US 20140193647A1

(19) **United States**

(12) **Patent Application Publication**

Hormadaly

(10) **Pub. No.: US 2014/0193647 A1**

(43) **Pub. Date: Jul. 10, 2014**

(54) **COATINGS FOR SOLAR APPLICATIONS**

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(21) Appl. No.: **14/006,142**

(22) PCT Filed: **Mar. 25, 2012**

(86) PCT No.: **PCT/IL2012/000130**

§ 371 (c)(1),
(2), (4) Date: **Feb. 25, 2014**

Related U.S. Application Data

(60) Provisional application No. 61/466,998, filed on Mar. 24, 2011.

Publication Classification

(51) **Int. Cl.**
F24J 2/48 (2006.01)

(52) **U.S. Cl.**
CPC ***F24J 2/485*** (2013.01)
USPC **428/433**; 428/426; 252/582; 427/372.2; 427/383.7

(57) **ABSTRACT**

The present invention discloses coating compositions comprising: I) at least one highly absorbing material selected from the group consisting of ruthenium, iridium and osmium compounds, and mixtures thereof; II) an inorganic glass binder or a precursor thereof; III) a ceramic filler comprising metal oxides, metal powders and mixtures thereof; and V) a liquid organic vehicle. The invention further discloses methods for preparing these coatings and uses thereof in solar applications.

COATINGS FOR SOLAR APPLICATIONS

[0001] An ideal solar absorber is a coating with very high absorptance in the solar portion of the spectrum (UV, VIS and near IR), low emissivity at the working temperature, high chemical durability, good mechanical stability and low cost.

[0002] Most of the materials in use today have some drawbacks such as thermal degradation at high temperature, instability on exposure to UV radiation, oxidation, and some materials do not protect the steel pipes used in the solar collector from corrosion.

[0003] For solar tower applications and other applications which are based on absorption of the solar energy and its conversion to heat, there is a need for high temperature black material as solar absorber which is compatible with steel such as carbon steel, stainless steel and Inconel™. The solar absorber should also have high absorption in the solar portion of the spectrum (UV, VIS and near IR), exhibit stability at high temperatures (e.g. 400-700° C.), withstand thermal cycling between room temperature to temperatures in the range of 400-700° C. and be easily applied onto metal substrates.

[0004] Presently known solar absorbers are divided into mid- and high-temperature materials (Kennedy, C. E., 2002, *Review of Mid-to High-Temperature Solar Selective Absorber Materials*, NREL/TP-520-31267, Golden, Colo.: National Renewable Energy Laboratory). Earlier examples of solar energy applications were reported in U.S. Pat. No. 4,211,210.

[0005] Recent publications describe porcelain-enamel coatings consisting of spinel type black pigments embedded in borosilicate glass medium (H. J. Brown-Shaklee et al., Solar Energy Materials & Solar Cells 93 (2009) 1404-1410). Additional examples of solar absorbers include Tantalun carbide absorbers (Elisa et al, Journal of Renewable and Sustainable Energy (2011), 3(6), 063107, 6 pp.) and nitride absorbers (Lei et al. (Science China: Technological Sciences (2010), 53(6), 1507-1512) and spectrally selective TiAl/TiAlN/TiAlON/TiAlO coatings (Lei et al, Chinese Science Bulletin (2009), 54(8), 1451-1454).

[0006] However, all of these coatings suffer from instability (such as oxidation or degradation) at high temperatures and/or gradually loses the adhesion to the metallic substrate.

[0007] Thus, there is a long and felt need to provide novel compositions to be used as coatings for solar absorbers, such that these compositions would be devoid of the deficiencies described hereinabove, namely that they would be well adhered to the metal substrates and remain stable at high temperatures and during many thermal cycles.

[0008] The inventor has now successfully designed a novel composition that can be used as a coating of a solar absorber, and have successfully shown the application of this coating in solar applications.

[0009] Thus, according to one aspect of the present invention, there is provided a coating composition comprising:

[0010] I) at least one highly absorbing material selected from the group consisting of ruthenium, iridium and osmium compounds, and mixtures thereof;

[0011] II) an inorganic glass binder, or a precursor thereof;

[0012] III) a ceramic filler, comprising metal oxides, metal powders and mixtures thereof; and

[0013] IV) a liquid organic vehicle.

[0014] This composition can be formulated as a paste or paint, to be applied on a metal substrate, for example in a solar tower. Suitable metal substrate are made from a metal, such as steel, stainless steel, inconel type alloys and other alloys which can withstand high temperatures in the range of 600-800° C.

[0015] As noted above, the coating composition described herein contains a highly absorbing material selected from either a ruthenium compound, an iridium compound or an osmium compound, and mixtures thereof.

[0016] The term "highly absorbing material", as used herein, refers to a component of a ceramic coating which makes the coating to have high absorption (as inferred from reflectance) in 400-2500 nm spectral range (UV, VIS and near IR) of 90-98%.

[0017] Without being bound to a specific theory, these compounds or mixtures thereof act as the functional (absorbing) phase in the coating composition.

[0018] As noted above, the at least one highly absorbing material is selected from the group consisting of ruthenium, iridium and osmium compounds, and mixtures thereof.

