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(54) **MULTI-LAYERED ELASTOMER ARTICLE AND METHOD FOR MAKING THE SAME**  
**MEHRSCICHTIGER ELASTOMERARTIKEL UND VERFAHREN ZUR HERSTELLUNG**  
**ARTICLE ÉLASTOMÈRE MULTICOUCHE ET MÉTHODE DE FABRICATION**

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• **GIH-KEONG LAU ET AL: "Dielectric elastomer**  
**unimorph using flexible electrodes of**  
**electrolessly deposited (ELD) silver", SENSORS**  
**AND ACTUATORS A, ELSEVIER SEQUOIA S.A.,**  
**LAUSANNE, CH, vol. 169, no. 1, 19 April 2011**  
**(2011-04-19), pages 234-241, XP028233493, ISSN:**  
**0924-4247, DOI: 10.1016/J.SNA.2011.04.037**  
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**Description**

**[0001]** This application claims priority from European application No. 14193990.0, filed on 20th November 2014.

5 Technical Field

**[0002]** The present invention relates to a multi-layered elastomer article and to a method for its manufacturing.

10 Background of the invention

**[0003]** (Per)fluoroelastomers are known to be relatively chemically inert, thermally stable polymers, owing primarily to the strength of the carbon-fluorine bonds present in the molecule.

**[0004]** Because of their properties, the (per)fluoroelastomers are desirable in many applications which require elastomeric materials able to provide high performances, such as withstanding to high temperatures.

15 **[0005]** However, a great number of applications in the field of oil and gas, electronics, automotive, and aerospace require the (per)fluoroelastomers, for example, to have electrical and thermal conductivity or to provide a barrier to gases and liquids.

**[0006]** With the aim to provide (per)fluoroelastomers having the above properties, it has been proposed in the art to adhesively bond metals to (per)fluoroelastomers.

20 **[0007]** Conventional approaches, such as for example vapour coating, sputtering or ion bombardment processes, comprise chemically or physically roughen the metal surface, followed by a thermal fusion or adhering with the intermediary of an adhesive layer (also called primer) between the outmost fluoropolymer layer and the metal, which also has to possess outstanding adhesion properties towards additional top-coat (outer) layers made from fluoropolymers.

25 **[0008]** For example, WO 2013/101822 (3M INNOVATIVE PROPERTIES CO.) discloses a fluoroelastomer material bearing a conductive metal overlayer bound to said fluoroelastomer material through a thin layer of titanium. The method for making said material comprises the steps of (a) providing a fluoroelastomer material, optionally (d) exposure of the fluoroelastomer to oxygen plasma, (b) applying a layer of titanium metal to the fluoroelastomer material by a vapour coating method, (c) applying a metal overlayer to the fluoroelastomer material by a vapour coating method, and optionally (e) electroplating the fluoroelastomer.

30 **[0009]** However, high performing polymers - including, in particular, (per)fluoroelastomers and silicone rubbers - have low surface energy, and consequently poor adhesion with respect to metal materials.

**[0010]** Thus, the high performing polymers coated with metal layers using conventional approaches can suffer of problems such as easy peeling of the metallic coating from the substrate and poor durability of the coating.

35 **[0011]** In the field of semi-crystalline polymers, WO 2014/154733 (SOLVAY SPECIALTY POLYMERS S.P.A.) discloses a multilayer mirror assembly made of ethylene-chloro-trifluoro-ethylene (ECTFE), a semi-crystalline partially fluorinated polymer, treated by a radio-frequency plasma discharge process, and then coated with metallic nickel by electroless plating.

40 **[0012]** However, semi-crystalline polymers, such as ECTFE, and elastomers have different chemical-physical properties and are used in different applications. Also, semi-crystalline polymers do not undergo to elongation and, hence, they are not affected by the problems typically encountered when using elastomers.

**[0013]** In particular, defects in the metallic layer applied on the surface of the elastomer can become particularly evident when the elastomer undergoes to elongation, resulting in a loss of continuity in the metal layer and consequent decrease or loss of the properties imparted by the metal coating, such as for example barrier to fluids and thermal/electrical conductivity.

45 **[0014]** FR 2139998 (DR. ING. MAX SCHLOTTER) discloses plastics and articles made therefrom which are metal plated by conditioning their surface by a treatment with sulfur trioxide vapor or a sulfur trioxide containing atmosphere. In particular, Example 23 discloses the treatment of a soft rubber plate, which is first exposed to the sulfur trioxide vapor phase, then treated with an activating solution, a reducing solution and then chemically nickel plated. Then, the metal layer is reinforced by electroplating with a copper deposit. The authors concluded that "when heating the plates after copper plating to 80°C for two hours, the adherence of the copper layer to the plate is such that the metal layer does not separate from the rubber plate but that the rubber plate itself becomes torn".

50 **[0015]** US 2009/0017319 A (FRAMATOME CONNECTORS INT.) discloses a process for metallizing support media made from plastic material, particularly from high temperature plastic material such as those for electronic industry, notably semi-crystalline polymer or liquid crystal polymers or polybutylene terephthalate (PBT) or polyphenylene sulphide (PPS) or syndiotactic polystyrene (SPS). However, this document is completely silent about the treatment of elastomers or article obtained therefrom.

**[0016]** EP 2 626 448 discloses a process for forming a metal film comprising a step (X) of applying an agent containing a compound (a) onto the surface of a base and a step (Y) of forming a metal film on the surface of the compound (a) by

a wet-mode plating technique, wherein the compound (a) is a compound having either an OH group or an OH-generating group, an azide group and a triazine ring per molecule, and the base comprises a polymer.

## Summary of the invention

**[0017]** The Applicant faced the problem to provide an elastomer article having high adhesion to a metallic layer, such that defects in the metallic layer are avoided or at least minimized even after the elastomer has undergone to elongation.

**[0018]** Thus, in a first aspect, the present invention relates to a multi-layered article made of an elastomeric composition [composition (C)] comprising at least one elastomer, said article having at least one surface [surface (S)] comprising:

- nitrogen-containing groups [groups (N)] and
- at least one layer [layer (L1)] adhered to said surface (S) comprising at least one metal compound [compound (M)] selected from the group consisting of: Cu, Ni, Pd, Co, Zn, Ag, Au, Pt, Sn;

wherein said elastomer comprises recurring units derived from at least one (per)fluorinated monomer, characterized in that said nitrogen-containing groups (N) are grafted onto said surface (S) via an atmospheric plasma process performed in the presence of a nitrogen-containing gas, which is a mixture of N<sub>2</sub> and H<sub>2</sub>.

**[0019]** As said above, said groups (N) are grafted onto said surface (S).

**[0020]** Without being bounded by any theory, the Applicant believes that at least part of said groups (N) grafted onto said surface (S) form chemical bonds with said at least one compound (M), thus obtaining an outstanding adhesion between said surface (S) comprising groups (N) and said layer (L1) comprising compound (M).

**[0021]** The expression "chemical bonds" is intended to indicate any type of chemical bond, such as for example covalent bond, ionic bond, dipolar (or coordinate) bond, between at least part of groups (N) grafted on the surface of the elastomer and compound (M).

**[0022]** Advantageously, the article according to the present invention comprising said layer (L1) adhered to said surface (S) provides electrical and thermal conductivity and a barrier to gases and liquids, and can withstand extreme environmental conditions due to chemical resistance, abrasion resistance and wear resistance, while maintaining its typical flexibility and mechanical properties.

**[0023]** Then, in a second aspect, the present invention relates to a method for manufacturing a multi-layered article, said method comprising the steps of:

(i) providing an article made of an elastomeric composition [composition (C)] comprising at least one elastomer, wherein said elastomer comprises recurring units derived from at least one (per)fluorinated monomer, said article having at least one surface [surface (S-1)];

(ii) forming nitrogen-containing groups [groups (N)] on said at least one surface (S-1) so as to provide an elastomer article having at least one nitrogen-containing surface [surface (S-2)], wherein said nitrogen-containing groups (N) are grafted onto said surface (S-2) via an atmospheric plasma process performed in the presence of a nitrogen-containing gas, which is a mixture of N<sub>2</sub> and H<sub>2</sub>;

(iii) contacting said at least one surface (S-2) with a first composition [composition (C1)] comprising at least one metallization catalyst, so as to provide an article having at least one surface [surface (S-3)] containing groups (N) and at least one metallization catalyst; and

(iv) contacting said at least one surface (S-3) with a second composition [composition (C2)] containing at least one metal compound [compound (M1)], so as to provide a multi-layered article having at least one surface [surface (S)] comprising groups (N) and at least one layer (L1) adhered to said surface (S) comprising at least one metal compound (M) selected from the group consisting of: Cu, Ni, Pd, Co, Ag, Au, Pt, Sn and alloys thereof.

