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(54) **SOL-GEL FORMULATIONS ENHANCING CORROSION RESISTANCE AND LUBRICATION PROPERTIES OF PRESSURE EQUIPMENT.**

(57) Abstract: The present invention discloses a compression fitting with double ferrule (Figure 1) whose nut (1) is coated with coatings providing corrosion resistance and lubrication properties. Those particular properties are provided by a sol-gel formulation comprising at least one titanium derivative, a first silicon-based derivative, an organic-based derivative. Said formulation further comprises a second and a third silicon-based derivative which are different from said first silicon-based derivative. Fig. 1

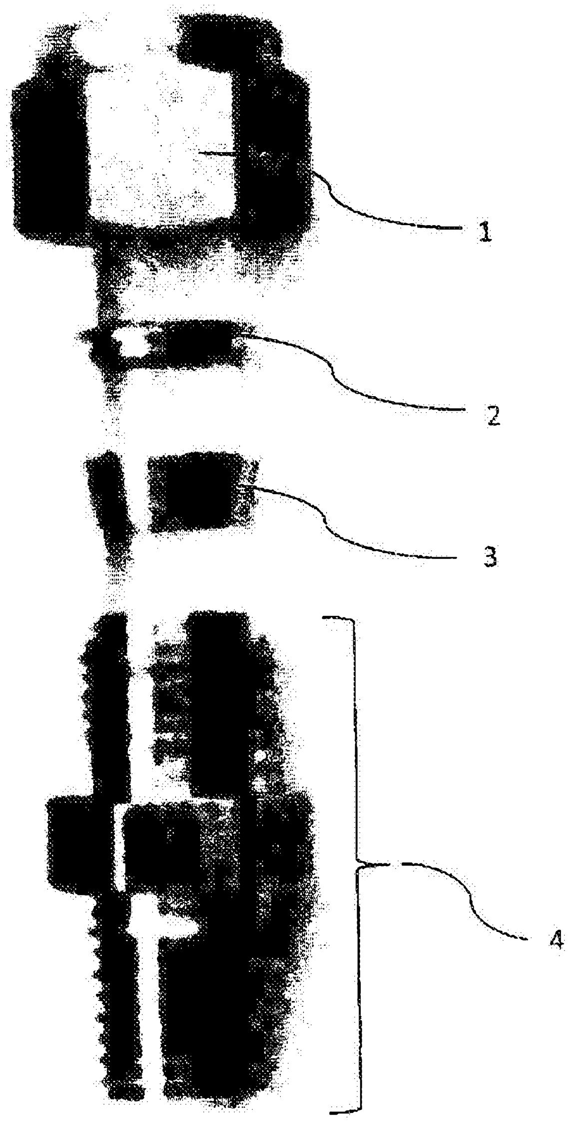

Fig. 1

Sol-gel formulations enhancing corrosion resistance and lubrication properties of pressure equipment

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[0001] Technical field

[0002] The invention is directed to formulations for coatings for pressure equipment and transportable pressure equipment. More particularly, those coatings are based on sol-gel formulations and are adapted for improving corrosion resistance and lubrication properties.

[0003] Background art

[0004] US patent application published US 2013/0071626 A1 relates to a coating which provides corrosion resistance, wear resistance, and, optionally, lubrication, for deposition on a threaded article. The coating comprises a polymer matrix, such as a polyimide, which is modified with small amounts of fluorine containing polymer modifier, as well as other compounds, such as glycidoxypropyltriethoxy silane (GPTES). Nanoparticles of titanium dioxide (TiO_2) may be employed to incorporate reinforcements into the polymer matrix. The coating can further comprise a solid lubricant or an anticorrosion compound, such as molybdenum disulfide (MoS_2), which is dispersed within the polymer matrix. The coatings may be deposited according to techniques generally understood in the art, like atomization or spray coating and dip coating.

[0005] US patent application published US 2013/0167965 A1 relates to coating which alter the surface properties relevant to fluid flow, such that the overall energy loss in fluid transport system can be minimized. The coatings comprise an intermediate layer, which is a lubricant layer with anticorrosion properties comprising any of ceramic materials, in particular titanium dioxide (TiO_2). The coatings further comprise a surface layer, which is composed of lubricant particles in solid, gel, or liquid form which subsequently cures or which creates coating and/or cures upon heating. The lubricant materials are resistant to degradation and are oleophobic with stable ratings at, or greater than, 300°C. This lubricant material may be applied in the form of sol-gel mixture, comprising at least one silane and/or alkoxysilane, and at least one fluoroalkylsilane and/or fluoroalkoxysilane, in a solvent including but not limited to alcohol, such as ethanol, water, acid and mixtures thereof. The lubricant particles might also be molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2). The lubricant material is deposited through a gaseous process, for example chemical vapor deposition (CVD), plasma enhanced chemical vapor deposition (PECVD), or any other vapor based deposition process known in the art. 92802

[0006] International patent application published WO 2007/003828 A2 relates to a sol-gel formulation comprising at least one organometallic compound, a first organosilane compound, at least one compound selected among acids, bases, glycols and ethoxyethanol and demineralized or distilled water to make up 100%. Additional compounds might be added, such as talc, micas, surfactants, kaolin, a second organosilane compound or a fluorosilane.

[0007] Summary of the invention

[0008] The invention has for technical problem to provide a sol-gel formulation adapted for coatings with an enhanced corrosion resistance showing therefore enhanced autolubrification properties as well as improved anticorrosion properties.

[0009] It is one object of the present invention to disclose a sol-gel formulation, adapted for coatings, with corrosion resistance and lubrication properties. Said sol-gel formulation comprises at least one titanium derivative, a first silicon-based derivative, and an organic-based derivative. Said sol-gel formulation further comprises a second silicon-based derivative which is different from said first silicon-based derivative. Said sol-gel formulation is remarkable in that it further comprises a third silicon-based derivative which is different from said first and second silicon-based derivatives.

[0010] More particularly, one or any combination of the following is true: said one titanium derivative is titanium isopropoxide; said first silicon-based derivative is 3-(trimethoxysilyl)propyl methacrylate; said organic-based derivative is methyl methacrylate; said second silicon-based derivative is an orthosilicate derivative; and said third silicon-based derivative is a dipodal silane. 92802

[0011] In one embodiment, the molar concentration of titanium isopropoxide is comprised between 0.20M and 0.80M, preferentially between 0.30M and 0.70M, more preferentially between 0.40M and 0.60M and even more preferentially between 0.45M and 0.55M. Preferably, the molar concentration of titanium isopropoxide is 0.50M.

[0012] In one embodiment, the molar concentration of 3-(trimethoxysilyl)propyl methacrylate is comprised between 0.10M and 1.20M, preferentially either between 0.10M and 0.50M or between 0.80M and 1.20M, more preferentially either between 0.20M and 0.40M or between 0.90M and 1.10M, even more preferentially either between 0.25M and 0.35M or between 0.95M and 1.05M. Preferably, the molar concentration of 3-(trimethoxysilyl)propyl methacrylate is 1.00M.

[0013] In one embodiment, the molar concentration of methyl methacrylate is comprised between 0.01M and 1.20M, preferentially either between 0.01M and 0.19M or between 0.80M and 1.20M, more preferentially either between 0.05M and 0.15M or between 0.90M and 1.10M, even more preferentially either between 0.07M and 0.13M or between 0.95M and 1.05M. Preferably, the molar concentration of methyl methacrylate is 1.00M.

[0014] In one embodiment, the molar concentration of the orthosilicate derivative is comprised between 0.20M and 0.55M, preferentially either between 0.22M and 0.28M or between 0.27M and 0.33M or between 0.45M and 0.55M, more preferentially either between 0.23M and 0.27M or between 0.28M and 0.32M or between 0.48M and 0.52M, even more preferentially either between 0.24M and 0.26M or between 0.29M and 0.31M or between 0.49M and 0.51M. Preferably, the molar concentration of the orthosilicate derivative is 0.25M.

[0015] In one embodiment, said orthosilicate derivative is tetraethyl orthosilicate or tetramethyl orthosilicate, preferentially tetramethyl orthosilicate.

[0016] In one embodiment, the molar concentration of the dipodal silane is comprised between 0.10M and 0.60M, preferentially either between 0.10M and 0.30M or between 0.40M and 0.60M, more preferentially either between 0.15M and 0.28M or between 0.45M and 0.55M. Preferably, the molar concentration of the dipodal silane is 0.25M.

[0017] In one embodiment, said dipodal silane is 1,2-bis(triethoxysilyl)ethane.

[0018] In one embodiment, the sol-gel formulation further comprises a corrosion inhibitor, preferentially 2-mercaptobenzothiazole. The concentration of 2-mercaptobenzothiazole is comprised between 0.1 $mg.ml^{-1}$ and 0.3 $mg.ml^{-1}$, preferentially between 0.15 $mg.ml^{-1}$ and 0.25 $mg.ml^{-1}$. Preferably, the concentration of 2-mercaptobenzothiazole is 0.2 $mg.ml^{-1}$.

[0019] In one embodiment, said corrosion inhibitor is comprised in an organic vesicle, preferentially made of polyethyleneimine. The concentration of polyethyleneimine is comprised between 0.5 $mg.ml^{-1}$ and 1.5 $mg.ml^{-1}$. Preferably, the concentration of polyethyleneimine is 1 $mg.ml^{-1}$.