[0019] Examples of suitable Ru, Ir and Os highly absorbing materials, which are useful for the present invention, include, but are not limited to, the following classes:

[0020] dioxides MO_2, wherein M=Ru, Ir, Os;

[0021] mixed oxides, such as spinels of Ru, Ir and Os such as Co_2RuO_4, $Co_{2+x}Ru_{1-x}O_4$ where x=0 to 0.5;

[0022] $Co_{2+x-y}M_yM'_{1-x}O_4$ where M=Ru, Ir, Os and M'=transition metals such as Cu, Zn, Fe, Mn, Cr and y=0 to 0.75;

[0023] pervoskites such as $M'MO_3$ where M'=Ca, Sr, Ba and M=Ru, Ir, Os;

[0024] mixed oxides such as Sr_2MO_4 where M=Ru, Ir, Os;

[0025] alkali ruthenates; pyrochlores and substituted pyrochlores of Ru, Ir, Os such as the compounds taught in U.S. Pat. No. 3,583,931 and U.S. Pat. No. 3,681,262 and those reported by Longo et al. (Materials Research Bulletin 4,191 (1969));

[0026] any precursor compound of Ru, Ir, Os which converts to an oxidized form of these metals upon firing, such as MO_2, $M'MO_3$ etc. where M=Ru, Ir, Os and M'=Ca, Sr, Ba, examples of such precursors are the chlorides of Ru, Ir and Os;

[0027] nitrites salts of Ru, Ir and Os; and

[0028] resinates of Ru, Ir and Os.

[0029] According to one preferred embodiment of the present invention, the highly absorbing material contains at least one Ru compound.

[0030] Examples of suitable Ru compounds, include, but are not limited to, RuO_2, $BaRuO_3$, pyrochlore-like Ru compounds, $CaRuO_3$, $SrRuO_3$, Sr_2RuO_4 and any mixtures thereof.

[0031] According to one preferred embodiment of the invention, the highly-absorbing material is selected from RuO_2, $BaRuO_3$, and pyrochlore-like Ru compounds.

[0032] The term "pyrochlore-like" refers to compounds have the same crystal structure as pyrochlore.

[0033] For example, the pyrochlore-like Ru compound can be $Nd_{1.75}Cu_{0.25}Ru_2O_{6+\delta}$, as exemplified below. In this case, the term $6+\delta$ indicates that in some cases the structure has 6 oxygen units, and in some it has 7 oxygen units.

[0034] The amount of the highly absorbing material in the afore-mentioned compositions ranges from 1 to 99.5% weight of the paste weight. Preferably the highly absorbing material concentration ranges from 5 to 50% weight of the

paste weight. More preferably the highly absorbing material concentration ranges from 7 to 30% weight, on a paste basis. It should be noted that additional black materials, having the same crystal structure as RuO_2, are also known to a person skilled in the art to have similar properties as RuO_2 and to therefore can be just as suitable for the purpose of the invention. Some exemplary compounds are hence IrO_2 and OsO_2 and other compounds of Ir and Os.

[0035] As noted above, the coating composition described herein further contains an inorganic glass binder or a precursor thereof.

[0036] This glass binder phase is preferably a multi-component inorganic glass.

[0037] The glass component of the coating composition of the invention may be any, glass which is compatible with the substrate and has the durability for use in such applications requiring many thermal cycles from room temperature to temperatures in the range of 300-800° C. or higher.

[0038] Examples of suitable glasses, include, but are not limited to, borosilicates of Na, K, Li, Ca, Sr, Mg, Ba, with or without transition metals oxides; Silicates of Na, K, Li, Ca, Sr, Mg, Ba, with or without transition metals oxides, and boroaluminosilicates of Na, K, Li, Ca, Sr, Mg, Ba, with or without transition metals oxides.

[0039] According to one preferred embodiment of the invention, the inorganic glass binder or the precursor thereof, is selected from borosilicates of Na, K, Li, Ca, Sr, Mg, Ba, with or without transition metals oxides.

[0040] Some suitable glasses useful for the invention are identified in the table below (in terms of the glass ingredients and their respective molar concentrations):

TABLE 1

Ingredients	Range in mole %	Preferred range in mole %
Na_2O	0.1-15.0	0.1-12.0
Li_2O	0-15.0	0-12.0
K_2O	0.1-15	0.1-12.0
ZnO	0-12.0	0-10.0
CaO	0-18.0	0-15.0
SrO	0-18.0	0-15.0
BaO	0.1-15.0	0.1-12.0
MgO	0-8.0	0-4.0
Al_2O_3	0.1-4.0	0.1-4.0
B_2O_3	0.1-15.0	0.1-10.0
SiO_2	40.0-65.0	40.0-65.0
TiO_2	0.1-8.0	0.1-8.0
ZrO_2	0-5.0	0-3.0
Bi_2O_3	0-5.0	0-4.0
*TM (oxides)	0-20.0	0-18.0

*TM (oxides) = CuO, CoO, Cr_2O_3, Fe_2O_3, MnO_x (various oxides of manganese), V_2O_5.

[0041] It should be noted that one or more of the alkali oxides within the glass composition, as indicated in Table 1, may be substituted by the corresponding fluorides, for example, NaF may be a substitute for Na_2O, LiF may be a substitute for Li_2O and KF may be a substitute for K_2O. Thus, the term "metal oxides", as used herein also includes the corresponding metal fluorides.