**[0024]** Optionally, the above method comprises after step (iv), step (v) of applying a third composition [composition (C3)] containing at least one metal compound [compound (M2)] onto said surface (S).

## Detailed description of the invention

**[0025]** Preferably, said multi-layered article is in the form of a film or a shaped article.

**[0026]** The thickness of said film is not particularly limited. For example, said film can have a thickness of between 0.5 mm and 10 mm.

**[0027]** The term "elastomer" as used within the present description and in the following claims indicates amorphous polymers or polymers having a low degree of crystallinity (crystalline phase less than 20% by volume) and a glass transition temperature value (T<sub>g</sub>), measured according to ASTM D3418, below room temperature. More preferably, the elastomer according to the present invention has a T<sub>g</sub> below 5°C, even more preferably below 0°C.

**[0028]** As said in the claims, said elastomer comprises recurring units derived from at least one at least one (per)fluorinated monomer. In a preferred embodiment, said monomers are free of nitrogen atoms.

**[0029]** By the expression "at least one (per)fluorinated monomer, it is hereby intended to denote a polymer comprising recurring units derived from one or more than one (per)fluorinated monomers. In the rest of the text, the expression "(per)fluorinated monomers" is understood, for the purposes of the present invention, both in the plural and the singular, that is to say that it denote both one or more than one fluorinated monomers as defined above. The prefix "(per)" in the expression "(per)fluorinated monomer" and in the term "(per)fluoroelastomer" means that the monomer or the elastomer can be fully or partially fluorinated.

**[0030]** Non limitative examples of suitable (per)fluorinated monomers include, notably, the followings:

- C<sub>3</sub>-C<sub>8</sub> perfluoroolefins, such as tetrafluoroethylene (TFE) and hexafluoropropene (HFP);
- C<sub>2</sub>-C<sub>8</sub> hydrogenated fluoroolefins, such as vinylidene fluoride (VDF), vinyl fluoride, 1,2-difluoroethylene and trifluoroethylene (TrFE);
- chloro- and/or bromo- and/or iodo-C<sub>2</sub>-C<sub>6</sub> fluoroolefins, such as chlorotrifluoroethylene (CTFE);
- CH<sub>2</sub>=CH-R<sub>f0</sub> wherein R<sub>f0</sub> is a C<sub>1</sub>-C<sub>6</sub> (per)fluoroalkyl or a C<sub>1</sub>-C<sub>6</sub> (per)fluorooxyalkyl having one or more ether groups;
- CH<sub>2</sub>=CFOR<sub>f1</sub>, wherein R<sub>f1</sub> is a C<sub>1</sub>-C<sub>6</sub> fluoro- or perfluoroalkyl group, such as CF<sub>3</sub>, C<sub>2</sub>F<sub>5</sub>, C<sub>3</sub>F<sub>7</sub>;
- CF<sub>2</sub>=CFOR<sub>f2</sub>, wherein R<sub>f2</sub> is a C<sub>1</sub>-C<sub>6</sub> fluoro- or perfluoroalkyl group, such as CF<sub>3</sub>, C<sub>2</sub>F<sub>5</sub>, C<sub>3</sub>F<sub>7</sub>; or a C<sub>1</sub>-C<sub>12</sub> oxyalkyl or a C<sub>1</sub>-C<sub>12</sub> (per)fluorooxyalkyl group comprising one or more ether groups, such as perfluoro-2-propoxypropyl; or a group of formula -CF<sub>2</sub>OR<sub>f3</sub> in which R<sub>f3</sub> is a C<sub>1</sub>-C<sub>6</sub> fluoro- or perfluoroalkyl or a C<sub>1</sub>-C<sub>6</sub> (per)fluorooxyalkyl group comprising one or more ether groups, such as -C<sub>2</sub>F<sub>5</sub>-O-CF<sub>3</sub>;
- CF<sub>2</sub>=CFOR<sub>f4</sub>, wherein R<sub>f4</sub> is a C<sub>1</sub>-C<sub>12</sub> alkyl or (per)fluoroalkyl group; a C<sub>1</sub>-C<sub>12</sub> oxyalkyl; or a C<sub>1</sub>-C<sub>12</sub> (per)fluorooxyalkyl; said R<sub>f4</sub> comprising a carboxylic or sulfonic acid group, in its acid, acid halide or salt form;
- fluorodioxoles, such as perfluorodioxoles;
- fluorosilanes, such as CF<sub>3</sub>-C<sub>2</sub>H<sub>4</sub>-Si(R<sub>f5</sub>)<sub>3</sub> or Ar-Si(R<sub>f5</sub>)<sub>3</sub> wherein each of R<sub>f5</sub> is independently selected from Cl, C<sub>1</sub>-C<sub>3</sub> alkyl or C<sub>1</sub>-C<sub>3</sub> alkoxy, and Ar is a phenyl ring optionally substituted with a C<sub>1</sub>-C<sub>6</sub> fluoro- or perfluoroalkyl group, e.g. CF<sub>3</sub>, C<sub>2</sub>F<sub>5</sub>, C<sub>3</sub>F<sub>7</sub> or a C<sub>1</sub>-C<sub>6</sub> (per)fluorooxyalkyl group comprising one or more ether groups, such as -C<sub>2</sub>F<sub>5</sub>-O-CF<sub>3</sub>; and CH<sub>2</sub>=CH<sub>2</sub>-Si(R<sub>f6</sub>)<sub>3</sub> wherein each of R<sub>f6</sub> is independently selected from H, F and C<sub>1</sub>-C<sub>3</sub> alkyl, provided that at least one of said R<sub>f6</sub> is F.

**[0031]** Preferably, said (per)fluoro-elastomer has a T<sub>g</sub> of less than 0°C, more preferably of less than -10°C, as measured as measured according to ASTM D-3418.

**[0032]** Typically, said (per)fluoro-elastomer comprises recurring units derived from the (per)fluorinated monomers cited above.

**[0033]** More preferably, said (per)fluoro-elastomer comprises recurring units derived from:

- C<sub>3</sub>-C<sub>8</sub> perfluoroolefins, such as tetrafluoroethylene (TFE) and hexafluoropropene (HFP);
- C<sub>2</sub>-C<sub>8</sub> hydrogenated fluoroolefins, such as vinylidene fluoride (VDF), vinyl fluoride, 1,2-difluoroethylene and trifluoroethylene (TrFE);
- CF<sub>2</sub>=CFOR<sub>f1</sub>, wherein R<sub>f1</sub> is a C<sub>1</sub>-C<sub>6</sub> fluoro- or perfluoroalkyl group, such as CF<sub>3</sub>, C<sub>2</sub>F<sub>5</sub>, C<sub>3</sub>F<sub>7</sub>, or a group of formula -CFOCF<sub>2</sub>OR<sub>f2</sub> wherein R<sub>f2</sub> is a C<sub>1</sub>-C<sub>6</sub> fluoro- or perfluoroalkyl group, e.g. CF<sub>3</sub>, C<sub>2</sub>F<sub>5</sub>, C<sub>3</sub>F<sub>7</sub>;
- fluorosilanes, such as CF<sub>3</sub>-C<sub>2</sub>H<sub>4</sub>-Si(R<sub>f3</sub>)<sub>3</sub> wherein each of R<sub>f3</sub> is independently selected from Cl, C<sub>1</sub>-C<sub>3</sub> alkyl or C<sub>1</sub>-C<sub>3</sub> alkoxy, and CH<sub>2</sub>=CH<sub>2</sub>-Si(R<sub>f4</sub>)<sub>3</sub> wherein each of R<sub>f4</sub> is selected from H, F and C<sub>1</sub>-C<sub>3</sub> alkyl.

