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(54) Title: A METHOD FOR PREVENTING CORROSION OF METAL ARTICLES

(57) Abstract: The present invention concerns a method for preventing the corrosion of metal articles and alloys comprising applying thereon a composition formed by a curable epoxy resin and a curing agent in admixture with at least two ionisable amorphous polymers having a low T_g , and then curing this composition after application. The thus obtained coating layer, when subjected to mechanical damage, such as a scratch, allows the polymers to form an ionic network that protects the underlying metal surface from corrosion.

WO 2019/101697 A1

Description**Title****A METHOD FOR PREVENTING CORROSION OF METAL ARTICLES****Cross-Reference to Related Application**

This application claims priority to European application No. 17306632.5 filed November 23, 2017, the whole content of this application being incorporated herein by reference for all purposes.

5 Technical Field

The present invention relates to a method for preventing the corrosion of metal articles and to compositions for carrying out this method.

Background Art

It is known that metals and alloys undergo corrosion when exposed to certain
10 environmental conditions. Usually, metals undergo electrochemical oxidation by contact with an oxidant, like oxygen or sulphur, and convert to more stable forms, such as their oxides, hydroxides or sulphides. The most common example of electrochemical oxidation is rusting, which consists in the formation of iron oxides or salts on a metal surface and imparts a typical orange coloration. One of the methods
15 used to prevent the oxidation of metals and metal alloys is to apply a polymeric film on their surface.

The US Patent Application published with No. 2004/265603 (SCHLENOFF, JOSEF B) discloses an anticorrosion polymer coating to be applied on a metallic surface, said coating comprising a positively-charged polyelectrolyte and a negatively-charged
20 polyelectrolyte forming a complex. The polyelectrolytes used for making the coating are copolymers having a combination of charged and neutral repeat units. There is no disclosure or suggestion of polymers comprising a neutral polymer chain and one charged unity at each end of the chain. Furthermore, the coating disclosed in this document can be formed either by exposing a surface to alternating oppositely charged
25 polyelectrolyte solutions or using a pre-formed polyelectrolyte complex, which can be obtained by mixing the oppositely charged polyelectrolytes. The pre-formed complex precipitates and is then dissolved or re-suspended in a suitable solvent/liquid to form a polyelectrolyte complex solution/dispersion. Such solution or dispersion is then applied

to the substrate surface and the solvent/liquid is evaporated, leaving behind a film comprising the polyelectrolyte complex.

It is also known that fully or partially fluorinated polyethers, commonly referred to in the polymer field as (per)fluoropolyethers (herein after abbreviated as "PFPEs"), are very versatile polymers. The most widely known PFPEs can be obtained by means of processes comprising either the homopolymerization of hexafluoropropylene oxide (HFPO) or 2,2,3,3-tetrafluorooxetane or the photooxidation of tetrafluoroethylene (TFE) and/or hexafluoropropylene (HFP).

PFPEs comprises a fully or partially fluorinated polyoxyalkylene chain (PFPE chain) that contains recurring units having at least one catenary ether bond and at least one fluorocarbon moiety. PFPEs can be divided into non-functional and functional; the former comprise a PFPE chain having at least two ends, wherein such ends bear (per)haloalkyl groups, while the latter comprise a PFPE chain having at least two ends, wherein at least one end comprises a functional group. Functional PFPEs can be used as starting materials for the manufacture of other functional PFPEs that are used as such for a variety of industrial applications, e.g. as additives for lubricant compositions, or as building blocks for the manufacture of block copolymers.

For example, the use of functional PFPEs in the lubrication field is disclosed in US 5498547 (HITACHI, LTD) 12/03/1996, related to a rotary magnetic recording medium having a lubricating film layer on its surface. The lubricating film layer comprises a fluoropolyether lubricant having at least two acidic functional groups in one molecule and a fluoropolyether lubricant having at least two basic functional groups in one molecule. This document teaches that the two fluoropolyether lubricants form a stable network structure on the medium surface by an appropriate combination of the lubricant having the acidic groups and the one having the basic groups. It is herein pointed out that magnetic recording media typically comprise a substrate, a magnetic layer and a protective carbon overcoat laid on the magnetic layer and lubricants are applied onto the carbon overcoat in order to prevent wear by contact with a magnetic head floating over the surface of the medium during recording and reproduction, or by contact with dust generated during such contact. Magnetic materials used in the manufacture of recording media are metal oxides, such as ferromagnetic oxides, in

admixture with a binder and further additives.

WO 2013/017470 (SOLVAY SPECIALTY POLYMERS ITALY SPA) discloses compositions comprising two ionisable fluoropolymers, each comprising recurring fluorinated blocks and recurring blocks comprising at least one ionisable anionic or cationic group, wherein at least one ionizable recurring block is comprised between two fluorinated blocks. The two fluoropolymers in the composition are present at an ionic ratio ranging from 1.1 to 0.9. Such compositions are able to form elastomeric materials, which, in certain instances, advantageously show a self-repairing behaviour. There is no disclosure or suggestion of compositions comprising fluoropolymers having a chain of recurring fluorinated blocks, said chain having two ends, each end comprising one ionisable anionic or cationic group. No reference is made is to anti-corrosion properties of these compositions.

WO 2014/090646 (SOLVAY SPECIALTY POLYMERS ITALY SPA) discloses compositions comprising:

- two ionisable fluoropolymers, each comprising recurring fluorinated blocks and recurring blocks comprising at least one ionisable anionic or cationic group, wherein at least one ionizable recurring block is comprised between two fluorinated blocks;
- at least one fluorinated solvent; and
- at least one alcohol.

Such compositions are stable even after addition of a cross-linking agent and can be used for the manufacture of polymeric materials endowed with high chemical stability, improved mechanical properties and, in some instances, self-healing properties. Mono-epoxy-silanes and mono-epoxy acrylates are taught as useful cross-linking agents. There is no disclosure or suggestion of compositions comprising fluoropolymers having a chain of recurring fluorinated blocks, said chain having two ends, each end comprising one ionisable anionic or cationic group. There is also no hint to anti-corrosion properties.

International application published as WO2016/150942 (Solvay Specialty Polymers Italy SpA) discloses a non-aqueous fluoropolymer composition [composition (FC)] comprising:

- at least one fluorinated ionisable polymer [polymer (A)] comprising recurring

(per)fluorinated blocks [blocks (F)], recurring functional blocks [blocks (Ba)] and at least one curable group [group (C)], said blocks (Ba) comprising at least one ionisable anionic group [group (I^-)];

- at least one fluorinated ionisable polymer [polymer (B)] comprising recurring (per)fluorinated blocks [blocks (F)], recurring functional blocks [blocks (Bb)] and at least one curable group [group (C)], said blocks (Bb) comprising at least one ionisable cationic group [group (I^+)];

- at least one fluorinated solvent [solvent (F)]; and

- at least one solvent [solvent (S)] different from said solvent (F).

10 This non aqueous composition (FC) can be used for example for preparing polymeric articles, preferably amorphous articles, endowed with elastic properties. In some embodiments, the articles are endowed with self-healing properties. No possible anti-corrosion properties are described.

Yu L. *et al.* in Proc. SPIE 9430, Electroactive Polymer Actuators and
15 Devices (EAPAD) 2015, disclose an ionic polymer based on two polydimethylsiloxane(PDMS)-derivatives, i.e. a couple of an acid- and a base-functionalised PDMS, which is useful as silicone elastomer system with high dielectric permittivity. Nevertheless, this document does not mention anti-corrosion properties.

In the field of anti-corrosion coatings, it is also known in the art the use of microspheres
20 as self-healing additives in a polymeric matrix. These microspheres can break after scratch providing self-healing of the damaged part of the polymer matrix, and in some cases also anti-corrosion properties. None of the systems discloses the formation of ionic networks formed *in situ*. An example is disclosed in *Eur. Pol. J.* 49 (2013) 2467-76 reporting of microcapsules based on Zn with active components inside that are free
25 isocyanate. These systems suffer from the high sensitivity to humidity of the free isocyanate that causes a very short life-time of the formulation because of the premature solidification of the active component.

Summary of the Invention

The Applicant has now found that ionisable polymers having a low glass transition
30 temperature (hereinafter referred to as " T_g "), when incorporated in a curable epoxy resin formulation, are able to form a particularly effective coatings on metal articles that

are protective against corrosion.

A subject of the present invention is therefore a method [method (M)] for making a coated article [article (A)], said method comprising:

- i) applying to at least a part of the surface of a metal substrate a composition
5 [composition (C)] comprising, and preferably consisting of:
- a) at least one polymer [polymer (P1)] comprising a polymer chain [chain (R)] consisting of a plurality of non-ionisable recurring units [units (U)], said chain having two ends, each end comprising at least one ionisable acid group;
 - b) at least one polymer [polymer (P2)] comprising a polymer chain [chain (R)]
10 consisting of a plurality of non-ionisable recurring units [units (U)], said chain (R) being equal or different from that of polymer (P1) and having two ends, each end comprising at least one ionisable amino group;
 - c) at least a curable epoxy resin; and
 - d) optionally, at least a curing agent for said curable epoxy resin;

15 wherein:

said polymers (P1) and (P2) are amorphous and have a T_g lower than -35°C , preferably ranging from -35°C to -120°C and

and where the ratio between the equivalents of polymer (P1) and the equivalents of polymer (P2) in said composition (C) preferably ranges from 1.4 to 0.6, more
20 preferably from 1.2 to 0.8, most preferably from 1.1 to 0.9;

ii) curing said composition (C), so as to obtain the article (A).

Method (M) has been found particularly effective for protecting metal substrate against corrosion.

In a further aspect, the invention relates to a composition (C), as above detailed, which
25 is adapted for performing the method (M).

In a still further aspect, the invention relates to a coated article [article (A)] comprising a metal substrate and a coating resulting from curing of composition (C).

Detailed Description of the Invention

General definitions, symbols and abbreviations

30 In the present invention, by the acronym "PFPE" is meant "(per)fluoropolyether", i.e. fully or partially fluorinated polyether. When this acronym is used as substantive in

the plural form, it is referred to as "PFPEs".

The term "(per)haloalkyl" denotes a fully or partially halogenated straight or branched alkyl group.

Unless otherwise indicated, the term "halogen" includes fluorine, chlorine,
5 bromine and iodine.

In the present invention, unless otherwise indicated, the following terms are to be meant as follows:

- a "cycloalkyl group" is a univalent group derived from a cycloalkane by removal of an atom of hydrogen; the cycloalkyl group thus comprises one end which is a free
10 electron of a carbon atom contained in the cycle, which able to form a linkage with another chemical group;

- a "divalent cycloalkyl group" or "cycloalkylene group" is a divalent radical derived from a cycloalkane by removal of two atoms of hydrogen from two different carbons in the cycle; a divalent cycloalkyl group thus comprises two ends, each being
15 able to form a linkage with another chemical group;

- the adjective "aromatic" denotes any mono-or polynuclear cyclic group (or moiety) having a number of π electrons equal to $4n+2$, wherein n is 0 or any positive integer; an aromatic group (or moiety) can be an aryl or an arylene group (or moiety);

- an "aryl group" is a hydrocarbon monovalent group consisting of one core
20 composed of one benzene ring or of a plurality of benzene rings fused together by sharing two or more neighbouring ring carbon atoms, and of one end. Non-limitative examples of aryl groups are phenyl, naphthyl, anthryl, phenanthryl, tetracenyl, triphenyl, pyrenyl, and perylenyl groups. The end of an aryl group is a free electron of
25 a carbon atom contained in a (or the) benzene ring of the aryl group, wherein an hydrogen atom linked to said carbon atom has been removed. The end of an aryl group is capable of forming a linkage with another chemical group;

- an "arylene group" is a hydrocarbon divalent group consisting of one core composed of one benzene ring or of a plurality of benzene rings fused together by
30 sharing two or more neighbouring ring carbon atoms, and of two ends. Non-limitative examples of arylene groups are phenylenes, naphthylenes, anthrylenes,

phenanthrylenes, tetracenylenes, triphenylylenes, pyrenylenes, and perylenylenes. An end of an arylene group is a free electron of a carbon atom contained in a (or the) benzene ring of the arylene group, wherein a hydrogen atom linked to said carbon atom has been removed. Each end of an arylene group is capable of forming a linkage
5 with another chemical group.

Cycloalkyl, cycloalkylene, aryl and arylene groups can be substituted with one or more straight or branched alkyl or alkoxy groups and/or halogen atoms and/or can comprise one or more heteroatoms, like nitrogen, oxygen and sulphur, in the ring.

The use of parentheses “(...)” before and after names of compounds, symbols or
10 numbers identifying formulae or parts of formulae like, for example “polymer (P1)”, “chain (R)”, etc..., has the mere purpose of better distinguishing those names, symbols or numbers from the rest of the text; thus, said parentheses could also be omitted.

The expression “average functionality (F)” denotes the average number of functional groups per polymer molecule and can be calculated according to methods
15 known in the art. For example, the average functionality (F) of PFPE alcohols can be calculated following the method reported in EP 1810987 B (SOLVAY SOLEXIS SPA) 7/25/2007 or in S.Turri, E. Barchiesi, M. Levi Macromolecules 28, 7271, (1995). In particular, the average functionality of polymers (P1) and (P2) according to the present invention was determined following the teaching of the latter reference.

20 When ranges are indicated, range ends are included.

The expression “as defined above” is intended to comprise all generic and specific or preferred definitions referred to by that expression in preceding parts of the description, unless indicated otherwise.

As intended herein, “corrosion” means the conversion of a metal into its
25 corresponding oxide(s), hydroxide(s) or sulphide(s) or mixtures thereof.