[0020] In one embodiment, the sol-gel formulation further comprises a solid lubricant, preferentially tungsten disulfide. The weight concentration of the solid lubricant is comprised between 0.05% and 0.15%. Preferably, the weight concentration of the solid lubricant is 0.1%.

[0021] In one embodiment, the sol-gel formulation further comprises an hydrophobic silane. Said hydrophobic silane is chosen among a fluorosilane, said fluorosilane being preferentially perfluoroalkylsulfonyl ketone silane. The weight concentration of said hydrophobic silane is comprised between 0.5% and 1.5%. Preferably, the weight concentration of said hydrophobic silane is 1%.

[0022] In one embodiment, the sol-gel formulation further comprises a fourth silicon-based derivative, which is different from said first, said second and said third silicon-based derivatives. Said fourth silicon-based derivative is 3-(glycidoxypropyl)methyldiethoxysilane. The molar concentration of 3-(glycidoxypropyl)methyldiethoxysilane is comprised between 0.40M and 1.00M, preferentially between 0.50M and 0.90M, more preferentially between 0.60M and 0.80M, even more preferentially between 0.65M and 0.75M. Preferably, the molar concentration of 3-(glycidoxypropyl)methyldiethoxysilane is 0.70M.

[0023] In one embodiment, the sol-gel formulation further comprises diethylenetriamine, at a concentration comprised between 3 $mg.ml^{-1}$ and 7 $mg.ml^{-1}$, preferentially at a concentration comprised between 4 $mg.ml^{-1}$ and 6 $mg.ml^{-1}$. Preferably, the concentration of diethylenetriamine is 5 $mg.ml^{-1}$.

[0024] In one embodiment, the sol-gel formulation further comprises a surfactant, preferentially montmorillonite. The weight concentration of the surfactant is comprised between 0.05% and 0.15%. Preferably, the weight concentration of the surfactant is 0.1%. 92802

[0025] In one embodiment, the sol-gel formulation is further adapted to coat an alloy. Said alloy is chosen from the group consisting of ferrous alloys, steel alloys, stainless steel alloys, 316L stainless steel alloys, nickel alloys, copper alloys, brass alloys, bronze alloys or aluminium alloys, preferentially 316L stainless steel alloys, brass alloys or aluminium alloys, more preferentially 316L stainless steel alloys. Said alloy forms a compression fitting with double ferrule.

[0026] It is another object of the present invention to disclose a process of coating an alloy with a sol-gel formulation with corrosion resistance and lubrication properties. Said process comprises the step of deposition of a sol-gel formulation onto an alloy, and the step of polymerization of said sol-gel formulation onto said alloy. Said process is remarkable in that said sol-gel formulation is in accordance with the first object of the present invention.

[0027] In one embodiment, the step of deposition of the sol-gel formulation is a step of dip-coating or a step of atomization onto said alloys.

[0028] In one embodiment, the sol-gel formulation is dissolved into ethanol. The concentration of ethanol is comprised between 5M and 45M, preferentially either between 5M and 15M or between 25M and 45M, more preferentially either between 8M and 12M or between 30M and 40M. Preferably, the concentration of ethanol is 35 M.

[0029] In one embodiment, the step of polymerization is performed by ultraviolet reticulation or by thermal curing, preferentially by ultraviolet reticulation. Said ultraviolet reticulation is performed during ten minutes with an ultraviolet light power of 50 W/m^2 or 250 W/m^2, preferentially with an ultraviolet light power of 250 W/m^2.

[0030] In one embodiment, the alloy is chosen from the group consisting of ferrous alloys, steel alloys, stainless steel alloys, 316L stainless steel alloys, nickel alloys, copper alloys, brass alloys, bronze alloys or aluminium alloys, preferentially 316L stainless steel alloys, brass alloys or aluminium alloys, more preferentially 316L stainless steel alloys. 92802

[0031] In one embodiment, the alloy consists of a compression fitting with double ferrule, said compression fitting with double ferrule comprising a nut (1), a back ferrule (2), a front ferrule (3) and a threaded body (4).

[0032] All features of the above described aspects of the invention may be combined or replaced with one another.

[0033] Brief description of the drawings

[0034] In the following, we briefly describe the figures according to the embodiments of the present invention. Further details are given in the detailed description of the embodiments. The figures have the purpose of illustrating the invention and should not be understood in a limiting sense.

[0035] Figure 1 A compression fitting with double ferrule.

[0036] Figure 2 Tafel Curves on flat surfaces of 316L stainless steel alloy coated with the sol-gel formulation of the invention.

[0037] Figure 3 Corrosion potential curves in function of time of 316L stainless steel alloy coated with the sol-gel formulation of the invention.

[0038] Figures 4-9 Bode plots for flat surfaces of 316L stainless steel alloy coated with the sol-gel formulation of the invention through UV reticulation. The number of the figures corresponds respectively to the samples disclosed in table I.

[0039] Figure 10 Bode plot for a flat surface of 316L stainless steel alloy coated with the sol-gel formulation of the invention through thermal curing.

[0040] Detailed description of the embodiments

[0041] The following description is merely exemplary in nature and is in no way intended to limit the present teachings, application, or uses.

[0042] Pressure equipment and/or transportable pressure equipment, such as, for example, the compression fitting with double ferrule depicted in Figure 1, needs to show corrosion resistance and lubrication properties. 92802

[0043] Figure 1 describes the compression fitting with double ferrule. It comprises a nut (1), a back ferrule (2), a front ferrule (3) and a threaded body (4). A pipe (not shown) might be connected to the threaded body (4) which is itself connected to a source of fluid. The fluid might be a liquid or a gas. The back ferrule (2) and the front ferrule (3) ensure a correct sealing (without any leaks) with the pipe. The nut (1) is used for tightening the pipe to the threaded body (4). Those four elements, but more particularly the nut (1) of the compression fitting need to demonstrate corrosion resistance for durability as well as lubrication properties for adequate connection of the different elements between each other.

[0044] The compression fitting with double ferrule of figure 1 and its elements are usually made of alloys. Those alloys are usually chosen from the group consisting of ferrous alloys, steel alloys, stainless steel alloys, 316L stainless steel alloys, nickel alloys, copper alloys, brass (Cu/Zn) alloys, bronze (Cu/Sn) alloys and/or aluminium alloys.

[0045] The above mentioned alloys need to be coated by a coating for enhancing the corrosion resistance and the lubrication properties of these materials. This can be done by applying several techniques which are generally understood in the art. The coatings which are chosen are coatings formed by a sol-gel formulation.

[0046] In the present invention, the coatings are deposited on the nut (1) of the compression fitting with double ferrule either by dip-coating, either by atomization or spray-coating. Alternatively, the coatings of the present invention can be deposited on flat surfaces.

[0047] <u>Components of the sol-gel formulation</u>

[0048] The sol-gel formulation for the coating comprises one titanium derivative, which confers to the formulation anticorrosion properties as well as lubricant properties. This titanium derivative, for example, titanium isopropoxide, is incorporated into a network formed of different silicon-based derivatives and one organic-based derivative. 92802

[0049] A first silicon-based derivative is 3-(trimethoxysilyl)propyl methacrylate (TMSM).

[0050] The organic-based derivative of the sol-gel formulation comprises methyl methacrylate (MMA).

[0051] A second silicon-based derivative is an orthosilicate derivative. This orthosilicate derivative is chosen from tetramethyl orthosilicate (TMOS) or from tetraethyl orthosilicate (TEOS). Preferentially, TMOS is employed.

[0052] A third silicon-based derivative is a dipodal silane, namely 1,2-bis(triethoxysilyl)ethane. This dipodal silane strengthen the sol-gel formulation by preventing water diffusion into the formulation and therefore the swelling of the sol-gel formulation.

[0053] Optionally, the sol-gel formulation further comprises a corrosion inhibitor. This corrosion inhibitor is 2-mercaptobenzothiazole (MBT). Preferentially, this corrosion inhibitor is encapsulated into an organic vesicle, made of polyethyleneimine (PEI). The corrosion resistance and lubrication properties of the sol-gel formulation happen to be enhanced with these additional elements.

[0054] Optionally, a solid lubricant or an anticorrosion compound of the type of molybdenum disulphide (MoS_2) or tungsten disulfide (WS_2) is added to the sol-gel formulation. Preferentially, WS_2 is employed.

[0055] Optionally, an hydrophobic silane is added to the sol-gel formulation. The hydrophic silane is chosen among fluorosilane, preferentially perfluoroalkylsulfonyl ketone silane ($C_{17}H_{22}F_{17}O_5NSSi$), also known as FC-922. This component also provides lubricant properties to the sol-gel formulation.

[0056] Optionally, a fourth silicon-based derivative is 3-(glycidoxypropyl)methyl diethoxysilane (GPTMS). This component provides enhanced wettability properties and subsequently optimizes the deposition onto an alloy surface.

[0057] Optionally, a surfactant can be added. The surfactant is montmorillonite (MMT). This component provides enhanced wettability properties and subsequently optimizes the deposition onto an alloy surface. 92802

[0058] Coating of the sol-gel formulation on flat surfaces

[0059] The coating of the sol-gel formulation on flat surfaces is achieved by means of the spray-coating technique.

[0060] In this technique, an airbrush is used to pulverize the sol-gel formulation onto the flat, two-dimensional surfaces. The distance between the airbrush and the surface determines the thickness of the layer.