**[0034]** Optionally, said (per)fluoroelastomer further comprises recurring units derived from at least one bis-olefin.

**[0035]** Non limiting examples of suitable bis-olefins are selected from those of formulae below:

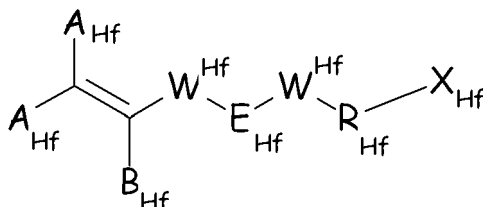
- R<sub>1</sub>R<sub>2</sub>C=CH-(CF<sub>2</sub>)<sub>j</sub>-CH=CR<sub>3</sub>R<sub>4</sub> wherein j is an integer between 2 and 10, preferably between 4 and 8, and R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, equal or different from each other, are -H, -F or C<sub>1</sub>-C<sub>5</sub> alkyl or (per)fluoroalkyl group;
- A<sub>2</sub>C=CB-O-E-O-CB=CA<sub>2</sub>, wherein each of A, equal or different from each other, is independently selected from -F, -Cl, and -H; each of B, equal or different from each other is independently selected from -F, -Cl, -H and -OR<sub>B</sub>, wherein R<sub>B</sub> is a branched or straight chain alkyl radical which can be partially, substantially or completely fluorinated or chlorinated; E is a divalent group having 2 to 10 carbon atoms, optionally fluorinated, which may be inserted with ether linkages; preferably E is a -(CF<sub>2</sub>)<sub>z</sub>- group, with z being an integer from 3 to 5; and -R<sub>6</sub>R<sub>7</sub>C=CR<sub>5</sub>-E-O-CB=CA<sub>2</sub>, wherein E, A and B have the same meaning as above defined; R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, equal or different from each other, are -H, -F or C<sub>1</sub>-C<sub>5</sub> alkyl or fluoroalkyl group.

**[0036]** When a bis-olefin is employed, the resulting (per)fluoroelastomer typically comprises from 0.01% to 5% by moles of units deriving from the bis-olefin with respect to the total amount of units in the polymer.

[0037] Optionally, said (per)fluoroelastomer may comprise cure sites, either as pendant groups bonded to certain recurring units or as ends groups of the polymer chain, said cure sites comprising at least one iodine or bromine atom, more preferably at least one iodine atom.

[0038] Among cure-site containing recurring units, mention can be notably made of:

(CSM-1) iodine or bromine containing monomers of formula:

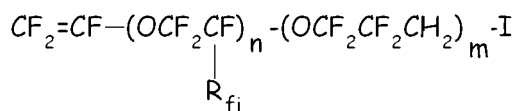


wherein each of  $A_{Hf}$ , equal to or different from each other and at each occurrence, is independently selected from F, Cl, and H;  $B_{Hf}$  is any of F, Cl, H and  $OR_{Hf}^B$ , wherein  $R_{Hf}^B$  is a branched or straight chain alkyl radical which can be partially, substantially or completely fluorinated or chlorinated; each of  $W_{Hf}$  equal to or different from each other and at each occurrence, is independently a covalent bond or an oxygen atom;  $E_{Hf}$  is a divalent group having 2 to 10 carbon atom, optionally fluorinated;  $R_{Hf}$  is a branched or straight chain alkyl radical, which can be partially, substantially or completely fluorinated; and  $X_{Hf}$  is a halogen atom selected from the group consisting of Iodine and Bromine; which may be inserted with ether linkages; preferably E is a  $-(CF_2)_m-$  group, with m being an integer from 3 to 5;

(CSM-2) ethylenically unsaturated compounds comprising cyanide groups, possibly fluorinated.

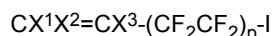
[0039] Among cure-site containing monomers of type (CSM1), preferred monomers are those selected from the group consisting of:

(CSM1-A) iodine-containing perfluorovinylethers of formula:



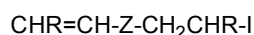
with m being an integer from 0 to 5 and n being an integer from 0 to 3, with the proviso that at least one of m and n is different from 0, and  $R_{fi}$  being F or  $CF_3$ ; (as notably described in patents US 4745165 (AUSIMONT SPA), US 4564662 (MINNESOTA MINING) and EP 199138 (DAIKIN IND LTD) ; and

(CSM-1B) iodine-containing ethylenically unsaturated compounds of formula:



wherein each of  $X^1$ ,  $X^2$  and  $X^3$ , equal to or different from each other, are independently H or F; and p is an integer from 1 to 5; among these compounds, mention can be made of  $CH_2=CHCF_2CF_2I$ ,  $I(CF_2CF_2)_2CH=CH_2$ ,  $ICF_2CF_2CF=CH_2$ ,  $I(CF_2CF_2)_2CF=CH_2$ ;

(CSM-1C) iodine-containing ethylenically unsaturated compounds of formula:



wherein R is H or  $CH_3$ , Z is a  $C_1$ - $C_{18}$  (per)fluoroalkylene radical, linear or branched, optionally containing one or more ether oxygen atoms, or a (per)fluoropolyoxyalkylene radical; among these compounds, mention can be made of  $CH_2=CH-(CF_2)_4CH_2CH_2I$ ,  $CH_2=CH-(CF_2)_6CH_2CH_2I$ ,  $CH_2=CH-(CF_2)_8CH_2CH_2I$ ,  $CH_2=CH-(CF_2)_2CH_2CH_2I$ ;

(CSM-1D) bromo and/or iodo alpha-olefins containing from 2 to 10 carbon atoms such as bromotrifluoroethylene or bromotetrafluorobutene described, for example, in US 4035565 (DU PONT) or other compounds bromo and/or iodo alpha-olefins disclosed in US 4694045 (DU PONT).

[0040] Among cure-site containing monomers of type (CSM2), preferred monomers are those selected from the group consisting of:

(CSM2-A) perfluorovinyl ethers containing cyanide groups of formula  $\text{CF}_2=\text{CF}-(\text{OCF}_2\text{CFX}^{\text{CN}})_m-\text{O}-(\text{CF}_2)_n-\text{CN}$ , with  $\text{X}^{\text{CN}}$  being F or  $\text{CF}_3$ , m being 0, 1, 2, 3 or 4; n being an integer from 1 to 12;  
 (CSM2-B) perfluorovinyl ethers containing cyanide groups of formula  $\text{CF}_2=\text{CF}-(\text{OCF}_2\text{CFX}^{\text{CN}})_m-\text{O}-\text{CF}_2-\text{CF}(\text{CF}_3)-\text{CN}$ , with  $\text{X}^{\text{CN}}$  being F or  $\text{CF}_3$ , m' being 0, 1, 2, 3 or 4.

**[0041]** Specific examples of cure-site containing monomers of type CSM2-A and CSM2-B suitable to the purposes of the present invention are notably those described in patents US 4281092 (DU PONT), US 5447993 (DU PONT) and US 5789489 (DU PONT).

**[0042]** Preferably, said (per)fluoroelastomer comprises iodine or bromine cure sites in an amount of 0.001 to 10% wt. Among these, iodine cure sites are those selected for maximizing curing rate, so that (per)fluoroelastomers comprising iodine cure-sites are preferred.

**[0043]** According to this embodiment, for ensuring acceptable reactivity it is generally understood that the content of iodine and/or bromine in the (per)fluoroelastomer should be of at least 0.05 % wt, preferably of at least 0.1 % weight, more preferably of at least 0.15 % weight, with respect to the total weight of the (per)fluoroelastomer.

**[0044]** On the other side, amounts of iodine and/or bromine not exceeding preferably 7 % wt, more specifically not exceeding 5 % wt, or even not exceeding 4 % wt, with respect to the total weight of the (per)fluoroelastomer, are those generally selected for avoiding side reactions and/or detrimental effects on thermal stability.

**[0045]** These iodine or bromine cure sites of these preferred embodiments of the invention might be comprised as pending groups bound to the backbone of the (per)fluoroelastomer polymer chain (by means of incorporation in the (per)fluoroelastomer chain of recurring units derived from monomers of (CSM-1) type, as above described, and preferably of monomers of (CSM-1A) to (CSM1-D), as above detailed) or might be comprised as terminal groups of said polymer chain.

**[0046]** According to a first embodiment, the iodine and/or bromine cure sites are comprised as pending groups bound to the backbone of the (per)fluoroelastomer polymer chain. The (per)fluoroelastomer according to this embodiment generally comprises recurring units derived from iodine or bromine containing monomers (CSM-1) in amounts of 0.05 to 5 mol per 100 mol of all other recurring units of the (per)fluoroelastomer, so as to advantageously ensure above mentioned iodine and/or bromine weight content.

