Process for protecting a metal substrate from corrosion under insulation

The invention relates to a process for protecting a metal substrate from corrosion under insulation. In particular, the invention relates to a process for protecting a metal substrate from corrosion under insulation by providing the metal substrate under thermal insulation with a specific coating. The invention also relates to a metal substrate provided with thermal insulation wherein a specific coating layer is applied between the metal substrate and the thermal insulation.

In industrial applications, metal substrates are often provided with a layer of thermal insulation. This applies to all kinds of industrial equipment, including pipelines, storage vessels, reactors, heat exchangers, and other equipment. Layers of thermal insulation are generally relatively thick. This is necessary to ensure that the layer insulates adequately. One problem with thermal insulation is that it sometimes becomes detached from the underlying substrate. This creates the risk of water or other corrosive chemicals getting between the metal substrate and the layer of thermal insulation. This can give rise to corrosion, also referred to as "corrosion under insulation." Corrosion under insulation is particularly troublesome for a number of reasons. First, the atmosphere in the space between the metal substrate and the thermal insulation layer is often such that corrosion is favored, for example, due to high humidity, relatively high temperature, and possibly the presence of salts. The detachment of the thermal insulation and the entry of water or other corrosive chemicals between the metal substrate and thermal insulation is not always easy to see externally, making it difficult to take timely action. Furthermore, to repair the corrosion, it is necessary to remove the thermal insulation, with associated costs and downtime.

There is therefore a need for a process for protecting a metal substrate from corrosion under insulation. The invention provides such a process.

The invention pertains to a process for protecting a metal substrate from corrosion under insulation comprising the steps of

- applying a layer of a coating composition to a metal substrate,
- curing of the coating composition, and
- application of a layer of thermal insulation

wherein the coating composition comprises

- metal particles with an average diameter in the range of 20-120 microns, in an amount of 50-95 wt.%, calculated on the total weight of the coating composition,
- curable resin, in an amount of 5-50 wt.%, calculated on the total weight of the coating composition, wherein the curable resin is selected from the group of epoxy resins, acrylic resins, and polyester resins,
- catalyst suitable for accelerating curing of the curable resin,
- and the coating layer after curing has a total layer thickness of 50-2000 microns.

It has been found that a metal substrate is coated with a composition as described above, a coating is obtained that gives excellent results in protecting a metal substrate from corrosion under insulation. The coating has excellent adhesion properties, wear properties, and anti-corrosion properties. The coating can be easily applied by spraying and cured under relatively mild conditions. Additionally, it has been found that the coating used in the present invention is able to withstand severe expansion and contraction of the underling substate. This is important because the substrates are often part of apparatus which may be subject to large changes in temperature. It has further been found that the coating shows self-healing properties.

The invention and the advantages associated therewith are further explained below.

The coating composition comprises metal particles. The metal particles may be particles of any known metal. It is preferred if the metal particles are selected from the group of aluminium, zinc, tin, magnesium and combinations, and where applicable, alloys thereof. The use of aluminium and/or zinc is particularly preferred.

It is particularly preferred if of the total metal particles at least 50 wt.% are aluminium particles, in particular at least 70 wt.%, more particularly at least 80 wt.%, preferably at least 90 wt.%. In one embodiment, all metal particles are aluminium particles. Aluminium has a lower density than zinc, giving the coating a lower weight for a defined thickness. Moreover, a coating with aluminium particles appears to be easier to spray in thick layers, up to, say, 500 microns without intermediate drying, and on vertical surfaces than a coating with zinc particles, without the coating running off or sagging. It also appears that the life of a coating with aluminium particles is longer than the life of a coating with zinc particles. A coating based on aluminium particles applied in one layer with a wet thickness of 500 microns and a thickness after drying of 450 microns has a theoretical lifetime of 60 years.
A further advantage of using aluminium particles is that the coating composition in the pot is less prone to sagging than when zinc particles are used. This means that the "pot-life" of the

coating composition is longer. It has also been shown that a coating with aluminium particles has high flexibility. This means not only that the coating layer is more resistant to impact, bending, and denting, but also that it is possible to further process coated sheets, by bending and even rolling, without damaging the coating layer.

The metal particles have an average diameter in the range of 20-120 microns. The average diameter is the D50, that is, the value at which 50% of the particles have a larger diameter and 50% have a lower diameter. Particle size distribution can be determined as is conventional in the field, e.g. through laser diffraction. If the particles are too large, the homogeneity of the coating layer decreases, and thus the degree of coverage of the substrate. If the particle are too small, it is difficult to obtain a layer of sufficient thickness and homogeneity. The particle size distribution is determined by volume, as is conventional in this field.
It is preferred if the metal particles have an average diameter in the range of 20 to 100 microns, more preferably 30 to 90 microns, even more preferably 40 to 80 microns. Suitable metal particles are commercially available.

