

Coating

FIELD OF THE INVENTION

The present invention relates to a coating composition (e.g. a high emissivity coating composition), a package containing the composition and to a method for making
5 the composition. The invention also relates to a method for preparing a coated substrate comprising applying the coating composition, a coated substrate per se and to use of the coating composition to coat a substrate (e.g. a refractory).

BACKGROUND OF THE INVENTION

10 There is an increasing need for industrial energy users to reduce energy consumption.

In industries, such as the petrochemical sector, which rely heavily on the use of furnaces and fired heaters, there is a desire to improve furnace and heater efficiency, to reduce fuel consumption, and the emissions therefrom. High emissivity coatings have
15 become one established approach to help solve this problem. High emissivity coatings have, for example, been proven to reduce energy and production costs in a petrochemical furnace. The high emissivity coating is used to cover the inner surface of the furnace wall, enabling it to absorb and re-emit heat, and thereby increase thermal efficiency. An increase in thermal efficiency arising from the increased emissivity of the
20 interior of a heater or furnace results, in turn, in decreases in fuel consumption and overall energy demand.

High emissivity coatings present on the inner surface of furnaces and other heaters are required to satisfy a number of criteria, in addition to improving the emissivity of the surface. Such coatings are required to improve emissivity across a wide spectral
25 range, as well as across a range of temperatures. Achieving high emissivity at high temperatures (e.g. $>1000\text{ }^{\circ}\text{C}$), can be a particular challenge because many coatings can only tolerate temperatures of up to around $1000\text{ }^{\circ}\text{C}$ before the temperature causes instability in the coating, which may manifest in blistering or disintegration. High emissivity coatings must also possess strong adhesion to the underlying substrate,
30 typically a refractory, abrasion resistance, thermal shock resistance and thermal resistance in order to provide longevity of performance.

Conventionally, chromium oxide (Cr_2O_3) is used in high emissivity coatings for furnaces, but it can only tolerate temperatures of $1100\text{ }^{\circ}\text{C}$ or lower. Above this temperature, the high vapor pressure of chromium causes the coating material to
35 become unstable and start to disintegrate, causing the rest to melt. Moreover, the use of

chromium products has been banned in Europe and in some Asian countries, due to the environmental and health problems caused if chromium escapes into the environment.

SUMMARY OF THE INVENTION

5 Viewed from a first aspect the present invention provides a coating composition, preferably a high emissivity coating composition, and more preferably a high emissivity coating composition in the form of a suspension, comprising:

- (i) 2-20 wt% of a first emissivity agent selected from oxides of Mn, Ce, Co and mixtures thereof;
- 10 (ii) 0-5 wt%, preferably 0-1 wt%, more preferably 0-0.01 wt% and still more preferably 0-0.001 wt% of an oxide of Cr;
- (iii) 0-5 wt% Fe_2O_3 ;
- (iv) 10-35 wt% filler selected from aluminium silicate, oxides of Al, oxides of Si and mixtures thereof; and
- 15 (v) 10-20 wt% binder;

wherein the total content of emissivity agents in said composition is preferably 15-45 wt%, and preferably wherein the weight ratio of said first emissivity agent to said filler is 0.12:1 to 0.5:1.

20 Viewed from a further aspect the present invention provides a coating composition, preferably a high emissivity coating composition, and more preferably a high emissivity coating composition in the form of a powder, comprising:

- (i) 5-25 wt% of a first emissivity agent selected from oxides of Mn, Ce, Co and mixtures thereof;
- (ii) 0-5 wt%, preferably 0-1 wt%, more preferably 0-0.01 wt%, and still more
- 25 preferably 0-0.001 wt% of an oxide of Cr;
- (iii) 0-5 wt% Fe_2O_3 ; and
- (iv) 30-60 wt% filler selected from aluminium silicate, oxides of Al, oxides of Si and mixtures thereof;

30 wherein the total content of emissivity agents in said composition is preferably 40 to 75 wt%, based on the total weight of the composition, and preferably wherein the weight ratio of said first emissivity agent to said filler is 0.12:1 to 0.5:1.

Viewed from a further aspect the present invention provides a package containing a composition as hereinbefore defined.

35 Viewed from a further aspect the present invention provides a method for preparing a coating composition as hereinbefore defined, comprising mixing:

a first emissivity agent selected from oxides of Mn, Ce, Co and mixtures thereof, 0-5 wt% of oxide of Cr, 0-5 wt% Fe_2O_3 , a filler selected from aluminium silicate, oxides of Al, oxides of Si and mixtures thereof, and optionally binder.

Viewed from a further aspect the present invention provides a method for preparing a coated substrate, comprising the steps:

- a) providing a substrate;
- b) applying a coating composition as hereinbefore defined onto at least one surface of said substrate; and
- c) heating said coating composition to form the coated substrate.

Viewed from a further aspect the present invention provides a coated substrate obtainable by, or obtained by, the method as hereinbefore defined.

Viewed from a further aspect the present invention provides a coated substrate comprising a composition as hereinbefore defined, preferably a coated refractory (e.g. a coated shaped refractory, a coated unshaped refractory), a coated insulating material or a coated ceramic fiber.

Viewed from a further aspect the present invention provides a method for preparing a coated substrate, preferably a coated refractory, a coated insulating material or a coated ceramic fiber, wherein said coating is derived from a coating composition comprising:

- (i) 2-20 wt% of a first emissivity agent selected from oxides of Mn, Ce, Co and mixtures thereof;
- (ii) 0-5 wt%, preferably 0-1 wt%, more preferably 0-0.01 wt% and still more preferably 0-0.001 wt% of an oxide of Cr;
- (iii) 0-5 wt% Fe_2O_3 ;
- (iv) 10-35 wt% filler selected from aluminium silicate, oxides of Al, oxides of Si and mixtures thereof; and
- (v) 10-20 wt% binder;

wherein the total content of emissivity agents in said composition is preferably 15-45 wt%, and preferably wherein the weight ratio of said first emissivity agent to said filler is 0.12:1 to 0.5:1.

Viewed from a further aspect the present invention provides a furnace comprising a coated substrate as hereinbefore defined.

Viewed from a further aspect the present invention provides the use of a coating composition as hereinbefore defined to coat a substrate.

DEFINITIONS

As used herein, the term “emissivity” refers to the effectiveness of a material to emit energy as thermal radiation. Emissivity may be defined as the ratio of energy radiated by a particular material to energy radiated by a blackbody at the same temperature.

As used herein, the term “emissivity agent” refers to a material that provides the emissivity to a coating composition to which it is added.

As used herein, the term “filler” refers to a material that provides the resistance to stress and thermal stress in a high emissivity coating in which it is present.

As used herein, the term “wt%” is based on the total weight of the composition (e.g. the first or second composition), unless otherwise specified. The total wt% of the composition should be 100%.

