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(54) Title: ELECTRODEPOSITION MATERIAL, PROCESS FOR PROVIDING A CORROSION-PROTECTIVE LAYER OF TiO₂ ON AN ELECTRICALLY CONDUCTIVE SUBSTRATE AND METAL SUBSTRATE COATED WITH A LAYER OF TiO₂

(57) Abstract: The present invention relates to an electrodeposition material for the electrochemical deposition of a corrosion-protective layer of TiO₂ on an electrically conductive substrate comprising a titanium compound, a complexing agent, water and optionally an accelerator, organic solvents, buffering agents and one or more additives, characterized in that the titanium compound is titanyl sulfate and/or titanyl oxalate, the complexing agent is selected from the group consisting of gluconic acid, gluconates, polyhydroxy-polycarbonic acids, ethylenediaminetetraacetate, methylglycinediacetate, iminodisuccinate, nitrilotriacetic acid and nitrilotriacetate, triethanolamine, phosphonic acid and phosphonates, poly-aspartic acid and polyaspartates, polyacrylic acid and polyacrylates and the accelerator is selected from the group consisting of hydroxylamines and their derivatives, nitrates, H₂O₂ and organic peroxides. The invention further relates to a process for providing a corrosion-protective layer of TiO₂ on an electrically conductive substrate and to a metal substrate coated with a layer of TiO₂.

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**Electrodeposition material, process for
providing a corrosion-protective layer of TiO₂ on an electrically
conductive substrate and metal substrate coated with a layer of TiO₂**

The present invention relates to an electrodeposition material for the electrochemical deposition of a corrosion-protective layer of TiO₂ on an electrically conductive substrate comprising a titanium compound, a complexing agent, water and optionally an accelerator, organic solvents, buffering agents and one or more additives. Such TiO₂ layer deposited electrochemically may serve as an appropriate primer layer for subsequent coating treatment (e.g. coating with organic materials, such as for instance lacquers, varnishes, paints, organic polymers, adhesives, etc.).

Further, according to a second aspect of the invention, the present invention relates to a process for providing a corrosion-protective layer of TiO₂ on an electrically conductive substrate by electrodeposition of a electrodeposition material comprising a titanium compound, a complexing agent, water and optionally an accelerator, organic solvents, buffering agents and one or more additives.

Finally, according to a third aspect of the invention, the present invention relates to a metal substrate coated with a layer of TiO₂ produced by the process of the invention.

The very common industrial task involves providing metallic or non-metallic substrates with a first coating, which has a corrosion-inhibiting effect and/or which constitutes a primer for the application thereon of a subsequent coating containing e.g. organic polymers. An example of such a task is the pre-treatment of metals prior to lacquer coating, for which various processes are available in the art. Examples of such processes are layer-forming or non-layer-forming phosphating, chromating or a chromium-free conversion treatment, for example using complex fluorides of titanium, zirconium, boron or silicon. Technically simpler to perform,

but less effective, is the simple application of a primer coat to a metal prior to lacquer-coating thereof. An example of this is the application of red lead. An alternative to so-called „wet“ processes are so-called „dry“ processes, in which a corrosion-protection or coupling layer is applied by gas phase deposition. Such processes are known, for example, as PVD or CVD processes. They may be assisted electrically, for example by plasma discharge.

A layer produced or applied in this way may serve as a corrosion-protective primer for subsequent lacquer coating. However, the layer may also constitute a primer for subsequent bonding. Metallic substrates in particular, but also substrates of plastics or glass, are frequently pre-treated chemically or mechanically prior to bonding in order to improve adhesion of the adhesive to the substrate. For example, in vehicle or equipment construction, metal or plastics components may be bonded metal to metal, plastics to plastics or metal to plastics. At present, front and rear windscreens of vehicles are as a rule bonded directly into the bodywork. Other examples of the use of coupling layers are to be found in the production of rubber/metal composites, in which once again the metal substrate is as a rule pre-treated mechanically or chemically before a coupling layer is applied for the purpose of bonding with rubber.

