EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:

(21) Application number: 04741765.4

(22) Date of filing: 09.06.2004

(51) Int Cl.:  
C09D 4/00 (2006.01)  
C09D 183/08 (2006.01)  
C09D 183/04 (2006.01)

(54) TWO-COMPONENT COATING SYSTEM FOR EQUIPPING SMOOTH SURFACES WITH EASY-TO-CLEAN PROPERTIES

2-K-LACK ZUR AUSRÜSTUNG VON GLATTEN OBERFLÄCHEN MIT REINIGUNGSLEICHTEN EIGENSCHAFTEN

SYSTEME DE PEINTURE A DEUX COMPOSANTS PERMETTANT DE CONFERER DES PROPRIETES D'E FACILITE D'E NETTOYAGE A DES SURFACES LISSES

(84) Designated Contracting States:  
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PL PT RO SE SI SK TR

(30) Priority: 05.08.2003 DE 10336544

(43) Date of publication of application: 03.05.2006 Bulletin 2006/18

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(56) References cited:  

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Description

| [0001] | The present invention relates to a new system for equipping surfaces with an oil, water, and dirt repellent coating. The invention further relates to a method of applying the new system to surfaces, and also to the use of the new system. |
| [0002] | Surfaces with oil, water, and dirt repellency properties are referred to in the everyday art as "easy to clean". |
| [0004] | The most suitable of the existing coating systems in terms of the easy-to-clean properties are those based on fluoroorganofunctional silanes and/or siloxanes. Systems described for producing an easy-to-clean coating include 100% systems, solvent-containing systems, emulsions, and aqueous systems. |
| [0005] | For the majority of users, however, the known easy-to-clean coatings are awkward and complicated to implement. |
| [0006] | For preparing such coating systems the ingredients, such as solvent, fluoroalkylsilane, water, and catalyst, whose safety aspects must be observed, are generally first weighed out into a suitable stirred vessel and reacted with stirring under control for several hours. The majority of end users are unable to carry out this complicated procedure. |
| [0007] | Generally the coatings must also be baked at high temperatures (DE 101 35 684), so making them unsuitable for certain applications, on windshields for example. Other products on the market, which do not have these disadvantages, nevertheless have a short storage stability or low abrasion resistance in coatings obtained from them (EP 0 846 715). |
| [0008] | Furthermore, some of the known coating materials contain toxic and environmentally objectionable solvents, such as halogenated hydrocarbons or benzine. |
| [0009] | Further, the application of an aqueous composition of a metal oxide, particularly a cerium oxide slurry, as a polishing agent for improving the adhesion properties of glass coatings has been known for a long time (Glass Technology, Vol. 12, No. 5, October 1971, pp. 131-135). |
| [0010] | It was an object of the present invention to provide a coating system for easy-to-clean applications which is convenient for the end user and at the same time is effective. A particular concern of the invention was to provide a system suitable for easy-to-clean coating on smooth surfaces. |
| [0011] | The object posed is achieved in accordance with the invention as specified in the claims. |
| [0012] | Thus it has been found, surprisingly, that an easy-to-clean coating can be applied effectively, durably, and in a simple and user friendly fashion to a surface, in particular a smooth surface, by using a special two-component system based on organofunctional silicon compounds if |
| [0013] | - the surface to be treated is cleaned and if desired pretreated, i.e., the cleaned surface is advantageously polished with a definitely abrasive, water-containing composition, the surface not being visibly optically roughened and the number of reactive surface groups being additionally increased, |
| [0014] | - the mixture is reacted for at least 2 minutes, preferably from 3 to 5 minutes, and is advantageously effective generally for up to 100 hours after the formulations of the two-component system have been combined, and |
| [0015] | - the mixture is reacted for at least 2 minutes, preferably from 3 to 5 minutes, and is advantageously effective generally for up to 100 hours after the formulations of the two-component system have been combined, and |
| [0016] | - thereafter the mixture is applied to the surface and reacted. |
| [0017] | The two-component system of the invention, composed of a substantially water-free formulation 1 and of a formulation 2, advantageously possesses a storage stability of more than one year. |
| [0018] | Furthermore, in accordance with the invention, the mixture to be applied to the surface to be treated, based on the two-component system, is readily amenable to the user, is activated generally after just 2 to 5 minutes, and advantageously is ready to use successfully for up to around 100 hours (this is also called the pot life). In addition to this an outstanding coating quality with substantially reproducible application properties is obtained. Moreover, coatings obtainable in accordance with the invention have outstanding easy-to-clean properties, but in particular outstanding hydrophobic and oleophobic properties. A particularly noteworthy feature is that coatings obtainable in accordance with the invention also have, unexpectedly, a comparatively high, excellent abrasion resistance. |
| [0019] | Thus it is possible with particular advantage in accordance with the invention to equip smooth surfaces, such as windshields, grass shower cubicles, glass facades one houses, and also wall tiles and sanitary ceramics with an easy-to-clean coating in an advantageous and durable fashion. |
| [0020] | In addition to these qualities, easy-to-clean coatings obtainable in accordance with the invention are notable for outstanding abrasion resistance. |
| [0021] | The present invention accordingly provides a two-component system for equipping surfaces with an oil, water,
and dirt repellent coating, the two-component system being composed of a formulation 1

