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(54) Title: CERAMERS, THEIR APPLICATION AND USE

(57) Abstract: New ceramers, comprising aqueous suspensions of titanium oxide and/or zirconium oxide possibly in combination with other metals in the form of nanometric particles, are described.

CERAMERS, THEIR APPLICATION AND USE

Field of the invention

This invention relates to the field of coating materials (hereinafter coatings) for application to metal surfaces in general so as to give them anti-adherent, scratch-resistant and antibacterial properties.

The prior art

Nanotechnologies are now widely used in various sectors, for creating hybrid compositions known as *ceramers*. In the preparation process for these organic substances, as oligomers or polymers, they are intimately mixed with inorganic material (oxides, silicates), so as to obtain compositions that present typical properties of both ceramics (high temperature resistance, rigidity, etc.) and of plastics (plasticity, low-density, ease of transformation, etc.).

The production of these hybrids essentially takes place by means of sol-gel processes. This method allows formation of the inorganic network at temperatures significantly lower than the degradation temperatures of any organic components. The chemical reactions involved in this process may be hydrolysis and simultaneous condensation in solution (sol), of a metal alkoxide network-former until the formation of a three-dimensional network (gel), possibly combined with the polymerization reactions of unsaturated monomers. The incorporation during the formation of the inorganic network of an organic phase that can consist of both low-molecular weight product and of functionalised and non-functionalised oligomers and polymers therefore leads to the formation of true composite materials, wherein the organic and inorganic part constitute separate yet intimately interconnected phases. In the great majority of cases the inorganic component of these structures is represented by silica.

One field in which they are widely used in the polymer coating field where they are used to give the material flame-retardant, scratch-resistant, UV-resistance, gas-barrier properties, etc.

A new field of application of these materials, currently in strong expansion, is that of the treatment of metal surfaces, such as for example aluminium coating for the creation of pots and pans with non-stick properties for domestic use. Indeed, scientific studies have demonstrated that Teflon, normally used as an internal

coating for pans, saucepans, etc., has a high toxicity and various companies have therefore launched on the market items having a ceramer coating with non-stick properties to replace this material.

These are generally mixtures containing a silane composition, nanoparticles of silica, an organic acid, a composition from the family of polydimethylsiloxanes, water and a water-miscible solvent and in some cases a pigmenting component of an inorganic nature. The mixture that is obtained is deposited on the metal, which is followed by a drying phase. The coating can be achieved in both one and two layers, depositing a first layer of a mixture not containing the polydimethylsiloxane composition and subsequently one layer of the mixture containing the polydimethylsiloxane composition.

A coating of this type presents significant non-stick and scratch-resistant characteristics that can be associated with the fact that there is less danger associated with the use of the material The limitation of use of this material lies in the fact that if the metal surface does not present a sufficient degree of porosity and/or roughness, the coating has gripping difficulties and tends to manifest chalking phenomena (detachment of the ceramer film). This is linked to the low-elasticity of the ceramer, which cannot therefore be used on perfectly smooth surfaces.

Summary of the invention

Ceramers comprising titanium and/or zirconium oxide in the form of nanometric particles deriving from aqueous suspensions of titanium or zirconium oxide are described.

Detailed description of the invention

This invention allows the aforementioned drawbacks to be overcome thanks to new ceramers comprising titanium and/or zirconium oxide in the form of nanometric particles, deriving from aqueous suspensions of titanium or zirconium oxide.

The nanometric titanium oxide indeed succeeds in giving the ceramer itself an extremely high substrate adhesion, and therefore chalking resistance (anti-chalking), extremely high elasticity and excellent smoothness while the zirconium oxide gives the ceramer greater mechanical strength and scratch resistance.

According to a particular embodiment of the invention, the aqueous suspensions of titanium oxide in the form of nanometric particles as indicated above are those obtained as described in Patent Application EP 1 996 515 in the name of the same Applicant.

In short, as explained in greater detail in the abovementioned application, these are aqueous suspension of nanoparticles of titanium oxide obtained via of a process in which a titanium alkoxide is reacted by heating in water in the presence of a mineral acid and a non-ionic surfactant, and optionally by evaporating the solvent when obtaining the solid product is desired.

The titanium alkoxide used as the starting product in the present process may for example be chosen from the group consisting of titanium methoxide, ethoxide, normal-propoxide, iso-propoxide, normal-butoxide and isobutoxide, titanium isopropoxide being preferred.

The non-ionic surfactants used are tensioactive substances consisting of a non-polar portion and a non-ionizable polar functionality, ethers, esters, ether-esters, with Triton X-100 (TX-100) being particularly preferred.

