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(71) Applicant (for all designated States except US):
ARKEMA [FR/FR]; 4-8, cours Michelet, F-92800
Puteaux (FR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BONNET, Anthony**
[FR/FR]; 14, rue du Mont Rôti, F-27170 Beaumont Le
Roger (FR). **WERTH, Michael** [FR/FR]; 7, Allée Paul
Gauguin, F-27300 Bernay (FR).

(74) Agent: **SENNINGER, Thierry**; Arkema, Département
Propriété Industrielle, 4-8, Cours Michelet, La Défense 10,
F-92091 Paris La Défense Cedex (FR).

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(54) Title: METAL SURFACES COATED WITH FLUOROPOLYMERS

(57) Abstract: The invention relates to a metal surface coated with, in succession a layer (L1) comprising at least one primer, placed on the metal surface; a layer (L2) comprising at least one radiation grafted fluoropolymer and optionally at least one unmodified fluoropolymer; an optional layer (L3) comprising at least one unmodified fluoropolymer. According to one embodiment, it is a metal surface coated with, in succession a layer (L2) comprising at least one primer, at least one radiation grafted fluoropolymer and optionally at least one unmodified fluoropolymer, placed on the metal surface; an optional layer (L3) comprising at least one unmodified fluoropolymer. The invention more particularly relates to a metal tube having on its internal and/or external surface a coating with the layers described above that is (L1) / (L2) / optionally (L3) or (L2) / optionally (L3). The invention also relates to a blend of at least one functionalized fluoropolymer and at least one flexible fluoropolymer having a tensile modulus between 50 and 1000 MPa (as measured according to ISO R 527 at 23°C), preferably between 100 and 750 MPa and even more preferably between 200 and 600 MPa. The invention also relates to a structure of a layer comprising said blend adhering to an inorganic surface or to the surface of a plastic. It relates also to the use of said blend to make a coating on an inorganic surface or on the surface of a plastic.

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METAL SURFACES COATED WITH FLUOROPOLYMERS

Field of the invention

The present invention relates to the coating of a metal surface with a fluoropolymer modified by radiation grafting. It also relates to a blend of a functionalized PVDF and a flexible fluoropolymer.

Technical problem

Fluoropolymers, in particular polyvinylidene fluoride (PVDF), are used in applications requiring high heat resistance, high chemical resistance and good liquid and gas barrier properties. Thus, they are very useful for protecting metal substrates. However, it is known that fluoropolymers suffer from a problem of adhesion to metals. In general, this problem is solved by applying a primer layer having good adhesion to the metal surface allowing bonding to the polymer. In the case of fluoropolymers, particularly PVDF, several systems allowing PVDF to bond onto metal substrates are known, but the effectiveness of these systems is lower than with a fluoropolymer modified by radiation grafting (for simplicity's sake, the expression "radiation grafted fluoropolymer" is used).

The grafting of a graftable compound onto a polymer chain is a well-known operation that has already been employed widely to modify the physico-chemical properties of polymers. Thus, maleic anhydride is grafted onto a polyolefin (polyethylene or polypropylene) in the melt state in an extruder. To do this, a radical initiator, the decomposition temperature of which must be carefully chosen, is added to the molten compound. The grafting by means of a radical initiator onto a fluoropolymer that has hydrogen atoms in its structure is much less easy. This therefore explains the fact why there has been little description of maleic anhydride being grafted onto PVDF. In addition, the contents of maleic anhydride grafted onto PVDF are generally low. Radiation-assisted grafting makes it possible to obtain more effective grafting than grafting assisted by a radical initiator, resulting in improved adhesion properties.

The present invention relates to a coating on a metal surface to which a primer has been attached, comprising a radiation grafted fluoropolymer. The invention also relates to a blend having superior adhesion on metals and also on different types of substrates, obtained by blending a functionalized fluoropolymer, preferably a radiation grafted fluoropolymer, and a flexible fluoropolymer. It also relates to a structure of a layer comprising said blend adhering to an inorganic surface or to the surface of a plastic. It relates also to the use of said blend to make a coating on an inorganic surface or on the surface of a plastic.

10 Prior art

Patent **EP 404 752** discloses structures consisting in succession of a substrate, a primer and a PVDF layer. The primer is a blend of an epoxy resin with a polymer compatible with PVDF. The compatible polymer may itself be PVDF or else an acrylic polymer such as PMMA (the usual abbreviation for polymethyl methacrylate) or a methyl methacrylate/ethyl acrylate copolymer.

Patent **EP 354 822** discloses compositions based on an epoxy and/or epoxy-phenolic resin and on an acrylic resin serving as adhesion primer for improving the adhesion of fluororesins to metals.

20

Application **WO 9727260** discloses structures consisting in succession of a metal substrate, a primer and a PVDF layer. The primer is a blend of at least two of the following three polymers, namely (i) a PVDF homopolymer, (ii) a PVDF copolymer containing at least 50 mol% of VDF and (iii) an acrylic polymer having carboxylic acid functional groups such as, for example, methyl methacrylate/acrylic acid copolymers.

Application **WO 97/49777** discloses similar structures. However, the addition of the acrylic polymer reduces the chemical resistance and the temperature resistance of the coating.

30

Patent **GB 1 255 493** discloses a composition containing a fluoropolymer, a monomer containing at least two double bonds and at least one silicon-based compound. The composition, once crosslinked using a radical initiator or by radiation, is used as an adhesive for metals.

5

In these documents of the prior art, there is no mention of a radiation grafted fluoropolymer. In addition, the presence of an acrylic resin has a tendency to reduce the chemical resistance and the temperature resistance of the coating.

10 Patent **US 5 576 106** discloses the radiation grafting of a compound that can be grafted onto the surface of particles of a fluoropolymer powder. The grafting does not take place in the bulk.

15 Application **EP 1484346 A1** describes a radiation grafted fluoropolymer used alone or blended with another fluoropolymer or with an acrylic polymer. All examples relate to a radiation grafted fluoropolymer used alone.

20 Application **EP 1508927 A1** describes a radiation grafted fluoropolymer which, according to a preferred embodiment, is blended with another fluoropolymer. In the examples, the radiation grafted fluoropolymer and the fluoropolymer are of the same type (for instance, a modified Kynar 761 is blended with Kynar 761 or a modified Kynarflex 2801 is blended with Kynarflex 2801).

25 Application **EP 1537989 A1** describes a radiation grafted fluoropolymer that may be blended with a fluoropolymer. All examples relate to a radiation grafted fluoropolymer used alone.

30 Application **EP 1541343 A1** describes a radiation grafted fluoropolymer that may be blended with a fluoropolymer. The two examples relate to a radiation grafted fluoropolymer used alone.

International application **WO 2005/068522 A1** describes a radiation grafted fluoropolymer that may be blended with a fluoropolymer or with an acrylic polymer. All examples relate to a radiation grafted fluoropolymer used alone.

- 5 In none of these applications, it is suggested the adhesion is improved when the radiation grafted fluoropolymer is blended with a flexible fluoropolymer.

Brief description of the invention

The invention relates to a metal surface coated with, in succession :

- 10 • a layer (L1) comprising at least one primer, placed on the metal surface;
- a layer (L2) comprising at least one radiation grafted fluoropolymer and optionally at least one unmodified fluoropolymer;
- 15 • an optional layer (L3) comprising at least one unmodified fluoropolymer.

According to one embodiment, it is a metal surface coated with, in succession :

- a layer (L2) comprising at least one primer, at least one radiation grafted fluoropolymer and optionally at least one unmodified fluoropolymer, placed on the metal surface;
- 20 • an optional layer (L3) comprising at least one unmodified fluoropolymer.

The invention more particularly relates to a metal tube having on its internal and/or external surface a coating with the layers described above that is (L1) / (L2) / optionally (L3) or (L2) / optionally (L3).

25

The invention also relates to a blend of at least one functionalized fluoropolymer and at least one flexible fluoropolymer having a tensile modulus between 50 and 1000 MPa (as measured according to ISO R 527 at 23°C), preferably between 100 and 750 MPa and even more preferably between 200 and 600 MPa.

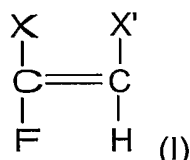
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The invention also relates to a structure of a layer comprising said blend adhering to an inorganic surface or to the surface of a plastic. It relates also to the use of said blend to make a coating on an inorganic surface or on the surface of a plastic.

Detailed description of the invention

French patent application 04.11066 and US patent provisional application 60/647310 are incorporated herein by reference.

- 5 **The term fluoromonomer** refers to an unsaturated monomer of formula (I) :



in which X and X' can be, independently of one another, a hydrogen atom, a halogen, in particular fluorine or chlorine, or a perhalogenated, in particular perfluorinated, alkyl.

