

NOVEL COATING FOR METAL SURFACES AND METHOD FOR
IMPLEMENTING IT

BACKGROUND OF THE INVENTION

5 The present invention relates to a novel coating for metal surfaces and a method for implementing the coating. The invention particularly relates to a three-layer coating for metal surfaces, comprising a primary epoxy layer, an adhesive layer and a polyolefin layer. The
10 invention also relates to a method for coating metal surfaces.

 Three-layer coating for metal surfaces are already known in the prior art, notably for coating metal tubes. The first layer consists of an epoxy primer which
15 initially forms a gel and then cross-links. The second layer consists of a polymer adhesive, and is generally arranged over the primer before the latter gels. The third layer generally consists of a thermoplastic polymer, most frequently a polyolefin.

20 Thus, the following patents: EP-A-0,057,823, EP-A-0,205,395, FR-A-2,184,321, FR-A-2,529,829 disclose such three-layer systems, which enable the advantages of epoxy resins and polyolefins to be combined, specifically high adherence and good shock-resistance and cathodic
25 disbondment resistance. However, in those patents, there is no mention of problems associated with epoxy/adhesive reactivity and to the time that passes between application of the epoxy layer and the adhesive layer.

 WO-92/03,234 discloses a method for coating metal
30 tubes in which the adhesive is applied over a partially cross-linked epoxy resin so as to favour epoxy/adhesive reactions and thus adhesion. It is additionally recommended to apply the adhesive before cross-linking, but after the epoxy gels. However, no example or
35 numerical value is given.

 Additionally, when the adhesive is arranged over the epoxy primer after it gels, salt water withstand tests show that, in the case of these conventional three-layer

systems, total disbondment occurs at the metal/epoxy interface, accompanied by significant corrosion. It is essential to avoid this negative effect in many applications, notably the transport of hydrocarbons through underwater pipes. If, on the other hand, the adhesive is arranged over the primer after the latter gels, then salt water withstand tests show that no more disbondment at the metal/epoxy interface occurs, and nor does the associated corrosion; however, this time, disbondment at the epoxy/adhesive interface is observed.

There is thus a need for coatings that simultaneously have good adhesion and good water withstand properties.

It appears from the prior art that the choice of the epoxy/adhesive pair is an essential parameter. Indeed, to obtain high adhesion between the epoxy primer and the adhesive, the latter requires to be applied rapidly before the primer gels in order to ensure a high level of reaction with the epoxy primer. This means that the time between the epoxy/adhesive layers must be relatively short, and below the gelling time of the primer. This criterion is sometimes difficult to satisfy on industrial production lines as a result of their design (proportioning of application equipment, linear speed of the tube) or for large-diameter coating (low rotational and linear speed of the tube). There is thus a requirement for adhesive compositions having high adhesion which is independent of the nature and origin of the primer and/or of the thermoplastic polymer, but also of the conditions of application at time level, between the epoxy-adhesive primary layers.

SUMMARY OF THE INVENTION

The above problems are resolved in a surprising manner by the invention. Thus, the present invention provides a coating for a metal surface comprising:

- (i) a primer able to gel and set;
 - (ii) an adhesive; and
 - (iii) a thermoplastic polymer;
- in which said adhesive contains a catalyst.

According to one embodiment, said adhesive is a polymer functionalized by grafting or copolymerization with a functional monomer chosen from:

- (i) unsaturated carboxylic acids
- 5 (ii) unsaturated dicarboxylic acid anhydrides
- (iii) derivatives of these acids or anhydrides, or
- (iv) unsaturated epoxides.

According to one embodiment, said adhesive is a copolymer of:

- 10 ethylene,
- optionally one or several monomers selected from:
 - unsaturated carboxylic acid esters
 - vinyl esters of saturated carboxylic acids, and
 - alpha-olefins, and
- 15 said functional monomer being copolymerized.

In one embodiment, the said adhesive is an ethylene/C1-C4 alkyl (meth)acrylate/maleic anhydride terpolymer.

According to another embodiment, said adhesive is
20 polyethylene grafted with maleic anhydride or polypropylene grafted with maleic anhydride.

In one embodiment, said catalyst is present in an amount of 0.005% to 2.5% by weight based on the adhesive weight.

25 In another embodiment, said catalyst is 1,4-diazabicyclo[2,2,2] octane (DABCO) or methyl-2-imidazole (M2ID).

In a further embodiment, said primer is an epoxy primer.

30 In yet a further embodiment, said thermoplastic polymer is polyethylene or polypropylene.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The invention is now described in detail in the description that follows.

35 The primer is any conventional primer used in the art of three-layer coating. Examples that can be mentioned are epoxy, polyester or acrylic resins. Conventionally, an epoxy resin is used with advantage.