As used herein, the term “heating” includes heating and heat-treating.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a coating composition comprising:

- (i) 2-20 wt% of a first emissivity agent selected from oxides of Mn, Ce, Co and mixtures thereof;
- (ii) 0-5 wt%, preferably 0-1 wt%, more preferably 0-0.01 wt% and still more preferably 0-0.001 wt% of an oxide of Cr;
- (iii) 0-5 wt% Fe_2O_3 ;
- (iv) 10-35 wt% filler selected from aluminium silicate, oxides of Al, oxides of Si and mixtures thereof; and
- (v) 10-20 wt% binder;

wherein the total content of emissivity agents in said composition is preferably 15-45 wt%, and preferably wherein the weight ratio of said first emissivity agent to said filler is 0.12:1 to 0.5:1.

Preferably the coating composition is in the form of a suspension.

Preferably the coating composition comprises water.

The present invention advantageously provides a high emissivity coating composition, and in particular, a coating composition that yields coatings that possess high emissivity both at high temperatures (e.g. $>1000\text{ }^\circ\text{C}$) as well as across the whole spectral range (i.e. $400\text{-}12,000\text{ cm}^{-1}$). The coating compositions of the present invention also provide coatings with excellent adhesion as well as abrasion, thermal shock and

thermal resistance properties. These are essential properties for the coating composition to perform well as coatings on, e.g. refractories in industrial furnaces.

The present invention also provides a coating composition, preferably a high emissivity coating composition, and more preferably a high emissivity coating composition in the form of a powder, comprising:

- (i) 5-25 wt% of a first emissivity agent selected from oxides of Mn, Ce, Co and mixtures thereof;
- (ii) 0-5 wt%, preferably 0-1 wt%, more preferably 0-0.01 wt%, and still more preferably 0-0.001 wt% of an oxide of Cr;
- (iii) 0-5 wt% Fe_2O_3 ; and
- (iv) 30-60 wt% filler selected from aluminium silicate, oxides of Al, oxides of Si and mixtures thereof;

wherein the total content of emissivity agents in said composition is preferably 40 to 75 wt%, based on the total weight of the composition, and preferably wherein the weight ratio of said first emissivity agent to said filler is 0.12:1 to 0.5:1.

Advantageously this second coating composition, preferably a powder coating composition, may be used to prepare the first coating composition hereinbefore described. The second coating composition, preferably a powder coating composition, is a mixture of the emissivity agents and fillers present in the first coating composition hereinbefore described. Binder, and optionally water, may be added to the second coating composition, e.g. shortly before application of the coating, to prepare the first coating composition.

First coating composition

Although Cr_2O_3 is one of the most commonly used emissivity agents in furnace coatings, the first coating composition of the present invention advantageously comprises less than 5 wt% of oxides of Cr, based on the total weight of the first composition. Preferably the first coating composition of the present invention comprises 0-4 wt%, more preferably 0.1-3.5 wt%, and still more preferably 0.1-2 wt% oxides of Cr, based on the total weight of the first composition. More preferably the first coating composition of the present invention comprises less than 5 wt% of an oxide of Cr selected from CrO , Cr_2O_3 , CrO_2 , CrO_3 , CrO_5 and mixtures thereof, based on the total weight of the first composition. Still more preferably the first coating composition of the present invention comprises 0-4 wt%, more preferably 0.1-3.5 wt% and still more preferably 0.1-2 wt% of an oxide of Cr selected from CrO , Cr_2O_3 , CrO_2 , CrO_3 , CrO_5 and

mixtures thereof, based on the total weight of the first composition. Another preferred first coating composition of the present invention comprises 0-1 wt%, more preferably 0-0.01 wt% and still more preferably 0-0.001 wt% oxides of Cr selected from CrO, Cr₂O₃, CrO₂, CrO₃, CrO₅ and mixtures thereof, based on the total weight of the first composition.

5 Particularly preferably the first coating composition of the present invention comprises less than 5 wt% Cr₂O₃, based on the total weight of the first composition. Preferably the first coating composition of the present invention comprises 0-4 wt%, more preferably 0.1-3.5 wt%, and still more preferably 0.1-2 wt% Cr₂O₃, based on the total weight of the first composition. Another preferred first coating composition of the present
10 invention comprises 0-1 wt%, more preferably 0-0.01 wt% and still more preferably 0-0.001 wt% Cr₂O₃, based on the total weight of the first composition. Yet more preferably the first coating composition of the present invention does not comprise Cr₂O₃. This is beneficial because chromium is banned for use in industrial products in many EU and Asian countries due to the ecological harm it causes.

15 A preferred first coating composition of the present invention comprises 0-1000 ppm wt Cr, more preferably 0-500 ppm wt Cr and more preferably 0 ppm wt Cr.

Fe₂O₃ is also a commonly used emissivity agent. However, a preferred first coating composition of the present invention advantageously comprises less than 5 wt% Fe₂O₃, based on the total weight of the first composition. Preferably the first coating
20 composition of the present invention comprises 0-4 wt% Fe₂O₃, more preferably 0.1-3.5 wt% Fe₂O₃, and still more preferably 0.1-2 wt% Fe₂O₃, based on the total weight of the first composition. Particularly preferably the first coating composition of the present invention does not comprise Fe₂O₃. The absence of Fe₂O₃ from the coating compositions of the present invention has been found to improve the thermal shock
25 performance of the coatings produced therefrom.

A preferred first coating composition of the present invention comprises 0-1000 ppm wt Fe, more preferably 0-500 ppm wt Fe and still preferably 0 ppm wt Fe.

In one preferred first coating composition of the present invention the first emissivity agent is selected from an oxide of Mn. Representative examples of oxides of
30 Mn include MnO, MnO₂, Mn₃O₄, Mn₂O₃, MnO₃, Mn₂O₇, Mn₅O₈, Mn₇O₁₂ and Mn₇O₁₃. When the first emissivity agent is an oxide of Mn, it is preferably MnO₂.

In another preferred first coating composition of the present invention the first emissivity agent is selected from an oxide of Ce. Representative examples of oxides of Ce include CeO₂, Ce₂O₃ and Ce₃O₄. When the first emissivity agent is an oxide of Ce, it
35 is preferably CeO₂.

In another preferred first coating composition of the present invention the first emissivity agent is selected from an oxide of Co. Representative examples of oxides of Co include CoO, Co₂O₃ and Co₃O₄. When the first emissivity agent is an oxide of Co, it is preferably CoO.

5 In another preferred first coating composition of the present invention, the first emissivity agent is selected from an oxide of Ce, Co and mixtures thereof. Such coating compositions preferably comprise a first emissivity agent selected from CeO₂, CoO and mixtures thereof.