[0061] **Coating of the sol-gel formulation on non-flat surfaces**

[0062] The coating of the sol-gel formulation on non-flat surfaces is achieved by means of the dip-coating technique and/or the spray-coating technique.

[0063] In this technique, the geometry and the complexity of the non-flat, three-dimensional surfaces are important parameters that have to be considered when performing the coating.

[0064] Preparation of sol-gel formulation

[0065] The above components of the sol-gel formulation are mixed together in a solvent, for example ethanol (EtOH). The concentration of the solvent is 35 mol.l^{-1}(M). Once all the components are mixed together in the solvent, a thermal curing is performed. The thermal curing is performed during 1 hour at a temperature which is comprised between 20°C and 150°C, preferentially at 120°C. Alternatively, instead of the thermal curing previously described, a UV reticulation is performed. This UV reticulation is performed during 10 minutes.

[0066] The sol-gel formulation is prepared as following:

A solution of 3-(trimethoxysilyl)propyl methacrylate (1.00M), methyl methacrylate (1.00M) and titanium isopropoxide (0.50M) is achieved into ethanol (35M). Then tetramethyl orthosilicate (0.25M) and 1,2-bis(triethoxysilyl)ethane (0.25M) is added. Then, reticulation is achieved with UV light during 10 minutes.

Optionally, the organic vesicle made of polyethyleneimine (1 $mg.ml^{-1}$) encapsulating the corrosion inhibitor 2-mercaptobenzothiazole (0.2 $mg.ml^{-1}$) is added to the above formulation prior to UV reticulation. 92802

Optionally, the solid lubricant compound WS_2 is added at a weight concentration of 0.1%.

Optionally, the hydrophobic silane chosen among the fluorosilane FC-922, is added at a weight concentration of 0.1%.

Optionally, the surfactant montmorillonite is added at a weight concentration of 0.1%.

[0067] The transformation of a liquid sol-gel formulation to a 3D solid network can be achieved by supplying thermal energy or photon. This polymerization step can be carried out at 120 °C for 1 hour. This method, which gives good results towards the anticorrosion properties of the films (see figure 2, "thermal curing"), however, is tedious. In addition, it is necessary to have an oven for carrying out this step of the preparation of sol-gel films.

[0068] One has therefore envisioned a photo-polymerization, *i.e.* the use of UV light so that the mechanism of reticulation occurs. In this case, the photosensitive sol-gel formulations should contain a photoinitiator for absorbing UV light and converting the light energy in a chemical energy in the form of reactive intermediates such as free radicals, which will later initiate polymerization. The main photo-polymerization reactions fall into two main categories: the free radical reaction and cationic reaction. These two types of reaction take place in three stages: photoinitiating, propagation and termination. From reactive moieties typically used, acrylates react by radical polymerization, while the epoxy groups obey to a cationic polymerization. This photo-polymerization eliminates immovably material like an oven and enables the performing of the crosslinking step with simple systems such as a portable UV lamp.

[0069] In this study, the crosslinking reaction was performed by UV light with a power of 250 $W.m^{-2}$ on 316L stainless steel alloy samples. The power of the UV light can be adjusted, depending on the alloy to be coated. For example, if the crosslinking reaction has to be performed onto a brass alloy, the power of the UV light is of 50 $W.m^{-2}$. 92802

[0070] For comparison purposes, the polymerization reaction was also achieved on 316L stainless steel alloy samples with a pre-layer of titanium nitride (TiN) or which a pre-layer of nickel (Ni) which were deposited prior to any further deposition of the sol-gel formulation.

[0071] After some preliminary tests, the presence of a photoinitiator has been demonstrated to be non-essential, and the best results were therefore obtained without adding such components.

[0072] The sol-gel formulation comprising the following components was therefore prepared and cross-linked by photo-polymerization using UV light during 10 minutes. The step of photo-polymerization is carried out in a solvent, such as ethanol, at a concentration of 35M.

3-(trimethoxysilyl)propyl methacrylate (1.00M)
methyl methacrylate (1.00M)
titanium isopropoxide (0.50M)
tetramethyl orthosilicate (0.25M)
1,2-bis(triethoxysilyl)ethane (0.25M)
polyethyleneimine (1 $mg.ml^{-1}$)
2-mercaptobenzothiazole (0.2 $mg.ml^{-1}$)
WS_2 (0.1 % weight)
fluorosilane FC-922 (0.1 % weight)

This sol-gel formulation corresponds to the sol-gel formulation indicated at entry 3 of table V.

[0073] <u>Analyses of the coatings</u>

[0074] Once the flat or non-flat surfaces have been coated with the sol-gel formulation, different tests have been performed to determine the efficacy of the process and the effect on the corrosion resistance and lubrication properties.

[0075] Analyses of the flat surfaces by electrochemistry tests 92802

[0076] Three types of measures have been performed in electrochemistry for determining the corrosion resistance properties of the surfaces coated with the sol-gel formulation:

a) the determination of Tafel curves, which can characterize quantitatively the corrosion phenomenon;

b) the corrosion potential, which is a measure of the evolution of the potential of the sample in function of time; and

c) the determination of Bode plots, which is a measure of the variation of the electrochemical impedance in function of the variation of frequency to determine the system's frequency response.

To achieve those electrochemical measurements, the experiment is carried out in a three-electrode cell comprising a reference electrode, which is a saturated calomel electrode (SCE), and an auxiliary electrode, or counter-electrode, in platinum, which serves merely to carry the current flowing through the cell. The third electrode of the electrochemical cell is the working electrode, namely the sample to analyse.

[0077] Figure 2 details the Tafel curves obtained for flat surfaces on 316L stainless steel alloys coated with the above described sol-gel formulation. The numbers 1 to 6 on the figure correspond to the entries of Table I.

Table I: Indication of the results of thickness and the intensity of corrosion obtained by Tafel curves determinations of flat surface of 316L stainless steel alloy coated with the sol-gel formulation. 92802

	Pre-layer of TiN	Pre-layer of Ni	Thickness (μm)	Intensity of corrosion (10^{-8} A/cm²)
1	No	No	14	0.11
2	Yes	No	14	1.60
3	Yes	No	8	0.28
4	Yes	No	40	168.4
5	No	Yes	19	347.1
6	No	No	14	n.d.

n.d.: non-determined

Table I and figure 2 show that when UV reticulation was performed, excellent corrosion currents were obtained. These corrosion currents have the value of about 10^{-9} A/cm² for the samples 1 and 3.

The presence of a pre-layer of TiN does not improve the corrosion resistance properties for identical thickness (comparison between samples 1 and 2).

However, the presence of a pre-layer of TiN allows to obtain this optimal corrosion current (about 10^{-9} A/cm²) when the thickness of the layer is smaller (see sample 3).

When the thickness becomes larger, the anticorrosion properties become less interesting (see sample 4).

When nickel is used as a pre-layer, there is no benefit because the flat surfaces do not present good anticorrosion results (see sample 5).

[0078] Figure 2 also indicates the Tafel curves for a flat surface of 316L stainless steel alloy which was coated with the sol-gel formulation with thermal curing for 1 hour. In this case, it is clear that when thermal curing is processed, the anticorrosion properties are improved.

[0079] Figure 3 indicates the corrosion potential in function of time for a flat surface of 316L stainless steel alloy coated with the sol-gel formulation of the invention. More the corrosion potential is cathodic, better the anticorrosion properties are. 92802

Those results confirm the one obtained through the Tafel curves. The flat surface of 316L stainless steel alloy which was coated with the sol-gel formulation with thermal curing presents more important anticorrosion properties than the flat surfaces which were coated through UV reticulation. Indeed, the corrosion potential is -0.40 V, which is rather a cathodic value of the corrosion potential.

Moreover, when the thickness of the sample is large (case of sample 5), the corrosion potential is rather anodic (-0.33 V), which means that this sample demonstrated weak anticorrosion properties.

The cathodic corrosion potential of the samples 1, 2, 3, 4 and 6 (by referring to table I) is comprised between -0.355 V and -0.375 V.

[0080] Figures 4 to 9 show the Bode plots for the flat surfaces of 316L stainless steel alloy which were coated with the sol-gel formulation through UV reticulation. Figures 4 to 9 correspond respectively to samples 1 to 6 of the Table I.

Figure 10 shows the Bode plot for a flat surface of 316L stainless steel alloy which was coated with the sol-gel formulation through thermal curing.

Those Bode plots were determined after 24 hours of immersion of the sample into the electrochemical cell.

The global resistance of the system has been determined to be 10^{-3} Ω. Figure 9 representing the Bode plot of sample 6, namely the Bode plot of a flat surface of 316L stainless steel alloy coated with 14µm of the sol-gel formulation through UV reticulation during 10 minutes, shows a larger resistance than these 10^{-3} Ω.

[0081] <u>Analyses of the non-flat surfaces by pitting corrosion</u>

[0082] Pitting corrosion is a form of extremely localized corrosion that leads to the creation of small holes in the metal.

[0083] The elements of the compression fitting with double ferrule of figure 1 have been immersed into an aqueous solution of iron(III) chloride (100g of $FeCl_3$ in 900 mL of demineralized water) during 72 hours at room temperature. 92802

[0084] For comparison purposes, the elements of the compression fitting with double ferrule have been tested in pitting corrosion in a non-coated status and in with a silver layer. Those results are also compared with the standardized norms (Total Group).

