料剂。

13. 权利要求 1 所述的金属板，其中所述固化的涂层进一步包含至多 6 重量%的反射颜料。

14. 权利要求 1 所述的金属板，其中所述固化的涂层进一步包含石墨烯碳颗粒。

15. 权利要求 14 所述的橡胶制剂，其中所述固化的涂层包含至多 5 重量%的所述石墨烯碳颗粒。

16. 权利要求 1 所述的金属板，其中所述金属是卷材的形式。

17. 权利要求 1 所述的金属板，其中所述金属基材包括金属屋顶板。

18. 权利要求 1 所述的金属板，其中所述金属基材包括镀锌钢材。

19. 权利要求 1 所述的金属板，其中所述经涂覆的金属板具有至少 65 的日光反射率。

20. 权利要求 1 所述的金属板，其中所述金属板具有至少 40%的热发射率。

21. 经涂覆的屋顶板材，包含：

板状金属基材；和

覆盖该板状金属基材的至少一部分的涂层，其中所述涂层基本上由固化的胶乳树脂组成，并且其中所述经涂覆的屋顶板材具有至少 65%的日光反射率，至少 40%的热发射率，和当经受 ASTMB117 盐雾测试时至少 500 小时没有腐蚀点的耐腐蚀性。

22. 权利要求 21 所述的经涂覆的屋顶板材，其中所述板状金属基材包括镀锌钢材。

23. 权利要求 22 所述的经涂覆的屋顶板材，其中所述镀锌钢材是卷材的形式。

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24. 权利要求 21 所述的经涂覆的屋顶板材，其中所述涂层由包含胶乳树脂的组合物沉积并具有至少 1 微米的干膜厚度。

25. 涂覆板状金属基材的方法，包括：

以至少 1 微米的湿膜厚度将基本上不含反射颜料的包含胶乳树脂的涂料组合物施涂于所述板状金属基材；和

固化所述涂料组合物以产生具有至少 65 的日光反射指数和当经受 ASTMB117 盐雾测试时至少 500 小时没有腐蚀点的耐腐蚀性的经涂覆的金属板。

26. 权利要求 25 所述的方法，其中所述涂料组合物是水性的。

27. 权利要求 25 所述的方法，其中所述涂料组合物进一步包含聚结剂、蜡、粘度增强剂和 / 或增稠剂。

28. 权利要求 25 所述的方法，其中所述涂料组合物具有在室温由 4 号蔡氏杯测量的至少 10 秒的粘度。

29. 权利要求 25 所述的方法，其中所述胶乳树脂具有低于 50℃的玻璃化转变温度。

30. 权利要求 25 所述的方法，其中所述涂料组合物包含小于 5 重量%的挥发性有机溶剂。

31. 权利要求 25 所述的方法，其中所述涂料组合物具有小于 1.5 的 VOC。

32. 权利要求 25 所述的方法，其中所述涂料组合物是疏水的。

33. 权利要求 25 所述的方法，其中所述涂料组合物基本上不含铬和金属磷酸盐。

34. 权利要求 25 所述的方法，其中所述涂料组合物通过辊涂施涂。

35. 权利要求 34 所述的方法，其中所述涂料组合物以至少 200ft/min 的速率施涂。

36. 权利要求 25 所述的方法，其中所述涂料在低于 250° 的温度固化少于 10 秒的时间。

37. 权利要求 25 所述的方法，进一步包括使经涂覆的金属板形成卷材。

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具有高日光反射指数和耐腐蚀性的经涂覆的板材，及其制造方法

[0001] 相关申请的交叉引用

[0002] 本申请要求2012年6月19日提交的美国临时专利申请序列号61/661,532的权益，其通过引用并入本文。

发明领域

[0003] 本发明涉及具有高日光反射指数和耐腐蚀性的经涂覆的板材，以及制造这种经涂覆的板材的方法。

[0004] 发明背景

[0005] 建筑和其它应用中使用的板材经常需要耐腐蚀性质。例如，钢和其它类型的金属屋顶板材必须长期耐受暴露于环境条件。镀锌钢材屋顶板通常由含铬的组合物预处理以增加耐腐蚀性。这种预处理可以在钢材的长条上进行，然后将钢材绕成卷供随后使用。

[0006] 镀锌钢材和其它类型的金属屋顶材料可具有高日光反射率性质，但是当暴露于太阳光时，由于它们低的热发射率性质，它们倾向于变热。由于这种日光的加热，下面的结构可要求显著量的能量以冷却，例如，通过空气调节。

[0007] 几个最近的美国和州政府法规要求金属屋顶满足特定的日光反射指数值以防止过热。日光反射指数(SRI)基于日光反射率和热发射率的组合计算，且要求65、70或更高的SRI值以满足特定的政府法规。日光反射率作为日光辐射在从表面反射的电磁波谱的可见光、红外光和紫外光区域中的百分比测量，且0或0%的值对应于零反射率以及1或100%的值对应于全反射率。热发射率作为表面散发热量的能力测量，且0或0%的值对应于零热发射率并且1或100%的值对应于总热发射率。为了减少过热，具有相对较高的日光反射率和热发射率的金属屋顶是期望的。

[0008] 常规的金属屋顶未能满足某些政府能量法规，并且常规的预处理的使用将日光反射指数减少至低于未经处理的金属的日光反射指数。

[0009] 发明概述

[0010] 本发明的一方面提供了包含金属基材和固化的涂层的经涂覆的金属板，所述固化的涂层覆盖至少一部分金属基材，其中：(a)固化的涂层：(i)由包含胶乳树脂的组合物沉积，(ii)是基本上透明的，(iii)基本上不含反射颜料，和(iv)具有至少1微米的干膜厚度；和(b)经涂覆的金属板具有至少65的日光反射指数和当经受ASTMB117盐雾测试时至少500小时没有腐蚀点的耐腐蚀性。

[0011] 本发明的另一方面提供了包含板状金属基材和涂层的经涂覆的屋顶板材，所述涂层覆盖至少一部分板状金属基材，其中所述涂层基本上由固化的胶乳树脂组成，并且其中经涂覆的屋顶板材具有至少65%的日光反射率，至少40%的热发射率，和当经受ASTMB117盐雾测试时至少500小时没有腐蚀点的耐腐蚀性。

[0012] 本发明的进一步的方面提供了涂覆板状金属基材的方法，其包括以至少1微米的湿膜厚度将基本上不含反射颜料的包含胶乳树脂的涂料组合物施涂于板状金属基材，以及

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固化所述涂料组合物以生产具有至少65的日光反射指数和当经受ASTMB117盐雾测试时至少500小时没有腐蚀点的耐腐蚀性的经涂覆的金属板。

