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(54) METHOD OF PROVIDING A MULTIFUNCTIONAL COATING ON A METAL SUBSTRATE

VERFAHREN ZUR BEREITSTELLUNG EINER MULTIFUNKTIONSBESCHICHTUNG AUF EINEM
METALLSUBSTRAT

PROCÉDÉ FOURNISSANT UN REVÊTEMENT MULTIFONCTIONNEL SUR UN SUBSTRAT
MÉTALLIQUE

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Description

[0001] The present invention relates to a method of providing a multifunctional coating on a metal substrate.

[0002] It is generally known in the art to apply a surface treatment, e.g. an oil or chemical surface passivation such as chromate or phosphate to a metal substrate, e.g. steel, zinc and zinc alloy coated steel, tinplate, hot dip galvanised steel to confer corrosion protection of the respective metal or alloy during storage and transport. Such a surface treatment may affect further downstream processes such as shaping and painting. The friction of the metal surface thus treated can assist or detract from any mechanical deformation process such as simple bending, roll-forming, stamping and deep drawing. Regarding painting, the surface may or may not be directly paintable.

[0003] Metal substrates that have been surface passivated, generally require the use of lubricants, typically an oil-in-water emulsion comprising a hydrocarbon in water, in order to provide a low coefficient of friction to effect three dimensionally (3D) shaping operations, such as roll-forming or deep-drawing. After such a 3D forming step frequently the lubricant may need to be removed by degreasing in preparation for subsequent finishing step such as paint pre-treatment of the product and final painting thereof. Using oil based lubricants and corresponding degreasing fluids results in wastes that have a serious impact on the environment.

[0004] Thin organic coatings (TOCs) having thicknesses typically ranging from 1-5 micrometer are known in the art for application to hot dip galvanized steel in order to offer corrosion protection and colour to the underlying metal. A disadvantage of these TOCs is that they are often up to 10 times more expensive than commercially available traditional passivation systems. Furthermore, in forming operations oil-based lubricants may still be required.

[0005] EP 1 634 932 A1 describes a method of providing a coating to a metal substrate, comprising at least the subsequent steps of applying a first layer to the surface of the metal substrate, and then applying a second layer that can contain solid lubricants and pigments, wherein the first layer contains watersoluble phosphate.

[0006] It is an object of the invention to provide a method of coating a metal substrate, which does not show the above drawbacks or which shows these to a lesser extent.

[0007] It is another object to provide a method of coating a metal substrate, in particular a passivated surface thereof, allowing to reduce the impact on the environment during further processing steps.

[0008] A further object is to provide a method of modifying a metal substrate in order to offer improved corrosion resistance, colour, inherent lubricity and direct paintability properties.

[0009] Yet another object is to provide a method of producing a three-dimensional product from a flat metal

substrate, e.g. by one or more 3D deformation steps, that does not need an additional lubricant.

[0010] One or more of the above objects are satisfied by the present invention, which according to a first aspect defines a method of providing a coating to a passivated surface of a metal substrate, comprising at least the subsequent steps of applying a lubricating layer to the passivated surface of the metal substrate and applying a dyeing layer to the lubricating layer as described in claim 1.

[0011] According to the invention a passivated surface of a metal substrate is subjected to a multistep coating process for achieving a multifunctional coated metal substrate having useful properties for further processing in addition to corrosion resistance derived from the passivated surface. In a first step a lubricating compound is permanently, chemically, preferably covalently bonded to the passivated surface thereby providing an inherent lubricating property to the metal substrate obviating the need for any additional fluid lubricant, in particular an organic one, in a further forming operation. If needed, water may be used as a coolant for the equipment used. Thus reduction of chemical waste generation, in particular organic lubricant and degreasing compositions, in further processing steps can be achieved.

[0012] With conventional emulsion-based lubricants water is present as a dispersant for the organic components but also acts as a coolant. When water is applied on the coated metal substrate of the invention, the lubricating layer, preferably having hydrophobic properties, repels the water molecules such that an aqueous buffer layer is formed between the two metal surfaces. Although not strictly necessary, the inventors found that providing water on the lubricating layer further increases the lubricating properties of the lubricating layer.