[0042] Alternatively, the binder phase of the composition can also be also provided by a precursor of silicon dioxide, which can yield silicon dioxide upon heat treatment. A suitable SiO_2 precursor can be any silicone resin which can be formulated to a paint consistency when combined with the compounds of Ru, Ir, Os, their mixtures and solvents. Examples of silicon resins are polydimethylsiloxanes, polymethydro-dimethylsiloxane copolymer, vinyl terminated silicone polymers and vinyl backbone silicone polymers.

[0043] The amount of the inorganic glass binder in the afore-mentioned compositions ranges from 5 to 80% weight of the paste weight. Preferably the glass binder concentration ranges from 10 to 60% weight of the paste weight. More preferably the glass binder concentration ranges from 15 to 55% weight of the paste weight.

[0044] The composition of the present invention also includes a ceramic filler, comprising metal oxides, metal powders and mixtures thereof.

[0045] The term "ceramic coating" usually refers to an inorganic, essentially non-metallic protective coating, on metal suitable for use at or above red heat. However, the term ceramics both with regard to a ceramic filler, and the cured coating of this invention, includes all engineering materials or products that are chemically inorganic, except metals and metal alloys, and also includes composites, such as ceramic-metal combinations and other combinations of ceramic fillers involving organic materials.

[0046] The ceramic fillers are, for example, selected from among oxides of groups IVB and VB of the periodic table and transition metal oxides, especially oxides of ZrO_2, Nb_2O_5 and Co_3O_4.

[0047] Without being bound to any specific theory, it appears that the one or more oxides of groups IVB and VB of the periodic table present in the composition function as nucleating agents, expansion modifiers which, when dissolved in the glass, enhance its durability. Thus, the transition metal oxide, e.g., Co_3O_4, functions as an absorber and also enhances the binding of the glass and the ceramic to the metallic substrates.

[0048] The weight of these ceramic fillers is preferably not higher than 30% of the total weight of solids dispersed in the organic medium. Preferably, the ceramic filler concentration ranges from 0.1 wt % to 30 wt % of the total weight of solids dispersed in the organic medium.

[0049] As noted hereinabove, the ceramic filler may also include metals or metal powders.

[0050] Suitable metals or metal powders to be used as part of the present invention are those metals which have a low emissivity, and also must not oxidize at high temperatures, thereby limiting the choice of appropriate metals to the precious metals only.

[0051] Some examples of suitable metal powders include, but are not limited to, Ag powder, Pd powder and their mixtures. Other metals which can be used are Au and Pt but they are more expensive.

[0052] As can be seen in the Examples section which follows, the ceramic filler is preferably a combination of silver and/or and any of the oxides provided hereinabove.

[0053] The amount of this ceramic filler ranges from 0.1 wt %-30 wt % of the total weight of solids dispersed in the organic medium.

[0054] As noted hereinabove, the compositions of the invention further comprise a liquid organic vehicle. However, in principle any inert liquids can be used.

[0055] Organic liquid vehicles can be used with or without thickening and/or stabilizing agents and/or other common additives.

[0056] Suitable organic liquids are aliphatic alcohols or esters thereof, terpens such as pine oil, terpineol and the like, solutions of resins such as the polymethylacrylates of lower alcohols and solutions of ethyl cellulose in solvents such as

pine oil and the monobutyl ether of ethylene glycol monoacetate. Preferred liquid organic vehicles are ethyl cellulose solutions in terpineol and butyl ethers of ethylene glycol.

[0057] As can be seen in the Examples which follow, the liquid organic vehicle is often a combination of several liquid vehicles. One such combination, which is advantageous in its clean burning pattern, is the combination of ethyl cellulose, terpineol and dibutylcarbitol. However, other suitable carriers and/or combinations of carriers may be used, as known to any person skilled in the art.

[0058] The amount of the liquid organic vehicle ranges from 10-50 wt %. Preferably, it ranges from 15% weight to 40% weight of the total weight of the composition.

[0059] Some preferred coating compositions of the invention comprise (in Wt % after firing): from 1 to 99.5 RuO_2;
from 5 to 80 glass particles [composed of SiO_2 (40.0-65.0 mole %), B_2O_3 (0.1-15.0 mole %), Al_2O_3 (0.1-4.0 mole %), TiO_2 (0.1-8.0 mole %), K_2O (0.1-15.0 mole %), Na_2O (0.1-15.0 mole %), and BaO (0.1-15.0 mole %)];

[0060] The amounts of the liquid organic vehicle and of the ceramic filler, are as described hereinabove.

[0061] Thus, according to one preferred embodiment of the invention, there is provided a composition comprising from 1 to 99.5% weight RuO_2, from 5 to 80% weight glass particles, from 0.1% weight to 30% weight of the ceramic filler and from 10% weight to 50% weight of the liquid organic vehicle.

[0062] The chosen ceramic filler in many of the examples contains
from 0.1 to 12.0 Co_3O_4;
from 0.1 to 12.0 Nb_2O_5; and
from 0 to 12.0 ZrO_2.

[0063] In some preferred embodiments, the ceramic filler optionally further contains up to 20% silver powder.

[0064] The compositions of the invention are prepared by combining together at least one of the Ru, Ir, Os compounds, the glass binder component, one or more ceramic fillers comprising oxides of group IVB & VB of the periodic table, or transition metal oxides and/or metal powder(s), and an organic vehicle.