**[0047]** According to a second preferred embodiment, the iodine and/or bromine cure sites are comprised as terminal groups of the (per)fluoroelastomer polymer chain; the fluoroelastomer according to this embodiment is generally obtained by addition to the polymerization medium during fluoroelastomer manufacture of anyone of:

- iodinated and/or brominated chain-transfer agent(s); suitable chain-chain transfer agents are typically those of formula  $\text{R}_f(\text{I})_x(\text{Br})_y$ , in which  $\text{R}_f$  is a (per)fluoroalkyl or a (per)fluorochloroalkyl containing from 1 to 8 carbon atoms, while x and y are integers between 0 and 2, with  $1 \leq x+y \leq 2$  (see, for example, patents US 4243770 (DAIKIN IND LTD) and US 4943622 (NIPPON MEKTRON KK) ; and
- alkali metal or alkaline-earth metal iodides and/or bromides, such as described notably in patent US 5173553 (AUSIMONT SRL).

**[0048]** Among specific compositions of said (per)fluoroelastomer, which are suitable for the purpose of the present invention, mention can be made of fluoroelastomers having the following compositions (in mol %):

- (i) vinylidene fluoride (VDF) 35-85 %, hexafluoropropene (HFP) 10-45 %, tetrafluoroethylene (TFE) 0-30 %, perfluoroalkyl vinyl ethers (PAVE) 0-15 %, bis-olefin (OF) 0-5 %;
- (ii) vinylidene fluoride (VDF) 50-80 %, perfluoroalkyl vinyl ethers (PAVE) 5-50 %, tetrafluoroethylene (TFE) 0-20 %, bis-olefin (OF) 0-5 %;
- (iii) vinylidene fluoride (VDF) 20-30 %,  $\text{C}_2\text{-C}_8$  non-fluorinated olefins (OI) 10-30 %, hexafluoropropene (HFP) and/or perfluoroalkyl vinyl ethers (PAVE) 18-27 %, tetrafluoroethylene (TFE) 10-30 %, bis-olefin (OF) 0-5 %;
- (iv) tetrafluoroethylene (TFE) 50-80 %, perfluoroalkyl vinyl ethers (PAVE) 20-50 %, bis-olefin (OF) 0-5 %;
- (v) tetrafluoroethylene (TFE) 45-65 %,  $\text{C}_2\text{-C}_8$  non-fluorinated olefins (OI) 20-55 %, vinylidene fluoride 0-30 %, bis-olefin (OF) 0-5 %;
- (vi) tetrafluoroethylene (TFE) 32-60 % mol %,  $\text{C}_2\text{-C}_8$  non-fluorinated olefins (OI) 10-40 %, perfluoroalkyl vinyl ethers (PAVE) 20-40 %, fluorovinyl ethers (MOVE) 0-30 %, bis-olefin (OF) 0-5 %;
- (vii) tetrafluoroethylene (TFE) 33-75 %, perfluoroalkyl vinyl ethers (PAVE) 15-45 %, vinylidene fluoride (VDF) 5-30 %, hexafluoropropene HFP 0-30 %, bis-olefin (OF) 0-5 %;
- (viii) vinylidene fluoride (VDF) 35-85 %, fluorovinyl ethers (MOVE) 5-40 %, perfluoroalkyl vinyl ethers (PAVE) 0-30 %, tetrafluoroethylene (TFE) 0-40 %, hexafluoropropene (HFP) 0-30 %, bis-olefin (OF) 0-5 %;
- (ix) tetrafluoroethylene (TFE) 20-70 %, fluorovinyl ethers (MOVE) 30-80 %, perfluoroalkyl vinyl ethers (PAVE) 0-50 %, bis-olefin (OF) 0-5 %.

**[0049]** Suitable examples of (per)fluoroelastomers are the products sold by SOLVAY SPECIALTY POLYMERS S.p.A. under the trade name Tecnoflon®, such as for example Tecnoflon® PL 855.

**[0050]** As an alternative, not within the scope of the present invention, said elastomer can be a silicone elastomer. Preferably, said silicone elastomer has a  $T_g$  of less than  $-10^\circ\text{C}$ , more preferably of less than  $-30^\circ\text{C}$ , and even more preferably of less than  $-50^\circ\text{C}$  as measured according to ASTM D-3418.

**[0051]** Typically, said silicone elastomer comprises recurring units derived from silicon-containing monomers, and optionally further hydrogenated monomers and/or (per)fluorinated monomers as disclosed above.

**[0052]** By the expression "silicon-containing monomer", it is hereby intended to denote a linear or branched monomer containing alternating silicon and oxygen atoms.

**[0053]** Examples of suitable silicon-containing monomers include:

- silane, such as  $\text{CH}_2=\text{CH}_2\text{-Si(R}_{17}\text{)}_3$  wherein each of  $\text{R}_{17}$  is independently selected from H, F and  $\text{C}_1\text{-C}_3$  alkyl;
- siloxane of formula  $(\text{R})_3\text{Si-O-Si(R)}_3$  and  $(\text{R})_2\text{Si(OH)}_2$ , wherein each R is independently selected from H, linear or branched alkyl groups having from 1 to 6 carbon atoms, preferably methyl group, or phenyl group.

**[0054]** Typically, said silicone elastomer is a polyorganosiloxane-based silicone rubber base, such as a polydimethyl siloxane containing crosslinking groups having hydroxyl, vinyl or hexenyl groups, or a polymethylphenyl siloxane.

**[0055]** Suitable examples of silicone elastomers are the products sold by Dow Corning Corp. (U.S.A.) under the trade name Silastic, such as Silastic 35U and Silastic TR-55 (dimethyl vinyl terminated, dimethyl organosiloxane).

**[0056]** Said nitrogen-containing groups (N) are not particularly limited, provided that it contains at least one nitrogen atom. Examples said of groups (N) are amino, amide, imino, nitrile, urethane and urea groups.

**[0057]** The thickness of said layer (L1) is not particularly limited. For example, said layer (L1) has a thickness of from 1 nm to 10  $\mu\text{m}$ .

**[0058]** Preferably, said layer (L1) is a continuous layer, completely covering said surface (S). However, depending on the application, said layer (L1) can be a discontinuous layer, partially covering said surface (S), i.e. said surface (S) comprises at least one area that is not covered by said layer (L1).

**[0059]** Examples of said compound (M) are the following comprises at least one metal selected from the group consisting of: Rh, Ir, Ru, Ti, Re, Os, Cd, Tl, Pb, Bi, In, Sb, Al, Ti, Cu, Ni, Pd, V, Fe, Cr, Mn, Co, Zn, Mo, W, Ag, Au, Pt, Ir, Ru, Pd, Sn, Ge, Ga and alloys thereof.

**[0060]** According to the invention, said compound (M) comprises at least one metal selected from the group consisting of Ni, Cu, Pd, Co, Ag, Au, Pt, Sn and alloys thereof. Even more preferably, said compound (M) comprises Cu and Pd.

**[0061]** Under step (i) of the process of the present invention, said elastomeric composition (C) typically comprises at least one elastomer, for example in the form of slabs, powder, crumbs, liquids, gels; and further ingredients.

**[0062]** Suitable further ingredients and their amounts can be selected by the skilled person, depending on the type of elastomer used, the conditions used in the cross-linking step and/or the properties desired in the final article.

**[0063]** Typically, further ingredients can be selected from the following:

- curing agents, such as polyhydroxylic compounds (for example Bisphenol A), triallyl-isocyanurate (TAIC) and organic peroxide (for example di-tertbutyl peroxide, 2,4-dichloro benzoyl peroxide, dibenzoyl peroxide, bis(1,1-diethylpropyl)peroxide, bis(1-ethyl-1-methylpropyl)peroxide, 1,1-diethylpropyl-1-ethyl-1-methylpropyl-peroxide, 2,5-dimethyl-2,5-bis(tert-amylperoxy)hexane, dicumyl peroxide, di-tert-butyl perbenzoate, bis[1,3-dimethyl-3-(tert-butylperoxy)butyl] carbonate and 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, which is sold under the trade name Luperox® 101XL45);
- metal compounds, in particular bivalent metal oxides and/or hydroxide, such as  $\text{MgO}$ ,  $\text{ZnO}$  and  $\text{Ca(OH)}_2$ ; salts of a weak acid, such as Ba, Na, K, Pb, Ca stearate, benzoates, carbonates, oxalates, or phosphites; and mixtures thereof; and
- conventional additives, in particular fillers, such as carbon black and fumed silica; accelerators, such as ammonium, phosphonium and aminophosphonium salt; thickeners; pigments; antioxidant; stabilizers; processing aids.

