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(54) METHOD FOR PRODUCING MULTIFUNCTIONAL PROTECTIVE FILM

(57) The present invention relates to technological methods for coating surfaces of a solid material (a solid body) and producing a multifunctional protective nano-sized film, in particular for modifying surfaces with the purpose of improving the properties thereof, and can be used in instrument engineering, electronics, mechanical engineering, a fuel and energy complex, housing and utilities, and other industries, for example, in microelectronics, when producing parts with pre-determined properties, and for AI systems. The method for producing a protective film on at least part of the surface of a solid body comprises a pre-treatment of the surface, the application of a composition formulation based on a fluorine-containing surfactant to the solid body surface which has been heated further following the pre-treatment and which has a roughness Ra from 0.001 μm to 2.5 μm, and curing the substance. The technical result that can be achieved by using the invention is an increase in the technological effectiveness of protective film production while extending the application scope.

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Description

FIELD OF THE INVENTION

[0001] This invention relates to technological methods that are used for coating surfaces of a solid material (a solid body), and producing a multi-functional nano-scale protective film, in particular, for modifying surfaces with the purpose of improving the properties thereof, and may be used in instrument engineering, electronics, mechanical engineering, a fuel and energy complex, housing and utilities, and other industry sectors, for example, in microelectronics, when manufacturing parts with pre-determined properties, and artificial intelligence systems.

BACKGROUND

[0002] In the background the RU patent No. 2095386 is known, published on 10.11.1997, IPC C09D5/18, that discloses a method for producing fire-protective coatings on various surfaces, which includes applying a composite compound and curing it. A composite compound used for coating comprises a polymeric binder, a fibrous filler, a powder filler, a fire retardant, sludge flotation and water. Disadvantages of the known method are its multi-stage processing, which does not ensure sufficient coating adhesion to a surface thus reducing wear resistance of produced coatings.

[0003] In the background the RU patent No. 2429284 is known, published on 27.08.2010, IPC C10M 147/04, that discloses a method for producing lubricant and inhibitory coatings, which includes surface degreasing, drying and subsequent spraying the composition from a distance of 0.1 to 0.5 m. After the composition spraying a lubricated surface is held at a temperature of +16 to +32°C until light fractions of a coolant fully evaporate. The method is intended for applying the compositions on metal surfaces in order to provide them with corrosion protection. By selecting a composition volume and amount of time for the final readiness of the lubricated surface a monomolecular film, 1.0 to 7.0 nm in thickness, is formed on the prepared surface.

[0004] In the background the RU patent No. 2269557 is known, published on 20.02.2005, IPC C09D127/1, for the invention "Operational deposit inhibitory coating and method for producing it". The patent discloses a method for producing inhibitory coatings on metal surfaces. A surface to be coated is thoroughly cleaned, in particular, it is decontaminated with acetone or white spirit by 3-4 times immersing a plate into a solvent bath, whereupon the product is kept in air for 5-10 minutes to remove solvent vapours. The plate is preheated prior to spray coating. The heating temperature depends on the thickness of a metal product wall, and exceeds the operating temperature of the coating. After reaching a required temperature the product is kept in the furnace for 30 minutes. 3-layer inhibitory polymer coatings are produced by spraying in an electrostatic field. After melting the last layer the plate coated with the polymer is held in the process vessel for 5-6 hours at a temperature of 220-230°C. The thickness of the produced coating is 210-240 μm. A 3-4 layered coating is used as the inhibitory coating. This coating is made of powdered dried to a moisture content of max. 3 wt% polytetrafluoroethylene or polytrifluorochloroethylene stabilized in acetylene by wetting the polymer powder with a solution of Diafen NN stabilizer. The solution is produced by dissolving Diafen NN stabilizer in acetone being heated to 40°C. Then the polymer-stabilizer mixture is dried at ambient temperature, finally it is dried at 80-100°C for 5 hours, torrefied at 210°C for 1 hour, and held at a temperature of 220-230°C for 5-6 hours.

[0005] A disadvantage of the known method is its low processability due to the complicated multi-stage treatment of a surface. Besides, the inhibitory composition being used does not contain a liquid substance, which considerably limits the applicability of the known method.

[0006] The RU patent No. 2139902 (prototype) is known, publ. on 20.10.1999, IPC C09D127/12, that discloses "Method for producing anti-friction polymer coating" (Author(s): Gurinovich E.G., et al.), describing a method for producing the anti-friction polymer coating [3], which includes surface cleaning with an agent for degreasing, drying the treated surface at 20-200°C, applying an anti-friction composition epilame - 0.1-10.0% solution of an organofluoric surfactant (fluorine surfactant) - perfluoropolyoxyalkylene or perfluorinated polyalkylene oxide compound by immersing a product into the solution or by aerosol spraying and heat treatment of the coating. A disadvantage of the given method is that in applying a freon-containing ozone-destroying composition (use of ozone-depleting freons is prohibited under the Montreal Agreement) by immersing or spraying (including aerosol spraying) without heating a treated surface it is impossible to succeed in production of a coating which would be uniform and equal in thickness and performance properties. The method is not applicable with respect to safety requirements for processing the large-size and heavy products with a hight degree of surface roughness without using the special-purpose facilities.

[0007] Besides, a disadvantage of the comparable methods listed above is the impossibility to apply coatings on surfaces in hardly accessible places of an object to be coated.

BRIEF DESCRIPTION

[0008] The object of the invention is intended to achieve is to create a new technological method for producing a multi-functional protective nano-film (coating) for many fields of application.

[0009] The technical result to be achieved by using the invention is both to improve the processability in producing a protective film, and to extend the field of application.