including at least one fluoroalkylsilane of the general formula I

\[ R^1-Y_u-(\text{CH}_2)_2\text{Si}(\text{CH}_3)_q(R^2)_{3-q} \]  \hspace{1cm} (I)

in which \( R^1 \) is a linear, branched or cyclic and also mono-, oligo- or perfluorinated alkyl group having 1 to 13 carbon atoms or a mono-, oligo- or perfluorinated aryl group, \( Y \) is a \(-\text{CH}_2\), \( O \) or \( S \) group and \( u \) is 0 or 1, \( R^2 \) is a chlorine atom or an alkoxy group having 1 to 4 carbon atoms, and \( q \) is 0 or 1,

and/or at least one alkylsilane of the general formula II

\[ R^3\text{Si}(\text{CH}_3)_p(R^4)_{3-p} \]  \hspace{1cm} (II),

in which \( R^3 \) is a linear, branched or cyclic alkyl group having 1 to 18 carbon atoms, \( R^4 \) is a chlorine atom or an alkoxy group having 1 to 4 carbon atoms, and \( p \) is 0 or 1.

and a formulation 2,

wherein formulation 2 contains water, an organic or inorganic acid, and a solvent or diluent, and both formulations being mixed together shortly before application.

Generally speaking, the two-component system on the invention is obtained by combining the respective ingredients for formulation 1 and, separately, combining the respective ingredients for formulation 2. Formulations 1 and 2 of the two-component system are generally kept in two separate, preferably sealable, vessels until shortly before they are used, and can be stored thus at room temperature in outstanding fashion for a year or more without loss of activity.

Formulation 1 of the two-component system of the invention suitably includes at least one fluoroalkylsilane of the general formula I

\[ R^1-Y_u-(\text{CH}_2)_2\text{Si}(\text{CH}_3)_q(R^2)_{3-q} \]  \hspace{1cm} (I)

in which \( R^1 \) is a linear, branched or cyclic and also mono-, oligo- or perfluorinated alkyl group having 1 to 13 carbon atoms or a mono-, oligo- or perfluorinated aryl group, \( Y \) is a \(-\text{CH}_2\), \( O \) or \( S \) group and \( u \) is 0 or 1, \( R^2 \) is a chlorine atom or an alkoxy group having 1 to 4 carbon atoms, preferably methoxy, ethoxy, propoxy, isopropoxy, butoxy and/or 2-methoxyethoxy, and \( q \) is 0 or 1,

and/or at least one alkylsilane of the general formula II

\[ R^3\text{Si}(\text{CH}_3)_p(R^4)_{3-p} \]  \hspace{1cm} (II),

In which \( R^3 \) is a linear, branched or cyclic alkyl group having 1 to 18 carbon atoms, \( R^4 \) is a chlorine atom or an alkoxy group having 1 to 4 carbon atoms, and \( p \) is 0 or 1, preferably methoxy, ethoxy, propoxy, isopropoxy, butoxy and/or 2-methoxyethoxy.

In formulation 1 the amount of silane of the formula I and/or II is preferably from 0.1 to 60% by weight, based on formulation 1, more preferably from 0.5 to 10% by weight, very preferably from 1 to 4% by weight.

Formulation 1 of the invention of the present two-component system may also include at least one silane, preferably a silicic ester, of the general formula III

\[ \text{Si}(R^5)_4 \]  \hspace{1cm} (III)

in which groups \( R^5 \) are identical or different and \( R^5 \) is a chlorine atom or an alkoxy group having 1 to 4 carbon atoms, preferably methoxy, ethoxy, propoxy, isopropoxy, butoxy and/or 2-methoxyethoxy, and/or at least one oligomeric silicic ester, preferably an alkyl silicate, such as DYNASIL® 40, of the general formula IV

\[ (R^6)_n\text{SiO}_{(4-n)/2} \]  \hspace{1cm} (IV),

in which groups \( R^6 \) are identical or different and \( R^6 \) is a hydroxyl group or an alkoxy group having 1 to 4 carbon atoms, preferably methoxy, ethoxy, propoxy, isopropoxy, butoxy and/or 2-methoxyethoxy, and \( n \) is 1, 2 or 3. It being possible for such oligomeric silanes to possess suitably an average degree of oligomerization of from 2 to 40, preferably from 3 to 20, i.e., number of Si units per molecule, and to be present in linear, branched or cyclic form and also a three-dimensional structure,

and/or condensates and/or cocondensates of aforementioned silicon compounds of the formulae I to IV and/or mixtures of aforementioned silicon compounds.

In formulation 1 the amount silane of formula III and/or of a silicic ester of formula IV may suitably total \( \leq 10\% \)
by weight, based on formulation 1, and the amount is preferably from 0.001 to 2% by weight, more preferably from 0.1 to 0.6% by weight.