The conventional wet or dry coating processes in each case exhibit particular disadvantages. For example, chromating processes are disadvantageous from both an environmental and an economic point of view owing to the toxic properties of the chromium and the occurrence of highly toxic sludge. However, chromium-free wet processes, such as phosphating, as a rule, also result in the production of sludge containing heavy metals, which has to be disposed of at some expense. Another disadvantage of conventional wet coating processes is the actual coating stage frequently has to be preceded or followed by further stages, thereby increasing the amount of space required for the treatment line and the consumption of chemicals. For example, phosphating, which is used virtually exclusively in automobile construction, entails several cleaning stages, an

activation stage and generally a post-passivation stage. In all these stages, chemicals are consumed and waste is produced which has to be disposed of.

Although dry coating processes entail fewer waste problems, they have the disadvantage of being technically complex to perform (for example requiring a vacuum) or of having high energy requirements. The high operating costs of these processes are therefore a consequence principally of plant costs and energy consumption.

Further, it is known from the prior art that thin layers of metals compounds, for example oxide layers, may be produced electrochemically on an electrically conductive substrate. For example, the article by Y. Zhou and J. A. Switzer entitled „Electrochemical Deposition and Microstructure of Copper (I) Oxide Films“, Scripta Materialia, Vol. 38, No. 11, pages 1731 to 1738 (1998), describes the electrochemical deposition and microstructure of copper (I) oxide films on stainless steel. The article investigates above all the influence of deposition conditions on the morphology of the oxide layers; it does not disclose any practical application of the layers.

According to Blandeu et al. in Thin Solid Film, 42, 147 (1997) (Abstract), TiO₂-layers are obtained on a Ti-sheet from H₂SO₄ aqueous solution by anodic oxidation method. This is obtained at potentials below 50 V. However, this process can produce TiO₂ only on Ti-substrates by anodic oxidation.

According to Nogami et al. in J. Electrochem. Soc., 135, 3008 (1988) (Abstract), TiO₂ is obtained on a Ti-sheet from an aqueous solution containing 0.5 mol/L H₂SO₄ and 0.03 mol/L HNO₃ by anodic oxidation method (titanium anodization). Constant current is 1 mA/cm². The oxidation is performed in a cooled bath of 278 K to 283 K. However, this process can produce TiO₂ only on a Ti-substrate by anodic oxidation.

Further EP 1 285 105 B1 discloses a process for producing a coating comprising at least two layers on an electrically conductive surface wherein in a first stage a chromium-free layer of at least one X-ray crystalline inorganic compound of at least one metal is electrochemically deposited on an electrically conductive surface from a solution containing the metal in dissolved form. Besides many other metals titanium is disclosed.

According to the applicant's not yet published application PCT/EP2004/014140 corrosion-protective layers of TiO_2 are electrochemically deposited on a metal substrate from an electrodeposition material comprising titanyl sulfate or titanyl oxalate as titanium component, citrate or citric acid, tartaric acid and tartrates, lactic acid and lactates as chelating agents and hydroxylamines and their derivatives or nitrates as accelerators.

It is an object of the present invention to provide further electrodeposition materials for the electrochemical deposition of a corrosion-protective layer of TiO_2 on an electrically conductive substrate which result in TiO_2 layers providing excellent corrosion protection and which may serve as an excellent primer layer for subsequent coating treatment.

Surprisingly this object can be achieved by the use of titanyl sulfate and/or titanyl oxalate as the titanium component combined with a special combination of complexing agents and accelerators.

Subject-matter of the present invention therefore is an electrodeposition material as specified above characterized in that the titanium compound is titanyl sulfate and/or titanyl oxalate, the complexing agent is selected from the group consisting of gluconic acid, gluconates, polyhydroxy-polycarbonic acids, ethylenediaminetetraacetate, methylglycinediacetate, iminodisuccinate, nitrilotriacetic acid and nitrilotriacetate, triethanolamine, phosphonic acid and phosphonates, poly-aspartic acid and polyaspartates, polyacrylic acid and

polyacrylates and the accelerator is selected from the group consisting of hydroxylamines and their derivatives, nitrates, H_2O_2 and organic peroxides.