**[0064]** Preferably, in composition (C), said curing agents are in an amount of from 0.5 to 15 phr (i.e., parts by weight per 100 parts by weight of the elastomer), more preferably of from 2 to 10 phr.

**[0065]** Preferably, in composition (C), said metal compounds are in an amount of from 0.5 to 15 phr, more preferably of from 1 to 10 phr.

**[0066]** Preferably, in composition (C), said conventional additives are in an amount of from 0.5 to 50 phr, more preferably of from 3 to 40 phr.

**[0067]** Said composition (C) is typically manufactured by using standard methods.

**[0068]** Typically, all the ingredients are first mixed together. Mixer devices such as internal mixers or open mill mixers can be used.

**[0069]** Under step (i) of the process of the present invention, said article is obtained by curing said composition (C).

**[0070]** The conditions for the curing of said composition (C) can be selected by the skilled person depending on the elastomer and the curing agent used.

**[0071]** For example, when the elastomer is a fluoroelastomer, curing can be performed at a temperature of from 100°C to 250°C, preferably from 150°C to 200°C, for a time of from 5 to 30 minutes.

**[0072]** In the method according to the present invention, said step (ii) is performed by treating said surface (S-1) in the presence of a nitrogen-containing gas.

**[0073]** Said nitrogen-containing gas can be for example N<sub>2</sub>, NH<sub>3</sub> or mixtures thereof, optionally in admixture with nitrogen-free gas such as CO<sub>2</sub> and/or H<sub>2</sub>. Under step (ii) of the present invention, said nitrogen-containing gas is a mixture of N<sub>2</sub> and H<sub>2</sub>.

**[0074]** The gas rate can be selected by the skilled person. Good results have been obtained by using gas flow between 5 nl/min and 15 nl/min, preferably of about 10 nl/min.

**[0075]** According to the invention, said step (ii) is performed by an atmospheric plasma process.

**[0076]** Preferably, said atmospheric plasma process is performed under atmospheric pressure and with an equivalent corona dose of from 50 Wmin/m<sup>2</sup> to 30,000 Wmin/m<sup>2</sup>, more preferably of from 500 Wmin/m<sup>2</sup> to 15000 Wmin/m<sup>2</sup>.

**[0077]** Advantageously, said at least one surface (S-1) is continuously treated by said atmospheric plasma process in the presence of a nitrogen-containing gas, so as to provide a nitrogen-containing surface (S-2).

**[0078]** The Applicant has found that the so-treated surface (S-2) provides outstanding adhesion with a layer (L1) comprising at least one metal compound, applied thereto as disclosed below.

**[0079]** Preferably, under step (iii) of the present invention, said composition (C1) is in a solution or a colloidal suspension of the metallization catalyst in a suitable solvent, such as water.

**[0080]** Preferably, step (iii) is performed by dipping the elastomer as obtained in step (ii) in said composition (C1).

**[0081]** Preferably, compounds that may be employed as metallization catalysts in the method of the present invention are selected in the group comprising Pd, Pt, Rh, Ir, Ni, Cu, Ag and Au catalysts.

**[0082]** More preferably, the metallization catalyst is selected from Pd catalysts, such as PdCl<sub>2</sub>.

**[0083]** Preferably, under step (iv), said composition (C2) is an electroless metallization plating bath, comprising at least one compound (M1), at least one reducing agent, at least one liquid medium and, optionally, one or more additives.

**[0084]** Preferably, said compound (M1) comprises one or more metal salts. More preferably, said compound (M1) preferably comprises one or more metal salts of the metals listed above with respect to compound (M).

**[0085]** Preferably, said reducing agent is selected from the group comprising formaldehyde, sodium hypophosphite, hydrazine, glycolic acid and glyoxylic acid.

**[0086]** Preferably, said liquid medium is selected from the group comprising water, organic solvents and ionic liquids.

**[0087]** Among organic solvents, alcohols are preferred such as ethanol.

**[0088]** Non-limitative examples of suitable ionic liquids include, notably, those comprising as cation a sulfonium ion or an imidazolium, pyridinium, pyrrolidinium or piperidinium ring, said ring being optionally substituted on the nitrogen atom, in particular by one or more alkyl groups with 1 to 8 carbon atoms, and on the carbon atoms, in particular by one or more alkyl groups with 1 to 30 carbon atoms.

**[0089]** Preferably, the ionic liquid is advantageously selected from those comprising as anion those chosen from halides anions, perfluorinated anions and borates.

**[0090]** Preferably, additives are selected from the group comprising salts, buffers and other materials suitable for enhancing stability of the catalyst in the liquid composition.

**[0091]** Preferably, said step (iv) is performed at a temperature above 30°C, for example between 40°C and 50°C.

**[0092]** Preferably, said step (iv) is performed so as to provide a continuous layer (L1), which completely covers said surface (S), for example by dipping the elastomer as obtained in step (iii) in said composition (C2). However, depending on the application of the multi-layered article, said step (iv) may be performed so as to provide a discontinuous layer (L1), which partially covers said surface (S).

**[0093]** Preferably, said steps (iii) and (iv) are performed as a single step [step (iii-D)], more preferably by electroless deposition.

**[0094]** By "electroless deposition" it is meant a redox process typically carried out in a plating bath between a metal cation and a proper chemical reducing agent suitable for reducing said metal cation in its elemental state.

**[0095]** The preferred conditions disclosed above with respect to step (iii) and step (iv) apply whether steps (iii) and (iv) are performed separately or when step (iii) and step (iv) are performed as a single step (iii-D).

**[0096]** Preferably, said composition (C3) is an electrolytic solution, comprising at least one compound (M2), at least one metal halide and, optionally, at least one ionic liquid as defined above.

**[0097]** Said compound (M2) can be the same or different from said compound (M1).

**[0098]** Preferably, said compound (M2) is a metal salt deriving from Al, Ni, Cu, Ag, Au, Cr, Co, Sn, Ir, Pt and alloys thereof.

**[0099]** Preferably, said metal halide is PdCl<sub>2</sub>.

**[0100]** Preferably, said step (v) is performed by electro-deposition.



**[0101]** Within the present description and in the following claims, by "electro-deposition" it is meant a process using electrical current to reduce metal cations from an electrolytic solution.

**[0102]** The present invention will be now described in more detail with reference to the following examples, whose purpose is merely illustrative and not limitative of the scope of the invention.

## Examples

### Materials

**[0103]** Tecnoflon® PL855 fluoroelastomer: TFE/PMVE/MOVE terpolymer having Mooney viscosity of about 54 and Tg of about -30°C, supplied by Solvay Specialty Polymers Italy S.p.A.

**[0104]** Luperox® 101XL45: 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, blend with calcium carbonate and silica, with 45 wt.% of solid content TAIC: triallyl isocyanurate, with 75 wt.% of solid content

**[0105]** Commercial copper electroless solution Printoganth PV, supplied by Atotech

### Example 1 - Production of an elastomer article [Plaque 1C]

**[0106]** The ingredients listed in the following Table 1 were mixed together in an open mill mixer.

**Table 1**

Ingredients	Amount (phr)
Tecnoflon® PL855	100
Carbon Black N990	30
ZnO	5
Luperox® 101XL45	3
TAIC	4

**[0107]** The composition thus obtained was press-cured for 10 minutes at 170°C, so as to form plaques of 2 mm thick and 130 mm of side. The plaques were then post-cured in an oven (in air) for 24 hours at 250°C.

**[0108]** The plaques thus obtained were then cleaned with a lab cloth soaked with isopropyl alcohol (IPA), in order to remove dirt and contaminants.