10 In a preferred first coating composition of the present invention, the total amount of the first emissivity agent is 3 to 15 wt%, e.g. 4 to 12 wt%, preferably 5 to 12 wt%, still more preferably 4 to 6 wt% and yet more preferably 5 to 6 wt%, based on the total weight of the first coating composition.

One preferred first coating composition of the invention comprises a single first emissivity agent. Another preferred first coating composition comprises more than one
15 (e.g. two or three, preferably two) first emissivity agent. When the first coating composition comprises two different first emissivity agents, the weight ratio of the oxides is preferably 30:70 to 70:30, more preferably 40:60 to 60:40 and still more preferably about 50:50. For example, a preferred first coating composition comprising two first emissivity agents comprises CeO₂ to CoO or CeO₂ to MnO₂ in a weight ratio of 30:70 to
20 70:30, more preferably 40:60 to 60:40 and still more preferably about 50:50.

In a preferred first coating composition of the present invention, the ratio of the first emissivity agent to filler is preferably 0.15:1 to 0.4:1, more preferably 0.18:1 to 0.35:1 and still more preferably 0.25:1 to 0.32:1.

A preferred first coating composition of the present invention further comprises a
25 second emissivity agent which is a metallic oxide, and preferably a metallic oxide selected from titanium dioxide, nickel oxide, magnesium oxide, copper oxide, terbium oxide, and mixtures thereof. Particularly preferably the second emissivity agent is titanium oxide, especially TiO₂. The second emissivity agent must be a different metallic oxide to the first emissivity agent.

30 In a preferred first coating composition of the present invention, the total amount of the second emissivity agent which is a metallic oxide is 10 to 22 wt%, preferably 13 to 18 wt%, and still more preferably 16 to 18 wt%, based on the total weight of the first coating composition.

35 A preferred first coating composition of the present invention therefore comprises:

(i) 2-20 wt% of a first emissivity agent selected from oxides of Mn, Ce, Co and mixtures thereof;

(ia) 10-22 wt% of a second emissivity agent, which is a metallic oxide, preferably selected from titanium dioxide, nickel oxide, magnesium oxide, copper oxide, terbium oxide and mixtures thereof;

(ii) 0-5 wt%, preferably 0-1 wt%, more preferably 0-0.01 wt%, and still more preferably 0-0.001 wt% of an oxide of Cr;

(iii) 0-5 wt% Fe_2O_3 ;

(iv) 10-35 wt% filler selected from aluminium silicate, oxides of Al, oxides of Si and mixtures thereof; and

(v) 10-20 wt% binder;

wherein the total content of emissivity agents in said composition is preferably 15-45 wt%, and preferably wherein the weight ratio of said first emissivity agent to said filler is 0.12:1 to 0.5:1.

In a preferred first coating composition of the present invention, the total amount of first emissivity agent and second emissivity agent, which is a metallic oxide, is 15 to 40 wt%, more preferably 18 to 35 wt% and still more preferably 20 to 30 wt%, based on the total weight of the first coating composition.

One preferred first coating composition of the present invention solely comprises metallic oxide emissivity agents.

Another preferred first coating composition of the present invention, further comprises a third emissivity agent, and preferably a third non-metallic oxide emissivity agent. Preferably the third non-metallic oxide emissivity agent is selected from silicon carbide (SiC), boron silicide (B_4Si), boron carbide (B_4C), silicon hexaboride (SiB_6), molybdenum disilicide (MoSi_2), tungsten disilicide (WSi_2), zirconium diboride (ZrB_2), and mixtures thereof. More preferably, such coating compositions of the present invention further comprise a third non-metallic oxide emissivity agent selected from boron silicide (B_4Si), boron carbide (B_4C), silicon hexaboride (SiB_6), molybdenum disilicide (MoSi_2), tungsten disilicide (WSi_2), zirconium diboride (ZrB_2), and mixtures thereof.

A particularly preferred first coating composition of the invention does not comprise silicon carbide (SiC).

Another particularly preferred first coating composition of the invention comprises silicon carbide (SiC).

In a preferred first coating composition of the present invention, the total amount of a third non-metallic oxide emissivity agent is 0 to 18 wt%, preferably 0 to 15 wt%, more

preferably 10-15 wt% and still more preferably 12-14 wt%, based on the total weight of the first coating composition.

In a preferred first coating composition of the present invention, the total amount of emissivity agents is 15 to 45 wt%, more preferably 15 to 40 wt%, still more preferably 20 to 38 wt% and yet more preferably 24 to 38 wt%, based on the total weight of the first coating composition.

A preferred first coating composition of the present invention therefore comprises:

- (i) 2-20 wt% of a first emissivity agent selected from oxides of Mn, Ce, Co and mixtures thereof;
- (ia) 10-22 wt% of a second emissivity agent, which is a metallic oxide, preferably selected from titanium dioxide, nickel oxide, magnesium oxide, copper oxide, terbium oxide and mixtures thereof;
- (ib) 0-18 wt% of a third non-metallic oxide emissivity agent selected from silicon carbide (SiC), boron silicide (B_4Si), boron carbide (B_4C), silicon hexaboride (SiB_6), molybdenum disilicide ($MoSi_2$), tungsten disilicide (WSi_2), zirconium diboride (ZrB_2), and mixtures thereof
- (ii) 0-5 wt%, preferably 0-1 wt%, more preferably 0-0.01 wt%, and still more preferably 0-0.001 wt% of an oxide of Cr;
- (iii) 0-5 wt% Fe_2O_3 ;
- (iv) 15-35 wt% filler selected from aluminium silicate, oxides of Al, oxides of Si and mixtures thereof; and
- (v) 10-20 wt% binder;

wherein the total content of emissivity agents in said composition is preferably 15-45 wt%, and preferably wherein the weight ratio of said first emissivity agent to said filler is 0.12:1 to 0.5:1.

A particularly preferred first coating composition of the present invention comprises, preferably consists of, the following mixtures of emissivity agents:

- MnO₂, TiO₂ and SiC;
- CeO₂, CoO and TiO₂;
- CoO and TiO₂;
- CoO, TiO₂ and SiC
- CeO₂, TiO₂ and SiC.

The first coating composition of the present invention further comprises at least one filler. The filler is selected from aluminium silicate, oxides of Al, oxides of Si and

mixtures thereof, e.g. aluminium silicate and an oxide of Al, different oxides of Al, an oxide of Al and an oxide of Si etc. Preferred fillers include aluminium silicate, alumina, silica, and mixtures thereof.

5 Preferably, the first coating composition comprises 15 to 35 wt%, more preferably 15 to 33 wt%, still more preferably 19 to 33 wt% and yet more preferably 19-30 wt%, of at least one filler, based on the total weight of the first coating composition.

10 The first coating composition of the present invention further comprises binder. Preferably the first coating composition comprises 10 to 18 wt%, more preferably 10 to 15 wt% and still more preferably 11 to 14 wt% binder, based on the total weight of the first coating composition.

