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(54) Title: METHOD FOR THE TREATMENT OF METAL SURFACES FOR BESTOWING THEREON A HIGH HYDROPHOBICITY AND OLEOPHOBICITY

(57) Abstract: A method for the treatment of metal surfaces comprising in succession: - a step of depositing a coating of metal oxide, in which on a metal surface a sol is deposited made from a colloidal suspension in water of one or more metal alkoxides M(OR)<sub>n</sub> in the presence of an acid catalyst, in which: M is comprised in the group consisting of Al, Ti, Si, Y, Zn, Zr; R is a linear or branched aliphatic chain C1-C4; - a step of consolidation, wherein the coating is subjected to a temperature between 150 °C and 900 °C; - a step of functionalization, in which the coating is treated with boiling water and/or steam for the realization of hydroxyl groups; - a second step of consolidation, wherein the coating is subjected to a temperature between 150 °C and 900 °C, and - a step of fluorination, wherein the coating is treated with a fluorinated compound.

METHOD FOR THE TREATMENT OF METAL SURFACES FOR  
BESTOWING THEREON A HIGH HYDROPHOBICITY AND  
OLEOPHOBICITY

\* \* \*

5           The present invention relates to a method for the treatment of metal surfaces.

          In many industrial fields it is since a long time felt the need to intervene on the metal surfaces, for the purpose of bestowing thereon high characteristics of hydrophobicity (water repellency) and oleophobicity  
10           (repellency to oil). As is known to the technicians of different industrial sectors, wherein the metals or their alloys constitute important structural parts and interfaces, the possibility of providing a metal surface of a high hydrophobicity results in the advantages of preventing the adhesion of dirt and contaminants of different nature, also of biological origin, avoiding the  
15           formation of ice and frost in adverse environmental conditions, effectively limiting the phenomena of wear and corrosion, reducing, or even avoiding, fouling phenomena due to different agents, allowing more favorable flow conditions in the vicinity of the surface, with consequent gains also in terms of energy.

20           From the benefits listed above it can result immediately that the fields of navigation, marine in general and aerospace are among the most sensitive in research that aims to impart to the metal surfaces a high hydrophobicity and oleophobicity.

          It is known that the hydrophobicity of a surface and, therefore, its  
25           degree of repulsion towards water, depends by the appropriate combination between the structural characteristics, in terms of size of the roughness, and the energy of the same surface, in turn linked to the chemistry. Conventionally, a surface is defined hydrophobic when the contact angle ( $\theta$ ) that the same form with a drop of water is greater than  
30           90°, hydrophobicity is said gradually increasing as the contact angle  $\theta$  goes beyond this threshold. The super hydrophobicity is achieved when the contact angle of the surface with a drop of water is greater than 150°.

Similarly, the higher the contact angle that the surface forms with a drop of oil, the higher is the degree of oleophobicity.

In addition to the evaluation of the static contact angle  $\theta$  (static hydrophobicity), there are other dynamic parameters that define the hydrophobic behavior of a surface (dynamic hydrophobicity). The dynamic hydrophobicity is related to the ability of a drop of water to “roll” or “slide” along a surface, and then leave the same once the angle of inclination starts to increase. Experimentally, the dynamic hydrophobicity can be expressed in two ways, by means of the minimum value of the angle of inclination that the surface must present in order to cause the “rolling” or the “sliding” of a drop of known size, or by means of the measurement of the hysteresis value (difference) between the contact angle with which a drop of known volume advances ( $\vartheta_A$ ) on an inclined plane and the angle of recession ( $\vartheta_R$ ).

In this respect, in order to activate a real self-cleaning mechanism on the surface, it is necessary that the water droplets that are deposited then have the ability to “abandon” the surface itself, bringing with them, with a rolling or sliding mechanism, the dirt particles and removing their debris from the surface. Consequently, in order that the removal of dirt has the maximum effectiveness, the sliding or rolling of the drops on the surface must be able to occur for low angles of inclination of the surface (low inclination angle is equivalent to a high dynamic hydrophobicity). In literature, the dynamic hydrophobicity is measured by reference to the behavior of a water droplet of 30  $\mu\text{l}$ .

The pertinent literature shows how the relationship between static hydrophobicity and dynamic hydrophobicity is complex and, in many cases, even if the static contact angle is sufficiently high ( $> 150^\circ$ ), it does not correspond to a sufficient dynamic hydrophobicity. This is because if the interaction of the droplet with the surface depends in a more or less direct manner from the surface roughness and energy, its movement on the same is affected by additional parameters, such as physical

inhomogeneity, differences in chemistry and composition, particle size, etc., the influence of which is difficult to interpret.