[0024] Preferred monomeric or oligomeric silicon compounds of formulae I, II, III or IV are: tridecafluoro-1,1,2,2-
tetraydrooctytrimethoxysilane, tridecafluoro-1,1,2,2-tetraydrooctytrimethoxysilane, n-propyltrimethoxysilane, n-propyl-
triethoxysilane, n-butyltriethoxysilane, n-butyltrimethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, n-octyltri-
ethoxysilane, n-octyltrimethoxysilane, isooctyltriethoxysilane, isooctyltrimethoxysilane, hexadecytrimethoxysilane, hex-
adecyltriethoxysilane, octadecytrimethoxysilane, octadecytriethoxysilane, tetraethoxysilane, and tetraethyl orthosili-
cate, ethyl polysilicate, such as DYNASIL® 40.

[0025] Formulation 1 of the two-component system of the invention may further contain at least one solvent or diluent
in an amount of from 40 to 99.9% by weight, based on formulation 1. Formulation 1 contains preferably from 90 to 99.5%
by weight of solvent and/or diluent, more preferably from 96 to 99% by weight.

[0026] Formulation 2 of the two-component system of the invention contains water preferably in an amount of from
0.001 ppm by weight to 99.9% by weight, based on formulation 2, more preferably from 1 to 99.9% by weight, very
preferably from 10 to 99.9% by weight.

[0027] Formulation 2 of the two-component system of the invention further suitably contains an organic or inorganic
acid, preferably in an amount of from 0.001 to 10% by weight, based on formulation 2. Particular preference is given in
this context to from 0.05 to 1% by weight, in particular from 0.1 to 0.2% by weight. Thus, for example, an acid of type
HXX where X is a carboxylic acid, such as formic acid, acetic acid, nitric acid, hydrochloric acid, sulfuric acid, and phosphoric acid. It is also possible here to use a chlorosilane which under hydrolysis conditions gives off HCl, an example being SiCl4.

[0028] Formulation 2 also contain a solvent or diluent in an amount of < 100% by weight, based on formulation 2. Preference is given in this context to from 0.01 to 90% by weight, more preferably from 0.1 to 20% by weight, solvent and/or diluent.

[0029] By way of example, but not exclusively, one formulation or both formulations of the two-component system of
the invention may comprise at least one chlorine-free solvent and/or diluent from the group of the alcohols, such as
methanol, ethanol, propanol, isopropanol, 1-methoxy-2-propanol or butanol, the glycols, such as butyl glycol, ethyl glycol,
propyl glycol or butyl glycol, the ethylene glycol ethers, the propylene glycol ethers, the ketones, such as acetone or
ethyl ketone, and the esters, such as ethyl acetate. Ethanol and isopropanol are used with particular preference.

[0030] Moreover, formulation 1 or 2 may contain a wetting aid, such as butyl glycol, 1-methoxy-2-propanol or a polyether
siloxane, alcohol alkoxylates, polyethers, and polyether modified trisiloxanes for example, in an amount of ≤ 10% by
weight, based on the respective formulation, preferably from 2 to 6% by weight.

[0031] Generally speaking, formulations 1 and 2 of the two-component system of the invention can be obtained simply
and economically by mixing the respective ingredients. Amounts (% by weight) specified here refer in each case to the
corresponding formulation, with the respective ingredients of one formulation together making not more than 100% by
weight.

[0032] The present invention likewise provides a method of equipping surfaces with an oil, water, and dirt repellent
coating, which comprises

- cleaning and if desired pretreating the surface,
- combining and mixing formulations 1 and 2 of the two-component system,
- reacting the mixture for at least 2 minutes, and
- thereafter applying the mixture to the surface.

[0033] The surface to be treated in accordance with the invention is suitably first precleaned, using a fat-dissolving
liquid, such as isopropanol, acetone or a conventional glass cleaner to clean or polish the surface, for example.

[0034] In addition the surface can also be pretreated. For carrying out a pretreatment in the method of the invention
preference is thus given to an abrasive, aqueous composition suitably comprising oxide particles having an average
diameter (d50) of less than 6 μm, preferably from 0.05 to 5 μm. Said abrasive compositions may be in the form of a
slurry or dispersion and, called metal oxide slurry hereinbelow. In the method of the invention it is particularly
preferred to use an aqueous or aqueous/alcoholic metal oxide slurry comprising preferably cerium oxide, aluminum
oxides, aluminum hydroxide, aluminum oxide hydroxide, magnesium oxide, iron oxides, titanium oxides, titanium dioxide
for example, metatitanic acid, zirconium oxides, tin dioxide, silicates, aluminum silicates for example, silicon oxides,
pyrogenic silica, such as AEROSIL®, for example, or precipitated silica, or a mixture of aforementioned oxides.

[0035] It is thus possible in accordance with the invention to equip surfaces, in particular smooth surfaces, such as
windshields, glass shower cubicles, glass facades on houses, and also wall tiles and sanitary ceramics with an abrasion-
resistant, easy-to-clean coating in an advantageous and durable fashion.

[0036] After cleaning and/or pretreatment, the mixture of the two-component system of the invention is suitably applied.
Application of the mixture formed from formulations 1 and 2 to the surface takes place preferably by spraying, brushing,
flowcoating, dipping, knife coating or polishing.