Preferably, the binder is phosphoric acid (H_3PO_4), a sodium aluminosilicate and/or a potassium aluminosilicate to form, for instance, $\text{Al}_2(\text{H}_2\text{P}_2\text{O}_7)$, $\text{Al}(\text{PO}_3)_3$, AlPO_4 , and/or KAlSi_3O_8 . A particularly preferred binder is phosphoric acid (H_3PO_4). The phosphoric acid is preferably in the form of an aqueous solution.

15 A preferred first coating composition of the present invention further comprises water. A preferred coating composition of the present invention further comprises 1 to 35 wt% water, and more preferably 20 to 35 wt% water (e.g. around 30 wt%), based on the total weight of the first coating composition.

20 A particularly preferred first coating composition of the present invention therefore comprises:

(i) 2-20 wt% of a first emissivity agent selected from oxides of Mn, Ce, Co and mixtures thereof;

25 (ia) 10-22 wt% of a second emissivity agent, which is a metallic oxide, preferably selected from titanium dioxide, nickel oxide, magnesium oxide, copper oxide, terbium oxide and mixtures thereof;

(ib) 0-18 wt% of a third non-metallic oxide emissivity agent selected from silicon carbide (SiC), boron silicide (B_4Si), boron carbide (B_4C), silicon hexaboride (SiB_6), molybdenum disilicide (MoSi_2), tungsten disilicide (WSi_2), zirconium diboride (ZrB_2), and mixtures thereof

30 (ii) 0-5 wt%, preferably 0-1 wt%, more preferably 0-0.01 wt%, and still more preferably 0-0.001 wt% of an oxide of Cr;

(iii) 0-5 wt% Fe_2O_3 ;

(iv) 15-35 wt% filler, preferably 15 to 33 wt% filler, selected from aluminium silicate, oxides of Al, oxides of Si and mixtures thereof;

35 (v) 10-20 wt% binder, preferably phosphoric acid; and

(vi) 1-35 wt% water,

wherein the total content of emissivity agents in said composition is preferably 15-40 wt%, and preferably wherein the weight ratio of said first emissivity agent to said filler is 0.12:1 to 0.5:1.

5 The first coating composition of the present invention is a high emissivity coating composition, meaning that it is able to efficiently absorb and re-emit heat. The first coating composition of the present invention preferably produces coatings having a relatively constant emissivity across a range of temperatures, e.g. 500-1500 °C.

10 The first coating composition of the present invention also possesses the other properties necessary to function as high emissivity coatings, e.g. thermal resistance, thermal shock resistance, abrasion resistance and adhesion.

Second coating composition

15 As described above, the second coating composition herein described is preferably a powder coating composition. It is a mixture of the emissivity agents and fillers present in the first coating composition hereinbefore described. Binder, and optionally, water may be added to the second coating composition, e.g. shortly before application of the coating.

20 The second coating composition of the present invention advantageously comprises less than 5 wt% of oxides of Cr, based on the total weight of the second coating composition. Preferably the second coating composition of the present invention comprises 0-4 wt% oxides of Cr, more preferably 0.1-3.5 wt%, and still more preferably 0.1-2 wt% oxides of Cr, based on the total weight of the second coating composition. More preferably the second coating composition of the present invention comprise less than 5 wt% of an oxide of Cr selected from CrO, Cr₂O₃, CrO₂, CrO₃, CrO₅ and mixtures thereof, based on the total weight of the second coating composition. Still more preferably the second coating composition of the present invention comprises 0-4 wt%, more preferably 0.1-3.5 wt% and still more preferably 0.1-2 wt% of an oxide of Cr selected from CrO, Cr₂O₃, CrO₂, CrO₃, CrO₅ and mixtures thereof, based on the total weight of the second coating composition. Another preferred second coating composition of the present invention comprises 0-1 wt%, more preferably 0-0.01 wt% and still more preferably 0-0.001 wt% oxides of Cr selected from CrO, Cr₂O₃, CrO₂, CrO₃, CrO₅ and mixtures thereof, based on the total weight of the second coating composition.

35 Particularly preferably the second coating composition of the present invention comprises less than 5 wt% Cr₂O₃, based on the total weight of the second coating

composition. Preferably the second coating composition of the present invention comprises 0-4 wt%, more preferably 0.1-3.5 wt%, and still more preferably 0.1-2 wt% Cr_2O_3 , based on the total weight of the second coating composition. Another preferred second coating composition of the present invention comprises 0-1 wt%, more preferably 0-0.01 wt% and still more preferably 0-0.001 wt% Cr_2O_3 , based on the total weight of the second coating composition. Yet more preferably the second coating composition of the present invention does not comprise Cr_2O_3 . This is beneficial because chromium is banned for use in industrial products in many EU and Asian countries due to the ecological harm it causes.

10 A preferred second coating composition of the present invention comprises 0-1000 ppm wt Cr, more preferably 0-500 ppm wt Cr and more preferably 0 ppm wt Cr.

Fe_2O_3 is also a commonly used emissivity agent. However, a preferred second coating composition of the present invention advantageously comprises less than 5 wt% Fe_2O_3 , based on the total weight of the second coating composition. Preferably the second coating composition of the present invention comprises 0-4 wt% Fe_2O_3 , more preferably 0.1-3.5 wt% Fe_2O_3 , and still more preferably 0.1-2 wt% Fe_2O_3 , based on the total weight of the second coating composition. Particularly preferably the second coating composition of the present invention does not comprise Fe_2O_3 . The absence of Fe_2O_3 from the second coating composition of the present invention has been found to improve the thermal shock performance of the coatings produced therefrom.

20 A preferred second coating composition of the present invention comprises 0-1000 ppm wt Fe, more preferably 0-500 ppm wt Fe and still preferably 0 ppm wt Fe.

In one preferred second coating composition of the present invention the first emissivity agent is selected from an oxide of Mn. Representative examples of oxides of Mn include MnO , MnO_2 , Mn_3O_4 , Mn_2O_3 , MnO_3 , Mn_2O_7 , Mn_5O_8 , Mn_7O_{12} and Mn_7O_{13} . When the first emissivity agent is an oxide of Mn, it is preferably MnO_2 .

In another preferred second coating composition of the present invention the first emissivity agent is selected from an oxide of Ce. Representative examples of oxides of Ce include CeO_2 , Ce_2O_3 and Ce_3O_4 . When the first emissivity agent is an oxide of Ce, it is preferably CeO_2 .

30 In another preferred second coating composition of the present invention the first emissivity agent is selected from an oxide of Co. Representative examples of oxides of Co include CoO , Co_2O_3 and Co_3O_4 . When the first emissivity agent is an oxide of Co, it is preferably CoO .