[0085] Before evaluation of the weight loss, the elements were rinsed with ethanol and demineralized water.

Table II: Indication of the weight loss of the different elements, depending on the type of coating (pitting corrosion studies).

	Type of element	weight loss when non-coated (%)	weight loss when coated with silver (%)	weight loss when coated with sol-gel formulation (%)	standard (%)
1	nut (1)	1.08	2.01	1.16 ; 0.96	2-5
2	back ferrule (2)	0.01	0.16	0.72 ; 0.01	< 1
3	front ferrule (3)	2.29	3.98	5.58 ; 5.08	0.3-2.5
4	threaded body (4)	2.61	2.39	1.48 ; 1.54	0.7-2

The nut (1), the threaded body (4) and the back ferrule (2) shows results which are consistent with the norms imposed by the Total Group. However, the front ferrule does not fall into the standard imposed by the Total Group.

[0086] Analyses of the non-flat surfaces by crevice corrosion

[0087] Crevice corrosion refers to corrosion occurring in confined spaces to which the access of the working fluid from the environment is limited.

[0088] The working fluid is an aqueous solution of iron(III) chloride (100g of $FeCl_3$ in 900 mL of demineralized water). The test of crevice corrosion is performed during 72 hours at room temperature. 92802

[0089] In a first experiment, the elements of the compression fitting with double ferrule were screwed after deposition of the sol-gel formulation.

[0090] For comparison purposes, the elements of the compression fitting with double ferrule have been tested in crevice corrosion in a non-coated state and with a silver layer. Those results are also compared with the standardized norms (Total Group).

[0091] Before evaluation of the weight loss, the elements were rinsed with ethanol and demineralized water.

<u>Table III</u>: Indication of the weight loss of the different elements, depending on the type of coating (crevice corrosion studies, screwing after deposition).

	Type of element	Weight loss (%)				standard (%)
		uncoated	coating with silver layer	coating with sol-gel formulation		
				by thermal curing	by UV reticulation	
1	nut (1)	2.77	4.57	2.00	2.05	2-5
2	back ferrule (2)	n.d.	n.d.	n.d.	0.02	< 1
3	front ferrule (3)	n.d.	n.d.	n. d.	0.15	0.3-2.5
4	threaded body (4)	1.92	1.58	1.44	1.67	0.7-2
5	whole system	1.77	2.00	1.30	1.44	/

n.d.: non-determined

The nut (1), the threaded body (4) and the back ferrule (2) shows results which are consistent with the norms imposed by the Total Group. However, the front ferrule does not fall into the standard imposed by the Total Group.

It is interesting to note that when the non-flat surface is coated with silver, the corrosion phenomenon increases.

[0092] The whole system, *i.e.* the compression fitting with double ferrule, such as the 92802
one depicted on Figure 1, was then set up and the weight loss has been determined (see table III, entry 5).

[0093] It has been thus observed that, when the whole system has been coated with the sol-gel formulation of the present invention through UV reticulation during 10 minutes, the weight loss is the less important compared to the weight loss in case of the whole system without any coatings or with a silver layer. Therefore, it is clear that the whole system shows improved corrosion resistance when coated with the sol-gel formulation of the present invention.

[0094] In a second experiment, the elements of the compression fitting with double ferrule were screwed prior deposition of the sol-gel formulation.

[0095] For comparison purposes, the results are compared with the standardized norms (Total Group).

[0096] Before evaluation of the weight loss, the elements were rinsed with ethanol and demineralized water.

<u>Table IV</u>: Indication of the weight loss of the different elements when coated with the sol-gel formulation, (crevice corrosion studies, screwing prior deposition).

	Type of element	Weight loss (%)		standard (%)
		coating by thermal curing	coating by UV reticulation	
1	nut (1)	2.59	0.72	2-5
2	back ferrule (2)	n.d.	n.d.	< 1
3	front ferrule (3)	n.d.	n.d.	0.3-2.5
4	threaded body (4)	1.85	1.06	0.7-2
5	whole system	1.65	0.91	/

n.d.: non-determined

The nut (1) and the threaded body (4) of the compression fitting with double ferrule show anticorrosion properties in an accepted range, the range being the one imposed by the norms of Total Group.

[0097] The weight loss of the whole system, *i.e.* the compression fitting with double ferrule has been determined (see entry 5 of table IV). 92802

When the sol-gel formulation has been coated by UV reticulation during 10 minutes, the anticorrosion properties of the compression fitting with double ferrule are enhanced.

[0098] Other variants regarding the composition of the sol-gel formulation can be envisioned in the present invention (see table V).

Table V: Variants regarding the composition of the sol-gel formulation and the concentration of the components. All the values in the table are the molar concentration (M) except for DETA whose concentration is expressed in $mg.ml^{-1}$ and for WS_2 whose concentration is expressed in weight percentages. Ethanol is the solvent in which the sol-gel formulation is dissolved and in which the polymerization is performed.

	TMSM	MMA	TIP	Ethanol	TMOS	Dipodal	GPTMS	DETA	WS_2
1	1	1	0.5	35	0.5	/	/	5	/
2	1	1	0.5	35	0.5	/	/	5	0.1
3	1	1	0.5	35	0.25	0.25	/	/	0.1
4	1	1	0.5	35	0.25	0.5	/	/	0.1
5	0.3	0.1	0.7	10	0.3	/	0.7	5	0.1

TMSM: 3-(trimethoxysilyl)propyl methacrylate

MMA: methyl methacrylate

TIP: titanium isopropoxide

TMOS: tetramethyl orthosilicate

Dipodal: 1,2-bis(triethoxysilyl)ethane

GPTMS: 3-(glycidoxypropyl)methyldiethoxysilane

DETA: diethylenetriamine

The sol-gel formulations 1 to 5 further comprise polyethyleneimine (1 $mg.ml^{-1}$), 2-mercaptobenzothiazole (0.2 $mg.ml^{-1}$) and perfluoroalkylsulfonyl ketone silane (1% wt.).

[0099] The invention has been described with reference to best modes of carrying out the invention. Obviously, modifications and alterations will occur to others when reading and understanding this specification. It is intended to include all such modifications and alterations in so far as they come within the scope of the appended claims or the equivalents thereof. 92802

[00100] In any case the above described embodiments shall not be understood in a limiting sense. In particular, the features of the above embodiments may also be replaced or combined with one another.

1. Formulation sol-gel ayant des propriétés de résistance à la corrosion et de lubrification adaptée pour des revêtements, comprenant au moins
   a. un dérivé de titane,
   b. un premier dérivé à base de silicium,
   c. un dérivé de type organique, et
   d. un second dérivé à base de silicium qui est différent dudit premier dérivé à base de silicium,

   caractérisée en ce que ladite formulation comprend en outre
   e. un troisième dérivé à base de silicium, qui est différent desdits premier et second dérivés à base de silicium.

2. Formulation sol-gel selon la revendication 1, caractérisée en ce qu'un de ce qui suit ou une combinaison quelconque de ce qui suit est vrai:
   ledit dérivé de titane est l'isopropoxyde de titane,
   ledit premier dérivé à base de silicium est le méthacrylate du 3-triméthoxysilyle de propyle,
   ledit dérivé organique est le méthacrylate de méthyle,
   ledit second dérivé à base de silicium est un dérivé orthosilicate, et
   ledit troisième dérivé à base de silicium est un silane dipodal.

3. Formulation sol-gel selon la revendication 2, caractérisée en ce que la concentration molaire de l'isopropoxyde de titane est comprise entre 0,20 M et 0,80 M, de préférence entre 0,30 M et 0,70 M, plus préférentiellement entre 0,40 M et 0,60 M et encore plus préférentiellement entre 0,45 M et 0,55 M.

4. Formulation sol-gel selon la revendication 2, caractérisée en ce que la concentration molaire du méthacrylate du 3-triméthoxysilyle de propyle est comprise entre 0,10 M et 1,20 M, de préférence soit entre 0,10 M et 0,50 M ou entre 0,80 M et 1,20 M, plus préférentiellement soit entre 0,20 M et 0,40 M ou entre 0.90M et 1.10M, encore plus préférentiellement soit entre 0,25 M et 0,35 M ou entre 0,95 M et 1,05 M.

5. Formulation sol-gel selon la revendication 2, caractérisée en ce que la concentration molaire du méthacrylate de méthyle est comprise entre 0,01 M et 1,20 M, de préférence soit entre 0,01 M et 0,19 M ou entre 0,80 M et 1,20 M, et plus préférentiellement entre 0,05 M et 0,15 M ou entre 0.90 M et 1.10 M, encore plus préférentiellement soit entre 0,07 M et 0,13 M ou entre 0,95 M et 1,05 M.

6. Formulation sol-gel selon la revendication 2, caractérisée en ce que la concentration molaire du dérivé orthosilicate est comprise entre 0,20 M et 0,55 M, de préférence entre 0,22 M et 0,28 M ou entre 0,27 M et 0,33 M ou entre 0,45 M et 0,55 M, plus préférentiellement soit entre 0,23 M et 0,27 M ou entre 0,28 M et 0,32 M ou entre 0,48 M et 0.52 M, encore plus préférentiellement soit entre 0,24 M et 0,26 M ou entre 0,29 M et 0.31 M ou entre 0,49 M et 0,51 M.

