(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 803 297 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
29.10.1997 Bulletin 1997/44

(51) Int. Cl.^{6}: **B05D 7/14**

(21) Application number: **97201023.5**

(22) Date of filing: **07.04.1997**

(84) Designated Contracting States:
DE ES FR GB IT SE

(30) Priority: **25.04.1996 EP 96201109**

(71) Applicant: **Akzo Nobel N.V.**
6824 BM Arnhem (NL)

(72) Inventor: **Durand, Dominique**
91580 Etrechy (FR)

(74) Representative: **Schalkwijk, Pieter Cornelis et al**
AKZO NOBEL N.V.
Patent Department (Dept. APTA)
P.O. Box 9300
6800 SB Arnhem (NL)

(54) Anticorrosive multilayer coating system for metal surfaces

(57) Proposed is an anticorrosive multilayer coating system for metal surfaces, more particularly pipes and storage tanks, comprising at least a primer coat (a) based on a non-conductive binder, followed by a second or further top coats (b), characterised in that the primer coat (a) is an electroinsulating powder coating layer based on an epoxy resin, alkyd resin, polyester resin, melamine-containing resin, polyurethane resin and/or polyacrylate resin, and, optionally, a filler, pigment and/or adjuvant, and the outer top coat (b) is an electrically conductive powder coating layer based on an epoxy resin, alkyd resin, polyester resin, melamine-containing resin, polyurethane resin and/or polyacrylate resin incorporating 0,1 to 50% by weight of an electrically conductive resin, filler, pigment and/or adjuvant capable of providing a conductive outer layer with, optionally, a structured and/or wrinkle finish, calculated on the overall weight of this outer layer.

Printed by Rank Xerox (UK) Business Services
2.14.18/3.4

Description

The invention pertains to an anti-corrosive multilayer coating system for metal surfaces, more particularly pipes and storage tanks, comprising at least a primer coat (a) based on a non-conductive binder, followed by a second or further top coatings (b).

A multilayer coating system for protecting underground pipes and tanks has been described in CA-1013625. The system disclosed in this document comprises at least three layers, i.e., a prime coating layer comprising a non-conductive binder as well as particles of metal more anodic than the metal of the structure, an intermediate coating comprising a non-conductive film-forming material and a filler provided thereon, and a top coating based on a non-conductive, abrasion and moisture resistant layer.

Although this multilayer coating system offers sound protection, under certain circumstances there may be such a great difference in voltage between the tank's contents and the surrounding area as will cause breakdown. This means that at the place where breakdown has occurred the metal surface will no longer be protected, with all its corrosive consequences.

The invention now provides a multilayer coating system by which the aforementioned problems are obviated wholly or for the most part.

The invention consists in that in a coating system of the known type mentioned in the opening paragraph the primer coat (a) is an electroinsulating powder coating layer based on an epoxy resin, alkyd resin, polyester resin, melamine-containing resin, polyurethane resin and/or polyacrylate resin, and the outer top coat (b) is an electrically conductive smooth or non-smooth powder coating layer based on an epoxy resin, alkyd resin, polyester resin, melamine-containing resin, polyurethane resin and/or polyacrylate resin incorporating 0,1 to 50 wt.% of an electrically conductive or non-conductive resin or adjuvant capable of providing a conductive outer layer with, optionally, a structured and/or wrinkle finish, calculated on the overall weight of this outer layer.

When the difference in voltage between the metal surface to be protected and the surrounding area becomes so great as to create a risk of breakdown, the provision of an outer, electrically conductive top coat based on one or more of the aforementioned powder coatings serves to confine the breakdown to the layers situated between the substrate and the conductive top coat. The rougher the surface of the outer coating layer is, the greater its specific surface will be. In this way the risk of breakdown is reduced considerably owing to a discharge taking place from the electrically conductive top coat to the surroundings.