Metal particles are present in the coating composition in an amount of 50-95 wt.%, calculated on the total weight of the coating composition before application to the substrate.
It is one of the advantages of the invention that the coating composition has a relatively high metal content, so the final coating layer contains a lot of metal. This contributes to the good corrosion-resistant results of the composition in the application against corrosion under insulation. Therefore, it is preferred if the composition contains at least 60 wt.% metal, preferably at least 65 wt.%, sometimes even at least 70 wt.%. On the other hand, there must be enough space for the resin, catalyst, and any further components. Therefore, the amount of metal particles is at most 95 weight %, and it may be desirable if the composition comprises at most 90 weight % metal particles, or at most 85 weight % metal particles.

The exact amount of metal particles also depends on the particle size of the metal particles, and further properties. In some cases, particularly if the metal is aluminium or if particles with an average particle size greater than 55 microns are used, it may be preferable if the composition contains 50-80 wt.% of metal particles, particularly 50-70 wt.%

The composition contains a curable resin selected from the group of epoxy resins, acrylic resins, and polyester resins. Polyester resins are preferred, among others because their flexibility makes them particularly suitable for use on substrates which contract and expand. A heat-curable resin is preferred. It is particularly preferred for the resin to be curable at a

temperature of at most 100ºC, in particular at most 60ºC, more in particular at most 45ºC, or at most 40ºC. Suitable resin compositions are well known and need no further explanation. The presence of curable resins other than those mentioned is neither necessary nor desirable. Therefore, in one embodiment, the coating composition does not contain more than 10 wt.%, particularly not more than 5 wt.% of curable resins other than those specified above.

The resin is present in an amount of 5-50 wt.%, calculated on the amount of the coating composition. If less than 5 wt.% resin is present, insufficient binding is obtained. If more than 50 wt.% resin is present, there is insufficient space for the other components of the composition, especially for the metal particles. It is preferable if the resin is present in an amount of 5-40 wt.%, particularly 5-30 wt.%, even more particularly 5-25 wt.%, calculated as resin polymer to the total weight of the composition.

The composition also contains a catalyst. The catalyst is chosen to suit the curing mechanism of the resin. A catalyst for a heat-curable resin is preferred. Suitable catalysts are known and need no further explanation. The catalyst is applied in the usual amounts known in the field, generally in the range of 0.001 – 2 wt.%, calculated on the weight of the coating composition.

The coating composition may contain an organic diluent, for example in an amount of 2-40 wt.% calculated on the total coating composition. This is often desirable to give the composition good processing properties, particularly a sufficiently low viscosity. Application of less than 2 wt.% diluent usually does not achieve the effect of the diluent. Application of more than 40 wt.% of diluent detracts from the quantities of the other ingredients. It may be attractive to use at least 5 wt.% diluent, and/or at most 35 wt.%, more preferably at most 30 wt.%.

Suitable diluents include, for example, organic diluents such as alcohols with, for example, 2-10 carbon atoms, such as ethanol, propanol, butanol, and octanol. Other suitable diluents include alkyl esters and alkyl ethers, for example, ethyl acetate, ethyl acetate, methyl ethyl ketone, and methyl isobutyl ketone, and alkyl ethers of glycols. Aromatic hydrocarbons, such as benzene, toluene and xylene can also be used, as well as mixtures of aromatic solvents derived from petroleum.

Preferably, the coating composition contains 5-40 wt.% of a diluent with a boiling point or decomposition point above 60ºC, preferably above 80ºC. Compared to low-boiling solvents such as ethanol, this has the advantage that the diluents remain in the composition for a long

time, thus maintaining good workability. The ranges given above for the total amount of diluent also apply here.

One class of diluents that is particularly preferred are synthetic and natural oils . Suitable natural oils include vegetable oils such as cottonseed oil, peanut oil, coconut oil, cocoa butter, pumpkin seed oil, flaxseed oil, corn oil, olive oil, palm kernel oil, palm oil, rapeseed oil, sesame oil, soybean oil, sunflower oil, grapeseed oil, walnut oil, and wheat germ oil. Animal oils such as fish oil can also be used, as can oil from algae. Suitable oils also include petroleum products such as petroleum fractions, for example, with a boiling point in the range of 50-400ºC, particularly 50-250ºC. Suitable petroleum fractions include gasoline, diesel, and kerosene.
Application of vegetable oils is preferred because they are durable and provide good results. Application of peanut oil, flaxseed oil, corn oil, olive oil, palm oil, rapeseed oil, sunflower oil, sesame oil, or soybean oil is preferred.
Mixtures of different diluents and/or different oils can be used.

It is preferable if the composition includes a total of 5-40 wt.% of synthetic oil and/or natural oil, especially a vegetable oil as indicated above. The ranges given above for the total amount of diluent also apply here.

It is also preferred that of the total amount of diluent in the composition at least 30 wt.% be a synthetic oil or natural oil, in particular a vegetable oil as indicated above, more preferably at least 50 wt.%, even more preferably at least 60 wt.%, or at least 70 wt.%, or at least 80 wt.%.