10

Suitable exemplary fluoromonomers for use according to the invention include, but are not limited to, vinylidene fluoride (VDF, $\text{CH}_2=\text{CF}_2$), vinyl fluoride, trifluoroethylene, tetrafluoroethylene (TFE), hexafluoropropylene (HFP) and chlorotrifluoroethylene (CTFE). Mention may also be made of, 2-
 15 chloropentafluoro-propene, perfluoroalkyl vinyl ethers, such as $\text{CF}_3\text{-O-CF}=\text{CF}_2$ or $\text{CF}_3\text{-CF}_2\text{-O-CF}=\text{CF}_2$, 1-hydropentafluoropropene, 2-hydropentafluoropropene, dichlorodifluoroethylene, trifluoroethylene, 1,1-dichlorofluoroethylene and perfluoro-1,3-dioxoles, such as those described in
 20 **US 4 558 142**. Fluorine-comprising diolefins can be mentioned as well, for example diolefins, such as perfluorodiallyl ether and perfluoro-1,3-butadiene.

The term fluoropolymer refers to polymer and copolymers (including polymers having two or more different monomers, such as terpolymers) containing at least 50 mole percent of fluoromonomer units derived from fluoromonomer (I).
 25 The polymers and copolymers are obtained by the radical polymerization of at least one fluoromonomer of formula (I). Unsaturated olefinic monomers not comprising fluorine, such as ethylene, propylene, butylene and higher homologues, may also be used as comonomers.

The fluoropolymer is produced by processes known in the state of the art. The fluoropolymer can be prepared in aqueous emulsion or in aqueous suspension. The emulsion comprise, for example, a water-soluble initiator, such as an alkali metal or ammonium persulfate or an alkali metal permanganate, which produce free radicals, and also comprise one or more emulsifiers, such as alkali metal or ammonium salts of a perfluorooctanoic acid. Other aqueous colloidal suspension processes use initiators which are essentially soluble in the organic phase, such as dialkyl peroxides, alkyl hydroperoxides, dialkyl peroxydicarbonates or azoperoxides, the initiator being used in combination with colloids of the following types: methylcelluloses, methylhydroxypropylcelluloses, methylpropylcelluloses and methylhydroxyethylcelluloses. In particular, patents **US 3553185** and **EP 0120524** disclose processes for the synthesis of PVDF by suspending VDF in water and polymerizing it. Patents **US 4 025 709**, **US 4 569 978**, **US 4 360 652**, **US 626 396** and **EP 0 655 468** disclose processes for the synthesis of PVDF by emulsifying VDF in water and polymerizing it.

Preferably, the fluoropolymer is a PVDF, that is a homo- or copolymer of VDF containing at least 50 mole% VDF, advantageously at least 75% VDF by weight and preferably at least 85% VDF. PVDF is preferred as it provides very good chemical and thermomechanical resistance and it is easily extruded. As regards the PVDF copolymers, they are obtained through the copolymerization of VDF and at least one comonomer selected from the group consisting of vinyl fluoride, trifluoroethylene, tetrafluoroethylene (TFE), hexafluoropropylene (HFP), chlorotrifluoroethylene (CTFE), 2-chloropentafluoro-propene, perfluoroalkyl vinyl ethers, such as $\text{CF}_3\text{-O-CF=CF}_2$ or $\text{CF}_3\text{-CF}_2\text{-O-CF=CF}_2$, 1-hydropentafluoropropene, 2-hydropentafluoropropene, dichlorodifluoroethylene, 1,1-dichlorofluoroethylene and perfluoro-1,3-dioxoles, such as those described in **US 4 558 142**. Fluorine-comprising diolefins can be mentioned as well, for example diolefins, such as perfluorodiallyl ether and perfluoro-1,3-butadiene.

The PVDF can be a copolymer of VDF and HFP or a terpolymer of VDF, HFP and TFE. Preferably, the PVDF is a homopolymer or a VDF/HFP copolymer.

5 The PVDFs commercialized under the brand name KYNAR® can be used. For example, we mention more particularly the following products: KYNAR 710, KYNAR 720, KYNAR 740, KYNAR 2850 and KYNAR 3120.

10 In the specification, the expression "unmodified fluoropolymer" is used to denote a fluoropolymer that has not been modified by radiation grafting. The definition of the term fluoropolymer applies equally for both the "unmodified fluoropolymer" and the fluoropolymer from which the radiation grafted fluoropolymer is derived.

15 **The radiation grafted fluoropolymer** is a fluoropolymer that has been chemically modified by radiation grafting. The grafting is carried out in the bulk of the polymer and not on its surface according to the following process:

- a) melt-blending a fluoropolymer and at least one graftable compound;
- b) the blend obtained is made in the form of granules or powder;
- c) irradiating this blend in the solid state by irradiation (which can be a γ or β radiation) with a dose of between 1 and 15 Mrad, optionally after having removed the residual oxygen; and
- 20 d) optionally removing the graftable compound that has not grafted and the residues liberated by the grafting, especially HF.

25 The blend is obtained by any melt blending techniques known in the art, preferably using an extruder.

30 The irradiation is done with an electron or photon source. The radiation dose is between 10 and 200 kGray, preferably between 10 and 150 kGray. Irradiation using a cobalt bomb is preferred. During step c), it is preferable to prevent oxygen from being present, for instance by flushing the fluoropolymer/graftable compound blend with nitrogen or argon.

The graftable compound is grafted in an amount of 0.1 to 5% by weight (i.e. the grafted graftable compound corresponds to 0.1 to 5 parts per 99.9 to 95 parts of fluoropolymer), advantageously 0.5 to 5% and preferably 1 to 5%. The content of grafted graftable compound depends on the initial content of the graftable compound in the fluoropolymer/graftable compound blend to be irradiated. It also depends on the grafting efficiency, and therefore on the duration and the energy of the irradiation.

Step d) can sometimes be optional if the amount of graftable compound that has not been grafted is low or not detrimental to the adhesion of the modified fluoropolymer. Step d) may be carried out using techniques known to those skilled in the art. Vacuum degassing may be applied, optionally heating at the same time. It is also possible to dissolve the modified fluoropolymer in a suitable solvent, such as for example N-methylpyrrolidone, and then to precipitate the polymer in a non-solvent, for example in water or else in an alcohol.

One of the advantages of this radiation grafting process is that it is possible to obtain higher contents of grafted graftable compound than with conventional grafting processes using a radical initiator. Thus, typically, with the radiation grafting process it is possible to obtain contents of greater than 1% (1 part of graftable compound per 99 parts of fluoropolymer), or even greater than 1.5%, whereas with a conventional grafting process carried out in an extruder the content is lower and sometimes is not feasible.

The radiation grafting takes place "cold", typically at temperatures below 100°C, or even below 70°C, so that the fluoropolymer/graftable compound blend is not in the melt state, as in the case of a "conventional" grafting process that is carried out in an extruder. One essential difference with a "conventional" grafting process is therefore that, in the case of a semicrystalline fluoropolymer (as is the case with PVDF for example), the grafting takes place in the

amorphous phase and not in the crystalline phase, whereas homogeneous grafting is produced in the case of grafting carried out in an extruder. The graftable compound is therefore not distributed among the fluoropolymer chains in the same way in the case of radiation grafting as in the case of grafting carried out in an extruder. The modified fluoropolymer product therefore has a different distribution of the graftable compound among the fluoropolymer chains compared with a product that would be obtained by grafting carried out in an extruder. This makes it possible to obtain better adhesion properties than grafting using a radical initiator.

With regard to the **graftable compound**, this possesses at least one double bond $C=C$, and at least one polar functional group that may be one of the following functional groups:

- a carboxylic acid;
- a carboxylic acid salt;
- a carboxylic acid anhydride;
- an epoxide;
- a carboxylic acid ester;
- a silyl;
- an alkoxy silane;
- a carboxylic amide;
- a hydroxyl;
- an isocyanate.

It is also possible to envisage mixtures of several graftable compounds.

As examples of graftable compounds, we mention methacrylic acid, acrylic acid, undecylenic acid, zinc, calcium or sodium undecylenate, maleic anhydride, dichloromaleic anhydride, difluoromaleic anhydride, itaconic anhydride, citraconic anhydride, crotonic anhydride, glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether and vinylsilanes, such as vinyltrimethoxysilane, vinyltriethoxysilane, vinyltriacetoxysilane and γ -methacryloxypropyltrimethoxysilane.

Preferably, to obtain good adhesion, an anhydride or else zinc, calcium or sodium undecylenates will be chosen. These graftable compounds also have the advantage of being solids, which makes it easier to introduce them into an extruder. Maleic anhydride is most particularly preferred as it allows good adhesion properties to be achieved.

Because of the presence of a C=C double bond in the graftable compound, polymerization of the graftable compound, to give polymer chains either grafted onto the fluoropolymer, or free chains, that is to say those not attached to the fluoropolymer, is not excluded. The term "polymer chain" is understood to mean a chain-linking of more than ten units of the graftable compound. Within the context of the invention, it is preferable to limit the presence of grafted or free polymer chains, and therefore to seek to obtain chains with fewer than ten units of the graftable compound. Chains limited to fewer than five graftable compound units will be preferred, and those having fewer than two graftable compound units will be even more preferred. Grafting only one compound unit is most preferred.