Another functional property of great interest for the metal surfaces is oleophobicity, ie the repellency against oils, fats, etc. The provision of this additional property to a metal surface allows to physically prevent the adhesion of dirt and grease particles, in order to further implement the performance of "self-cleaning". The degree of oleophobicity of a surface depends strongly on the energy of the surface itself, or better, on the difference between the surface tension of the oily substance and the energy of the surface itself; the lower will be the latter, the greater the repellency of the surface towards adhesion of substances with higher surface tension. In literature, the difficulty is documented of generating oleophobic surfaces, especially because of the need to have extremely low surface energies (<5mN/m) [Tsujii K. Et al. *Angewandte Chemie-International Edition in English* 1997 36 (9), 1011-1012)].

Up to now, the solutions to impart a high hydrophobicity to metal surfaces have resulted to be particularly complex and expensive and, therefore, not suitable to be applied on an industrial scale. In fact, these solutions typically require expensive materials, long preparation times and multistep procedures, besides resulting in dynamic contact angles generally greater than 10°. Moreover, generally the treatments of the prior art provide for the need of using organic solvents, which, as is known, on an industrial scale involve a number of environmental issues, as well as problems related to safety and health of workers in charge of the treatment.

Purpose of the present invention is to provide metal surfaces presenting a high hydrophobicity and oleophobicity without compromising their realization on an industrial scale.

Object of the present invention is a method for the treatment of metal surfaces, characterised in that it comprises in succession:

- a step of depositing a coating of metal oxide, wherein on a metal surface is deposited a sol made from a colloidal suspension in water of one or more metal alkoxides  $M(OR)_n$  in the presence of an acid catalyst,

in which:

5 M is comprised in the group consisting of Al, Ti, Si, Y, Zn, Zr;

R is a linear or branched  $C_1$ - $C_4$  aliphatic chain;

- a step of consolidation, in which said coating is subjected to a temperature comprised between 150 °C and 400 °C;

10 - a step of functionalization, in which said coating is treated with boiling water and/or steam for forming hydroxyl groups;

- a second step of consolidation, in which said coating is subjected to a temperature comprised between 150 °C and 400 °C, and

15 - a step of superficial chemical activation, in which said coating is treated with an alkylsilane compound. Preferably, in said step of superficial chemical activation, said alkylsilane compound is fluorinated.

Preferably, the method includes a third step of consolidation, in which, after being treated with an alkylsilane compound, the said coating is subjected to a temperature comprised between 50 °C and 300 °C.

20 Preferably, the step of deposition provides that said sol is deposited by dipcoating or spray coating or spin-coating.

Preferably, said coating has a thickness comprised between 50 and 500nm.

Preferably, in said step of fluorination said coating is treated with a fluorinated compound by dipcoating or spray coating or spin-coating.

25 Preferably, said fluorinated compound is a fluorine alkyl silane.

A further object of the present invention is a metal component having a surface coating made by the method forming object of the present invention.

30 For a better understanding of the invention some embodiments are given below for illustrative and not limiting purposes.

#### EXAMPLES

Below is described a method for the treatment of metal surfaces according to a preferred embodiment of the present invention. For purposes of comparison the method was also applied on a ceramic surface and on a glass surface.

5 Always for purposes of comparison, the method was repeated on the same metal surfaces with the only change that in the step of preparation of the sol, isopropyl alcohol was used as a solvent instead of water.

10 In particular, the metal surface used is aluminum, and the ceramic surface used is porcelain stoneware and the glass surface is a sodium-calcium glass (Superfrost-Carlo Erba), all suitably degreased and pre-treated.

Below are reported the procedural steps of a preferred embodiment of the method object of the present invention.

15 Preparation of a sol comprising nano particles of alumina ( $Al_2O_3$ )

A colloidal suspension of alumina was prepared by peptization of aluminum tri-sec butoxide 0.5M in aqueous solution in the presence of nitric acid as the acid catalyst. The reactions of hydrolysis and condensation which lead to the formation of the sol occur keeping the system under stirring at 80 °C. The molar ratios of the sol are as follows:

aluminum tri-sec-butoxide:water:nitric acid = 1:100:0,07

#### Treatment

25 The surfaces takeb ubder examination (metal, ceramic and glass) were subjected to an operation of "dip coating" in the sol at room temperature. The operation of "dip coating" was realized with a speed of immersion and emersion of 120 mm/min and a soak time in the sol of 5 seconds. Once every single substrate has emerged from the sol, the solvent water is evaporated promoting the transition to the state of gel formed by nano particles of partially hydrolyzed  $Al_2O_3$ .