7. Formulation sol-gel selon les revendications 2 ou 6, caractérisée en ce que ledit dérivé orthosilicate est l'orthosilicate de tétraéthyle ou l'orthosilicate de tétraméthyle, préférentiellement l'orthosilicate de tétraméthyle.

8. Formulation sol-gel selon la revendication 2, caractérisée en ce que la concentration molaire du silane dipodal est comprise entre 0,10 M et 0,60 M, de préférence soit entre 0,10 M et 0,30 M et 0,40 M ou entre 0,40 M et 0,60 M, plus préférentiellement encore entre soit 0,15 M et 0,28 M ou entre 0,45 M et 0,55 M.

9. Formulation sol-gel selon les revendications 2 ou 8, caractérisée en ce que ledit silane dipodal est le 1,2-bis-triéthoxysilyle éthane.

10. Formulation sol-gel selon l'une quelconque des revendications 1 à 9, caractérisée en ce que ladite formulation comprend en outre un inhibiteur de corrosion, de préférence le 2-mercaptobenzothiazole.

11. Formulation sol-gel selon la revendication 10, caractérisée en ce que la concentration du 2-mercaptobenzothiazole est comprise entre 0,1 $mg.ml^{-1}$ et 0,3 $mg.ml^{-1}$, préférentiellement entre 0,15 $mg.ml^{-1}$ et 0,25 $mg.ml^{-1}$.

12. Formulation sol-gel selon l'une quelconque des revendications 10 à 11, caractérisée en ce que ledit inhibiteur de corrosion est compris dans une vésicule organique, de préférence en polyéthylène-imine.

13. Formulation sol-gel selon la revendication 12, caractérisée en ce que la concentration de polyéthylène-imine est comprise entre 0,5 $mg.ml^{-1}$ et 1,5 $mg.ml^{-1}$.

14. Formulation sol-gel selon l'une quelconque des revendications 1 à 13, caractérisée en ce que ladite formulation comprend en outre un lubrifiant solide, de préférence le disulfure de tungstène.

15. Formulation sol-gel selon la revendication 14, caractérisée en ce que la concentration en poids de lubrifiant solide est comprise entre 0,05% et 0,15%.

16. Formulation sol-gel selon l'une quelconque des revendications 1 à 15, caractérisée en ce que ladite formulation comprend en outre un silane hydrophobe.

17. Formulation sol-gel selon la revendication 16, caractérisée en ce que ledit silane hydrophobe est choisi parmi un silane fluoré, ledit fluorosilane étant de préférence une cétone perfluoroalkylsulfonyle de silane.

18. Formulation sol-gel selon l'une quelconque des revendications 16 à 17, caractérisée en ce que la concentration en poids dudit silane hydrophobe est comprise entre 0,5% et 1,5%.

19. Formulation sol-gel selon l'une quelconque des revendications 1 à 18, caractérisée en ce que ladite formulation comprend en outre un quatrième dérivé à base de silicium, qui est différent desdits premier, second et troisième dérivés à base de silicium.

20. Formulation sol-gel selon la revendication 19, caractérisée en ce que ledit quatrième dérivé à base de silicium est le méthyle diéthoxysilane 3-glycidoxypropyle.

21. Formulation sol-gel selon la revendication 20, caractérisée en ce que la concentration molaire du méthyle diéthoxysilane 3-glycidoxypropyle est comprise entre 0,40 M et 1,00 M, de préférence entre 0,50 M et 0,90 M, plus préférentiellement entre 0,60 M et 0,80 M, encore plus préférentiellement entre 0,65 M et 0,75 M.

22. Formulation sol-gel selon l'une quelconque des revendications 1 à 21, caractérisée en ce que ladite formulation comprend en outre le diéthylène triamine, de préférence à une concentration comprise entre 3 $mg.ml^{-1}$ et 7 $mg.ml^{-1}$, plus préférentiellement à une concentration comprise entre 4 $mg.ml^{-1}$ et 6 $mg.ml^{-1}$.

23. Formulation sol-gel selon l'une quelconque des revendications 1 à 22, caractérisée en ce que ladite formulation comprend en outre un agent tensioactif, de préférence le montmorillonite.

24. Formulation sol-gel selon la revendication 23, caractérisée en ce que la concentration en poids de l'agent tensioactif est comprise entre 0,05% et 0,15%.

25. Formulation sol-gel selon l'une quelconque des revendications 1 à 24, caractérisée en ce que ladite formulation sol-gel est en outre adaptée pour revêtir un alliage.

26. Formulation sol-gel selon la revendication 25, caractérisée en ce que ledit alliage est choisi dans le groupe constitué des alliages ferreux, des alliages d'acier, des alliages d'acier inoxydable, des alliages d'acier inoxydable 316L, des alliages de nickel, des alliages de cuivre, des alliages de laiton, des alliages de bronze ou des alliages d'aluminium, de préférence des alliages d'acier inoxydable 316L, des alliages de laiton ou des alliages d'aluminium, plus préférentiellement des alliages d'acier inoxydable 316L.

27. Formulation sol-gel selon l'une quelconque des revendications 25 à 26, caractérisée en ce que ledit alliage forme un raccord à compression à double bague.

28. Procédé de revêtement d'un alliage avec une formulation sol-gel ayant des propriétés de résistance à la corrosion et de lubrification, ledit procédé comprenant les étapes suivantes
    a. déposition d'une formulation sol-gel sur ledit alliage, et
    b. polymérisation de ladite formulation sol-gel sur ledit alliage

    ledit procédé est caractérisé en outre en ce que ladite formulation sol-gel est conforme à l'une quelconque des revendications 1 à 27.

29. Procédé de revêtement d'un alliage, selon la revendication 28, caractérisé en ce que ladite étape de dépôt de ladite formulation sol-gel est une étape de trempage ou une étape de pulvérisation sur lesdits alliages. 92802

30. Procédé de revêtement d'un alliage selon l'une quelconque des revendications 28 à 29, caractérisé en ce que ladite formulation sol-gel est dissoute dans l'éthanol.

31. Procédé de revêtement d'un alliage, selon la revendication 30, caractérisé en ce que la concentration en éthanol est comprise entre 5 M et 45 M, de préférence soit entre 5 M et 15 M ou entre 25M et 45M, et plus préférentiellement entre soit 8M et 12M ou entre 30M et 40M.

32. Procédé de revêtement d'un alliage selon l'une quelconque des revendications 28 à 31, caractérisé en ce que ladite étape de polymérisation est effectuée par réticulation aux ultraviolets ou par durcissement thermique, de préférence par réticulation aux ultraviolets.

33. Procédé de revêtement d'un alliage, selon la revendication 32, caractérisé en ce que ladite réticulation aux ultraviolets est effectuée pendant dix minutes avec une lumière ultraviolette de puissance de 50 W/m^2 ou 250 W/m^2, de préférence avec lumière ultraviolette de puissance de 250 W/m^2.

34. Procédé de revêtement d'un alliage selon l'une quelconque des revendications 28 à 33, caractérisé en ce que ledit alliage est choisi dans le groupe constitué des alliages ferreux, des alliages d'acier, des alliages d'acier inoxydable, des alliages d'acier inoxydable 316L, des alliages de nickel, des alliages de cuivre, des alliages de laiton, des alliages de bronze ou des alliages d'aluminium, de préférence des alliages d'acier inoxydable 316L, des alliages de cuivre ou des alliages d'aluminium, plus préférentiellement des alliages d'acier inoxydable 316L.

35. Procédé de revêtement d'un alliage selon l'une quelconque des revendications 28 à 34, caractérisé en ce que ledit alliage est constitué d'un raccord à compression à double bague, ledit raccord à compression à double bague comprenant un écrou (1), une bague arrière (2), une bague avant (3) et un corps fileté (4).