As acid mineral, according to the invention, we mean for example an acid chosen from the group comprising: hydrochloric acid, nitric acid, sulphuric acid, perchloric acid, hydrobromic acid and hydriodic acid; halogen acids, and hydrochloric acid in particular, being preferred.

The molar titanium oxide/mineral acid ratio is of between 0.005 and 15, preferably between 5 and 6.

The reaction temperature is between 15°C and 95°C, preferably between 45°C and 55°C.

Reaction times are between 12 h and 72 h, preferably 24 hours.

The aqueous suspensions of zirconium oxide according to the invention can be prepared by dissolving in water a soluble zirconium salt (such as for example zirconyl nitrate or chloride) in a concentration range of between 0.1 and 0.6M, heating and boiling for at least 48h, thus obtaining a stable suspension of zirconium oxide nanoparticles. If necessary, an organic salt having a complexing function such as sodium citrate can be added (up to 10% by weight for example) so as to modify the pH of the suspension.

In addition, if desired, the suspension of zirconium nanoparticles, in particular those that have been subject to the above-described pH modification treatment, may be purified by filtration with osmosis membranes and possible reintegration of the water to maintain the concentration of nanoparticles in the suspension constant.

The ceramers according to the present invention are thus obtained starting from a mixture of a silane composition (trimethoxymethylsilane, triethoxymethylsilane, etc.) with an aqueous suspension of titanium and/or zirconium oxide nanoparticles, as described above, in the presence of an organic acid or an aqueous solution of NaOH (normally 1 – 15%), of a water-soluble organic solvent and possibly of a micrometric pigment or of an inorganic micrometric opacifier.

Of the organic acids, formic acid and acetic acid are preferred.

Ethyl alcohol and isopropyl alcohol can be preferably used as organic water-soluble solvent.

Lastly, possible examples of inorganic opacifier in micrometric form are: $ZrSiO_4$, CeO_2 TiO_2, while as regards the inorganic pigments, those known in the prior art can be used, preferably yellow, titanate-based pigments, blue cobalt and zinc illuminate-based pigments, brown and black iron, chromium and cobalt oxide-based pigments, iridescent Iriondin© based pigments produced by the company Merck).

The black pigment, if desire, is obtained with carbon black and carbon nanotubes.

To prepare the ceramers according to the invention, a suspension of titanium dioxide containing 6.0% nanoparticles by weight (10-40% by weight) obtained as previously described, is mixed with deionised water (10-30% by weight) and possibly isopropyl alcohol (0-10% by weight).

A silane is diluted into the mixture with stirring, preferably trimethoxymethylsilane or triethoxymethylsilane (35-70% by weight) and an aqueous sodium hydroxide solution at 10% (0-2% by weight) is then added so as to bring the pH to approximately 4.5. Finally, any pigment or opacifier (5-10% by weight) is added. After stirring, the coating is filtered and is ready for application to the desired surface.

It should also be noted that, where it should be deemed necessary, nanomaterials can be added to the composition, for example nano-Ag^0, nano-Cu^0 or nano-CeO_2, nano Al_2O_3, nanoferrites having the formula $M^{II}M^{III}_2O_4$, where $M^{II} = Fe^{2+}$, Co^{2+}, $M^{III}= Fe^{3+}$, nano-hydroxyapatite (HA), silica, capable of exercising their intrinsic action: antibacterial action, without UV light irradiation (Ag^0), thermo-catalytic action (CeO_2), increase in resistance (Al_2O_3) or magnetic action (nanoferrites).

These further materials can therefore be added to the ceramer composition mixture or can be present as dopants of the titanium oxide in suspension and in such cases can be obtained via the addition of a salt thereof in stage i) or alternatively in stage iii) of the process as described above, that will in this way lead to the formation of a TiO_2 dispersion doped with Ag^0, Cu^0 o CeO_2, Al_2O_3, nanoferrites, nano-hydroxyapatite.

The above-described metals in nanometric form can be obtained with the processes of the prior art.

One example of the obtainment process is described in patent application WO2010/100107, in this case operating in an aqueous environment at ambient pressure, heating to a reaction temperature of between 25 - 90°C with a microwave apparatus, placing a metal precursor salt in the reaction environment already heated to the reaction temperature and containing a reducing agent, a chelating agent and a catalyser.

The reducing agent is preferably chosen from; glucose, galactose, maltose, lactose, sucrose.