**[0109]** One of the plaque thus obtained was used as reference plaque (hereinafter referred to as "Plaque 1C").

### Example 2 - Manufacture of a multi-layered elastomer article

**[0110]** One of the plaques obtained according to the procedure described in Example 1 was treated as follows.

#### Step (a) [Plaque AP]

**[0111]** An atmospheric plasma treatment was performed on one surface of the plaque by means of a Dielectric Barrier Discharge (DBD) device with mobile upper electrode, in the following conditions:

electrode distance 3mm

gas flow 10 nL/min

gas composition 95% N<sub>2</sub> + 5% H<sub>2</sub>

source power 400W

mobile electrode speed 2m/min and 3 passes

**[0112]** The treatment resulted in an equivalent corona dose of about 8700 W min/m<sup>2</sup>.

**[0113]** The plaque thus obtained will be hereinafter referred to as "Plaque AP".

#### Step (b) [Plaque 2]

**[0114]** Plaque AP obtained according to the procedure disclosed in step (a) was subjected to electroless deposition

in order to obtain a layer of metallic copper.

[0115] The plaque was cleaned by dipping in a suitable solution containing isopropyl alcohol and, then, contacted with a  $\text{PdCl}_2$  solution.

[0116] The palladium ions were reduced to metallic palladium. Then, electroless deposition of copper was performed by dipping the sample in the bath containing the Atotech's Printogant PV solution, for 90 seconds, at 45°C, so as the metallic copper was deposited on the surface of the plaque.

[0117] The plaque thus obtained will be hereinafter referred to as "Plaque 2".

### Comparative Example 3 - Manufacture of a comparative multi-layered elastomer article [Plaque 3C]

[0118] One plaque obtained according to the procedure described in Example 1 above was treated according to the procedure described in Example 2, step (b), without performing the atmospheric plasma treatment.

[0119] The plaque thus obtained will be hereinafter referred to as "Plaque 3C".

### Comparative Example 4 - Manufacture of a comparative multi-layered elastomer article [Plaque 4C]

[0120] One plaque obtained according to the procedure described in Example 1 above was deposited with a copper layer by sputtering technique, i.e. in particular by eroding copper atoms from a copper electrode using an argon plasma and depositing said copper onto the plaque.

[0121] The plaque thus obtained will be hereinafter referred to as "Plaque 4C".

### Example 5 - Surface analysis

#### 5a - Surface analysis by ATR-FTIR

[0122] Attenuated total reflection (ATR) is a sampling technique used in conjunction with infrared (IR) spectroscopy which enables samples to be examined directly in the solid or liquid state. Fourier transform infrared (FTIR) spectroscopy is a measurement technique that allows to record IR spectra.

[0123] The surface of Plaque AP obtained after step (a) of Example 2 was analysed by ATR-FTIR, as follows.

[0124] A piece measuring 20mm x 30mm of the treated plaque was subjected to measurements performed with Ge crystal, with a resolution of  $2\text{cm}^{-1}$  and 256 scans.

[0125] The same analysis was performed on the surface of Plaque 1C, obtained following the procedure disclosed in Example 1 and having the same measures of Plaque AP.

[0126] The results were compared by performing spectral subtraction between the spectra obtained for Plaque AP and Plaque 1C, and weak positive bands were observed in the region at about  $3300\text{ cm}^{-1}$  and from  $1680\text{ cm}^{-1}$  to  $1500\text{ cm}^{-1}$ , which were compatible with the presence of chemical groups containing nitrogen atoms like amide, urethanes and ureas.

[0127] The comparison of the peaks in the functional region of ATR-FTIR spectra is showed in Table 2.

Table 2

Plaque	Positive peak at $3300\text{ cm}^{-1}$	Positive peaks between $1680\text{ cm}^{-1}$ and $1500\text{ cm}^{-1}$
1C(*)	-	-
AP	Compatible with N containing groups	Compatible with N containing groups
(*) comparison		

[0128] The above results showed that atmospheric plasma treatment modified the surface of the elastomer plaque, by introducing nitrogen-containing groups.

#### Example 5b - Surface analysis by X-Ray (XPS)

[0129] X-ray Photoelectron Spectroscopy (XPS) is a surface analysis, which provides quantitative and chemical state information from the surface of the material being studied. The average depth of analysis was approximately 5 nm, so that it was possible to obtain the actual composition of the sample surface.

[0130] The surface of Plaque 2 obtained after step (b) of Example 2 was analysed by XPS.

[0131] The same analysis was performed on the surface of Plaque 1C, obtained following the procedure disclosed in

Example 1.

**[0132]** The comparison between Nitrogen, Palladium and Copper concentration observed on Plaque 1C and Plaque 2 is showed in Table 3.

**Table 3**

Plaque	Atomic concentration (%)		
	N	Pd	Cu
1C(*)	0%	0%	0%
2	1.32%	0.46%	4.77%
(*) comparison			

**[0133]** The above results showed that Plaque 2, which is an examples of the multilayer article according to the present invention, contains the nitrogen-containing groups, as well as palladium and copper atoms.

#### Example 6 - Evaluation of adhesion of the metallic layer

**[0134]** The adhesion of the metallic layer was evaluated on the following plaques:

- Plaque 2 obtained according to the procedure described in Example 2,
- Plaque 3C obtained according to the procedure described in Comparative Example 3 and
- Plaque 4C obtained according to the procedure described in Comparative Example 4.

**[0135]** The adhesion was evaluated as follows: using a cutting tool, two series of perpendicular cuts were performed on the metallic layer of Plaque 2, Plaque 3C and Plaque 4C, in order to create a lattice pattern on them. A piece of tape was then applied and smoothened over the lattice and removed with an angle of 180° with respect to the metallic layer.

**[0136]** The adhesion of metallic layer was then assessed for Plaque 2, Plaque 3C and Plaque 4C by comparing the lattice of cuts with the ASTM D3359 standard procedure. The classification of test results ranged from 5B to 0B, whose descriptions are depicted in Table 4 herein below.

**Table 4**

ASTM D3359 Classification	Description
<b>5B</b>	The edges of the cuts are completely smooth; none of the squares of the lattice is detached.
<b>4B</b>	Detachment of flakes of the coating at the intersections of the cuts. A cross cut area not significantly greater than 5% is affected.
<b>3B</b>	The coating has flaked along the edges and/or at the intersection of the cuts. A cross cut area significantly greater than 5%, but not significantly greater than 15% is affected.
<b>2B</b>	The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross cut area significantly greater than 15%, but not significantly greater than 65%, is affected.
<b>1B</b>	The coating has flaked along the edges of the cuts in large ribbons and/or some squares have
	detached partly or wholly. A cross cut area significantly greater than 35%, but not significantly greater than 65%, is affected.
<b>0B</b>	Any degree of flaking that cannot be classified even by classification 1B.

**[0137]** The adhesion value obtained for the plaques was as follows:

- Plaque 2 = 5B;
- Plaque 3C = 1B;
- Plaque 4C = 1B

[0138] The above results demonstrated the excellent adhesion achieved in the elastomer article according to the present invention.

#### Example 7 - Evaluation of mechanical properties

[0139] The mechanical properties of Plaque 2 obtained according to the procedure described in Example 2 and Plaque 1C obtained according to the procedure described in Example 1 were evaluated with tensile tests following the DIN 53504 S2 standard procedure.

[0140] The measured mechanical properties are showed in Table 5.

Table 5

	Plaque 1C(*)	Plaque 2
Stress at 20% of strain [MPa]	4.6	4.9
Stress at 50% of strain [MPa]	7.7	8.0
Stress at 100% of strain [MPa]	14.7	14.9
Stress at break [MPa]	20.5	22.1
Strain at break [%]	137	140
(*) comparison		

[0141] By visual assessment made during and after the test, it was verified that the metal layer remained completely adherent to the surface of Plaque 2 and that it followed the elongation of the same.

[0142] The above results demonstrated that the mechanical properties of Plaque 1C(\*) comprising the pristine elastomer were not altered by the procedure described in Example 2 and that an excellent adhesion was achieved in multi-layered elastomer article according to the present invention.

#### Claims

1. A multi-layered article made of an elastomeric composition (C) comprising at least one elastomer, said article having at least one surface (S) comprising:

- nitrogen-containing groups (N) and
- at least one layer (L1) adhered to said surface (S) comprising at least one metal compound (M) selected from the group consisting of: Cu, Ni, Pd, Co, Zn, Ag, Au, Pt, Sn;

wherein said elastomer comprises recurring units derived from at least one (per)fluorinated monomer, **characterized in that** said nitrogen-containing groups (N) are grafted onto said surface (S) via an atmospheric plasma process performed in the presence of a nitrogen-containing gas, which is a mixture of N<sub>2</sub> and H<sub>2</sub>.