The principle of epoxy resins is for example described in Kirk-Othmer Encyclopedia of Chemical Technology, vol. 9, pp 267-289, 3rd Ed. These resins are most frequently polyphenol polyglycidylethers.

5 One for example can use:

- condensation products of bisphenol A and epichlorhydrine;
- epoxy-cresol novolac (ECN) resins;
- epoxy phenol novolacs;
- 10 - resins derived from bisphenol F;
- derivatives of polynuclear phenols and glycidyl-ethers;
- cycloaliphatic resins;
- resins derived from aromatic amines such as :
- 15 tetraglycidylmethylenedianiline derivatives;
- triglycidyl-p-aminophenol derivatives,
- triazine derivatives such as triclycidyl isocyanate;
- resins derived from hydantoine.

The epoxy resins used in the present invention can be
 20 resins able to cross-link at elevated temperatures, typically from 160°C to 250°C, conventionally from 180 to 220°C. The epoxy resins could also be resins able to cross-link at ambient temperature, with, for example, amines or amides.

25 The gelling time of these primers or epoxy resins can be comprised between 15 and 45 sec., for example between 20 and 30 sec., at the temperature at which said epoxy resin is applied. Gelling time is determined as in French Afnor standard NFA 49-706; it is the time needed
 30 to bring about rapid increase in viscosity at a determined temperature.

The glass transition temperature, Tg, when the latter is defined, is conventionally comprised between 80°C and 120°C.

35 These primers, typically epoxy resins, can be deposited in powder or liquid form on the metal surface, with conventional techniques.

In this present specification, the term "additive" stands for products commonly known as (co-extrusion) binders, thermoplastic binders, hot-melt bonding agents, etc.

5 By way of examples, one can cite (co)polyolefins modified with an unsaturated carboxylic acid derivative (modification being by copolymerization, terpolymerization or grafting. For the adhesive, certain functionalized polyolefins can also be employed provided
10 that the functional group content is sufficient to ensure adhesion between the layer. Mixtures of adhesives are also suitable.

Example of such adhesives are given in the following patent, this list being non-limiting, EP-A-210307, EP-A-
15 33220, EP-266994, FR-A-2,132,780, EP-A-171,777, US-A-4, 758,477, US-A-4,762,890, US-A-4,966,810, US-A-4,452,942 and US-A-3,658,948.

Examples of such adhesives are:

- copolymers of ethylene copolymerized with butene,
20 hexene, octene, optionally mixed with ethylene-propylene copolymers, grafted with maleic anhydride, said ethylene/alpha-olefin copolymers containing, for example, 35 to 80% by weight ethylene, the anhydride grafting rate being comprised between 0.01 and 1% by weight, for
25 example between 0.05 and 0.5% based on the total weight of the polymer;

- copolymers of ethylene and vinyl acetate (EVA), with or without addition of maleic anhydride, (the maleic anhydride being grafted or terpolymerised), containing
30 more particularly up to 40% by weight of vinyl acetate, 0.01 to 1% by weight grafted maleic anhydride or 0.1 to 10% by weight terpolymerised maleic anhydride, based on the total copolymer weight;

- polyolefins such as polyethylene (LLDPE, LDPE,
35 VLDPE, etc.) or polypropylene, the polyolefins being grafted with a carboxylic acid derivative such as maleic anhydride, the grafting rate being comprised between 0.005% and 1% by weight;

- terpolymers of ethylene and alkyl (meth)acrylate (such as methyl, ethyl or butyl acrylate) and maleic anhydride containing up to 40% by weight of alkyl (meth)acrylate and 0.01 to 10% by weight of maleic anhydride, based on the total terpolymer weight, the maleic anhydride being grafted or copolymerized.

The grafted polyethylenes and polypropylenes, and the terpolymers of ethylene/alkyl (meth)acrylate/maleic anhydride are the preferred additives in this invention.

10 The adhesives can be mixed with each other or with polyethylenes (VLDPE, etc.).

The term "catalyst" as used in this invention stands for any compound able to speed up the reaction at the epoxy-adhesive interface between the remaining epoxy functions and the functional groups present on the adhesive.

As examples of the catalyst, we can mention: 1,4-diazabicyclo[2,2,2] octane (DABCO), methyl-2-imidazole (M2ID), H₃BO₃, stearic acid, calcium stearate, B₄Na₂O₇ (Borax), NaH₂PO₄, Sb₂O₃, TNPP, APTS, DLBBE, etc.

The catalyst is added in an amount sufficient to catalyze the reaction at the interface. Generally speaking, the catalyst is effective at very low concentrations, for example 0.005% by weight, based on the adhesive weight. The concentration able to be used in the present invention is from 0.005 to 2.5% by weight, advantageously from 0.01 to 1% by weight, for example between 0.05 and 0.5% by weight based on the adhesive weight.