[0065] The amount and type of the organic vehicle can be adjusted to determine the consistency of the composition, thereby obtaining the specific properties of a coating composition in the form of paste or paint. The working examples below illustrate the preparation of several useful paste or paint compositions.

[0066] Thus, according to another aspect of the present invention there is provided a highly absorbing paste. The paste comprises at least one of the Ru, Ir, Os compounds, finely divided glass particles as described hereinabove, dispersed in an organic medium or vehicle, together with additional solids (metal oxides and metal(s) powders) selected according to the intended use of the formulation. The solids dispersed in the organic medium contain from about 0.5 to 80% glass particles, from about 1 to 99.5% particles of the highly absorbing materials, such as the compounds of Ru, Ir and Os, and from about 0.1% to 30.0% of a ceramic filler.

[0067] In addition, the composition of the invention can be formulated into a paint, for example, by the addition of suitable solvents.

[0068] Thus, according to another aspect of the present invention there is provided a highly absorbing paint.

[0069] The term "paint", as used herein, is considered as a composition with a lower viscosity than paste. By thinning down as paste (having more solvents in the composition), any composition can be made have paint-like properties and consistency.

[0070] Both the pastes and paints of the present invention can be used for coating metallic substrates for absorption of solar energy, especially solar applications such as generation of electricity in solar towers, troughs, Stirling engines and as heat absorber in solar collectors for domestic uses.

[0071] Thus, according to another aspect of the invention, there is provided a method of coating a metal substrate, said method comprising applying the coating composition described herein on a metal substrate, and curing it by heating it.

[0072] The term "metal substrate", as used herein, refers to any substrate that can be used in such applications which requires many thermal cycles from room temperature to temperatures in the range of 300-800° C. or higher.

[0073] The term "thermal cycle", as used herein, refers to heating to 300-800° C. and cooling to room temperature.

[0074] In the presently sought thermal applications, such as solar towers, stirling engines and troughs, the coating must withstand at least 5 years of service, i.e. at least 1800 cycles.

[0075] For domestic solar collectors, the temperature is lower (around 100° C. or less), and therefore the cycles required should be at least 3600 (about 10 years of service).

[0076] Preferably, the metal substrate is selected from carbon steel, stainless steel, inconel type alloys and other alloys which can be used in the range of 300-800° C.

[0077] According to one preferred embodiment, the metal substrate is steel, such as carbon steel or stainless steel.

[0078] According to another preferred embodiment, the metal substrate is Inconel™.

[0079] Inconel™ (a registered trademark of Special Metals Corporation) refers to a family of high-performance alloys (or superalloys) where nickel and chromium are the two primary metals. There are many variations of Inconcel, all with high strength and high temperature resistance, corrosion resistance, and oxidation resistance.

[0080] The term "Inconel™ 625" refers to a super alloy material comprising at least 58% nickel, 20-23% chromium, 0.1% carbon, 0.5% manganese, 0.5% silicon, no more than 5.0% iron, no more than 0.015% sulfur, no copper, no more than 0.40% aluminum, no more than 0.40% titanium, no more than 0.015% lead, no more than 1% cobalt, 3.15-4.15% niobium, no boron, and 8.0-10.0% molybdenum.

[0081] The term "Inconel™ 718" refers to a super alloy material comprising 50-55% nickel and cobalt, 17-21% chromium, 4.75-5.5% niobium and tantalum, 2.8-3.3% molybdenum, 0.65-1.15% titanium, 0.2-0.8% aluminum, balance* iron (*Reference to the 'balance' of a composition does not guarantee this is exclusively of the element mentioned but that it predominates and others are present only in minimal quantities).

[0082] The term "super alloy" refers to an alloy both inert and non-inert that provides resistance to abrasion and corrosion and that has a low iron content. A low iron content means an alloy having an iron content of less than 25%. The super alloy contains 10-30% chromium and less than 30% molybdenum. Nickel comprises at least 40% of the super alloy and is the highest element percentage. Examples are materials having the names Inconel™ and Hastelloy®.

[0083] Today there are three basic forms of solar thermal power stations in use: dish-Sterling systems, solar tower power station systems, and parabolic trough systems.

[0084] In solar towers, the present compositions can be used as an efficient coating for the metallic parts which contain and shield the fluid. The fluid can be water or steam, molten salt or other fluids which can survive high temperatures.

[0085] Parabolic trough power stations feature a large number of collectors, which have long concentrators with a small lateral dimension, and thus possess not a focal point, but rather a focal line; this fundamentally differentiates this design from that of the dish-Sterling and solar tower power stations.

[0086] Along the focal line runs an absorber pipe for the concentrated heat (as a rule up to about 400° C.); the pipe transports this heat to the power station. A fluid such as, for example, thermo oil or superheated stream comes into consideration as the transport medium; this circulates in the absorber pipework.

[0087] Although a trough collector is preferably designed as a parabolic trough collector, trough collectors with spherical or only approximately parabolic designs of concentrators are often used, since an exact parabolic concentrator with the dimensions cited above can only be manufactured with great effort that is not really justified economically. The cured compositions and some or the absorbing materials may be useful as absorbing materials in the multilayer of materials used to fabricate the coating of the central pipe of any trough as described hereinabove.

[0088] Stirling Engines are constructed of a hot and cold modules. The present coatings can be applied on the hot component of the engine, to absorb the sun energy and convert it to heat.