The expression “ionisable amino group” and “ionisable acid groups” identify amino or acid groups able to form ionic groups, namely cationic and anionic groups respectively. In greater detail, an ionisable amino group identifies a primary, secondary or tertiary amino group, while an “ionisable acid group” identifies an acid group
30 comprising at least one hydroxyl function in its protonated form, i.e. a protic acid group.

The expression “non-ionisable recurring unit” identifies a chemical moiety that is

not able to form an ionic group with the at least one ionisable amino group or the at least one ionisable acid group in each end of polymers (P1) and (P2).

THE METAL SUBSTRATE

The nature of the metal substrate is not particularly limited. The metal substrate
5 which can be used in this invention may be any of those metal materials which are generally used in various apparatuses, appliances and instruments which may be exposed to corrosive/harsh environment. Non limiting examples of metal substrates which can be coated with composition (C) are shaped metal parts used for instance in architecture (including e.g. frame rails, joists, girders, etc.), industrial plants (e.g. pipes,
10 flanges, valves...), in the automotive industry.

Suitable metal substrates include for example, structural materials, electrically conductive materials, valve metals with corrosion resistance.

Examples of metal constituents of the metal substrate are titanium, tantalum, zirconium and niobium, alloys composed mainly, e.g., containing more than about 50%
15 by weight, of these metals, e.g. Ti-Ta alloys, Ti-Ta-Nb alloys, Ti-Ta-Zr alloys, Ti-Pd alloys, etc., and lower-cost metal materials with good workability, such as iron, nickel, cobalt, copper or alloys composed mainly, e.g., containing more than about 50% by weight, of these metals, e.g., carbon steel, stainless steel, Ni-Cu alloys, brass, etc.

Low-melting metals such as aluminium, magnesium and lead can also be used.

20 Metal substrate may be solely constituted by an individual metallic material (be it a metal in its zero oxidation state, or an alloy of metals in their zero oxidation state, or a composition including one or more than one metals in their zero oxidation state) or may comprise a superficial anti-corrosion coating, such as e.g. anodized layers or other metal coating layers.

25 Anodized layers are created on the metal substrate through an electrochemical process that converts the surface of the metal substrate into durable, corrosion-resistant, anodic oxide finish. Aluminum is ideally suited to anodizing, although other nonferrous metals, such as magnesium and titanium, also can be anodized. So, metal substrates of Aluminum, Magnesium, Titanium may comprise anodized surfaces.

30 Anodizing is accomplished by immersing the metal support into an acid electrolyte bath and passing an electric current through the medium. A cathode is

mounted to the inside of the anodizing tank; the metal support acts as an anode, so that oxygen ions are released from the electrolyte to combine with the metal atoms at the surface of the metal support being anodized.

Otherwise, suitable metals which can be coated on the surface of the metal
5 substrate are any of those metals which have inherent corrosion resistance and can be alloyed with the metal substrate. Suitable coating metals include tantalum, zirconium, niobium, titanium, molybdenum, tungsten, vanadium, chromium, nickel, silicon, and alloys composed mainly of these metals.

Generally, the metal substrate is an iron substrate, such as a cast iron substrate
10 (e.g. grey cast iron, white cast iron, malleable iron, ductile or nodular iron, Ni-hard type iron, Ni-resist type iron), or a steel substrate, such as a stainless steel or carbon steel substrate.

The metal substrate may have any shape; e.g. it may be under the form of a wire, a sheet or film or may have a different three-dimensional shape, e.g. it may have a
15 tubular shape, or whichever other geometry, including irregular shapes.

POLYMER (P1)

Polymer (P1) can be represented with formula (P1) here below:



wherein:

- 20 - R is a polymer chain consisting of a plurality of non-ionisable recurring units [units (U)], equal to or different from one another and
- E1 and E1', equal to or different from one another, are end groups each comprising at least one ionisable acid group. Recurring units (U) are hydrocarbon units, which can further comprise non-ionisable atoms or non-ionisable functional groups, including one
25 or more of halogen atoms, preferably fluorine atoms, ethereal oxygen atoms, alkyl or alkoxy silane groups, carbonate, ester, urethane and acrylate groups.

Non limiting examples of polymers (P1) are those wherein chain (R) is independently selected from a fully or partially fluorinated polyoxyalkylene chain, a polyalkylsiloxane chain, a polyoxyalkylene chain, a polycarbonate chain, a polyester
30 chain, a polyacrylate chain and a polybutadiene chain, as described in greater detail here below.

Examples of chains (R)*Fully or partially fluorinated polyoxyalkylene chains (R_F)*

As intended herein, a fully or partially fluorinated polyoxyalkylene chain [herein after otherwise referred to as “chain (R_F)”, “(per)fluoropolyether chain” or “PFPE chain”]
 5 comprises recurring units [units (U_F)] having at least one catenary ether bond and at least one fluorocarbon moiety; typically, chain (R_F) comprises repeating units (U_F) selected from:

- (U_F - i) -CFXO-, wherein X is F or CF₃;
 (U_F - ii) -CFXCFXO-, wherein X, equal or different at each occurrence, is F or CF₃, with
 10 the proviso that at least one of X is -F;
 (U_F - iii) -CF₂CF₂CW₂O-, wherein each of W, equal or different from each other, is F, Cl, H,
 (U_F - iv) -CF₂CF₂CF₂CF₂O-;
 (U_F - v) -(CF₂)_j-CFZ-O- wherein j is an integer from 0 to 3 and Z is a group of general
 15 formula -OR_f*T, wherein R_f* is a fluoropolyoxyalkylene chain comprising a number of repeating units from 0 to 10, said recurring units being chosen among the followings :
 -CFX*O-, -CF₂CFX*O-, -CF₂CF₂CF₂O-, -CF₂CF₂CF₂CF₂O-, with each of each of X* being independently F or CF₃ and T being a C₁-C₃ perfluoroalkyl group.

When recurring units [units (U_F)] are different from one another, they are
 20 randomly distributed along the chain.

Preferably, chain (R_F) complies with formula (R_F-I):

(R_F-I) -



wherein:

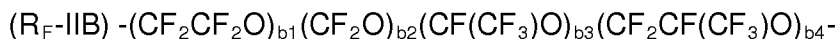
- 25 - X₁ is independently selected from -F and -CF₃;
 - X₂, X₃, equal or different from each other and at each occurrence, are independently -F, -CF₃, with the proviso that at least one of X is -F;
 - g₁, g₂, g₃, and g₄, equal or different from each other, are independently integers ≥0, selected in such a way that the average number molecular weight (M_n) ranges from
 30 400 to 10,000; should at least two of g₁, g₂, g₃ and g₄ be different from zero, the different recurring units are generally statistically distributed along the chain.

More preferably, chain (R_F-I) is selected from chains of formulae (R_F-IIA) - (R_F-IIE):



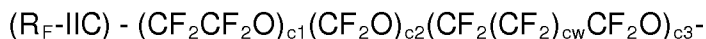
wherein:

- 5 - a1 and a2 are independently integers ≥ 0 such that the number average molecular weight (M_n) ranges from 400 to 10,000, preferably from 400 to 5,000; both a1 and a2 are preferably different from zero, with the ratio a1/a2 being preferably ranging from between 0.1 to 10;



10 wherein:

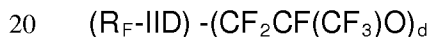
- b1, b2, b3, b4, are independently integers ≥ 0 such that the number average molecular weight (M_n) ranges from 400 to 10,000, preferably from 400 to 5,000; preferably b1 is 0, b2, b3, b4 are > 0 , with the ratio b4/(b2+b3) being ≥ 1 ;



15 wherein:

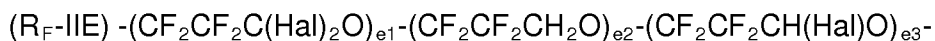
- cw = 1 or 2;

c1, c2, and c3 are independently integers ≥ 0 such that the number average molecular weight (M_n) ranges from 400 to 10,000, preferably from 400 to 5,000; preferably c1, c2 and c3 are all > 0 , with the ratio c3/(c1+c2) being generally lower than 0.2;



wherein:

- d is an integer > 0 such that the number average molecular weight (M_n) ranges from 400 to 10,000, preferably from 400 to 5,000;



25 wherein:

- Hal, equal or different at each occurrence, is a halogen selected from fluorine and chlorine atoms, preferably a fluorine atom;

- e1, e2, and e3, equal to or different from each other, are independently integers ≥ 0 selected in such a way that the (e1+e2+e3) number average molecular weight (M_n)

30 ranges from 400 to 10,000.

Still more preferably, chain (R_F) complies with formula (R_F-III) here below:



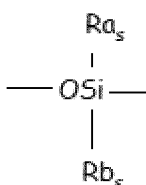
wherein:

- a1, and a2 are integers > 0 such that the number average molecular weight (M_n) ranges from 400 to 4,000, with the ratio $a2/a1$ generally ranging from 0.2 to 5.

5 *Polyalkylsiloxane chains (R_S)*

As intended herein, a polyalkylsiloxane chain [herein after otherwise referred to as chain (R_S)] comprises recurring units [units (U_S)] of formula:

(U_S)



10 in which R_{a_s} and R_{b_s} , equal to or different from one another, are independently selected from hydrogen, straight or branched (halo)alkyl and aryl, with the proviso that at least one of R_{a_s} and R_{b_s} is not hydrogen.

Preferred R_{a_s} and R_{b_s} groups are straight or branched alkyl groups comprising from 1 to 4 carbon atoms; more preferably, both R_{a_s} and R_{b_s} are methyl, i.e. chain (R_S) is a polydimethylsiloxane chain [chain (R_{S-I})], which essentially consists of a sequence of
15 recurring units of formula (U_{S-i}) here below:



Minor amount (e.g. < 1 % wt, based on the weight of chain (R_{S-I})) of spurious units, defects or recurring unit impurities may be comprised in chain (R_{S-I}) without this affecting chemical properties of this chain.

20 Chain (R_S) has a number average molecular weight (M_n) typically ranging from 500 to 10,000, preferably from 500 to 5,000.

Polyoxyalkylene chains (R_{OA})

As intended herein, a polyoxyalkylene chain [herein after otherwise referred to as chain (R_{OA})] is a straight or branched polymer chain consisting of repeating
25 hydrocarbon units comprising at least one catenary ether bond [units (U_{OA})]; non-limiting examples of chain (R_{OA}) are chains comprising, preferably essentially consisting of a sequence of units of formula $-OR_{OA}^{\sim}-$, wherein each of $R_{OA}^{\sim}$, equal to or

different from each other, is, independently at each occurrence, an hydrocarbon divalent group, possibly comprising additional heteroatom(s), and preferably a divalent alkylene group, which may be linear or branched.

Preferred chains (R_{OA}) are polyoxyethylene chains comprising, preferably essentially consisting of recurring units of formulae (U_{OA-i}) as below detailed, polyoxypropylene chains comprising, preferably essentially consisting of recurring units of formulae (U_{OA-ii}) - (U_{OA-iv}) here below, a polytetramethylene glycole chain, comprising, preferably essentially consisting of recurring units of formula (U_{OA-v}) here below, or a chain comprising, preferably essentially consisting of, a mixture of any of oxyethylene, oxypropylene, oxytetramethylene units (U_{OA-i}) - (U_{OA-v}):

(U_{OA-i}): $-OCH_2CH_2-$

(U_{OA-ii}): $-OCH_2CH_2CH_2-$

(U_{OA-iii}): $-OCH(CH_3)CH_2-$

(U_{OA-iv}): $-OCH_2CH(CH_3)-$

(U_{OA-v}): $-OCH_2CH_2CH_2CH_2-$.

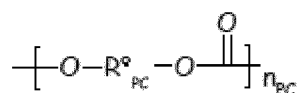
The expression "essentially consisting of" when used in connection with chain (R_{OA}) is hereby understood to indicate that said chain (R_{OA}) may comprise, in addition to the listed recurring units, impurities, defects or spurious groups in a minor amount (e.g. < 5 % moles, wrt to total amount of recurring units), these impurities, defects or spurious groups having generally no peculiar effect on properties of chain (R_{OA}).

Preferred chains (R_{OA}) according to the invention are polyoxypropylene chains. Chain (R_{OA}) has a number average molecular weight (M_n) typically ranging from 500 to 10,000, preferably from 500 to 5,000.

Polycarbonate chains (R_{PC})

As intended herein, a polycarbonate chain [herein after otherwise referred to as chain (R_{PC})] consists of repeating units [units (U_{PC})] of formula:

(U_{PC})



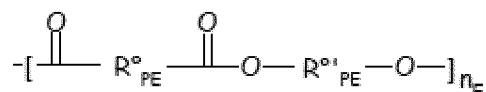
wherein R_{PC}° represents:

- a straight or branched alkylene chain, optionally comprising one or more cycloalkyl, divalent cycloalkyl group, aryl or arylene group as defined above, and wherein n_{PC} is an integer such that the polycarbonate chain has a number average molecular weight (M_n) typically ranging from 500 to 10,000, preferably from 500 to 5,000.

Polyester chains (R_{PE})

As intended herein, a polyester chain [herein after otherwise referred to as chain (R_{PE})] comprises recurring units [units (U_E)] of formula:

(U_E)



wherein R°_{PE} and $R^{\circ'}_{PE}$, equal to or different from one another, represent a straight or branched alkylene chain, optionally comprising one or more cycloalkyl, divalent cycloalkyl group, aryl or arylene groups as defined above.

Chain (R_{PE}) has a number average molecular weight (M_n) typically ranging from 500 to 10,000, preferably from 500 to 5,000.