2. The multi-layered article according to claim 1, wherein said at least one (per)fluorinated monomer is selected from the group comprising:

- C<sub>3</sub>-C<sub>8</sub> perfluoroolefins;
- C<sub>2</sub>-C<sub>8</sub> hydrogenated fluoroolefins;
- chloro- and/or bromo- and/or iodo-C<sub>2</sub>-C<sub>6</sub> fluoroolefins;
- CH<sub>2</sub>=CH-R<sub>f0</sub> wherein R<sub>f0</sub> is a C<sub>1</sub>-C<sub>6</sub> (per)fluoroalkyl or a C<sub>1</sub>-C<sub>6</sub> (per)fluorooxyalkyl having one or more ether groups;
- CH<sub>2</sub>=CFOR<sub>f1</sub>, wherein R<sub>f1</sub> is a C<sub>1</sub>-C<sub>6</sub> fluoro- or perfluoroalkyl group;
- CF<sub>2</sub>=CFOR<sub>f2</sub>, wherein R<sub>f2</sub> is a C<sub>1</sub>-C<sub>6</sub> fluoro- or perfluoroalkyl group; or a C<sub>1</sub>-C<sub>12</sub> oxyalkyl or a C<sub>1</sub>-C<sub>12</sub> (per)fluorooxyalkyl group comprising one or more ether groups; or a group of formula -CF<sub>2</sub>OR<sub>f3</sub> in which R<sub>f3</sub> is a C<sub>1</sub>-C<sub>6</sub> fluoro- or perfluoroalkyl or a C<sub>1</sub>-C<sub>6</sub> (per)fluorooxyalkyl group comprising one or more ether groups;
- CF<sub>2</sub>=CFOR<sub>f4</sub>, wherein R<sub>f4</sub> is a C<sub>1</sub>-C<sub>12</sub> alkyl or (per)fluoroalkyl group; a C<sub>1</sub>-C<sub>12</sub> oxyalkyl; or a C<sub>1</sub>-C<sub>12</sub> (per)fluorooxyalkyl; said R<sub>f4</sub> comprising a carboxylic or sulfonic acid group, in its acid, acid halide or salt form;
- fluorodioxoles; and

- fluorosilanes.

3. A method for manufacturing a multi-layered article, said method comprising the steps of:

- (i) providing an article made of an elastomeric composition (C) comprising at least one elastomer, wherein said elastomer comprises recurring units derived from at least one (per)fluorinated monomer, said article having at least one surface (S-1);
- (ii) forming nitrogen-containing groups (N) on said at least one surface (S-1) so as to provide an elastomer article having at least one nitrogen-containing surface (S-2), wherein said nitrogen-containing groups (N) are grafted onto said surface (S-2) via an atmospheric plasma process performed in the presence of a nitrogen-containing gas, which is a mixture of N<sub>2</sub> and H<sub>2</sub>;
- (iii) contacting said at least one surface (S-2) with a first composition (C1) comprising at least one metallization catalyst, so as to provide an article having at least one surface (S-3) containing groups (N) and at least one metallization catalyst; and
- (iv) contacting said at least one surface (S-3) with a second composition (C2) containing at least one metal compound (M1), so as to provide a multi-layered article having at least one surface (S) comprising groups (N) and at least one layer (L1) adhered to said surface (S) comprising at least one metal compound (M) selected from the group consisting of: Cu, Ni, Pd, Co, Ag, Au, Pt, Sn and alloys thereof.

4. The method according to Claim 3, wherein said composition (C2) is an electroless metallization plating bath, comprising at least one compound (M1), at least one reducing agent, at least one liquid medium and, optionally, one or more additives.

5. The method according to any one of claims 3 to 4, wherein said steps (iii) and (iv) are performed as a single step (iii-D).

6. The method according to any one of claims 3 to 5, wherein said method comprises after step (iv), step (v) of applying a third composition (C3) containing at least one metal compound (M2) onto said surface (S).

7. The method according to claim 6, wherein said composition (C3) comprises at least one compound (M2), at least one metal halide and, optionally, at least one ionic liquid.

## Patentansprüche

1. Mehrschichtiger Gegenstand aus einer Elastomerzusammensetzung (C), die wenigstens ein Elastomer umfasst, wobei der Gegenstand wenigstens eine Oberfläche (S) aufweist, die umfasst:

- stickstoffhaltige Gruppen (N) und
- wenigstens eine Schicht (L1), die an der Oberfläche (S) haftet, umfassend wenigstens eine Metallverbindung (M) ausgewählt aus der Gruppe bestehend aus: Cu, Ni, Pd, Co, Zn, Ag, Au, Pt, Sn;

wobei das Elastomer Wiederholungseinheiten umfasst, die von wenigstens einem (per)fluorierten Monomer abgeleitet sind,

**dadurch gekennzeichnet, dass** die stickstoffhaltigen Gruppen (N) durch ein atmosphärisches Plasmaverfahren, das in Gegenwart eines stickstoffhaltigen Gases, das ein Gemisch von N<sub>2</sub> und H<sub>2</sub> ist, durchgeführt wird, auf die Oberfläche (S) gepfropft sind.

2. Mehrschichtiger Gegenstand gemäß Anspruch 1, wobei das wenigstens eine (per)fluorierte Monomer ausgewählt ist aus der Gruppe umfassend:

- C<sub>3</sub>-C<sub>8</sub>-Perfluorolefine;
- hydrierte C<sub>2</sub>-C<sub>8</sub>-Fluorolefine;
- Chlor- und/oder Brom- und/oder Iod-C<sub>2</sub>-C<sub>6</sub>-fluorolefine;
- CH<sub>2</sub>=CH-R<sub>f0</sub>, wobei R<sub>f0</sub> ein C<sub>1</sub>-C<sub>6</sub>- (Per) fluoralkyl oder ein C<sub>1</sub>-C<sub>6</sub>- (Per) fluoroxyalkyl mit einer oder mehreren Ethergruppen ist;
- CH<sub>2</sub>=CFOR<sub>f1</sub>, wobei R<sub>f1</sub> eine C<sub>1</sub>-C<sub>6</sub>-Fluor- oder -Perfluoralkylgruppe ist;
- CH<sub>2</sub>=CFOR<sub>f2</sub>, wobei R<sub>f2</sub> eine C<sub>1</sub>-C<sub>6</sub>-Fluor- oder -Perfluoralkylgruppe; oder eine C<sub>1</sub>-C<sub>12</sub>-Oxyalkyl- oder eine C<sub>1</sub>-C<sub>12</sub>-(Per)fluoroxyalkylgruppe, die eine oder mehrere Ethergruppen umfasst; oder eine Gruppe der Formel

- CF<sub>2</sub>OR<sub>f3</sub> ist, wobei R<sub>f3</sub> eine C<sub>1</sub>-C<sub>6</sub>-Fluor- oder -Perfluoralkyl- oder eine C<sub>1</sub>-C<sub>6</sub>-(Per)fluoroxyalkylgruppe ist, die eine oder mehrere Ethergruppen umfasst;
- CF<sub>2</sub>=CFOR<sub>f4</sub>, wobei R<sub>f4</sub> eine C<sub>1</sub>-C<sub>12</sub>-Alkyl- oder - (Per) fluoralkylgruppe; ein C<sub>1</sub>-C<sub>12</sub>-Oxyalkyl; oder ein C<sub>1</sub>-C<sub>12</sub>-(Per) fluoroxyalkyl ist; wobei das R<sub>f4</sub> eine Carbon- oder Sulfonsäuregruppe in ihrer Säure-, Säurehalogenid- oder Salzform umfasst;
- Fluordioxole; und
- Fluorsilane.