[0089] The compositions of this invention can be applied onto the substrates by brushing, dipping, automatic printing or a hand printing employing conventional techniques.

[0090] The printed pattern is then dried at below 200° C., preferably at about 150° C., for 5-15 minutes before heating it.

[0091] Heating of the composition can be done either by firing in a box furnace, or by natural curing, for example by using solar power.

[0092] The temperature used for heating and curing of the composition depends on the heating method, but should generally be at least 600° C., as shown hereinbelow.

[0093] Firing the treated substrate to effect sintering of both the inorganic binder and the finely divided particles of compounds of Ru, Ir and Os, is preferably done in a box furnace with a temperature profile that will allow burnout of the organic matter at about 300° C.-450° C., lasting about 5-15 minutes, followed by a controlled ramp to temperature in the range of 650-1000° C. lasting 10-60 minutes and cool-down cycle.

[0094] Natural curing of the treated substrate can take place for example when the metallic parts of a solar tower (such as pipes and plates), which contain fluid, are coated by the composition of the invention, and are let to dry by the sun. Then the solar tower is allowed to operate (to be heated by the sun). During the warm up process the solar tower itself can reach temperatures in the range of 600-700° C. In this temperature range the composition cures to obtain the cured ceramic coating. Some examples conducted by the inventors have shown that during heat treatment in the temperatures range of 600° C. to 700° C., a ceramic coating was obtained even after 30 minutes at 600-700° C. range.

[0095] Thus, according to another preferred embodiment, the heating is conducted at a temperature which is lower than 750° C.

[0096] Another aspect of the invention therefore relates to a coated substrate, wherein the coating present on the substrate comprises the fired (or cured) form of the composition set forth above, namely, a ceramic coating comprising crystallized glass, one or more ruthenium, iridium and osmium compounds, one or more oxides of groups IVB and VB of the periodic table and transition metal oxide and metal(s) powder. The substrate is preferably steel, such as carbon steel, stainless steel and Inconel™.

[0097] The invention also provides a coated substrate in a solar collector comprising a steel substrate coated with the ceramic coating set forth above.

[0098] The parts of the solar tower to be coated include pipes and other parts of the solar tower which are exposed to concentrated solar power.

[0099] The following examples are given for the purpose of illustration, and are not intended to limit the scope of the invention.

EXAMPLES

Methods and Analysis

[0100] The processes of glass melting and grinding are known in the art, and are described, for example in U.S. Pat. No. 6,171,987 and U.S. Pat. No. 6,989,111.

[0101] A Hegman gauge was used to determine the state of dispersion of the particles in the paste. This instrument consists of a channel in a block of steel that was 25 □m deep (1 mil) on one end and ramps up to 0" depth at the other end. A blade is used to draw down paste along the length of the channel. Scratches will appear in the channel where the agglomerates' diameter is greater than the channel depth. A satisfactory dispersion will give a fourth scratch point of 10-18 μm typically. A fourth scratch measurement of >10 μm indicates a poorly dispersed suspension.

[0102] The reflection was measured on USB 4000 miniature fiber optic spectrometer and the emissivity was measured in emissiometer (manufactured by Devices and Services Company, USA). Refection spectrum and emissivity of the fired samples were measured in the range 400-1100 nm. The solar absorptivity and the emissivity (300° K) were also measured by: 410-Solar Reflectometer and emissiometer, (Surface Optics Corporation). These were used also to measure reflectance in the range of 400-2500 nm and emissivity at room temperature

Preparation Example 1

Preparation of Glass Powder Compositions

[0103] Glass compositions coded Glass A, Glass B and Glass C were prepared in a platinum crucible at 1300° C. The compositions of the three glasses are specified below (in terms of mole % of each ingredient present in the glass):

TABLE 2

Ingredients	Glass A	Glass B	Glass C
SiO_2	52	53	52
B_2O_3	4	4	4.3
Al_2O_3	4	4	—

TABLE 2-continued

Ingredients	Glass A	Glass B	Glass C
La_2O_3	—	—	5.0
TiO_2	6	7	2.35
ZrO_2	—	—	2.35
K_2O	12	11	—
Na_2O	12	11	—
Li_2O	—	—	10
BaO	10	10	24

[0104] One method for preparing the glasses consists of mixing together in the desired proportions the oxide or fluoride precursors, melting the mixture and pouring the molten composition into water to form the frit. An oxide or fluoride precursor may, of course, be any compound that will yield the desired oxide or fluoride under the usual conditions of frit production. For example, boric oxide will be obtained from boric acid; silicon dioxide will be produced from flint; barium oxide will be produced from barium carbonate; etc. The glass was preferably milled in a ball mill with water to reduce the particle size. As is well known in the art, melting was conducted at a peak temperature and for a time such that the melt becomes entirely liquid and homogeneous.

[0105] In preparing the glasses used in the present invention, the components were premixed by shaking in a polyethylene jar with plastic balls, and were then melted in a platinum or a high purity alumina crucible at the desired temperature. The melt was maintained at a peak temperature of 1100° C.-1400° C. for a period of 1.5-3.0 hours. The melt was then poured into cold water. The maximum temperature of the water during quenching was kept as low as possible by increasing the volume of water to melt ratio. The crude frit after separation from water was freed from residual water by drying in air, or by displacing the water by rinsing with methanol. The crude frit was then ball milled for 3-24 hours in alumina containers using alumina balls. Alumina picked up by the materials, if any, was not within the observable limit as measured by X-ray diffraction analysis. After discharging the milled slurry from the frit, the powder was air-dried at 120-150° C. range. The dried powder was then screened through a 325 mesh screen to remove any large particles.