Likewise, it is not excluded for there to be more than one C=C double bond in the graftable compound. Thus, for example, graftable compounds such as allylmethacrylate, trimethylolpropane trimethacrylate or ethylene glycol dimethacrylate may be used. However, the presence of more than one double bond in the graftable compound may result in crosslinking of the fluoropolymer, and therefore in a modification of the rheological properties, or even the presence of gels, which is not desirable. It may then be difficult to obtain a high grafting efficiency while still limiting crosslinking. Thus, the graftable compounds containing only a single C=C double bond are preferred. The preferred graftable compounds are therefore those possessing a single C=C double bond and at least one polar functional group.

From this standpoint, maleic anhydride and also zinc, calcium and sodium undecylenates constitute good graftable compounds as they have little tendency to polymerize or even to give rise to crosslinking. Maleic anhydride is most particularly preferred.

5

The radiation grafted fluoropolymer retains the very good chemical and oxidation resistance along with the thermomechanical behaviour of the fluoropolymer before grafting.

10 **The term "primer"** denotes a substance that is applied to a metal surface so as to improve the adhesion to this surface. It is also called an "adhesion primer".

The primer may be :

- an epoxy ;
- an epoxy-phenolic ;
- 15 - a polyurethane resin ;
- an acrylic resin.

The acrylic resin denotes homo- and copolymers of methyl methacrylate containing at least 50% methyl methacrylate by weight. As examples of
20 comonomers, mention may be made, for example, of alkyl (meth)acrylates, acrylonitrile, butadiene, styrene and isoprene. Examples of alkyl (meth)acrylates are described in Kirk-Othmer, Encyclopedia of Chemical Technology, 4th edition in Volume 1 on pages 292-293 and in Volume 16 on pages 475-478. Advantageously, the acrylic resin may contain 0 to 20% and preferably 5 to 15%
25 by weight of at least one other alkyl (meth)acrylate such as, for example, methyl acrylate and/or ethyl acrylate. The acrylic resin may be functionalized, that is to say it contains, for example, acid, acid chloride, alcohol, anhydride and ureido functional groups. These functional groups may be introduced by grafting or by copolymerization. As regards acid functional groups, it is advantageous to have
30 an acid functional group provided by the acrylic or methacrylic acid comonomer. Two adjacent acrylic acid functional groups may lose water to form an anhydride functional group which would not be a problem to apply. The

proportion of functional groups may be from 0 to 15% by weight of the acrylic resin comprising the optional functional groups.

5 The acrylic resin may optionally also contain from 5 to 30% by weight of impact modifiers, these being well known to those skilled in the art.

Preferably, the primer is an epoxy or epoxy-phenolic. The term "epoxy or epoxy-phenolic primer" is understood to mean the product resulting from the reaction between a thermosetting epoxy resin and a hardener. The principle of this chemistry is described, for example, in Kirk-Othmer Encyclopedia of Chemical Technology 3rd edition, Volume 9 on pages 267-289.

15 The epoxy primer may be defined as any product resulting from the reaction between an epoxy resin and a hardener. The term "epoxy resin" is understood to mean any organic compound possessing at least two oxirane functional groups that is ring-opening polymerizable.

The term "epoxy resins" denotes any of the standard epoxy resins liquid at room temperature (23°C) or at higher temperature. These epoxy resins may be monomeric or polymeric on the one hand, and aliphatic, cycloaliphatic, heterocyclic or aromatic on the other. As examples of such epoxy resins, mention may be made of the diglycidyl ether of resorcinol, the diglycidyl ether of bisphenol A, triglycidyl-*p*-aminophenol, the diglycidyl ether of bromobisphenol F, the triglycidyl ether of *m*-aminophenol, tetraglycidyl methylene dianiline, the triglycidyl ether of (trihydroxyphenyl)methane, the polyglycidyl ethers of phenol-formaldehyde novolac, polyglycidyl ethers of orthocresol novolac and tetraglycidyl ethers of tetraphenylethane. Mixtures of at least two of these resins may also be used.

30 Epoxy resins possessing at least 1.5 oxirane functional groups per molecule, and more particularly epoxy resins containing between 2 and 4 oxirane functional groups per molecule, are preferred. Epoxy resins possessing at least

one aromatic ring, such as diglycidyl ethers of bisphenol A, are also preferred. Owing to the reactions involved during the reaction of the oxirane functional groups with the hardener, what is obtained is a crosslinked material corresponding to a three-dimensional network of greater or lesser density depending on the basic characteristics of the resins and hardeners employed.

With regard to the hardener, it is general practice to use those hardeners for epoxy or epoxy-phenolic resins that react at room temperature or at temperatures above room temperature. As non-limiting examples, mention may be made of:

- acid anhydrides, including succinic anhydride;
- aromatic or aliphatic polyamines, including diaminodiphenylsulphone (DDS) or methylenedianiline or 4,4'-methylenebis-(3-chloro-2,6-diethylaniline) (MCDEA);
- dicyandiamide and its derivatives;
- imidazoles;
- polycarboxylic acids;
- polyphenols.

Preferably, dicyandiamide and its derivatives are preferred for the epoxy primers and polyphenols for the epoxy-phenolic primers.

The resins used in the present invention can be crosslinked between 150 and 280°C, preferably between 180 and 250°C. The gel time is defined by the AFNOR NFA 49-706 standard. This is the time needed to cause a rapid increase in the viscosity at a defined temperature. The gel time is advantageously between 20 and 60 seconds.

Advantageously, the measured glass transition temperature, denoted by T_g , is above 120°C. These resins may be in the form of powder or liquid that is sprayed onto the metal surface.

Advantageously, these are one-component resin powders, which are conventionally obtained as follows:

- the epoxy resin (which is solid at room temperature, e.g. DGEBA of high molecular weight), is melt-blended with the hardener, the optional accelerators, fillers, etc. There is precrosslinking during this step, but without going as far as the gel point;
- after blending, the compound is cooled so as to stop the crosslinking;
- the homogeneous solid obtained is ground to a powder.

10

What is thus obtained is a one-component powder which can be applied by standard methods and which completes its crosslinking on contact with the hot metal. For these applications, systems that crosslink only at high temperature (180-240°C) are generally preferred so that at room temperature there is no storage problem (pot life : 6 months-1 year).

15

These resins may include additives such as silicones, pigments such as titanium dioxide, iron oxides and carbon black, and fillers such as calcium carbonate, talc and mica.

20

It is also possible to add to the primer a catalyst capable of increasing the reactivity of the reactive functional groups of the primer. This catalyst may for example be 1,4-diazabicyclo[2.2.2]octane (DABCO) or methyl-2-imidazole (M2ID). These catalysts are described in patent **FR 2 745 733**.

25

The tie of the layer (L2) may be manufactured by melt-blending the various constituents in standard blending devices for thermoplastics, and then used thereafter or else recovered, after cooling, in the form of powder or granules.

30

With regard to the metal of which the metal surface is made, this may be any metal such as for example iron, copper, aluminium, titanium, lead, tin, cobalt, silver, tungsten, nickel and zinc. The term "metal" also covers mixtures

of these metals and also their alloys. Possible alloys are steels, such as for example carbon steel, nickel steel, chromium steel, nickel-chromium steel, chromium-molybdenum steel, silicon steel, stainless steel, cast iron, Permalloy. Aluminium alloys are, for example, aluminium-magnesium, aluminium-silicon, aluminium-copper-nickel-magnesium and aluminium-silicon-copper-nickel-magnesium. Copper alloys are, for example, brass, bronze, silicon bronze, silicon brass and nickel bronze. Nickel alloys are, for example, nickel-manganese (nickel D), nickel-aluminium (nickel Z), nickel-silicon, Monel and Hastelloy alloys. Aluminium alloys also include aluminium oxides and also, for example, aluminium-copper, aluminium-silicon, aluminium-manganese and aluminium-copper-nickel and manganese alloys.

Preferably, the metal will be aluminium, steel and stainless steel.

- 15 The expression "metal surface" applies to any type of surface of any geometry and of any shape. It therefore includes, for example, flat surfaces and also the internal and/or external surfaces of metal tubes, pipes or ducts. The object of the present invention is therefore also a metal tube covered on its internal and/or external surface with a coating according to the invention or its variants.
- 20 If the external surface of the tube is coated, the coated tube therefore has, in radial cross section going from the centre towards the outside of the tube, the following succession of concentric layers: external metal surface of the tube / primer layer (L1) / tie layer (L2) / coating layer (L3). If the internal surface of the tube is coated, the coated tube therefore has, in radial cross section going from the centre towards the outside of the tube, the following succession of concentric layers: coating layer (L3) / tie layer (L2) / primer layer (L1) / internal metal surface of the tube. All the variants of the invention described above are also applicable for metal tubes.
- 25
- 30 The metal surface may be pretreated before the layers described above are applied. The possible pretreatment of the metal surface may be a mechanical and/or chemical treatment. Possible pretreatments are the following : alkaline

cleaning, solvent cleaning using solvents such as trichloroethylene, brushing, shot-peening, phosphating, chromating, anodizing, chromic anodizing, silanizing, abrasion, pickling, and especially sulphochromic pickling. The pretreatment may also consist of a combination of these treatments. Apart from
5 cleaning and shot-peening, steel may be chromated or silanized in order to improve primer anchoring.