Because the metal content of the coating is important for the effect, and the inclusion of solid particles other than the metal particles may adversely affect the workability and effect of the composition, it is preferable that of the solid particles in the composition at least 80 wt.% consist of metal particles with an average diameter in the range of 20-120 microns, in particular at least 90 wt.%, even more particularly at least 95 wt.%, or at least 98 wt.%.

The use of glass particles in coating compositions has been described in the literature. For the composition according to the invention, their presence is neither necessary nor desirable. The presence of glass particles occupies volume taken up by metal particles in the coating composition according to the invention. It is therefore preferable if the composition comprises not more than 7 wt.%, preferably not more than 5 wt.%, more preferably not more than 2 wt.% in particular not more than 1 wt.% of glass particles.

In one embodiment, the total of metal particles, resin, catalyst and diluent constitutes at least at least 70 wt.%, in particular at least 80 wt.%, more particularly at least 90 wt.%, specifically at least 95 wt.% of the coating composition.

The substrate that is coated in the process according to the invention is a metal substrate, in particular a metal substrate that may be susceptible to corrosion. Suitable substrates include, for example, steel substrates including ordinary steel, stainless steel (SS), in particular SS 300 series ((304, 316, 316L), and carbon steel. Because the process according to the invention is intended to provide corrosion protection under insulation, the substrate will often be intended for applications in industry, in particular the chemical industry, including the petrochemical industry, such as pipes for water or other industrial liquids or gases, storage vessels, reactors, heat exchangers, and other applications where thermal insulation is used.

The substrate may have been provided with a primer, but this is not required. In one embodiment, the coating composition is applied directly onto a metal substrate, without intermediate layers being present.

The coating composition can be applied in a conventional manner, such as by spraying, rolling, pouring, ironing, and dipping. Application by spraying is preferred because it is a fast and accurate way to apply a coating composition that produces even results. Airless spraying is particularly preferred because it is a known process of spraying large areas. It has been found that the coating composition as used herein can be handled excellently by spraying, in particular airless spraying.

The coating composition may be applied in one or more layers, such as in one, two, three, four, or five layers. In the present specification, a single layer is a layer that has been applied without intermediate curing. If the composition is applied in more layers, the composition must be at least partially cured in between. Depending on the curing mechanism, this can be done easily. It has appeared that that the coating composition as used herein can be applied to a relatively high total layer thickness without intermediate curing being required. This applies in particular to aluminium-based coatings.

After application of the composition, a curing step takes place. How this is done depends on the curing mechanism of the resin used. Curing with heat is preferred. In this case it is preferable if the curing takes place at a temperature from 5-100ºC, in particular 10-60ºC, more particularly 15-45ºC, for example 20-40ºC . The time required depends on the chosen temperature (the lower the temperature, the more time is required). Curing time generally

takes 1-48 hours, more specifically 2-36 hours, for example 4-30 hours. At lower temperatures, the curing time will be longer than at higher temperatures.

After curing, the composition has a total layer thickness of 50-2000 microns. This is the total of all applied layers. At layer thicknesses below 50 microns, the protection against corrosion under insulation is not obtained. Layer thicknesses above 2000 microns often provide no additional benefit. The total layer thickness is preferably at least 75 microns, more preferably at least 100 microns, particularly above 150 microns. The total layer thickness is preferably at most 1500 microns, more preferably at most 1200 microns. The coating thickness to be selected depends on the desired life of the coating layer. In some cases, a layer thickness of at most 1000 microns may be sufficient, or at most 800 microns, or at most 600 microns, or at most 400 microns. It is found that the coating layer according to the invention provides adequate protection even in relatively thin layers.

After application and curing, one or more post-processing steps may optionally be performed. Suitable finishing steps include sanding or polishing to obtain a surface with a metallic appearance. If desired, one or more further coating layers may be applied, but this is not necessary.

The invention also relates to a metal substrate provided with a layer of thermal insulation, wherein between the metal substrate and the layer of thermal insulation a coating layer comprising metal particles and a resin is present, wherein the coating layer is obtained by applying and curing a coating composition, wherein the coating composition comprises

- metal particles with an average diameter in the range of 20-120 microns, in an amount of 50-95 wt.%, calculated on the total weight of the coating composition,
- curable resin, in an amount of 5-50 wt.%, calculated on the total weight of the coating composition, wherein the curable resin is selected from the group of epoxy resins, acrylic resins, and polyester resins,
- catalyst suitable for accelerating curing of the curable resin,
- and the coating layer after curing has a total layer thickness of 50-2000 microns.

The preferences expressed above for the nature of the substrate, the coating composition, layer thicknesses and other features also apply to this embodiment of the present invention.