[0106] The glass obtained was suitable for use in the preparation of the coating compositions of the invention, as described in the following examples.

Preparation Example 2

Preparation of Highly Absorbing Pastes

[0107] Powders of the title glasses were formulated to pastes which were used to prepare the solar absorbing coatings. Typical compositions of pastes are provided in Table 3 below.

TABLE 3

Ingredients	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Glass A*	51.98	—	44.98	29.53	29.70
Glass B**	—	51.98	—		—
Co_3O_4	4.03	4.03	4.03	2.37	2.30
Nb_2O_5	7.00	7.00	7.00	4.00	4.00
ZrO_2	7.00	7.00	7.00	4.00	4.00
RuO_2	—	—	7.00	30.00	30.00
solution of ethyl cellulose (10%) in 1:1 mixture of terpineol and dibutylcarbitol	15.00	15.00	15.00	15.00	15.00
terpineol	7.50	7.50	7.50	7.50	7.50
dibutylcabitol	7.50	7.50	7.50	7.50	7.50

*The milled form of Glass A

**The milled form of Glass B

[0108] The preparation of the paste formulations according to the present invention was carried as follows. The particulate inorganic solids were mixed with the organic liquids and dispersed with suitable equipment, such as a Muller, to form a suspension, resulting in a composition for which the viscosity was in the range of about 100-150 pascalseconds at a shear rate of 4 sec^{-1}.

[0109] The organic liquid used was a mixture of diethylene glycol dibutyl ether, terpineol, and ethyl cellulose.

[0110] The ingredients of the formulation, minus about 5 weight percent of the organic components, were weighed together in a container. The components were then vigorously mixed to form a uniform blend; then the blend was passed through dispersing equipment, such as a Muller, to achieve a good dispersion of particles. The remaining 5% consisting of organic components of the paste was then added, and the resin content was adjusted to bring the viscosity, when fully formulated, to between 140 and 200 Pa·s at a shear rate of 4 sec^{-1}. The composition was then applied onto a substrate, such as carbon steel, stainless steels and Inconel™ substrate, usually by the process of screen printing, brushing or dipping to the desired thickness, typically to 5-100 μm.

Preparation Example 3

Application of the Highly Absorbing Pastes on a Substrate to Form a Coated Substrate

[0111] The paste of Sample 4 was printed on inconel 718 and 625 substrates. Two Inconel™ 625 substrates were used: one was sandblasted and the second had no treatment.

[0112] The nine coated substrates of Inconel™ 718 were fired at 700° C., 900° C. and 1000° C. for 30 minutes at peak temperature, three coated substrates were used for each temperature. Ramp was 20° C./minute to peak temperature and cool down was 20° C./minute.

[0113] The coated substrates were tested for their reflectivity and emissivity, showing that the samples fired at 1000° C. had the highest reflectivity (lowest absorption) and emissivity of 82% for the paste fired on Inconel™ 718. Fired samples at 700° C. had the lowest reflectivity, lower than Pyromark® 2500 and emissivity of 83% for the paste fired on Inconel™ 718. Samples fired at 900° C. had also low reflectivity, lower than the commercial Pyromark 2500®, emissivity was 83% for the sample on Inconel™ 718. Pyromark® 2500 has emissivity of 87%.

[0114] The paste composition of Sample 4 was also printed on Inconel™ 718 substrates and fired at peak temperature of 750° C., 800° C. and 850° C. Ramp was 20° C./minute to peak temperature and cool down was 20° C./minute. Data of solar

absorptivity and emissivity were collected, showing very high solar absorptivity and emissivity lower than Pyromark 2500®.

Preparation Example 4

[0115] Samples 5 (reference JH-041-114) composition was printed on Inconel™ 718 and fired at 750° C.; 800° C. & 850° C. peak temperatures. Ramp was 20° C./minute to reach peak temperature, kept at peak temperature for 30 minutes and cooled down to room temperature at 20° C./minute

[0116] The solar absorptivity and the emissivity (300° K) were measured by: 410-Solar Reflectometer and emissiometer, Surface Optics Corporation.

[0117] Summarized data are given below in Table 4 (Samples 6, 7 and 8):

TABLE 4

Sample No.	Composition	Peak firing (° C.)	Solar Absorptivity	Emissivity (300° K)
6	Samples 5	750	97.2%	83.4%
7	Samples 5	800	96.9%	84.0%
8	Samples 5	850	96.7%	84.6%

[0118] The above data show that composition of Sample 5 when fired in the 750-850° C. range, has very high solar absorptivity.