The chelating agent is preferably chosen from polyvinyl alcohol PVA, polyvinylpyrrolidone PVP, sodium lauryl sulphate, sodium dodecyl benzene sulphonate SDBS, cetyltrimethylammonium bromide CTAB, tetraoctylammonium bromide TOAB, triton X-100, polyethylene glycol PEG, ethylenediaminetetraacetic acid EDTA, starch, β-cyclodextrin β-CD, while the catalyser is chosen from: alkaline metal hydroxides, carbonates, ammonia, urea.

The chelating agent/metal ratio is of between 1 – 10, while the reducer/metal ratio is of between 1 and 2.

The catalyser/metal ratio is of between 1.4 and 7.9.

This application is used in the coating of various metal supports, such as aluminium, steel, brass, bronze, on glass surfaces, ceramics, on wood and on plastic.

Application takes place according to known procedures for the application of these products and can be carried out in such a way as to create one or more superimposed layers.

The nanometric Ag^0 is preferably applied as the last external layer so that it may better exercise its antibacterial action as described in example 26.

Various examples of the preparation of ceramers according to the invention and of ceramers also containing a composition from the polydimethylsiloxanes family, referring to applications of two-layer coatings, are provided below,

Example 1

Preparation of zirconium suspensions

(reference example)

a) 31 kg of a zirconyl nitrate solution is placed in a reactor together with 129 kg of purified water. The solution is brought to the boil and left in this condition for 48 h. The solution is left to cool and a nanoparticle zirconia suspension is recovered.

b) 45 kg of the suspension obtained are taken and stirred with a mechanical stirrer. 5 kg of sodium citrate are slowly added and then left to mix for 2 h.

c) 10 kg of the suspension obtained in step (b) are taken and placed in the tank of the diafiltration machine. Diafiltration is initiated eliminating the aqueous solution containing the dissolved salts, the suspension retained in the tank is recovered and the tank is topped up with water while maintaining the weight of the tank constant at 10 kg. The process ends when at least 10 kg of ultrapure water have been added. A nanoparticle zirconia suspension is recovered at the same concentration as the initial suspension.

d) 10 kg of the suspension of step (c) are taken and placed in the tank of the diafiltration machine. The aqueous solution that passes through the membrane is discarded and the tank is topped up with ultrapure water. The process ends when 5 kg of product remains in the tank. A nanoparticle zirconia suspension, having double the concentration of the original suspension, is recovered.

Example 2

Preparation of a suspension of titanium dioxide in nanometric form (reference example)

In a 2 l reactor, heated by diathermic oil circulating in the external sleeve, 5 g conc. HCl, 75 g of TX-100 and water are added until the weight of 750 g is reached. The temperature is brought to 50°C. Subsequently 50 g of $Ti[OCH(CH_3)_2]_4$ (TIP) are very quickly added and the formation of a white, flocky precipitate is immediately observed.

After 7 hours there is the formation of a very stable transparent sol.

Example 3 (two-layer ceramic coating, composition of the underlying layer)

37.77 g of a nanometric titanium dioxide suspension according to example 2 in aqueous solution brought to 6.0% by weight by means of further dilution in water, having pH of around 1, are mixed with 10.75 g of deionised water and with 5.10 g of isopropyl alcohol (IP97, Brentagg). The mixture is stirred and 37.20 g of trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are added. At this point, 2.07 g of an aqueous sodium hydroxide solution at 10% by weight is added so as to bring the pH to approximately 4.5. Finally, 7.10 g of white pigment (MMO 300, anatase, Tioxide) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 20-25 μm.

Example 4 (two-layer ceramic coating, composition of the underlying layer)

Some sodium citrate is added to the nanometric titanium dioxide produced according to example 2 to a pH of 5.5-6.0 and is thus subjected to dialysis using 500 kilo Dalton membranes so as to eliminate some of the salts and to concentrate the suspension to 16% in nanoparticle weight.

37.92 g of the nanometric titanium dioxide suspension in aqueous solution at 16.0% by weight, having a pH of around 5.5-6.0, are mixed with 15.76 g of deionised water. The mixture is stirred and 1.70 g of glacial acetic acid (Aldrich) are added, bringing the pH to approximately 4.5. 37.33 g of trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are subsequently added. Finally, 7.29 g of white pigment (MMO 300, anatase, Tioxide) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 20-25 μm.

Example 5 (two-layer ceramic coating, composition of the underlying layer)

Some sodium citrate is added to the nanometric zirconium produced according to example 1 to a pH of 5.5-6.0 and is thus subjected to dialysis using 500 kilo Dalton membranes so as to eliminate some of the salts and to concentrate the suspension to 10% in nanoparticle weight.