According to a preferred embodiment of the invention, the nonconductive primer powder coating is composed of:

a) 5 to 65 parts by weight of an epoxy resin and/or polyester resin which may be modified or not,
b) 2 to 25 parts by weight of a curing agent based on dicyandiamide, a phenol, triglycidyl isocyanurate or a polyisocyanate,
c) 1 to 80 parts by weight of a pigment, and
d) 0,2 to 3 parts by weight of a degassing medium.

The outer, electrically conductive powder coating layer is preferably composed of:

a) 5 to 65 parts by weight of an epoxy resin and/or polyester resin which may be modified or not,
b) 2 to 25 parts by weight of a curing agent based on dicyandiamide, a phenol, triglycidyl isocyanurate or a polyisocyanate,
c) 1 to 80 parts by weight of a conductive or non-conductive pigment,
d) 0,2 to 3 parts by weight of a degassing medium, and
e) 0,1 to 50 parts by weight of an electrically conductive or non-conductive adjuvant capable of giving a structured and/or wrinkle finish.

To create thorough protection the first non-conductive powder coating layer is generally applied in a thickness ranging from 60 μm to 600 μm. The thickness of the second, electrically conductive top coat after curing is generally in the range of 100 μm to 1000 μm.

The preparation of the powder coatings according to the invention is carried out in the conventional manner known in the art. It comprises weighing the raw materials, followed by pre-mixing of the raw materials and an extrusion process, optionally followed by a grinding process and storage.

Suitable epoxy resins include epoxy resins based on epichlorohydrin and 2,2-bis-(4-hydroxyphenol)-propane with softening points of between 40 and 90°C and an epoxy equivalent weight of between 450-2000. The softening point is particularly between 50 and 70°C. Other suitable epoxy resins are for example epoxydised phenolnovolac resins with an epoxy equivalent weight of between 160 and 250 and with a softening point of between 40 and 90°C. The softening point is preferably between 50 and 70°C. Preferably, a diglycidyl ether of bisphenol-A (DGEBA) novolac modified epoxy resin is used.

Suitable curing agents for epoxy resins are for instance dicyandiamide, imidazole derivatives and imidazoline derivatives, acid anhydrides of trimellitic acid, pyromellitic acid, benzophenone tetracarboxylic acid, tetrahydrophthalic acid, cyclopentane dicarboxylic acid, hexahydrophthalic acid, partially esterified adducts of said carboxylic acids, aromatic amines, phenolic resins (cresol or novolac), and epoxy resin-phenol adducts, alone or in combination.

The curing agents can be applied in amounts between 2 and 25% by weight (calculated on the overall weight of the powder coating layer).

The multilayer coating system according to the invention further contains fillers, adjuvants, and 1 to 80 parts by weight of one or more pigments.

Suitable fillers are generally well-known in the art and include quartz powder, aluminium silicates, calcium silicates, and magnesium silicates, calcium carbonate, barium sulphate, calcium sulphate, and aluminium oxide, mixtures of these, optionally with smaller amounts of, e.g., aluminium hydroxide, ammonium polyphosphate, and the like.

Suitable adjuvants include flow-promoting agents, accelerators, curing agents, release agents, viscosity reducing agents and/or corrosion protective additives.

Flow-promoting agents are well-known in the art and include, by preference, liquid polyacrylates, such as polybutyl acrylate and polyethyl acrylate. Other suitable flow-promoting agents include fluorinated polymers, such as esters of polyethylene glycol and perfluoroctanoic acid, polymeric siloxanes, such as polydimethyl siloxane or polymethylphenyl siloxane.

Corrosion protective additives are well-known in the art and include zinc dust and/or silica-containing additives. A suitable compound is "Shieldex" (ex Grace), which can be applied in amounts between for example 0,5 and 10% by weight (calculated on the first powder coating layer).

Suitable pigments are, for instance, titanium dioxide, iron oxide (yellow, brown, red, black), carbon black, and organic pigments.