30 After the water evaporated, the substrates were heat treated in an oven at 400 °C for 10 minutes in order to remove organic residues and promote the densification of the formed coating.

To optimize the adhesion between the film and the surface, before the deposition the substrate is preferably cleaned and activated, for example by means of acid/basic attacks of the surfaces, heat treatment in air, machining or other.

5           Subsequently, to promote the reactivity of the surface with the formation of hydroxyl functional groups and to modulate the surface roughness on the nanometric scale, the treated surfaces were immersed in boiling water for 30 minutes and again thermally treated in an oven at 400 °C for 10 minutes.

10           Alternatively to the immersion in boiling water, part of metal surfaces have been treated with a steam jet for a time of 30 min to be subsequently heat treated in an oven at 400 °C for 10 minutes as described above.

15           Finally, the treated surfaces were subjected to a further operation of "dip coating" in a solution containing an alkylsilane compound. In particular, the compound used is a fluorine alkyl silane marketed by the company EVONIK with the code F8263.

The operation of "dip coating" has been realized with a speed of immersion and emersion of 120 mm/min and a soak time of 2 minutes.

20           Once emerged from the solution containing a fluorine alkyl silane compound, the treated surfaces were kept in a stove at 150 °C for 15 minutes in order to promote the chemical activation of the surface of the film of alumina.

25           This last step in an oven can also be avoided. Indeed, the cross linking of the polymer to the inorganic surface can also occur at room temperature with, of course, longer reaction times.

30           Each of the surfaces treated with the method described above has presented a totally transparent coating. This requirement ensures the bestowing of desired properties without compromising the aesthetic characteristics (color, appearance, etc.) on the surfaces involved in the treatment.

Test of hydrophobicity and olephobicity

The surfaces treated as described above were subjected to tests to verify the characteristics of: static hydrophobicity with water (contact angle with water ( $\theta_{st}$ )); dynamic hydrophobicity (expressed both as a minimum inclination angle of the surface for which the sliding starts of a water droplet of 30  $\mu$ l ( $\vartheta_{dn}$ ) and as hysteresis values ( $\vartheta_A - \vartheta_R$ )); oleophobicity (contact angle with paraffin oil ( $\theta_{ol}$ )); surface energy; static hydrophobicity after abrasion.

The abrasion was carried out by simulating the standardized operating procedure in the case of coated glass for buildings (UNI EN 1096-2, Appendix E: Test of resistance to abrasion). In particular, it has been used an abrasive felt rotating pad (thickness 10 mm  $\pm$  1 mm) with a diameter of 5,0 cm  $\pm$  0,5 cm and operated at a speed of 30 rounds/minute. In these conditions the felt pad was applied to the treated surfaces with a force equal to 4N and for a time equal to 30 seconds.

Table I shows the measured values of the above characteristics.

In Table I with SM1 it is indicated the metal surface treated with the step of immersion in boiling water; with SM2 it is indicated the metal surface treated with the step of applying a jet of steam; with SC it is indicated the treated ceramic surface; with SV it is indicated the treated glass surface; with SMalc it is indicated the treated metal surface having used isopropyl alcohol instead of water in the step of preparation of the sol.

TABLE I

	$\theta_{st}$ (°)	$\vartheta_{dn}$ (°)	$\vartheta_A - \vartheta_R$ (°)	$\theta_{ol}$ (°)	Surface energy (mN/m)	$\theta_{st}$ (°) after abrasion
SM1	172 $\pm$ 8	5	0,4	130 $\pm$ 3	0,34	168 $\pm$ 3
SM2	164 $\pm$ 8	6	1,0	121 $\pm$ 3	0,58	150 $\pm$ 4
SMalc	158 $\pm$ 4	10	6,2	110 $\pm$ 2	0,18	142 $\pm$ 3
SC	161 $\pm$ 13	47,5	1,4	121 $\pm$ 8	0,50	123 $\pm$ 6
SV	116 $\pm$ 1	48	1,1	102 $\pm$ 3	0,55	115 $\pm$ 1



The values reported in Table I show the unexpected and surprising effects of the method forming object of the present invention.

In fact, it can be seen both as the method is more effective when applied on metal surfaces rather than on ceramic surfaces or glass, and as the use of water in the step of preparation of the sol produces better effects than the use of an alcohol. This evidence is particularly surprising, emphasizing at the same time one of the most important advantages of the present invention. In fact, the present invention, not using organic solvents but water, not only provides getter features of hydrophobicity and oleophobicity to metal surfaces, but in an industrial dimension also involves enormous advantages in terms of safety, health of personnel, production management, environmental and economic sustainability.