37.80 g of the nanometric titanium dioxide suspension in aqueous solution at 10% by weight, having a pH of around 5.5-6.0, are mixed with 15.71 g of deionised water. The mixture is stirred and 2.00 g of glacial acetic acid (Aldrich) are added, bringing the pH to approximately 4.5. 37.23 g of trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are subsequently added. Finally, 7.29 g of white pigment (MMO 300, anatase, Tioxide) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 20-25 μm.

Example 6 (two-layer ceramic coating, composition of the underlying layer)

37.77 g of a nanometric titanium dioxide suspension according to example 2 in aqueous solution brought to 6.0% by weight by means of further dilution in water, having pH of around 1, are mixed with 5.75 g of deionised water and with 5.10 g of isopropyl alcohol (IP97, Brentagg). The mixture is stirred and 42.20 g of trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are added. At this point, 2.07 g of an aqueous sodium hydroxide solution at 10% by weight is added so as to bring the pH to approximately 3.5. Finally, 7.10 g of white pigment (MMO 300, anatase, Tioxide) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 20-25 μm.

Example 7 (two-layer ceramic coating, composition of the underlying layer)

37.77 g of a nanometric titanium dioxide suspension according to example 2 in aqueous solution brought to 6.0% by weight by means of further dilution in water, having pH of around 1, are mixed with 2.75 g of deionised water and with 5.10 g of isopropyl alcohol (IP97, Brentagg). The mixture is stirred and 45.20 g of trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are added. At this point, 2.07 g of an aqueous sodium hydroxide solution at 10% by weight is added so as to bring the pH to approximately 3.5. Finally, 7.10 g of white pigment (MMO 300, anatase, Tioxide) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 20-25 μm.

Example 8 (two-layer ceramic coating, composition of the underlying layer)

37.77 g of a nanometric titanium dioxide suspension according to example 2 in aqueous solution brought to 6.0% by weight by means of further dilution in water, having pH of around 1, are mixed with 10.75 g of deionised water and with 5.10 g of isopropyl alcohol (IP97, Brentagg). The mixture is stirred and 37.20 g of trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are added. At this point, 2.07 g of an aqueous sodium hydroxide solution at 10% by weight is added so as to bring the pH to approximately 4.5. Finally, 7.10 g of white pigment (Zircobit MO/S, zircon, Colorobbia) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 20-25 μm.

Example 9 (two-layer ceramic coating, composition of the underlying layer)

Some sodium citrate is added to the nanometric titanium dioxide produced according to example 2 to a pH of 5.5-6.0 and is thus subjected to dialysis using 500 kilo Dalton membranes so as to eliminate some of the salts and to concentrate the suspension to 16.0% in nanoparticle weight.

19.36 g of the nanometric titanium dioxide suspension in aqueous solution at 16% by weight, having a pH of around 5.5-6.0, are mixed with 21.59 g of deionised water. The mixture is stirred and 51.14 g of triethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are added. Subsequently, 0.33 of glacial acetic acid (Aldrich) are added, bringing the pH to approximately 4.5. Finally, 7.58 of white pigment (MMO 300, anatase, Tioxide) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 20-25 μm.

Example 10 (two-layer ceramic coating, composition of the underlying layer)

Some sodium citrate is added to the nanometric zirconium produced according to example 1 to a pH of 5.5-6.0 and is thus subjected to dialysis using 500 kilo Dalton membranes so as to eliminate some of the salts and to concentrate the suspension to 10.0% in nanoparticle weight.

23.35 g of the nanometric zirconium dioxide suspension in aqueous solution at 10% by weight, having a pH of around 5.5-6.0, are mixed with 21.74 g of deionised water. The mixture is stirred and 46.71 g of trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are added. Subsequently, 0.83 of glacial acetic acid (Aldrich) are added, bringing the pH to approximately 4.5. Finally, 7.36 of

white pigment (MMO 300, anatase, Tioxide) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 20-25 μm.

Example 11 (two-layer ceramic coating, composition of the underlying layer)

The nanometric titanium dioxide produced according to example 2 is concentrated to a nanoparticle weight of 16%.

17.46% of a titanium dioxide suspension in aqueous solution at 16.0% by weight, having a pH or around 1.0, are mixed with 14.45 g of deionised water and with 6.85 g of isopropyl alcohol (IP97, Brentagg). The mixture is stirred and 49.95 g of trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are added. At this point, 1.76 g of an aqueous sodium hydroxide solution at 10.0% by weight are added so as to bring the pH to approximately 4.5. Finally, 9.54 g of white pigment (Zircobit MO/S, zircon, Colorobbia) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 20-25 μm.

Example 12 (two-layer ceramic coating, composition of the underlying layer)

Some sodium citrate is added to the nanometric titanium dioxide produced according to example 2 to a pH of 5.5-6.0 and is thus subjected to dialysis using 500 kilo Dalton membranes so as to eliminate some of the salts and to concentrate the suspension to 16.0% in nanoparticle weight.