[0013] The dyeing layer is applied to the lubricating layer. It has unexpectedly been discovered that adding dyes to the coating system can further improve lubricity and corrosion resistance, as well as providing surface colour, at least temporarily. In addition to the aesthetic benefit of a coloured metal substrate, the dye offers a tool for quality control by identifying where the lubricating surface treatment has taken place. The dye, preferably an ionic dye, is believed to covalently bond to sites of the passivated surface not occupied by the lubricating compound, as well as possibly to the lubricating compound itself.

[0014] The surface treatment according to the invention affords a multifunctional coating, the functions comprising at least two of corrosion protection, inherent lubricity, colour and direct paintability.

[0015] In the context of this description "inherent lubricity" means that additional oil-based lubricants are not needed. Water may be required as a coolant for cooling the tool(s) used, in particular in shaping operations., "Direct paintability" means that the product can be painted directly without the need for further surface preparation or pre-treatment.

[0016] Advantageously the lubricating and/or dyeing layers are applied at monomolecular level.

[0017] The lubricating compound has a hydrophobic nature offering a good lubricating property between the metal substrate treated according to the invention and a shaping tool without needing an additional oil-based fluid lubricant.

[0018] The metal substrate to which the present method is applied has a passivated surface. In view of environmental considerations chromium free passivation systems are preferred, in particular for hot dip galvanised steel products.

[0019] The non-chromium (VI) passivation layer of the metal substrate can be obtained by applying a metal phosphate, metal silicate, metal titanate, metal zirconate or other metal oxide type layer, as well as Cr³⁺ based passivation layers. Surface oxidation of the metal substrate is also possible. The coating weight of such a passivation layer typically ranges from tens of milligrams up to about 1 gram per square meter. Advantageously the passivation layer is rich in oxide/hydroxide at the surface for bonding of the lubricant and/or dye in the surface treatment according to the invention.

[0020] The lubricating compound generally comprises a linker group capable of forming a covalent bond to typically a metal oxide surface. Optionally said surface may have been hydroxylated. Suitable linker groups include silanes, carboxylic acids, sulphates, phosphates. A hydrocarbon chain, preferably a saturated one like alkyl, is directly attached to the linker group. Relatively long chained alkyl groups are more preferred. The hydrocarbon chain may be substituted, in particular halogenated. Substituting one or more hydrogen atoms by fluorine atoms in order to obtain a mono- or polyfluorinated derivative is preferred. Another suitable substituent may be selected from anionic substituents like carboxylic acids, sulphates, phosphates in order to control the surface tension of the resultant surface layer. E.g. covalently bonding of a polyfluorinated lower carboxylic acid to an oxide/hydroxide rich passivation layer may involve a condensation reaction involving loss of water and the formation of an ester link. Silanes may react via a sol-gel reaction to form a silyl ether linkage.

[0021] In a preferred embodiment the saturated hydrocarbon chain contains 2 - 20 carbon atoms, preferably 3 - 18 carbon atoms.

[0022] The lubricant, advantageously soluble in water, is preferably selected from the group comprising pentafluoropropionic acid, chloroethyldimethyl silane, ethyldimethylchlorosilane, octadecyldimethylchlorosilane, pentadecafluorooctanoic acid and stearic acid. Of this group pentadecafluorooctanoic acid is particularly preferred in view of its hydrophobicity and solubility in water.

[0023] An indication of the inherent lubricating property is hydrophobicity, illustrated by the contact angle between a droplet of water and the surface treated. The higher the contact angle, the less water spreads out, the better the auto-lubricating property.

[0024] The dye is preferably an ionic dye suitable for covalent binding to unoccupied sites of the passivated surface and to the lubricating compound. Preferred examples of useful anionic dyes comprise rhodamine and copper (II) phthalocyanine-tetrasulphonic acid tetra sodium salt.

[0025] Advantageously the coating method is carried out in a continuous manner on a moving metal strip, such as hot dip galvanised steel strip.