[0010] The object of the invention and the required technical result are achieved by means of the method for producing a protective film at least on a portion of the surface of a solid body, including preliminary preparation of the surface, application of a composite compound based on a surfactant and heat-setting of the agent. According to the invention a composite compound is applied on the prepared and afterwards additionally heated surface of a solid body with roughness (Ra) of 0.001 to 2.5 μm.

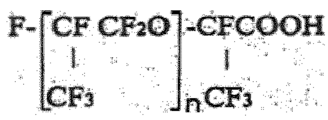
[0011] Additional aspect characterizing the invention is that the surface heating is performed within the temperature range of 28 to 48°C.

[0012] In one more aspect the invention is characterized in that the application a composite compound is performed so as to produce a 3-10 nm, preferably 1-8 nm thick protective film, and with the arithmetic average surface roughness within 2.4 to 3.7 nm, preferably within 1.6 to 2.3 nm.

[0013] Another aspect, in which the invention is also characterized, is that a composite compound is applied on a surface by immersing, spraying, spreading, aerosol spraying, active or passive swabbing, and the spraying is performed manually or in automated facilities.

[0014] One more aspect, in which the invention is characterized, is that the composite compound used is a solution of fluorine-containing surfactant, additionally including at least one modifying additive.

[0015] A further aspect, in which the invention is also characterized, is that the fluorine-containing surfactant used is a polymer of the perfluoropolyether group with a molecular weight of more than 2000, and the following general structural formula



where, n - total number of the element within the range of 1-13, inclusively.

or

$$X_1\text{-}[CF_2O]_n\text{-}[C_2F_4O]_m\text{-}[C_3F_6O]_l\text{-}X_2$$

where, n + m + l = 5÷50, but each of X_1 and X_2 is independently selected from the group: CF_3, $-C_2F_5$ or $-C_3F_7$.

[0016] In one more aspect the invention is characterized by using the solution comprising a fluorine-containing surfactant in amount of 0.2 to 18.5 wt%, wherein the surfactant used is freon, alcohol, Khladis, water or any possible combination of them, and a corrosion inhibitor, an anti-friction additive, a bactericidal additive or any possible combination of them is used as the modifying additive.

[0017] In another aspect, the invention is also characterized by the heat setting performed within the temperature range of 67 to 114°C during 45 to 117 minutes.

[0018] A further aspect, in which the invention is also characterized, is that after the application of a composite compound additionally drying in open air is preformed within the temperature range of 22 to 39°C during 3 to 5 minutes.

[0019] A significant difference of the claimed invention is a one-stage process of laying a protective film on a heated surface of a solid body with roughness (Ra) of 0.001 to 2.5 μm, during which each molecule of the film independently interacts with the surface thus producing a chemisorbed multi-functional nano-film. The proposed method makes it possible to produce a higher level of monomolecularity and continuity of the coating. A multi-functional nano-scale film produced by the proposed method reduces coefficient of friction and decreases abrasion of surfaces in assemblies of tribological systems, provides corrosion protection, reduces the effects of salt spray, vapour, radiation, and eliminates activity of micro-organisms. Separation of the coating from a surface, if it happens, also proceeds molecule-by-molecule thus precluding the presence of large-sized non-soluble agglomerates in oil. The proposed method, providing a new physically and chemically based interaction between composite compounds and surfaces, makes it possible to apply the indicated compound on metal, non-metallic and polymer surfaces, including current conducting and dielectric, in hardly accessible locations, for example, into interior portions of an electronic instrument, a microchip, a printed circuit with components installed, and thus as a whole to achieve the claimed technical result that is both to improve the processability in producing a protective film, and to extend the field of application.

LIST OF DRAWINGS

[0020]

Fig. 1a shows a protective film surface profile diagram.

Fig. 1b shows a protective film molecular density profile diagram.

Fig. 2 shows a model of chemisorption of a fluorine-containing surfactant after the application of a composite compound.

Fig. 3 shows composite compound consumption rates required for coating a surface to produce a multi-functional protective nano-film.

DETAIL DESCRIPTION

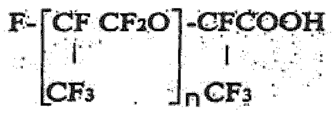
[0021] Surfaces used for application of a composite compound (composition) are surfaces of solid bodies with roughness of Ra of 0.001 to 2.5 μm, which may be, for example, metal, alloys, glass, plastic products, rubber products, fiberglass plastics, printed circuits, etc.

[0022] Surface of a solid body is thoroughly degreased with modern fluorine- or alcohol-containing solvents using ultrasonic equipment or special degreasing chambers. Cleaning and degreasing allow to open surface micropores for bringing into the active state of information and molecular absorption and activation of the surface modification.

[0023] Prior to the actual application of a composite compound, a clean and degreased surface is heated within the temperature range of 37 to 48°C. It is important to emphasize that surface heating to a temperature below 37°C does not result in surface micropores opening for adsorption of composite compound molecules, while surface heating to a temperature above 48°C does not ensures formation of a uniform sorption layer.

[0024] The composite compound used is a solution of a fluorine-containing surfactant, further comprising at least one modifying additive, for example, a corrosion inhibitor, an anti-friction additive, a bactericidal additive and other components. In a particular embodiment of the invention, the choice of additives is specified by a specific field of application of the proposed method, and any possible combination of modifying additives may be used.