19.36 g of the nanometric titanium dioxide suspension in aqueous solution at 16% by weight, having a pH of around 5.5-6.0, are mixed with 21.59 g of deionised water. The mixture is stirred and 51.14 g of triethoxymethylsilane (Xiameter OFS-6370 Silane, Dow Corning) are added. Subsequently, 0.33 of glacial acetic acid (Aldrich) are added, bringing the pH to approximately 4.5. Finally, 7.58 of white pigment (MMO 300, anatase, Tioxide) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 20-25 μm.

Example 13 (two-layer ceramic coating, composition of the underlying layer)

Some sodium citrate is added to the nanometric titanium dioxide produced according to example 2 to a pH of 5.5-6.0 and is thus subjected to dialysis using 500 kilo Dalton membranes so as to eliminate some of the salts and to concentrate the suspension to 16.0% in nanoparticle weight.

12.15 g of the nanometric titanium dioxide suspension in aqueous solution at 16% by weight, having a pH of around 5.5-6.0, are mixed with 13.15 g of deionised

water. The mixture is stirred and 66.52 g of triethoxymethylsilane (Xiameter OFS-6370 Silane, Dow Corning) are added. Subsequently, 0.21 of glacial acetic acid (Aldrich) are added, bringing the pH to approximately 4.5. Finally, 7.58 of white pigment (MMO 300, anatase, Tioxide) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 20-25 μm.

Example 14 (two-layer ceramic coating, composition of the underlying layer)

Some sodium citrate is added to the nanometric zirconium produced according to example 1 to a pH of 5.5-6.0 and is thus subjected to dialysis using 500 kilo Dalton membranes so as to eliminate some of the salts and to concentrate the suspension to 10% in nanoparticle weight.

23.35 g of the zirconium dioxide suspension in aqueous solution at 10% by weight, having a pH of around 5.5-6.0, are mixed with 21.74 g of deionised water. The mixture is stirred and 46.71 g of triethoxymethylsilane (Xiameter OFS-6370 Silane, Dow Corning) are added. Subsequently, 0.83 of glacial acetic acid (Aldrich) are added, bringing the pH to approximately 4.5. Finally, 7.36 of white pigment (MMO 300, anatase, Tioxide) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 20-25 μm.

Example 15 (two-layer ceramic coating, composition of the underlying layer)

37.77 g of a nanometric titanium dioxide suspension according to example 2 in aqueous solution brought to 6.0% by weight by means of further dilution in water, having pH of around 1.0, are mixed with 2.75 g of deionised water and with 5.10 g of isopropyl alcohol (IP97, Brentagg). The mixture is stirred and 45.20 g of trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are added. At this point, 2.07 g of an aqueous sodium hydroxide solution at 10% by weight is added so as to bring the pH to approximately 3.5. Finally, 7.10 g of Iriodin® 500 (10-60 μm, Merck) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 20-25 μm.

Example 16 (two-layer ceramic coating, composition of the underlying layer)

37.77 g of a nanometric titanium dioxide suspension according to example 2 in aqueous solution brought to 6.0% by weight by means of further dilution in water, having pH of around 1.0, are mixed with 2.75 g of deionised water and with 5.10 g of isopropyl alcohol (IP97, Brentagg). The mixture is stirred and 45.20 g of

trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are added. At this point, 2.07 g of an aqueous sodium hydroxide solution at 10% by weight is added so as to bring the pH to approximately 3.5. Finally, 7.10 g of carbon black (Xfast Schwarz 0066, Basf) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 20-25 μm.

Example 17 (two-layer ceramic coating, composition of the underlying layer)

37.77 g of a nanometric titanium dioxide suspension according to example 2 in aqueous solution brought to 6.0% by weight by means of further dilution in water, having pH of around 1.0, are mixed with 2.75 g of deionised water and with 5.10 g of isopropyl alcohol (IP97, Brentagg). The mixture is stirred and 45.20 g of trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are added. At this point, 2.07 g of an aqueous sodium hydroxide solution at 10.0% by weight is added so as to bring the pH to approximately 3.5. Finally, 7.10 g of a mixture comprising 87.5% by weight of yellow pigment (Zircobit MO/S, zircon, PGE6618, rutile, Colorobbia Spain) and 12.5% by weight of blue pigment (PGE61014, spinel, Colorobbia Spain) is added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 20-25 μm.