Preferred embodiments of the present invention are described in the dependent claims.

The electrodeposition material preferably comprises 0,05 to 0,3 mol/l titanium compound, 0,01 to 0,2 mol/l complexing agent and 0,02 to 0,2 mol/l accelerator.

The pH of the electrodeposition material preferably is 5 to 10, more preferably 6 to 9, most preferably 7,5 to 8,0.

The electrodeposition material preferably comprises a polymeric cationic binder in addition to the components specified above. As the cationic binder all electrodepositable resins known in the art may be used. Examples of such cationic film-forming resins include amine salt group-containing resins such as the acid-solubilized reaction products of polyepoxides and primary or secondary amines. Usually, these amine salt group-containing resins are used in combination with a blocked isocyanate curing agent. Besides amine salt group-containing resins, quaternary ammonium salt group-containing resins can also be employed. Examples of these resins are those which are formed from reacting an organic polyepoxide with a tertiary amine salt. Also, film-forming resins which cure via transesterification can be used. Further, cationic compositions prepared from Mannich bases can be used. From an electrodeposition material comprising the components of the present invention combined with a polymeric cationic binder a layer of TiO_2 and a resinous layer can be deposited simultaneously.

Preferably the electrodeposition material of the present invention comprises the polymeric cationic binder in an amount of 5 to 60 % by weight based on the total weight of the electrodeposition material.

The present invention further relates to a process for providing a corrosion-protective layer of TiO_2 on an electrically conductive substrate by electrodeposition of a electrodeposition material comprising a titanium compound, a complexing agent, water and optionally an accelerator, organic solvents, buffering agents and one or more additives, characterized in that the titanium compound is titanyl sulfate and/or titanyl oxalate, the complexing agent is selected from the group consisting of gluconic acid, gluconates, polyhydroxy-polycarbonic acids, ethylenediaminetetraacetate, methylglycinediacetate, iminodisuccinate, nitrilotriacetic acid and nitrilotriacetate, triethanolamine, phosphonic acid and phosphonates, poly-aspartic acid and polyaspartates, polyacrylic acid and polyacrylates and the accelerator is selected from the group consisting of hydroxylamines and their derivatives, nitrates, H_2O_2 and organic peroxides.

Preferably the electrodeposition material of claims 2 to 5 may be used in that process.

The electrodeposition preferably is carried out under the following conditions current density: 0,01 to 100, preferably 0,1 to 20, more preferably 0,5 to 10 mA/cm^2 , coating time: 0,15 to 20, preferably 0,5 to 10, more preferably 1 to 4 minutes, temperature: 0 to 100, preferably 20 to 60 °C, pH: 5 to 10, preferably 6 to 9, more preferably 7,5 to 8,0.

The electroconductive substrate preferably is selected from the group consisting of steel, especially cold rolled steel and galvanized steel, and aluminium.

The TiO_2 -layer is deposited on the electrically conductive substrate preferably within essentially uniform layer thickness, calculated as weight per unit area, in the range of from 0,01 to 3,5 g/m^2 , more preferably in the range of from 0,5 to 1,4 g/m^2 .

Illustrating the invention are the following examples which, however, are not to be considered as limiting the invention to their details. All parts and percentages in

the following examples as well as throughout the specification are by weight unless otherwise indicated.

Example 1

Ti Compound	0,14 mol/l Titanium potassium oxalate dihydrate (50 g/L)
Complexing Agent	0,03 mol/L Gluconic acid (12 g/L 50% by weight)
Accelerator	0,04 mol/L H ₂ O ₂ (5 g/L 30% by weight)
Process Parameters	pH=7,5; Current density 0,5 – 1 mA/cm ² ; t= 5 min; T=60°C; Substrate: galvanized steel

Example 2

Ti Compound	0,14 mol/l Titanium potassium oxalate dihydrate (50 g/L)
Complexing Agent	0,03 mol/L L(+)-Tartaric acid (5 g/L)
Accelerator	0,04 mol/L H ₂ O ₂ (5 g/L 30% by weight)
Process Parameters	pH=7,5; Current density 0,5 – 1 mA/cm ² ; t= 5 min; T=60°C; Substrate: galvanized steel

Preparing of the electrodeposition material:

The titanium compound was dissolved in deionized water (accelerated by heating to 30 to 50°C)

The Complexing Agent was added.