[0025] The fluorine-containing surfactant used is a polymer of the perfluoropolyether group with a molecular weight of more than 2000, and the following general structural formula



where, n - total number of the element within the range of 1-13, inclusively; or

$$X_1\text{-}[CF_2O]_n\text{-}[C_2F_4O]_m\text{-}[C_3F_6O]_l\text{-}X_2$$

where, n + m + l = 5÷50, but each of X_1 and X_2 is independently selected from the group: CF_3, $-C_2F_5$ or $-C_3F_7$.

[0026] The polymer may be of several types or groups since a combined use of fluorine-containing surfactants of different structures, some of them have anionogenic properties, another ones - cationogenic properties, results in formation of sorption (adsorption) layers which extremely tightly bound to a metal surface (a solid body).

[0027] Preferably, fluorine-containing surfactants with end groups - CF_3, are used, as they are more active in the film forming. It is important to note, that the molecule length of an attached surfactant is selected on the basis of purposes of protective films: the longer a molecule the less effect of a solid surface. When molecules are short a surface may be additionally shielded. When molecules are long surfactant solubility is reduced. The chemical nature of a fluorine-containing surfactant (high C-O and C-F bonding strength, spatial protection provided by fluorine atoms) characterizes the high stability of the compounds, making them suitable for using in aggressive environments. It should also be noted that the use of fluorine-containing surfactants with a molecular weight of less than 2000 does not allow to produce the uniform layer of a film, as the insufficient molecular weight density of the composition substance is observed.

[0028] The solvent used is freon, alcohol, Khladis, water, or any possible combination of them. The choice of said substances as a solvent is due to the fact that it is required to ensure complete solubility of fluorine molecules and other structural elements provided that substances are fully compatible without degradation of functional properties. A fluorine-containing surfactant is used in a solution in amounts of 0.2 to 18.5 wt.% It is important to emphasize that using a fluorine-containing surfactant in amounts of less than 0.2 wt.% does not ensure formation of a uniform film layer. Using a fluorine-containing surfactant in amounts of more than 18.5 wt.% does not result in the observance of conditions for density of molecules distribution and spacings between them.

[0029] After the application of a composite compound heat-setting of the film is performed within the temperature range of 67 to 114°C during 45 to 11 minutes to ensure complete deposition of the compound and to build chemical bonds with the surface. Heat-setting is preceded by additionally drying in open air within the temperature range of 22 to 39°C during 3 to 5 minutes, in the process of which adsorption of the film monomolecular layer starts to proceed. It should be noted that the indicated temperature ranges and time frames for both heat-setting and drying are optimum for uniform heat-fixing of the film.

[0030] In particular embodiments of the invention, a composite compound may be applied at least on a portion of the surface, for example, of equipment or parts or on the entire surface of specified parts or equipment.

[0031] The proposed method of applying a protective film on the heated surface of a solid body with roughness (Ra) of 0.001 to 2.5 μm makes it possible to provide a higher level of monomolecularity and continuity of the coating on the surface profile in accordance with the normal distribution laws of Gauss and Laplace, where the probability of a molecule getting on a surface interval a, b is determined under the following principle:

$$P(\alpha < X < \beta) = \int_{\alpha}^{\beta} f(x)\,dx = \int_{\alpha}^{\beta} \frac{dx}{b-a} = \frac{\beta-\alpha}{b-a}.$$

[0032] The interval a and b defines parameters (boundaries) of distribution and represents a uniform distribution.

[0033] A surface profile diagram and a molecular density profile diagram are shown in Fig. 1a and in Fig. 1b, respectively. As it can be clearly seen, Fig. 1 a shows degree of coating and surface smoothing -formation of a uniform layer when the studied interval of surface general space dimensions is 40-60 nm and availability of a low thickness coating within dimensions not exceeding 120 nm associated with the current surface roughness. As it can be clearly seen, Fig. 16 shows degree of smoothing - profile a film when leveling the surface.

[0034] A film is uniformly fixed during heat-setting. A monomolecular interrelated coating produced as a result of heat-setting of a composite compound is uniform and dense, besides, it provides hydrophobic properties to the surface and prevents the surface, including current conducting, from any contact with moisture and other aggressive agents, and effects of radiation. The nature of produced coatings on average consistent with Langmuir-Blodgett's theoretical concept of surfaces. Height of "nap" ("Langmuir's palisade") is 3 to 10 nm, preferably 1 to 8 nm, the coating is uniform, without visible bumps; film coating surface roughness: root mean squared - 3.5 nm, preferably 2 nm, arithmetic average - 3.1 nm, preferably 1.6 nm. Illustration of the profile diagram of the surface of a multi-functional protective film of a fluorine-containing surfactant produced according to the process of the invention is shown in Fig. 1.

[0035] Composite compound molecules are arranged close to each other on the surface of a solid body. Spiral-shaped polar molecules of these substances are able to capture electrons during coating of hard metal surfaces. Fluorine molecules and modifying additives (e.g., corrosion inhibitors, bactericidal action polymers) of a composite compound enter into interaction with these electrons, forming a single chemical structure with a surface to be coated. In most cases of coating glass, ceramic, polymer, rubber, mineral and other non-metallic and polymer surfaces composite compound molecules are chemisorbed with a surface by means of interaction with ionic structure, hydrogen bridges, thermal crystallization, disperse and capillary forces. With regard to specific resistance of semiconductors within a wide range (10^{-4} to 10^{9} ohm*cm) some semiconductors (silicon carbide, selenium, tellurium, etc.) change their electrical resistance with increasing voltage applied to them or under the effect of light emissions. Coating with a composite compound does not change parameters of current conductivity and dielectric properties, contributes to reducing effects of external aggressive factors, thus expanding the applicability of the proposed method.

