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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 December 2013 (27.12.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/192180 A2

(51) International Patent Classification:
C09D 5/33 (2006.01)

(21) International Application Number:
PCT/US2013/046324

(22) International Filing Date:
18 June 2013 (18.06.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/661,532 19 June 2012 (19.06.2012) US
13/786,516 6 March 2013 (06.03.2013) US

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

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

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:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

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

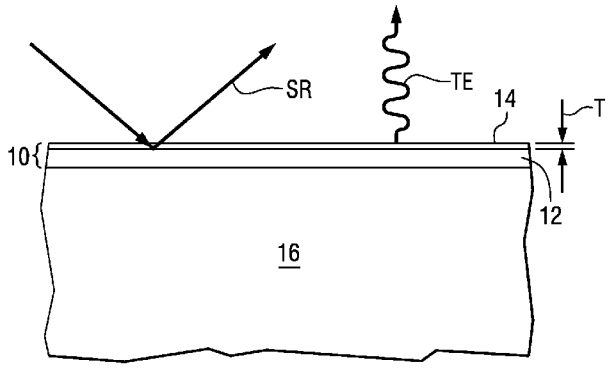


FIG. 1

(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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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.

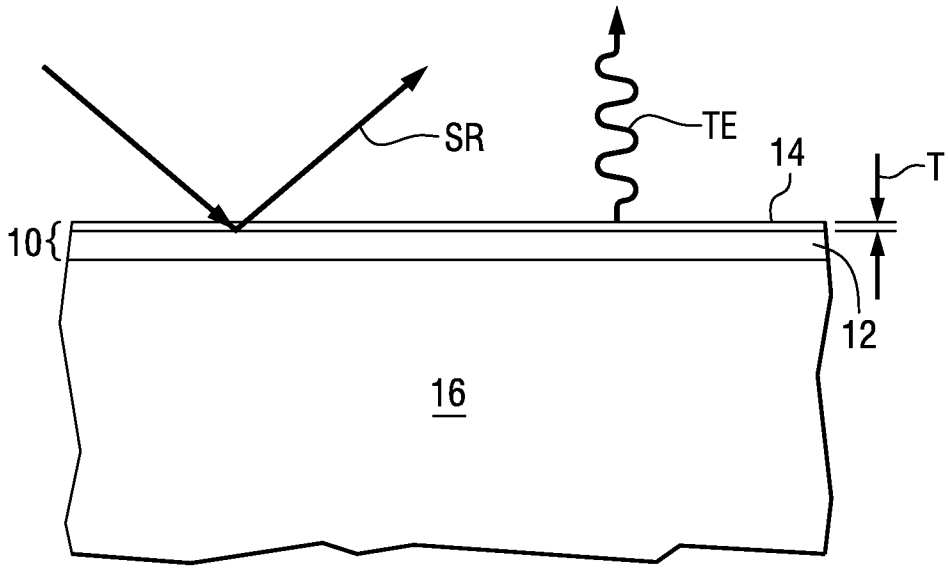


FIG. 1