A layer of thermal insulation is present in the invention. Materials suitable for thermal insulation are known in the field. The invention is suitable for application with all known

thermal insulation layers. In general, thermal insulation layers have a thickness from 0.5 cm to 50 cm, depending on the substrate on which they are applied.
Examples of suitable materials include materials that comprise insulating materials such as insulating fiber layers such as glass wool, rock wool or ceramic fibers, hollow spheres such as glass beads, or materials such as calcium silicate, expanded perlite, or organic or inorganic foams, where the materials may or may not also include a binder.
The thermal insulation can be applied as is known in the art for the various materials. The presence of the anti-corrosion coating according to the invention does not affect this. It is one of the advantages associated with the present invention that the coating layer is easy to apply, as is as described above, and that the presence of this layer does not interfere with the application of the layer of thermal insulation material. This means that the application of the coating layer according to the invention is easy to incorporate into existing manufacturing processes.

According to the invention, a metal substrate is protected from corrosion under insulation. That this effect is achieved is due to the excellent properties of the anti-corrosion coating used in the invention. It should be noted that, as is explained above, the requirements to protect

In one embodiment, the coating exhibits a rating of 0 to 2 in ISO 2409 (Adhesion test for artificial aging of carbon steel and stainless steel test panels, if the coating has a thickness of less than or equal to 250 microns, and where at a cross cut value of 2, a tensile test according to ISO 4624 will be performed).
In one embodiment, the coating shows In one embodiment, the coating shows no adhesive break in ISO2624 between steel and the primer (first coat) (unless pull-off values are 5 MPa or more).

In one embodiment , the coating after exposure according to ISO 9227 (neutral salt spray test) tested after 720 hours of exposure and/or after heat treatment after 480 hours of exposure shows a value 0 (S0) according to ISO 4628-2, a value Ri 0 according to ISO 4628-3, a value 0 (S0) according to ISO 4628-4, a value 0 (S0) according to ISO 4628-5, or a value 2/3 according to ISO 4628-8.
In one embodiment, the coating after exposure according to ISO 2812-2 (water immersion test), after 3000 hours of exposure and/or after heat treatment after 2000 hours of exposure shows a value 0 (S0) according to ISO 4628-2, a value Ri 0 according to ISO 4628-3, a value 0 (S0) according to ISO 4628-4, a value 0 (S0) according to ISO 4628-5, or a value 2/3 according to ISO 4628-8.

In one embodiment the coating shows a rating of 0 to 2 in ISO 2409 (Adhesion test after corrosion tests at ambient temperature for carbon steel test panels after 12 days in a standard atmosphere according to ISO 554, if the coating has a thickness of less than or equal to 250 microns, and where at a cross-cut value of 2 there will be a tensile test according to ISO 4624) .
In one embodiment, the coating shows no adhesive break in ISO2624 between steel and the primer (first coat) (unless pull-off values are 5 MPa or more), after 12 days in a standard atmosphere according to ISO 554.

In one embodiment, the coating satisfies the classification for CUI-1, CUI-2, or CUI-3 according to ISO 19277:2018, after 20 thermal cycles with a minimum temperature of 5ºC and a maximum temperature of 60ºC for CUI-1, after 20 thermal cycles with a minimum temperature of 5ºC and a maximum temperature of 150ºC for CUI-2, and after 20 thermal cycles with a minimum temperature of -5ºC and a maximum temperature of 204ºC for CUI-3, obtaining the following results: a value 0 (S0) according to ISO 4628-2, a value Ri 0 according to ISO 4628-3, a value 0 (S0) according to ISO 4628-4, and a value 0 (S0) according to ISO 4628-5.

In one embodiment, the coating meets the multiphase cyclic CUI test criteria for carbon steel vertical pipe tests in accordance with ISO19277:2018, for CUI-2, or even for CUI-3.

In one embodiment, the coating meets all requirements of CUI-1 of ISO 19277:2018 . In some embodiments, the coating meets all the requirements of CUI-2 of ISO 19277:2018, or even all the requirements of CUI-3 of ISO 19277:2018.

In some embodiments, the coating meets the requirements for cryogenic testing for CUI-1 Cryo, CUI-2 Cryo, or even CUI-3 Cryo, in particular addition to meeting the requirements for CUI-1, CUI-2, and/or CUI-3 according to ISO 19277:2018.

In some embodiments, the coating meets the requirements for insulation for vertical pipes for CUI-2 or even CUI-3 as shown in ISO 19277:2018, in particular addition to meeting the requirements for CUI-1, CUI-2, and/or CUI-3 according to ISO 19277:

It will be clear that preferences and options described for different aspects of the invention can be combined with each other unless they are mutually exclusive.

The invention will be elucidated by the following examples, without being limited thereto or thereby.

Examples

The coating composition tested

A coating composition comprising aluminium particles was prepared by mixing aluminium particles with a curable polyester coating, and a diluent. The composition also contained a catalyst. The aluminium particles had an average particle size of 45 microns. The coating composition contained 55 wt.% aluminium particles. The diluent was a vegetable oil, and was applied in an amount of about 11 wt.%, calculated on the total coating composition.