Example 18 (two-layer ceramic coating, composition of the overlying layer)

38.74 g of a nanometric titanium dioxide suspension according to example 2 in aqueous solution brought to 6.0% by weight by means of further dilution in water, having pH of around 1.0, are mixed with 11.0 g of deionised water and with 5.21 g of isopropyl alcohol (IP97, Brentagg). The mixture is stirred and 38.02 g of trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are added. At this point, 2.50 g of an aqueous sodium hydroxide solution at 10% by weight is added so as to bring the pH to approximately 4.5. Finally, 4.53 g of hydroxy-terminated polydimethylsiloxane (Xiameter PMX-0156 Silanol fluid, Dow Corning) are added. After stirring, the coating is filtered and applied to a steel plate onto which a pigmented ceramic layer having a thickness of 3-10 μm has been applied.

Example 19 (two-layer ceramic coating, composition of the overlying layer).

Some sodium citrate is added to the nanometric titanium dioxide produced according to example 2 to a pH of 5.5-6.0 and is thus subjected to dialysis using

500 kilo Dalton membranes so as to eliminate some of the salts and to concentrate the suspension to 16% nanoparticles by weight.

39.25 g of the nanometric titanium dioxide suspension in aqueous solution at 16.0% by weight, having a pH of around 5.5-6.0, are mixed with 16.31 g of deionised water. The mixture is stirred and 1.66 g of glacial acetic acid (Aldrich) are added, bringing the pH to approximately 4.5. 38.65 g of trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are subsequently added). 4.13 of a mixture comprising 1/3 by weight of hydroxy-terminated polydimethylsiloxane (Xiameter PMX-0156 Silanol fluid, Dow Corning) and 2/3 of isopropyl alcohol (IP97, Brentagg). After stirring, the coating is filtered and applied to a steel plate having a thickness of 3-10 μm.

Example 20 (two-layer ceramic coating, composition of the overlying layer).

Some sodium citrate is added to the nanometric titanium dioxide produced according to example 2 to a pH of 5.5-6.0 and is thus subjected to dialysis using 500 kilo Dalton membranes so as to eliminate some of the salts and to concentrate the suspension to 16.0% by weight of nanoparticles.

19.81 g of the nanometric titanium dioxide suspension in aqueous solution at 16% by weight, having a pH of around 5.5-6.0, are mixed with 22.10 g of deionised water. The mixture is stirred and 52.34 g of trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are added. Subsequently, 0.34 g of glacial acetic acid (Aldrich) are added, bringing the pH to approximately 4.5. Then 5.40 g of a mixture comprising 20% by weight of hydroxy-terminated polydimethylsiloxane (Xiameter PMX-0156 Silanol fluid, Dow Corning) and 80% by weight of isopropyl alcohol (IP97, Brentagg) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 3-10 μm.

Example 21 (two-layer ceramic coating, composition of the overlying layer)

Some sodium citrate is added to the nanometric zirconium produced according to example 1 to a pH of 5.5-6.0 and is thus subjected to dialysis using 500 kilo Dalton membranes so as to eliminate some of the salts and to concentrate the suspension to 10.0% nanoparticles by weight.

38.29 g of the zirconium dioxide suspension in aqueous solution at 10% by weight, having a pH of around 5.5-6.0, are mixed with 15.91 g of deionised water. The

mixture is stirred and 2.03 g of glacial acetic acid are added (Aldrich), bringing the pH to approximately 4.5. Subsequently, 37.70 g of trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are added. Subsequently, 4.05 g of isopropyl alcohol (IP97, Brentagg) and 2.03 g of hydroxy-terminated polydimethylsiloxane (Xiameter PMX-0156 Silanol fluid, Dow Corning) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 3-10 μm.

Example 22 (two-layer ceramic coating, composition of the overlying layer)

Some sodium citrate is added to the nanometric zirconium produced according to example 1 to a pH of 5.5-6.0 and is thus subjected to dialysis using 500 kilo Dalton membranes so as to eliminate some of the salts and to concentrate the suspension to 10.0% nanoparticles by weight.

23.88 g of the zirconium dioxide suspension in aqueous solution at 10% by weight, having a pH of around 5.5-6.0, are mixed with 22.24 g of deionised water. The mixture is stirred and 47.78 g of trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are added. Subsequently, 0.85 g of glacial acetic acid (Aldrich) are added, bringing the pH to approximately 4.5. Then 5.25 g of a mixture comprising 20% by weight of hydroxy-terminated polydimethylsiloxane (Xiameter PMX-0156 Silanol fluid, Dow Corning) and 80% by weight of isopropyl alcohol (IP97, Brentagg) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 3-10 μm.