In another preferred second coating composition of the present invention, the first emissivity agent is selected from an oxide of Ce, Co and mixtures thereof. Such coating compositions preferably comprise a first emissivity agent selected from CeO_2 , CoO and mixtures thereof.

5 In a preferred second coating composition of the present invention, the total amount of the first emissivity agent is 7 to 20 wt%, preferably 8 to 20 wt%, still more preferably 7 to 11 wt% and yet more preferably 8 to 11 wt%, based on the total weight of the second coating composition.

A preferred second coating composition of the invention comprises a single first
10 emissivity agent. Another preferred second coating composition comprises more than one (e.g. two or three, preferably two) first emissivity agent. When the second coating composition comprises two different first emissivity agents, the weight ratio of the oxides is preferably 30:70 to 70:30, more preferably 40:60 to 60:40 and still more preferably about 50:50. For example, a preferred second coating composition comprising two first
15 emissivity agents comprises CeO_2 to CoO or CeO_2 to MnO_2 in a weight ratio of 30:70 to 70:30, more preferably 40:60 to 60:40 and still more preferably about 50:50.

In a preferred second coating composition of the present invention, the ratio of the first emissivity agent to filler is preferably 0.15:1 to 0.4:1, more preferably 0.18:1 to 0.35:1 and still more preferably 0.25:1 to 0.32:1.

20 A preferred second coating composition of the present invention further comprises a second emissivity agent which is a metallic oxide, and preferably a metallic oxide selected from titanium dioxide, nickel oxide, magnesium oxide, copper oxide, terbium oxide, and mixtures thereof. Particularly preferably the second emissivity agent is titanium oxide, especially TiO_2 . The second emissivity agent must be a different
25 metallic oxide to the first emissivity agent.

In a preferred coating composition of the present invention, the total amount of the second emissivity agent which is a metallic oxide is 22 to 32 wt%, preferably 25 to 32 wt%, and still more preferably 28-32 wt%, based on the total weight of the second coating composition.

30 A preferred second coating composition of the present invention therefore comprises:

- (vi) 5-25 wt% of a first emissivity agent selected from oxides of Mn, Ce, Co and mixtures thereof;

(via) 22-32 wt% of a second emissivity agent, which is a metallic oxide, preferably selected from titanium dioxide, nickel oxide, magnesium oxide, copper oxide, terbium oxide and mixtures thereof;

5 (vii) 0-5 wt%, preferably 0-1 wt%, more preferably 0-0.01 wt%, and still more preferably 0-0.001 wt% of an oxide of Cr;

(viii) 0-5 wt% Fe_2O_3 ; and

(ix) 30-60 wt% filler selected from aluminium silicate, oxides of Al, oxides of Si and mixtures thereof;

10 wherein the total content of emissivity agents in said composition is preferably 40-75 wt%, and preferably wherein the weight ratio of said first emissivity agent to said filler is 0.12:1 to 0.5:1.

In a preferred second coating composition of the present invention, the total amount of first emissivity agent and second emissivity agent, which is a metallic oxide, is 20 to 55 wt%, more preferably 30 to 50 wt% and still more preferably 40 to 50 wt%,
15 based on the total weight of the second coating composition.

A preferred second coating composition of the present invention solely comprises metallic oxide emissivity agents.

Another preferred second coating composition of the present invention, further comprises a third emissivity agent, preferably a third non-metallic oxide emissivity agent.
20 The third non-metallic oxide emissivity agent is preferably selected from silicon carbide (SiC), boron silicide (B_4Si), boron carbide (B_4C), silicon hexaboride (SiB_6), molybdenum disilicide (MoSi_2), tungsten disilicide (WSi_2), zirconium diboride (ZrB_2), and mixtures thereof. More preferably, such coating compositions of the present invention further comprise a third non-metallic oxide emissivity agent selected from boron silicide (B_4Si),
25 boron carbide (B_4C), silicon hexaboride (SiB_6), molybdenum disilicide (MoSi_2), tungsten disilicide (WSi_2), zirconium diboride (ZrB_2), and mixtures thereof.

A particularly preferred second coating composition of the invention does not comprise silicon carbide (SiC).

30 Another particularly preferred second coating composition of the invention comprises silicon carbide (SiC).

In a preferred second coating composition of the present invention, the total amount of a third non-metallic oxide emissivity agent is 0 to 25 wt%, preferably 10 to 25 wt%, more preferably 17-25 wt% and still more preferably 21-25 wt%, based on the total weight of the second coating composition.

In a preferred second coating composition of the present invention, the total amount of emissivity agents is 40 to 75%, more preferably 40 to 70 wt% and still more preferably 42 to 67 wt%, based on the total weight of the second coating composition.

A preferred second coating composition of the present invention therefore comprises:

- (vi) 5-25 wt% of a first emissivity agent selected from oxides of Mn, Ce, Co and mixtures thereof;
- (via) 22-32 wt% of a second emissivity agent, which is a metallic oxide, preferably selected from titanium dioxide, nickel oxide, magnesium oxide, copper oxide, terbium oxide and mixtures thereof;
- (vib) 0-25 wt% of a third non-metallic oxide emissivity agent selected from silicon carbide (SiC), boron silicide (B₄Si), boron carbide (B₄C), silicon hexaboride (SiB₆), molybdenum disilicide (MoSi₂), tungsten disilicide (WSi₂), zirconium diboride (ZrB₂), and mixtures thereof
- (vii) 0-5 wt%, preferably 0-1 wt%, more preferably 0-0.01 wt%, and still more preferably 0-0.001 wt% of an oxide of Cr;
- (viii) 0-5 wt% Fe₂O₃; and
- (ix) 30-60 wt% filler selected from aluminium silicate, oxides of Al, oxides of Si and mixtures thereof;

wherein the total content of emissivity agents in said composition is preferably 40-75 wt%, and preferably wherein the weight ratio of said first emissivity agent to said filler is 0.12:1 to 0.5:1.

A particularly preferred second coating composition of the present invention comprises, preferably consists of, the following mixtures of emissivity agents:

- MnO₂, TiO₂ and SiC;
- CeO₂, CoO and TiO₂;
- CoO and TiO₂;
- CoO, TiO₂ and SiC
- CeO₂, TiO₂ and SiC.

The second coating composition of the present invention further comprises at least one filler. The filler is selected from aluminium silicate, oxides of Al, oxides of Si and mixtures thereof, e.g. aluminium silicate and an oxide of Al, different oxides of Al, an oxide of Al and an oxide of Si etc. Preferred fillers include aluminium silicate, alumina, silica, and mixtures thereof.

Preferably, the second coating composition comprises 30 to 52 wt%, more preferably 30 to 45 wt%, still more preferably 30 to 40 wt% and yet more preferably 30-35 wt%, of at least one filler, based on the total weight of the second coating composition.