The outer powder coating layer contains 0,1 to 50% by weight of structural adjuvants. As examples may be mentioned cellulose acetobutyrate, thermoplastic polymers, such as polyethylene or polypropylene, rubber compounds, such as butadiene-acrylonitrile, acrylate rubber, fillers, such as silica (Aerosil 380 ex Degussa), bentone, talc, high specific gravity pigments. When conductive structural adjuvants are employed, use should be made of one or more conductive fillers. Examples of suitable conductive fillers include specific carbon blacks, such as Printex XE2 (ex Degussa), graphite, conductive resins such as aniline resins, and/or metallic powders (aluminium, zinc).

The multilayer coating systems according to the invention were found to be preeminently suitable for obtaining top coats giving very long-term high corrosion resistance. It was found that protection against corrosion can be obtained for metal substrates based on iron, copper, and alloys of these metals.

The first powder coating layer can be applied by means of flame spraying, (electrostatic) fluidised bed methods, (electrostatic) spraying, plasma spraying, and tribocharging methods.

Electrostatic powder or tribo spraying methods charge the particles with the aid of a powder gun and spray them towards a grounded steel substrate. The powder is charged and the particles stick on the metal due to electrostatic attraction forces. Electrostatic charge is not always necessary when the substrate is preheated. The object can then be placed in an oven for curing of the powder coating. For some reactive powders, no oven is necessary.

The fluidised bed method is quite simple and best described as a "hot dip process." A preheated object is dipped in a fluidised bed of powder. The powder sticks and melts on the metal surface. Optionally, after dipping the object is placed in an oven for curing.

The powder coatings utilised for the second coating layer are preferably applied to the first coating layer by electrostatic/tribo spraying and cured at a temperature of 160-200°C, depending on the formulations. During the curing process, the powder coating melts and subsequently flows out to form a continuous coating film before substantial curing of the components, albeit a film with a wrinkle finish because of the presence of the structural adjuvants.

Suitable catalysts must guarantee rapid curing of the components but must be substantially inactive in the mixing of the polyester and the epoxy resins.

Prior to application of the second coating layer, the first layer can be a cured layer but also a non-cured or partially cured layer. One option of the present two-layer coating system is the possibility of curing both layers in a single step, in which case the first layer is applied as a base, over which the second electrically conductive powder coating is applied, after which the total system is cured under the aforementioned conditions.

Preferably, the thickness of the first corrosion protective powder coating layer is between 60 and 600 μm, and the thickness of the second electrically conductive powder coating layer is between 100 and 1000 μm.

The invention will be futher elucidated by means of the following examples, without, however, being limited thereto.

In order to determine the properties of the anticorrosive multilayer coating system according to the invention use was made of a cathodic disbonding test in accordance with British gas specification PS/CW6.

Example

Preparation of the first coating layer (system A)

The first coating layer was prepared using the following ingredients: (all parts are parts by weight)

epoxy resin	70,0 (663 UE, ex Dow)
substituted dicyandiamide	3,5
acrylate flow agent	0,3 (Resiflow PV88, ex Worlee)
Shieldex AC5	2,7
Calcium carbonate	14,4
Carbon black	0,3 (Printex 300, ex Degussa)
Titanium dioxide	6,3
Phthalocyanine blue	0,1
Iron oxide yellow	2, 4

The comparative second coating layer (system B) was prepared using the following ingredients:

epoxy resin	24,0 (663 UE, ex Dow)
carboxylic polyester	36,0 (P2230, ex DSM)
acrylate flow agent	0,3 (Resiflow PV 88, ex Worlee)
benzoin	1,0
titanium dioxide	3,0
carbon black	0,5 (Printex 300, ex Degussa)
acrylate rubber	12,8
$BaSO_4$	12,9
$CaCO_3$	9,5

The coating composition for the second coating layer according to the invention (system C) was prepared in the same manner as the coating composition for system B, the difference being that for system C use was made of 1,4 parts of a conductive carbon black (Printex XE2, ex Degussa) and of 8,6 parts of $CaCO_3$ instead of 9,5 parts.