[0026] A second aspect of the invention relates to a metal product having a multifunctional coating the product comprising a metal body, a lower passivation layer, a lubricating layer and an outer dye layer. The metal product according to the invention has a lubricating layer that is permanently bonded to the passivation layer. The lubricating layer is covered with the dye layer. The preferences explained above with respect to the method according to the invention are similarly applicable to the product according to the invention.

[0027] The invention also relates to a method of producing a three dimensional product starting from a flat metal substrate having a passivated surface, the method comprising at least the subsequent steps of applying a lubricating layer to the passivated surface of the metal substrate, applying a dyeing layer to the lubricating layer and 3D deforming of the dyed and lubricated metal substrate. The metal product thus produced may be painted directly in a subsequent step. Again the preferences explained hereinbefore are similarly applicable to this third aspect of the present invention.

[0028] The following examples illustrate the invention.

Figure 1 shows a metal substrate (1) provided with a passivating layer (2) and a lubricating compound (3) bonded to the passivating layer. Figure 1 also shows how the hydrocarbon chains of the lubricating compounds repel water molecules (4) to form a combined organic layer and aqueous buffer layer between the two metal surfaces.

Figure 2 shows a metal substrate (1) provided with a lubricant according to the prior art (oil in water emulsion). A thin layer of oil micelles (5) is formed at the surface that acts as a buffer between the two metal substrates.

Example 1

[0029] Samples of a hot dip galvanised steel strip were dipped into a solution of titanium isopropoxide in isopropanol, thereby obtaining a titanate passivation layer. Three different concentrations of isopropoxide were used 0.001 M, 0.01 M and 0.1 M. Then three lubricity compounds pentafluoropropionic acid, chlorethyldimethyl silane and ethyl dimethylchlorosilane were deposited on the substrates. To determine whether the samples had been successfully treated dye solutions (100 mg/L) were applied. Two dyes were used rhodamine and copper (II)

phthalocyanine-tetrasulfonic acid, tetra sodium salt having a pink and blue colour respectively. Where no titania had been deposited the metal surface retained its standard metal appearance, while the surfaces where titania and lubricant were present, had a pink or blue colour depending on the dye.

Example 2

[0030] Corrosion studies were performed with differently coated hot dip galvanised steel samples. All samples had in common that they had been treated with 0.01 M titanium isopropoxide in isopropanol by dipcoating to form a titanate passivated surface layer.

Experiment 1

[0031] A first sample A received only this passivating treatment. A second sample B was additionally coated with a chloroethyldimethyl silane lubricant. Another sample C received the lubricant followed by rhodamine dye.

[0032] The thus prepared samples were exposed to a 5 % sodium chloride solution for 72 hours.

[0033] It was observed that white rusting was present on sample A, but less on sample B while sample C showed the least white rust. The presence of the lubricant and dye have incrementally reduced the occurrence of white rusting. The pink colour of rhodamine was however lost.

Experiment 2

[0034] Experiment 1 was repeated, but using penta-decafluorooctanoic acid as a lubricant. A similar result with the lubricant and dye affording incremental corrosion protection was achieved.

Experiment 3

[0035] Experiment 1 was repeating, but using copper (II) phthalocyaninetetrasulphonic acid tetrasodium salt as blue dye. Similar results as in Experiments 1 and 2 were obtained.

Example 3

[0036] Linear friction tests (LFT) were performed with differently coated hot dip galvanised steel samples in line with the Renault "Multi Frottement test" D31-1738 and is accredited to the ISO 17025 standard. To assess lubricity the coated samples were pulled at a speed of 0.33 mm/s between a flat tool and a cylindrical tool pushed together with a force of 5 kN. The tool material used was DIN 1.3343 and the surface roughness (Ra) of each tool was 0.4 µm. Before each test the tools were cleaned with a tissue soaked in acetone or alcohol. The coated strips were drawn through the tools ten times along a testing distance of 55 mm; after each stroke the tools were re-

leased and the strips returned to the original starting position in preparation for the next stroke.

Experiment 4

[0037] A first sample (A) was coated with a titanate passivation layer. A second sample (B) additionally comprised a pentafluoropropionic acid lubricity compound and a third sample (C) comprised an octadecyldimethyl-chlorosilane lubricity compound. Each sample was tested dry, with deionised water and in the presence of four commercial lubricants (DA Stuart Drawsol 1050E 12% (L1), Castrol Cooledge B1 8% (L2), Gulf Vanishing Oil CN 100% (L3) and Rocol 8% (L4). The LFT results are shown in Table 1.