5 Packages

The present invention also provides a package containing a coating composition, e.g. a first or second coating composition, as hereinbefore described. Packages of the present invention include containers, drums, bottles, boxes, tins, jars, sachets etc.

10 Methods and coatings

The present invention also provides a method for preparing a coating composition, e.g. a first or second coating composition, as hereinbefore described, comprising mixing:

a first emissivity agent selected from oxides of Mn, Ce, Co and mixtures thereof;

15 0-5 wt%, preferably 0-1 wt%, more preferably 0-0.01 wt%, and still more preferably 0-0.001 wt% of an oxide of Cr;

0-5 wt% Fe_2O_3 ;

a filler selected from aluminium silicate, oxides of Al, oxides of Si and mixtures thereof; and optionally binder. A binder is used when preparing a first coating composition.

20 Preferably the first coating composition as hereinbefore described is prepared by mixing the second coating composition as hereinbefore described with binder, and optionally water.

Preferably, the first emissivity agent has a particle size of less than 150 μm , more preferably less than 100 μm . Even more preferably, the first emissivity agent has a
25 particle size in the range of 10 to 60 μm , more preferably in the range of 20 to 60 μm . Such particle sizes provide the coating produced from the coating composition with good mechanical properties. If present, the second emissivity agent, which is a metallic oxide, preferably has a particle size in the range of 10 to 60 μm , more preferably in the range of 20 to 60 μm . If present, the third non-metallic oxide emissivity agent preferably has a
30 particle size in the range of 10 to 60 μm , most preferably in the range of 20 to 60 μm . If necessary, the particle size of any of the emissivity agents may be reduced by grinding.

Preferably, filler has a particle size of less than 150 μm , more preferably less than 110 μm .

35 The present invention also provides a method for preparing a coated substrate, comprising the steps:

- a) providing a substrate;
- b) applying a first coating composition as hereinbefore defined onto at least one surface of said substrate; and
- c) heating said coating composition to form the coated substrate.

5 In preferred methods of the invention the substrate is selected from a shaped refractory, an unshaped or monolithic refractory, or an insulating or fiber material. Representative examples of shaped refractories include fireclay brick, silica brick, high alumina brick, and magnesia brick. Representative examples of unshaped or monolithic refractories include castable refractory, plastic refractory and ramming mix refractories.

10 Representative examples of insulating or fiber material include insulating firebricks, ceramic modules, fiberlite, fiber board and ceramic fibers. In preferred methods of the invention, the substrate is a refractory, preferably a fireclay brick, an insulating firebrick, a plastic refractory or a ceramic fiber.

15 The substrate may be an inner lining, structure and/or part of a furnace (e.g. a cracking furnace in a petrochemical plant), a fire heater, preheater, reformer, other refractory equipment in the field, ceramic automotive parts, refractory aerospace parts, or marine parts that are subjected to high temperature when in use. In preferred methods of the invention the coating and heating step is carried out on a refractory *in situ* in a furnace.

20 Optionally a primer is applied to the at least one surface of the substrate prior to application of the first coating composition of the invention. When a primer is employed, any conventional primer may be employed. However, an advantage of the first coating composition of the present invention, is that a primer is not required.

25 In preferred methods of the invention, the first coating composition is applied in step (b) by a method selected from spray coating, brush coating, dip coating or combinations thereof. More preferably, the first coating composition is applied in step (b) by spray coating, even more preferably by air spray coating or airless spray coating.

30 In preferred methods of the invention, step (c) provides a layer of coating composition having a thickness of 100 to 300 μm , more preferably 150 to 250 μm (e.g. 200 μm).

 In preferred methods of the invention, the step (c) heating is at a temperature of 500 °C to 1700 °C, more preferably 1000 °C to 1500 °C (e.g. 1200 °C).

 In preferred methods of the invention, the step (c) heating is for at least 1 hr.

The heating step (c) employed in the methods of the invention preferably removes water from the coating composition (e.g. by evaporation), increases coating strength and/or increases adhesion between coating and substrate.

5 The present invention also provides a coated substrate, preferably a coated refractory (e.g. a coated shaped refractory, a coated unshaped refractory), a coated insulating material or a coated ceramic fiber, obtainable by or obtained by the method hereinbefore described.

10 The present invention also provides a coated substrate, preferably a coated refractory (e.g. a coated shaped refractory, a coated unshaped refractory), a coated insulating material or a coated ceramic fiber, wherein said coating is derived from a first coating composition as hereinbefore described. Preferred coated substrates are derived from preferred first coating composition.

The present invention also provides a furnace comprising a coated substrate as hereinbefore described.

15 The present invention also provides the use of a coating composition as hereinbefore described to coat a substrate.

20 It will be appreciated that, although specific embodiments of the present invention have been described herein for the purposes of illustration, various modifications may be made without departing from the scope of the disclosure. Accordingly, the disclosure is not limited except as by the appended claims.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a graph showing total emissivity versus temperature for coatings of the invention as well as a comparative coating.

25

EXAMPLES

Materials

All starting materials were commercially available.

30 Measurement methods

Emissivity was measured across the spectral range of 400-12000cm⁻¹ using a system comprised of a computer controlled circular turntable equipped with a blackbody reference and a heating system based on a CO₂ laser. The system combines two spectrometers. The first one is used to obtain emittance spectra in far and mid infrared

ranges, while the second one is used to acquire emittance between mid-infrared and visible spectral ranges. The system provides emittance measurements in the spectral range from far infrared up to visible light and across a wide range of temperature. The total emissivity of coatings is computed by integrating the product of the spectral

5 emissivity and the black body energy over the measured entire spectrum.

Adhesion was measured according to ASTM-D4541-17 (published 2017), wherein a dolly comprising a layer of glue is brought into contact with a coated substrate to determine how strongly the coating is attached to the substrate.

Abrasion resistance was measured according to ASTM-D968-15 (published

10 2015), wherein a 10 kg load of SiC particles (size 1.4 to 2.0 mm) is dropped onto the coating and resultant weight loss from the coating is measured.

Thermal shock resistance was measured by heating a coated sample up to 1200 °C in a furnace, using a heating rate of 1 °C/min. The sample was then held at 1200 °C for 15 min before being taken out of the furnace and being allowed to cool at room

15 temperature. The sample weight was then evaluated. This process was repeated for 32 cycles, with the sample weight being measured, and the appearance of the coating being observed, at the end of each cycle.

Thermal resistance at 1500 °C was measured by heating a coated sample up to target temperature, using a heating rate of 1 °C/min. The sample was then held at target

20 temperature for 5 hours before being allowed to cool at room temperature, then being taken out of the furnace and the appearance of the coating being observed.