Thereafter, the accelerator and optionally the additives were added.

The pH was adjusted by the addition of KOH (0,5 to 1,5 mol/l) at a temperature of 45 to 60°C

Claims:

1. Electrodeposition material for the electrochemical deposition of a corrosion-protective layer of TiO_2 on an electrically conductive substrate comprising a titanium compound, a complexing agent, water and optionally an accelerator, organic solvents, buffering agents and one or more additives, characterized in that
the titanium compound is titanyl sulfate and/or titanyl oxalate,
the complexing agent is selected from the group consisting of gluconic acid, gluconates, polyhydroxy-polycarbonic acids, ethylenediaminetetraacetate, methylglycinediacetate, iminodisuccinate, nitrilotriacetic acid and nitrilotriacetate, triethanolamine, phosphonic acid and phosphonates, polyaspartic acid and polyaspartates, polyacrylic acid and polyacrylates and
the accelerator is selected from the group consisting of hydroxylamines and their derivatives, nitrates, H_2O_2 and organic peroxides.
2. Electrodeposition material according to claim 1, characterized in that it comprises 0,05 to 0,3 mol/l titanium compound, 0,01 to 0,2 mol/l complexing agent and 0,02 to 0,2 mol/l accelerator.
3. Electrodeposition material according to claim 1 or 2, characterized in that its pH is 5 to 10, preferably 6 to 9, more preferably 7,5 to 8,0.
4. Electrodeposition material according to claims 1 to 3, characterized in that it further comprises a polymeric cationic binder.
5. Electrodeposition material according to claim 4, characterized in that it comprises the polymeric cationic binder in an amount of 5 to 60 % by weight based on the total weight of the electrodeposition material.
6. Process for providing a corrosion-protective layer of TiO_2 on an electrically conductive substrate by electrodeposition of a electrodeposition material comprising titanium compound, a complexing agent, water and optionally an

accelerator, organic solvents, buffering agents and one or more additives, characterized in that

the titanium compound is titanyl sulfate and/or titanyl oxalate,

the complexing agent is selected from the group consisting of gluconic acid, gluconates, polyhydroxy-polycarbonic acids, ethylenediaminetetraacetate, methylglycinediacetate, iminodisuccinate, nitrilotriacetic acid and nitrilotriacetate, triethanolamine, phosphonic acid and phosphonates, polyaspartic acid and polyaspartates, polyacrylic acid and polyacrylates and

the accelerator is selected from the group consisting of hydroxylamines and their derivatives, nitrates, H_2O_2 and organic peroxides.

7. Process of claim 6 using the electrodeposition material of claims 2 to 5.
8. Process of claim 6 or 7, characterized in that the electrodeposition is carried out under the following conditions:
current density: 0,01 to 100, preferably 0,1 to 20, more preferably 0,5 to 10 mA/cm²
coating time: 0,15 to 20, preferably 0,5 to 10, more preferably 1 to 4 minutes
temperature: 0 to 100, preferably 20 to 60 °C
pH: 5 to 10, preferably 6 to 9, more preferably 7,5 to 8,0.
9. Process according to claims 6 to 8, characterized in that the electroconductive substrate is selected from the group consisting of steel, especially cold rolled steel and galvanized steel, and aluminium.
10. Process according to claims 6 to 9, characterized in that the TiO₂-layer is deposited on the electrically conductive substrate with an essentially uniform layer thickness, calculated as weight per unit area, in the range of from 0,01 to 3,5 g/m², preferably in the range of from 0,5 to 1,4 g/m².
11. A metal substrate coated with a layer of TiO₂ produced by the process of claims 6 to 10.