[0037] In the method of the invention the coating of the surface to be treated is carried out suitably at a (surface) temperature of from 0 to 50 °C, preferably from 5 to 25°C, the coating obtained is suitably crosslinked at room temperature. After the mixture formed from formulations 1 and 2 has been applied, however, it is also possible to carry out thermal aftertreatment. In addition. For instance, In order to accelerate complete crosslinking, it is possible to carry out heat treatment at a temperature of up to 330°C, preferably up to 280°C, in particular from 50°C to 150°C. For this purpose it is possible to use a fan, a heatable drying chamber, or a blow dryer for example.

[0038] The general procedure for the method according to the invention is that the substrate surface to be treated, generally a smooth substrate surface, is cleaned. If appropriate the surface can additionally be pretreated, i.e. activated. Formulations 1 and 2 of the two-component system are generally combined and mixed thoroughly, preferably by intense shaking or stirring, not until shortly before application, and at ambient temperature. For this purpose, formulations 1 and 2 can be adjusted in such a way that they can be mixed in a ratio of 1:1, advantageously both in volume terms and in weight terms. A mixture obtained in this way is suitably reacted for at least 2 minutes. This activating operation can also be assisted by intense shaking or stirring. Thereafter the mixture is applied to the surface. The pot life is generally up to one hour. Normally, however, the mixture can be employed effectively for up to 100 hours following combination. Furthermore, the coating obtained in this way can be thermally aftertreated.

[0039] The contact angle between a coating and a drop of liquid applied to it is a measure of the easy-to-clean properties of the surface and is generally determined in accordance with DIN EN 828. Coatings of the invention advantageously have a contact angle > 80°, preferably from 90 to 130°.

[0040] The coatings obtainable in accordance with the invention are accordingly distinguished by outstanding easy-to-clean properties and also by resistance to a wide variety of influences, such as weather, chemicals, solvents, and in particular by very good abrasion resistance.

[0041] The present invention hence also provides for the use of a two-component system of the invention for coating surfaces for equipping them with water, oil, and dirt repellency properties and also for improving the weather stability, the corrosion resistance, the abrasion resistance and scratch resistance, the chemical resistance, especially solvent resistance, and for protecting against graffiti, also referred to as antigraffiti effect.

[0042] The invention further provides for the use of a two-component system of the invention for the coating, likewise in accordance with the invention, of substrate surfaces, i.e., glass surfaces, windshields, window panes, glass facades, and shower cubicles, for example, ceramic surfaces, in particular glazes, metal surfaces, such as copper and aluminum, and polymer surfaces.

[0043] The present invention is illustrated by the following examples without being restricted in its subject-matter:

Comparative examples

[0044] The formulations as described in comparative examples 1 to 4 can be used directly for smooth surfaces.

Comparative example 1: DYNASYLAN® F 8263 from Degussa

[0045] The ready-to-use coating system based on activated fluoroalkylsilane possesses a storage stability of < 6 months.

[0046] Comparative example 2: CLEARSHIELD® from RITEC:

Coating system having the following composition from NMR analysis:

- about 10 mol% dimethylpolysiloxane
- about 32 mol% isopropanol
- about 58 mol% 1,1-dichloro-1-fluoroethane

Comparative example 3: CRYSTAL GUARD® from Chemetall:

[0047] 2.5-10 % triethoxyoctylsilane
1 - 2.5 % trimethoxyphenylsilane
> 50 % heptane
**Comparative example 4:** AQUAPERL® from PPG

[0048] composed of petroleum and a silane

**Inventive examples**

[0049] The following applies to examples 1 to 5:

[0050] For the preparation of a coating system first of all 2 formulations were prepared separately, using as mixing vessel a 11 glass bottle with screw closure in each case.

**Example 1:**

Formulation 1 (K-1):

[0051] 10.0 g of DYNASYLAN® F 8261 (tridecafluorooctyltriethoxysilane) were mixed with 240.0 g of isopropanol.

Formulation 2 (K-2):

[0052] 224.0 g of H₂O, 25.0 g of isopropanol, and 1.0 g of hydrochloric acid (37% strength) were mixed. Composition 2 possesses a melting point of - 4°C.

**Example 2:**

Formulation 1 (K-1):

[0053] 10.0 g of DYNASYLAN® F 8261 (tridecafluorooctyltriethoxysilane) and 1.5 g of DYNASIL® A (tetraethoxysilane) were mixed with 238.5 g of isopropanol.

Formulation 2 (K-2):

[0054] 224.0 g of H₂O, 25.0 g of isopropanol, and 1.0 g of hydrochloric acid (37% strength) were mixed.

**Example 3:**

Formulation 1 (K-1):

[0055] 10.0 g of DYNASYLAN® OCTEO (n-octyltriethoxysilane) were mixed with 240.0 g of isopropanol.

Formulation 2 (K-2):

[0056] 224.0 g of H₂O, 25.0 g of isopropanol, and 1.0 g of hydrochloric acid (37% strength) were mixed.

**Example 4:**

Formulation 1 (K-1):

[0057] 10.0 g of DYNASYLAN® F 8261 (tridecafluorooctyltriethoxysilane) were mixed with 240.0 g of ethanol.