Example 23 (single-layer ceramic coating)

Sodium citrate of up to pH 5.5-6.0 is added to the nanometric titanium dioxide produced according to example 2 and is therefore subjected to dialysis using 500 kilo membranes at 16% nanoparticles by weight.

37.42 g of the nanometric titanium dioxide suspension in aqueous solution at 16% by weight, having a pH of around 5.5-6.0, are mixed with 15.55 g of deionised water. The mixture is stirred and 1.68 g of glacial acetic acid (Aldrich) are added, bringing the pH to approximately 4.5. Subsequently 36.85 g of trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) and 1.31 g of hydroxy-terminated polydimethylsiloxane (Xiameter PMX-0156 Silanol fluid, Dow Corning) are subsequently added. Finally, 7.19 g of white pigment (MMO 300,

anatase, Tioxide) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 20-25 μm.

Example 24 Preparation of nanometre silver

2.76 of PVP k25 (Mwa=29000) are dissolved in 70 ml of water. Two solutions are separately prepared: one $AgNO_3$ 0.26 M (0.75 of salt in 17 ml of water) solution and one d(+)glucose 1.11 M (0.80 g of glucose in 4 ml of water) solution.

The glucose solution and 0.25 g of NaOH are added to the PVP solution which is then heated to 70°C in a microwave, setting a maximum power of 200W. When the system reaches 70°C, the aqueous $AgNO_3$ solution is injected and the reaction is allowed to proceed for 3 min. The molar ratios used are the following: $nPVP/nAgNO_3 = 5.5$; $nNaOH/nAgNO_3 = 1.4$; $nGlucose/nAgNO_3 = 1$.

With the addition of AgNO3 the solution immediately turns brown in colour, with intense yellow highlights. No precipitate is observed.

The concentration by weight of Ag^0 is equal to 0.5% by weight.

Example 25

Preparation of nanometre silver

5.90 g of PVP k30 (Mwa= 35,000-40,000) are dissolved in 76.39 ml of water and heated to 70°C. 0.53 g of NaOH flakes and 1.70 g of glucose powder (99.0% Cargill) are added to the solution. A solution obtained by dissolving 6.4 g of $AgNO_3$ in 9.08 g of di H_2O is added after 30'. It is then allowed to cool thus obtaining a 4.0% by weight Ag^0 nanoparticle suspension.

Example 26 (triple-layer ceramic coating, composition of all the layers)

a) Base: 37.77 g of a nanometric titanium dioxide suspension according to example 2 in aqueous solution brought to 6.0% by weight by means of further dilution in water, having pH of around 1, is mixed with 10.75 g of deionised water and with 5.10 g of isopropyl alcohol (IP97, Brentagg). The mixture is stirred and 37.20 g of trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are added. At this point, 2.07 g of an aqueous sodium hydroxide solution at 10% by weight is added so as to bring the pH to approximately 4.5. Finally, 7.10 g of white pigment (MMO 300, anatase, Tioxide) are added. After stirring, the coating is filtered and applied to a steel plate having a thickness of 20-25 μm.

b) Top: 38.74 g of a nanometric titanium dioxide suspension according to example 2 in aqueous solution brought to 6.0% by weight by means of further dilution in water, having pH of around 1.0, are mixed with 11.00 g of deionised water and with 5.21 g of isopropyl alcohol (IP97, Brentagg). The mixture is stirred and 38.02 g of trimethoxymethylsilane (Xiameter OFS-6070 Silane, Dow Corning) are added. At this point, 2.50 g of an aqueous sodium hydroxide solution at 10% by weight is added so as to bring the pH to approximately 4.5. Finally, 4.53 g of hydroxyl-terminated polydimethylsiloxane (Xiameter PMX-0156 Silanol fluid, Dow Corning) are added. After stirring, the coating is filtered and applied to a steel plate onto which a ceramic layer having a thickness of 3-10 μm has been applied as described in point (a).

c) a silver nanoparticle solution according to example 22 in aqueous solution at 4.0% by weight, is applied on top of the application of the top coat as described in point (b). The finish is thus treated at 120° for 30'.

Example 27

Preparation of a titanium dioxide suspension doped with silica in nanometric form (reference example)

In a 2l reactor heated by means of heated by diathermic oil circulating in the external sleevediathermic oil circulating in the external sleeve. 80 g of a nanometric suspension of TiO2 at 16% are placed together with 20 g of TEOS (tetraethoxysilane) and with 20g of ethyl alcohol and reacted for 2 hours. To the reaction batch thus obtained are added 400 g of ultrapure water. The system is vigorously stirred with the subsequent addition of 1000 g of a previously prepared solution, obtained by mixing 700 g of a nanometric nanoparticle silica suspension in water at 40% and 250 g of 0.1 molar sodium hydroxide. On conclusion of the addition a nanoparticle suspension having average dimensions of ca 20 nm and pH 9.4 is obtained.