Preparation Example 5

[0119] Sample 5 composition was printed on Inconel™ 718 substrates, fired at peak temperature of 900° C. for 30 minutes (ramp 20° C./min, held 30 minutes at 900° C. then cool down to room temperature 20° C./min). One fired part (Sample 9) was subjected to temperature cyclings (from room temperature to 700° C., in a box furnace, air atmosphere) and storage at 700° C. Total number of cyclings was 16 and the total time at 700° C. was 503.5 hours. Another fired part (Sample 10) was kept at room temperature as a reference. Solar absorptivities of the above two samples (Samples 9 and 10) were measured by 410-Solar reflectometer and emissiometer. Cycled sample (Sample 9) absorptivity was 94.6% and the reference (Sample 10) absorptivity was 94.3%. Data show that cyclings from room temperature to 700° C. and storage at 700° C. in air atmosphere did not change the absorbtivity after about 500 hrs.

Preparation Example 6

[0120] Two compositions (Samples 11&12) were formulated with barium ruthenate $BaRuO_3$, and are given in table 5:

TABLE 5

	Sample 11	Sample 12
$BaRuO_3$	30.0%	30.0%
Glass A	29.7%	37.7%
Co_3O_4	2.3%	2.3%
Nb_2O_5	4.0%	—
ZrO_2	4.0%	—
Organic vehicle*	30.0%	30.0

*Same Organic vehicle used in Samples 1-5.

[0121] Samples 11 & 12 compositions were printed on Inconel™ 718 substrates and fired in air at 700° C., 750° C., 800° C. and 900° C. Firings schedules were: ramp of 20° C./minute to peak temperature, hold 30 minutes at peak temperature and cool down room temperature 20° C./minute.

[0122] Absorptivities of fired compositions of Samples 11 and 12 at 4 peak firing temperatures 700° C., 750° C., 800° C. and 900° C. were measured by 410-Solar reflectometer and emissiometer, Surface Optics Corporation, and are given in table 6:

TABLE 6

Sample No.	Composition	Peak firing (° C.)	Solar Absorptivity
13	Samples 11	700	94.8%
14	Samples 11	750	94.9%
15	Samples 11	800	94.4%
16	Samples 11	900	91.3%
17	Samples 12	700	95.5%
18	Samples 12	750	95.4%
19	Samples 12	800	91.3%
20	Samples 12	900	89.3%

[0123] Data of table 4 show that compositions based on barium ruthenate have high solar absorptivity and in addition they illustrate the roles of Nb_2O_5 and ZrO_2; the later oxides are important to maintain high solar absorptivity even when fired at 800° C.

Preparation Example 7

[0124] Compositions (Samples 21& 22), similar to Sample 5 were prepared, printed on Inconel™ 718 and fired at peak temperature of 800° C. using the same firing schedule of: ramp 20° C./minute to 800° C., hold 30 minutes at 800° C. and cool down 20° C./minute to room temperature. Compositions and solar absorptivity are given in table 7.

TABLE 7

Ingredients	Sample 5	Sample 21	Sample 22
Glass A	29.70%	44.55%	40.84%
Co_3O_4	2.30%	3.45%	3.16%
Nb_2O_5	4.00%	6.00%	5.50%
ZrO_2	4.00%	6.00%	5.50%
RuO_2	30.00%	14.29%	21.43%
Organic* vehicle	30.00%	30.00%	30.00%
Solar absorptivity	96.9%	93.8%	93.9%

*Same Organic vehicle used in Samples 1-5.

[0125] Table 7 shows that useful absorptivities>93.0% that can be obtained by using less ruthenium oxide.

[0126] Sample 22 was also tested in field trials on a trough, for 2 months at a maximal temperature of 350 C, showing no change in both solar absorptivity and emissivity.

Preparation Example 8

[0127] Two compositions—Samples 23 and 24 were formulated with pyrochlore taught in U.S. Pat. No. 6,989,111, having the general formula $Nd_{1.75}Cu_{0.25}Ru_2O_{6+\delta}$. Compositions and solar absorptivity are given in table 8.

TABLE 8

Ingredients	Sample 23	Sample 24
$Nd_{1.75}Cu_{0.25}Ru_2O_{6+\delta}$	30.0%	30.0%
Glass A	30.0%	—
Glass C	—	30.0%
Co_3O_4	2.3%	2.3%
Nb_2O_5	4.0%	4.0%
Oragnics*	30.0%	30.0%

*Same Organic vehicle used in Samples 1-5.

[0128] Compositions of Samples 23 and 24 were printed on Inconel™ 718 and fired at peak temperature of 800° C. using the same firing schedule of: ramp 20° C./minute to 800° C., hold 30 minutes at 800° C. and cool down 20° C./minute to room temperature. Visual comparison has shown that coating based on Samples 23&24 were black and similar to Samples 13-15.

Preparation Example 9

[0129] Compositions containing ruthenium compounds and silver powder are exemplified by Samples 25-27 which are given in table 8. These compositions were formulated with larger amounts of organic materials to form paint like consistency. Samples 25-27 compositions were applied to Inconel® 718 and stainless steel 347 by a brush and fired at peak temperature of 700° C.; firing schedule was ramp of 20° C./minute to 700° C., hold 30 minutes at 700° C. and cool down 20° C./minute to room temperature. Visual inspection shows that black coating were obtained with no cracks.

[0130] Compositions taught in this application mature to a ceramic coating by thermal treatment in the range of 600-700° C.

[0131] Because of the low temperature required to form mature ceramics, these formulations can be applied directly on the metallic part of solar tower and mature during the operation of the solar tower.