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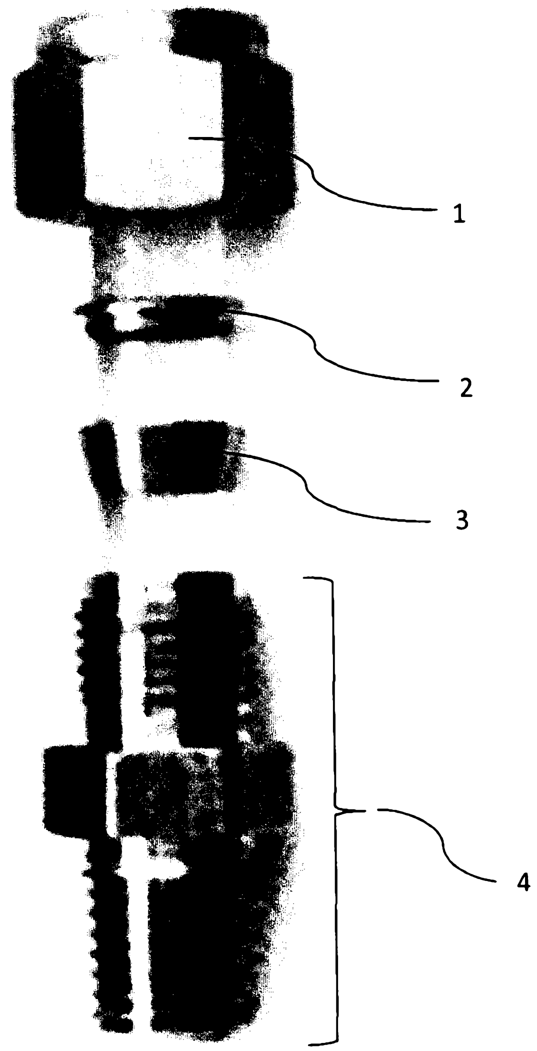
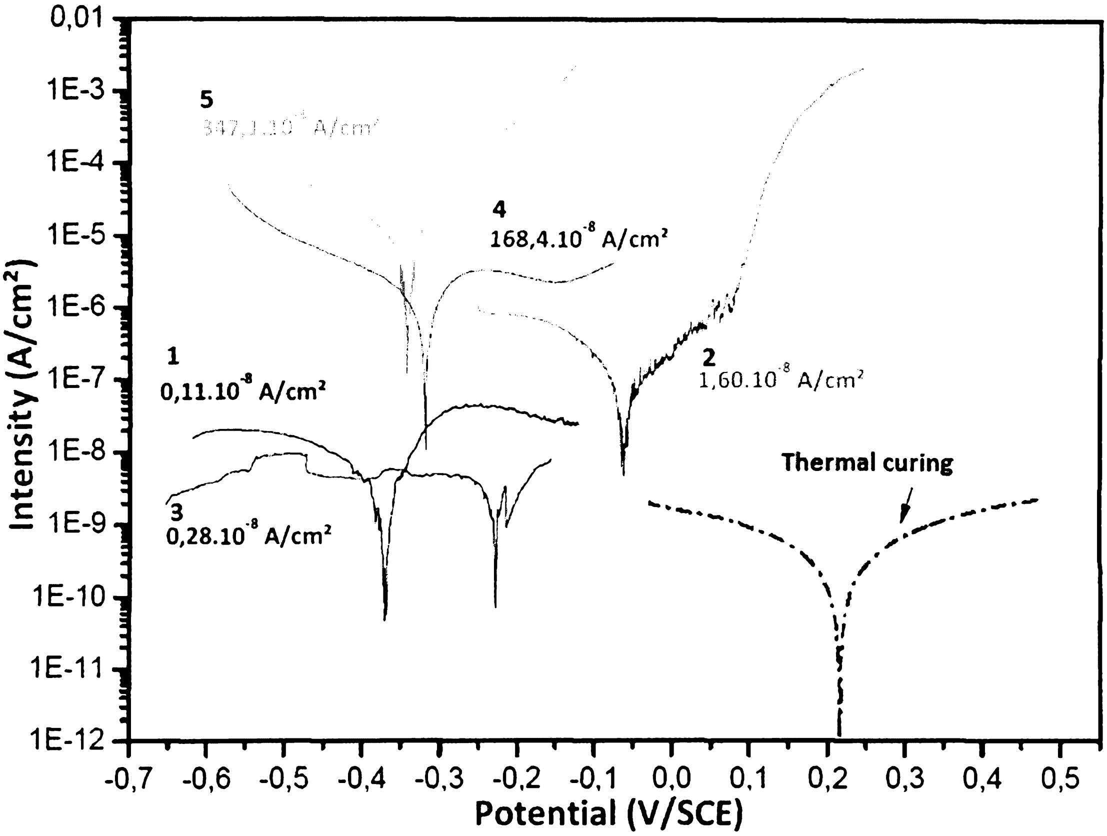
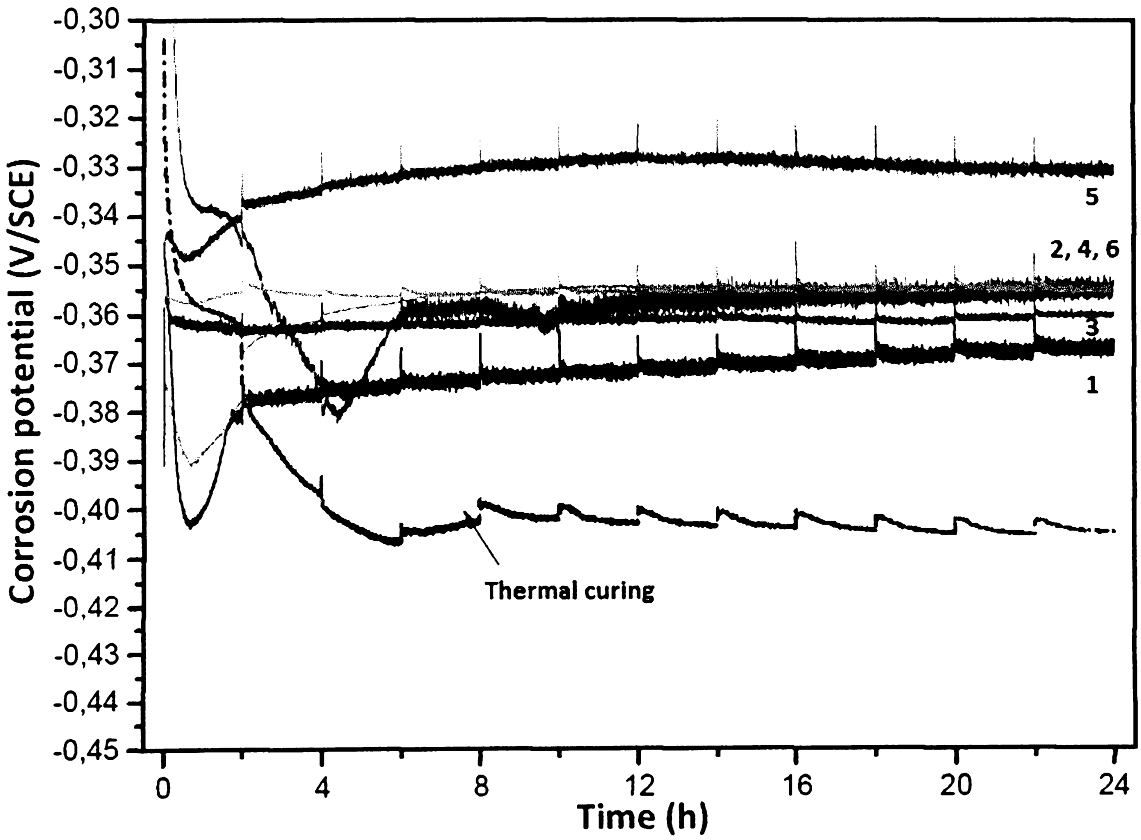


Fig. 1



0,01
1E-3
1E-4
1E-5
1E-6
1E-7
1E-8
1E-9
1E-10
1E-11
1E-12
Intensity (A/cm²)
-0,7 -0,6 -0,5 -0,4 -0,3 -0,2 -0,1 0,0 0,1 0,2 0,3 0,4 0,5
Potential (V/SCE)
5
4
168,4.10⁻⁸ A/cm²
1
0,11.10⁻⁸ A/cm²
2
1,60.10⁻⁸ A/cm²
3
0,28.10⁻⁸ A/cm²
Thermal curing

Fig. 2



-0,30
-0,31
-0,32
-0,33
-0,34
-0,35
-0,36
-0,37
-0,38
-0,39
-0,40
-0,41
-0,42
-0,43
-0,44
-0,45
Corrosion potential (V/SCE)
0 4 8 12 16 20 24
Time (h)
5
2, 4, 6
3
1
Thermal curing