The tie (L2) and the external layer (L3) may also be extruded using a "crosshead" surrounding the tube. The tie and optionally the external layer may
10 also be applied using a powder method.

It is not excluded for the coating of the invention as described above to be limited to the protection of only one side of the metal surface. In this case, the metal surface is covered on both sides with a coating corresponding to the
15 invention or else to one of its variants. As illustrative examples, the following succession of layers may be found:

(L3) / (L2) / (L1) / metal surface / (L1) / (L2) / (L3)
(L2) / (L1) / metal surface / (L1) / (L2).

20 **As regards the metal surface coated**

The present invention relates to a metal surface coated with, in succession :

- a layer (L1) comprising at least one primer, placed on the metal surface;
 - a layer (L2) of a tie comprising at least one radiation grafted
25 fluoropolymer optionally blended with at least one unmodified fluoropolymer.
- The invention therefore relates to the following succession of layers : metal / primer layer (L1) / tie layer (L2).

In a first variant, a coating layer (L3) comprising at least one fluoropolymer is
30 placed beside the tie layer. In this case, the following succession of layers is obtained : metal / primer layer (L1) / tie layer (L2) / coating layer (L3).

According to a second variant, at least said primer is incorporated with at least one radiation grafted fluoropolymer and optionally with at least one unmodified fluoropolymer in order to form the tie layer (L2). Thus, in this case, the following succession is obtained : metal / tie layer (L2). The tie layer (L2) is placed on the metal surface. According to this second variant, said primer, said radiation grafted fluoropolymer and optionally said fluoropolymer will have been powder blended beforehand using techniques known to those skilled in the art. Once the powder blend has been applied to the metal surface, it is not excluded for the primer and the radiation grafted fluoropolymer to chemically react with each other in the melt state, although this is not necessarily deleterious to the adhesion of the tie layer (L2) to the metal.

In a third variant, the primer is incorporated into the radiation grafted fluoropolymer and optionally into the unmodified fluoropolymer, in order to form the tie layer (L2), and a coating layer (L3) comprising the fluoropolymer is placed beside the tie layer (L2). The following succession of layers is obtained : metal / tie layer (L2) / coating layer (L3).

Table I below summarizes the invention and its variants :

20

Table I

	Structure
Invention	metal surface / primer layer (L1) comprising at least one primer / tie layer (L2) comprising at least one radiation grafted fluoropolymer and optionally at least one fluoropolymer
First variant	metal layer / primer layer (L1) comprising at least one primer / tie layer (L2) comprising at least one radiation grafted fluoropolymer and optionally at least one fluoropolymer / coating layer (L3) comprising at least one fluoropolymer
Second variant	metal surface / tie layer (L2) comprising at least one primer and at least one radiation grafted fluoropolymer and at least one fluoropolymer
Third variant	metal layer / tie layer (L2) comprising at least one primer and at least one radiation grafted fluoropolymer and at least one fluoropolymer / coating layer (L3) comprising at least one fluoropolymer

The tie layer (L2)

In the case of the invention and the first variant, the tie layer (L2) comprises a radiation grafted fluoropolymer that is optionally blended with an unmodified fluoropolymer. Thus, the tie layer (L2) comprises from 1 to 100 parts by weight of at least one radiation grafted fluoropolymer per 99 to 0 parts by weight of at least one unmodified fluoropolymer. Advantageously, it contains by weight from 10 to 90 parts, more preferably from 10 to 75 parts, and even more preferably from 10 to 50 parts, of at least one radiation grafted fluoropolymer per 90 to 10 parts, more preferably from 90 to 25 parts, and even more preferably 90 to 50 parts of at least one unmodified fluoropolymer.

To promote very strong adhesion of the tie layer (L2) on the primer layer (L1), it is possible for the blend to contain no unmodified fluoropolymer and only the radiation grafted fluoropolymer : thus the blend contains 100 parts of radiation grafted fluoropolymer per 0 part of unmodified fluoropolymer.

According to the second and third variants, the tie layer (L2) comprises from 1 to 70 parts by weight of the radiation grafted fluoropolymer and optionally of the unmodified fluoropolymer per 99 to 30 parts by weight of primer. In this case, the radiation grafted fluoropolymer and the unmodified fluoropolymer are in the same relative proportions as those given above in the case of the invention and its first variant.

The unmodified fluoropolymer of the layer (L2) may be chosen from the list of fluoropolymers described above. It is possible for it to be different from the fluoropolymer used for obtaining the radiation grafted fluoropolymer so as to combine mechanical and/or chemical properties.

The MFI (Melt Flow Index) of a radiation grafted fluoropolymer deriving from a PVDF homopolymer is advantageously between 5 and 40 g/10 min (at 230°C under a load of 5 kg) and between 5 and 30 g/10 min (at 230°C under a load of

5 kg) when the radiation grafted fluoropolymer derives from a VDF / HFP copolymer.

5 The MFI of the unmodified fluoropolymer is advantageously between 5 and 40 g/10 min and preferably between 8 and 20 g/10 min (at 230°C under a load of 5 kg). Advantageously, the melting point of the unmodified fluoropolymer is above 150°C. The highest possible melting point is preferred.

Layer (L3)

10 For the first and third variants, a layer (L3) comprising at least one unmodified fluoropolymer is placed against the tie layer (L2). The fluoropolymer may be chosen from the family of fluoropolymers described above. It is advantageously chosen among PVDF homopolymers and VDF/HFP copolymers containing at least 50% VDF by weight, advantageously at least 75% VDF by weight and
15 preferably at least 85% VDF by weight. Advantageously, it is a PVDF homopolymer or a VDF/HFP copolymer having a melting point of at least 165°C. Advantageously, the MFI is between 5 and 40 g/10 min and preferably between 8 and 20 g/10 min (at 230°C under a load of 5 kg).

20 One blend that is of particularly high performance in terms of adhesion, even in the boiling water resistance test, is a blend comprising 50% by weight of a KYNAR® 710 onto which 1% by weight of maleic anhydride has been radiation grafted and 50% by weight of KYNAR® 2751.

25 **As regards the thicknesses of the various layers (L1), (L2) and (L3),** these may be adjusted, by adjusting the process parameters known to those skilled in the art, such as, for example, the powder throughput through the gun or the molten polymer throughput through the extruder.

30 Table II specifies the thicknesses of the various layers (L1), (L2) and (L3).

Table II

Thicknesses in μm	(L1)	(L2)	(L3)
Invention	50-150	100-500	1000-5000
First variant	50-150	100-5000	XXXXXXXXXX
Second variant	XXXXXXXXXX	50-500	1000-5000
Third variant	XXXXXXXXXX	50-5000	XXXXXXXXXX

For the structures of the first and third variants in which the coating layer (L3) is absent, it is recommended that the tie layer (L2) be thicker than for the structures of the invention and of the second variant so as to preserve the chemical and mechanical resistance of the coating.

As regards the blend of the radiation grafted fluoropolymer and the unmodified fluoropolymer, it has been surprisingly discovered that a very strong and cohesive adhesion can be attained by blending a radiation grafted PVDF and a flexible fluoropolymer. The term flexible fluoropolymer relates to a fluoropolymer selected in the list given above having a tensile modulus between 50 and 1000 MPa (as measured according to ISO R 527 at 23°C), preferably between 100 and 750 MPa and even more preferably between 200 and 600 MPa.

More generally, this surprising effect can be observed not only with a radiation grafted PVDF but also with any functionalized PVDF, that is a PVDF comprising at least 50mole% of monomer units of VDF and monomer units of at least one functional monomer having a least one functional group that may be one of the following groups : a carboxylic acid, a carboxylic acid salt, a carbonate, a carboxylic acid anhydride, an epoxide, a carboxylic acid ester, a silyl, an alkoxysilane, a carboxylic amide, a hydroxyl, an isocyanate. The functionalized PVDF is prepared in suspension, in emulsion or in solution by copolymerizing VDF with said at least one functional monomer and optionally at least another comonomer. For instance, the functionalized PVDF may comprise monomer

units of VDF and of an unsaturated dibasic acid monoester or vinylene carbonate as is envisioned in **US 5415958**. Another example is a functionalized PVDF comprising monomer units of VDF and of itaconic or citraconic anhydride as is envisioned in **US 6703465 B2**. Such functionalized PVDFs may be
5 prepared in suspension, in emulsion or in solution.

Thus, the blend comprises by weight from 1 to 99 parts, advantageously from 10 to 90 parts, preferably from 10 to 75 parts, even more preferably from 10 to 50 parts of at least one functionalized PVDF per 99 to 1, advantageously from
10 90 to 10 parts, preferably from 90 to 25 parts, even more preferably from 90 to 50 parts of a flexible fluoropolymer.