Example 1: Testing in accordance with ISO19277 – classification environment CUI-1

The coating composition was applied to carbon steel and stainless steel substrates. The substrate properties and application conditions were as follows:

Substrate material	Carbon steel and stainless steel
Surface preparation	Abrasive blasted to Sa 2½ / Sa3 according to ISO 8501-1
Roughness	82 µm according to ISO 8503-5
Water soluble contaminants	17.8 / 18.7 mg/m2 according to ISO 8502-6/9
Dust contamination	D2/S2 according to ISO 8502-3
Coating 1st coat	Coating according to the invention
Method of application	Air spray
Dry film thickness	240 micron
Application environment	
Air temperature [°C]	19.9
Relative Humidity [%]	69.8
Steel temperature [°C]	20.0
Dew point [°C]	14.2

Curing took place under ambient conditions for at least 24 hours.

The following test methods were applied:

Heat conditioning	120 hours	ISO 19277
Neutral salt spray (AC)	720 hours	ISO 9227
Neutral salt spray (HC)	480 hours	ISO 9227
Thermal cycling	20 cycles	ISO 19277
Dry film thickness		ISO2808
Adhesion		ISO 4624
Blistering		ISO 4628-2
Rusting		ISO 4628-3
Cracking		ISO 4628-4
Flaking		ISO 4628-5
Scribe evaluation		ISO 4628-8

The following performance requirements apply:

Assessments before artificial ageing

- Adhesion
  - No adhesive break between steel and the primer (first coat) (unless pull-off values are 5 MPa or more)

Assessments after artificial ageing (neutral salt spray)

- Defect assessment
  - Blistering 0(S0) assessment immediately after artificial ageing
  - Rusting Ri 0 assessment immediately after artificial ageing
  - Cracking 0(S0) assessment immediately after artificial ageing
  - Flaking 0(S0) assessment immediately after artificial ageing
  - Scribe evaluation 2/3 assessment within 8 hours after artificial ageing
- Adhesion
  - No adhesive break between steel and the primer (first coat) (unless pull-off values are 5 MPa or more). assessment after 12 days in standard atmosphere as defined in ISO 554

Assessments after thermal cycling

- Defect assessment
  - Blistering 0(S0) assessment immediately after thermal cycling
  - Rusting Ri 0 assessment immediately after thermal cycling
  - Cracking 0(S0) assessment immediately after thermal cycling

- Flaking 0(S0) assessment immediately after thermal cycling

For CUI-1 heat conditioning included an exposure cycle which was repeated a total of 5 times, providing a total of 100 hours exposure at a maximum temperature of the CUI-1 classification of 60ºC and 20 hours of air cooling times. Each cycle includes 20 hours of exposure to the maximum temperature of the classification of 60ºC and 4 hours of exposure to air at 23ºC.

For CUI-1 thermal cycling included an exposure cycle which was repeated a total of 20 times, with each cycle including exposure to the maximum temperature of the classification of 60ºC and immediate exposure to ice water at 5ºC.

The results of the various tests are summarised below:

	Adhesion [MPa]	Mean calculated delamination/corrosion at scribe [mm]	Blistering, rusting, cracking, flaking?
Carbon steel, without heat conditioning, before artificial aging (3 samples)	10-11	Nd	Nd
Carbon steel, heat conditioned, before artificial aging (3 samples)	11-12	Nd	Nd
Stainless steel, without heat conditioning, before artificial aging (3 samples)	9-10	Nd	Nd
Stainless steel, heat conditioned, before artificial aging (3 samples)	7-8	Nd	Nd
Carbon steel, without heat conditioning, 720 hours neutral salt spray (3 samples)	8-10	0/0	No defects
Carbon steel, heat conditioned, 480 hours neutral salt spray (3 samples)	8-10	0/0	No defects in 2 samples, minor rusting in one sample
Carbon steel, without heat conditioning, 20 thermal cycles (3 samples)	Nd	Nd	No defects
Carbon steel, heat conditioned, 20 thermal cycles (3 samples)	Nd	Nd	No defects

Stainless steel, without heat conditioning, 20 thermal cycles (3 samples)	Nd	Nd	No defects
Stainless steel, heat conditioned, 20 thermal cycles (3 samples)	Nd	Nd	No defects

Thus, for all tests the panels meet the requirements of ISO19277 – classification environment CUI-1.

Example 2: Testing in accordance with ISO19277 – classification environment CUI-2

The coating composition, substrate properties, and application conditions were the same as for Example 1.