Formulation 2 (K-2):

[0058] 124.0 g of H₂O, 125.0 g of isopropanol, and 1.0 g of hydrochloric acid (37% strength) were mixed. This formulation 2, with a melting point of - 4°C, has an extremely low sensitivity to frost.

**Example 5:**

Formulation 1 (K-1):

[0059] 10.0 g of DYNASYLAN® F 8261 (tridecafluorooctyltriethoxysilane) were mixed with 240.0 g of isopropanol.
Formulation 2 (K-2):

- 187.15 g of H₂O, 62.5 g of isopropanol, and 0.35 g of hydrochloric acid (37% strength) were mixed.

At application the following procedure was carried out for examples 1 to 5:

The blending of formulations K-1 and K-2 of the two-component system was carried out by the respective user: thus, prior to application, first 250 g of K-2 were added to 250 g of K-1 (examples 1 to 4) or 20 ml of K-2 were added to 20 ml of K-1 (example 5), the lid was closed tightly, and the mixture was shaken for 2 minutes. After 2 minutes the solution was ready to use.

The individual formulations (K-1 and K-2) were hitherto stable on storage for around 1 year, and application systems produced from them can be used advantageously for about 2 days.

From the formulations described above, comparative examples 1 to 3 and inventive examples 1 to 5, coatings were produced on glass. The solutions of inventive examples 1 to 5 were applied in each case after a pot life of 2 minutes (directly after mixing), 15 minutes, 1 hour, and 6 hours. Approximately 50 ml in each case of the total formulations were required for coating.

The use formulations, in other words a solution formed from the blending of K-1 and K-2 or the solutions of the comparative examples, were each applied to the glass surfaces in order to test the resistance of the formulation. The solutions of inventive examples 1 to 5 were applied in each case after a pot life of 2 minutes (directly after mixing), 15 minutes, 1 hour, and 6 hours. Approximately 50 ml in each case of the total formulations were required for coating.

The ready to-use formulations were distributed as a liquid film on the glass surface, rubbed using a paper cloth, and then polished, leaving no residue. A hydrophobic effect came about generally after just 5 minutes at room temperature.

Performance tests:

Abrasion resistance (under water or an aqueous 3% by weight aluminum silicate slurry) after a defined number of abrasion cycles with Glitzi sponge scourer, 1 kg applied weight, and water.

Repeat measurement of the static contact angles (CA) with DI water and contact angle measuring instrument G-15 from KRUSS, before and after each abrasion test.

Table 1:

<table>
<thead>
<tr>
<th>Comparative example</th>
<th>Unexposed Contact angle [°]</th>
<th>After 5000 abrasion cycles under water Contact angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>98</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>94</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>87</td>
<td>59</td>
</tr>
</tbody>
</table>

Table 2:

<table>
<thead>
<tr>
<th>Example</th>
<th>Pot life [min.]</th>
<th>0 (unexposed)</th>
<th>24 000</th>
<th>32 000</th>
<th>56 000</th>
<th>80 000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>95</td>
<td>94</td>
<td>92</td>
<td>83</td>
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<td>1</td>
<td>15</td>
<td>96</td>
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<td>77</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>98</td>
<td>93</td>
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<td>76</td>
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<td>360</td>
<td>96</td>
<td>94</td>
<td>87</td>
<td>85</td>
<td>87</td>
</tr>
</tbody>
</table>
The abrasion test using an abrasive solution for the abrasion machine further illustrates the scratch resistance or abrasion resistance of the coating. Therefore the following examples were tested with a 3% strength by weight aqueous aluminum silicate solution (the aluminum silicate particles have a size of about 80 μm). At contact angles of less than 80°, the coatings are no longer referred to as easy-to-clean, and therefore the measurements were discontinued when this figure was reached.

Table 3: Abrasion cycles using an aqueous 3% strength by weight aluminum silicate slurry as lubricant for the abrasion machine

<table>
<thead>
<tr>
<th>Example</th>
<th>Pot life [min.]</th>
<th>0 (unexposed)</th>
<th>24 000</th>
<th>32 000</th>
<th>56 000</th>
<th>80 000</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2</td>
<td>106</td>
<td>92</td>
<td>96</td>
<td>95</td>
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<td>360</td>
<td>103</td>
<td>89</td>
<td>90</td>
<td>80</td>
<td>77</td>
</tr>
</tbody>
</table>

Table: Abrasion cycles using an aqueous 3% strength by weight aluminum silicate slurry as lubricant for the abrasion machine

<table>
<thead>
<tr>
<th>Example</th>
<th>Pot life [min.]</th>
<th>0</th>
<th>4 000</th>
<th>6 000</th>
<th>8 000</th>
<th>10 000</th>
<th>12 000</th>
</tr>
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<td>comp. 1</td>
<td>15</td>
<td>97</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>comp. 2</td>
<td>15</td>
<td>90</td>
<td>65</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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Claims

1. A two-component system for equipping surfaces with an oil, water, and dirt repellent coating, the two-component system being composed of a formulation I:

   $$R^1\cdot Y\cdot (CH_2)_2 Si(CH_3)_q(R^3)_3-q$$  \( (I) \)

   in which R1 is a linear, branched or cyclic and also mono-, oligo- or perfluorinated alkyl group having 1 to 13 carbon atoms or a mono-, oligo- or perfluorinated aryl group, Y is a -(CH2)_2 O or S group and u is 0 or 1, R2 is a chlorine atom or an alkyl group having 1 to 4 carbon atoms, and q is 0 or 1, and/or at least one alkylsilane of the general formula II:

   $$R^3 Si(CH_3)_p(R^4)_3-p$$  \( (II) \).
in which $R^3$ is a linear, branched or cyclic alkyl group having 1 to 18 carbon atoms, $R^4$ is a chlorine atom or an alkoxy group having 1 to 4 carbon atoms, and $p$ is 0 or 1,
and a formulation 2,
wherein formulation 2 contains water, an organic or inorganic acid, and a solvent or diluent,
and both formulations being mixed together shortly before application.