[0036] In the whole, a general model of chemisorption is shown in Fig. 2. Due to the spiral-shaped structure of the non-polar portion of a composite compound, according to the invention, fixed fluorine molecules are able to maintain lubricating properties, exclude dry friction by forming a boundary damping layer in friction zones and surface dynamics. Besides, effects of radiation and background charge, activity of bacteria growth on the surface, gas permeability and destruction of the surface are reduced. A multi-functional film of fluorine, according to the invention, occludes all micropores up to the grade of 4-5 nm, decontaminates them, protects the surface against aggressive substances, and thus inhibits galvanic corrosion without changing parameters of current conductivity and dielectric properties, which allows to expand the applicability of the proposed method.

[0037] After the treatment of a surface with a composite compound and the producing a multi-functional protective nano-film micropores and microcracks on the uppermost layer of the produced surface coating reduce level of distributed stress concentration, thus stop forming damage centres and points of surface energy accumulation. The proposed method by smoothing the surface energy of the laws of the uniform density provides formation of a multi-functional protective coating - production of a nano-film having higher wear resistance, antibacterial properties, resistance to corrosion, property to reduce effects of radiation and intellectual memory.

[0038] Quality control of coatings should be done by measuring wetting angle. Soft surfaces such as silicone or rubber may change in size after the application of a composite compound (increase in size at first), and then within 80 to 96 hours they restore original dimensions with new properties of chemical resistance to aggressive environments.

[0039] Processability is improved due to the single-stage operation used to apply a composite compound on an additionally heated surface with roughness (Ra) of 0.001 to 2.5 μm followed by the formation of a nano-film. After the compound getting at least on a portion of the surface of a solid body a solvent used is evaporated and a fluorine-containing surfactant itself enters into reaction with the surface. Then fluorine-containing surfactant molecules build structures of Langmuir (Langmuir's palisade) in the form of spirals with axes of molecules normally directed to surfaces, which allow not only provide reliable retaining of lubricating environments but also serve as a buffer between contacting surfaces. During adsorption, surface diffusion, and due to the evaporation of the solvent a monomolecular layer (monolayer) is formed as a 3 to 10 nm, preferably 1 to 8 nm thick film, besides the formation of the film is accompanied by a chemical reaction (chemisorption) in which the surface material reacts with the composite compound based on a fluorine-containing surfactant. In forming the film layer molecules of the fluorine-containing surfactant are ordered in a certain way of the spatial orientation, and physical and chemical properties of the coated surface are radically changed. Particles of the fluorine-containing surfactant are not separated from the surface due to the chemisorption bond. Thus, the proposed method provides a new physically and chemically based interaction between the composite compound and surfaces which makes it possible to apply the indicated compound on metal, non-metallic and polymer surfaces, including current conducting and dielectric in hardly accessible locations, for example, into interior portions of an electronic instrument, a microchip, a printed circuit with components installed, and thereby extending the field of application.

[0040] The proposed method for modification of a surface with a higher level of processability of coating allows to produce multi-functional (anti-friction, anti-adhesion, etc.) protective nano-films (3 to 10 nm, preferably 1 to 8 nm, in thickness) of a wide spectrum of the complex protection of surfaces on a surface with roughness (Ra) of 0.001 to 2.5 μm, thereby improving physical and chemical properties of the surface, economic characteristics of the coating, and extending the field of application.

[0041] A composition may be applied by immersing, spraying, spreading, aerosol spraying, active or passive swabbing. In addition to the above spraying may be performed manually or in automated facilities. Consumption rate of a composite compound is determined by the application algorithm shown in Fig. 3. This diagram shows a consumption rate of 1 kg composite compound (with density of 0.8-1.8 g/cm^3 at t = 20°C) for various methods of application (coating).

[0042] A technical and economic advantage of this invention is the increased effectiveness of the complex protection of surfaces with the same weight of structure and optimization of physical and chemical, and electrical properties - multi-functional protection of surfaces against dry friction, effects of moisture (hydrophobic properties, water repellency), radiation, bacteria and wear, and at the same time reduced both labour intensity for producing a protective nano-film and time for coating process.

Table 1 shows examples of methods for producing a protective film for the purpose to illustrate certain aspects of the invention embodiment which are not anywise intended to limit the extend of this invention.

Table 2 shows characteristics of coated with the film surfaces of metal products, rubber products, optical glass, a printed circuit with electronic components and an aluminium-magnesium alloy.

Table 3 shows results of measuring resistance (ohms) of insulation coated with the composite compound "Epilam "ElectronicS" produced by LLC "AVTOSTANKOPROM" according to TU 2412-002-13868195- 2012.

Table 4 shows technological features of coating with the use of a composition compound and producing a multi-functional protective nano-film of a fluorine-containing surfactant.

[0043] The modified surfaces produced by the proposed method were tested according to the applicable standards and GOST standards with respect to characteristics confirming that the stated technical result has been achieved:

- quality of a composition to be applied was evaluated according to TU 2412-001-13868195-2012, TU 2412-002-13868195-2012 and quality of coating applied - according to TI 1831-010/3.

[0044] The following examples show the processes of producing multi-functional protective nano-films on a surface with roughness (Ra) of 0.001 to 2.5 μm in accordance with the method proposed in the claims, as well as characteristics of the produced modified surfaces confirming that the stated technical result has been achieved.

Example 1. Method for producing a protective film on the metal surface of a supporting pair consisting of step bearings and step bearing needles with roughness (Ra) of 0.04 μm.