30 The catalyst is added to the adhesive by all means known in the art, such as for example compounding, carried out at a suitable temperature depending on the components.

The thermoplastic polymer employed in the present invention is any thermoplastic conventionally used in the art.

Examples of suitable thermoplastic polymers are the polyamides, polyolefins, polyamide alloys and their

mixtures. The thermoplastic polymer layer can additionally contain conventional fillers, such as glass fibers.

Here, the term polyamide stands for the condensation
5 products:

- of one or several alpha-omega-amino-acids such as those containing more than 5 carbon atoms, for example from 6 to 12 carbon atoms; or
- of one or several lactames corresponding to the
10 above amino-acids; or
- of one or several substantially stoichiometric combinations of one or several aliphatic and/or cycloaliphatic and/or aromatic-aliphatic diamines, or salts thereof, with one or several apliphatic or aromatic
15 carboxylic diacids or salts thereof; or
- any mixture of the above monomers; and
- any mixture of the resulting condensation products, optionally with other polymers compatible with the polyamides.

20 By way of example, the polyamide is PA6, PA6,6

Here, the term "polyolefin" covers homopolymers or copolymers of alpha-olefins or di-olefins.

Such olefins are, by way of example, ethylene, propylene, butene-1, octene-1, butadiene.

25 The following can be mentioned as typical examples:

- polyethylene PE, polypropylene PP, copolymers of ethylene and alpha-olefins. Such polymers can be grafted or copolymerized with unsaturated carboxylic acid anhydrides such as maleic anhydride or unsaturated
30 epoxides such as glycidyl methacrylate.

- copolymers of ethylene with one or several products selected from: (i) unsaturated carboxylic acids and salts or esters thereof; (ii) saturated carboxylic acid vinyl esters such as vinyl acetate; (iii) unsaturated di-
35 carboxylic acids and salts, esters, hemiesters, anhydrides thereof; and (d) unsaturated epoxides.

These ethylene (co)polymers can be grafted with unsaturated carboxylic acid anhydrides or unsaturated epoxides.

- styrene-based block copolymers, and notably those
5 comprising polystyrene and polybutadiene sequences (SBS), polystyrene and polyisoprene sequences (SIS), polystyrene and poly(ethylene-butylene) sequences (SEBS), such copolymers optionally being functionalized with maleic anhydride.

10 The above copolymers can be randomly copolymerized or sequenced, and have a linear or branched structure.

The term polyolefin also covers mixtures of several of the polyolefins mentioned above.

One can, for example, use the following in this
15 invention: polyethylene (HDPE, MDPE, LDPE or VLDPE), or polypropylene.

The molecular weight of the polyolefins can vary over a wide range as will be understandable to those skilled in the art.

20 When the thermoplastic is polyethylene, an ethylene-based adhesive is for example used, whereas when the thermoplastic is polypropylene, a propylene-based adhesive is for example used.

Alloys should be taken to mean products comprising a
25 polyamide such as described above; polyolefin such as described above and when the latter does not have sufficient functionality to ensure compatibility with the polyamide, a compatibilizing agent; the polyolefin is present in the form of a phase dispersed in the polyamide
30 phase, which is thus referred to as a polyamide matrix.

For example, the polyamide represents from 25 to 75% by weight of the alloy.

The compatibilizing agent is present in a sufficient amount to ensure compatibility, meaning dispersion of the
35 polyolefin in the polyamide matrix in the form of nodules, for example, up to 25% by weight of the polyolefin. Nodule diameter can be 0.1 to 5 μ m.

The compatibilizing agent is a product known per se for rendering polyamides and polyolefins compatible, for example as described in the following patent applications: FR-A-2,291,225, EP-A-0,342,066 and EP-A-
5 0,218,665 the content of which is incorporated herein by reference.

The thickness of the primer layer can be comprised between 20 and 400 μ m, for example between 50 and 150 μ m.

The thickness of the adhesive layer can be comprised
10 between 100 and 500 μ m, for example between 200 and 350 μ m.

The thickness of the thermo-plastic layer can be comprised between 0.5 and 5mm, for example between 1.5 and 3mm.

The invention also covers the case where conventional
15 additives and/or fillers such as CaCO₃, talc or mica, silicones, anti-UV agents, pigments such as TiO₂, FeOx or carbon black, stabilizers, fireproofing agents, etc. are added to the primer, the adhesive or the thermoplastic.

The present invention also provides a method for
20 applying a coating according to the invention comprising the steps consisting of:

- (i) applying a primer;
- (ii) applying the adhesive; and
- (iii) applying thermoplastic polymer.

25 Prior to applying the primer, the metal surface is conventionally degreased, optionally shot-blasted or sand-blasted, and heated. The pre-treatment (shot or sand-blasting) increases surface roughness and encourages keying of the primer.