[0013] 附图简述

[0014] 图1为根据本发明的实施方式的经涂覆的屋顶板材的部分示意性侧视图，其说明了日光反射率和热发射率性质。

[0015] 图2为部分示意性侧视图，其说明了在辊轧机中涂覆和卷起金属板的方法，包括根据本发明的实施方式使用辊涂机将涂料组合物施涂于板上。

[0016] 图3为根据本发明的实施方式的经涂覆的金属的总日光反射率(TSR)对干膜厚度(DFT)的图。

[0017] 图4为根据本发明的实施方式的经涂覆的金属的热发射率(TE)对DFT的图。

[0018] 图5为根据本发明的实施方式的经涂覆的金属的日光反射指数(SRI)对DFT的图。

[0019] 图6为根据本发明的实施方式的经涂覆的金属的TSR对DFT的图。

[0020] 图7为根据本发明的实施方式的经涂覆的金属的TE对DFT的图。

[0021] 图8为根据本发明的实施方式的经涂覆的金属的SRI对DFT的图。

[0022] 本发明实施方式的详细说明

[0023] 图1示意性地说明了根据本发明的实施方式的包括基板12和涂布层14的经涂覆的板材10。在某些实施方式中，经涂覆的板10可用于建筑应用，例如作为建筑物16或其它结构的屋顶板材。涂层14具有典型地大于1微米，例如，大于2或3微米的干膜厚度T。在某些实施方式中，涂层14的干膜厚度T可以是3到10或20微米。基板12可以是任意期望的厚度，例如0.5-3mm。例如，在某些实施方式中镀锌钢材屋顶板材的厚度的范围可在0.5-2mm。尽管显示于图1中的板12是平整的，但是可以提供任意其它的形状，例如波纹状、棱纹状等。

[0024] 如图1所示，在经涂覆的板10上，一部分入射日光辐射从其具有总日光反射率TSR值的表面反射。本文所使用的术语“总日光反射率”是指表面材料反射太阳光（包括可见光、红外光、和紫外光波长）的能量的量度（按0%-100%的等级）。在某些实施方式中，经涂覆的板10的总日光反射率TSR为至少60%，例如，至少62%或65%。

[0025] 如图1所进一步说明的，经涂覆的板10具有热发射率TE性质。本文所使用的术语“热发射率”是指材料释放吸收的热量的能力。0至1或0%至100%的数字被用于表述发射率。在某些实施方式中，经涂覆的板10的热发射率TE为至少0.3(30%)，例如，至少0.4(40%)或0.5(50%)。

[0026] 总日光反射率TSR和发射率TE性质，如图1示意性地说明，可以结合以得到日光反射指数（“SRI”）。本文所使用的术语“日光反射指数”是将日光反射率和发射率并入单一值以表示在阳光下的材料的温度的值。SRI量化了相对于标准黑和标准白的表面，表面将变得有多热。使用基于之前测得的日光反射率和发射率的值的等式（如美国材料与试验协会标准E1980中规定的）计算SRI。根据ASTM标准E1980，将TSR和TE的值输入标准等式以计算SRI值。在某些实施方式中，日光反射指数SRI为至少65，例如，至少70或75。

[0027] 根据本发明的实施方式，涂料组合物包含胶乳树脂。胶乳树脂可以是自交联的，或可以不是自交联的。胶乳树脂典型地占所述涂料组合物的20-60重量%，例如，约30-约50

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重量%。在某些实施方式中，用于制备胶乳树脂的合适的单体可包括乙烯基芳族单体例如苯乙烯，脂环族单体例如甲基丙烯酸环己酯，和长链脂族单体例如丙烯酸 2- 乙基己酯、MMA 和 / 或甲基丙烯酸 2- 乙基己酯。其它类型的单体包括环己烯、2- 乙基 -1- 己烯、环己醇、α - 甲基苯乙烯、2- 乙基己醇、醋酸 2- 乙基己酯、丁酸甲基 -4- 苯酯、十四酸甲酯和 / 或十六酸甲酯。

[0028] 在某些实施方式中，用于胶乳树脂的单体包括乙烯基芳族化合物，例如乙烯基芳族单体，该用于胶乳树脂的单体，在某些实施方式中，包括具有至少 100℃的计算 Tg 的化合物。乙烯基芳族化合物的具体例子为苯乙烯（其具有 100℃的计算 Tg）、α - 甲基苯乙烯（其具有 168℃的计算 Tg）、乙烯基甲苯、对甲基苯乙烯、乙基乙烯基苯、乙烯基萘、乙烯基二甲苯、α - 甲基苯乙烯二聚物（甲基）丙烯酸酯、五氟苯乙烯等。在某些实施方式中，苯乙烯或另一种乙烯基芳族单体可以以重量%计包含树脂的最主要的单体。

[0029] 在某些实施方式中，胶乳树脂的单体包括脂环族（甲基）丙烯酸酯单体，例如丙烯酸三甲基环己酯、丙烯酸叔丁基环己酯、（甲基）丙烯酸二环戊二烯酯、甲基丙烯酸三甲基环己酯（计算 Tg 为 98℃）、甲基丙烯酸环己酯（计算 Tg 为 83℃）、甲基丙烯酸异冰片酯（计算 Tg 为 110℃）、甲基丙烯酸 2- 乙基己酯、甲基丙烯酸四氢化糠酯、甲基丙烯酸 3,3,5- 三甲基环己酯（计算 Tg 为 125℃）、和 / 或甲基丙烯酸 4- 叔丁基环己酯等。

[0030] 在某些实施方式中，胶乳树脂的单体包括（甲基）丙烯酸烷酯，该胶乳树脂的单体，在某些实施方式中，包括具有至少 100℃的计算 Tg 的化合物。（甲基）丙烯酸烷酯的具体的例子为（甲基）丙烯酸 C_1-C_{24} 烷基酯，例如（甲基）丙烯酸甲酯（其具有 105℃的计算 Tg）、（甲基）丙烯酸丙酯、（甲基）丙烯酸丁酯、（甲基）丙烯酸异丁酯、（甲基）丙烯酸己酯、（甲基）丙烯酸 2- 乙基己酯、（甲基）丙烯酸辛酯、（甲基）丙烯酸癸酯、（甲基）丙烯酸十二烷基酯、（甲基）丙烯酸十五烷基酯、（甲基）丙烯酸十六烷基酯、（甲基）丙烯酸十八烷基酯、和（甲基）丙烯酸十九烷基酯、和它们的混合物。其它单体包括，例如，腈类，例如丙烯腈和 / 或甲基丙烯腈。

[0031] 可用于本发明的涂料组合物的胶乳树脂的一些非限制性的例子商购自 Nuplex，Lubrizol，Rohm and Haas，Alberdingk Boley Company，Omnova 和 DSM Neoresins，例如 Joncryl 1982，Caroboset CR-781，Alberdingk AC 2403，Alberdingk 2360，NeocrylXK-98 等。

[0032] 胶乳树脂可具有 50nm-300nm，例如 60nm-100 或 150nm 的平均粒度；-20 至 100℃，典型地为 0 至 20 或 50℃的玻璃化转变温度（T_g）；和 0-20，典型地 2-10 的酸值。