[0045] The surface was degreased with acetone GOST 2768-84, after which the surface was subjected to heating at a temperature of +39°C during 8 min. Then a composite compound was applied on the surface heated to the said temperature by immersing. The composite compound used was "Epilam SFC-05" wt.% solution of a fluorine-containing surfactant with a molecular weight of 2200 of the general formula.

$$F-\left[\begin{matrix}CF & CF_2O\\ | & \\ CF_3 & \end{matrix}\right]_n-\begin{matrix}CFCOOH\\ | \\ CF_3\end{matrix}$$

[0046] Solkane solvent was used as the solvent. The solution also included a polyphosphate-based amine corrosion inhibitor as the additive. The consumption rate was 74 g/m^2. Then the surface was subjected to heat-setting at a temperature of +97°C during 55 min. As the result a 7 nm thick film was produced with the arithmetic average roughness of 3.7 nm and the root mean square surface roughness of 3.4 nm, Ref. Table 1. The produced film was subjected to friction power tests. Refer to Table 2 for details.

<u>Example 2. Method for producing a protective film on the non-metallic surface of an instrument printed circuit with installed electronic elements and with roughness (Ra) of 0.16 μm.</u>

[0047] The method was performed as in Example 1, isopropyl alcohol GOST 9805-84 was used for degreasing, after which the surface was subjected to heating at a temperature of 28°C during 9 min., and the composite compound to be applied was "Epilam ElectronicS" wt.% solution of fluorine-containing surfactant with a molecular weight of 3000 of the general formula as in Example 1. Isopropyl alcohol in combination with freon Foran was used as the solvent. The solution also included an amine corrosion inhibitor as the additive. The consumption rate was 154 g/m^2. Then the surface was subjected to heat-setting at a temperature of +68°C during 60 min. The compound was applied to the surface by spraying without isolating conductor strips made of non-ferrous metals. Time and temperature parameters of the method, as well as thickness and roughness of the produced film are shown in Table 1. The produced film was subjected to moisture resistance tests in a climatic test chamber at a humidity level of 95-98%. Refer to Table 2 for details.

<u>Example 3. Method for producing a protective film on a rubber surface with roughness (Ra) of 0.70 μm.</u>

[0048] The method was performed as in Example 1, and the composite compound to be applied was "Epilam SFC-20" wt.% solution of a fluorine-containing surfactant with a molecular weight of 2200 of the general formula as in Example 1. Ozone-safe freon Foran 141 was used as the solvent. The solution also included a polyphosphate-based amine corrosion inhibitor as the additive. The consumption rate was 132 g/m^2. Then the surface was subjected to heat-setting at a temperature of + 85°C during 52 min. The compound was applied on the surface by immersing. Time and temperature parameters of the method, as well as thickness and roughness of the produced film are shown in Table 1. The produced film was subjected to chemical resistance tests. Refer to Table 2 for details.

<u>Example 4. Method for producing a protective film on the glass surface of an optical glass with roughness (Ra) of 0.012 μm.</u>

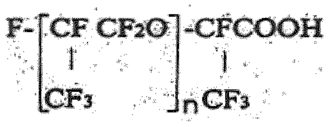
[0049] The method was performed as in Example 1, but with additional drying (prior to heat-setting). Drying was performed at a temperature of +29°C during 5 min. The composite compound to be applied was "Epilam Aqua" wt.% solution of a fluorine-containing surfactant with a molecular weight of 2500 of the general formula X_1-$[CF_2O]_n$-$[C_2F_4O]_m$$[C_3F_6O]_l$-$X_2$. Distilled non-potable water was used as the solvent. The solution also included a bactericidal additive. The consumption rate was 341 g/m^2. The compound was applied to the surface by spreading. Time and temperature parameters of the method, as well as thickness and roughness of the produced film are shown in Table 1. The produced film was subjected to tests for hydrophobic, anti-adhesion and bactericidal properties. Refer to Table 2 for details.

<u>Example 5. Method for producing a protective film on the metal surface of a guillotine cutter with roughness (Ra) of 0.020 μm.</u>

[0050] The method was performed as in Example 1, but with additional drying prior to heat-setting. Drying was performed at a temperature of + 37°C during 5 min. The composite compound to be applied was a composition 6SF-180-05 a wt.% solution of a fluorine-containing surfactant with a molecular weight of 2500 of the general formula X_1-$[CF_2O]_n$-$[C_2F_4O]_m$-$[C_3F_6O]_l$-X_2. Freon was used as the solvent. The solution also included a corrosion inhibitor as the additive. The consumption rate was 118 g/m^2. The compound was applied to the surface by immersing and by ultrasonic exposure. Time and temperature parameters of the method, as well as thickness and roughness of the produced film are shown in Table 1. The produced film was subjected to tests with measuring resistance to dry friction. Refer to Table 2 for details.

Example 6. Method for producing a protective film on the surface of an aluminium-magnesium alloy with roughness (Ra) of 0.040 μm.

[0051] The method was performed as in Example 1, but with additional drying prior to heat-setting. Drying was performed at a temperature of +34°C during 5 min. The composite compound to be applied was "Epilam ElectronicA" a wt.% solution of a fluorine-containing surfactant with a molecular weight of 2200 of the general formula



[0052] Isopropyl alcohol in combination with freon Foran was used as the solvent. The solution also included an atmospheric corrosion inhibitor as the additive. The consumption rate was 142 g/m^2. The compound was applied to the surface by manual swabbing. Time and temperature parameters of the method, as well as thickness and roughness of the produced film are shown in Table 1. The produced film was subjected to tests for effects of aggressive environments. Refer to Table 2 for details.

[0053] This method makes it possible to produce a damping coating when designing production nano-systems developed artificially with atomic-scale precision. It represents a "smart" coating - the coating-informer, which is able to transmit information about condition of the surface on which a composite compound has been applied or a surface mating with the surface.