Polybutadiene chains (R_{PBD})

As intended herein, a polybutadiene chain [herein after otherwise referred to as chain (R_{PBD})] is a chain comprising recurring units derived from 1,3-butadiene monomer, whereas the said recurring units may be formed by connecting the 1,3-butadiene monomers end-to-end, so-called 1,4-addition polymerisation, either in *cis* or *trans* configuration, yielding, respectively, 1,4-*cis* or 1,4-*trans* units, or by connecting 1,3-butadiene monomers via 1,2-addition polymerization, so providing 1,2-*vinyl* units.

The chain (R_{PBD}) may comprise recurring units derived from olefins and dienes other than 1,3-butadiene monomer, being nevertheless understood that chains (R_{PBD}) whereas 1,3-butadiene is the predominant monomer (e.g. at least 60 % moles, preferably at least 80 % moles, even more preferably 90 % moles) are preferred. Most preferably, chain (R_{PBD}) essentially consists of a sequence of recurring units derived from 1,3-butadiene.

According to a preferred embodiment, chain (R) of polymer ($P1$) is a chain (R_S) as defined above, preferably a chain (R_{S-I}).

Groups E1 and E1'

End groups E1 and E1' typically comprise at least one carboxylic acid group, phosphonic acid group or sulfonic acid group, said at least one acid group comprising at least one hydroxyl group in its protonated form, so that it is capable to form an anionic group via acid/base reaction with the at least one ionisable amino group at one of the ends of polymer (P2). E1 and E1' can be equal to or different from one another. Preferably, E1 and E1' are equal to one another.

The polymer (P1) may comprise from two to six end groups or more. According to a preferred embodiment of the present invention, the polymer (P1) comprises two or four acid end groups as defined above.

Preferably, groups E1 and E1' comply with formula (E1-A) here below:



wherein:

- B1 represents a chemical bond or a straight or branched alkylene chain, said alkylene chain preferably comprising from 1 to 20 carbon atoms, and optionally bearing one or more halogen atoms, one or more further -E_A groups and/or optionally comprising one or more heteroatoms or moieties independently selected from:

- cycloalkylene and arylene groups as defined above, -O-, -S-, -OC(O)O-, -OC(O)NH-, -OC(O)S-, -SC(O)S-, -NHC(O)NH- and -NHC(S)NH

and

- E_A represents a -COOH, a -P(O)(OR_{EA})₂ or a -S(O)₂OH group, wherein one of R_{EA} is hydrogen and the other one is hydrogen or straight or branched alkyl, preferably C₁-C₄ alkyl.

In a preferred embodiment, E_A is a -COOH group.

POLYMER (P2)

Polymer (P2) can be represented with formula (P2) here below:



wherein:

- R is a polymer chain as defined above and

- E2 and E2', equal to or different from one another, are end groups each comprising at least one ionisable amino group.

Chain (R) of polymer (P2) can be the same or different from chain (R) of polymer (P1). According to a preferred embodiment, chain (R) of polymer (P2) is a chain (R_S) as defined above, preferably a chain (R_S-I).

Groups E2 and E2'

5 End groups E2 and E2' typically comprise at least one ionisable primary, secondary or tertiary amino group. Groups E2 and E2' can be equal to or different from one another; preferably, groups E2 and E2' are equal to one another. "Ionisable primary, secondary or tertiary amino group" means that the amino group is in its free form, so that it is capable to form a cationic group via acid/base reaction with the at
10 least one a ionisable acid group at one of the ends of polymer (P1).

The polymer (P2) may comprise from two to six or more end groups. According to a preferred embodiment of the present invention, the polymer (P2) comprises two or four amino end groups as defined above.

Preferably, groups E2 and E2' comply with formula (E2-A) here below:

15 (E2-A) -B2-N(R_{P2})₂

wherein:

- B2 represents a chemical bond or a straight or branched alkylene chain, said alkylene chain preferably comprising from 1 to 20 and optionally bearing one or more halogen atoms, one or more further -N(R_{P2})₂ groups and optionally comprising one or more
20 heteroatoms or moieties independently selected from:

- cycloalkylene and arylene groups as defined above;

-N(R_{P2*})- wherein R_{P2*} represents hydrogen or straight or branched alkyl, preferably C₁-C₄ alkyl, more preferably methyl;

-O-, -S-, -OC(O)O-, -OC(O)NH-, -OC(O)S-, -SC(O)S-, -NHC(O)NH and -NHC(S)NH

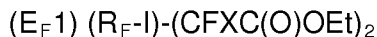
25 and

- R_{P2} represents hydrogen or straight or branched alkyl, preferably C₁-C₄ alkyl.

Polymers (P1) and (P2) wherein chain (R) is a chain (R_F) [herein after polymers (P_F1) and (P_F2)]

Polymers (P_F1) and (P_F2) can be prepared according to methods known in the
30 art for the synthesis of PFPEs. In particular, the synthesis of polymers (P_F1) and (P_F2) wherein chain (R_F) is a chain of formula (R_F-I) can be carried out by oxypolymerization

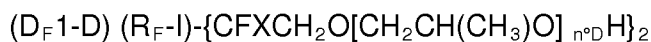
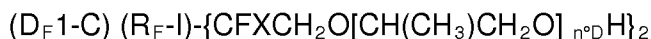
of fluoroolefins, followed by conversion of a resulting -CFXC(O)F terminated polymer ("acyl fluoride terminated polymer", wherein X is as defined above) into the corresponding ethyl ester of formula (E_F1):



5 Ester (E_F1) can be either hydrolyzed to provide an acid polymer (P_F1) wherein E and E' represent -CFXC(O)OH [herein after (P_F1-A)] or reduced to the corresponding PFPE diol ["diol (D_F1)] of formula (R_F-I)-(CFXCH₂OH)₂ [herein after "PFPE diol (D_F1-A)"]. The reduction of ester (E_F1) can be carried out according to methods known in the art, using reducing agents such as NaBH₄, or by catalytic hydrogenation,
10 as disclosed, for example, in US 6509509 A (AUSIMONT S.P.A.) 7/5/2001, US 6573411 (AUSIMONT S.P.A.) 11/21/2002, WO 2008/122639 A (SOLVAY SOLEXIS S.P.A.) 10/16/2008.

Polymer (P_F1-A) can be used as such in the manufacture of compositions (C).

Diols (D_F1-A) can be reacted with alkylene oxides, typically ethylene oxide and
15 propylene oxide, in the presence of a base, to provide further diols (D_F1-B) - (D_F1-D) of formulae:



20 wherein n^D is a positive number, preferably ranging from 1 to 10, more preferably ranging from 1 to 5. Diols (D_F1-B) - (D_F1-D) can also be used as precursors for polymers (P_F1) and (P_F2), as explained below in greater detail.

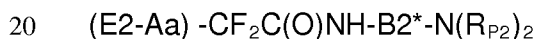
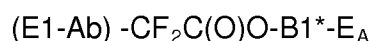
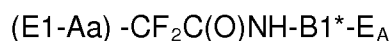
Diols (D_F1-A) and (D_F1-B) with a chain (R_F-III) and wherein in (D_F1-B) n^D ranges from 1 to 2 are available from Solvay Specialty Polymers Italy S.p.A. with the
25 tradename Fomblin® Z DOL. Other diols (D_F1-B) - (D_F1-D) can be obtained following the teaching of WO2014090649 (SOLVAY SPECIALTY POLYMERS ITALY SPA).

Throughout the present application, ester (E_F1), diols (D_F1) and polymers (P_F1) and (P_F2) are visually represented as bifunctional compounds. However, it is known to a person skilled in the art that ester (E_F1) and diols (D_F1) such are always obtained as
30 mixtures comprising the corresponding mono-functional and neutral esters or alcohols which form in the oxypolymerization reaction, i.e. compounds terminating with

(per)haloalkyl groups at one or both ends, typically C₁-C₃ perfluoroalkyl groups. Ester (E_F1) and diols (D_F1) are thus characterized by an average functionality (F) as defined above; the higher the average functionality, the higher the number of bifunctional species. As a consequence, polymers (P_F1) and (P_F2) obtained from ester (E_F1) or from diols (D_F1) are also in admixture with corresponding polymers wherein one end of chain (R_F) bears a (per)haloalkyl group and with neutral compounds present in the (E_F1) or diol (D_F1) used as starting material. Usually, neutral compounds that comprise (per)haloalkyl groups at both ends are present in an amount lower than 0.04% on a molar basis. For the purpose of the present invention, ester (E_F1), diols (D_F1) having an average functionality (F) higher than 1, preferably of at least 1.5 can be used.

PFPE ester (E_F1) and diols (D_F1) can be used as precursors for the synthesis of polymers (P_F1) and (P_F2) with suitable reaction partners, according to methods known in the art for the manufacture of PFPE derivatives.

For example, PFPE ester (E_F1) can be used as precursor for polymers (P_F1) or (P_F2) wherein groups (E1-A) and (E2-A) respectively comply with formulae (E1-Aa), (E1-Ab), (E2-Aa), (E2-Ab) herein below:



wherein:

- E_A and R_{P2} are as defined above and

- B1* and B2* represent straight or branched alkylene chains, said alkylene chain preferably comprising from 1 to 10 carbon atoms and optionally bearing one or more halogen atoms, and/or optionally comprising one or more heteroatoms or moieties independently selected from:

- cycloalkylene and arylene groups as defined above;

-O-, -S-, -OC(O)O-, -OC(O)NH-, -OC(O)S-, -SC(O)S-, -NHC(O)NH and -NHC(S)NH-.

B1* may also comprise one or more further E_A groups, while B2* may also comprise one or more further -N(R_{P2})₂ groups.

B2* may also comprise one or more -N(R_{P2}*)- moieties.

Polymers (P_{F1}) or (P_{F2}) wherein groups (E1-A) and (E2-A) comply with formulae (E1-Aa), (E1-Ab), (E2-Aa), (E2-Ab) as defined above can be manufactured by reacting ester (E_{F1}) with compounds of formulae NH₂- B1*-E_A and HO-B2*-N(R_{P2})₂,
 5 wherein B1*, E_A, B2* and N(R_{P2})₂ are as defined above.

Should B1* and B2* polymers (P_{F1}) or (P_{F2}) contain one or more of the aforementioned heteroatoms or moieties, end groups (E1-Aa), (E1-Ab), (E2-Aa), (E2-Ab) can also be build up by subsequent reactions of ester (E_{F1}) with suitable reaction partners. For example, a polymer (P_{F1}) wherein group (E1-Aa) comprises
 10 a -NHC(O) moiety can be obtained by reacting ester (E_{F1}) first with a diamine and then with an acid comprising two E_A groups. A polymer (P_{F1}) wherein group (E1-Ab) comprises one or more -O-C(O)-NH- moieties can be obtained by reacting ester (E_{F1}) first with a diol and then with a diisocyanate.

PFPE diols (D_{F1}) can be used, for example, as precursors of polymers (P_{F1})
 15 and (P_{F2}) wherein groups (E1-A) and (E2-A) respectively comply with the formulae listed below:



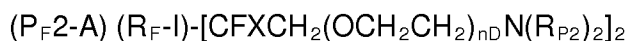
in which X, E_A and R_{P2} are as defined above and nD is 0 or a positive number,
 20 preferably from 1 to 10, more preferably from 1 to 5, while B1** and B2** represent a chemical bond or straight or branched alkylene chains, said alkylene chains preferably comprising from 1 to 10 carbon atoms and optionally bearing one or more halogen atoms, and/or comprising one or more heteroatoms or moieties independently selected from:

25 -cycloalkylene and arylene groups as defined above;
 -O-, -S-, -OC(O)O-, -OC(O)NH-, -OC(O)S-, -SC(O)S-, -NHC(O)NH- and -NHC(S)NH-.

B1** may also comprise one or more further E_A groups, while B2** may also comprise one or more further -N(R_{P2})₂ groups.

B2** may also comprise one or more -N(R_{P2}*)- moieties.

30 For example, starting from a PFPE diol (D_{F1}-A) or (D_{F1}-B), polymers (P_{F2}) can be obtained complying with formula (P_{F2}-A):

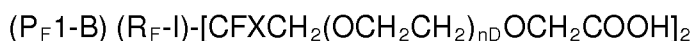


in which R_{F-I} , X, R_{P2} and nD are as defined above.

Conveniently, polymers (P_{F2-A}) can be obtained by converting a PFPE diol (D_{F1-A}) or (D_{F1-B}) into the corresponding sulfonic ester (like the trifluoromethanesulfonyl, perfluorobutylsulfonyl or p-toluenesulfonyl ester) and then reacting the sulfonic ester with an amine of formula $HN(R_{P2})_2$, following the procedure disclosed in US 6984759 B (SOLVAY SOLEXIS SPA).

Amines (P_{F2-A}) can be used as such in the manufacture of compositions (C) or can be used as precursors of other polymers (P_{F1}) or (P_{F2}) by reaction with suitable reaction partners according to methods known in the art. For example, convenient polymers (P_{F1}) can be obtained by reaction of an amine (P_{F2-A}) with an aromatic polycarboxylic acid or a derivative thereof able to form amido bonds, for example with trimellitic acid or a derivative thereof, such as trimellitic anhydride. Good results were obtained using a polymer (P_{F1}) obtained by reacting an amine (P_{F2-A}) of formula (R_{F-III})-(CF₂CH₂NH₂)₂ with trimellitic anhydride.

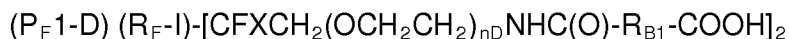
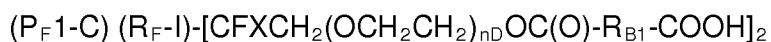
A further example of polymer which can be obtained from a PFPE diol (D_{F1}) is a polymer (P_{F1}) complying with formula (P_{F1-B}):



wherein (R_{F-I}), X and nD are as defined above by reaction of diol (D_{F1}) with an ester of a 2-halo-acetic acid, for example with 2-chloroethyl acetate. The reaction can be conveniently carried out as disclosed in US 7252740.