30 Step (i) is carried out by depositing the primer in liquid form, or, if the primer is in powder form, by projection, for example by electrostatic projection, deposition taking place on the heated metal surface.

Step (ii) is implemented by depositing adhesive in
35 the molten state on the primer layer, for example after hardening, or prior to hardening and after gelling, or prior to gelling. Conventionally, the adhesive is

extruded and applied in film form, or projected or sprayed if it is in powder form.

Step (iii) is carried out by depositing the thermoplastic on the adhesive. Conventionally, the thermoplastic is extruded to then be applied in film form by a banding operation.

The thus coated tube can then be submitted to a pressing operation, using rollers for example. The tube can then be cooled in a cooling chamber using, for example, a water spray. The time between applying the primer and cooling should be sufficient to ensure complete cross-linking of the epoxy primer, this being a guarantee of good anti-corrosion behavior (verification that $\Delta T_g \leq 5^\circ\text{C}$ according to French standards NFA 49710 or NFA 49711).

In one advantageous embodiment of the method of the invention, the adhesive is applied before the primer sets, but after the primer gels. The expression "after the primer gels" includes very brief periods, meaning immediately after gelling, at least partially, but also longer periods as well, which can for example be of the order of the primer gel time.

The present invention also provides a metallic object the surface of which is coated using a coating according to the invention, and in particular a metallic tube. This metal tube has a diameter of up to 0.8m and even 2.5m, and a thickness of 2 to 50 mm. Metal tubes with the coating according to the invention are completely suitable for transporting hydrocarbons, gas or water, such tubes being able to be buried and/or immersed.

The invention is illustrated in the following examples which should in no case be considered as limiting.

EXAMPLES

In the following examples, a production line is employed enabling steel tubes of outer diameter 11.4 cm and 5.5 mm thickness to be coated.

5 Several types of epoxy primer are employed, specifically:

 - epoxy 1: available from Bitumes Spéciaux under the general reference Eurokote® and having the following characteristics:

10 specific gravity 1.50 g/ml; Tg 105°C, gelling time 45 sec at 180°C; minimum and maximum substrate temperatures 180 and 220°C respectively, a hardening profile such that hardening time at 180°C is about 60 sec and at 220°C is about 20 sec.

15 - epoxy 2: available from Bitumes Spéciaux under the general reference Eurokote® and having the following characteristics:

 specific gravity 1.50 g/ml; Tg 105°C, gelling time 80 sec at 180°C; minimum and maximum substrate temperatures
20 180 and 220°C respectively, a hardening profile such that hardening time at 180°C is about 180 sec and at 220°C is about 60.

 - epoxy 3: available from BASF under the name Basepox® PE 508190, and having the following
25 characteristics:

 specific gravity 1.49 g/ml, gelling time 40 sec at 180°C; minimum and maximum substrate temperatures 180 and 210°C respectively.

 - epoxy 4: available from Zhong Yuan Oil Field
30 Construction Chemical Industry Co. under the name Beauté Eternelle®, and having the following characteristics:

 specific gravity 1.2-1.4 g/ml; gelling time 38 sec at 180°C; minimum and maximum substrate temperatures 180 and 210°C respectively.

35 - epoxy 5: available from Langfang Yannei Chemical Co. Ltd under the name PEY2® and having the following characteristics:

specific gravity 1.2-1.4 g/ml; gelling time 25 sec at 180°C; minimum and maximum substrate temperatures 180 and 210°C respectively.

- epoxy 5: available from Langfang Yannei Chemical Co. Ltd under the name PEY2® and having the following characteristics:

specific gravity 1.2-1.4 g/ml; gelling time 25 sec at 180°C; minimum and maximum substrate temperatures 180 and 210°C respectively.

10 Several types of adhesive are used, which will or will not be mixed with various types of catalyst, specifically:

- adhesive 1: available from Elf Atochem under the general name LOTADER®, which is an ethylene/butyl acrylate/maleic anhydride terpolymer in a weight ratio of 15 91/6/3, and a melt flow index MFI of 5 g/10 min (at 190°C under 2.16 kg);

- adhesive 2: available from Elf Atochem under the general name LOTADER®, which is mixture of 55% by weight 20 of an ethylene/butyl acrylate/maleic anhydride terpolymer in a weight ratio of 93.5/6/0.5 and an MFI of 2 g/10 min (at 190°C under 2.16 kg) and 45% by weight of VLDPE of density 0.910 and MFI of 0.9 g/10 min (at 190°C under 2.16 kg);

25 - adhesive 3: available from Elf Atochem under the general name OREVAC® which is a polypropylene grafted with maleic anhydride at a grafting rate of 0.15% by weight, and having an MFI of 2 g/10 min (at 190°C under 2.16 kg);