[0033] 本发明的涂料组合物可以是水性的。在某些实施方式中，水可占涂料组合物的 20-80 重量%，例如，50-65 重量%。在某些实施方式中，涂料组合物基于所述组合物的总重量计包含少于 10 重量%，例如，少于 7 或 4 重量%的有机溶剂。涂料组合物的树脂固体含量基于所述组合物的总重量计可以是相对较高的，例如，大于 35 或 40 重量%。

[0034] 涂料组合物可具有较少或没有挥发性有机成分 (VOC)。例如，涂料组合物基于所述组合物的总重量计可包含少于 1.5 重量%的 VOC，例如，少于 1 或 0.5 重量%的 VOC。在某些实施方式中，涂料组合物基本上不含 VOC。

[0035] 涂料组合物基于所述涂料组合物的总重量计可进一步以至多 10 重量%的量，例如，以 2-3 重量%的量包含至少一种聚结剂。合适的聚结剂的例子包括商购自 Dow Chemical

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Company 的丁基卡必醇、Dowanol DPM、Dowanol DPnB、Dowanol PPh、丁基溶纤剂或 Dowanol DPnP。根据本发明的实施方式，聚结剂在胶乳树脂颗粒周围形成了薄膜，这有助于它们聚结。胶乳树脂颗粒的改进的聚结导致产生非常细的粒度和均匀的微结构，这与其它类型的具有较大树脂粒度的涂层相比提供了改进的腐蚀防护。例如，根据本发明的某些实施方式，平均树脂粒度可以少于 150 纳米，例如，少于 100 或 80 纳米。

[0036] 在某些实施方式中，蜡基于所述涂料组合物的总重量计可以以至多 10 重量%，例如，0.5-3 重量%的量添加至涂料组合物中。合适的类型的蜡包括 Ceraflour 913、Worleeadd 352、Aquamat 272、Aquamat270、Aquacer 539、和它们的组合。例如，可以使用由 BYK Chemie 以 Aquamat 272 的名称出售的蜡。可以控制蜡的类型和用量以改进经涂覆的板材的耐刮性。例如，当经涂覆的板形成卷材时，蜡添加剂的使用可减少或防止在卷起和开卷工艺期间，以及在随后的经涂覆的板材的安装和使用期间的刮擦。在某些实施方式中，限制添加至涂料组合物中的蜡的量以避免当经涂覆的板被卷起时的不希望的滑移，例如，以防止不希望的卷材的“可伸缩”，由于相邻卷材层之间的低摩擦。

[0037] 多种其它添加剂可根据本发明的某些实施方式任选地添加至涂料组合物中。例如，合适的添加剂包括增稠剂、消泡剂、表面活性剂、防锈剂、pH 控制剂、二氧化硅、和染料剂。

[0038] 合适的增稠剂包括 Acrysol ASE-60、Aquatix 8421、DSX-1550、和 Laponite RD。当使用时，这种增稠剂基于所述涂料组合物的总重量计可以以至多 7 重量%，例如，0.5-4 重量%的量存在。

[0039] 合适的消泡剂为基于所述涂料组合物的总重量计以至多 2 重量%，例如，0.1-0.5 重量%的量，包括 BYK-011、BYK-20、BYK-32、BYK 34 和得自 Ashland 的 Drewplus L-419。

[0040] 合适的表面活性剂为基于所述涂料组合物的总重量计以至多 2 重量%，例如，0.1-0.5 重量%的量，包括得自 DuPont 的 Zonyl FSP，得自 Air Products 的 Surfynol 104E、BYK 346、和 BYK348。

[0041] 合适的防锈剂基于所述涂料组合物的总重量计为至多 1 重量%，例如，0.4-0.6 重量%的典型的量，包括 Halox 550、Halox Flash X-150、330、Halox SZP-391、苯甲酸铵、和亚硝酸钠。

[0042] 在某些实施方式中，涂料组合物基本上不含某些金属盐，例如金属磷酸盐、磷碳酸盐和磷硅酸盐。例如，所述组合物可以基本上不含磷酸锌、磷酸钙、磷硅酸钙和 / 或富含钙的二氧化硅。

[0043] 合适的 pH 控制剂基于所述涂料组合物的总重量计以至多 1 重量%，例如，0.01-0.2 重量%的典型的量包括任意水溶性的胺例如得自 Avecia 的二甲基乙醇胺 (DMEA)。

[0044] 根据本发明的某些实施方式，所述涂料基本上不含铬。在这种实施方式中，铬并不被有意地添加至涂料组合物中并且仅仅以痕量或作为杂质存在。

[0045] 在某些实施方式中，可以将含有铬酸盐的材料添加至涂料组合物中。这种含有铬酸盐的涂料组合物可特别地适用于作为底漆涂料。例如，可以基于所述涂料组合物的总重量计以至多 12 重量%，例如，0.2-1 重量%的量添加铬酸。这种含有铬酸锶的添加剂可提供改进的耐腐蚀性性质。当用作底漆涂层时，涂料组合物可进一步包括典型地用于底漆的着

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色剂和染色剂，例如二氧化钛等。

[0046] 在某些实施方式中，可以以例如 0.1 至 2 或 3 重量%或更多的量将二氧化硅添加至涂料组合物中。二氧化硅的一些例子包括来自 PPG Industries 的 Lo-Vel 275 二氧化硅和来自 Air Products Aerosil 200 的二氧化硅。

[0047] 在某些实施方式中，涂料组合物和固化的涂层基本上不含反射颜料。本文所使用的术语“反射颜料”是指板状或片状的干涉颜料，例如云母、硅酸盐、二氧化硅和氧化铝。来自 Eckart 的 Solarflair 9870 是反射颜料的一个例子。本文所使用的术语“基本上不含反射颜料”是指涂层没有或具有最少量的反射颜料，却能实现日光反射率和/或日光反射指数期望的水平。例如，固化的涂层可具有少于 2 或 1 重量%的反射颜料。尽管所述涂层可基本上不含反射颜料，但是它们仍然保持足够的日光反射率性质和例如，65 或更大的 SRI 的日光反射指数值。反射颜料添加剂的成本可因此避免，同时仍然提供日光反射率的期望的水平。

[0048] 在某些实施方式中，将至少一种着色的颜料或染料剂添加至涂料组合物中。着色的颜料和染色剂不同于反射干涉颜料并且包括标准的无机和有机颜料，例如发现于常规的油漆和底漆中的那些。例如，多种着色的颜料在 Dry Color Manufacturers Association(DCMA) 分类中列出。与具有相对较高纵横比的板状和薄板状的反射干涉颜料相比，这种着色的颜料和染色剂典型地包含具有基本上等轴的形态，例如，约 1 :1 的纵横比的颗粒。一种合适的类型的着色的颜料基于所述涂料组合物的总重量计以至多 35 重量%，例如，1-25 重量%的量包含 TiO_2。商购自 PPG Industries 的 Aquext 白色染料剂和商购自 Wayne Pigments Corrosperse 176E 铬染料剂是合适的染料剂的例子。