Polymer (P_{F1-B}) can be used as such in the manufacture of compositions (C) or it can in turn be used as precursor for the manufacture of other polymers (P_{F1}) and (P_{F2}).

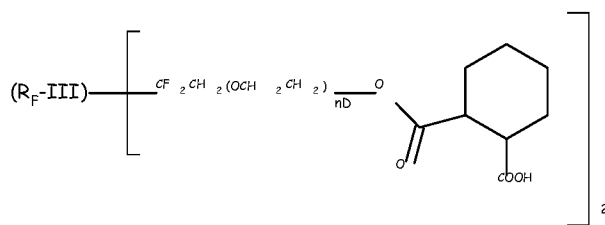
Further convenient polymers (P_{F1}) for the preparation of compositions (C) are those complying with the following formulae (P_{F1-C}) and (P_{F1-D}) herein below:



wherein R_{F-I} , X and nD are as defined above and R_{B1} is C₁-C₁₀ straight or branched alkylene, C₄-C₆ cycloalkylene as defined above or C₅-C₆ arylene as defined above, optionally comprising one or more -COOH groups. Preferably, chain (R_{F-I}) is a chain

(R_F-III) as defined above, X is F, nD is 0 or ranges from 1 to 5 and R_{B1} is selected from *o*-, *m*-, *p*-cyclohexylene and *o*-, *m*-, *p*-phenylene. Polymers (P_F1-C) and (P_F1-D) can be obtained from diols (D_F1-A), (D_F1-B) and from (P_F2-A) by reaction with a diacid of formula HOOC-R_{B1}-COOH wherein R_{B1} is as defined above or with a reactive derivative thereof, like a halide or an anhydride.

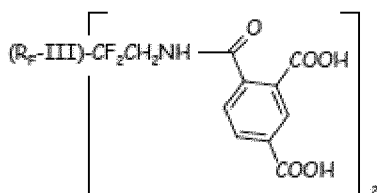
A convenient example of compound (P_F1-C) complies with formula (P_F1-Ca) here below:



(P_F1-Ca), with (R_F-III) as defined above, and nD being 0 or ranging from 1 to 5.

A convenient example of polymer (P_F1-D) complies with formula (P_F1-Da) here below:

(P_F1-Da)



Further convenient examples of polymers (P2) for the preparation of compositions (C) are those complying with the following formulae (P_F2-B) and (P_F2-C)

(P_F2-B) (R_F-I)-[CFXCH₂(OCH₂CH₂)_{nD}OC(O)-R_{B1}-N(R_{P2})₂]₂

wherein R_F-I, X, nD and N(R_{P2})₂ and R_{B1} are as defined above.

(P_F2-C) (R_F-I)-[CFXCH₂(OCH₂CH₂)_{nD}OC(O)NH-R_{B2}NHC(O)OR_{B3}-N(R_{P2})₂]

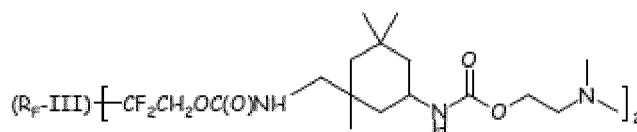
wherein R_F-I, X, nD and R_{P2} are as defined above, R_{B2} is straight or branched C₁-C₆ alkylene chain optionally comprising a C₄-C₆ cycloalkylene group as defined above or a C₅-C₆ arylene group as defined above and R_{B3} is C₂-C₁₀ straight or branched alkylene, optionally interrupted by one or more -N(RP2*)- groups as defined above.

Polymers (P_F2-B) can be obtained by reaction of a diol (D_F1-A) or (D_F1-B) with an amidoacid or with a reactive derivative thereof, such as a halide or anhydride.

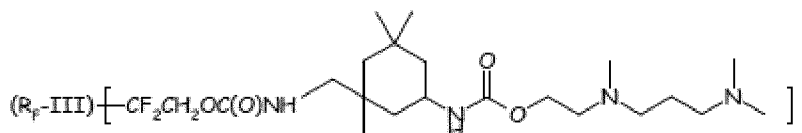
Polymers (P_F2-C) can be obtained by reaction of a diol (D_F1-A) or (D_F1-B) with a diisocyanate and an aminoalcohol.

Convenient examples of polymers (P_F2-C) comply with the formulae (P_F2-Ca) and (P_F2-Cb) here below:

5 (P_F2-Ca)



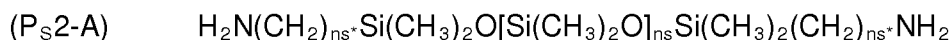
(P_F2-Cb)



Polymers (P₁) and (P₂) wherein chain (R) is a chain (R_S) [herein after polymers (P_S1) and (P_S-2)]

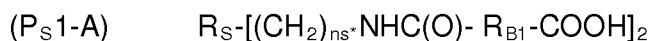
Polymers (P_S1) and (P_S2) are available on the market, or can be obtained according to methods known in the art. In particular, polymers (P_S1) and (P_S2) wherein Ra_s and Rb_s are both methyl can be obtained by hydrolysis of dimethyl chlorosilane to provide a dihydroxy-terminated poly(dimethylsiloxane) and derivatization of the same according to methods known in the art for the manufacture of amines and acids.

A convenient example of polymer (P_S2) is a polydimethyl siloxane of formula (P_S2-A) here below:



in which ns is a positive number selected in such a way that the number average molecular weight (M_n) of the [Si(CH₃)₂O]_{ns} chain ranges from 500 to 10,000, preferably from 500 to 5,000 and ns* is 0 or a positive number equal to or higher than 1, preferably ranging from 1 to 10. A polymer (P_S2-A) wherein ns* is 3 is available from Aldrich®.

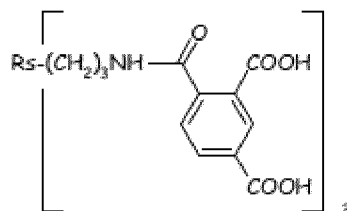
Polymer (P_S2-A) can be used as such in the manufacture of compositions (C) or can be used as precursor for the manufacture of other polymers (P_S1) and (P_S2). For instance, convenient polymers (P_S1) complying with the following formula (P_S1-A) here below:



wherein ns^* and R_{B1} are as defined above and R_S is a chain of formula $-Si(CH_3)_2O[Si(CH_3)_2O]_{ns}Si(CH_3)_2-$, with ns is a positive number selected in such a way that the number average molecular weight (M_n) of the $[Si(CH_3)_2O]_{ns}$ chain ranges from 500 to 10,000, preferably from 500 to 5,000, can be obtained by reaction of polymer (P_{S2-A}), as described above, with an acid of formula $HOOC-R_{B1}-COOH$, wherein R_{B1} is as defined above, or with a reactive derivative thereof, such as a halide or anhydride.

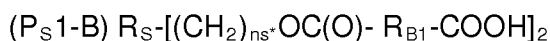
A convenient example of polymer (P_{S1-A}) is one complying with formula (P_{S1-Aa}) here below:

(P_{S1-Aa})



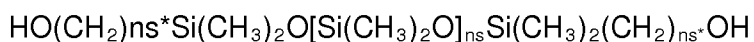
wherein R_S is a chain (R_{S-l}).

A further convenient example of polymer (P_{S1}) is a polymer complying with formula (P_{S1-B}):



wherein ns^* and R_{B1} are as defined above and R_S is a chain of formula $Si(CH_3)_2O[Si(CH_3)_2O]_{ns}Si(CH_3)_2-$.

Polymer (P_{S1-B}) can be obtained by reaction of a dihydroxy-terminated silane precursor of formula:



by reaction with an acid of formula $HOOC-R_{B1}-COOH$, wherein R_{B1} is as defined above, or with a reactive derivative thereof, such as a halide or anhydride.

Polymers (P1) and (P2) wherein chain (R) is a chain (R_{OA}) [herein after polymers ($P1_{OA}$) and ($P2_{OA}$)]

Polymers ($P1_{OA}$) and ($P2_{OA}$) are available on the market or can be obtained according to methods known in the art. Preferred examples of polymers ($P1_{OA}$) and ($P2_{OA}$) are those comprising a polyoxyethylene chain, a polyoxypropylene chain, a

polytetramethylene glycole chain, or a chain comprising a mixture of any of oxyethylene, oxypropylene, oxytetramethylene units.

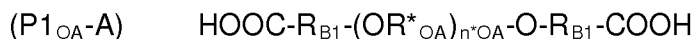
For example, starting from a polyoxyalkylene diol of formula (D_{OA}1):



- 5 wherein each of R^{*}_{OA}, equal to or different from each other, is, independently at each occurrence, a straight or branched alkylene divalent group, typically an ethylene, propylene or a tetramethylene group, and n^{*}_{OA} is an integer selected in such a way as the number average molecular weight ranges from 500 to 5,000, polymers (P_{OA}1) and (P_{OA}2) can be obtained by methods known in the art by reaction with suitable reaction
10 partners. A diol (D_{OA}-1) wherein R^{*}_{OA} is substantially at each occurrence an ethylene group is commercially available from Aldrich®.

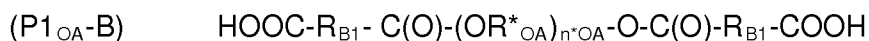
The expression "substantially at each occurrence" in connection with moieties R^{*}_{OA} of polymers (P1_{OA}) or (P2_{OA}) is meant to indicate that minor amounts (i.e. < 1 % in moles) of groups R^{*}_{OA} other than those specified may be present as impurities,
15 defects or spurious components, being understood that these impurities, defects or spurious component may not substantially affecting the properties of chain R^{*}_{OA}.

For example, polymers (P1_{OA}) complying with formula (P1_{OA}-A):



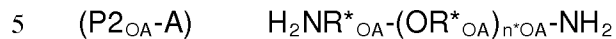
- wherein R_{B1}, R^{*}_{OA} and n^{*}_{OA} are as defined above, can be obtained by reaction of a
20 diol (D_{OA}1) with a halo-alkyl or haloalkylene acid X^o-R_{B1}-COOH wherein X^o is halogen and R_{B1} is a C₁-C₁₀ straight or branched alkylene, C₄-C₆ cycloalkylene as defined above or C₅-C₆ arylene, and preferably is selected from *o*-, *m*-, *p*-cyclohexylene and *o*-, *m*-, *p*-phenylene, as already defined above, or with a corresponding halide or ester. For example, a polymer (P1_{OA}-A) wherein R_{B1} is -CH₂- can be obtained by reaction of
25 diol (D_{OA}1) with a 2-halo acetic acid or halide or ester thereof, such as with 2-chloroacetic acid ethyl ester. A polymer (P1_{OA}-A) wherein R^{*}_{OA} is substantially at each occurrence an ethylene group and R_{B1} is -CH₂- is available from Aldrich®.

Polymers (P1_{OA}) complying with formula (P1_{OA}-B):



can be obtained by reaction of a diol (D_{OA-1}) with a diacid of formula $HOC(O)-R_{B1}-COOH$, wherein R_{B1} is as defined above, or with a reactive derivative thereof, such as an halide or anhydride.

Polymers ($P2_{OA}$) complying with formula ($P2_{OA}-A$):



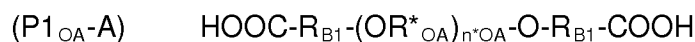
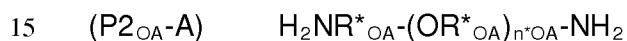
wherein R^*_{OA} and n^*_{OA} are as defined above can be obtained from a diol (D_{OA1}) by conventional reactions for the replacement of the hydroxyl group into an amino group. A polymer ($P2_{OA}-A$) wherein R^*_{OA} is substantially at each occurrence a propylene group of formula $-CH_2-CH_2-$ is available on the market from Aldrich®.

10 According to an embodiment of the invention, at least one of the following conditions (preferably both conditions) are satisfied:

(1) polymer (P1) complies with formula ($P1_{OA}-A$);

(2) polymer (P2) complies with formula ($P2_{OA}-A$)

wherein:



in which:

- each of R^*_{OA} , equal to or different from each other, is, independently at each occurrence, a straight or branched alkylene divalent group, typically an ethylene, propylene or a tetramethylene alkylene group,

20 $-n^*_{OA}$ is an integer selected in such a way as the number average molecular weight ranges from 500 to 5,000, and

- R_{B1} is C_1-C_{10} straight or branched alkylene, C_4-C_6 cyloalkylene or C_5-C_6 arylene, optionally comprising one or more $-COOH$ groups.

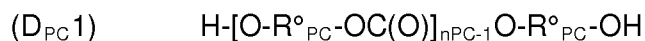
25 Preferably, the polymer (P1) and (P2) in composition (C) have respectively the formulae ($P1_{OA}-A$) and ($P2_{OA}-A$) as defined above, R^*_{OA} is substantially at each occurrence a propylene group of any of formulae $-CH_2CH_2CH_2-$, $-CH_2-CH(CH_3)-$ and $-CH(CH_3)-CH_2-$, and R_{B1} comprises one $-COOH$ group.

Polymers (P1) and (P2) wherein chain (R) is a chain (R_{PC}) [herein after polymers

30 ($P1_{PC}$) and ($P2_{PC}$)]

Polymers (P1_{PC}) and (P2_{PC}) can be manufactured by reaction of a diol of formula (D^o_{PC1}):

(D^o_{PC1}) HO-(R^o_{PC})-OH wherein (R^o_{PC}) is a straight or branched alkylene chain, preferably a C₂ – C₁₀ alkylene chain, optionally comprising ethereal oxygen atoms and a carbonate, typically diphenylcarbonate, to provide a dihydroxy-terminated polycarbonate of formula (D_{PC1}):



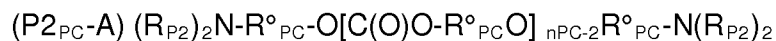
wherein R^o_{PC} and n_{PC} are as defined above which is subsequently reacted with suitable reaction partners according to methods known in the art to provide polymers (P1_{PC}) and (P2_{PC}).