30 Several types of thermoplastic polymer are used, here polyolefins, the thermoplastic layer being referred to as the top-coat, specifically:

- top-coat 1: polyethylene available from Elf Atochem under the general name Lacqtène®, low density (LDPE) 35 having a melt flow index MFI of 0.25 g/10 min (at 190°C under 2.16 kg) and a density of 0.934, with a heat stabilizer and an anti-UV agent;

- top-coat 2: polyethylene available from Elf Atochem under the general name Lacqtène®, medium density (MDPE) having a melt flow index MFI of 0.3 g/10 min (at 190°C under 2.16 kg) and a density of 0.937 with thermal stabilisation and anti-UV agent;

- top-coat 3: polyethylene available from UCC, high density (HDPE) having a melt flow index MFI of 0.6 g/10 min (at 190°C under 2.16 kg) and a density of 0.943 with thermal stabilisation and an anti-UV agent;

10 - top-coat 4: polypropylene available from Hoechst, under the name Hostalen® PP, having a melt flow index MFI of 1 g/10 min (at 230°C under 2.16 kg) and a density of 0.9 with thermal stabilisation and an anti-UV agent.

The coating is applied using the following method:
15 heating of the tube; electrostatic projection of the epoxy; extrusion of the adhesive; extrusion of the thermoplastic; roller pressing; cooling by water spray.

Peel-off strength is measured by peeling at 180°C at ambient temperature and at 100 m/min over a 5 cm width.
20 5 tests were done and the mean value adopted.

Example 1

In this example, two systems are compared, one in which the adhesive does not contain a catalyst and the
25 other in which the adhesive contains a catalyst. The catalyst is DABCO, added in an amount of 0.25% by weight based on adhesive weight. The adhesive/catalyst mixture is obtained by compounding the components at 130-140°C.

Adhesion is then determined, for variable epoxy-
30 adhesive times.

Table 1a (epoxy/adhesive time 22-25 seconds)

	temperature	nature	thickness	time
tube	180°C	-	-	-
layer 1	180°C	epoxy 1	70 μm	-
layer 2	225°C	adhesive 1	250-300 μm	-
layer 3	210°C	top-coat 1	2.5 mm	-
epoxy gel at 180°C				45 s
epoxy/adhesive	-	-	-	22-25 s
epoxy/cooling	-	-	-	90 s

The results are given in table 1b:

Temperature	Peel-off force (N/5 cm)	
	without catalyst	with catalyst
23°C	1071	945
50°C	600	663
70°C	300	326

Table 2a (epoxy/adhesive time 45 seconds) :

	temperature	nature	thickness	time
tube	180°C	-	-	
layer 1	180°C	epoxy 1	70 μm	
layer 2	225°C	adhesive 1	250 to 300 μm	-
layer 3	210°C	top-coat 1	2.5m	-
epoxy gel at 180°C	-	-	-	45 s
epoxy/adhesive	-	-	-	45 s
epoxy/cooling				110 s

The results are given in table 2b:

Temperature	Peel-off force (N/5 cm)	
	without catalyst	with catalyst
23°C	909	1233
50°C	515	682
70°C	240	350

Table 3a (epoxy/adhesive time 60 seconds) :

	temperature	nature	thickness	time
tube	180°C	-	-	-
layer 1	180°C	epoxy 1	70 μ m	-
layer 2	225°C	adhesive 1	250-300 μ m	-
layer 3	210°C	top-coat 1	2.5 mm	-
epoxy gel at 180°C				45 s
epoxy/adhesive	-	-	-	60 s
epoxy/cooling	-	-	-	125 s

The results are given in table 3b:

Temperature	Peel-off force (N/5 cm)	
	without catalyst	with catalyst
23°C	40	1156
50°C	448	725
70°C	255	375

Example 2

5 In this example, two systems are compared, one in which the adhesive does not contain a catalyst and the other in which the adhesive contains a catalyst. The catalyst is DABCO added in an amount of 0.25% by weight based on the adhesive weight. The adhesive/catalyst mixture is obtained by compounding the components at 130-140°C. Adhesion is then determined for variable epoxy/adhesive times.

10

Table 4a (epoxy/adhesive times 22-25 seconds) :

	temperature	nature	thickness	time
tube	200°C	-	-	-
layer 1	200°C	epoxy 2	70 μ m	-
layer 2	225°C	adhesive 1	250-300 μ m	-
layer 3	210°C	top-coat 1	2.5 mm	-
epoxy gel at 200°C				45 s
epoxy/adhesive	-	-	-	22-25 s
epoxy/cooling	-	-	-	90 s

The results are given in table 4b:

Temperature	Peel-off force (N/5 cm)	
	without catalyst	with catalyst
23°C	723	1132
50°C	665	731
70°C	400	278