### 3. Verfahren zur Herstellung eines mehrschichtigen Gegenstands, wobei das Verfahren die Schritte umfasst:

- (i) Bereitstellen eines Gegenstands aus einer Elastomerzusammensetzung (C), die wenigstens ein Elastomer umfasst, wobei das Elastomer Wiederholungseinheiten umfasst, die von wenigstens einem (per)fluorierten Monomer abgeleitet sind, wobei der Gegenstand wenigstens eine Oberfläche (S-1) aufweist;
- (ii) Bilden von stickstoffhaltigen Gruppen (N) auf der wenigstens einen Oberfläche (S-1), um einen Elastomergegenstand bereitzustellen, der wenigstens eine stickstoffhaltige Oberfläche (S-2) aufweist, wobei die stickstoffhaltigen Gruppen (N) durch ein atmosphärisches Plasmaverfahren, das in Gegenwart eines stickstoffhaltigen Gases, das ein Gemisch von N<sub>2</sub> und H<sub>2</sub> ist, durchgeführt wird, auf die Oberfläche (S-2) gepfropft sind;
- (iii) Inkontaktbringen der wenigstens einen Oberfläche (S-2) mit einer ersten Zusammensetzung (C1), die wenigstens einen Metallisierungskatalysator umfasst, um einen Gegenstand bereitzustellen, der wenigstens eine Oberfläche (S-3) aufweist, die Gruppen (N) und wenigstens einen Metallisierungskatalysator enthält; und
- (iv) Inkontaktbringen der wenigstens einen Oberfläche (S-3) mit einer zweiten Zusammensetzung (C2), die wenigstens eine Metallverbindung (M1) enthält, um einen mehrschichtigen Gegenstand bereitzustellen, der wenigstens eine Oberfläche (S), die Gruppen (N) umfasst, und wenigstens eine Schicht (L1), die an der Oberfläche (S) haftet und wenigstens eine Metallverbindung (M) ausgewählt aus der Gruppe bestehend aus: Cu, Ni, Pd, Co, Ag, Au, Pt, Sn und Legierungen davon umfasst, aufweist.

### 4. Verfahren gemäß Anspruch 3, wobei die Zusammensetzung (C2) ein Stromlose-Metallisierung-Plattierungsbad ist, das wenigstens eine Verbindung (M1), wenigstens ein Reduktionsmittel, wenigstens ein flüssiges Medium und gegebenenfalls einen oder mehrere Zusatzstoffe umfasst.

### 5. Verfahren gemäß einem der Ansprüche 3 bis 4, wobei die Schritte (iii) und (iv) als Einzelschritt (iii-D) durchgeführt werden.

### 6. Verfahren gemäß einem der Ansprüche 3 bis 5, wobei das Verfahren nach Schritt (iv) Schritt (v) des Aufbringens einer dritten Zusammensetzung (C3), die wenigstens eine Metallverbindung (M2) enthält, auf die Oberfläche (S) umfasst.

### 7. Verfahren gemäß Anspruch 6, wobei die Zusammensetzung (C3) wenigstens eine Verbindung (M2), wenigstens ein Metallhalogenid und gegebenenfalls wenigstens eine ionische Flüssigkeit umfasst.

## Revendications

### 1. Article multicouche fait d'une composition élastomérique (C) comprenant au moins un élastomère, ledit article possédant au moins une surface (S) comprenant :

- des groupes (N) contenant de l'azote et
- au moins une couche (L1) collée à ladite surface (S) comprenant au moins un composé métallique (M) choisi dans le groupe constitué par : Cu, Ni, Pd, Co, Zn, Ag, Au, Pt, Sn ;

ledit élastomère comprenant des motifs répétitifs issus d'au moins un monomère (per)fluoré, **caractérisé en ce que** lesdits groupes (N) contenant de l'azote sont greffés sur ladite surface (S) via un procédé au plasma atmosphérique réalisé en la présence d'un gaz contenant de l'azote, qui est un mélange de N<sub>2</sub> et H<sub>2</sub>.

### 2. Article multicouche selon la revendication 1, ledit au moins un monomère (per)fluoré étant choisi dans le groupe comprenant :

- des C<sub>3-8</sub>-perfluorooléfines ;

- des C<sub>2-8</sub>-fluorooléfines hydrogénées ;
- des chloro-C<sub>2-6</sub>-fluorooléfines et/ou des bromo-C<sub>2-6</sub>-fluorooléfines et/ou des iodo-C<sub>2-6</sub>-fluorooléfines ;
- CH<sub>2</sub>=CH-R<sub>f0</sub>, R<sub>f0</sub> étant un C<sub>1-6</sub>- (per) fluoroalkyle ou un C<sub>1-6</sub>- (per) fluorooxyalkyle possédant un ou plusieurs groupes éther ;
- CH<sub>2</sub>=CFOR<sub>f1</sub>, R<sub>f1</sub> étant un groupe C<sub>1-6</sub>-fluoroalkyle ou C<sub>1-6</sub>-perfluoroalkyle ;
- CF<sub>2</sub>=CFOR<sub>f2</sub>, R<sub>f2</sub> étant un groupe C<sub>1-6</sub>-fluoroalkyle ou C<sub>1-6</sub>-perfluoroalkyle ; ou un C<sub>1-12</sub>-oxyalkyle ou un groupe C<sub>1-12</sub>-(per) fluorooxyalkyle comprenant un ou plusieurs groupes éther ; ou un groupe de formule -CF<sub>2</sub>OR<sub>f3</sub> dans lequel R<sub>f3</sub> est un C<sub>1-6</sub>-fluoroalkyle ou C<sub>1-6</sub>-perfluoroalkyle ou un groupe C<sub>1-6</sub>- (per) fluorooxyalkyle comprenant un ou plusieurs groupes éther ;
- CF<sub>2</sub>=CFOR<sub>f4</sub>, R<sub>f4</sub> étant un groupe C<sub>1-12</sub>-alkyle ou C<sub>1-12</sub>-(per)fluoroalkyle ; un C<sub>1-12</sub>-oxyalkyle ; ou un C<sub>1-12</sub>-(per)fluorooxyalkyle ; ledit R<sub>f4</sub> comprenant un groupe acide carboxylique ou acide sulfonique, sous sa forme d'acide, d'halogénure d'acide ou de sel ;
- des fluorodioxoles ; et
- des fluorosilanes.

**3.** Procédé pour la fabrication d'un article multicouche, ledit procédé comprenant les étapes de :

- (i) mise à disposition d'un article fait d'une composition élastomérique (C) comprenant au moins un élastomère, ledit élastomère comprenant des motifs répétitifs issus d'au moins un monomère (per)fluoré, ledit article possédant au moins une surface (S-1) ;
- (ii) formation de groupes (N) contenant de l'azote sur ladite au moins une surface (S-1) afin d'obtenir un article d'élastomère possédant au moins une surface contenant de l'azote (S-2), lesdits groupes (N) contenant de l'azote étant greffés sur ladite surface (S-2) via un procédé au plasma atmosphérique réalisé en la présence d'un gaz contenant de l'azote, qui est un mélange de N<sub>2</sub> et H<sub>2</sub> ;
- (iii) mise en contact de ladite au moins une surface (S-2) avec une première composition (C1) comprenant au moins un catalyseur de métallisation, afin d'obtenir un article possédant au moins une surface (S-3) contenant des groupes (N) et au moins un catalyseur de métallisation ; et
- (iv) mise en contact de ladite au moins une surface (S-3) avec une deuxième composition (C2) contenant au moins un composé métallique (M1), afin d'obtenir un article multicouche possédant au moins une surface (S) comprenant des groupes (N) et au moins une couche (L1) collée à ladite surface (S) comprenant au moins un composé métallique (M) choisi dans le groupe constitué par : Cu, Ni, Pd, Co, Ag, Au, Pt, Sn et des alliages correspondants.

**4.** Procédé selon la revendication 3, ladite composition (C2) étant un bain de placage de métallisation autocatalytique, comprenant au moins un composé (M1), au moins un agent de réduction, au moins un milieu liquide et, éventuellement, un ou plusieurs additifs.

**5.** Procédé selon l'une quelconque des revendications 3 et 4, lesdites étapes (iii) et (iv) étant réalisées en une unique étape (iii-D).

**6.** Procédé selon l'une quelconque des revendications 3 à 5, ledit procédé comprenant après l'étape (iv), l'étape (v) d'application d'une troisième composition (C3) contenant au moins un composé métallique (M2) sur ladite surface (S).

**7.** Procédé selon la revendication 6, ladite composition (C3) comprenant au moins un composé (M2), au moins un halogénure métallique et, éventuellement, au moins un liquide ionique.

**REFERENCES CITED IN THE DESCRIPTION**

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