Dihydroxy-terminated polycarbonates (D_{PC1}) having an average number molecular weight (M_n) ranging from 500 to 3,000 are commercially available, for example, from UBE as Ethernacoll® PH.

For example, convenient polymers (P1_{PC}) can be obtained by reaction of (D_{PC1}) with a halo-alkyl or haloalkylene acid ester, preferably with an acid of formula X^o-R_{B1}-COOH wherein X^o is halogen and R_{B1} is as defined above, or an ester thereof, for example with 2-chloro acetic acid ethyl ester.

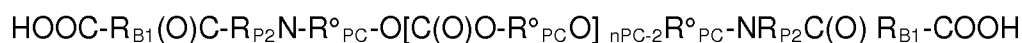
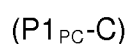
Further convenient polymers (P1_{PC}) [polymers (P1_{PC}-B)] can be manufactured by reaction of diol (D_{PC1}) with an acid of formula HOOC-R_{B1}-COOH wherein R_{B1} is as defined above, or with a reactive derivative thereof, such as a halide or an anhydride.

Convenient polymers (P2_{PC}) complying with formula (P2_{PC}-A):



wherein R_{P2}, R^o_{PC} and n_{PC} are as defined above can be manufactured from diol (D^o_{PC1}) by converting the terminal hydroxyl groups into amino groups according to methods known in the art.

Polymers (P2_{PC}-A) wherein at least one of R_{P2} is hydrogen can be used as precursors of further polymers (P1_{PC}) and (P2_{PC}). For example, polymers of formula (P1_{PC}-C):



can be obtained by reaction with a diacid of formula $\text{HOOC-R}_{\text{B1}}\text{-COOH}$ wherein R_{B1} is as defined above or with a reactive derivative thereof, such as a halide or anhydride.

Polymers (P1) and (P2) wherein chain (R) is a chain (R_{PE}) [herein after polymers (P1_{PE}) and (P2_{PE})"]

5 Polymers (P1_{PE}) and (P2_{PE}) can be prepared according to methods known in the art starting from a polyester diol [diol (D_{PE1})]. Diols (D_{PE1}) can be obtained by polycondensation of dicarboxylic acids or lactams and diols. Polyester diols are commercially available; for example, polycaprolactone diols are available from Perstop under the tradename CapaTM. Convenient polymers (P1_{PE}) can be obtained by reaction
10 of a diol (D_{PE1}) with a halo-alkyl or haloalkylene acid ester, preferably with an acid of formula $\text{X}^{\circ}\text{-R}_{\text{B1}}\text{-COOH}$ wherein X° is halogen and R_{B1} is as defined above, or an ester thereof, for example with 2-chloro acetic acid ethyl ester. Further convenient polymers (P_{PE1}) can be obtained by reaction of a diol (D_{PE1}) with an acid of formula $\text{HOOC-R}_{\text{B1}}\text{-COOH}$ wherein R_{B1} is as defined above, or with a reactive derivative
15 thereof, such as a halide or anhydride

Polymers (P_{PE2}) with $\text{-N(R}_{\text{P2}}\text{)}_2$ end groups can be obtained from diols (D_{PE1}) according to methods known in the art for the replacement of the hydroxyl group with an amino group. Polymers (P_{PE2}) thereby obtained can be in turn used as precursors for other polymers (P_{PE1}) or (P_{PE2}) by reaction with suitable precursors according to
20 methods known in the art.

Polymers (P1) and (P2) wherein chain (R) is a polybutadiene chain (R_{PBD}) [herein after "polymers (P_{PBD1}) and (P_{PBD2})"]

Polymers (P_{PBD1}) and (P_{PBD2}) can be obtained from dihydroxy terminated polybutadienes according to methods disclosed in the art.

25 Such polybutadienes are available, for example, from Cray Valley; one of them is marketed as Poly bd[®] R-45HTLO.

Convenient polymers (P_{PBD1}) can be obtained by reaction of a dihydroxy terminated polybutadiene [diol (D_{PBD1})] with a halo-alkyl or haloalkylene acid ester, preferably with an acid of formula $\text{X}^{\circ}\text{-R}_{\text{B1}}\text{-COOH}$ wherein X° is halogen and R_{B1} is as
30 defined above, or an ester thereof, for example with 2-chloro acetic acid ethyl ester.

Further convenient polymers (P_{PBD1}) can be obtained by reaction of a dihydroxy terminated polybutadiene with an acid of formula $HOOC-R_{B1}-COOH$ wherein R_{B1} is as defined above, or a reactive derivative thereof.

Polymers (P_{PBD2}) with $-N(R_{P2})_2$ end groups can be obtained from a dihydroxy terminated polybutadiene (D_{PBD1}) according to methods known in the art for the replacement of the hydroxyl groups with an amino group. Polymers (P_{PBD2}) thereby obtained can be in turn used as precursors for other polymers (P_{PBD1}) or (P_{PBD2}) by reaction with suitable precursors according to methods known in the art.

Epoxy resin and curing agent

Within the context of the present invention, the expression "curable epoxy resin" is used according to its usual meaning, i.e. to designate polymers comprising a plurality of epoxy groups, which may generate three-dimensional cross-linked thermoset structures by reaction of the said epoxy groups with each other and/or by reaction of the same with suitable curing agents.

Hence, suitable curable epoxy resins which may be used within the frame of the invention encompass low-molecular weight pre-polymers and high molecular weight polymers bearing a plurality of epoxide groups, either as side pendant groups or as terminal groups.

One curable epoxy resin or mixtures of more than one curable epoxy resin may be used in the present composition (C).

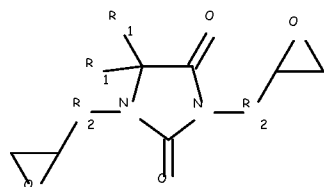
Preferred curable epoxy resins of possible use in the present invention may be selected from the group consisting of:

- polyglycidyl ether-type epoxies, including (i) polyglycidylethers of polyhydric phenols, including bisphenol A diglycidyl ethers, biphenol F diglycidyl ethers, and (ii) polyglycidyl ethers of polyhydric (cyclo)aliphatic alcohols, such as butanediol diglycidyl ether and trimethylolpropane triglycidyl ether;

- novolacs epoxy resins, such as epoxy phenol novolacs (EPN) and epoxy cresol novolacs (ECN);

- glycidylamine type epoxy resin, such as N,N',N'',N''' -tetraglycidyl-diaminodiphenylmethanes (e.g. N,N',N'',N''' -tetraglycidyl-bis-(4-

aminophenyl)-methane), triglycidyl isocyanurate, hydantoin type epoxy resin, such as the compounds of formula:



- with R_1 , equal to or different from each other, is independently at each occurrence, an aliphatic group, such as e.g. $-\text{CH}_3$; and R_2 , equal or different at each other, is independently at each occurrence an aliphatic divalent group, such as e.g. $-\text{CH}_2-$ or $-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-\text{CH}_2-$; N,N,N',N'-tetraglycidyl-m-xylenediamine, 1,3-bis(N,N-diglycidylaminomethyl)cyclohexane, aminophenol type epoxies such as N,N,O-triglycidyl-p-aminophenol, aniline type epoxies, and toluidine type epoxy resins, ;
- polymers of monomers having an epoxy group, possibly in combination with other monomers; specific examples of monomers having an epoxy group include glycidyl (meth)acrylate, 3,4-epoxycyclohexyl (meth)acrylate, and methylglycidyl (meth)acrylate. Specific examples of other monomers that can be copolymerized with a monomer having an epoxy group include (meth)acrylic acid, methyl (meth)acrylate, ethyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, iso-butyl (meth)acrylate, tert-butyl (meth)acrylate, cyclohexyl (meth)acrylate, benzyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, styrene, methylstyrene, chloromethylstyrene, (3-ethyl-3-oxetanyl)methyl (meth)acrylate, N-cyclohexylmaleimide, and N-phenylmaleimide. Specific, preferred examples of polymers of monomers having an epoxy group, as detailed above, include polyglycidyl methacrylate, a copolymer of methyl methacrylate and glycidyl methacrylate, a copolymer of benzyl methacrylate and glycidyl methacrylate, a copolymer of n-butyl methacrylate and glycidyl methacrylate, a copolymer of 2-hydroxyethyl methacrylate and glycidyl methacrylate, a copolymer of (3-ethyl-3-oxetanyl)methyl methacrylate and glycidyl methacrylate, and copolymer of styrene and glycidyl methacrylate;
- epoxy group-terminated polyesters, in particular epoxy group-terminated polyesters of dimerised monomeric unsaturated fatty acids and polyhydric alcohols, or epoxy group-terminated polyesters of aliphatic or aromatic polycarboxylic acids and polyhydric alcohols. Examples of such polycarboxylic acids are oxalic acid, succinic

acid, glutaric acid, adipic acid, pimelic acid, sebacic acid, suberic acid, azelaic acid or dimerised or trimerised linoleic acid. It is, however, also possible to use cycloaliphatic polycarboxylic acids such as tetrahydrophthalic acid, 4-methyltetrahydrophthalic acid, hexahydrophthalic acid or 4-methylhexahydrophthalic acid. Aromatic polycarboxylic acids can also be used, typically phthalic acid, isophthalic acid and terephthalic acid.

Good results have been obtained when the composition (C) comprised at least one polyglycidyl ether-type epoxy resin, in particular at least one polyglycidylether of polyhydric phenols, and more precisely, a bisphenol A diglycidyl ether.

As said, curing of the curable epoxy resin can be achieved with or without the addition of a curative; it is nevertheless preferred to use a curing agent in combination with the curable epoxy resin in the composition (C).

Common classes of curing agents for epoxy resins comprise amines (including polyamines), polyamidoamines, polyamides, acids, acid anhydrides, phenols, alcohols and thiols. Suitable curing agents can be selected amongst the curing agents for epoxy resins by any person of ordinary skills in this field, depending on the curable epoxy resin or mixture of resins chosen for use herein.

According to a preferred embodiment, curing agents are selected among those having only a limited or no reactivity at room temperature with the curable epoxy resin, but which are able to react with the epoxy groups of the curable epoxy resin at high temperature, so that the formulation of curable epoxy resin and curing agent may be prepared and stored for some time prior to use.

The composition (C) may further comprise, in addition to curing agents, epoxy curing accelerators, which may be e.g. added to composition (C) just before applying the same to the metal substrate. These compounds are known in the art.

Any type of pigments may be used in the composition (C) of the invention. Preferred pigments are, or will comprise, one or more of the following: titanium dioxide which is available from Whittaker, Clark & Daniels, South Plainfield, New Jersey, USA; Arctic blue #3, Topaz blue #9, Olympic blue #190, Kingfisher blue #211, Ensign blue #214, Russet brown #24, Walnut brown #10, Golden brown #19, Chocolate brown #20, Ironstone brown #39, Honey yellow #29, Sherwood green #5, and Jet black #1 available from Shepard Color Company, Cincinnati, Ohio, USA.;

black F-2302, blue V-5200, turquoise F-5686, green F-5687, brown F-6109, buff F-6115, chestnut brown V-9186, and yellow V-9404 available from Ferro Corp., Cleveland, Ohio, USA and METEOR® pigments available from Engelhard Industries, Edison, New Jersey, USA.

5 The composition (C) may comprise a liquid medium [medium (L)]. When composition (C) comprises a liquid medium, polymer (P1), polymer (P2) and curable epoxy resin may be, independently from each other, at least partially solubilized in the said medium (L). Otherwise, said polymer (P1), polymer (P2) and curable epoxy resin may be dispersed in the said medium (L).

10 According to certain embodiments composition (C) is a waterborne composition, that is to say that medium (L) comprises water as major liquid medium.

The amount of water, while complementing necessarily the other ingredients in the composition is generally of at least 30 % wt, preferably at least 35 % wt, more preferably at least 38 % wt, with respect to the total weight of the composition (C).

15 Upper amounts for water are not particularly limited, except because of the presence of the other listed mandatory ingredients.