[0049] 在某些实施方式中，涂层基本上不含着色的颜料和染料剂。例如，涂层可以是基本上透明和无色的。

[0050] 在某些实施方式中，可以基于所述涂料组合物的总重量计以 5 重量%，例如，1-2 重量%的量将导电颗粒（例如石墨烯碳颗粒）添加至涂料组合物中。这种石墨烯碳颗粒可提供改进的热发射率性质。该石墨烯碳颗粒可以从商业源获得，或可以根据描述于美国申请序列号 13/249,315 和 13/309,894 中的方法和设备制造，其通过引用并入本文。示例性的商购的石墨烯碳颗粒得自 Angstron and XG Sciences。

[0051] 本文所使用的术语“石墨烯碳颗粒”是指具有包含一或多层一个原子厚的平面层的 sp^2 键合的碳原子结构的碳颗粒，所述碳原子密集地填充在蜂窝晶格中。堆叠层的平均数可以小于 100，例如，小于 50。在某些实施方式中，堆叠层的平均数为 30 或更小，例如 20 或更小、10 或更小，或在某些情形下，5 或更小。所述石墨烯碳颗粒可以是基本上平的，然而，平面层的至少一部分可以基本上是弯曲的、卷曲的、褶皱的或搭扣的 (buckled)。所述颗粒典型地不具有球状的或等轴的形态。

[0052] 在某些实施方式中，存在于本发明的组合物中的石墨烯碳颗粒具有以垂直于碳原子层的方向测量的不大于 10 纳米、不大于 5 纳米，或在某些实施方式中，不大于 4 或 3 或 2 或 1 纳米，例如不大于 3.6 纳米的厚度。在某些实施方式中，石墨烯碳颗粒可以为 1 个原子层至 3、6、9、12、20 或 30 个原子层厚、或更多。在某些实施方式中，存在于本发明的组合物中的石墨烯碳颗粒具有以平行于碳原子层的方向测量的至少 50 纳米，例如大于 100 纳米，在某些情形下大于 100 纳米至 500 纳米、或大于 100 纳米至 200 纳米的宽度和长度。石墨

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烯碳颗粒可以以具有大于 3 :1，例如大于 10 :1 的相对较高的纵横比（纵横比被定义为颗粒的最长尺寸与颗粒的最短尺寸的比）的超薄片 (flake)，片粒 (platelet) 或层的形式提供。

[0053] 在某些实施方式中，本发明的组合物中使用的石墨烯碳颗粒具有相对较低的氧含量。例如，在本发明的组合物的某些实施方式中使用的石墨烯碳颗粒可以具有不大于 2 原子重量%，例如不大于 1.5 或 1 原子重量%、或不大于 0.6 原子重量，例如约 0.5 原子重量%的氧含量，即使当具有不大于 5 或不大于 2 纳米的厚度时也是如此。石墨烯碳颗粒的氧含量可以使用 X 射线光电子能谱分析法（例如描述于 D. R. Dreyer 等人，Chem. Soc. Rev. 39，228-240(2010)）测定。

[0054] 在某些实施方式中，本发明的组合物中使用的石墨烯碳颗粒具有至少 50 平方米每克，例如 70-1000 平方米每克，或在某些情形下，200-1000 平方米每克或 200-400 平方米每克的 B. E. T. 比表面积。本文所使用的术语“B. E. T. 比表面积”是指基于描述于期刊“The Journal of the American Chemical Society”，60，309(1938) 的 Brunauer-Emmett-Teller 方法根据 ASTMD 3663-78 标准通过氮气吸附测定的比表面积。

[0055] 在某些实施方式中，本发明的组合物中使用的石墨烯碳颗粒具有至少 1.1（例如至少 1.2 或 1.3）的拉曼光谱 2D/G 峰比。本文所使用的术语“2D/G 峰比”是指在 2692cm^{-1} 的 2D 峰的强度与在 1，580cm^{-1} 的 G 峰的强度的比。

[0056] 在某些实施方式中，本发明的组合物中使用的石墨烯碳颗粒具有相对较低的堆密度。例如，在本发明的组合物的某些实施方式中使用的石墨烯碳颗粒的特征在于具有小于 0.2g/cm^3，例如不大于 0.1g/cm^3 的堆密度（振实密度）。为了本发明的目的，通过将 0.4 克石墨烯碳颗粒置于具有可视刻度的玻璃量筒中测定石墨烯碳颗粒的堆密度。该量筒被提高大约一英寸且振实 100 次，通过在硬的表面上敲击量筒的底部，以使石墨烯碳颗粒在量筒内沉降。然后测量颗粒的体积，且通过将 0.4 克除以测得的体积计算出堆密度，其中所述堆密度以 g/cm^3 表述。

[0057] 在某些实施方式中，本发明的组合物中使用的石墨烯碳颗粒具有比石墨粉和某些类型的基本上平的石墨烯碳颗粒的压缩密度和百分比致密化小的压缩密度和百分比致密化。较低的压缩密度和较低的百分比致密化目前均被认为有助于比表现出较高的压缩密度和较高的百分比致密化的石墨烯碳颗粒更好的分散和 / 或流变性能。在某些实施方式中，石墨烯碳颗粒的压缩密度为 0.9 或更小，例如小于 0.8、小于 0.7，例如 0.6-0.7。在某些实施方式中，石墨烯碳颗粒的百分比致密化为小于 40%，例如小于 30%，例如 25-30%。

[0058] 为了本发明的目的，从给定质量的压缩后的颗粒测得的厚度计算出石墨烯碳颗粒的压缩密度。具体地，通过使 0.1 克石墨烯碳颗粒在 1.3 厘米的冲模中在 15，000 磅的力下经受冷压，持续 45 分钟（接触压力＝ 500MPa[兆帕] 压力）确定测得的厚度。然后根据以下公式从该测得的厚度计算出石墨烯碳颗粒的压缩密度：

[0059] 压缩密度 (g/cm^3) ＝ 0.1 克

[0060] $\Pi*(1.3cm/2)^2*$（以 cm 计的测得的厚度）

[0061] 然后，石墨烯碳颗粒的百分比致密化被确定为计算出的石墨烯碳颗粒的压缩密度（如上述测定的）与石墨的密度 2.2g/cm^3 的比。

[0062] 在某些实施方式中，紧接着混合之后和在较后的时间点，例如在 10 分钟、或 20 分钟、或 30 分钟、或 40 分钟，石墨烯碳颗粒具有至少 100 微西门子，例如至少 120 微西门子、

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例如至少 140 微西门子的测得的体积液体电导率。为了本发明的目的，如下测定石墨烯碳颗粒的体积液体电导率。首先，使用缸式超声波仪 (bath sonicator) 对包含在丁基溶纤剂中的 0.5％石墨烯碳颗粒的溶液的样品施加超声 30 分钟。超声处理之后，立即将样品置于经校准的标准电导池 (K = 1)。将 Fisher Scientific AB 30 电导率计引入至样品以测量样品的电导率。在约 40 分钟的期间绘制电导率。