[0054] Results of the insulation resistance tests of printed circuits with conductor strips, installed electronic components and sensors coated with the composite compound as per Example 3 ("Epilam ElectronicS") are shown in Table 3. The results of the insulation resistance tests clearly show that the studied values and characteristics of printed circuits have showed positive results - the invention may increase the lifetime of an electronic unit.

[0055] Parameters of the n-type and p-type conduction remain stable, which is a significant and determining factor when choosing competitive compositions for protection of printed circuits. Characteristics of "nap" - Langmuir's palisade - 3 to 10 nm, preferably 1 to 8 nm in thickness with a chemisorbed monomolecular layer of vertically directed fluorine molecules make it possible to maintain the n-type and p-type conduction according to programmed parameters even in the presence of donor (antimony, arsenic, phosphorus) and acceptor (indium, gallium, boron, etc.) impurities as part of materials.

[0056] Besides, substances included into a composite compound are able to bind with a surface through the process of chemisorption when subjected to temperatures, thus contributing both to further improvement of the processability and expanding the applicability of the proposed method. Table 4 shows the necessary and sufficient parameters and values of the practical application of the proposed process and the production of a multi-functional protective nano-films of a fluorine-containing surfactant. The values in Table 4 according to the proposed method allow specialists of a wide range of industry sectors of using the proposed method for producing a multi-functional protective nano-film.

[0057] The proposed method may be used in various industries to solve the complex protection issue and to give the appropriate properties to elements of artificial intelligence, to work surfaces and other equipment and parts of general mechanical engineering, instrument engineering, microelectronics and bio-energetics, to enhance the protection against wear, corrosion, moisture, for purposes of ensuring antibacterial protection and reducing effects of radiation, as well as for treatment of surfaces of high-load friction units, tools for metal cutting, for treatment of printed circuit boards, chips, sensors, etc. in order to provide them with wear resistance and durability when operating in aggressive environments.

Table 1

Example	Surface roughness, Ra	Heating, °C	Drying in open air		Heat-setting		Film thickness, nm	Film surface roughness, nm	
			°C	t,	°C	t, min		Arithmetic average	Root mean squared
1	0.04	39	-		97	55	7	3.7	3.4
2	0.16	28	-	-	68	60	5	2.4	2.1
3	0.7	39	-	-	85	52	6	2.7	2.5
4	0.01	40	29	5	110	50	4	1.7	1.6
5	0.02	39	37	5	100	60	8	1.9	1.9

(continued)

Example	Surface roughness, Ra	Heating, °C	Drying in open air		Heat-setting		Film thickness, nm	Film surface roughness, nm	
			°C	t,	°C	t, min		Arithmetic average	Root mean squared
6	0.04	40	34	5	90	75	5	2.3	2.2

Table 2

Example	Test	Characteristics without treatment	Characteristics after treatment	Conclusions and recommendations
1	Application on a supporting pair consisting of step bearings and step bearing needles	Appearance of adhering after 1.5-2 hours of operating	In operating conditions after heating to 300°C and Ptest of 25 kgf/cm2	Surface after coating and 1.5-2 hours of operation is clean, without adhering, scores and traces of rust, rotation is smooth
2	Application on an instrument printed circuit with installed electronic elements	Quality of connectors WF, SCM has been deteriorated after thermal influence. Values of Rave in milliohm before application: 9.35/2.37/ 4.87/8.16	Quality of connectors PWL, WF, SCM, BH connections has remained the same. Values of Rave in milliohm after application: 15.86/3.45/5.31/9.69	After the application (to provide hydrophobic properties and to prevent water from getting inside): quality of connectors has not been deteriorated after thermal influence
3	Application on a rubber part (collar)	Em brittlement, damage to surface in curing and removal from the mould	Chemical resistance, improvement of surface quality of conductive mixture STEP.	After the application the part was easily removed from the mould, surface quality has gained a polished profile.
4	Application on the glass surface of an optical glass	Dust adhesion and deterioration of the wave refractive indexes and spectral properties	Deduction of dust adhesion - 2.8 times; improvement of the refractive index; improvement of resistance to transparent IR emission;	After the application the functions are normal, improved properties and reduced wetting properties have been obtained.
5	Application on the metal surface of a guillotine cutter	Dulling of the cutting end (edges) after 164 operations	Cutter life - no dulling up to 281 operations	After the application an improvement of wear resistance of the guillotine cutter cutting end has been achieved.
6	Application on an aluminium magnesium alloy (Al-Mg alloy)	1. Disruption of a brazed seam; 2. After brazing and chemical oxidation a water-repellent treatment is required.	Results are positive after testing samples during 10 days and nights in the chamber under conditions of humidity of 96-98% at a temperature of 38-42°C	After the application and cycling variation tests no defects or chances of the coating have been revealed

Table 3.