Table 5a (epoxy/adhesive time 45 seconds) :

	temperature	nature	thickness	time
tube	200°C	-	-	-
layer 1	200°C	epoxy 2	70 μm	-
layer 2	225°C	adhesive 1	250-300 μm	-
layer 3	210°C	top-coat 1	2.5 mm	-
epoxy gel at 180°C				45 s
epoxy/adhesive	-	-	-	45 s
epoxy/cooling	-	-	-	110 s

The results are given in table 5b:

Temperature	Peel-off force (N/5 cm)	
	without catalyst	with catalyst
23°C	278	1102
50°C	257	711
70°C	157	312

Table 6a (epoxy/adhesive time 60 seconds) :

	temperature	nature	thickness	time
tube	200°C	-	-	-
layer 1	200°C	epoxy 2	70 μ m	-
layer 2	225°C	adhesive 1	250-300 μ m	-
layer 3	210°C	top-coat 1	2.5 mm	-
epoxy gel at 180°C				45 s
epoxy/adhesive	-	-	-	60 s
epoxy/cooling	-	-	-	125 s

The results are given in table 6b:

Temperature	Peel-off force (N/5 cm)	
	without catalyst	with catalyst
23°C	178	1072
50°C	165	634
70°C	120	386

5 Example 3

In this example, three systems are compared, one in which the adhesive does not contain a catalyst, the second in which the adhesive contains DABCO and the third in which the adhesive contains methyl-2-imidazole (M2ID).
 10 The catalyst is added in an amount of 0.25% by weight based on adhesive weight. The adhesive/catalyst mixture is obtained by compounding the components at 130-140°C.

Adhesion is then determined, for variable epoxy-adhesive times.

Table 7a (epoxy/adhesive time 22-25 seconds)

	temperature	nature	thickness	time
tube	200°C	-	-	-
layer 1	200°C	epoxy 2	70 μm	-
layer 2	225°C	adhesive 1	250-300 μm	-
layer 3	210°C	top-coat 1	2.5 mm	-
epoxy gel at 200°C				45 s
epoxy/adhesive	-	-	-	22-25 s
epoxy/cooling	-	-	-	90 s

The results are given in table 7b:

Temperature	Peel-off force (N/5 cm)		
	without catalyst	with DABCO	With M2ID
23°C	723	1132	> 1053
50°C	665	731	646
70°C	400	278	294

Table 8a (epoxy/adhesive time 45 seconds)

	temperature	nature	thickness	time
tube	200°C	-	-	-
layer 1	200°C	epoxy 1	70 μ m	-
layer 2	225°C	adhesive 1	250-300 μ m	-
layer 3	210°C	top-coat 1	2.5 mm	-
epoxy gel at 200°C				45 s
epoxy/adhesive	-	-	-	45 s
epoxy/cooling	-	-	-	110 s

The results are given in table 8b:

Temperature	Peel-off force (N/5 cm)		
	without catalyst	with DABCO	With M2ID
23°C	278	1102	> 975
50°C	257	711	467
70°C	157	312	268

5 Example 4

In this example two systems are compared, one in which the adhesive does not contain a catalyst, and the other in which the adhesive contains a catalyst. The catalyst is DABCO, added in an amount of 0.25% by weight based on the adhesive weight. The adhesive/catalyst mixture is obtained by compounding the components at 130-140°C. Adhesion is then determined.

Table 9a (epoxy/adhesive times 22-25 seconds) :

	temperature	nature	thickness	time
tube	180°C	-	-	-
layer 1	180°C	epoxy 3	70 μ m	-
layer 2	230°C	adhesive 1	250-300 μ m	-
layer 3	215°C	top-coat 1	2.5 mm	-
epoxy gel at 180°C				40 s
epoxy/adhesive	-	-	-	22-25 s
epoxy/cooling	-	-	-	90 s

The results are given in table 9b:

Temperature	Peel-off force (N/5 cm)	
	without catalyst	with catalyst
23°C	249	> 1065
50°C	523	> 790
70°C	375	459

5 Example 5

In this example two systems are compared, one in which the adhesive does not contain a catalyst, and the other in which the adhesive contains a catalyst. The catalyst is DABCO, added in an amount of 0.25% by weight based on the adhesive weight. The adhesive/catalyst mixture is obtained by compounding the components at 130-140°C. Adhesion is then determined.

Table 10a (epoxy/adhesive times 22-25 seconds) :

	temperature	nature	thickness	time
tube	180°C	-	-	-
layer 1	180°C	epoxy 1	70 μ m	-
layer 2	225°C	adhesive 2	250-300 μ m	-
layer 3	210°C	top-coat 2	2.5 mm	-
epoxy gel at 180°C				45 s
epoxy/adhesive	-	-	-	22-25 s
epoxy/cooling	-	-	-	90 s

The results are given in table 10b.