[0038] Table 1 shows that the coefficient of friction observed on the dry titania surface was 0.562 and that this value can be reduced by providing a commercial emulsion based lubricant on the titanate surface. The presence of water also reduces the coefficient of friction (0.275) compared to the dry sample.

[0039] The coefficient of friction observed for sample B comprising pentafluoropropionic acid was 0.538 when tested dry. The presence of a commercial lubricant reduced the coefficient of friction to between 0.132 and 0.168, whereas the presence of water reduces the coefficient of friction to a slightly lower level (0.249) than that of the titanate coated sample (0.275).

[0040] As shown in Table 1, the coefficient of friction observed for sample C (dry) was 0.101. When the sample was tested in the presence of commercial lubricants the observed CoF values were all higher than the value obtained for the dry sample (C). When tested in the presence of water, the observed coefficient of friction for sample C was 0.089. This value is much lower than the values obtained for the dry sample and the samples tested in the presence of the commercial lubricants.

[0041] Contact angle experiments were also performed on the surfaces of samples A, B and C (ASTM D7334 - 08) to assess their wettability. The contact angles measured for samples A, B and C were 109.7°, 112.8 and 124.8° respectively, which suggests an increase in surface hydrophobicity (A<B<C). The reduction in coefficient of friction values obtained for samples A, B and C has therefore been attributed, at least in part, to the increasing hydrophobicity of the surface. However, the length of the pendant alkyl chain of the lubricating compound and the angle that it forms with the substrate surface may also have an effect on lubricating properties.

Table 1

Lubricant	Sample		
	A	B	C
Dry	0.562	0.538	0.101
L1	0.135	0.139	0.111

(continued)

Lubricant	Sample		
	A	B	C
L2	0.135	0.132	0.110
L3	0.168	0.168	0.170
L4	0.137	0.142	0.125
Water	0.275	0.249	0.089

Claims

1. Method of providing a coating to a metal substrate, comprising at least the subsequent steps of applying a passivating layer to the surface of the metal substrate, applying a lubricating layer to the passivating layer on the metal substrate and applying a dyeing layer to the lubricating layer, wherein the passivating step comprises applying a metal oxide layer not based on chromium (VI), a metal phosphate layer, a metal silicate layer or metal titanate layer on the surface of the metal substrate and the lubricating step comprises chemically bonding a lubricating compound to the passivating layer, the lubricating compound having a hydrophobic nature.
2. Method according to claim 1, wherein the metal substrate is a hot dip galvanized steel strip.
3. Method according to claim 1 or 2, wherein the passivating step comprises applying a chromate free passivating layer.
4. Method according to any of the preceding claims, wherein the passivating layer is rich in oxide/hydroxide.
5. Method according to any one of the preceding claims, wherein chemically bonding comprises covalently bonding.
6. Method according to any one of the preceding claims, wherein the lubricating compound is applied at a molecular level.
7. Method according to any one of the preceding claims, wherein the lubricating compound comprises a linker group, which linker group comprises a silane, a carboxylic acid, a sulphate or a phosphate.
8. Method according to any one the preceding claims, wherein the lubricating compound comprises a hydrocarbon chain or a substituted hydrocarbon chain.
9. Method according to claim 8, wherein the hydrocarbon chain or substituted hydrocarbon chain is a saturated hydrocarbon chain containing 2 - 20 carbon atoms.
10. Method according to claim 8 or claim 9, wherein the substituted hydrocarbon chain comprises a halogen and/or an anionic substituent.
11. Method according to claim 10, wherein the halogen is selected from the group consisting of fluorine or chlorine and/or the anionic substituent comprises a carboxylic acid, a sulphate or a phosphate.
12. Method according to any one of the preceding claims, wherein the lubricating compound is selected from the group comprising pentafluoropropionic acid, chloroethyldimethyl silane and ethyldimethylchlorosilane, ootadecyldimethyl-chlorosilane, pentadecafluorooctanoic acid and stearic acid.
13. Method according to any of the preceding claims, wherein the dyeing layer comprises a dye compound selected from anionic dyes, in particular rhodamine and copper (II) phthalocyanine-tetrasulphonic acid, tetra sodium salt.
14. Coated metal product, the product comprising a metal body, a lower passivation layer, a lubricating layer and an outer dye layer, wherein the passivation layer is a metal oxide layer not based on chromium (VI), a metal phosphate layer, a metal silicate layer or a metal titanate layer and the lubricating layer comprises a lubricating compound chemically bonded to the passivating layer, the lubricating compound having a hydrophobic nature.
15. Coated metal product according to claim 14, wherein the lubricating layer is covalently bonded to the lower passivation layer.
16. Method of producing a three dimensional product from a flat metal substrate having a passivated surface, comprising at least the subsequent steps of applying a lubricating layer to the passivated surface of the metal substrate, applying a dyeing layer to the lubricating layer and three dimensionally deforming of the metal substrate thus coated, wherein the passivated surface comprises a metal oxide not based on chromium (VI), a metal phosphate, a metal silicate or a metal titanate and the lubricating step comprises chemically bonding a lubricating compound to the passivating surface the lubricating compound having a hydrophobic nature.