According to other embodiments, the medium (L) is a solvent medium, that is to say that medium (L) comprises one or more than one organic solvent as major liquid medium. The medium (L) typically comprises one or more organic solvents selected
20 from the group consisting of:

- aliphatic, cycloaliphatic or aromatic ether oxides, more particularly, diethyl oxide, dipropyl oxide, diisopropyl oxide, dibutyl oxide, methyltertbutylether, dipentyl oxide, diisopentyl oxide, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol dibutyl ether benzyl oxide; dioxane, tetrahydrofuran (THF),
- 25 - glycol ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monoisopropyl ether, ethylene glycol monobutyl ether, ethylene glycol monophenyl ether, ethylene glycol monobenzyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-butyl ether,
- 30 - glycol ether esters such as ethylene glycol methyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol monobutyl ether acetate,

- alcohols such as methyl alcohol, ethyl alcohol, diacetone alcohol,
- ketones such as acetone, methylethylketone, methylisobutyl ketone, diisobutylketone, cyclohexanone, isophorone,
- linear or cyclic esters such as methyl acetoacetate, dimethyl phthalate,
- 5 γ -butyrolactone,
- linear or cyclic carboxamides such as N,N-dimethylacetamide (DMAC), N,N-diethylacetamide, dimethylformamide (DMF), diethylformamide or N-methyl-2-pyrrolidone (NMP),
- organic carbonates for example dimethyl carbonate, diethyl carbonate, dipropyl
- 10 carbonate, dibutyl carbonate, ethylmethyl carbonate, ethylene carbonate, propylene carbonate, vinylene carbonate;
- organosulfur solvents, such as dimethyl sulfoxide (DMSO) and sulfolane (tetramethylene sulfone);
- diesters of formula (I_{de}), esteramides of formula (I_{ea}) and diamides of formula (I_{da}):
- 15 $R^1O(O)C-Z_{de}-C(O)OR^2$ (I_{de})
- $R^3O(O)C-Z_{ea}-C(O)NR^4R^5$ (I_{ea})
- $R^5R^4N(O)C-Z_{da}-C(O)NR^4R^5$ (I_{da})
- wherein:
- R¹ and R², equal to or different from each other, are independently selected from the
- 20 group consisting of C₁-C₃ hydrocarbon groups,
- R³ is selected from the group consisting of C₁-C₂₀ hydrocarbon groups, and
- R⁴ and R⁵, equal to or different from each other, are independently selected from the group consisting of hydrogen and C₁-C₃₆ hydrocarbon groups, optionally substituted, being understood that R⁴ and R⁵ might be part of a cyclic moiety including the nitrogen
- 25 atom to which they are bound, said cyclic moiety being optionally substituted and/or optionally comprising one or more heteroatoms, and mixtures thereof, and
- Z_{de}, Z_{ea} and Z_{da}, equal to or different from each other, are independently linear or branched C₂-C₁₀ divalent alkylene groups.

To the sake of ensuring suitable coated weight on the substrate, the

30 composition (C) generally possesses a liquid viscosity of at least 100, preferably at

least 250, more preferably at least 500 mPa.sec, when measured at 22°C, using a Brookfield viscometer operating at 10 rpm.

Conversely, in order to ensure acceptable liquid processability during coating via different coating techniques, it is generally preferred for the composition (C) to possess
5 a liquid viscosity of at most 5000 mPa.sec, at most 4700mPa.sec, when measured at 22° C, using a Brookfield viscometer operating at 10 rpm.

Optionally, the composition (C) can further comprise usual ingredients of coating compositions, notably :

- (i) thixotropic agents, otherwise referred to as rheological additives, i.e.
10 compounds which allow specific modification of the liquid viscosity of the composition, at various shear rate, matching hence requirements at different stages of processing;
- (ii) surfactants, i.e. compounds able to modify surface tension of the water-borne composition (C);
- 15 (iii) anti-foam agents/defoamers, preventing or suppressing formation of foam, such as notably tributylphosphate;
- (iv) inorganic fillers/hardeners, such as silicate compounds, e.g. metal silicate (aluminium silicate); particulate metal oxides, such as TiO_2 , Al_2O_3 and SiO_2 , zeolites, mica, talcum, kaolin; carbon fibres, glass
20 fibres, metal sulfates, such as BaSO_4 , CaSO_4 , SrSO_4 ;
- (v) organic fillers, preferably thermally stable polymers, like aromatic polycondensates;
- (vi) adhesion promoters, like colloidal silica and a phosphate compound, such as metal phosphate, e.g. Zn, Mn or Fe phosphate;
- 25 (vii) other special additives such as levelling agents, wetting agents, and the like.

In a preferred aspect, the present curable epoxy resin is a water-dispersible epoxy resin, preferably bisphenol A diglycidyl ether, and the curing agent is a water-soluble or water-dispersible, modified polyamidoamine or polyamide. In this preferred
30 embodiment, medium (L) comprises water as major liquid medium, and may comprise low amounts (e.g. less than 5 % wt, based on medium (L)) of organic solvents.

Composition (C) and preparation thereof

The composition (C) for carrying out the method (M) of the present invention comprises, besides the ionisable amorphous polymers having a low T_g described above, i.e. at least a polymer (P1) and at least a polymer (P2), at least a curable epoxy resin and optionally at least a curing agent for this curable epoxy resins.

By "low T_g " according to this invention is meant a T_g lower than -35°C , preferably ranging from -35°C to 120°C .

T_g is measured according to ASTM D3418 at midpoint by differential scanning calorimetry (DSC) with a scan rate at $20^\circ\text{C}/\text{min}$.

The equivalent ratio between polymer (P1) and polymer (P2) is advantageously such to maximize ionic bonding between acid groups of polymer (P1) and amine groups of polymer (P2). The composition (C) will hence comprise an overall amount of acid groups of polymer (P1) and an overall amount of amine groups of polymer (P2) which is substantially similar. In other terms, the ratio between the equivalents of polymer (P1) and the equivalents of polymer (P2) in said composition (C) will tend to be close to unitary, and will preferably range from 1.4 to 0.6, more preferably from 1.2 to 0.8, most preferably from 1.1 to 0.9. Most preferably the equivalent ratio is about 1.

For the avoidance of doubt, the ratio between the equivalents of polymer (P1) and the equivalents of polymer (P2) is referred to the acid/base reaction between the at least one ionisable acid group in each end group of polymer (P1) and the at least one ionisable amino group in each end of polymer (P2).

By the term "at least a polymer (P1)" is meant in the present invention that only one or more polymers (P1) may be used in the preparation of the present composition (C). "More polymers" means that polymers (P1) can be used differing from one another in the nature of units (U) of the chain (R), in the nature of end groups (E1) and (E1'), in the molecular weight, or in a plurality of the said features.

By the term "at least a polymer (P2)" is meant in the present invention that only one or more polymers (P2) may be used in the preparation of the present composition (C). "More polymers" means that polymers (P2) can be used differing from one another in the nature of chain (R), in the nature of end groups (E2) and (E2'), in the molecular weight, or in a plurality of the said features.

It is further understood that polymer(s) (P1) and polymer(s) (P2) of the inventive composition (C) may have polymer chains consisting of same recurring units (U) or may have polymer chains differing for nature of units (U) and/or molecular weight or any other structural feature.

5 As said, composition (C) comprises a curable epoxy resin, and a combination of polymer (P1) and polymer (P2): these two latter components are advantageously used in composition (C) as additives for improving the anti-corrosion performances of the epoxy coating resulting therefrom or in other terms, composition (C) can be essentially qualified as an epoxy formulation comprising certain combination of additives. This
10 means in general terms that polymer (P1) and polymer (P2) are present in the composition (C) as minor components, while the curable epoxy resin is present as major component, based on the combined weight of polymer (P1), polymer (P2) and curable epoxy resin.

The curable epoxy resin is hence present in the composition (C) in an amount of
15 at least 50 % wt, preferably at least 60 % weight, more preferably at least 70 % weight, based on the combined weight of polymer (P1), polymer (P2) and curable epoxy resin.

According to certain preferred embodiments, the overall amount of polymer (P1) plus polymer (P2) in the composition (C) is in the range of advantageously at least 1 % weight, preferably at least 2 % weight, more preferably at least 3 % weight, and of
20 advantageously at most 15 % weight, preferably at most 13 % weight, more preferably at most 12 % weight, with respect to the combined amount of polymer (P1), polymer (P2) and curable epoxy resin; most preferred amounts of combined weight of polymer (P1) and polymer (P2) are in the range of 4-10%, on same weight basis.

This composition (C) may be prepared by mixing the epoxy resin in a liquid
25 medium (L), as above detailed, with optionally the curing agent, thus obtaining a liquid formulation into which the polymers (P1) and (P2) may be incorporated directly as such. As an alternative, polymers (P1) and (P2) may be first pre-mixed with a medium (L), as above detailed, and then incorporated into a liquid formulation of curable epoxy resin with optionally curing agent, based on same or different
30 medium (L).

Any conventional mixing techniques, operated by appropriate mixing equipment,

may be used to achieve mixing the aforementioned components of the present composition (C).

According to a preferred embodiment of the present invention one polymer (P1) and one polymer (P2) are used in the manufacture of the composition (C); chain (R) of polymer (P1) can be the same or different from chain (R) of polymer (P2). Notably,
 5 chain (R) of polymer (P1) may comprise same recurring units as chain (R) of polymer (P2) and may possess same, similar or different molecular weight.

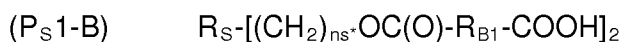
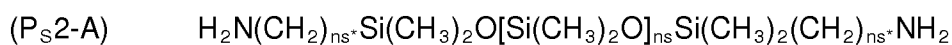
According to an embodiment, the chain (R) in either (P1) or (P2) is a chain (R_F) as defined above, preferably a chain of formula (R_{F-I}) as defined above, more preferably a chain of formula (R_{F1-III}) as defined above, while chain (R) in the other
 10 polymer is a chain (R_S) as defined above, preferably a chain (R_{S-I}) as defined above.

Convenient compositions (C) for carrying out the method (M) comprise a polymer (P1) and a polymer (P2) wherein, in both polymers, the chain (R) is a (per)fluoropolyether chain (R_F) as defined above, preferably a chain of formula (R_{F-I}) as defined above, more preferably a chain of formula (R_{F1-III}) as defined above.
 15

In another embodiment, the chain (R) in at least one of polymer (P1) and polymer (P2) is a chain (R_S) as defined above, preferably a chain (R_{S-I}), as detailed above. Preferably, the chain (R) in both polymer (P1) and polymer (P2) is a chain (R_S) as defined above, preferably a chain (R_{S-I}), as detailed above.

Very good results have been obtained with a composition (C) whereas chain ® of both polymer (P1) and polymer (P2) was a chain (R_S), in particular a chain (R_{S-I}), as detailed above, and wherein the composition (C) further comprised a curing agent.
 20

Particularly good results have been obtained when composition (C) comprised a polymer (P1) complying with formula (P_{S1-B}), and/or a polymer (P2) complying with formula (P_{S2-A}):
 25



wherein:

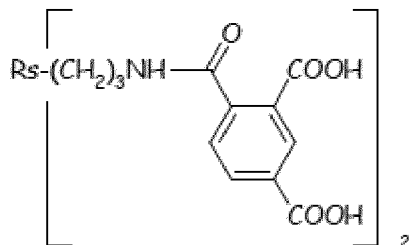
- ns is a positive number selected in such a way that the number average molecular weight (M_n) of the $[Si(CH_3)_2O]_{ns}$ chain ranges from 500 to 10,000;
 30

- ns* is 0 or a positive number equal to or higher than 1;

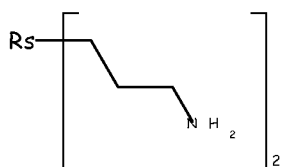
- R_S is a chain of formula $-\text{Si}(\text{CH}_3)_2\text{O}[\text{Si}(\text{CH}_3)_2\text{O}]_{ns}\text{Si}(\text{CH}_3)_2-$ with ns as defined above; and

- R_{B1} is C_1 - C_{10} straight or branched alkylene, C_4 - C_6 cycloalkylene or C_5 - C_6 arylene, optionally comprising one or more $-\text{COOH}$ groups.

- 5 An exemplary composition (C) having given very good results is a composition comprising a polymer (P1) complying with formula:



and a polymer (P2) complying with formula:



- 10 wherein R_S is, independently at each occurrence, a chain of formula $-\text{Si}(\text{CH}_3)_2\text{O}[\text{Si}(\text{CH}_3)_2\text{O}]_{ns}\text{Si}(\text{CH}_3)_2-$, with ns being a positive number selected in such a way that the number average molecular weight (M_n) of the chain R_S ranges from 500 to 10,000.

According to a preferred embodiment of the present invention, the
15 compositions (C) comprise one polymer (P1) and one polymer (P2) wherein one of them comprises two ionisable end groups and the other one comprises four end groups.

According to a most preferred embodiment, the present compositions (C)
comprise one polymer (P1) having four acidic end groups and one polymer (P2) having
20 two amino end groups.

The compositions (C) *per se* as defined above represent a further subject of the present invention.

Without being bound to theory, the Applicant believes that because polymer (P1) and polymer (P2) are dispersed in composition (C) including curable epoxy resin, when
25 this latter undergoes curing, polymer (P1) and polymer (P2) are then effectively

encapsulated in-situ by the cured epoxy coating, so existing as phase-separated domains. If, by an action such as scratching, content of said domains is mixed, it is believed that polymer (P1) and polymer (P2) are mixed together in the described equivalent ratio may, when exposed to each other because of said scratch in the epoxy matrix, form locally an infinite ionic network characterised by a much higher viscosity than that of the original components, so conferring healing behaviour and substantially improving corrosion resistance. The closer to 1 the equivalent ratio between polymer (P1) and polymer (P2) is, the higher is the efficiency in this network formation. Moreover, when at least one of the polymers (P1) or (P2) comprises more than two ionisable end groups, it is believed that a three-dimensional, cross-linked network can be formed, resulting in a higher protective barrier against corrosion.

Method (M) and Articles (A) coated with the composition (C)

The present method (M) can be carried out by a step i) of applying the composition (C) described above to at least a fraction of the surface of the metal substrate according to conventional techniques, followed by a step ii) of curing the composition (C). For example, composition (C) can be applied by casting composition (C), or can be applied by means of a dip-coater. Composition (C) can also be applied by spray coating or any other suitable technique that may be selected by any person of ordinary skills in the art.

After the step i) of applying the composition (C) on the metal article (A), the step ii) of curing is carried out by heating, thus also achieving the evaporation of any solvent comprised in composition (C) and formation of the desired protective film.

The curing step of method (M) may be carried out by heating for instance in industrial oven, at the most appropriate temperatures for the curable epoxy resin, which may be chosen by any skilled person. In an aspect, a temperature ranging from advantageously 25, preferably from at least 35°C to advantageously 150°C may be selected for curing composition (C); in a further aspect of the method (M) the temperature may be up to 200°C.