No. of electronic unit with the printed circuit, measurement point	Before tests; ohm normal value as per specifications - 10^4	In hot chamber; normal value as per specifications - 300	In moisture chamber;	48 hours after moisture chamber; normal value as per specifications - 10^4
Ref. 1-1; 2-2; 3-3; 4-4	2.0 10^5; 2.0 10^5; 2.0 10^5; 2.0 10^5	2.0 10^3; 0.3 10^4; 2.6 10^3; 2.5 10^3	110; 2.0 10^3; 240; 410	2.0 10^5; 1.7 10^5; 0.6 10^5; 0.7 10^5
1. With a film coated by the proposed method 1-1; 2-2; 3-3; 4-4	0.7 10^5; 0.8 10^5; 0.7 10^5; 0.6 10^5	2.4 10^3; 2.6 10^3; 2.5 10^3; 2.1 10^3	1.2 10^3; 680; 1.9 10^3; 70	0.7 10^5; 0.6 10^5; 0.7 10^5; 0.6 10^5
2. With a film coated by the proposed method 1-1; 2-2; 3-3; 4-4	1.2 10^5; 0.6 10^5; 0.5 10^5; 0.4 10^5	2.7 10^3; 2.8 10^3; 2.6 10^3; 2.9 10^3	2.1 10^3; 2.4 10^3; 53; 55	0.9 10^5; 0.4 10^5; 0.5 10^5; 0.4 10^5
3. With a film coated by the proposed method 1-1; 2-2; 3-3; 4-4	1.0 10^5; 0.7 10^5; 0.5 10^5; 2.3 10^5	2.8 10^3; 2.6 10^3; 2.5 10^3; 2.4 10^3	48; 440; 1.8 10^3; 840	1.0 10^5; 0.4 10^5; 0.5 10^5; 2.3 10^5

Table 4.

Treated surface description	Product dimension s, mm	Degreasi ng time, within the limits of, min	Drying time, within the limits of, min	Drying and heating temperat ure during applicatio n, °C	Applicatio n time, min	Temperat ure after the applicatio n, °C	Heat-setting temperatu re, °C	Heat-setting time, min
Metal (including non-ferrous metal alloys)	<3620	15-45	7-16	44	25-60	39	114	45
Non-metallic (glass, polymer, rubber, plastic, etc.)	<4870	15-45	7-16	48	25-60	37	95	87
Electrical (electronic units, printed circuits, integrated circuits, chips, etc.)	<948	24-52	6-14	37	20-45	22	67	117

Claims

1. Method for producing a protective film, at least on a portion of the surface of a solid body, including preliminary preparation of the surface, application of a composite compound based on a fluorine-containing surfactant and heat-setting of the agent, **characterized in that** the applying a composite compound on the prepared and afterwards additionally heated surface of a solid body with roughness (Ra) of 0.001 to 2.5 μm.

2. Method for producing a protective film according to claim 1, **characterized in that** the surface heating is performed within the temperature range of 28 to 48°C.

3. Method for producing a protective film according to claim 1, **characterized in that** the application of a composite compound is performed so as to produce a 3-10 nm, preferably 1-8 nm thick protective film.

4. Method for producing a protective film according to claim 1, **characterized in that** the application a composite compound is performed so as to produce a protective film with arithmetic average surface roughness within 2.4 to 3.7 nm, preferably within 1.6 to 2.3 nm.

5. Method for producing a protective film according to claim 1, **characterized in that** a composite compound is applied on a surface by immersing, spraying, spreading, aerosol spraying, active or passive swabbing.

6. Method for producing a protective film according to claim 5, **characterized in that** spraying is performed manually or in automated facilities.

7. Method for producing a protective film according to claim 1, **characterized in that** the composite compound used is a solution of fluorine-containing surfactant, that includes additionally at least one modifying additive.

8. Method for producing a protective film according to claim 7 **characterized in that** the fluorine-containing surfactant used is a polymer of the perfluoropolyether group with a molecular weight of more than 2000, and the following general structural formula

$$F-\left[\begin{array}{l}CF\ CF_2O\\ \ \ |\\ CF_3\end{array}\right]_n-\begin{array}{l}CFCOOH\\ \ \ |\\ CF_3\end{array}$$

where, n - total number of the element within the range of 1-13, inclusively; or

$$X_1\text{-}[CF_2O]_n\text{-}[C_2F_4\,O]_m\text{-}[C_3F_6O]_l\text{-}X_2$$

where, n + m + l = 5÷50, but each of X_1 and X_2 is independently selected from the group: CF_3, $-C_2F_5$ or $-C_3F_7$.

9. Method for producing a protective film according to claim 7, **characterized by** the using a solution comprising a fluorine-containing surfactant in amount of 0.2 to 18.5 wt.%

10. Method for producing a protective film according to claim 7, **characterized in that** the surfactant used is freon, alcohol, Khladis, water or any possible combination of them.

11. Method for producing a protective film according to claim 7, **characterized in that** a corrosion inhibitor, an anti-friction additive, a bactericidal additive or any possible combination of them is used as the modifying additive.

12. Method for producing a protective film according to claim 1, **characterized in that** the heat setting is performed within the temperature range of 67 to 114°C during 45 to 117 minutes.

13. Method for producing a protective film according to claim 1, **characterized in that** after the application of a composite compound additionally drying in open air is preformed within the temperature range of 22 to 39°C during 3 to 5 minutes.