[0063] 根据某些实施方式，在导电石墨烯碳颗粒之间发生定义为长程互联性的渗滤。这种渗滤可降低涂料组合物的电阻率。导电石墨烯颗粒可占据涂层内的最小体积以使得颗粒形成了连续，或接近连续的网络。在这种情形下，石墨烯碳颗粒的纵横比可影响渗滤所需的最小体积。此外，石墨烯碳颗粒的表面能可以相同或类似于弹性体橡胶的表面能。否则，当它们被加工时，颗粒可倾向于絮凝或分开。

[0064] 可以通过例如热加工制造本发明的组合物中使用的石墨烯碳颗粒。根据本发明的实施方式，由在热区被加热至高温的含碳前体材料生产石墨烯碳颗粒。例如，可以通过公开于美国专利申请序列号 13/249,315 和 13/309,894 中的体系和方法生产石墨烯碳颗粒。

[0065] 在某些实施方式中，可通过使用描述于美国专利申请序列号 13/249,315 中第 [0022]-[0048] 段的设备和方法制备石墨烯碳颗粒，引述的部分通过引用并入本文，其中 (i) 将能够形成两－碳段物质（例如正丙醇、乙烷、乙烯、乙炔、氯乙烯、1,2-二氯乙烷、烯丙醇、丙醛、和／或溴乙烯）的一种或多种烃前体材料引入至热区（例如等离子体）；和 (i i) 在热区中将烃加热到至少 1,000℃的温度以形成石墨烯碳颗粒。此外，可通过使用描述于美国专利申请序列号 13/309,894 中第 [0015]-[0042] 段的设备和方法制备石墨烯碳颗粒，引述的部分通过引用并入本文，其中 (i) 将甲烷前体材料（例如包含至少 50％的甲烷，或在某些情形下，至少 95 或 99％纯度或更高的气态或液态甲烷的材料）引入至热区（例如等离子体）；和 (ii) 在热区中加热甲烷前体以形成石墨烯碳颗粒。这种方法可以生产具有至少一些，在某些情形下具有所有上述特性的石墨烯碳颗粒。

[0066] 在通过上述方法生产石墨烯碳颗粒的期间，提供含碳前体作为可与惰性载气接触的进料材料。可在热区（例如，通过等离子体体系）中加热所述含碳前体材料。在某些实施方式中，将前体材料加热至 1,000℃ -20,000℃，例如 1,200℃ -10,000℃的温度。例如，热区的温度可以为 1,500-8,000℃，例如 2,000-5,000℃。尽管可通过等离子体体系产生热区，但是应理解可以使用任何其它合适的加热体系形成热区，例如各种类型的炉子，包括电加热的管式炉等。

[0067] 可以将气态料流与一种或多种骤冷料流接触，所述骤冷料流通过至少一种骤冷料流注射口被注射进等离子体腔室。所述骤冷料流可以冷却气态料流以促使石墨烯碳颗粒的形成或控制石墨烯碳颗粒的颗粒尺寸或形态。在本发明的某些实施方式中，在将气态产物料流与骤冷料流接触后，超细颗粒可以穿过会聚部件。在所述石墨烯碳颗粒离开等离子体系后，可以将它们收集。任何合适的装置（例如，袋式过滤器、旋风分离器或沉积于基材上）可别用于从气体流中分离石墨烯碳颗粒。

[0068] 不受任何理论的限制，现据信前述生产石墨烯碳颗粒的方法特别适用于生产如上所述的具有相对较低的厚度和相对较高的纵横比和相对较低的氧含量的石墨烯碳颗粒。此外，现据信这种方法可生产大量的具有基本上弯曲、卷曲、褶皱、或搭扣的形态（本文中称作“3D”形态）的石墨烯碳颗粒，而不是生产主要具有基本上二维（或平的）形态的颗粒。

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该特性据信反映于前述的压缩密度特性且据信在本发明的密封剂组合物应用中是有益的，现据信，当石墨烯碳颗粒的大部分具有 3D 形态时，可促使在组合物内石墨烯碳颗粒之间的“边缘对边缘”和“边缘对面”的接触。这被认为是由于与具有二维形态的颗粒相比，具有 3D 形态的颗粒更不可能在组合物中团聚（由于较低的范德华力）。此外，现据信甚至在具有 3D 形态的颗粒之间“面对面”接触的情形下，由于颗粒可具有多于一个面平面，整个颗粒表面没有参与与另一单一颗粒的单一“面对面”的相互作用，但可参与与其它颗粒的相互作用，包括在其它平面的其它“面对面”的相互作用。因此，具有 3D 形态的石墨烯碳颗粒现被认为提供本发明组合物中的最好的导电通路且现被认为可用于获得本发明所需的电导率特性，特别当石墨烯碳颗粒以以下描述的相对较低的量存在于组合物中时。

[0069] 图 2 示意性地说明了根据本发明的实施方式将涂料组合物施涂于板材之上的辊涂方法。在显示的实施方式中，涂覆操作可在常规的辊轧机中进行。金属板材（例如镀锌钢材等）在反向转动的涂布辊 20 和 22 之下经过的长带 5 上提供，所述涂布辊由涂料组合物 24 的供应来进料。未经涂覆的带 5 在涂布辊 20 和 22 之下经过，在那里涂料组合物 24 的层沉积于板材的上表面。经涂覆的板材 10 可形成用于储存和运输的卷材 26 以用于各种应用，例如镀锌钢材屋顶板材。

[0070] 在辊涂工艺期间，将涂料组合物典型地施涂于板材 5，且具有至少 1 微米，典型地至少 1 或 5 微米的湿膜厚度。在某些实施方式中，涂层材料的湿膜厚度为 5 至 15 或 20 微米。在某些实施方式中，涂料组合物的沉积率可以是至少 200ft/min，典型地至少 300ft/min 或 350ft/min。

[0071] 在施涂之后，涂料组合物典型地快速地干燥和固化，伴随着极少的 VOC 释放。固化时间典型地为少于 1 分钟，例如，少于 10 或 5 秒。典型的固化温度低于 300 °F，例如，低于 275° 或 250 °F。在某些实施方式中，固化时间在 225 °F 或 200 °F 的温度可以少于 3 或 2 秒，或更少。

[0072] 固化的涂层的干膜厚度典型地为至少 1 微米到至多 15 或 20 微米。例如，干膜厚度可以是 5-10 微米。根据本发明，已发现这种相对较薄的涂布层可显著地增加金属屋顶板材的日光反射指数。

[0073] 以下的实施例说明了本发明各种方面，但并不旨在限制本发明的范围。

实施例

[0074] 如下表 1-4 所述制备和测试涂料组合物。

[0075] 表 1

[0076] 涂料组合物 1-3 号

[0077]

组分	样品号 1	样品号 2	样品号 3
丙烯酸类胶乳树脂	198.10	199.18	165.41
去离子水	15.23	17.84	85.30

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消泡剂	0.48	0.48	0.51
Surfynol 表面活性剂	1.04	1.04	1.06
表面活性剂	1.04	1.04	1.06
聚结剂	10.01	10.01	10.15
铬染料剂	5.98	-	5.98
白色染料剂	-	-	154.63
防锈剂	2.41	2.43	2.46
增稠剂	3.55	3.55	5.36
去离子水	3.55	3.55	0.54
pH 控制剂	0.53	0.53	0.54
去离子水	0.53	0.53	0.54
蜡	3.64	3.64	10.52
以克计的总重量	246.09	243.82	444.06