The following test methods were applied:

Heat conditioning	120 hours	ISO 19277
Neutral salt spray (AC)	720 hours	ISO 9227
Neutral salt spray (HC)	480 hours	ISO 9227
Thermal cycling	20 cycles	ISO 19277
Dry film thickness		ISO2808
Adhesion		ISO 4624
Blistering		ISO 4628-2
Rusting		ISO 4628-3
Cracking		ISO 4628-4
Flaking		ISO 4628-5
Scribe evaluation		ISO 4628-8

The following performance requirements apply:

Assessments before artificial ageing

- Adhesion
    - No adhesive break between steel and the primer (first coat) (unless pull-off values are 5 MPa or more)

Assessments after artificial ageing (neutral salt spray)

- Defect assessment
    - Blistering 0(S0) assessment immediately after artificial ageing

- Rusting Ri 0 assessment immediately after artificial ageing
- Cracking 0(S0) assessment immediately after artificial ageing
- Flaking 0(S0) assessment immediately after artificial ageing
- Scribe evaluation 2/3 assessment within 8 hours after artificial ageing

- Adhesion
  - No adhesive break between steel and the primer (first coat) (unless pull-off values are 5 MPa or more). assessment after 12 days in standard atmosphere as defined in ISO 554

Assessments after thermal cycling

- Defect assessment
  - Blistering 0(S0) assessment immediately after thermal cycling
  - Rusting Ri 0 assessment immediately after thermal cycling
  - Cracking 0(S0) assessment immediately after thermal cycling
  - Flaking 0(S0) assessment immediately after thermal cycling

For CUI-2 heat conditioning includes an exposure cycle which was repeated a total of 5 times, providing a total of 100 hours exposure at a maximum temperature of the CUI-2 classification of 150ºC and 20 hours of air cooling times. Each cycle includes 20 hours of exposure to the maximum temperature of the classification of 60ºC and 4 hours of exposure to air at 23ºC.

For CUI-2 thermal cycling included an exposure cycle which was repeated a total of 20 times, with each cycle including exposure to the maximum temperature of the classification of 150ºC and immediate exposure to ice water at 5ºC.

The results of the various tests are summarised below:

	Adhesion [MPa]	Mean calculated delamination/corrosion at scribe [mm]	Blistering, rusting, cracking, flaking?
Carbon steel, without heat conditioning, before artificial aging (3 samples)	11-13	Nd	Nd
Carbon steel, heat conditioned, before artificial aging (3 samples)	12-14	Nd	Nd

Stainless steel, without heat conditioning, before artificial aging (3 samples)	8-9	Nd	Nd
Stainless steel, heat conditioned, before artificial aging (3 samples)	11-12	Nd	Nd
Carbon steel, without heat conditioning, 720 hours neutral salt spray (3 samples)	9-10	0/0 (2 samples) 0/1 (1 sample)	No defects
Carbon steel, heat conditioned, 480 hours neutral salt spray (3 samples)	9-10	0/0	No defects in 2 samples, minor rusting in one sample
Carbon steel, without heat conditioning, 20 thermal cycles (3 samples)	Nd	Nd	No defects
Carbon steel, heat conditioned, 20 thermal cycles (3 samples)	Nd	Nd	No defects
Stainless steel, without heat conditioning, 20 thermal cycles (3 samples)	Nd	Nd	No defects
Stainless steel, heat conditioned, 20 thermal cycles (3 samples)	Nd	Nd	No defects

Thus, for all tests the panels meet the requirements of ISO19277 – classification environment CUI-2.

Example 3: Testing in accordance with ISO19277 – classification environment CUI-3

The coating composition, substrate properties, and application conditions were the same as for Example 1.

The following test methods were applied:

Heat conditioning	120 hours	ISO 19277
Neutral salt spray (AC)	720 hours	ISO 9227
Neutral salt spray (HC)	480 hours	ISO 9227
Thermal cycling	20 cycles	ISO 19277
Dry film thickness		ISO 2808

Adhesion		ISO 4624
Blistering		ISO 4628-2
Rusting		ISO 4628-3
Cracking		ISO 4628-4
Flaking		ISO 4628-5
Scribe evaluation		ISO 4628-8

The following performance requirements apply:

Assessments before artificial ageing

- Adhesion
  - No adhesive break between steel and the primer (first coat) (unless pull-off values are 5 MPa or more)

Assessments after artificial ageing (neutral salt spray)

- Defect assessment
  - Blistering 0(S0) assessment immediately after artificial ageing
  - Rusting Ri 0 assessment immediately after artificial ageing
  - Cracking 0(S0) assessment immediately after artificial ageing
  - Flaking 0(S0) assessment immediately after artificial ageing
  - Scribe evaluation 2/3 assessment within 8 hours after artificial ageing
- Adhesion
  - No adhesive break between steel and the primer (first coat) (unless pull-off values are 5 MPa or more). assessment after 12 days in standard atmosphere as defined in ISO 554

Assessments after thermal cycling

- Defect assessment
  - Blistering 0(S0) assessment immediately after thermal cycling
  - Rusting Ri 0 assessment immediately after thermal cycling
  - Cracking 0(S0) assessment immediately after thermal cycling
  - Flaking 0(S0) assessment immediately after thermal cycling

For CUI-3 heat conditioning included an exposure cycle which was repeated a total of 5 times, providing a total of 100 hours exposure at a maximum temperature of the CUI-3 classification of 204ºC and 20 hours of air cooling times. Each cycle includes 20 hours of

exposure to the maximum temperature of the classification of 204ºC and 4 hours of exposure to air at 23ºC.