Temperature	Peel-off force (N/5 cm)	
	without catalyst	with catalyst
23°C	> 720	> 845
50°C	> 657	856
70°C	324	489
80°C	232	316

5

Example 6

In this example two systems are compared, one in which the adhesive does not contain a catalyst, and the other in which the adhesive contains a catalyst. The catalyst is DABCO, added in an amount of 0.25% by weight based on the adhesive weight. The adhesive/catalyst mixture is obtained by compounding the components at 130-140°C. Adhesion is then determined.

Table 11a (epoxy/adhesive times 22-25 seconds) :

	temperature	nature	thickness	time
tube	180°C	-	-	-
layer 1	185°C	epoxy 4	70 μm	-
layer 2	225°C	adhesive 2	250-300 μm	-
layer 3	250°C	top-coat 3	2.5 mm	-
epoxy gel at 180°C				38 s
epoxy/adhesive	-	-	-	22-25 s
epoxy/cooling	-	-	-	3 min

The results are given in table 11b.

Temperature	Peel-off force (N/5 cm)	
	without catalyst	with catalyst
23°C	617	694
50°C	380	440
70°C	225	325

Example 7

In this example two systems are compared, one in which the adhesive does not contain a catalyst, and the other in which the adhesive contains a catalyst. The catalyst is DABCO, added in an amount of 0.25% by weight based on the adhesive weight. The adhesive/catalyst mixture is obtained by compounding the components at 130-140°C. Adhesion is then determined.

10 Table 12a (epoxy/adhesive times 22-25 seconds) :

	temperature	nature	thickness	time
tube	180°C	-	-	-
layer 1	180°C	epoxy 5	70 μ m	-
layer 2	230°C	adhesive 2	250-300 μ m	-
layer 3	250°C	top-coat 3	2.5 mm	-
epoxy gel at 180°C				25 s
epoxy/adhesive	-	-	-	22-25 s
epoxy/cooling	-	-	-	3 min

The results are given in table 12b.

Temperature	Peel-off force (N/5 cm)	
	without catalyst	with catalyst
23°C	329	780
50°C	290	637
70°C	240	363

Example 8

15 In this example two systems are compared, one in which the adhesive does not contain a catalyst, and the other in which the adhesive contains a catalyst. The catalyst is M2ID, added in an amount of 0.25% by weight based on the adhesive weight.

The adhesive/catalyst mixture is obtained by compounding the components at 130-140°C. Adhesion is then determined.

5 Table 13a (epoxy/adhesive times 22-25 seconds) :

	temperature	nature	thickness	time
tube	200°C	-	-	-
layer 1	200°C	epoxy 2	70 μ m	-
layer 2	235°C	adhesive 3	250-300 μ m	-
layer 3	250°C	top-coat 4	2.5 mm	-
epoxy gel at 200°C				45 s
epoxy/adhesive	-	-	-	22-25 s
epoxy/cooling	-	-	-	3 min

The results are given in table 13b.

Temperature	Peel-off force (N/5 cm)	
	without catalyst	with catalyst
80°C	825	1056
110°C	726	713

Table 14a (epoxy/adhesive time 45 seconds) :

	temperature	nature	thickness	time
tube	200°C	-	-	-
layer 1	200°C	epoxy 2	70 μ m	-
layer 2	235°C	adhesive 3	250-300 μ m	-
layer 3	250°C	top-coat 4	2.5 mm	-
epoxy gel at 200°C				45 s
epoxy/adhesive	-	-	-	45 s
epoxy/cooling	-	-	-	3 min

The results are given in table 14b.

Temperature	Peel-off force (N/5 cm)	
	without catalyst	with catalyst
80°C	945	1005
110°C	679	730

5 Example 9

In this example, the results are given for variable amounts of catalyst (DABCO), specifically 0.05% and 0.1% DABCO respectively.

Table 15a (epoxy/adhesive time 80 seconds) :

	temperature	nature	thickness	time
tube	200°C	-	-	-
layer 1	200°C	epoxy 2	70 μm	-
layer 2	230°C	adhesive 1	250-300 μm	-
layer 3	230°C	top-coat 1	2.5 mm	-
epoxy gel at 180°C				45 s
epoxy/adhesive	-	-	-	80 s
epoxy/cooling	-	-	-	3 min

The results are given in table 15b:

Temperature	Peel-off force (N/5 cm)	
	0.05% DABCO	0.1% DABCO
23°C	366	> 1025
50°C	400	> 786
70°C	258	345

Example 10

In this example, the results are given for catalyst (DABCO) concentrations of 0 and 0.25% respectively.