Fig. 3

92802

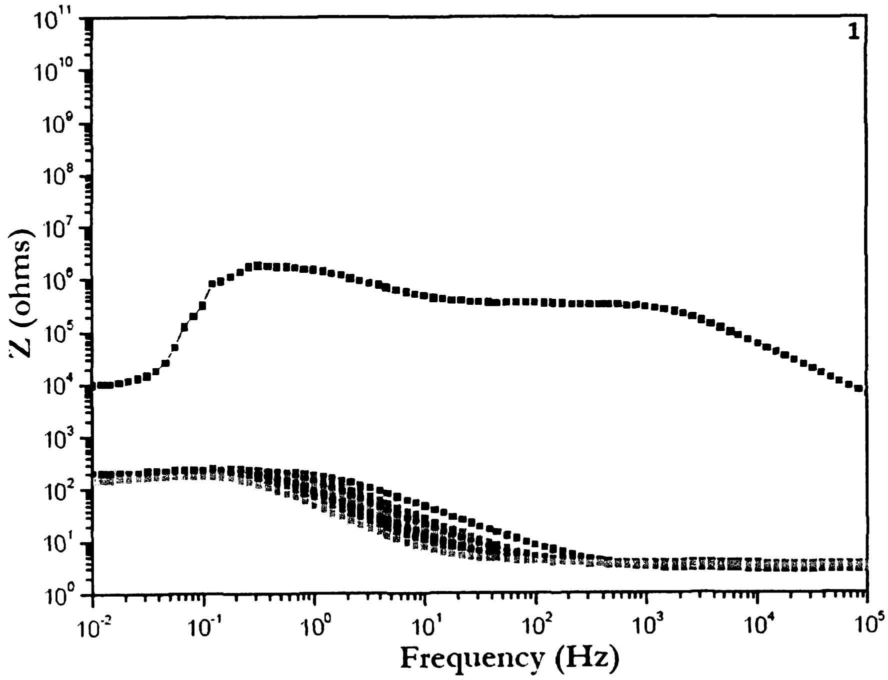


Fig. 4

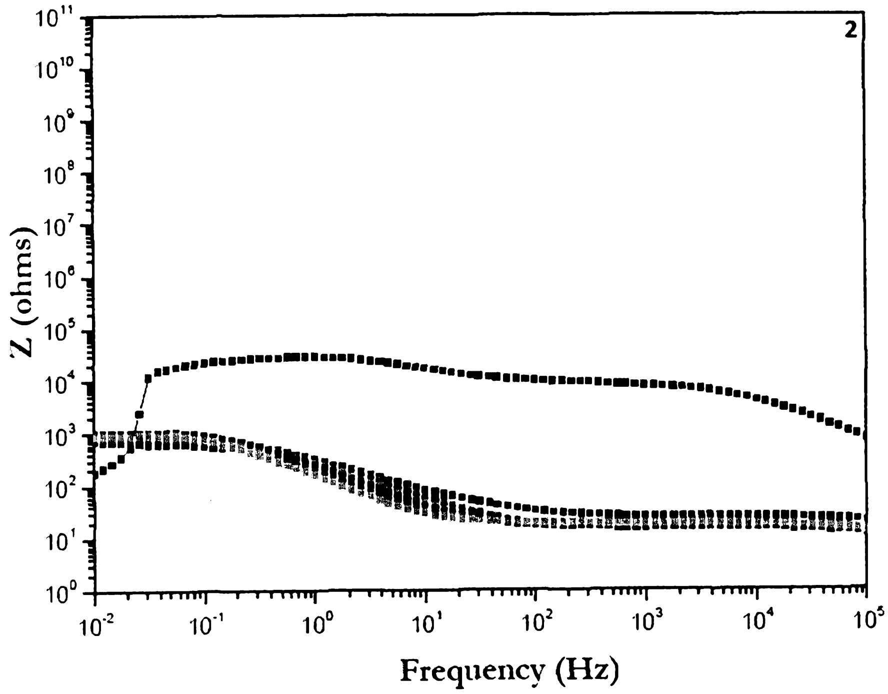


Fig. 5

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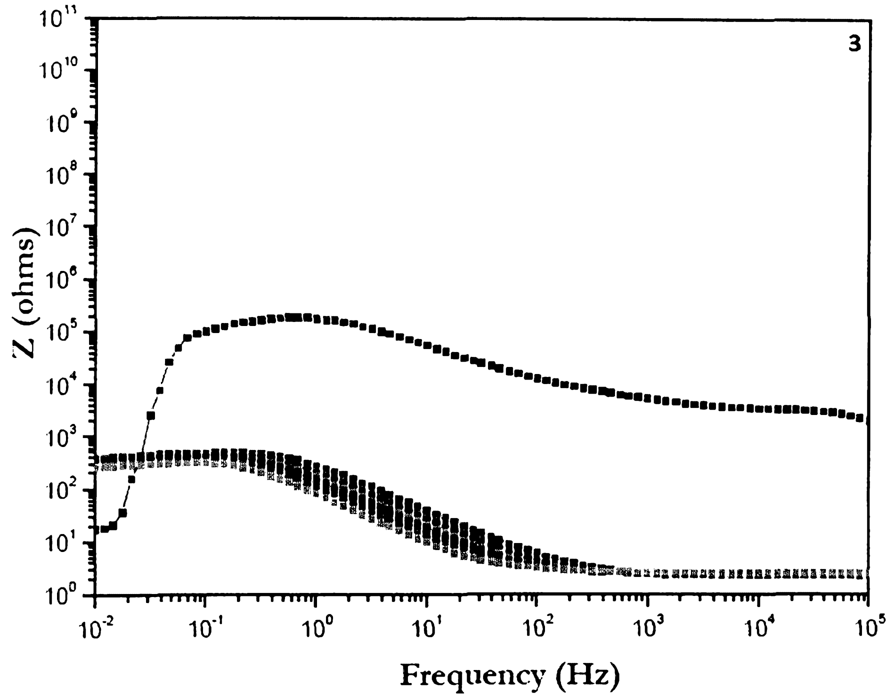