For CUI-3 thermal cycling included an exposure cycle which was repeated a total of 20 times, with each cycle including exposure to the maximum temperature of the classification of 204ºC and immediate exposure to ice water at 5ºC.

The results of the various tests are summarised below:

	Adhesion [MPa]	Mean calculated delamination/corrosion at scribe [mm]	Blistering, rusting, cracking, flaking?
Carbon steel, without heat conditioning, before artificial aging (3 samples)	11-12	Nd	Nd
Carbon steel, heat conditioned, before artificial aging (3 samples)	12-13	Nd	Nd
Stainless steel, without heat conditioning, before artificial aging (3 samples)	8-9	Nd	Nd
Stainless steel, heat conditioned, before artificial aging (3 samples)	10-11	Nd	Nd
Carbon steel, without heat conditioning, 720 hours neutral salt spray (3 samples)	7-10	0/0 (2 samples) 0/1 (1 sample)	No defects in one sample, minor rusting in 2 samples
Carbon steel, heat conditioned, 480 hours neutral salt spray (3 samples)	0-10	0/0	Minor rusting in all samples
Carbon steel, without heat conditioning, 20 thermal cycles (3 samples)	Nd	Nd	No defects
Carbon steel, heat conditioned, 20 thermal cycles (3 samples)	Nd	Nd	No defects
Stainless steel, without heat conditioning, 20 thermal cycles (3 samples)	Nd	Nd	No defects
Stainless steel, heat conditioned, 20 thermal cycles (3 samples)	Nd	Nd	No defects

Thus, for most tests the panels meet the requirements of ISO 19277 – classification environment CUI-3.

39737 HS

CLAIMS

1. Process for protecting a metal substrate from corrosion under insulation comprising the steps of
- applying a layer of a coating composition to a metal substrate,
- curing of the coating composition, and
- application of a layer of thermal insulation
wherein the coating composition comprises
- metal particles with an average diameter (D50) in the range of 20-120 microns, in an amount of 50-95 wt.%, calculated on the total weight of the coating composition,
- curable resin, in an amount of 5-50 wt.%, calculated on the total weight of the coating composition, wherein the curable resin is selected from the group of epoxy resins, acrylic resins, and polyester resins,
- catalyst suitable for accelerating curing of the curable resin,
- and the coating layer after curing has a total layer thickness of 50-2000 microns.

2. Process according to claim 1, wherein the curable resin is an acrylic resin.

3. Process according to claim 1, wherein the curable resin is a polyester resin.

4. Process according to any one of the preceding claims, wherein the metal particles are selected from the group consisting of aluminum, zinc, tin, magnesium and combinations, and where applicable, alloys thereof, wherein the use of aluminum and/or zinc is particularly preferred.

5. Process according to claim 4, wherein of the total metal particles at least 50 wt.% are aluminium particles, more particularly at least 70 wt.%, more particularly at least 80 wt.%, preferably at least 90 wt.%.

6. Process according to any of the preceding claims, wherein the metal particles have an average diameter in the range of 20 to 100 microns, preferably 30 to 90 microns, more preferably 40 to 80 microns.

7. Process according to any one of the preceding claims, wherein the coating composition comprises metal particles in an amount of 60-95 wt.%, calculated on the total

weight of the coating composition, in particular 65-90 wt.%, more particularly 70-85 wt.%, or, in particular if the metal is aluminium or if particles with an average particle size of more than 55 microns are used, 50-80 wt.% metal particles, more particularly 50-70 wt.%.

8. Process according to any of the preceding conclusions, wherein the curable resin is a heat-curable resin.

9. Process according to any of the preceding claims, wherein the resin is present in an amount of 5-40 wt.%, in particular 5-30 wt.%, still more particularly 5-25 wt.%, calculated as resin polymer on the total weight of the composition.

10. Process according to any of the preceding claims, wherein the coating composition further comprises an organic diluent, for example, in an amount of 2-40 wt.%, preferably at least 5 wt.%, and/or at most 35 wt.%, more preferably at most 30 wt.%.

11. Process according to claim 10, wherein the diluent is selected from synthetic or natural oils, preferably vegetable oils and/or petroleum fractions, especially vegetable oils.

12. Process according to any of the preceding claims, wherein the substrate is a metallic substrate for applications in industry, in particular the chemical industry, including the petrochemical industry, such as pipes for water or other industrial liquids or gases, storage vessels, reactors, heat exchangers, and other applications where thermal insulation is used.

13. Process according to any of the preceding claims, wherein the coating composition is applied by spraying, rolling, pouring, ironing, dipping, in particular by spraying, more particularly by airless spraying.

14. Process according to any of the preceding claims, wherein the coating composition is cured at a temperature of 5-100ºC, in particular 10-60ºC, more particularly 15-45ºC, for example 20-40ºC, for 1-48 hours, in particular 2-36 hours, for example 4-30 hours.

15. Process according to any of the preceding claims, wherein the total layer thickness of the coating compostion is at least 75 microns, preferably at least 100 microns, in particular more than 150 microns and/or at most 1500 microns, preferably at most 1200 microns, or at most 1000 microns, or at most 800 microns, or at most 600 microns, or at most 400 microns.