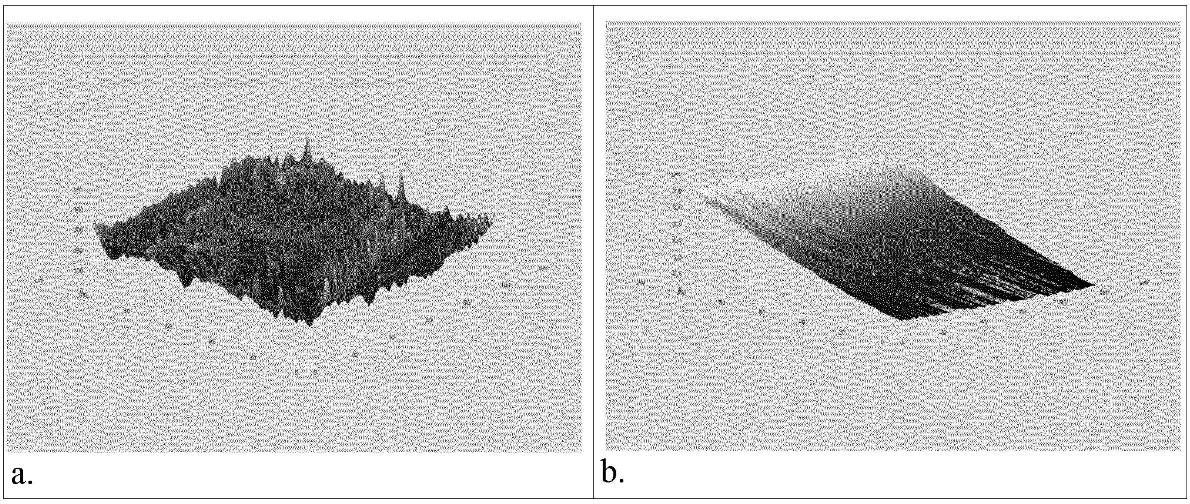

a.
b.

Fig. 1

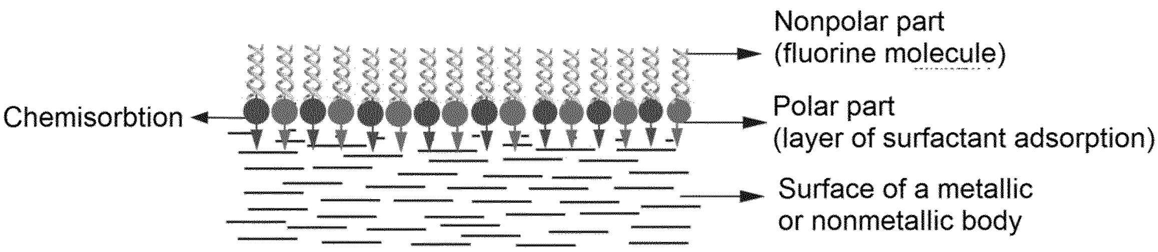

Nonpolar part
(fluorine molecule)
Chemisorbtion
Polar part
(layer of surfactant adsorption)
Surface of a metallic
or nonmetallic body

Fig. 2

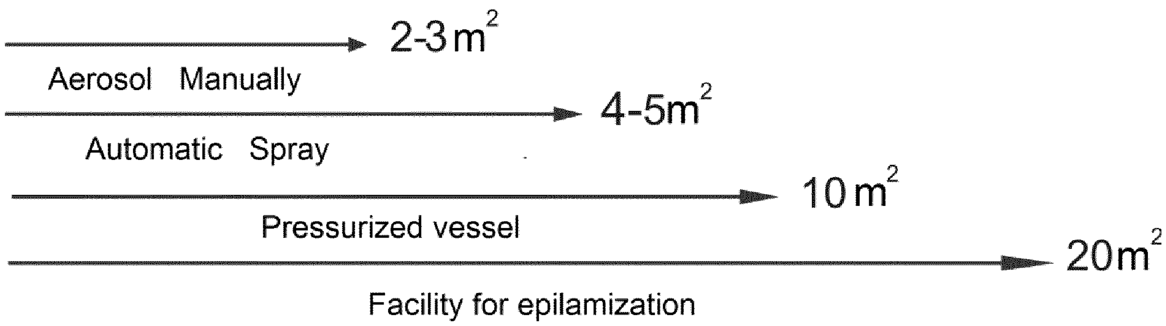

2-3 m2
Aerosol Manually
4-5m2
Automatic Spray
10 m2
Pressurized vessel
20m2
Facility for epilamization

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EA 2013/000015

A. CLASSIFICATION OF SUBJECT MATTER
C09D 127/12 (2006.01); B05D 5/02 (2006.01); B05D 5/08 (2006.01); B05D 3/10 (2006.01); C10M 147/04 (2006.01)
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D 127/12, B05D 5/02, 5/08, 3/10, C10M 147/04, B82B 1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatSearch (RUPTO internal), USPTO, PAJ, Esp@cenet, DWPI, EAPATIS, PATENTSCOPE, Information Retrieval System of FIPS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	RU 2139902 C1 (GOSUDARSTVENNOE UNITARNOE PREDPRIYATIE,OSNOVANNOE NA PRAVE KHOZYAISTVENNOGO VEDENIYA-TSENTRALNOE DISPETCHERSKOE UPRAVLENIE NEFTYANOI PROMYSHLENNOSTI) 20.10.1999, the abstract, the claims, p. 3, example 1	1-13
A	YAKOVLEV A. D. Khimiya i tekhnologiya lakokrasochnykh pokrytii. Leningrad "Khimiya", Leningradskoe otdelenie, 1981, p. 24-25, 32	1-13
A	RU 2286853 C2 (INSTITUT ORGANICHESKOGO SINTEZA URALSKOGO OTDELENIIA ROSSYSKOI AKADEMII NAUK) 10.11.2006, the abstract, the claims	1-13
A	RU 2429284 C2 (OBSCHESTVO S OGRANICHENNOI OTVETSTVENNOSTJU "AVTOSTANKOPROM") 20.09.2011, the abstract, the claims	1-13
A	RU 2401287 C2 (GAIDAR SERGEI MIKHAILOVICH et al.) 10.10.2010	1-13

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 March 2014 (11.03.2014)	27 March 2014 (27.03.2014)
Name and mailing address of the ISA/ RU	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (April 2005)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- RU 2095386 **[0002]**
- RU 2429284 **[0003]**
- RU 2269557 **[0004]**
- RU 2139902 **[0006]**