Fig. 6

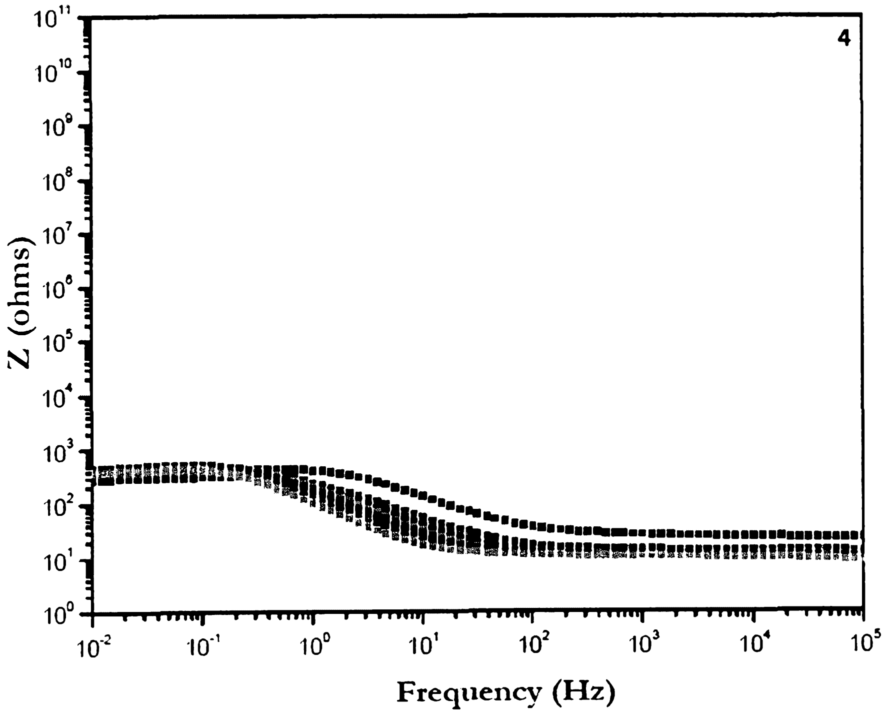

Fig. 7

92802

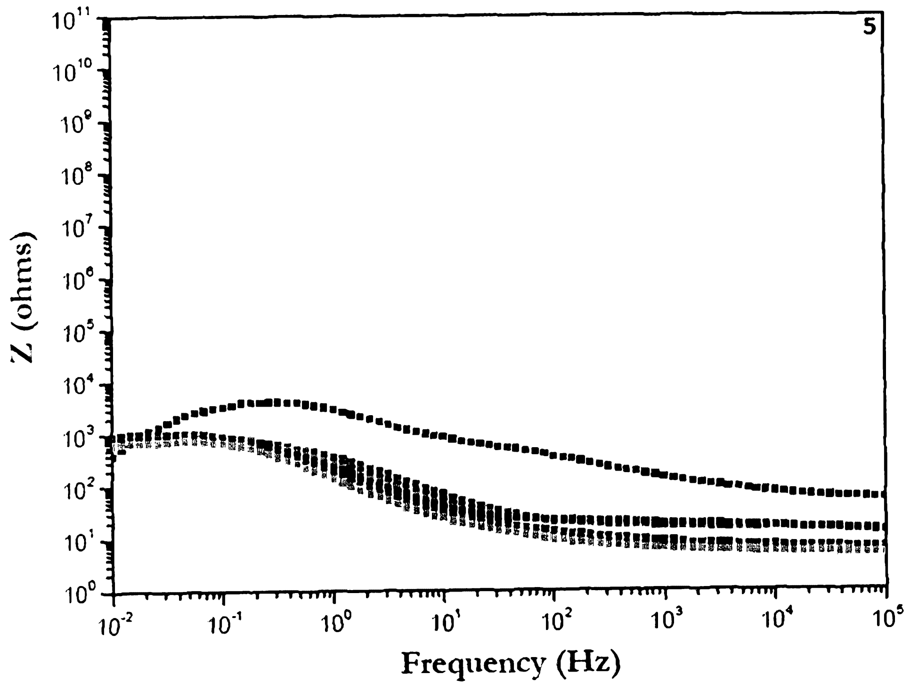

Fig. 8

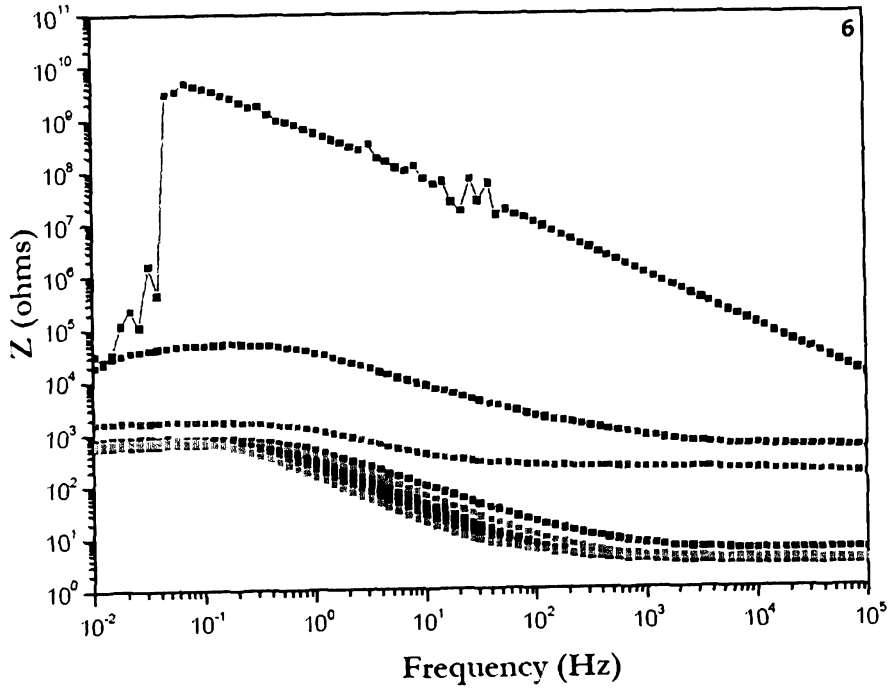

Fig. 9

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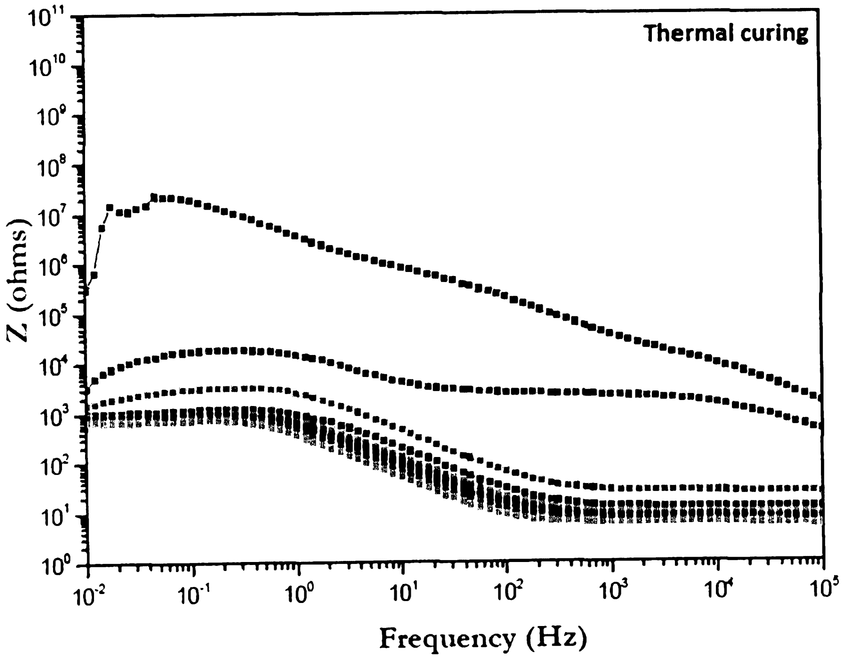
Thermal curing
Z (ohms)
Frequency (Hz)
10^11
10^10
10^9
10^8
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
10^-2
10^-1
10^0
10^1
10^2
10^3
10^4
10^5

Fig. 10

Abstract 92802

The present invention discloses a compression fitting with double ferrule (Figure 1) whose nut (1) is coated with coatings providing corrosion resistance and lubrication properties. Those particular properties are provided by a sol-gel formulation comprising at least one titanium derivative, a first silicon-based derivative, an organic-based derivative. Said formulation further comprises a second and a third silicon-based derivative which are different from said first silicon-based derivative.

Fig. 1

LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie
et du Commerce extérieur

National Application Number

LO 1185
LU 92802

SEARCH REPORT

in accordance with Article 35.1 a)
of the Luxembourg law on patents
dated 20 July 1992

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 0 620 255 A1 (LUCKY LTD [KR]) 19 October 1994 (1994-10-19) * claims 1-3,6,8 * * page 13 - page 14; examples 11-20 *	1,2	INV. C09D5/08 C09D5/02 C09D4/00 C09D133/12 C09D143/04 B01J13/14 C09D1/00
Y	US 2014/106155 A1 (IANDOLI ESPINOSA ANTONIO FRANCISCO [BR]) 17 April 2014 (2014-04-17) * claims 1,10,13,36 * * page 4, paragraph 40 - paragraph 42 * * page 10; example 10; table 11 *	1-35	
Y	DINESH BALGUDE ET AL: "Sol-gel derived hybrid coatings as an environment friendly surface treatment for corrosion protection of metals and their alloys", JOURNAL OF SOL-GEL SCIENCE AND TECHNOLOGY, KLUWER ACADEMIC PUBLISHERS, BO, vol. 64, no. 1, 14 July 2012 (2012-07-14), pages 124-134, XP035127802, ISSN: 1573-4846, DOI: 10.1007/S10971-012-2838-Z * page 130; table 2 * * the whole document *	1-35	**TECHNICAL FIELDS SEARCHED (IPC)** C09D B01J
A	US 5 316 855 A (WANG BING [US] ET AL) 31 May 1994 (1994-05-31) * claims 1-4 *	1-35	
A	EP 2 048 195 A1 (NOF CORP [JP]) 15 April 2009 (2009-04-15) * claims 1,10,14 *	1-35	

The present search report has been drawn up for all claims

	Date of completion of the search	Examiner
	6 May 2016	Mill, Sibel

CATEGORY OF CITED DOCUMENTS

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

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

& : member of the same patent family, corresponding document

ANNEX TO THE SEARCH REPORT
ON LUXEMBOURG PATENT APPLICATION NO.

LO 1185
LU 92802

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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06-05-2016

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie
et du Commerce extérieur

WRITTEN OPINION

File No.	Filing date *(day/month/year)*	Priority date *(day/month/year)*	Application No.
LO1185	19.08.2015		LU92802

International Patent Classification (IPC)
INV. C09D5/08 C09D5/02 C09D4/00 C09D133/12 C09D143/04 B01J13/14 C09D1/00

Applicant
LUXEMBOURG PATENT COMPANY S.A.

This report contains indications relating to the following items:

- ☒ Box No. I — Basis of the opinion
- ☐ Box No. II — Priority
- ☐ Box No. III — Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV — Lack of unity of invention
- ☒ Box No. V — Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI — Certain documents cited
- ☐ Box No. VII — Certain defects in the application
- ☐ Box No. VIII — Certain observations on the application

Examiner
Mill, Sibel

Form LU237A (Cover Sheet) (January 2007)

Application No.
LU92802

WRITTEN OPINION

Box No. I Basis of the opinion

1. This opinion has been established on the basis of the latest set of claims filed before the start of the search.
2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the application and necessary to the claimed invention, this opinion has been established on the basis of:

   a. type of material:

   ☐ a sequence listing

   ☐ table(s) related to the sequence listing

   b. format of material:

   ☐ on paper

   ☐ in electronic form

   c. time of filing/furnishing:

   ☐ contained in the application as filed.

   ☐ filed together with the application in electronic form.

   ☐ furnished subsequently.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

Box No. V Reasoned statement with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Yes:	Claims	3-35
	No:	Claims	1, 2
Inventive step	Yes:	Claims	
	No:	Claims	1-35
Industrial applicability	Yes:	Claims	1-35
	No:	Claims	

2. Citations and explanations

   see separate sheet

Reference is made to the following documents:

D1 EP 0 620 255 A1 (LUCKY LTD [KR]) 19 October 1994 (1994-10-19)

D2 US 2014/106155 A1 (IANDOLI ESPINOSA ANTONIO FRANCISCO [BR]) 17 April 2014 (2014-04-17)

D3 DINESH BALGUDE ET AL: "Sol-gel derived hybrid coatings as an environment friendly surface treatment for corrosion protection of metals and their alloys", JOURNAL OF SOL-GEL SCIENCE AND TECHNOLOGY, KLUWER ACADEMIC PUBLISHERS, BO, vol. 64, no. 1, 14 July 2012 (2012-07-14), pages 124-134, XP035127802, ISSN: 1573-4846, DOI: 10.1007/S10971-012-2838-Z

Item V

1. Novelty

D1 discloses in its examples 11-20 on pp. 13-14 sol-gel formulations comprising an organic compound (a copolymer) with three different silanes, which are silicon-based derivatives, see also table 1 on p.10 and l. 13-21 of p. 10. the catalyst can be a titanate derivative, se claim 6.

So D1 discloses all features of claims 1-2 of the present application.

So the subject-matter of claims 1-2 is not novel in light of D1.

2. Inventive step

3.1 D2 can be seen as closest prior art, since it discloses also anticorrosion coating compositions with sol-gel compositions comprising a silane, a titanate and a silicate. The difference to claim 3 lies in the absence of the third silicon derivative, which is absend in D2.

3.2 Starting from D2, the technical objective problem is to provide an alternative formulation for anticorrosive coatings.

Since D2 discloses different silanes in claims 13, 14 and allows the use of their mixtures, the person skilled in tha art would try out combinations of silanes and arrive at the subject matter of claim 3 of the present application, by combining the teaching within D2 alone.

3.3 Alternatively, starting from D2, the teaching of D3, which is a review disclosing different sol-gel compositions comprising different silanes and also titanates and organic components, see table 2, shows that several combinations of silanes lead successfully to organic-inorganic hybrid sol-gel formulations for corrosion protection.

3.4 At the moment, none of the technical features of the dependent claims seems to be linked with a technical and surprising effect. So an inventive step of the claims 4-35 cannot be acknowledged either.

4. Industrial application

The subject-matter of claims 1- 35 is industrially applicable.