Patentansprüche

1. Verfahren zum Bereitstellen einer Beschichtung für

- ein Metallsubstrat, umfassend mindestens die folgenden Schritte des Aufbringens einer Passivierungsschicht auf die Oberfläche des Metallsubstrats, des Aufbringens einer Schmierschicht auf die Passivierungsschicht auf dem Metallsubstrat und des Aufbringens einer Färbeschicht auf die Gleitschicht, wobei der Passivierungsschritt das Aufbringen einer Metalloxidschicht nicht auf Basis von Chrom (VI), einer Metallphosphatschicht, einer Metallsilikatschicht oder einer Metaltitanatschicht auf die Oberfläche des Metallsubstrats umfasst und der Schmierschritt das chemische Binden eines Schmiermittels an die Passivierungsschicht umfasst, wobei das Schmiermittel von hydrophober Natur ist.
2. Verfahren nach Anspruch 1, wobei das Metallsubstrat ein feuerverzinktes Stahlband ist.
 3. Verfahren nach Anspruch 1 oder 2, wobei der Passivierungsschritt das Aufbringen einer chromatfreien Passivierungsschicht umfasst.
 4. Verfahren nach einem der vorangegangenen Ansprüche, wobei die Passivierungsschicht reich an Oxid/Hydroxid ist.
 5. Verfahren nach einem der vorangegangenen Ansprüche, wobei das chemische Binden kovalentes Binden umfasst.
 6. Verfahren nach einem der vorangegangenen Ansprüche, wobei das Schmiermittel auf molekularer Ebene aufgebracht wird.
 7. Verfahren nach einem der vorangegangenen Ansprüche, wobei das Schmiermittel eine Linker-Gruppe umfasst, wobei die Linker-Gruppe ein Silan, eine Carbonsäure, ein Sulfat oder ein Phosphat umfasst.
 8. Verfahren nach einem der vorangegangenen Ansprüche, wobei das Schmiermittel eine Kohlenwasserstoffkette oder eine substituierte Kohlenwasserstoffkette umfasst.
 9. Verfahren nach Anspruch 8, wobei die Kohlenwasserstoffkette oder die substituierte Kohlenwasserstoffkette eine gesättigte Kohlenwasserstoffkette mit 2-20 Kohlenstoffatomen ist.
 10. Verfahren nach Anspruch 8 oder 9, wobei die substituierte Kohlenwasserstoffkette ein Halogen und/oder einen anionischen Substituent umfasst.
 11. Verfahren nach Anspruch 10, wobei das Halogen aus der Gruppe gewählt wird bestehend aus Fluor oder Chlor und/oder der anionische Substituent eine Carbonsäure, ein Sulfat oder ein Phosphat umfasst.
 12. Verfahren nach einem der vorangegangenen Ansprüche, wobei das Schmiermittel aus der Gruppe gewählt wird bestehend aus Pentafluorpropansäure, Chlorethyltrimethylsilan und Ethyldimethylchlorsilan, Octadecyldimethylchlorsilan, Pentadecafluorooctansäure und Stearinsäure.
 13. Verfahren nach einem der vorangegangenen Ansprüche, wobei die Färbeschicht eine Farbverbindung umfasst, die aus der Gruppe gewählt wird, bestehend aus anionischen Farbstoffen, insbesondere Rhodamin und Kupfer-(II)-phthalocyanin-Tetrasulfonsäure, Tetranatriumsalz.
 14. Beschichtetes Metallprodukt, wobei das Produkt einen Metallkörper, eine untere Passivierungsschicht, eine Schmierschicht und eine äußere Farbschicht umfasst, wobei die Passivierungsschicht eine Metalloxidschicht nicht auf Basis von Chrom (VI), eine Metallphosphatschicht, eine Metallsilikatschicht oder eine Metaltitanatschicht ist und die Schmierschicht ein Schmiermittel umfasst, die chemisch an die Passivierungsschicht gebunden ist, wobei das Schmiermittel von hydrophober Natur ist.
 15. Beschichtetes Metallprodukt nach Anspruch 14, wobei die Schmierschicht kovalent an die untere Passivierungsschicht gebunden ist.
 16. Verfahren zur Herstellung eines dreidimensionalen Produkts aus einem flachen Metallsubstrat mit einer passivierten Oberfläche, umfassend mindestens die folgenden Schritte des Aufbringens einer Schmierschicht auf die passivierte Oberfläche des Metallsubstrats, des Aufbringens einer Färbeschicht auf die Schmierschicht und des dreidimensionalen Verformens des so beschichteten Metallsubstrats, wobei die passivierte Oberfläche ein Metalloxid nicht auf Basis von Chrom (VI), ein Metallphosphat, ein Metallsilikat oder ein Metaltitanat umfasst und der Schmierschritt das chemische Binden eines Schmiermittels an die passivierende Oberfläche umfasst, wobei das Schmiermittel von hydrophober Natur ist.