2. The two-component system as claimed in claims 1,
wherein in formulation 1 the amount of silane of formula I and/or II is from 0.1 to 60\% by weight, based on formulation 1.

3. The two-component system as claimed in claim 1 or 2,
with formulation 1 including at least one silane of the general formula III

$$Si(R^5)_4 \quad (III)$$

in which groups $R^5$ are identical or different and $R^5$ is a chlorine atom or an alkoxy group having 1 to 4 carbon atoms,
and/or at least one oligomeric silicic ester of the general formula IV

$$R^6)_nSiO(4-n)/2 \quad (IV),$$
in which groups $R^6$ are identical or different and $R^6$ is a hydroxyl group or an alkoxy group having 1 to 4 carbon atoms, and $n$ is 1 or 2 or 3.

4. The two-component system as claimed in any one of claims 1 to 3,
wherein in formulation 1 the amount of silane of formula III and/or of a silicic ester of formula IV is $\leq$ 10\% by weight, based on formulation 1.

5. The two-component system as claimed in any one of claims 1 to 4,
wherein formulation 1 contains a solvent or diluent in an amount of from 40 to 99.9\% by weight, based on formulation 1.

6. The two-component system as claimed in any one of claims 1 to 5,
wherein formulation 2 contains water in an amount of from 0.001 ppm by weight to 99.9\% by weight, based on formulation 2.

7. The two-component system as claimed in any one of claims 1 to 6,
wherein formulation 2 contains an organic or inorganic acid in an amount of from 0.001 to 10\% by weight, based on formulation 2.

8. The two-component system as claimed in any one of claims 1 to 7,
wherein formulation 2 contains a solvent or diluent in an amount of $\leq$ 100\% by weight, based on formulation 2.

9. The two-component system as claimed in any one of claims 1 to 8,
comprising at least one solvent and/or diluent from the group of the alcohols, the glycols, the ethylene glycol ethers, the propylene glycol ethers, the ketones, and the esters.

10. The two-component system as claimed in any one of claims 1 to 9,
wherein formulation 1 or 2 contains a wetting agent in an amount of $\leq$ 10\% by weight, based on the respective formulation.

11. A method of equipping surfaces with an oil, water, and dirt repellent coating as set forth in any one of claims 1 to 10, which comprises

- cleaning and if desired pretreating the surface to be treated,
- combining and mixing formulations 1 and 2 of the two-component system,
- reacting the mixture for at least 2 minutes, and
- thereafter applying the mixture to the surface.

12. The method as claimed in claim 11,
wherein the surface is degreased and a metal oxide slurry is used for carrying out the pretreatment.

13. The method as claimed in claim 19 or 12, wherein coating is carried out at a temperature of from 0 to 50°C.

14. The method as claimed in any one of claims 11 to 13, wherein the mixture formed from formulations 1 and 2 is applied to the surface by spraying, brushing, flowcoating, dipping, knife coating or polishing.

15. The use of a two-component system as set forth in any of claims 1 to 10 for coating surfaces for equipping them with water, oil, and dirt repellency properties or for improving the weather stability, corrosion resistance, abrasion resistance and/or chemical resistance, or protecting against graffiti.

16. The use of a two-component system as claimed in claims 1 to 10 for coating glass surfaces, ceramic surfaces, metal surfaces or polymer surfaces.

Patentansprüche

1. Zweikomponentensystem zur Ausstattung von Oberflächen mit einer Öl, Wasser sowie Schmutz abweisenden Beschichtung, wobei das Zweikomponentensystem aus einer Zubereitung 1 die mindestens ein Fluoralkylsilan der allgemeinen Formel I

\[ R^1 \cdot Y \cdot (CH_2)_2Si(CH_3)_q(R^2)_{3-q} \] (I)

worin \( R^1 \) eine lineare, verzweigte oder cyclische sowie mono-, oligo- oder perfluorierte Alkylgruppe mit 1 bis 13 C-Atomen oder eine mono-, oligo- oder perfluorierte Arylgruppe darstellt, \( Y \) für eine -(CH_2)-, O- oder S-Gruppe steht und \( u \) gleich 0 oder 1 ist, \( R^2 \) für ein Chloratom oder eine Alkoxygruppe mit 1 bis 4 C-Atomen steht und q gleich 0 oder 1 ist, und/oder mindestens ein Alkylsilan der allgemeinen Formel II

\[ R^3Si(CH_3)_p(R^4)_{3-p} \] (II),

worin \( R^3 \) eine lineare, verzweigte oder cyclische Alkylgruppe mit 1 bis 18 C-Atomen darstellt, \( R^4 \) für ein Chloratom oder eine Alkoxygruppe mit 1 bis 4 C-Atomen steht und p gleich 0 oder 1 ist, und einer Zubereitung 2 besteht, wobei Zubereitung 2 Wasser, eine organische oder anorganische Säure und ein Löse- oder Verdünnungsmittel enthält, und beide Zubereitungen kurz vor der Anwendung zueinander gemischt werden.