EXAMPLE 28 (two-layer ceramic coating, composition of the underlying layer)

Component A:

Composite Ex. 27 69.6%

Ultrapure H2O purified by reverse osmosis 12.3%

Pigment d50 ca. 1 micron 18.1%

The components are mixed in the specified proportions with the aid of a ball mill so as to disperse the pigment in a correct manner.

The duration of the dispersion process is of 1 h.

At the end of the dispersion process the liquid product obtained is filtered using a steel, 1000-mesh filter and placed in drums.

Component B :

Methyltetraethoxysilane	79.0%
Glacial Acetic Acid	7.4%
Isopropanol	13.6%

The components, all in liquid state, are perfectly miscible and are therefore mixed and placed in drums. It is not necessary to filter the formulation.

The simplicity of the process also allows direct dosage of the components into the drum in which it is to be transported.

Example 29 (ceramic two-layer coating, composition of the overlying layer)

Component A:

Composite Ex. 27	85%
Ultrapure H2O purified by reverse osmosis	15%

The components, all in liquid state, are perfectly mixable and are therefore mixed and placed in drums. It is not necessary to filter the formulation.

The simplicity of the process also allows direct dosage of the components into the drum in which it is to be transported.

Component B:

Methyltetraethoxysilane	80.3%
Glacial Acetic Acid	5.1%
Isopropanol	9.5%
Polydimethylsiloxane	5.1%

The components, all in liquid state, are perfectly miscible and are therefore mixed and placed in drums. It is not necessary to filter the formulation.

The simplicity of the process also allows direct dosage of the components into the drum in which it is to be transported.

The products obtained are then applied as described in the foregoing examples.

CLAIMS

1. Ceramers comprising titanium oxide and/or zirconium oxide in the form of nanometric particles derived from aqueous suspensions of titanium oxide or zirconium oxide.

2. Ceramers according to claim 1, wherein said aqueous suspensions of titanium oxide in the form of nanometric particles are obtained via a process in which a titanium alkoxide is reacted by heating in water in the presence of a mineral acid and a non-ionic surfactant and optionally by evaporating the solvent when obtaining the solid product is desired.

3. Ceramers according to claim 2, wherein said alkoxides are chosen from: titanium methoxide, ethoxide, normal-propoxide, iso-propoxide, normal-butoxide, and isobutoxide.

4. Ceramers according to claim 2, wherein said mineral acid is chosen from: hydrochloric acid, nitric acid, sulphuric acid, perchloric acid, hydrobromic acid and hydriodic acid.

5. Ceramers according to claim 2, wherein said non-ionic surfactants are tensioactive substances consisting of a non-polar portion and a non-ionizable polar functionality, ethers, esters, ether-esters.

6. Ceramers according to claim 1, wherein said aqueous suspensions of zirconium oxide are obtained by dissolving a soluble zirconium salt in water and maintaining the boiling for at least 48 h.

7. Ceramers according to claims 1-6 also comprising nanomaterials, consisting of metals chosen from Ag^0, Cu^0, CeO_2 Al_2O_3, ferrites ($M^{II}M^{III}{}_2O_4$, M^{II} = Fe^{2+}, Co^{2+}, M^{III}= Fe^{3+}), hydroxyapatite (HA), silica or mixtures thereof.

8. Ceramers according to claim 7, wherein said metals are added to the mixture of ceramer composition or are present as dopants of the titanium oxide in suspension.

9. Process for preparing ceramers according to claims 1-8, wherein:

- a suspension of titanium dioxide in the form of nanoparticles, optionally in combination with the other nanometric metal particles as defined in claim 7, is mixed with deionized water and isopropyl alcohol.

- trimethoxymethylsilane is diluted in the mixture with stirring, and an aqueous sodium hydroxide solution is added thereto so as to bring the pH to approximately 4.5.

- the optional pigment and/or opacifier is added and, after stirring, the coating is filtered.

10. Use of ceramers according to claims 1-8 for application to metal surfaces.

11. Use according to claim 10, wherein said application consists of one or more superimposed ceramer layers.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2012/050997

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D5/00
ADD.

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

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)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 2010/110726 A1 (VAELINGE INNOVATION AB [SE]; BRUMMERSTEDT IVERSEN STEEN [DK]; RASMUSSE) 30 September 2010 (2010-09-30) claims; examples 1-11 page 3, line 15 - page 10, line 33 -----	1-11
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

International application No
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