Both coating layers (system B and system C) were used as a top coat to protect the outside of a gas tank coated with a first coating layer according to system A.

Application of the first coating layer (system A)

First, the tank's steel was subjected to sandblasting. Next, the tank was pre-heated to 240°C, whereupon the powder coating of system A was applied by electrostatic spraying in a layer thickness of 100 μm.

Application of the second coating layer (system B or system C)

The second layer according to system B or system C was applied in a layer thickness of 800 μm. There was 10 minutes of curing at a temperature of 200°C.

The cathodic disbonding test

The three gas tanks were subjected to the cathodic disbonding test.

The diameter of the coating which has lost adhesion was measured, as well as the surface.

	diameter (mm)	surface (cm^2)
System A:	8	0,2
System (A+B):	7	0,1
System (A+C):	6	0

From the results mentioned in the above table it appears that only the coating containing system (A+C) displays a satisfactory cathodic disbonding test. The initial hole of 6 mm remained intact when use was made of the system (A+C).

Claims

1. An anticorrosive multilayer coating system for metal surfaces, more particularly pipes and storage tanks, comprising at least a primer coat (a) based on a non-conductive binder, followed by a second or further top coats (b), characterised in that the primer coat (a) is an electroinsulating powder coating layer based on an epoxy resin, alkyd resin, polyester resin, melamine-containing resin, polyurethane resin and/or polyacrylate resin, and, optionally, a filler, pigment and/or adjuvant, and the outer top coat (b) is an electrically conductive powder coating layer based on an epoxy resin, alkyd resin, polyester resin, melamine-containing resin, polyurethane resin and/or polyacrylate resin incorporating 0,1 to 50% by weight of an electrically conductive resin, filler, pigment and/or adjuvant capable of providing a conductive outer layer with, optionally, a structured and/or wrinkle finish, calculated on the overall weight of this outer layer.

2. Anticorrosive coating system according to claim 1, characterised in that the insulating powder coating layer is composed of:

   a) 5 to 65 parts by weight of an epoxy resin and/or polyester resin which may be modified or not,
   b) 2 to 25 parts by weight of a curing agent based on dicyandiamide, a phenol, triglycidyl isocyanurate or a polyisocyanate,
   c) 1 to 80 parts by weight of a pigment, and
   d) 0,2 to 3 parts by weight of a degassing medium.

3. Anticorrosive coating system according to claim 1, characterised in that the outer, electrically conductive powder coating layer is composed of:

   a) 5 to 65 parts by weight of an epoxy resin and/or polyester resin which may be modified or not,
   b) 2 to 25 parts by weight of a curing agent based on dicyandiamide, a phenol, triglycidyl isocyanurate or a polyisocyanate,
   c) 1 to 80 parts by weight of a conductive or non-conductive pigment,
   d) 0,2 to 3 parts by weight of a degassing medium, and
   e) 0,1 to 50 parts by weight of an electrically conductive or non-conductive adjuvant capable of giving a structured and/or wrinkle finish.

4. Anticorrosive coating system according to claim 1, characterised in that the first powder coating layer has a thickness in the range of 60 µm to 600 µm.

5. Anticorrosive coating system according to claim 1, characterised in that the second powder coating layer has a thickness in the range of 100 µm to 1000 µm.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 20 1023

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	DE 31 01 778 A (MAIER JOSEF) 26 August 1982 * the whole document *	1	B05D7/14
A	EP 0 487 438 A (BENARD AIME ;WENDLING JEAN (FR)) 27 May 1992 * the whole document *	1	
D,A	CA 1 013 625 A (HOOKER CHEMICALS PLASTICS CORP) 12 July 1977 * the whole document *	1	
A	WO 82 02155 A (POLYMER CORP) 8 July 1982 * the whole document *	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

B05D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 August 1997	Brothier, J-A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)