[0078] 表 2

[0079] 涂料组合物 4 号

[0080]

组分	样品号 4
胶乳树脂	201.14
UC 中间体 [1]	22.27
去离子水	3.70
消泡剂	0.13
防锈剂颜料	8.05
表面活性剂	0.24
二氧化硅	1.08
去离子水	0.10

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以克计的总重量	236.62

[0081] [1]丙烯酸类乳液 Joncryl538(98.88)；消泡剂 (0.74)；去离子水 (5.0)；二氧化硅 (25.11)；腐蚀颜料 (49.78)；反射颜料 (25.11)；和消泡剂 (0.26)。

[0082] 将列于上表 1 和 2 中的组分在温和的搅拌下依各表中描述的顺序添加在一起。使涂料组合物平衡过夜，之后进行板的制备。第二天检测粘度和 pH。使用涂覆 (drawdown) 绕线棒将涂料组合物施涂于镀锌钢材基材。将经涂覆的板置于链条式平炉中，该链条式平炉设置于在两秒停留时间（线速）内获得 190 °F 的峰值金属温度的温度。测试了经涂覆的板，其结果显示于下表 3 中。

[0083] 表 3

[0084] 实验结果

[0085]

	样品号 1	样品号 2	样品号 3	样品号 4
% 重量固体	41.82	41.62	45.0	44.03
粘度（秒）（在室温下使用 4 号蔡氏杯测量）	10-15	10-15	12-20	9-25
干燥厚度	0.15-0.20（密尔） 3.8-5.1（微米）	0.15-0.20（密尔） 3.8-5.1（微米）	0.4-0.5（密尔） 10.2-12.7（微米）	0.15-0.25（密尔） 3.8-6.4（微米）
铅笔硬度	HB-F	HB-F	HB-F	B
T 型弯曲	1/3np/nc	1/3np/nc	1/3np/nc	1/3np/nc
反向冲击	通过	通过	通过	通过
交叉线腐蚀	通过	通过	通过	通过
巴特勒浸没	没有腐蚀	没有腐蚀	没有腐蚀	腐蚀-失败
盐雾	无黑点	无黑点	无黑点	腐蚀-失败
湿烟囱	无压力斑迹	无压力斑迹	无压力斑迹	压力斑迹，黑点
TSR(%)	66.8	65	70.7	66.8
TE(%)	54	58	78	54
SRI	71	69	84	71

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[0086] 根据铅笔硬度测试 ASTM D3363，使铅笔以 45 度的角度牢固抵靠涂层并且将该铅笔以 0.25 英寸的行程从操作者推离。向下和向前施加足够的压力以切割或刮擦膜。以递减的硬度范围重复该过程直到发现铅笔不能切入膜以达到基材。硬度的范围 :6B（非常软）到 6H（非常硬）。

[0087] 根据巴特勒浸没测试 ASTM D870，将带有切边的板置于一满杯自来水中，并且将其在湿度箱 100F/100％湿度中放置 1000 小时。然后，将板从水中取出，并且目视评估任何红色或白色的锈、黑点和 / 或板的表面或边缘的鼓泡。

[0088] 根据盐雾测试 ASTMB117，将板与用胶带粘住的切边在 95F/5％ NaCl 溶液箱中放置 1000 小时。然后，该板从箱中取出并且目视评估任何红色或白色的锈、黑点和板表面的鼓泡缺陷。

[0089] 根据湿堆叠测试，ASTM D7376-10A，用去离子水对板进行喷雾，将它们面对面地堆叠，并且夹在一起成束，以模拟被卷绕的卷材。然后将各束在 100F/100％湿度箱中放置 1000 小时。然后取出各束并且目视评估暗斑或白斑（压力斑迹）。

[0090] 在各种干膜厚度 (DFT) 下测试由类似于上述的样品 1 和 2 号的组合物涂覆的镀锌钢板的 TSR、TE 和 SRI 性质。结果显示于图 3、4 和 5 的曲线中。

[0091] 在各种干膜厚度 (DFT) 下测试由类似于上述的样品 1 和 2 号的组合物涂覆的镀锌钢板（但是基于所述涂料组合物的总重量计以 5 重量％的量添加了以名称 SolarFlair 得自 Eckart 的干涉颜料）的 TSR、TE 和 SRI 性质。结果显示于图 6、7 和 8 中的曲线。

[0092] 以 1 重量％的量将不同类型的石墨烯碳添加至类似于上述样品 1 号的涂料组合物中。样品 5 号包含根据美国专利申请序列号 13/309,894 生产的石墨烯碳颗粒。样品 6 号包括以名称 N-006-010-P 出售的来自 Angstron 的石墨烯碳颗粒。样品 7 号包含以名称 X-GNP-M-25 出售的来自 XG Sciences 的石墨烯碳颗粒。通过以 5 微米的膜厚度涂覆 (drawdown) 镀锌钢材基材来制备该板。然后使用输送履带式烘箱将该板在 190 ℉ 的峰值金属温度固化 2 秒。测试该板，且结果显示于下表 4 中。

[0093] 表 4

[0094] 实验结果

[0095]

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样品号	% 石墨烯	石墨烯类型	直径（微米）	厚度 (nm)	SRV	TE	SRI	盐雾-1000h
1	0%	NA	NA	NA	66.3	0.55	70	极好的
5	1%	石墨烯碳颗粒			59.7	0.54	59	非常少的鼓泡
6	1%	商购的 N-006-010-P 石墨烯碳	<14	10-20	42.2	0.72	41	极好的
7	1%	商购的 X-GNP-M-25 石墨烯碳	25	6	59.5	0.56	60	密集的鼓泡

[0096] 为了该详细说明的目的，除了在有相反的说明的情况下之外，应理解由本公开内容提供的实施方式可假设各种备选的变化形式和步骤顺序。此外，除了在任意实施例中、或在另有说明的情况下，否则用于表达例如在说明书和权利要求书中使用的成分的量的全部数值应理解为在所有情况下被术语“约”修饰。因此，除非有相反的说明，否则在下面的说明书和所附权利要求书中给出的数值参数是可取决于本发明所获得的期望的性能来变化的约数。最起码，并且不试图限制对权利要求的范围适用等同原则，各数值参数应该至少按照报道的有效数字的数值并采用普通的舍入技术来解释。

[0097] 尽管设定本发明的宽范围的数值范围和参数是约数，但是在具体实施例中给出的数值是尽量精确地报导的。然而，任何数值本身含有必然地从在它们各自试验测量中存在的标准偏差产生的必然的误差。