5 Table 16a (epoxy/adhesive time 80 seconds) :

	temperature	nature	thickness	time
tube	200°C	-	-	-
layer 1	200°C	epoxy 2	70 μ m	-
layer 2	225°C	adhesive 1	250-300 μ m	-
layer 3	210°C	top-coat 1	2.5 mm	-
epoxy gel at 180°C				45 s
epoxy/adhesive	-	-	-	80 s
epoxy/cooling	-	-	-	3 min

The results are given in table 16b:

Temperature	Peel-off force (N/5 cm)	
	without catalyst	with catalyst
23°C	178	1072
50°C	165	634
70°C	120	386

Example 11

In this example, the results are given for catalyst (DABCO) concentrations of 0 and 0.25% respectively.

5 Table 17a (epoxy/adhesive time 22-25 seconds):

	temperature	nature	thickness	time
tube	200°C	-	-	-
layer 1	200°C	epoxy 2	70 μ m	-
layer 2	235°C	adhesive 3	250-300 μ m	-
layer 3	250°C	top-coat 4	2.5 mm	-
epoxy gel at 180°C				45 s
epoxy/adhesive	-	-	-	22-25 s
epoxy/cooling	-	-	-	3 min

The results are given in table 17b:

Temperature	Peel-off force (N/5 cm)	
	without catalyst	with catalyst
80°C	925	1181
110°C	726	727

Table 18a (epoxy/adhesive time 45 seconds) :

	temperature	nature	thickness	time
tube	200°C	-	-	-
layer 1	200°C	epoxy 2	70 μ m	-
layer 2	235°C	adhesive 3	250-300 μ m	-
layer 3	250°C	top-coat 4	2.5 mm	-
epoxy gel at 200°C				45 s
epoxy/adhesive	-	-	-	45 s
epoxy/cooling	-	-	-	3 min

The results are given in table 18b:

Temperature	Peel-off force (N/5 cm)	
	without catalyst	with catalyst
80°C	945	1130
110°C	679	761

5 Example 12

In this example, salt water withstand ability is compared for different coatings. Metal/epoxy peel-off is determined after 1000 hours at 65°C in 3% NaCl salt water.

10 It is noted that ability to withstand salt water improves as epoxy/adhesive time increases (adhesive applied after gelling time); for systems without catalyst, adhesion decreases whereas, for systems with catalyst, adhesion remains high.

15 The present three-layer coatings thus have a good ability to withstand water, as well as high adhesion.

Obviously, the present invention is not limited to the examples given, but may undergo numerous variations readily available to the person skilled in the art.

For example the invention also covers the embodiment in which the adhesive and thermoplastic layers only form one and the same layer. According to a first alternative embodiment, the adhesive and the thermoplastic are substantially of the same nature, only the adhesive layer including the catalyst. In a second alternative embodiment, the adhesive can be mixed with the thermoplastic and only form one single layer.

What is claimed is:

- 1.- A coating for a metal surface comprising:
(i) a primer able to gel and set;
(ii) an adhesive; and
5 (iii) a thermoplastic polymer;
in which said adhesive contains a catalyst.
- 2.- The coating according to claim 1, in which said
adhesive is a polymer functionalized by grafting or
10 copolymerization with a functional monomer chosen from:
(i) unsaturated carboxylic acids
(ii) unsaturated dicarboxylic acid anhydrides
(iii) derivatives of these acids or anhydrides, or
(iv) unsaturated epoxides.
- 15 3.- The coating according to claim 2, in which said
adhesive is a copolymer of:
ethylene,
optionally one or several monomers selected from:
20 unsaturated carboxylic acid esters
vinyl esters of saturated carboxylic acids, and
alpha-olefins, and
said functional monomer being copolymerized .
- 25 4.- The coating according to one of claims 1 to 3, in
which said adhesive is an ethylene/C1-C4 alkyl
(meth)acrylate/maleic anhydride terpolymer.
- 5.- The coating according to claim 2, in which said
30 adhesive is polyethylene grafted with maleic anhydride or
polypropylene grafted with maleic anhydride.
- 6.- The coating according to one of claims 1 to 5, in
which said catalyst is present in an amount of 0.005% to
35 2.5% by weight based on the adhesive weight.
- 7.- The coating according to one of claims 1 to 6, in
which said catalyst is DABCO or M2ID.



- 8.- The coating according to one of claims 1 to 7, in which said primer is an epoxy primer.
- 5 9.- The coating according to one of claims 1 to 8, in which said thermoplastic polymer is polyethylene or polypropylene.
- 10 10.- A metal object the surface of which is coated using a coating according to any one of claims 1 to 9.
- 11.- The object according to claim 10, consisting of a metal tube.
- 15 12.- A method for applying a coating according to any one of claims 1 to 9, comprising the steps consisting of:
 (i) applying a primer;
 (ii) applying the adhesive; and
 (iii) applying thermoplastic polymer.
- 20 13.- The method according to claim 12, in which the adhesive is applied before the primer sets, but after the primer gels.