The thus obtained protective film may have a thickness ranging from 0.1 to 300 µm.

As said, another aspect of the invention relates to a coated article [article (A)]

comprising a metal substrate, as described above, and a coating resulting from curing of composition (C) adhered to at least a part of the surface of said metal substrate.

As intended herein "a coated article" is an article including a metal substrate and a coating, without limitation in its dimension and shape.

5 Coated articles including a coating resulting from composition (C) showed highly resistant to corrosion, even after the cured resin is damaged, e.g. removed by scratching. Without being bound to theory, it is believed that this high resistance is due to the formation of an ionic, three-dimensional network formed by the polymers (P1) and (P2) reacting together and able to protect any exposed metal substrates. This
10 advantageous feature of the protective film obtained by the present method is present throughout the coating. It was indeed observed, by using a microscope as described in detail in the following experimental part, that the polymers (P1) and (P2) are incorporated in the formulation of epoxy resin and curing agent thereof thus yielding the composition (C) that is in the form of an emulsion of droplets of the polymers having
15 size ranging between 1 and 50 μm , well dispersed in the water-borne resin formulation. During the step ii) of curing this composition (C) on the metal substrate, an *in situ* encapsulation of the polymers (P1) and (P2) in the resin matrix occurs. This cured coating film showed properties of high adhesion to the metal substrate and of anti-corrosion creating a great chemical and physical barrier against permeation of
20 potentially aggressive species or of water, e.g. sea water.

In a preferred embodiment of the present invention, the polymers (P1) and (P2) are incorporated into the composition (C) with a stoichiometry of 1:1 acid to amine end-groups and a content of approximately 5% by weight of the polymers with respect to the total weight of the dry composition (C) applied by method (M).

25 Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

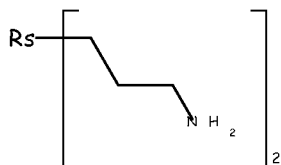
The invention is described in greater detail in the following experimental section
30 by means of non-limiting examples.

EXPERIMENTAL SECTION

Materials and methodsMaterials

Trimellitic anhydride was purchased from Aldrich® and used as received.

- 5 Poly(dimethylsiloxane), bis(3-aminopropyl) terminated ($M_n = 3000$) [herein after (Ps-Am)], i.e. a compound of formula:



- whereas R_s is a chain essentially consists of a sequence of recurring units of $-\text{OSi}(\text{CH}_3)_2-$ was purchased from Aldrich® and was used as received.
- 10 Polymer (Ps-Am) has an amine equivalent weight of 1500, and comprise 2 ionizable primary amine groups per molecule, one at each chain ends, and was found to possess a T_g of -118°C .

Butyl acetate (anhydrous $> 99\%$) was purchased from Aldrich® and was used as received.

- 15 Epoxy resin EPI-REZ® 6520-WH-53 is a 53 % wt solids aqueous dispersion of a bisphenol-A-type epoxy resin, further comprising minor amounts of acetone and propylene glycol monomethylether, which was supplied by Hexion® and used as received.

- EPIKURE® 6870-W-53 is a 53% solids, non-ionic aqueous dispersion of a modified polyamine adduct epoxy curing agent, commercially available from Hexion^(R) and used as received.
- 20

Defoaming additive BYK-024 was supplied by BYK-Chemie® and used as received.

Methods

- 25 Analytical procedure for the titration of acid polymers (Ps-Ac) (direct acid/base titration)

Sample: 1- 3 g (exactly weighed)

Solvent: HFX/IPA 50 /10 ml

Titration agent: tetramethylammonium hydroxide TMAH 0.1M in CH_3OH

Electrode: DG115SC Mettler Toledo

Analytical procedure for basic polymers (P2) (direct acid/base titration)

Sample: 1 -3 g (exactly weighed)

Solvent: HFX/IPA 50 /10 ml

5 Titrating agent: HCl 0.1M in IPA

Electrode: DG115SC Mettler Toledo

Viscosity

Rheological measurements were carried out with a “Dynamic mechanical spectrometer Rheometric ARES” Instrument

10 Geometry: Cone & Plate (25 mm)

Mode: Steady rate sweep test

Shear rate: from 1×10^{-02} to $1 \times 10^{+03}$ (1/s)

Temperature: 25°C

GPC

15 Gel permeation Chromatography (GPC) was carried out with a Waters Model 5900 instrument equipped with a set of “Ultrastyrigel” columns using THF at 40°C as solvent (elution rate 1 ml/min).

DSC analysis

20 The glass transition temperature (T_g) was determined according to ASTM D3418 by means of a Perkin-Elmer DSC 2C Instrument, and reported as midpoint by scans between -160°C and 20°C at a scanning speed of 20°C/min; the low temperature range was calibrated with reagent grade n-hexane.

Corrosion tests

25 It is known that epoxy primer coating protects metal substrates from corrosion by acting as a physical barrier, effectively isolating the metal substrate from any potentially corrosive environment. However, if the coating is scratched or damaged so that the metal surface becomes exposed, corrosion is likely to occur.

30 The corrosion tests for the metal substrates coated by the method of the invention and in parallel for metal substrates coated with reference compositions have been carried out after scratching down the coatings to the metal surface as follows. The film coatings to be tested were scratched by using a razor blade along a length of

approximately 3 cm and throughout the film thickness, i.e. down to the metal surface of the substrates. For a first series of corrosion tests two scratches were made in the form of a cross "X" while just one scratch was made on the tested substrates for a second series of tests. These scratched substrates were then left at room temperature for 24 hours prior to the corrosion test.

The coated metal substrates tested all had a part of the surface not coated, which was masked with adhesive tape before corrosion testing, so as to leave only the film coating fully exposed to the corrosive environment.

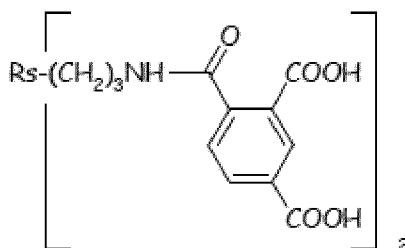
The corrosion tests were performed by immersing the substrates in 20 g/L of a NaCl solution at room temperature.

For the first series of tests the samples were immersed for a total time of 72 hours, with a visual inspection by macroscopic and microscopic imaging of the samples carried out at regular intervals of immersion at 24 hours, 48 hours and 72 hours.

For the first series of tests the samples were immersed for a total time of 144 hours, with a visual inspection by macroscopic and microscopic imaging of the samples carried out at regular intervals of immersion at 24 hours, 48 hours, 72 hours and 144 hours.

Synthesis examples

Example 1 – Synthesis of a polymer (P_S -Ac) of formula:



wherein R_s is a chain (R_s -I), i.e. a chain essentially consists of a sequence of recurring units of $-\text{OSi}(\text{CH}_3)_2-$ [herein after (P_S -Ac)] containing 1.19 eq/kg of acid groups

A glass reactor was charged with 20 g (13 meq) of (P_S -Am), as detailed above, and was warmed up to 70°C, under mechanical stirring, and dried under vacuum for two hours. Trimellitic anhydride (3.0 g 15 meq) was melted at 40°C and was added in the glass reactor. The reaction mass was warmed up to 130°C and kept at this

temperature for two hours. The completion of the reaction was monitored by $^1\text{H-NMR}$. The acid content, measured by titration according to the procedure described in the Methods section, was 1.19 eq/kg. All analyses confirmed the obtainment of the title product, with purity higher than 98%, a carboxylic acid equivalent weight of 838 g/eq and M_n 3,350. The product, consistently with its formula above, comprises 4 ionizable carboxylic groups per molecule. The material appears as opaque viscous liquid, differential Scanning Calorimetry (DSC) shows that the product has a Glass Transition at -115°C .

10 *Preparation of the compositions (C) of the invention and application on metal substrates*

All the compositions (C) of the invention were prepared by mixing manually, with a stirring rod, an epoxy resin (primer) and a curing agent for epoxy resins (hardener) in a mixing container. The two ionisable amorphous polymers (Ps-Am) and (Ps-Ac), were then incorporated into this formulation as follows.

15 The polymer (Ps-Am) was directly emulsified into the epoxy resin formulation prepared as illustrated above, by direct addition of the polymer and manual mixing using a stirring rod.

The polymer (Ps-Ac) was pre-mixed with butyl acetate in amount of 10% by weight with respect to the total weight of the mixture, to lower the polymer's viscosity. 20 The thus obtained pre-mixture was then emulsified into the epoxy resin formulation by direct addition and manual mixing using a stirring rod.

The relative amount of the two polymers (Ps-Ac) and (Ps-Am) added to the epoxy resin formulation was chosen so as to yield substantially same number of acidic end-groups of (Ps-Ac) and of basic end-groups of (Ps-Am) in the composition and hence in 25 the final coating resulting from the application of the composition onto the metal surface.

Following the emulsification of the two polymers (Ps-Ac) and (Ps-Am) in the epoxy resin formulation, the final composition (C) was obtained. Water could be used to adjust the viscosity.

30 Two different compositions of the invention (C-Ex 1) and (C-Ex 2) illustrated in the following Table 1 were thus prepared, as well as two control compositions Control-1

and Control-2, not including polymers (Ps-Ac) and (Ps-Am) but all other components of (C-Ex 1) and (C-Ex 2) respectively.

Table 1

EXAMPLES		Control-1	(C-Ex 1)	Control-2	(C-Ex 2)
Material	Solids (% w/w)	amount (g)	amount (g)	amount (g)	amount (g)
Part A					
EPI-REZ Resin 6520-WH-53	53	12.6	12.6	12.6	12.6
water	0	3.3	3.3	3.3	3.3
Part B					
EPIKURE 6870-WH-53	53	4.0	4.0	4.0	4.0
(P _S -Am)	100	0	0.31	0	0.31
(P _S -Ac) + 10%w/w butyl acetate	90	0	0.17	0	0.17
water	0	3	3	4	4
BYK-024 defoamer	100	0	0	0.10	0.10
Total A & B		22.9	23.4	24.	24.

EXAMPLE	Control-1	(C-Ex 1)	Control-2	(C-Ex 2)
	% wt with respect to weight sum (Ps-Am)+(Ps-Ac) + epoxy in EPI-REZ			
P _S -Am	0	4.34	0	4.34
Ps-Ac	0	2.14	0	2.14

5

Before application of the compositions prepared as described above on iron sample substrates, these substrates were degreased by using isopropanol and a laboratory tissue, then they were dried.

Two different methods for the application of the compositions (C-Ex 1), (C- Ex 2), Control-1 and Control-2 were used: (1) a direct deposition of the wet film on the substrate by using a pipette and (2) a spray application of the wet film by using a spray bottle with a pump vaporizer. After the film's application the samples were placed in an oven and cured at 80°C for 50 minutes. After this curing treatment, the samples were kept at room temperature and then subjected to the following anti-corrosion tests.

15 Microscopic observation of the samples' surface

A spray application of the compositions (C-Ex 1) and (C-Ex 2) of the invention was also carried out on microscope slides, which were cured under the same conditions used for the iron substrates. The films so obtained were then observed

under a microscope in order to estimate the size distribution of the polymers' droplets incorporated in the resin matrix. Micro-droplets of polymers (Ps-Ac) and (Ps-Am) in the size range from approximately 1 to approximately 50 μm were clearly visible for both compositions (C-Ex 1) and (C-Ex 2) throughout the bulk of the primer's film coating.

5 Anticorrosion tests

Corrosion test 1

 The composition of the invention (C-Ex 1) and the Control-1 composition were applied onto iron substrates by means of a pipette and then cured at 80°C as described above, thus resulting in dry films applied on the metal substrates having a thickness of
10 approximately 200 μm .

 Two samples of coated metal substrate were prepared for each composition tested. These substrates were scratched and then left to stand for 24 hours then they were immersed in separate solutions of 20 g/L NaCl and observed at regular intervals as described above.

15 After 24 hours the films prepared by using the Control-1 composition showed extensive corrosion in the region of the scratched surface, whereas the films prepared by using the (C-Ex 1) composition of the invention showed no corrosion.

 After 48 hours the films prepared by using the Control-1 composition showed a maximum corrosion in the region of the scratched surface. The films prepared by using
20 the (C-Ex 1) composition of the invention showed no / little signs of corrosion.

 After 72 hours the films prepared by using the Control-1 composition remained with maximum corrosion in the region of the scratched surface. The films prepared by using the (C-Ex 1) composition of the invention began to corrode in the region of the scratched surface; however, the intensity of the corrosion observed was less than that
25 observed for the Control-1 composition films after 24 hours.

Corrosion test 2

 The composition of the invention (C-Ex 2) and the Control-2 composition were applied onto iron substrates by spray application of the wet film using a spray bottle with a pump vaporizer and then cured at 80°C as described above, thus resulting in dry
30 films applied on the metal substrates having a thickness of approximately 130 μm .

Two samples of coated metal substrate were prepared for each composition tested. These substrates were scratched and then left to stand for 24 hours then they were immersed in separate solutions of 20 g/L NaCl and observed at regular intervals as described above.

5 After 24 hours the films prepared by using the Control-2 composition showed corrosion in the region of the scratched surface, whereas the films prepared by using the (C-Ex 2) composition of the invention showed no corrosion.

10 After 48 hours the films prepared by using the Control-2 composition showed extensive corrosion in the region of the scratched surface. The films prepared by using the (C-Ex 2) composition of the invention showed no corrosion.

After 72 hours the films prepared by using the Control-2 composition showed further extensive corrosion in the region of the scratched surface. The films prepared by using the (C-Ex 2) composition of the invention still showed no corrosion.