Substrates

Emissivity was tested using sapphire as the substrate to obtain the intrinsic

25 emissivity of the coating. The sapphire (single crystal of Al_2O_3) wafer had a thickness of 0.5 mm +/- 0.05 mm

Otherwise the substrates selected for testing were HI28 and SK34. HI28 is an insulating firebrick according to ASTM C 155, Group No. 28 widely used as linings in petrochemical boilers. SK34 is a super-duty fireclay brick according to ASTM C27,

30 regular type. SK34 was used as a representative substrate for usage in other pyrolysis industries.

No primer was applied to the substrates prior to application of the coating composition.

Coating compositions and coatings

35

Coating compositions were prepared by mixing all the ingredients together at room temperature (25 °C). The amounts of the various ingredients present in each of the coating compositions is set out in Table 1 below. Amounts are given in wt%, based on the total weight of the coating composition.

5 Comparative coating compositions were also prepared. Comparative example 1 (CE1) is a conventional high emissivity coating composition comprising chromium oxide as the emissivity agent. Comparative example 2 (CE2) is another conventional high emissivity coating composition comprising iron oxide as the emissivity agent.

10 The coating compositions were applied to a sapphire wafer for emissivity testing and to a substrate (HI28 and/or SK34) for adhesion, abrasion, and thermal shock testing as described below. The performance of the coatings was tested and the results are shown in Figure 1 and in Table 2 below.

- Preparation of sample for testing emissivity

15 The substrate (length 9 mm x width 9 mm x thickness 0.5 mm) was spray coated with the coating composition using an air spray gun. The coated substrate was dried at room temperature (25 °C) overnight (12 hours). The dried coating was calcined at 1200°C for 5 hours (heating rate 1°C/min) in a furnace, and then cooled down to room temperature (25 °C). The final coated substrate was removed from the furnace. The coating
20 thickness was 200 micron.

- Preparation of a coated substrate for testing adhesion, abrasion, and thermal shock

25 The substrates(HI28 and SK34) (length 115 mm x width 75 mm x thickness 15 mm) was spray coated with the coating composition using an air spray gun. The coated substrate was dried at room temperature (25 °C) overnight (12 hours). The dried coating was calcined at 1200 °C for 5 hours (heating rate 1°C/min) in furnace, and then cooled down to room temperature (25 °C). The final coated substrate was removed from the furnace. The coating thickness was 200 micron.

30

- Preparation of coated substrate for testing thermal resistance

35 The substrates (HI28 and SK34) (length 115 mm x width 75 mm x thickness 15 mm) was spray coated with the coating composition using an air spray gun. The coated substrate was dried at room temperature (25 °C) overnight (12 hours). The coating thickness was 200 micron.

Ingredient	Function	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	CE 1	CE 2
Al ₂ O ₃	Filler	22	26	15	15	16	16	16	16
SiO ₂	Filler	3	3	3	7	3	3	3	3
3Al ₂ O ₃ 2SiO ₂	Filler	-	-	13	9	14	-	-	14
SiC	Emissivity agent	12	10	-	-	-	14	14	-
Cr ₂ O ₃	Emissivity agent	-	-	-	-	-	-	6	-
MnO ₂	Emissivity agent	4	5	-	-	-	-	-	-
CeO ₂	Emissivity agent	-	-	6	6	-	-	-	-
CoO	Emissivity agent	-	-	6	6	6	6	-	-
Fe ₂ O ₃	Emissivity agent	-	-	-	-	-	-	-	6
TiO ₂	Emissivity agent	16	13	17	17	18	18	18	18
Phosphoric acid	Binder	15	15	14	14	15	15	15	15
Suspension media	Water	28	28	26	26	28	28	28	28
Total weight (g)		100	100	100	100	100	100	100	100
wt% first emissivity agent		4	5	12	12	6	6	-	-
wt% metal oxide emissivity agent		20	18	29	29	24	24	24	24
Total wt% emissivity agent		32	28	29	29	24	38	38	24

Table 1

	Blank (no coating)	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	CE 1	CE 2
Adhesion/PSI on HI28	121	130	144	188	148	170	147	136	169
Adhesion/PSI on SK34	635	888	913	747	819	866	1161	725	850
Abrasion (weight loss/g) on HI28	0.245	0.06	0.06	0.05	0.07	0.01	0.02	0.05	0.01
Abrasion (weight loss/g) on SK34	0.08	0.01	0.01	0.03	0.05	0.02	0.05	0.04	0.02
Thermal shock at 32 Cycles on HI28	NA	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Fail at 21 Cycles
Appearance of coating after heating at 1500 °C, 30 minutes on HI28	NA	NA	NA	Pass	Pass	Pass	Pass	Blistering	Pass
Appearance of coating after heating at 1500 °C, 30 minutes on SK34	NA	NA	NA	Pass	Pass	Pass	Pass	Blistering	Pass

Table 2

The results in Figure 1 and Table 2 show that coating compositions of the invention comprising MnO_2 , CeO_2 , CoO or mixtures thereof, and lacking Cr_2O_3 and Fe_2O_3 , produce coatings of comparable, or even improved, performance to conventional emissivity coatings containing Cr_2O_3 and/or Fe_2O_3 . More specifically, the coating compositions of the invention produce coatings with high-emissivity at high temperature (i.e. $>1000\text{ }^\circ\text{C}$), as well as adhesion to refractory substrates, abrasion resistance and thermal shock resistance. These are the properties required of high emissivity coatings for use in furnaces.

The results in Figure 1 show that examples 1, 3 and 6 of the present invention possess higher emissivity than the Blank (no coating). Example 6 also shows higher emissivity than CE.1, which contains Cr_2O_3 . Example 3 possesses an emissivity comparable to CE.1. Example 1 possess lower emissivity than CE. 1 but provides improved emissivity over the blank, whilst still lacking Cr_2O_3 .

Overall, the coating compositions of examples 1 and 2 perform similarly to a conventional Cr-containing coating (CE1) whilst examples 3-6 outperform the coating composition of CE1 on emissivity at high temperature and resistance to high temperatures.

Advantageously, the coating compositions of the invention do not require the presence of SiC to achieve the properties making them useful as high emissivity coatings (e.g. see example 4).

CLAIMS:

1. A coating composition, preferably a high emissivity coating composition, and more preferably a high emissivity coating composition in the form of a suspension, comprising:

- (i) 2-20 wt%, preferably 3-15 wt%, of a first emissivity agent selected from oxides of Mn, Ce, Co and mixtures thereof;
- (ii) 10-22 wt% of a second emissivity agent which is a metallic oxide selected from titanium dioxide, nickel oxide, magnesium oxide, copper oxide, terbium oxide, and mixtures thereof;
- (iii) 0-18 wt% of a third emissivity agent which is a non-metallic oxide emissivity agent selected from silicon carbide (SiC), boron silicide (B₄Si), boron carbide (B₄C), silicon hexaboride (SiB₆), molybdenum disilicide (MoSi₂), tungsten disilicide (WSi₂), zirconium diboride (ZrB₂), and mixtures thereof;
- (iv) 0-0.01 wt% of an oxide of Cr;
- (v) 0-1000 ppm Fe₂O₃;
- (vi) 10-35 wt% filler selected from aluminium silicate, oxides of Al, oxides of Si and mixtures thereof; and
- (vii) 10-20 wt% binder;

wherein the total content of said first, second and third emissivity agents in said composition is 15-45 wt%, based on the total weight of the composition.