Revendications

1. Procédé fournissant un revêtement sur un substrat métallique, comprenant au moins les étapes consécutives consistant à appliquer une couche de passivation sur la surface du substrat métallique, à appliquer une couche de lubrification sur la couche de passivation sur le substrat métallique et à appliquer une couche de teinture sur la couche de lubrification, ladite étape de passivation comprenant l'application d'une couche d'oxyde métallique n'étant pas à base de chrome (VI), une couche de phosphate métalli-

- que, une couche de silicate métallique ou une couche de titanate métallique sur la surface du substrat métallique et ladite étape de lubrification comprenant la liaison chimique d'un composé lubrifiant à la couche de passivation, le composé lubrifiant étant de nature hydrophobe. 5
2. Procédé selon la revendication 1, ledit substrat métallique étant une bande d'acier galvanisée à chaud. 10
 3. Procédé selon la revendication 1 ou 2, ladite étape de passivation comprenant l'application d'une couche de passivation sans chromate.
 4. Procédé selon l'une quelconque des revendications précédentes, ladite couche de passivation étant riche en oxyde/hydroxyde. 15
 5. Procédé selon l'une quelconque des revendications précédentes, ladite liaison chimique comprenant une liaison covalente. 20
 6. Procédé selon l'une quelconque des revendications précédentes, ledit composé lubrifiant étant appliqué à l'échelle moléculaire. 25
 7. Procédé selon l'une quelconque des revendications précédentes, ledit composé lubrifiant comprenant un groupe lieur, ledit groupe lieur comprenant un silane, un acide carboxylique, un sulfate ou un phosphate. 30
 8. Procédé selon l'une quelconque des revendications précédentes, ledit composé lubrifiant comprenant une chaîne hydrocarbonée ou une chaîne hydrocarbonée substituée. 35
 9. Procédé selon la revendication 8, ladite chaîne hydrocarbonée ou ladite chaîne hydrocarbonée substituée étant une chaîne hydrocarbonée saturée contenant 2 à 20 atomes de carbone. 40
 10. Procédé selon la revendication 8 ou 9, ladite chaîne hydrocarbonée substituée comprenant un halogène et/ou un substituant anionique. 45
 11. Procédé selon la revendication 10, ledit halogène étant choisi dans le groupe constitué par le fluor ou le chlore et/ou ledit substituant anionique comprenant un acide carboxylique, un sulfate ou un phosphate. 50