Preferably, the viscosity of the functionalized PVDF (measured at 230°C at a shear rate of 100 s^{-1} using a capillary rheometer) ranges from 100 Pa.s to
15 1500 Pa.s, preferably from 200 to 1000 Pa.s and even more preferably from 500 to 1000 Pa.s.

Preferably, the viscosity of the flexible fluoropolymer (measured at 230°C at a shear rate of 100 s^{-1} using a capillary rheometer) is from 100 to 1500 Pa.s,
20 preferably from 200 to 1000 Pa.s and even more preferably from 500 to 1000 Pa.s.

Preferably, the crystallization temperature of the flexible fluoropolymer (measured by DSC according to ISO 11357-3) is from 50 to 120°C, more
25 preferably from 85 to 110°C.

The blend may also comprise a PMMA (polymethyl methacrylate) homo- or copolymer containing at least 50 wt% methyl methacrylate. The proportion of PMMA may be, by weight, from 0 to 30 parts per 100 to 70 parts of the
30 functionalized PVDF and the flexible fluoropolymer. As examples of comonomers, mention may be made, for example, of alkyl (meth)acrylates, acrylonitrile, butadiene, styrene and isoprene. Examples of alkyl (meth)acrylates

are described in Kirk-Othmer, Encyclopedia of chemical technology, 4th edition in Volume 1, pages 292-293 and in Volume 16, pages 475-478. Advantageously, the PMMA may contain, by weight, 0 to 20% and preferably 5 to 15% of at least one other alkyl (meth)acrylate such as, for example methyl acrylate and/or ethyl acrylate. The PMMA may be functionalized, that is to say it contains, for example, acid, acid chloride, alcohol, anhydride or ureido functional groups. These functional groups may be introduced by grafting or by copolymerization. As regards acid functional groups, these are advantageously an acid functional group provided by the acrylic or methacrylic acid comonomer.

Two adjacent acrylic acid functional groups may undergo dehydration to form an anhydride.

The PMMA may itself contain an acrylic elastomer used to reinforce the impact resistance. There are in fact commercially available grades of PMMA called "impact grades" that contain acrylic impact modifiers, usually of the core/shell type. These acrylic impact modifiers may also be present in the PMMA because they have been introduced during its polymerization or prepared simultaneously with its polymerization. This proportion of acrylic elastomer may be, by weight, from 0 to 30 parts per 100 to 70 parts of PMMA respectively.

Preferably, the functionalized PVDF is a radiation grafted PVDF. Preferably, the radiation grafted fluoropolymer is derived from a PVDF containing at least 80 mole% of VDF, advantageously at least 90%, preferably at least 95%, even more preferably at least 98%. Most preferably, it is derived from a PVDF homopolymer (100% VDF).

Preferably, the flexible fluoropolymer is a PVDF copolymer, more particularly a VDF/HFP copolymer.

The blend is prepared by any melt blending technique known in the art, preferably using an extruder. The blend can be in the form of pellets or in the

form of a powder. The powder is obtained for instance by cryo-grinding pellets of the blend.

5 The strong and cohesive adhesion is observed not only on metals having a primer attached to them but also on any inorganic surface, like for example glass, quartz, ceramic, concrete or silicon. The adhesion may also be observed on the surfaces of plastics, preferably having chemical groups able to react with the functional groups of the functionalized fluoropolymer. As way of example, the adhesion is also observed when a layer comprising the blend is attached to
10 a layer comprising a functionalized polyolefin, a polyamide, a polyurethane resin, an epoxy resin, an epoxy-phenolic resin or an acrylic resin.

The invention relates also to the structure of a layer comprising the blend adhering to an inorganic surface or to the surface of a plastic. It also relates to
15 the use of the blend to make a coating on an inorganic surface or on the surface of a plastic.

As regards the process to apply the coating, it is also a subject of the present invention. Within the context of the invention and of its first variant, the
20 metal surface to be coated may firstly undergo a pretreatment so as to increase the adhesion of the primer layer (L1). This pretreatment step is known to those skilled in the art involved in the adhesion to metals. If the state of the metal surface does not require pretreatment, the primer layer (L1) is applied directly.

25 The primer of the layer (L1) is deposited on the metal surface in liquid form, by spraying or dipping, or if it is in the form of a powder, by electrostatic spraying. In electrostatic spraying, the powder is introduced into a gun in which it is conveyed by compressed air and passes through a nozzle raised to a high potential, generally between about ten and about one hundred kilovolts. The
30 applied voltage may be of positive or negative polarity. The powder flow rate through the gun is generally between 10 and 200 g/min, preferably between 50 and 120 g/min. During its passage through the nozzle, the powder becomes

charged with a certain amount of electricity and the powder particles conveyed by the compressed air are applied to the metal surface to be coated, the said surface itself being earthed, i.e. at a zero electrostatic potential. The powder particles are retained on this surface by their electrostatic charge and the electrostatic attraction forces are enough for the object coated with the powder to be able to be moved to an oven and heated therein.

Next, the tie layer (L2) is deposited, either by electrostatic spraying if it is in powder form or by coating or roll coating if it is in the form of a molten polymer. The adhesion between the layers (L1) and (L2) may sometimes be better if on the surface of (L1) there are chemical functional groups capable of reacting with the polar group of the graftable compound. Thus, when the primer is obtained after a crosslinking step, for example when it is an epoxy or epoxy-phenolic primer, there may remain, on the layer (L1), chemical functional groups that would not have reacted during the crosslinking step and that would be capable of reacting with those of the layer (L2). It may therefore be recommended to deposit the binder of the layer (L2) before the end of complete crosslinking.

Within the context of the second and third variants, the metal surface to be coated may firstly undergo a pretreatment so as to increase the adhesion of the tie layer (L2). This pretreatment step is known to those skilled in the art involved in the adhesion to metals. If the state of the metal surface does not require pretreatment, the tie layer (L2) is applied directly.

The tie (L2) is deposited on the metal surface by electrostatic spraying. The primer, the radiation grafted fluoropolymer and optionally the unmodified fluoropolymer will have been powder blended beforehand using the techniques known to those skilled in the art. If there is a coating layer (L3), this is applied either by electrostatic spraying or by coating or roll coating.

30

The subject of the present invention is also a process for manufacturing coated metal tubes. Within the context of the invention and of its first variant, the

pretreatment step and the step of applying the primer layer (L1) are identical to those explained in the case of the metal surface. The tie of the tie layer (L2) is then deposited either by spraying if it is available in powder form or extruded in an annular die (also called a crosshead) concentrically placed around the metal tube. The tie of the layer (L2) may also be extruded in a sheet die producing a continuous ribbon that is wound around a tube, for example by rotating the tube about itself. Optionally, the unmodified fluoropolymer of the coating layer (L3) is deposited in the same fashion.

Within the context of the second and third variants, the pretreatment step and the step of applying the tie layer (L2) are identical to those explained in the case of the metal surface. The coating layer (L3) is then deposited either by spraying if it is available in powder form or extruded in an annular die (also called a crosshead) placed concentrically around the metal tube. Optionally, the tie for the coating layer (L3) may also be extruded in a sheet die producing a continuous ribbon that is wound around a tube, for example by rotating the tube about itself.

The coating of the invention can be easily produced on a conventional coating line, owing to the excellent processability of fluoropolymers, in particular of PVDF. The coating may be applied continuously, at a speed of at least 50 cm/minute, at a temperature below 250°C, a temperature allowing all the initial properties of the metal to be maintained. The easy processability is an advantage over other known solutions using thermostable polymers, such as polysulphone, polyphenylene ether or polyetherimide which require either high temperatures or difficult and lengthy processing with reactive solvents (postcuring).

If there is a coating layer (L3), this is applied in the same way as the layer (L2).

Additives and/or fillers may be added in each of the layers of the coating so as to enhance the mechanical properties, adhesion or the ageing resistance. The additives may for example be pigments, plasticizers, impact modifiers or additives to improve ageing resistance, such as UV stabilizers. The fillers may
5 be titanium oxide, talc or carbon black.

As regards the coating, it exhibits good impact strength and scratch resistance, while still maintaining flexibility allowing the metal substrate to deform without the coating debonding, and excellent adhesion of the coating to
10 the metal, even at a high temperature (up to 150°C). These good properties are maintained during exposure to aqueous agents such as, for example, a salt fog or else an acid medium, at high temperatures (up to 100°C) and for long periods. The coating therefore allows the metal surface to be protected against corrosion.

15 The coating is strongly bonded to the metal surface due to the presence of the radiation grafted fluoropolymer.

Examples illustrating the invention

20 The following examples further illustrate the best mode contemplated by the inventors for the practice of their invention and are intended to be illustrative and not in limitation thereof.

The materials used were the following:

25 **STEEL TUBE:**

Welded steel tube (E36-4 grade): length 3 metres; outside diameter 114 mm and thickness 6.3 mm, supplied by Van Leeuwen Tubes (45120 Chalette sur Loing, France).

