ANTICORROSION COATING COMPOSITION IN AQUEOUS DISPERSION COMPRISING AN ORGANIC TITANATE AND/OR ZIRCONATE

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ABSTRACT

The present invention relates to an anticorrosion coating composition for metallic parts based on particulate metal in aqueous dispersion comprising an organic titanate or zirconate compatible in aqueous phase or in organic phase, optionally a silane-based binder, and water. The present invention likewise relates to an anticorrosion coating of metallic parts obtained from the coating composition according to the invention as well as a metallic substrate provided with this anticorrosion coating. The invention additionally relates to an aqueous composition of C_{1-8} tetraalkyl titanate, intended for the preparation of a coating composition of a metallic substrate in aqueous dispersion, as well as the process for preparation of such a composition.
ANTICORROSION COATING COMPOSITION IN AQUEOUS DISPERSION COMPRISING AN ORGANIC TITANATE AND/OR ZIRCONATE

[0001] The present invention relates to an anticorrosion coating composition for metal parts, which is based on particulate metal in aqueous dispersion comprising an organic titanate or zirconate compatible in aqueous phase or in organic phase, optionally a silane-based binder, and water.

[0002] In the sense of the present invention, the expressions “titanate(s) compatible in organic phase” and “zirconate(s) compatible in aqueous phase” are understood as meaning every organic titanate and zirconate not compatible with water, that is to say not soluable in an aqueous composition and which in addition is sensitive to moisture and to water (hydrolysis reaction).

[0003] In the sense of the present invention, the expressions “titanate(s) compatible in aqueous phase” and “zirconate(s) compatible in aqueous phase” are understood as meaning every organic titanate and zirconate compatible with water, that is to say soluable or emulsifiable or dispersible in an aqueous composition. These are generally organic titanates and organic zirconates which have been stabilized by chelation. They are likewise named “chelated (organic) titanate(s)” and “chelated (organic) zirconate(s)”.

[0004] The organic titanates, as well as the organic zirconates, compatible in organic phase can be used in anhydrous compositions as catalysts, reticulating agents, surface-treatment agents, adhesion promoters or anticorrosion agents. However, these organic titanates, as well as the organic zirconates, have the disadvantage of being very sensitive to water and to moisture inasmuch as they are hydrolysed very rapidly. For example, in the case of the hydrolysis of tetra-n-butyl titanate, the following reactions occur:

\[
\text{Ti(OCH}_3)_4 + 4\text{H}_2\text{O} \rightarrow \text{Ti(OH)}_4 + 4\text{C}_2\text{H}_5\text{OH}
\]

[0005] 1) conversion of the organic titanate to hydrated titanium oxide \(\text{Ti(OH)}_4\):

\[
\text{Ti(OCH}_3)_4+4\text{H}_2\text{O} \rightarrow \text{Ti(OH)}_4+4\text{C}_2\text{H}_5\text{OH}
\]

[0006] 2) then, formation of titanium dioxide \(\text{TiO}_2\):

\[
\text{Ti(OH)}_4 \rightarrow \text{TiO}_2+2\text{H}_2\text{O}
\]

[0007] In order to avoid the formation of titanium dioxide, the titanates and zirconates compatible in organic phase must thus be employed under rigorously anhydrous conditions. Consequently, the preparation of anhydrous compositions comprising a titanate or a zirconate compatible in organic phase is accompanied by very constraining handling precautions if it is wished to avoid the hydrolysis of the organic titanate to titanium dioxide on contact with air, moisture or traces of water.

[0008] The moisture resistance of titanates or zirconates compatible in organic phase can be improved by substituting two alkoxy groups by chelating agents. These chelating agents contain functional groups containing oxygen or nitrogen atoms which happen to stabilize the organic titanate or zirconate. These organic titanates or zirconates in chelated form can likewise be soluble in water, preferably in the presence of a weak acid of the acetic acid type. For example, the patent U.S. Pat. No. 4,495,156 describes titanates in aqueous chelated form (TYZOR AA which is a titanate compatible in organic phase, TYZOR LA and TYZOR TE which are titanates compatible in aqueous phase) which allow the adhesion to a substrate of a composition comprising them to be improved.