2. Zweikomponentensystem nach Anspruch 1, bei dem in Zubereitung 1 der Gehalt an Silan gemäß Formel I und/oder II 0,1 bis 60 Gew.-%, bezogen auf die Zubereitung 1, beträgt.

3. Zweikomponentensystem nach Anspruch 1 oder 2, wobei Zubereitung 1 mindestens ein Silan der allgemeinen Formel III

\[ Si(R^5)_4 \] (III)

worin Gruppen \( R^5 \) gleich oder verschieden sind und \( R^5 \) für ein Chloratom oder eine Alkoxygruppe mit 1 bis 4 C-Atomen steht, und/oder mindestens einen oligomeren Kieselsäureester der allgemeinen Formel IV

\[ (R^6)_nSiO(4-n)/2 \] (IV),

worin Gruppen \( R^6 \) gleich oder verschieden sind und \( R^6 \) für eine Hydroxygruppe oder eine Alkoxygruppe mit 1 bis 4 C-Atomen steht und n gleich 1 oder 2 oder 3 ist, enthält.
4. Zweikomponentensystem nach einem der Ansprüche 1 bis 3, bei dem in Zubereitung 1 die Menge an Silan der Formel III und/oder einem Kieselsäureester der Formel IV $\leq 10$ Gew.-%, bezogen auf die Zubereitung 1, beträgt.

5. Zweikomponentensystem nach einem der Ansprüche 1 bis 4, bei dem die Zubereitung 1 ein Löse- oder Verdünnungsmittel in einer Menge von 40 bis 99,9 Gew.-%, bezogen auf die Zubereitung 1, enthält.

6. Zweikomponentensystem nach einem der Ansprüche 1 bis 5, bei dem die Zubereitung 2 Wasser in einer Menge von 0,001 Gew.-ppm bis 99,9 Gew.-%, bezogen auf die Zubereitung 2, enthält.

7. Zweikomponentensystem nach einem der Ansprüche 1 bis 6, bei dem die Zubereitung 2 eine organische oder anorganische Säure in einer Menge von 0,001 bis 10 Gew.-%, bezogen auf die Zubereitung 2, enthält.

8. Zweikomponentensystem nach einem der Ansprüche 1 bis 7, bei dem die Zubereitung 2 ein Löse- oder Verdünnungsmittel in einer Menge von $< 100$ Gew.-%, bezogen auf die Zubereitung 2, enthält.


10. Zweikomponentensystem nach einem der Ansprüche 1 bis 9, bei dem die Zubereitung 1 oder 2 ein Netzhilfsmittel in einer Menge von $\leq 10$ Gew.-%, bezogen auf die jeweilige Zubereitung, enthält.

11. Verfahren zur Ausstattung von Oberflächen mit einer Öl, Wasser sowie Schmutz abweisenden Beschichtung nach einem der Ansprüche 1 bis 10, bei dem man

- die zu behandelnde Oberfläche reinigt und gegebenenfalls vorbehandelt,
- die Zubereitungen 1 und 2 des Zweikomponentensystems zusammengibt und mischt,
- die Mischung mindestens 2 Minute reagieren lässt und
- danach die Mischung auf die Oberfläche aufbringt.

12. Verfahren nach Anspruch 11, bei dem man die Oberfläche entfettet und für die Durchführung der Vorbehandlung eine Metalloxidschlemme einsetzt.

13. Verfahren nach Anspruch 11 oder 12, bei dem man die Beschichtung bei einer Temperatur von 0 bis 50°C durchführt.

14. Verfahren nach einem der Ansprüche 11 bis 13, bei dem man die Mischung aus den Zubereitungen 1 und 2 durch Sprühen, Streichen, Fluten, Tauchen, Rakeln oder Einpolieren auf die Oberfläche aufbringt.

15. Verwendung eines Zweikomponentensystems nach den Ansprüchen 1 bis 10 für die Beschichtung von Oberflächen zur Ausstattung mit Wasser, Öl und Schmutz abweisenden Eigenschaften sowie zur Verbesserung der Wetterbeständigkeit, der Korrosionsbeständigkeit, der Abriebbeständigkeit und/oder der Chemikalienbeständigkeit sowie zum Schutz vor Graffiti.