2. A coating composition, preferably a high emissivity coating composition, and more preferably a high emissivity coating composition in the form of a powder, comprising:

- (i) 5-25 wt% of a first emissivity agent selected from oxides of Mn, Ce, Co and mixtures thereof;
- (ii) 22-32 wt% of a second emissivity agent which is a metallic oxide selected from titanium dioxide, nickel oxide, magnesium oxide, copper oxide, terbium oxide, and mixtures thereof;
- (iii) 0-25 wt% of a third emissivity agent which is a non-metallic oxide emissivity agent selected from silicon carbide (SiC), boron silicide (B₄Si), boron carbide (B₄C), silicon hexaboride (SiB₆), molybdenum disilicide (MoSi₂), tungsten disilicide (WSi₂), zirconium diboride (ZrB₂), and mixtures thereof;
- (iv) 0-0.01 wt%, of an oxide of Cr;

(v) 0-1000 ppm Fe_2O_3 ; and

(vi) 30-60 wt% filler selected from aluminium silicate, oxides of Al, oxides of Si and mixtures thereof;

wherein the total content of said first, second and third emissivity agents in said composition is 40 to 75 wt%, based on the total weight of the composition.

3. A composition as claimed in claim 1 or 2, wherein said composition comprises 0-0.001 wt% of an oxide of Cr.

10 4. A composition as claimed in claim 1 or 2, wherein said composition does not comprise an oxide of Cr selected from CrO , Cr_2O_3 , CrO_2 , CrO_3 , CrO_5 and mixtures thereof.

15 5. A composition as claimed in claim 1, and any one of claims 3 or 4 when dependent on claim 1, wherein the total content of said first, second and third emissivity agents in said composition is 16-38 wt%, based on the total weight of the composition.

20 6. A composition as claimed in claim 1, and any one of claims 3-5 when dependent on claim 1, wherein the amount of said filler is 15 to 35 wt%, based on the total weight of the composition.

25 7. A composition as claimed in claim 1, and any one of claims 3-6 when dependent on claim 1, wherein the amount of binder is 10 to 15 wt%, based on the total weight of the composition and/or wherein said binder is phosphoric acid (H_3PO_4).

8. A composition as claimed in claim 1, and any one of claims 3-7 when dependent on claim 1, comprising water, preferably 10-40 wt% water.

30 9. A composition as claimed in claim 2, and any one of claims 3 or 4 when dependent on claim 2, comprising one of the following mixtures of emissivity agents:

MnO_2 , TiO_2 and SiC ;

CeO_2 , CoO and TiO_2 ;

CoO and TiO_2 ;

CoO , TiO_2 and SiC ; and

35 CeO_2 , TiO_2 and SiC .

10. A composition as claimed in claim 2, and any one of claims 3, 4 or 9 when dependent on claim 2, wherein the total content of said first, second and third emissivity agents in said composition is 40-70 wt%, based on the total weight of the composition.

5 11. A composition as claimed in any preceding claim, wherein the weight ratio of said first emissivity agent to said filler is 0.12:1 to 0.5:1, preferably 0.15:1-0.4:1, more preferably 0.18:1-0.35:1 and still more preferably 0.25:1-0.32:1.

12. A package containing a composition as claimed in any one of claims 1-11.

10

13. A method for preparing a coating composition as claimed in any one of claims 1-11, comprising mixing:

a first emissivity agent selected from oxides of Mn, Ce, Co and mixtures thereof;

a second emissivity agent which is a metallic oxide selected from titanium dioxide, nickel oxide, magnesium oxide, copper oxide, terbium oxide, and mixtures thereof;

15

a third emissivity agent which is a non-metallic oxide emissivity agent selected from silicon carbide (SiC), boron silicide (B₄Si), boron carbide (B₄C), silicon hexaboride (SiB₆), molybdenum disilicide (MoSi₂), tungsten disilicide (WSi₂), zirconium diboride (ZrB₂), and mixtures thereof;

20

0-0.01 wt% wt% of an oxide of Cr;

0-1000 ppm Fe₂O₃;

a filler selected from aluminium silicate, oxides of Al, oxides of Si and mixtures thereof; and optionally binder

25

14. A method for preparing a coated substrate, comprising the steps:

a) providing a substrate;

b) applying a coating composition as defined in claim 1 or any one of claims 3 to 11 when dependent on claim 1, onto at least one surface of said substrate; and

c) heating said coating composition to form the coated substrate.

30

15. A coated substrate obtainable by or obtained by the method according to claim 14.

35

16. A coated substrate comprising a composition as defined in claim 1, or any one of claims 3 to 11 when dependent on claim 1, preferably a coated shaped refractory, a coated unshaped refractory, a coated insulating material or a coated ceramic fiber.

17. A coated substrate, preferably a coated refractory, wherein said coating is derived from a coating composition comprising:

- 5 (i) 2-20 wt% of a first emissivity agent selected from oxides of Mn, Ce, Co and mixtures thereof;
- (ii) 10-22 wt% of a second emissivity agent which is a metallic oxide selected from titanium dioxide, nickel oxide, magnesium oxide, copper oxide, terbium oxide, and mixtures thereof;
- 10 (iii) 0-18 wt% of a third emissivity agent which is a non-metallic oxide emissivity agent selected from silicon carbide (SiC), boron silicide (B₄Si), boron carbide (B₄C), silicon hexaboride (SiB₆), molybdenum disilicide (MoSi₂), tungsten disilicide (WSi₂), zirconium diboride (ZrB₂), and mixtures thereof;
- (iv) 0-0.01 wt%, and still more preferably 0-0.001 wt% of an oxide of Cr;
- (v) 0-1000 ppm Fe₂O₃;
- 15 (vi) 10-35 wt% filler selected from aluminium silicate, oxides of Al, oxides of Si and mixtures thereof; and
- (vii) 10-20 wt% binder;

wherein the total content of said first, second and third emissivity agents in said composition is preferably 15-45 wt%, based on the total weight of the composition and
20 preferably wherein the weight ratio of said first emissivity agent to said filler is 0.12:1 to 0.5:1.

18. A furnace comprising a coated substrate according to any one of claims 15 to 17.

25 19. Use of a coating composition as defined in claim 1 or any one of claims 3 to 11 when dependent on claim 1, to coat a substrate.