30 **CHROMATING:**

Accomet PC chromating system supplied by Brent Europe Ltd (address: Ridgeway, Iver, Buckinghamshire, SLO 9JJ, UK).

EPOXY PRIMERS OF THE LAYER (L1)

5 **EUROKOTE® 798** : epoxy powder primer produced by BS Coating; gel time of 45 ±5 s at 180°C and T_g of 120-140°C (measured by DSC on crosslinked film).

SCOTCHKOTE® 6258: novolac epoxy powder primer produced by 3M®; gel time of 26 s at 182°C and T_g of 166°C (measured by DMA on crosslinked film).

PRODUCTS USED FOR THE TIE LAYER (L2)

10 **UNMODIFIED FLUOROPOLYMER**

KYNAR® 3120-15 : HFP/VDF copolymer (containing 10% HFP) produced by ARKEMA of melt flow rate MFI = 8 g/10 min at 230°C / 5 kg and melting point 165°C.

15 **KYNAR® 2850-04**: HFP/VDF copolymer (containing 4% HFP) produced by ARKEMA of melt flow rate MFI = 20 g/10 min at 230°C / 5 kg and melting point 158°C.

KYNAR® 2751: HFP/VDF copolymer (containing 16% HFP) produced by ARKEMA of melt flow rate MFI = 4-14 g/10 min at 230°C / 12.5 kg.

20 **RADIATION GRAFTED FLUOROPOLYMERS**

KYNAR® ADX 120 : modified PVDF containing 1% grafted maleic anhydride obtained according to the operating method described below, starting with a KYNAR® 720, a PVDF homopolymer of MFI = 14 g/10 min at 230°C / 5 kg and melting point 169°C.

25 **KYNAR® ADX 110** : modified PVDF containing 1% grafted maleic anhydride obtained according to the operating method described below, starting with a KYNAR® 710 which is a PVDF homopolymer of MFI = 20 g/10 min at 230°C / 5 kg and melting point 169°C.

30 **KYNAR® ADX 220** : modified PVDF containing 0.5% grafted zinc undecylenate obtained according to the operating method described below, starting with a KYNAR® 720, a PVDF homopolymer of MFI = 20 g/10 min at 230°C / 5 kg and melting point 169°C.

ACRYLIC POLYMER

OROGLAS® HT121 : an acrylic polymer produced by ALTUGLAS INTERNATIONAL consisting of methyl methacrylate, ethyl acrylate and acrylic acid, with a melt flow index of 2 g/10 min at 230°C / 3.8 kg.

PRODUCT USED FOR THE LAYER (L3)

KYNAR® 740 : a vinylidene fluoride homopolymer produced by ARKEMA with a melt flow rate MFI = 2 g/10 min at 230°C / 5 kg and melting point 168°C.

Preparation of KYNAR® ADX 120:

A blend of KYNAR® 720 PVDF and of 2 wt% maleic anhydride was prepared. This blend was prepared using a twin-screw extruder operating at 230°C and 150 rpm with a throughput of 10 kg/h. The granulated product thus prepared was bagged, in aluminium-lined sealed bags, and then the oxygen was removed by flushing with a stream of argon. These bags were then irradiated by γ radiation (Co⁶⁰ bomb) at 3 Mrad (10 MeV acceleration) for 17 hours. A 50% grafting level was determined, this level being checked after a step of dissolving the material in N-methylpyrrolidone and then precipitation in a water/THF mixture (50/50 by weight). The product obtained after the grafting operation was then placed in a vacuum overnight at 130°C in order to remove the residual maleic anhydride and the hydrofluoric acid released during the irradiation. The final grafted maleic anhydride content was 1% (determined by infrared spectroscopy on the C=O band at around 1870 cm⁻¹).

Preparation of KYNAR® ADX 110:

The operating conditions used for KYNAR® ADX 120 were repeated, but the KYNAR® 720 was replaced with KYNAR® 710. The final grafted maleic anhydride content was 1% (determined by infrared spectroscopy on the C=O band at around 1870 cm⁻¹).

Preparation of KYNAR® ADX 220 :

A blend of KYNAR® 720 PVDF and of 1 wt% zinc undecylenate was prepared. This blend was prepared using a twin-screw extruder operating at 230°C and 300 rpm with a throughput of 60 kg /h. The product thus prepared was bagged in aluminium-lined sealed bags. These bags were then irradiated by γ irradiation (Co⁶⁰ bomb) at 3 Mrad (10 MeV acceleration) for 17 hours. A 50% grafting level was determined, this level being checked after a step of dissolving the material in N-methylpyrrolidone and then precipitation in a water/THF mixture (50/50 by weight). The fluoropolymer modified by the zinc undecylenate was then vented under a hood in order to remove the very small amounts of gas coming from the irradiation. The final grafted zinc undecylenate content was 0.5% (determined by infrared spectroscopy).

PEEL FORCE MEASUREMENTS

The peel forces were determined after cutting the tubes – i.e. a circumferential peel. For each test temperature (110, 130 and 150°C), three rounds were peeled. The mean force and the standard deviation were calculated on the three values obtained.

Failure modes observed:

CF_t = cohesive failure in the tie

CF_p = cohesive failure in the tie near the primer layer interface

+ cr = with creep of the peel arm

AF = adhesive failure on the primer layer side.

STRUCTURES WITH TIE

Example 1: KYNAR[®] 3120-15 and KYNAR[®] ADX 120 were blended in a Fairex Super 2/50 single-screw extruder in proportions of 85/15 by weight. The blended compound was granulated on leaving the extruder.

5

The steel tube (114 mm outside diameter) to be coated was cleaned with trichloroethylene and then shot-peened.

10

Immediately after this operation, the tube, mounted on a portal frame rotating at 10 rpm and moving at 50cm/min, was heated to 200°C in an induction oven and coated with EUROKOTE[®] 798 powder primer sprayed by an electrostatic gun. The crosshead-extruded tie was wound around the tube onto the primer about 10-20 s after the deposition of the latter. The Kynar[®] 740, also crosshead-extruded, immediately covered the first two layers. A press roll ensured that there was good contact between the various layers. The coated tube was then cooled in water for 3 minutes.

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The throughputs in the gun and the two extruders were adjusted so as to obtain a primer layer 70-100 µm in thickness, a tie layer 250-350 µm in thickness and a KYNAR[®] 740 layer 1250-1500 µm in thickness.

In summary, the structure of the coating obtained was the following :

EUROKOTE[®] 798 / tie {85% KYNAR[®] 3120-15 / 15% KYNAR[®] ADX 120} / KYNAR[®] 740 with thicknesses of 80 µm / 300 µm / 1400 µm.

25

The peel results and the failure modes are given in Table I.

Example 2

30

A tube coated in the same way as in Example 1 was prepared, in order to obtain the following structure:

Eurokote 798 / tie {70% KYNAR[®] 3120-15 / 30% KYNAR[®] ADX 120} / KYNAR[®] 740 with thicknesses of 80 µm / 300 µm / 1400 µm.

Example 3

A tube coated in the same way as in Example 1 was prepared, but with a tube chromated using Accomet PC solution. The Accomet PC chromating solution was applied with a brush to the steel tube after the latter had been shot-peened. Passing the tube through the induction oven at 200°C was sufficient to ensure proper drying before application of the primer.

The structure obtained was the following :

EUROKOTE® 798 / Tie {85% KYNAR® 3120-15 / 15% KYNAR® ADX 120} / KYNAR® 740 with thicknesses of 80 µm / 300 µm / 1400 µm.

Example 4

A tube coated in the same way as in Example 3 was prepared, but with a thicker outer layer. The structure obtained was then the following:
EUROKOTE® 798 / Tie {85% KYNAR® 3120-15 / 15% KYNAR® ADX 120} / KYNAR® 740 with thicknesses of 80 µm / 300 µm / 2000 µm.

Example 5

A tube coated in the same way as in Example 3 was prepared, but with SCOTCHKOTE® 6258. The structure obtained was then the following:
SCOTCHKOTE® 6258 / Tie {85% KYNAR® 2850-04 / 15% KYNAR® ADX 120} / KYNAR® 740 with thicknesses of 80 µm / 300 µm / 1400 µm.

Example 6

A tube coated in the same way as in Example 1 was prepared, with the following structure :
EUROKOTE® 798 / Tie {85% KYNAR® 2850-04 / 15% KYNAR® ADX 120} / KYNAR® 740 with thicknesses of 80 µm / 300 µm / 1400 µm.

Example 7

A tube coated in the same way as in Example 3 was prepared, with the following structure: SCOTCHKOTE® 6258 / Tie {85% KYNAR® 2850-04 / 15% KYNAR® ADX 220} / Kynar 740 with thicknesses of 80 µm / 300 µm / 1 400 µm.

5

Example 8

KYNAR® 3120-15 and KYNAR® ADX 120 were blended in a Fairex Super 2/50 single-screw extruder in proportions of 85/15 by weight. The blended compound was granulated on leaving the extruder.