TABLE 9

Ingredients	Sample 25	Sample 26	Sample 27
$BaRuO_3$	26.90%	—	—
$Nd_{1.75}Cu_{0.25}Ru_2O_{6+\delta}$	—	26.90%	—
RuO_2	—	—	26.90%
Glass A	25.56%	25.56%	25.56%
Ag Powder	6.28%	6.28%	6.28%
Co_3O_4	1.35%	1.35%	1.35%
ZrO_2	1.35%	1.35%	1.35%
Nb_2O_5	1.35%	1.35%	1.35%
Organic vehicle	37.22%	37.22%	37.22%

Preparation Example 10

[0132] Compositions containing ruthenium compounds and larger concentration of silver powder are also exemplified by Samples 28-30 which are given in table 10.

[0133] These compositions were formulated with larger amounts of organic materials to form paint like consistency. Samples 28-30 compositions were applied to stainless steel 347 by a brush and fired at peak temperature of 700° C.; firing schedule was ramp of 20° C./minute to 700° C., hold 30 minutes at 700° C. and cool down 20° C./minute to room temperature. Visual inspection shows that black-gray coatings were obtained for Samples 28, 29 and black coating for Sample 30. All Samples 28-30 formed good coatings with no cracks and very good adhesion to the stainless steel substrate

TABLE 10

Ingredients	Sample 28	Sample 29	Sample 30
$BaRuO_3$	27.03%	—	—
$Nd_{1.75}Cu_{0.25}Ru_2O_{6+\delta}$	—	27.03%	—
RuO_2	—	—	27.03%
Glass A	19.37%	19.37%	19.37%
Ag Powder	12.61%	12.61%	12.61%
Co_3O_4	1.35%	1.35%	1.35%
ZrO_2	1.35%	1.35%	1.35%
Nb_2O_5	1.35%	1.35%	1.35%
Organic vehicle	36.94%	36.94%	36.94%

1. A coating composition comprising:

I) at least one highly absorbing material selected from the group consisting of ruthenium, iridium and osmium compounds, and mixtures thereof;

II) an inorganic glass binder or a precursor thereof;

III) a ceramic filler comprising metal oxides, metal powders and mixtures thereof; and

IV) a liquid organic vehicle.

2. The composition of claim **1**, wherein said highly absorbing material contains one or more Ru compounds.

3. The composition of claim **1**, wherein said highly absorbing material ranges from 7 to 30% weight.

4. The composition of claim **2**, wherein said Ru compound is selected from RuO_2, $BaRuO_3$, and pyrochlore-like Ru compounds, or mixtures thereof.

5. The composition of claim **1**, wherein said inorganic glass binder is selected from boroaluminosilicates of Na, K, Li, Ca, Sr, Mg, Ba, with or without transition metals oxides.

6. The composition of claim **1**, wherein said precursor of said silicon dioxide binder is a silicon resin selected from polydimethylsiloxanes, polymethydro-dimethylsiloxane copolymer, vinyl terminated silicone polymers and vinyl backbone silicone polymers.

7. The composition of claim **1**, wherein said inorganic glass binder or said precursor thereof ranges from 15 to 55% weight.

8. The composition of claim **1**, wherein said liquid organic vehicle is selected from aliphatic alcohols or esters thereof, terpens, terpineols, solutions of resins.

9. The composition of claim **1**, wherein the amount of said liquid organic vehicle ranges from 25% weight to 50% weight of the total weight of the composition.

10. The composition of claim **1**, wherein the amount of said ceramic filler ranges from 0.1% weight to 30% weight of the total weight of solids dispersed in said composition.

11. The composition of claim **1**, comprising from 1 to 99.5% weight RuO_2, from 5 to 80% weight glass particles, from 0.1% weight to 30% weight of said ceramic filler and from 10% weight to 50% weight of said liquid organic vehicle.

12. The composition of claim **1**, wherein said ceramic filler contains from 0.1 to 12.0% weight Co_3O_4; from 0.1 to 12.0% weight Nb_2O_5; and from 0 to 12.0% weight ZrO_2.

13. The composition of claim **12**, wherein said ceramic filler optionally further contains up to 20% silver powder.

14. The composition of claim **1**, being in the form of a paste or a paint.

15. A method of coating a metal substrate, said method comprising applying the coating composition of claim **1** on a metal substrate, and curing said composition by heating thereof.

16. The method of claim **15**, wherein said metal substrate is selected from a solar tower coated parts which are exposed to concentrated solar power, a trough pipe, a stirling engine or a domestic solar collector.

17. The method of claim **15**, wherein said metal substrate is composed of a carbon steel, stainless steel, Inconel™ and super alloys.

18. The method of claim **17**, wherein said heating is conducted by firing said composition.

19. The method of claim **17**, wherein said heating is conducted by naturally curing said composition.

20. The method of claim **19**, wherein said heating is conducted at a temperature which is lower than 750° C.

21. A metal substrate coated by a ceramic coating, said coating comprising at least one highly absorbing material selected from the group consisting of ruthenium, iridium and osmium compounds, and mixtures thereof, crystallized glass, and one or more a ceramic filler comprising metal oxides, metal powders and mixtures thereof.

22. A solar absorber coated by a ceramic coating, said coating comprising at least one highly absorbing material selected from the group consisting of ruthenium, iridium and osmium compounds, and mixtures thereof, crystallized glass, and one or more a ceramic filler comprising metal oxides, metal powders and mixtures thereof.

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