It should also be highlighted how the values of dynamic hydrophobicity result to be surprisingly better than those obtained on the ceramic surface or on the glass surface.

The values of dynamic hydrophobicity which can be found on metal surfaces treated with the method of the present invention are such as to ensure high repulsion to dirt and contaminants of various kinds, also of biological origin, avoid in adverse environmental conditions the formation of ice and frost, effectively limiting phenomena of wear and corrosion, reduce, or even avoid, phenomena of fouling due to different agents, allow more favorable fluid dynamic conditions in the vicinity of the surface, with consequent gains in terms of energy.

In addition, the surfaces indicated as SM1 and SM2 were tested for freezing/unfreezing according to UNI EN 539-2 (2006). In particular, the surfaces SM1 and SM2 have been subjected to successive cycles of freezing/unfreezing in a climatic chamber in which continuous thermal excursions from +11 °C to -17 °C occurs and in which the step of unfreezing occurs by means of immersion in water and the subsequent phase of freezing occurs after the water has been drained from inside the climatic chamber. The number of cycles of freezing/unfreezing to which the surfaces SM1 and SM2 were subjected was equal to: 36, 119, 234,

345, 447. The evaluation of the resistance to cycles of freezing/unfreezing is based on the measures of static hydrophobicity (static contact angle) and dynamic hydrophobicity (hysteresis) after each of the said cycles of freezing/unfreezing. In Table II are reported the detected values of static contact angle and hysteresis.

Table II

Number of cycles	Static contact angle (°)	Hysteresis (°)
36	145 ± 3	12 ± 3
119	140 ± 2	12 ± 2
234	140 ± 5	11 ± 3
345	140 ± 5	19 ± 5
447	134 ± 3	7 ± 4

From the values reported in Table II it is possible to understand how even after cycles of freezing/unfreezing the surfaces treated with the method forming object of the present invention continue to show high characteristics of hydrophobicity.

The result obtained from tests of freezing/unfreezing is a further proof of the nanoscale structure of the coating confirmed by the observations made in a scanning electron microscope with field emission source (SEM-FEG), of the effectiveness of the method of the present invention and of its potential in the industry.

## CLAIMS

1. Method for the treatment of metal surfaces for bestowing thereon a high hydrophobicity and oleophobicity, both static and dynamic, characterised in that it comprises in succession:

5           - a step of depositing a coating of metal oxide, wherein on a metal surface a sol is deposited made from a colloidal suspension in water of one or more metal alkoxides  $M(OR)_n$  in the presence of an acid catalyst,

in which:

M is comprised in the group consisting of Al, Ti, Si, Y, Zn, Zr;

10           R is a linear or branched aliphatic chain  $C_1-C_4$ ;

and in which the transition of sol to gel is promoted by evaporation of said water from said coating;

- a step of consolidation, in which said coating is subjected to a temperature between 150 °C and 400 °C;

15           - a step of functionalization, in which said coating is treated with boiling water and/or steam for the realization of the hydroxyl groups and to modulate the surface roughness on the nanometric scale;

- a second step of consolidation, in which said coating is subjected to a temperature between 150 °C and 400 °C, and

20           - a step of superficial chemical activation, wherein said coating is treated with an alkylsilane compound.

2. Method for the treatment of metal surfaces according to claim 1, characterised in that in said deposition step, M is Al.

25           3. Method for the treatment of metal surfaces according to claim 1 or 2, characterised in that in said step of functionalization, said coating is treated with boiling water and/or steam for a time of at least 30 min.

4. Method for the treatment of metal surfaces according to any of the preceding claims, characterised in that in said step of superficial chemical activation said alkylsilane compound is fluorinated.

30           5. Method for the treatment of metal surfaces according to any of the preceding claims, characterised in that it comprises a third step of

consolidation, in which after being treated with an alkylsilane compound, said coating is subjected to a temperature between 50 °C and 300 °C.

6. Method for the treatment of metal surfaces according to any of the preceding claims, characterised in that the deposition step provides  
5 that said sol is deposited by means of dip coating or spray coating or spin-coating.

7. Method for the treatment of metal surfaces according to any of the preceding claims, characterised in that said coating has a thickness  
between 50 and 500nm.

10 8. Method for the treatment of metal surfaces according to any of the preceding claims, characterised in that in said step of superficial chemical activation said coating is treated with a fluorinated compound by means of dip coating or spray coating or spin-coating.

15 9. Method for the treatment of metal surfaces according to claim 8, characterised in that said fluorinated compound is a fluorine alkyl silane.

10. Metallic element having a surface coating made by the method according to any of the preceding claims.