10

The steel tube (114 mm outside diameter) to be coated was cleaned with trichloroethylene and then shot-peened. Immediately after this operation the tube, mounted on a portal frame rotating at 10 rpm and moving at 50 cm/min, was heated to 200°C in an induction oven and coated with the tie. The latter was crosshead-extruded and wound around the tube. The KYNAR® 740, also crosshead-extruded, immediately afterwards covered the first layer. A press roll ensured that there was good contact between the various layers. The coated tube was cooled in water for 3 minutes.

15

20 The two extruders were adjusted so as to have thicknesses of the order of 250-350 µm of tie and 1250-1500 µm of KYNAR®740.

In summary, the structure of the coating obtained was the following :

tie {85% KYNAR® 3120-15 / 15% KYNAR® ADX 120} / KYNAR® 740 with
25 thicknesses of 300 µm / 1 400 µm.

Comparative Example 9

The steel tube (114 mm outside diameter) to be coated was cleaned with trichloroethylene and then shot-peened. Immediately after this operation, the tube, mounted on a portal frame rotating at 10 rpm and moving at 50 cm/min, was heated to 200°C in an induction oven. The KYNAR® 740 was crosshead-extruded and immediately afterwards covered the tube. A press roll ensured

30

that there was good contact. The coated tube was cooled in water for 3 minutes. The extruder was adjusted so as to obtain a KYNAR® 740 thickness of 1800 µm.

5 Comparative Example 10

KYNAR® 3120-15 and OROGLAS® HT121 were blended in a Fairex Super 2/50 single-screw extruder in proportions 85/15 by weight. The blended compound was granulated on leaving the extruder.

- 10 The steel tube (114 mm outside diameter) to be coated was cleaned in trichloroethylene and then shot-peened. Immediately after this operation, the tube, mounted on a portal frame rotating at 10 rpm and moving at 50 cm/min, was heated to 200°C in an induction oven and coated with EUROKOTE® 798 powder primer sprayed by an electrostatic gun. The crosshead-extruded tie was
- 15 wound around the tube onto the primer 10-20 s after deposition of the latter. The KYNAR® 740, also crosshead-extruded, immediately afterwards covered the first 2 layers. A press roll ensured that there was good contact between the various layers. The coated tube was cooled in water for 3 minutes.
- 20 The throughputs in the gun and the two extruders were adjusted so as to obtain primer thicknesses of 70-100 µm, tie thicknesses of 250-350 µm and Kynar® 740 thicknesses of 1250-1500 µm.

To summarize, the structure of the coating obtained was the following:

- 25 EUROKOTE® 798 / Tie {85% KYNAR® 3120-15 / 15% OROGLAS® HT121} / KYNAR® 740 with thicknesses of 80 µm / 300 µm / 1400 µm.

Comparative Example 11

- 30 The steel tube (114 mm outside diameter) to be coated was cleaned and then shot-peened. Immediately after this operation, the tube, mounted on a portal frame rotating at 10 rpm and moving at 50 cm/min, was heated to 200°C in an induction oven and covered with the EUROKOTE® 798 powder primer sprayed

by an electrostatic gun. The KYNAR[®] 740, also crosshead-extruded, immediately afterwards covered the first layer. A press roll ensured that there was good contact between the various layers. The coated tube was cooled in water for 3 minutes. The throughputs in the gun and the two extruders were
5 adjusted so as to have a primer thickness of 70-100 µm and a Kynar 740 thickness of 1250-1500 µm.

In summary, the structure of the coating obtained was the following:
EUROKOTE[®] 798 / KYNAR[®] 740 with thicknesses of 80 µm / 1400 µm.

10

Example 12 : boiling water resistance

An aluminium plate, cleaned and then shot-peened, maintained at 200°C, was coated by electrostatic powder coating with EUROKOTE[®] 798 powder primer then, 20 seconds afterwards, a film of KYNAR[®] ADX 120 was deposited and compressed
15 at 230°C for 30 s. A cross-shaped notch was made so as to favour the diffusion of water into the various interfaces. This structure was immersed in boiling water for 30 minutes. No loss of cohesion was observed.

Example 13 : boiling water resistance

20 An aluminium plate, cleaned and then shot-peened, and maintained at 200°C, was coated by electrostatic powder coating with EUROKOTE[®] 798 powder primer and then, 20 seconds afterwards, a film formed from 50% KYNAR[®] ADX 110 / 50% KYNAR[®] 2751 was deposited and compressed at 230°C for 30 s. A cross-shaped notch was made so as to favour diffusion of water into the various interfaces. This
25 structure was immersed in boiling water for 30 minutes. No loss of cohesion was observed.

Comparative Example 14 : boiling water resistance

An aluminium plate, cleaned and then shot-peened, and maintained at 200°C, was
30 coated by electrostatic powder coating with EUROKOTE[®] 798 powder primer and then, 20 seconds afterwards, a film of KYNAR[®] 740 was deposited and compressed at 230°C for 30 s. A cross-shaped notch was made so as to favour diffusion of water

into the various interfaces. This structure was immersed in boiling water for 1 minute. The film spontaneously debonded after 1 minute.

Comparative Example 15 : boiling water resistance

- 5 An aluminium plate, cleaned in trichloroethylene and then shot-peened, and maintained at 200°C, was coated by electrostatic powder coating with EUROKOTE® 798 powder primer and then, 20 seconds afterwards, a monolayer film consisting of a miscible blend of KYNAR® 740 (85%) and OROGLAS® HT121 PMMA (15%) was deposited and compressed at 230°C for 30 s. A cross-shaped notch was made so as
- 10 to favour diffusion of water into the various interfaces. This structure was immersed in boiling water for 5 minutes. The film spontaneously debonded after 5 minutes.

TABLE IV. Peel test results in N/cm and failure modes at 110, 130 and 150°C.

Structure	Example 8	Example 9 (comparative)	Example 10 (comparative)	Example 11 (comparative)
110°C average	150	5	146	50
Standard deviation	±7	±5	±7	±9
Mode	CF _p	AF	CF _p	AF
130°C average	110	0	105	30
Standard deviation	±9		±10	±7
Mode	CF _p		CF _p	AF
150°C average	42	0	39	10
Standard deviation	±7		±10	±9
Mode	CF _p		AF	AF

Examples of blends providing strong adhesion

To illustrate the strong adhesion that is observed with blends having two different types of PVDF, concentric tubes having the following structure with 4 different layers were prepared :

KYNAR® 720 / layer comprising the radiation grafted PVDF / LOTADER® AX8840 / PEX

The layer of KYNAR® 720 is the inner layer and the layer of PEX is the outer layer. PEX denotes a cross-linked polyethylene. The cross-linking is due to the reaction of silanes groups that are present on the polyethylene backbone. The layer of PEX is obtained from a mixture comprising 95% by weight of BORPEX ME-2510 and 5% of MB-51, both products from BOREALIS.

LOTADER® AX8840 is a copolymer of ethylene (92%) and glycidyl methacrylate (8%) prepared under high-pressures ($P > 1000$ bar) by ARKEMA, having a melt-flow rate of 5 (under ASTM D1238).

Comparative xample 1 :

A tube having the following structure was prepared:

KYNAR® 720 (130 μm) / KYNAR® ADX 120 (50 μm) / LOTADER® AX8840 (50 μm) / PEX (780 μm)

The tube is obtained by coextruding a layer of a polyethylene modified by silane groups (temperature of extrusion around 230°C), a layer of LOTADER® AX8840 (temperature of extrusion around 250°C), a layer of KYNAR® ADX 120 (temperature of extrusion around 250°C) and a layer of KYNAR® 720 (temperature of extrusion around 250°C). The tube is placed in a heated bath to activate the cross-linking.

The peel results and the failure modes are given in Table V.

Examples of blends providing strong adhesion

To illustrate the strong adhesion that is observed with blends having two different types of PVDF, concentric tubes having the following structure with 4 different layers were prepared :

KYNAR® 720 / layer comprising the radiation grafted PVDF / LOTADER® AX8840 /
PEX

The layer of KYNAR® 720 is the inner layer and the layer of PEX is the outer layer.

PEX denotes a cross-linked polyethylene. The cross-linking is due to the reaction of silanes groups that are present on the polyethylene backbone. The layer of PEX is obtained from a mixture comprising 95% by weight of BORPEX ME-2510 and 5% of MB-51, both products from BOREALIS.

LOTADER® AX8840 is a copolymer of ethylene (92%) and glycidyl methacrylate (8%) prepared under high-pressures ($P > 1000$ bar) by ARKEMA, having a melt-flow rate of 5 (under ASTM D1238).

Comparative xample 1 :

A tube having the following structure was prepared:

KYNAR® 720 (130 μm) / KYNAR® ADX 120 (50 μm) / LOTADER® AX8840 (50 μm) /
PEX (780 μm)

The tube is obtained by coextruding a layer of a polyethylene modified by silane groups (temperature of extrusion around 230°C), a layer of LOTADER® AX8840 (temperature of extrusion around 250°C), a layer of KYNAR® ADX 120 (temperature of extrusion around 250°C) and a layer of KYNAR® 720 (temperature of extrusion around 250°C). The tube is placed in a heated bath to activate the cross-linking.