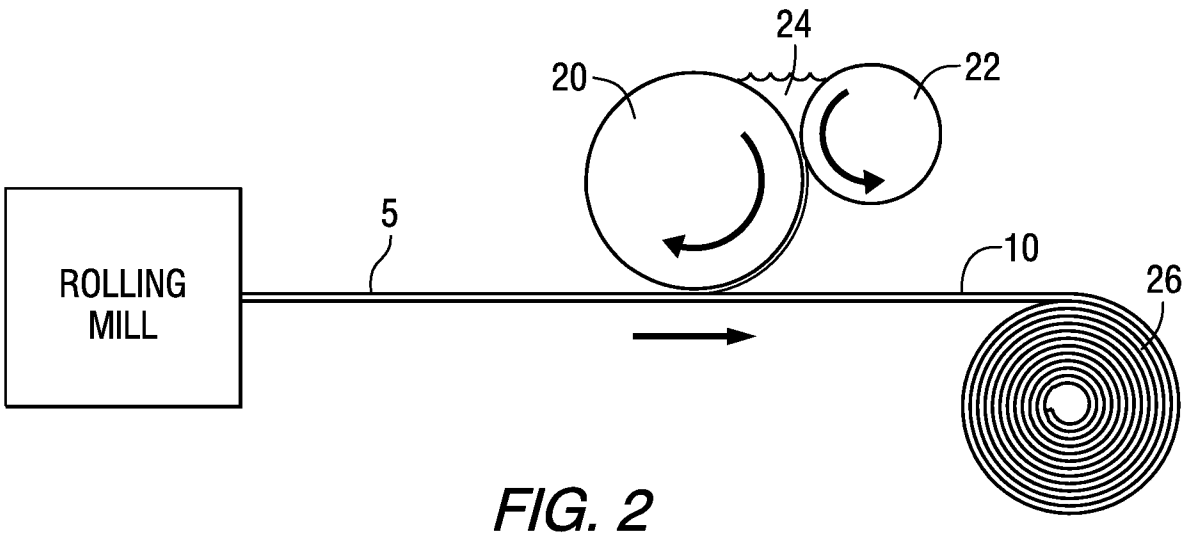


FIG. 2

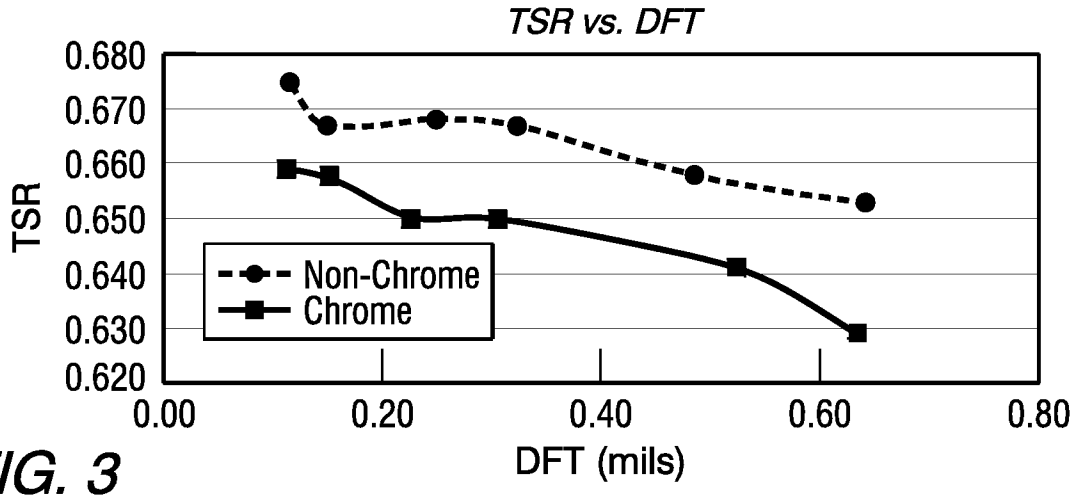


FIG. 3

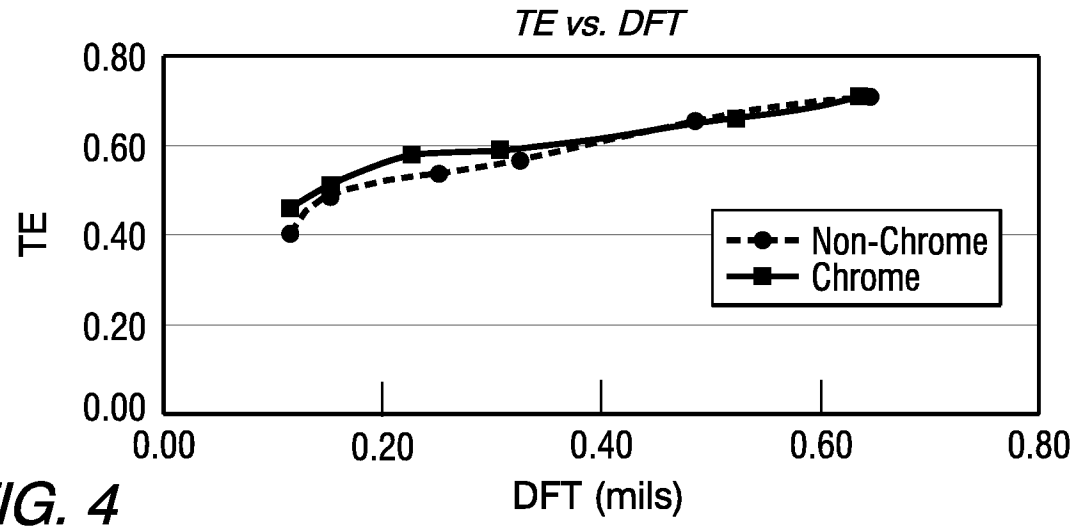


FIG. 4

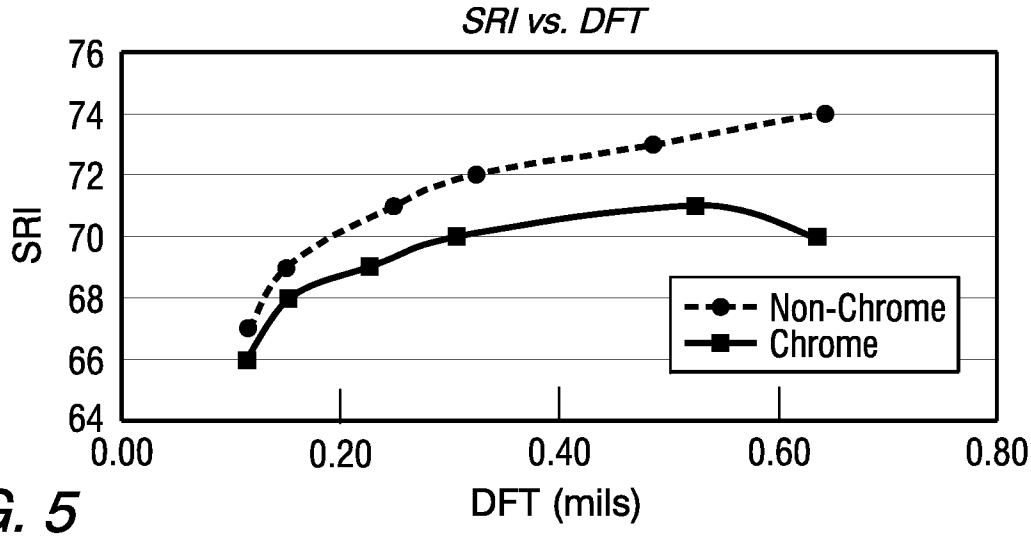


FIG. 5

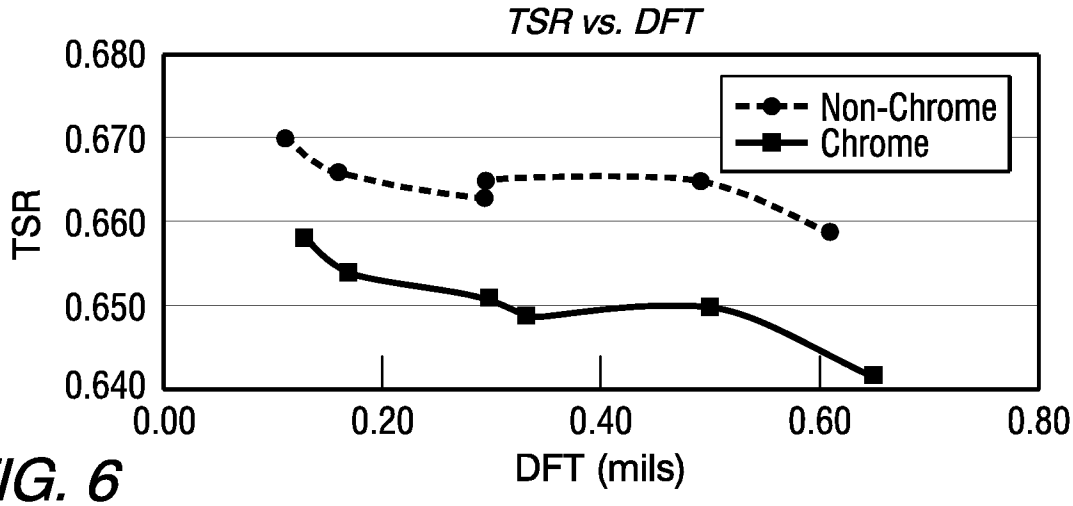


FIG. 6

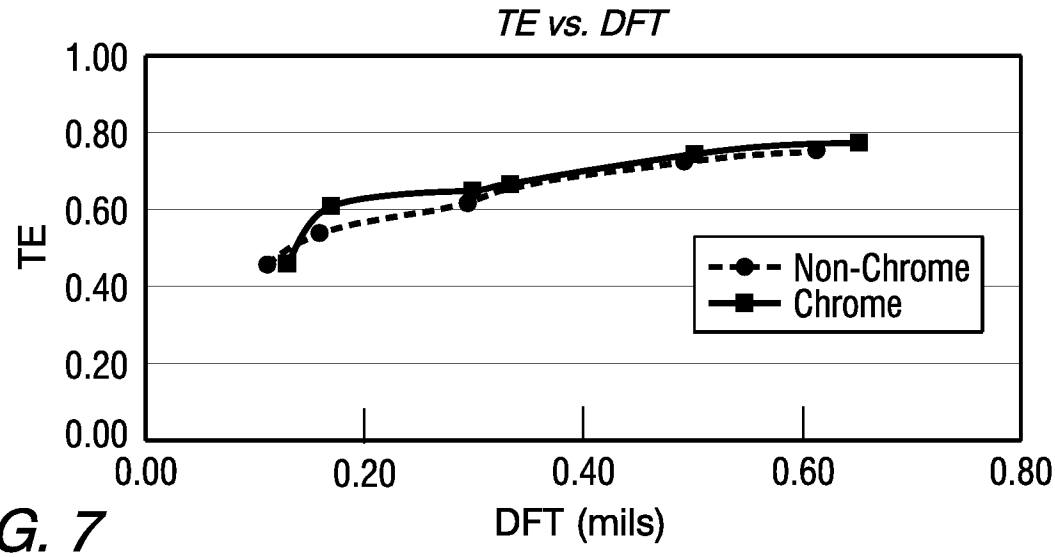


FIG. 7

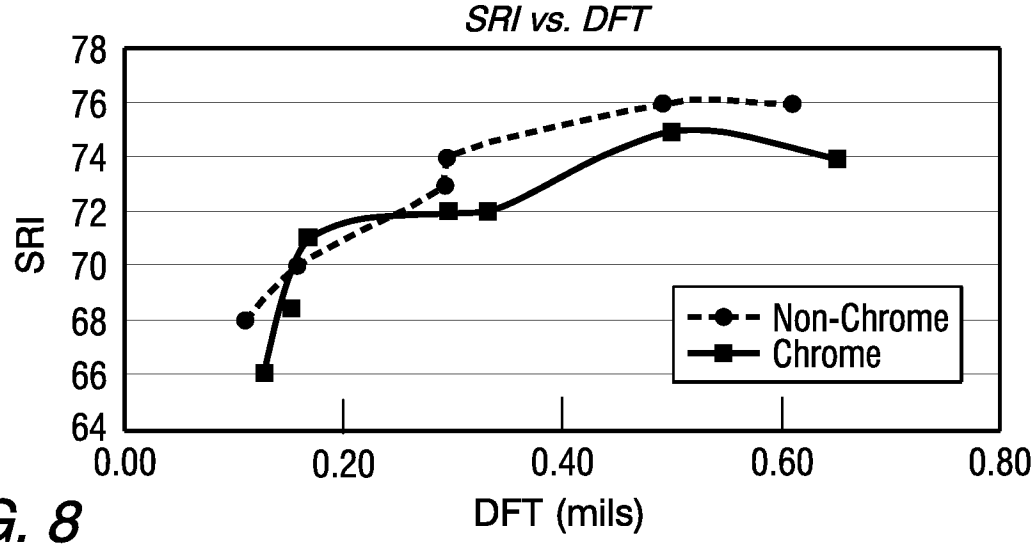


FIG. 8