 12. Procédé selon l'une quelconque des revendications précédentes, ledit composé lubrifiant étant choisi dans le groupe comprenant l'acide pentafluoropropionique, le chloroéthyl diméthylsilane et l'éthyl diméthylchlorosilane, l'octadécyl diméthylchlorosilane, l'acide pentadécafluorooctanoïque et l'acide stéarique. 55
 13. Procédé selon l'une quelconque des revendications précédentes, ladite couche de teinture comprenant un composé colorant choisi parmi les colorants anioniques, en particulier la rhodamine et le sel de tétrasodium d'acide phtalcyanine tétrasulfonique de cuivre (II).
 14. Produit métallique enduit, ledit produit comprenant un corps métallique, une couche de passivation inférieure, une couche de lubrification et une couche de teinture externe, ladite couche de passivation étant une couche d'oxyde métallique n'étant pas à base de chrome (VI), une couche de phosphate métallique, une couche de silicate métallique ou une couche de titanate métallique et ladite couche de lubrification comprenant un composé lubrifiant lié chimiquement à la couche de passivation, ledit composé lubrifiant étant de nature hydrophobe.
 15. Produit métallique enduit selon la revendication 14, ladite couche de lubrification étant liée par covalence à la couche de passivation inférieure.
 16. Procédé de fabrication d'un produit tridimensionnel à partir d'un substrat métallique plat comportant une surface passivée, comprenant au moins les étapes consécutives consistant à appliquer une couche de lubrification sur la surface passivée du substrat métallique, appliquer une couche de teinture sur la couche de lubrification et déformer de façon tridimensionnelle le substrat métallique ainsi enduit, ladite surface passivée comprenant un oxyde métallique n'étant pas à base de chrome (VI), un phosphate métallique, un silicate métallique ou un titanate métallique et l'étape de lubrification comprenant la liaison chimique d'un composé lubrifiant à la surface de passivation, ledit composé lubrifiant étant de nature hydrophobe.

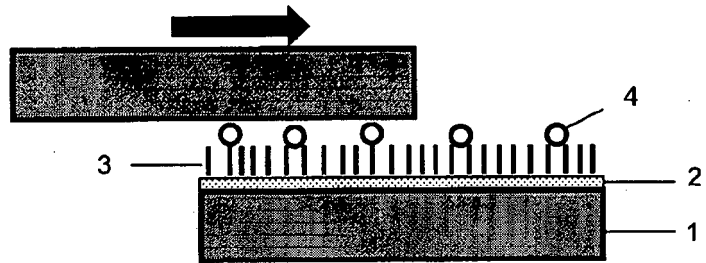


FIG. 1

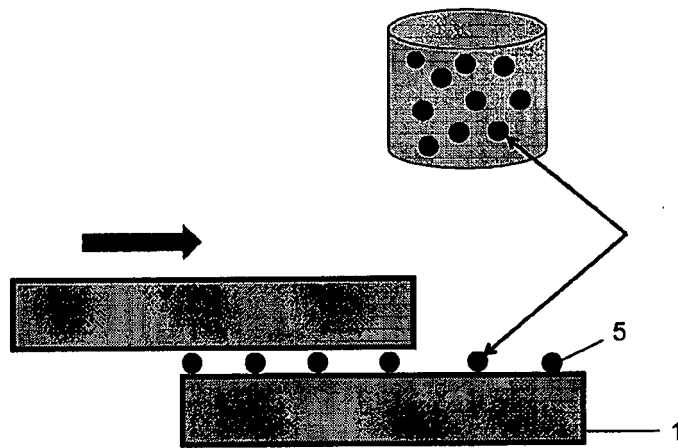


FIG. 2

REFERENCES CITED IN THE DESCRIPTION

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