[0098] 同样地，应理解本文所引述的任何数值范围都意图包含含在其中的所有子范围。例如，范围“1-10”意图包括所引述的最小值 1 和所引述的最大值 10 之间（并且包括 1 和 10）的所有子范围，即，具有等于或者大于 1 的最小值和等于或者小于 10 的最大值。

[0099] 在本申请中，除非另有说明，单数的使用包括复数，且复数包括单数。此外，在本申请中，“或”的使用是指“和 / 或”，但是“和 / 或”在某些情况下可以是明确使用的。

[0100] 本领域技术人员将容易地领会本发明可在没有背离前述说明书公开的概念的情况下作出改变。除非权利要求以它们的语言另有明确的说明，应认为这种改变包括在以下的权利要求范围内。因此，本文具体描述的特定实施方式仅仅是示例性的并且不限制本发明的范围，本发明被给与所附权利要求以及它们的任意和所有的等价体的完全的范围。

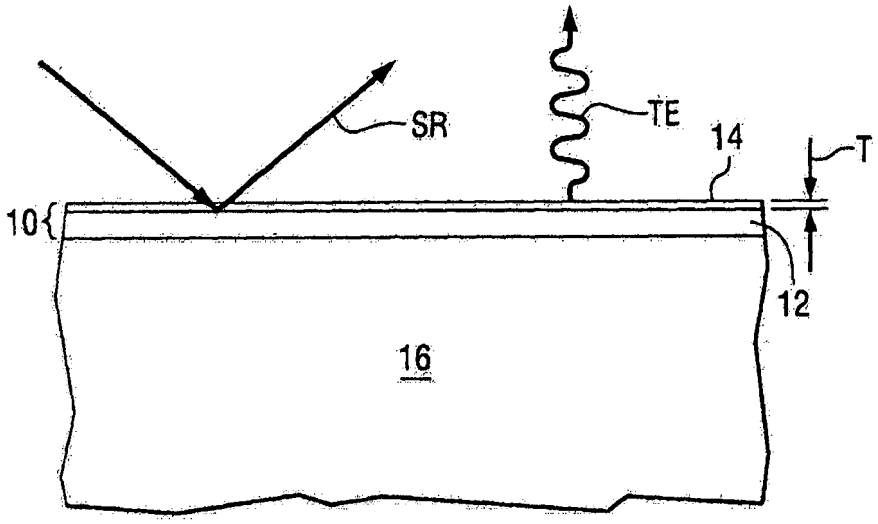


图 1

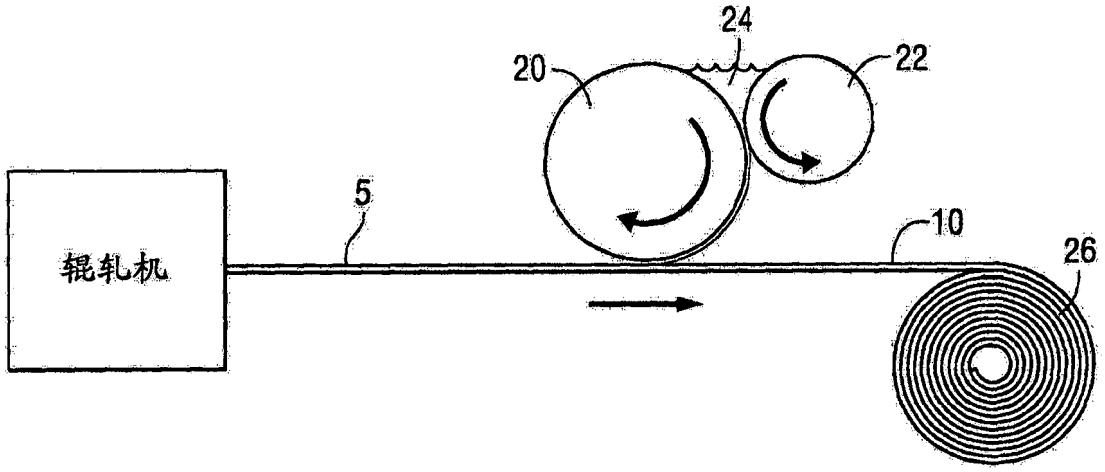


图 2

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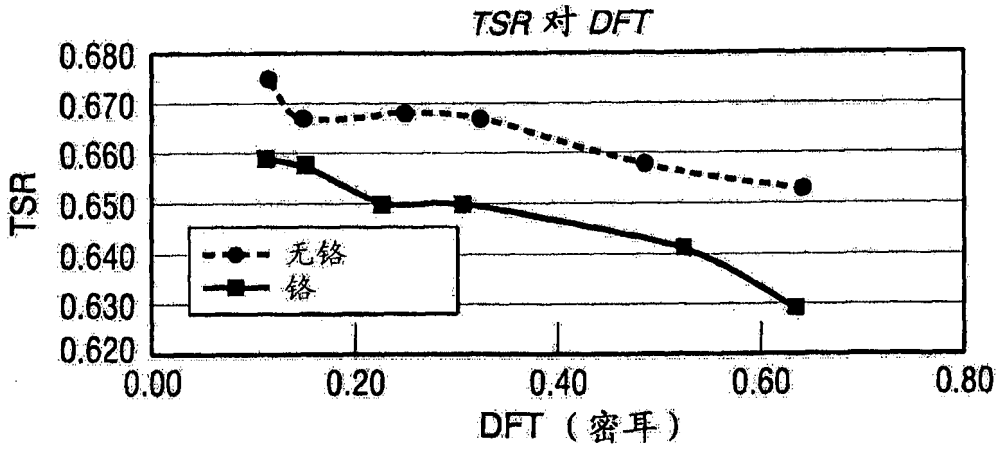