15 After 144 hours the films prepared by using the Control-2 composition showed a maximum corrosion in the region of the scratched surface. The films prepared by using the (C-Ex 2) composition of the invention began to corrode in the region of the scratched surface.

CLAIMS

Claim 1. A method [method (M)] for making a coated article [article (A)], said method comprising:

i) applying to at least a part of the surface of a metal substrate a composition
5 [composition (C)] comprising, and preferably consisting of:

- a) at least one polymer [polymer (P1)] comprising a polymer chain [chain (R)] consisting of a plurality of non-ionisable recurring units [units (U)], said chain having two ends, each end comprising at least one ionisable acid group;
- b) at least one polymer [polymer (P2)] comprising a polymer chain [chain (R)]
10 consisting of a plurality of non-ionisable recurring units [units (U)], said chain (R) being equal or different from that of polymer (P1) and having two ends, each end comprising at least one ionisable amino group;
- c) at least a curable epoxy resin; and
- d) optionally, at least a curing agent for said curable epoxy resin;

15 wherein:

said polymers (P1) and (P2) are amorphous and have a T_g lower than -35°C , preferably ranging from -35°C to -120°C and

and where the ratio between the equivalents of polymer (P1) and the equivalents of polymer (P2) in said composition (C) preferably ranges from 1.4 to 0.6, more
20 preferably from 1.2 to 0.8, most preferably from 1.1 to 0.9; and

ii) curing said composition (C), so as to obtain the article (A).

Claim 2. The method according to claim 1, wherein said polymer (P1) and said polymer (P2) have the following formulae:

(P1) E1-R-E1'
25 (P2) E2-R-E2'

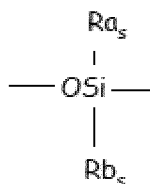
wherein:

-E1 and E1', equal or different from one another, are end groups each comprising at least one ionisable acid group;

-E2 and E2', equal or different from one another, are end groups each comprising at
30 least one ionisable amino group.

Claim 3. The method according to claim 1 or 2 wherein said chain (R) of the polymer (P1) and polymer (P2) is independently selected from a fully or partially fluorinated polyoxyalkylene chain, a polyalkylsiloxane chain, a polyoxyalkylene chain, a polycarbonate chain, a polyester chain and a polybutadiene chain.

5 **Claim 4.** The method according to claim 3, wherein said chain (R) of both polymers (P1) and (P2) is a polyalkylsiloxane chain comprising recurring units [units (U_s)] of formula:



(U_s)

10 in which R_{a_s} and R_{b_s} , equal to or different from one another, are independently selected from hydrogen, straight or branched (halo)alkyl and aryl, with the proviso that at least one of R_{a_s} and R_{b_s} is not hydrogen.

Claim 5. The method according to any one of claims 3 and 4, wherein the polyalkylsiloxane chain is a polydimethylsiloxane chain [chain (R_S -I)], which essentially consists of a sequence of recurring units of formula (U_{S-i}) here below:

15 (U_{S-i}): $-\text{OSi}(\text{CH}_3)_2-$.

Claim 6. The method according to claim 5, wherein polymer (P1) complies with formula (P_{S1-B}), and/or polymer (P2) complies with formula (P_{S2-A}):

(P_{S2-A}) $\text{H}_2\text{N}(\text{CH}_2)_{n_s^*}\text{Si}(\text{CH}_3)_2\text{O}[\text{Si}(\text{CH}_3)_2\text{O}]_{n_s}\text{Si}(\text{CH}_3)_2(\text{CH}_2)_{n_s^*}\text{NH}_2$

(P_{S1-B}) $R_S-[(\text{CH}_2)_{n_s}\text{OC(O)}-R_{B1}\text{-COOH}]_2$

20 in which:

- n_s is a positive number selected in such a way that the number average molecular weight (M_n) of the $[\text{Si}(\text{CH}_3)_2\text{O}]_{n_s}$ chain ranges from 500 to 10,000;

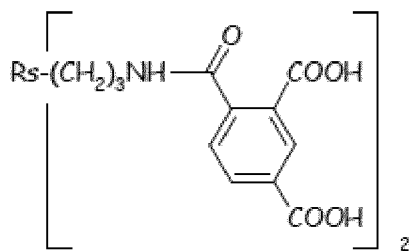
- n_s^* is 0 or a positive number equal to or higher than 1;

- R_S is a chain of formula $-\text{Si}(\text{CH}_3)_2\text{O}[\text{Si}(\text{CH}_3)_2\text{O}]_{n_s}\text{Si}(\text{CH}_3)_2-$ with n_s as defined above;

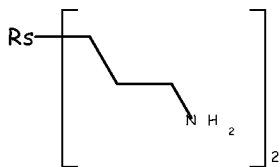
25 and

- R_{B1} is C_1 - C_{10} straight or branched alkylene, C_4 - C_6 cycloalkylene or C_5 - C_6 arylene, optionally comprising one or more $-\text{COOH}$ groups.

Claim 7. The method according to claim 6, wherein composition (C) comprises a polymer (P1) complying with formula:



and a polymer (P2) complying with formula:



5

wherein R_s independently at each occurrence is a chain of formula $-\text{Si}(\text{CH}_3)_2\text{O}[\text{Si}(\text{CH}_3)_2\text{O}]_{ns}\text{Si}(\text{CH}_3)_2-$, with ns being a positive number selected in such a way that the number average molecular weight (M_n) of the chain R_s ranges from 500 to 10,000.

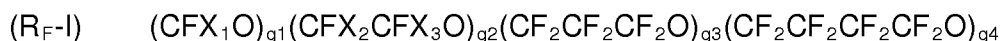
10 **Claim 8.** The method according to claim 3, wherein the fully or partially fluorinated polyoxyalkylene chain [chain (R_F)] comprises repeating units [units (U_F)] selected from:

- (i) $-\text{CFXO}-$, wherein X is F or CF_3 ;
- (ii) $-\text{CFXCFXO}-$, wherein X , equal or different at each occurrence, is F or CF_3 , with the proviso that at least one of X is $-\text{F}$;
- 15 (iii) $-\text{CF}_2\text{CF}_2\text{CW}_2\text{O}-$, wherein each of W , equal or different from each other, is F , Cl , H ,
- (iv) $-\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$;
- (v) $(\text{CF}_2)_j\text{-CFZ-O-}$ wherein j is an integer from 0 to 3 and Z is a group of general formula $-\text{OR}_f^*\text{T}$, wherein R_f^* is a fluoropolyoxyalkene chain comprising a number of repeating units from 0 to 10, said recurring units being chosen among the followings: $-\text{CFXO}-$, $-\text{CF}_2\text{CFXO}-$, $-\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$, $-\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$, with each of each of X being independently F or CF_3 and T being a C_1 - C_3 perfluoroalkyl group.

20

Claim 9. The method according to claim 7, wherein said chain (R_F) has the following formula ($\text{R}_F\text{-I}$):

25



wherein:

- X_1 is independently selected from -F and -CF₃;

- X_2 , X_3 , equal or different from each other and at each occurrence, are independently -F, -CF₃, with the proviso that at least one of X is -F;

- g_1 , g_2 , g_3 , and g_4 , equal or different from each other, are independently integers ≥ 0 , selected in such a way as the average number molecular weight (M_n) ranges from 400 to 10,000; should at least two of g_1 , g_2 , g_3 and g_4 be different from zero, the different recurring units are generally statistically distributed along the chain.

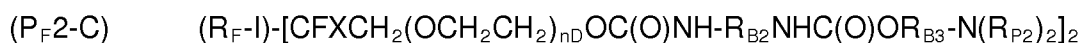
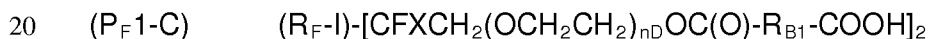
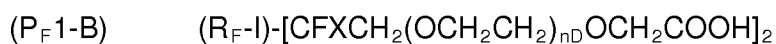
Claim 10. The method according to claim 9, wherein said chain (R_F) has the following formula (R_F -III):



wherein:

- a_1 , and a_2 are integers > 0 such that the number average molecular weight (M_n) ranges from 400 to 4,000, with the ratio a_2/a_1 generally ranging from 0.2 to 5.

Claim 11. The method according to claim 9, wherein said polymer (P1) complies with any of formulae (P_F1-B), (P_F1-C) and (P_F1-D); and/or said polymer (P2) complies with any of formulae (P_F2-A), (P_F2-B) and (P_F2-C);:



wherein:

- n_D is 0 or an integer higher than 1;

- R_{B1} is C₁-C₁₀ straight or branched alkylene, C₄-C₆ cycloalkylene or C₅-C₆ arylene, optionally comprising one or more -COOH groups;

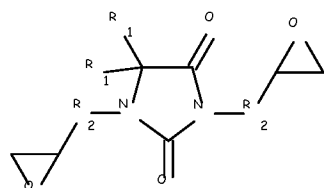
- R_{B2} is straight or branched C₁-C₆ alkylene chain optionally comprising a C₄-C₆ cycloalkylene group or a C₅-C₆ arylene group;

- R_{B3} is a C₂-C₁₀ straight or branched alkylene chain, optionally interrupted by one or

more $-N(R_{P2^*})-$ groups wherein R_{P2^*} represents hydrogen or straight or branched alkyl; and $-R_{P2}$ represents hydrogen or straight or branched alkyl.

Claim 12. The method according to any one of the previous claims, wherein said curable epoxy resin is selected from the group consisting of:

- 5 - polyglycidyl ether-type epoxies, including (i) polyglycidylethers of polyhydric phenols, including bisphenol A diglycidyl ethers, biphenol F diglycidyl ethers, and (ii) polyglycidyl ethers of polyhydric (cyclo)aliphatic alcohols, such as butanediol diglycidyl ether and trimethylolpropane triglycidyl ether;
- novolacs epoxy resins, such as epoxy phenol novolacs (EPN) and epoxy cresol
- 10 novolacs (ECN);
- glycidylamine type epoxy resin, such as N,N',N'',N''' -tetraglycidyl-diaminodiphenylmethanes (e.g. N,N',N'',N''' -tetraglycidyl-bis-(4-aminophenyl)-methane), triglycidyl isocyanurate, hydantoin type epoxy resin, such as the compounds of formula:



15

with R_1 , equal to or different from each other, is independently at each occurrence, an aliphatic group, such as e.g. $-\text{CH}_3$; and R_2 , equal or different at each other, is independently at each occurrence an aliphatic divalent group, such as e.g. $-\text{CH}_2-$ or $-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-\text{CH}_2-$; N,N,N',N' -tetraglycidyl-m-xylenediamine, 1,3-bis(N,N -

20 diglycidylaminomethyl)cyclohexane, aminophenol type epoxies such as N,N,O -triglycidyl-p-aminophenol, aniline type epoxies, and toluidine type epoxy resins, ;

- polymers of monomers having an epoxy group, possibly in combination with other monomers;

- epoxy group-terminated polyesters, in particular epoxy group-terminated polyesters of

25 dimerised monomeric unsaturated fatty acids and polyhydric alcohols, or epoxy group-terminated polyesters of aliphatic or aromatic polycarboxylic acids and polyhydric alcohols.

Claim 13. The method according to claim 12, wherein the composition (C) comprises at least one polyglycidyl ether-type epoxy resin, in particular at least one

polyglycidylether of polyhydric phenols, and more precisely, a bisphenol A diglycidyl ether; and/or wherein composition (C) comprises at least one curing agent for said curable epoxy resin selected from the group consisting of amines, polyamidoamines, polyamides, acids, acid anhydrides, phenols, alcohols and thiols.

5 **Claim 14.** A composition [composition (C)] comprising:

- a) at least one polymer [polymer (P1)] comprising a polymer chain [chain (R)] consisting of a plurality of non-ionisable recurring units [units (U)], said chain having two ends, each end comprising at least one ionisable acid group;
- b) at least one polymer [polymer (P2)] comprising a polymer chain [chain (R)]
10 consisting of a plurality of non-ionisable recurring units [units (U)], said chain (R) being equal to or different from that of polymer (P1) and having two ends, each end comprising at least one ionisable amino group;
- c) at least one curable epoxy resin; and
- d) optionally, at least one curing agent for said curable epoxy resin;

15 wherein:

- polymers (P1) and (P2) are amorphous, have a T_g lower than -35°C ;
- the ratio between the equivalents of polymer (P1) and the equivalents of polymer (P2) in said composition (C) preferably ranges from 1.4 to 0.6, more preferably from 1.2 to 0.8, most preferably from 1.1 to 0.9; and
- 20 - said curable epoxy resin is present in the composition (C) in an amount of at least 50 % wt, preferably at least 60 % weight, more preferably at least 70 % weight, based on the combined weight of polymer (P1), polymer (P2) and curable epoxy resin, said composition (C) possessing preferably the features described in anyone of Claims 1 to 13.

25 **Claim 15.** A coated article [article (A)] comprising a metal substrate, and a coating resulting from curing of composition (C) according to Claim 14, said coating being adhered to at least a part of the surface of said metal substrate.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/081823

A. CLASSIFICATION OF SUBJECT MATTER INV. C09D163/00 C08G77/388 C23F11/00 C09D5/08 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C09D C08G C23F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	abstract; examples 1-10 -----	7
T	Lyle A Chandler ET AL: "Multiple Glass Transitions in Butadiene-Acrylonitride Copolymers*", JOURNAL OF APPLIED POLYMER SCIENCE VOL, 1 January 1969 (1969-01-01), pages 1585-1593, XP055476216, Retrieved from the Internet: URL:https://onlinelibrary.wiley.com/doi/pdf/10.1002/app.1969.070130801 table 1 ----- -/--	1-15
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search	Date of mailing of the international search report	
26 November 2018	13/12/2018	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Dalet, Pierre	

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2018/081823

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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