16. Verwendung eines Zweikomponentensystems nach den Ansprüchen 1 bis 10 für die Beschichtung von Oberflächen aus Glas, aus Keramik, aus Metall oder aus Polymeren.
Revendications

1. Système à deux composants pour équiper des surfaces d’un revêtement oléophobe, hydrophobe, et antisolissure, le système à deux composants se composant de
   une formulation 1
   contenant au moins un fluoroalkylsilane ayant la formule générale I
   \[ R^1-Y_u-(CH_2)_2Si(CH_3)q(R^2)_{3-q} \] (I)
   dans laquelle R\(^1\) est un groupe alkyle linéaire, ramifié ou cyclique et aussi monofluoré, oligofluoré ou perfluoré comportant de 1 à 13 atomes de carbone ou un groupe aryle monofluoré, oligofluoré ou perfluoré, Y est un groupe -(CH\(_2\))\(_\text{o}S\) et u vaut 0 ou 1, R\(^2\) est un atome de chlore ou un groupe alkoxy comportant de 1 à 4 atomes de carbone, et q vaut 0 ou 1,
   et/ou au moins un alkylsilane ayant la formule générale II
   \[ R^3-Si(CH_3)p(R^4)_{3-p} \] (II)
   dans laquelle R\(^3\) est un groupe alkyle linéaire, ramifié ou cyclique comportant de 1 à 18 atomes de carbone, R\(^4\) est un atome de chlore ou un groupe alkoxy comportant de 1 à 4 atomes de carbone, et p vaut 0 ou 1,
   et une formulation 2,
   la formulation 2 contenant de l’eau, un acide organique ou inorganique, et un solvant ou un diluant,
   et les deux formulations étant mélangées l’une avec l’autre peu avant l’application.

2. Système à deux composants selon la revendication 1,
   dans lequel, dans la formulation 1, la quantité de silane ayant la formule I et/ou II est de 0,1 % à 60 % en poids, relativement à la formulation 1.

3. Système à deux composants selon la revendication 1 ou 2,
   la formulation 1 contenant au moins un silane ayant la formule générale III,
   \[ Si(R^5)_{4} \] (III)
   dans laquelle les groupes R\(^5\) sont identiques ou différents et R\(^5\) est un atome de chlore ou un groupe alkoxy comportant de 1 à 4 atomes de carbone,
   et/ou au moins un ester silicique oligomère ayant la formule générale IV,
   \[ (R^6)_{n}SiO(4-n)/2 \] (IV)
   dans laquelle les groupes R\(^6\) sont identiques ou différents et R\(^6\) est un groupe hydroxyle ou un groupe alkoxy comportant de 1 à 4 atomes de carbone, et n vaut 1 ou 2 ou 3.

4. Système à deux composants selon l’une quelconque des revendications 1 à 3,
   dans lequel, dans la formulation 1, la quantité de silane ayant la formule III et/ou d’un ester silicique ayant la formule IV est inférieure ou égale à 10 % en poids, relativement à la formulation 1.

5. Système à deux composants selon l’une quelconque des revendications 1 à 4,
   dans lequel la formulation 1 contient un solvant ou un diluant dans une quantité de 40 % à 99,9 % en poids, relativement à la formulation 1.

6. Système à deux composants selon l’une quelconque des revendications 1 à 5,
   dans lequel la formulation 2 contient de l’eau dans une quantité de 0,001 ppm en poids à 99,9 % en poids, relativement à la formulation 2.

7. Système à deux composants selon l’une quelconque des revendications 1 à 6,
   dans lequel la formulation 2 contient un acide organique ou inorganique dans une quantité de 0,001 % à 10 % en poids, relativement à la formulation 2.

8. Système à deux composants selon l’une quelconque des revendications 1 à 7,
dans lequel la formulation 2 contient un solvant ou un diluant dans une quantité strictement inférieure à 100 % en poids, relativement à la formulation 2.


10. Système à deux composants selon l’une quelconque des revendications 1 à 9, dans lequel la formulation 1 ou 2 contient un agent mouillant dans une quantité inférieure ou égale à 10 % en poids, relativement à la formulation respective.

11. Procédé pour équiper des surfaces d’un revêtement oléophobic, hydrophobe, et antisalissure selon l’une quelconque des revendications 1 à 10, lequel comprend

- le nettoyage et, si on le souhaite, le prétraitement de la surface à traiter,
- la combinaison et le mélange des formulations 1 et 2 du système à deux composants,
- le fait de laisser le mélange réagir pendant au moins 2 minutes, et
- après cela, l’application du mélange sur la surface.

12. Procédé selon la revendication 11, dans lequel la surface est dégraissée et une suspension d’oxyde métallique est utilisée pour réaliser le prétraitement.

13. Procédé selon la revendication 11 ou 12, dans lequel le revêtement est réalisé à une température de 0 à 50 °C.

14. Procédé selon l’une quelconque des revendications 11 à 13, dans lequel le mélange formé des formulations 1 et 2 est appliqué sur la surface par pulvérisation, au pinceau, par arrosage, par trempage, par enduction à la racle ou par polissage.

15. Utilisation d’un système à deux composants selon l’une quelconque des revendications 1 à 10 pour revêtir des surfaces afin de leur conférer des propriétés d’hydrophobie, d’oléophobic et de résistance à la salissure ou pour améliorer la stabilité aux intempéries, la résistance à la corrosion, la résistance à l’abrasion et/ou la résistance aux substances chimiques, ou pour protéger contre les graffitis.

REFERENCES CITED IN THE DESCRIPTION

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