The peel results and the failure modes are given in Table V.

Example 2:

A tube similar to the tube of example 1 was prepared except the KYNAR[®] ADX 120 is replaced by a blend consisting of 50% by weight of KYNAR[®] ADX 120 and 50% of a copolymer of VDF and HFP having by weight 16% of HFP and a viscosity of 900 Pa.s (measured at 230°C and 100 s⁻¹).

Example 3:

A tube similar to the tube of example 1 was prepared except the KYNAR[®] ADX 120 is replaced by a blend consisting of 50% by weight of KYNAR[®] ADX 110 and 50% of a copolymer of VDF and HFP having by weight 16% of HFP and a viscosity of 900 Pa.s (measured at 230°C and 100 s⁻¹).

Comparative example 4:

A tube similar to the tube of example 1 was prepared except the KYNAR[®] ADX 120 is replaced by a blend consisting of 50% by weight of KYNAR[®] ADX 110 and 50% of a copolymer of VDF and HFP having by weight 16% of HFP and a viscosity of 2300 Pa.s (measured at 230°C and 100 s⁻¹).

Table V.

ex.	Layer	Peel strength * (N/cm)	Failure mode
1 (comp.)	KYNAR [®] ADX 120 (MFI = 14 g/10 min)	15	adhesive
2 (inv.)	50% KYNAR [®] ADX 120 (MFI =14 g/10 min) + 50% VDF/HFP copolymer (16% HFP, viscosity 900 Pa.s)	42	cohesive
3 (inv.)	50% KYNAR [®] ADX 110 (MFI =20 g/10 min) + 50% VDF/HFP copolymer (16% HFP, viscosity 900 Pa.s)	45	cohesive
4 (comp.)	50% KYNAR [®] ADX 110 (MFI =20 g/10 min) + 50% VDF/HFP copolymer (16% HFP, viscosity 2300 Pa.s)	20	cohesive

* peel strength between the layer of LOTADER[®] AX8840 and the layer comprising the radiation grafted PVDF

As shown in Table III, the adhesion is greatly enhanced when the radiation grafted PVDF is diluted in a PVDF copolymer (see ex. 1 and 2). The bond is even stronger when the radiation grafted PVDF is of a lower viscosity (see ex. 2 and 3). Example 4
5 illustrates the influence of the viscosity of the unmodified PVDF.

10

15

CLAIMS

1. Metal surface coated with, in succession :

- a layer (L1) comprising at least one primer, placed on the metal surface;
- a layer (L2) comprising at least one radiation grafted fluoropolymer and optionally at least one unmodified fluoropolymer;
- an optional layer (L3) comprising at least one unmodified fluoropolymer.

2. Metal surface coated with, in succession :

- a layer (L2) comprising at least one primer, at least one radiation grafted fluoropolymer and optionally at least one unmodified fluoropolymer, placed on the metal surface;
- an optional layer (L3) comprising at least one unmodified fluoropolymer.

3. Coated metal surface according to Claim 1 or 2, in which the layer (L2) comprises from 1 to 100 parts by weight of at least one radiation grafted fluoropolymer per 99 to 0 parts by weight of an unmodified fluoropolymer.

4. Coated metal surface according to Claim 2, in which the tie layer (L2) comprises from 1 to 70 parts by weight of the radiation grafted fluoropolymer and of the unmodified fluoropolymer, per 99 to 30 parts by weight of primer.

5. Coated metal surface according to Claims 3 or 4, in which the unmodified fluoropolymer has a tensile modulus between 50 and 1000 MPa (as measured according to ISO R 527 at 23°C), preferably between 100 and 750 MPa and even more preferably between 200 and 600 MPa.

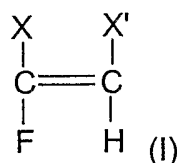
6. Coated metal surface according to Claim 5, in which the viscosity of the radiation grafted fluoropolymer (measured at 230°C at a shear rate of 100 s⁻¹ using a capillary rheometer) ranges from 100 Pa.s to 1500 Pa.s, preferably from 200 to 1000 Pa.s and even more preferably from 500 to 1000 Pa.s.

7. Coated metal surface according to Claims 5 or 6, in which the viscosity of the flexible fluoropolymer (measured at 230°C at a shear rate of 100 s⁻¹ using a capillary rheometer) ranges from 100 to 1500 Pa.s, preferably from 200 to 1000 Pa.s and even more preferably from 500 to 1000 Pa.s.

8. Coated metal surface according to Claims 5 to 7, in which the crystallization temperature of the flexible fluoropolymer (measured by DSC according to ISO 11357-3) is from 50 to 120°C, more preferably from 85 to 110°C.

9. Coated metal surface according to any one of the preceding claims, characterized in that it is covered on both sides.

10. Coated metal surface according to any one of the preceding claims, in which the unmodified fluoropolymer or the fluoropolymer from which the radiation grafted fluoropolymer is derived, is a polymer or copolymer containing at least 50 mole% of fluoromonomer units derived from fluoromonomer (I)



in which X and X' can be, independently of one another, a hydrogen atom, a halogen, in particular fluorine or chlorine, or a perhalogenated, in particular perfluorinated, alkyl.

11. Coated metal surface according to Claim 10 in which the fluoropolymer is a homo- or copolymer of VDF containing at least 50 mole% VDF.

5 12. Coated metal surface according to Claims 10 or 11 in which the fluoropolymer is a copolymer of VDF and HFP.

10 13. Coated metal surface according to any one of the preceding claims, in which the graftable compound possesses at least one C=C double bond and at least one polar functional group that may be a carboxylic acid, carboxylic acid salt, carboxylic acid anhydride, epoxide, carboxylic acid ester, silyl, alkoxysilane, carboxylic amide, hydroxyl or isocyanate functional group.

15 14. Coated metal surface according to Claim 13, in which the graftable compound possesses only a single C=C double bond.

20 15. Coated metal surface according to Claim 13 or 14, in which the graftable compound is an anhydride, preferably maleic anhydride, or zinc, calcium or sodium undecylenate.

25 16. Coated metal surface according to any one of the preceding claims, in which the metal surface is the internal and/or external surface of a tube, pipe or duct.

17. Metal tube coated on its internal and/or external surface with a coating according to any one of the Claims 1 to 16.

30 18. Blend of at least one functionalized PVDF and at least one flexible fluoropolymer, having a tensile modulus between 50 and 1000 MPa (as measured according to ISO R 527 at 23°C), preferably between 100 and 750 MPa and even more preferably between 200 and 600 MPa.

19. Blend according to Claim 18, in which the blend comprises by weight from 1 to 99 parts, advantageously from 10 to 90 parts, preferably from 10 to 75 parts, even more preferably from 10 to 50 parts of at least one functionalized PVDF per 99 to 1, advantageously from 90 to 10 parts, preferably from 90 to 25 parts, even more preferably from 90 to 50 parts of a flexible fluoropolymer.
20. Blend according to Claims 18 or 19, in which the viscosity of the functionalized PVDF (measured at 230°C at a shear rate of 100 s⁻¹ using a capillary rheometer) ranges from 100 Pa.s to 1500 Pa.s, preferably from 200 to 1000 Pa.s and even more preferably from 500 to 1000 Pa.s.
21. Blend according to any one of Claims 18 to 21, in which the viscosity of the flexible fluoropolymer (measured at 230°C at a shear rate of 100 s⁻¹ using a capillary rheometer) is from 100 to 1500 Pa.s, preferably from 200 to 1000 Pa.s and even more preferably from 500 to 1000 Pa.s.
22. Blend according to any one of Claims 18 to 21, in which the crystallization temperature of the flexible fluoropolymer (measured by DSC according to ISO 11357-3) is from 50 to 120°C, more preferably from 85 to 110°C.
23. Blend according to any one Claims 18 to 22, in which the blend comprises from 0 to 30 parts of PMMA homo- or copolymer per 100 to 70 parts of the functionalized PVDF and the flexible fluoropolymer.
24. Blend according to any one of Claims 18 to 23, in which the functionalized PVDF is a radiation grafted PVDF.

25. Blend according to any one of Claims 18 to 24, in which the PVDF from which the radiation grafted PVDF is derived, contains at least 80 mole% of VDF, advantageously at least 90%, preferably at least 95%, even more preferably at least 98%.

26. Blend according to any one of Claims 18 to 25, in which the PVDF from which the radiation grafted PVDF is derived, is a PVDF homopolymer.

27. Blend according to any one of Claims 18 to 26, in which the flexible fluoropolymer is a PVDF copolymer.

28. Structure of a layer comprising the blend according to any one of Claims 18 to 27, the layer adhering to an inorganic surface or to the surface of a plastic.

29. Use of the blend to make a coating on an inorganic surface or on the surface of a plastic.