16. Metal substrate provided with a layer of thermal insulation, wherein between the metal substrate and the layer of thermal insulation a coating layer comprising metal particles and a resin is present, wherein the coating layer is obtained by applying and curing a coating composition, wherein the coating composition comprises
- metal particles with an average diameter in the range of 20-120 microns, in an amount of 50-95 wt.%, calculated on the total weight of the coating composition,
- curable resin, in an amount of 5-50 wt.%, calculated on the total weight of the coating composition, wherein the curable resin is selected from the group of epoxy resins, acrylic resins, and polyester resins,
- catalyst suitable for accelerating curing of the curable resin,
- and the coating layer after curing has a total layer thickness of 50-2000 microns.

17. Metal substrate according to claim 16, wherein the thermal insulation layer has a thickness of 0.5-50 cm.

18. Metal substrate according to any of claims 16-17, wherein the thermal insulation layer comprises an insulating material, in particular a material selected from the group of insulating fiber layers such as glass wool, rock wool or ceramic fibers, hollow spheres such as glass spheres, or materials such as calcium silicate, expanded perlite, or organic or inorganic foams, wherein the materials may or may not also comprise a binder.

19. Process according to any of claims 1-15 or metal substrate according to any of claims 16-18, wherein the coating meets one or more of the following standards and requirements:
- immediately after application, the coating has a rating of 0 to 2 in ISO 2409 (Adhesion test for artificial aging of carbon steel and stainless steel test panels, if the coating has a thickness of less than or equal to 250 microns, and where at a cross-cut value of 2 a tensile test according to ISO 4624 will be performed);
- immediately after application, the coating shows no adhesive break in ISO2624 between steel and the primer (first coat) (unless pull-off values are 5 MPa or more);
- the coating shows after exposure according to ISO 9227 (neutral salt spray test) tested after 720 hours of exposure and/or after heat treatment after 480 hours of exposure a value 0 (S0) according to ISO 4628-2, a value Ri 0 according to ISO 4628-3, a value 0 (S0) according to ISO 4628-4, a value 0 (S0) according to ISO 4628-5, or a value 2/3 according to ISO 4628-8;
- the coating shows after exposure according to ISO 2812-2 (water immersion test), after 3000 hours of exposure and/or after heat treatment after 2000 hours of exposure a value 0 (S0) according to ISO 4628-2, a value Ri 0 according to ISO

4628-3, a value 0 (S0) according to ISO 4628-4, a value 0 (S0) according to ISO 4628-5, or a value 2/3 according to ISO 4628-8;

- the coating exhibits a rating of 0 to 2 in ISO 2409 (Adhesion test after corrosion tests at ambient temperature for carbon steel test panels after 12 days in a standard atmosphere according to ISO 554, if the coating has a thickness of less than or equal to 250 microns, and where at a cross-cut value of 2 a tensile test according to ISO 4624 will be performed);
- the coating shows In one embodiment, the coating shows no adhesive break in ISO2624 between steel and the primer (first coat) (unless pull-off values are 5 MPa or more) after 12 days in a standard atmosphere according to ISO 554;
- the coating meets the classification for CUI-1, CUI-2, or CUI-3, after 20 thermal cycles with a minimum temperature of 5ºC and a maximum temperature of 60ºC for CUI-1, after 20 thermal cycles with a minimum temperature of 5ºC and a maximum temperature of 150ºC for CUI-2, and after 20 thermal cycles with a minimum temperature of -5ºC and a maximum temperature of 204ºC for CUI-3, obtaining the following results: a value 0 (S0) according to ISO 4628-2, a value Ri 0 according to ISO 4628-3, a value 0 (S0) according to ISO 4628-4, and a value 0 (S0) according to ISO 4628-5.
- the coating meets the multiphase cyclic CUI test criteria for carbon steel vertical pipe test in accordance with ISO19277:2018, for CUI-2, or even for CUI-3.
- the coating meets all the requirements of CUI-1 of ISO 19277:2018, or all the requirements of CUI-2 of ISO 19277:2018, or even all the requirements of CUI-3 of ISO 19277:2018.
- the coating meets the requirements for cryogenic testing for CUI-1 Cryo, CUI-2 Cryo, or even CUI-3 Cryo, in particular addition to meeting the requirements for CUI-1, CUI-2, and/or CUI-3 according to ISO 19277:2018;
- the coating meets the requirements for insulation for vertical pipes for CUI-2 or even CUI-3 as shown in ISO 19277:201, 8, in particular addition to meeting the requirements for CUI-1, CUI-2, and/or CUI-3 according to ISO 19277:2018.

20. Process or metal substrate according to claim 19, wherein the coating meets all the requirements of CUI-1 of ISO 19277:2018, or all the requirements of CUI-2 of ISO 19277:2018, or even all the requirements of CUI-3 of ISO 19277:2018.