图 3

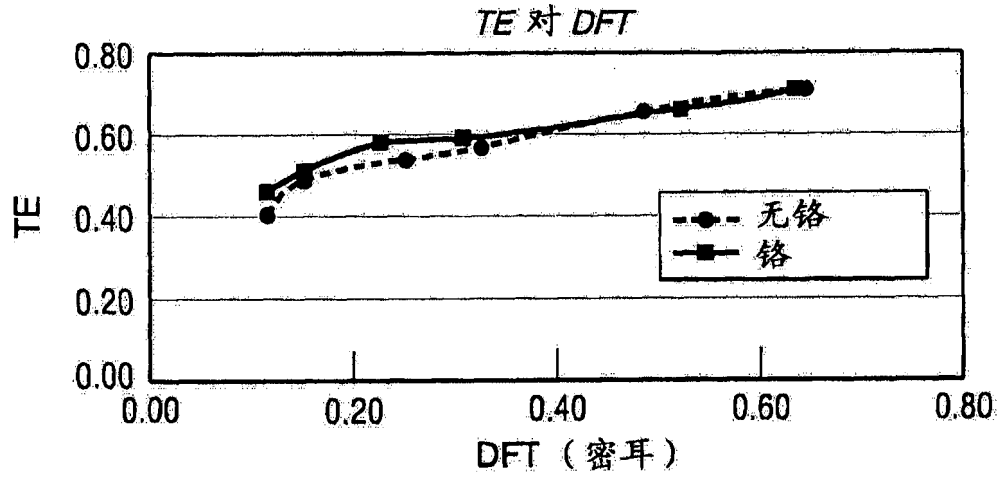


图 4

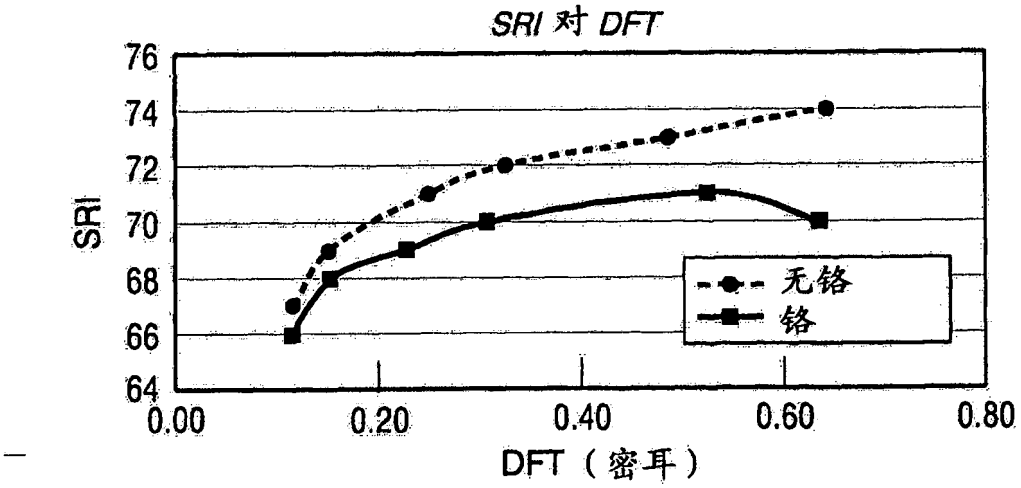

SRI 对 DFT
SRI
76
74
72
70
68
66
64
0.00
0.20
0.40
0.60
0.80
DFT（密耳）
无铬
铬

图 5

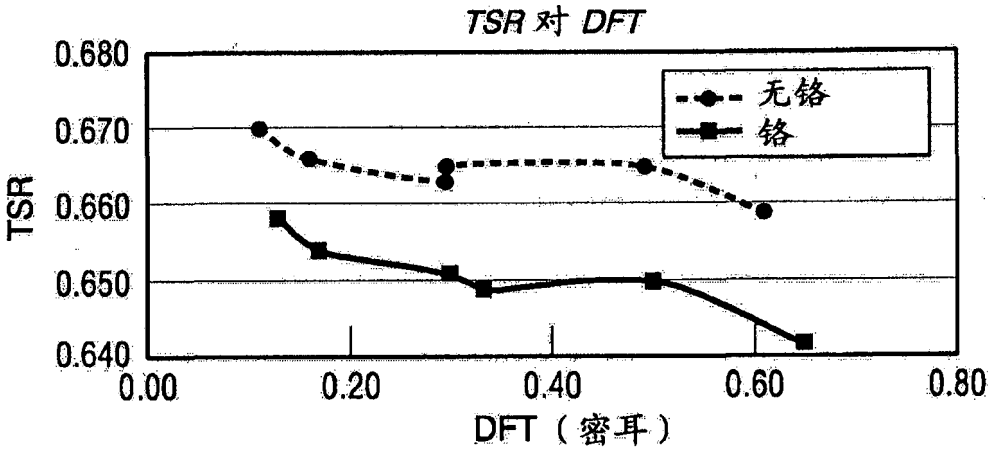

TSR 对 DFT
TSR
0.680
0.670
0.660
0.650
0.640
0.00
0.20
0.40
0.60
0.80
DFT（密耳）
无铬
铬

图 6

打印ID7583181 Pg 19

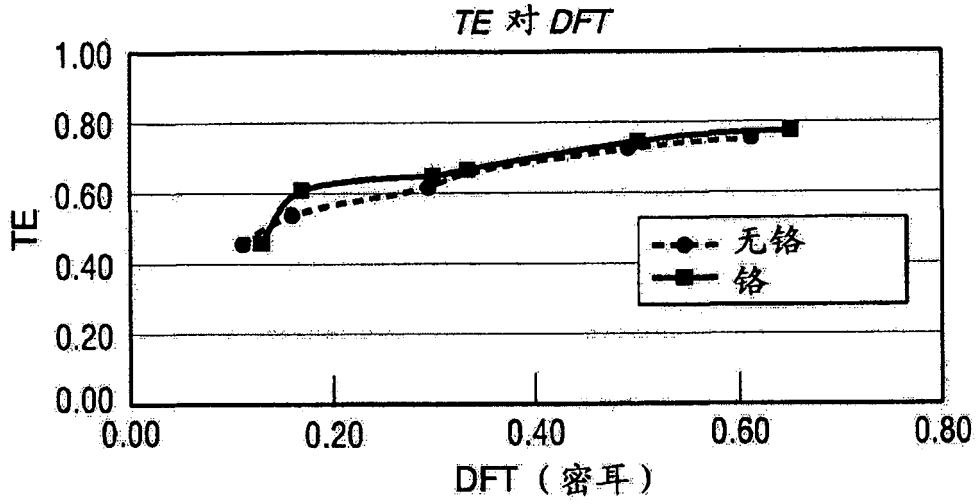


图 7

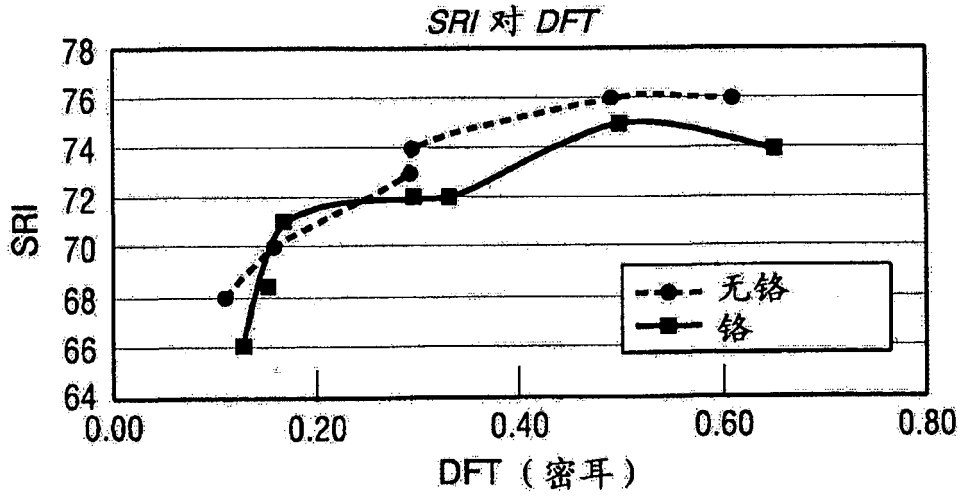


图 8