[0009] The hydrolysis rate of the organic titanates and zirconates depends on the size and the complexity of the alkyl group (the more the size of the alkyl group increases, the more the hydrolysis rate decreases). This is the reason why the organic titanates and zirconates in chelated form are less sensitive to hydrolysis than the tetraalkyl titanates or the tetra-alkyl zirconates.

[0010] The patent U.S. Pat. No. 4,224,213 describes coating compositions comprising a short-chain alkyl silicate of formula \(\text{Si(OR)}_3\), a short-chain alkyl titanate or zirconate and zinc powder. This coating composition is reticulated by reaction of the silicate and the titanate with moisture from the air. The examples of this patent teach that the addition of silicate allows the moisture resistance of organic titanates to be improved. This coating composition is an organic composition which does not contain any water. The silicate, contrary to the silane, does not allow the adhesion of a composition comprising it to a substrate.

[0011] The patent EP 0 808 883 describes an aqueous coating composition based on particulate metal, free from chromium, intended to be applied to a substrate. This composition, once applied to the substrate, undergoes hardening in heat in order to provide the said substrate with protection against corrosion. In order to increase the corrosion resistance of this coated substrate, the coated substrate can optionally be coated with a supplementary layer comprising, for example, a silica material.

[0012] Surprisingly, the inventors have succeeded in incorporating into an aqueous composition organic titanates and/or organic zirconates, whether they are in chelated or non-chelated form and compatible or not compatible in aqueous phase. They have likewise discovered that the application to a metallic substrate of an aqueous coating composition based on particulate metal comprising organic titanates and/or organic zirconates allows the resistance to corrosion of the substrate to be improved. The anticorrosion results being sufficient, a substrate coated by such a composition does not need any supplementary layer of anticorrosion coating. In addition, a coating is obtained whose flexibility and resistance to shocks is of very good quality, which is particularly advantageous in the case of anticorrosion coating of screws.

[0013] The present invention relates to an anticorrosion coating composition of metal parts based on particulate metal in aqueous dispersion comprising, in the following proportions (percentages by mass):

[0014] an organic titanate and/or zirconate : 0.3 to 24%;

[0015] a particulate metal or a mixture of particulate metals 10 to 40%;

[0016] a silane-based binder : 1 to 25%;

[0017] water : q.s.p. 100%.

with the condition that the sum of the organic titanate and/or the organic zirconate and of the silane-based binder is between 5 and 25%.

[0018] The composition advantageously comprises 0.5 to 19% by weight, with respect to the total weight of the
composition, of organic titanate and/or zirconate and 1 to 20% by weight, with respect to the total weight of the composition, of silane-based binder, on condition that the sum of organic titanate and/or zirconate and silane-based binder is between 7 and 20% by weight, with respect to the total weight of the composition.

The organic titanates can be chosen from the group constituted by the organic titanates compatible in organic phase and the organic titanates compatible in aqueous phase.

The organic titanates compatible in organic phase are advantageously \( \text{C}_1-\text{C}_8 \) tetraalkyl titanates which can be represented by the following formula (I):

\[
\begin{align*}
R_1 & \quad O \\
R_3 & \quad O \\
R_2 & \quad Ti \\
R_4 & \quad O \\
\end{align*}
\]

in which \( R_1, R_2, R_3 \) and \( R_4 \) independently represent an optionally substituted \( \text{C}_1-\text{C}_8 \) alkyl radical. The \( \text{C}_1-\text{C}_8 \) tetraalkyl titanate is advantageously chosen from the group comprising tetraethyl titanate (TE, \( \text{Ti} (\text{OC}_2\text{H}_5)_4 \)), tetra-n-butylen titanate (\( \text{Ti} (\text{OC}_{2n}\text{H}_{2n+1})_4 \)) and ethylene glycol titanate (\( \text{OGT, Ti(OC}_2\text{H}_{5} (\text{CH}_2)_{n}\text{OH})_4 \)).

The organic titanates compatible in organic phase can likewise be organic titanates in chelated form not compatible with water. As examples of organic titanates in chelated form not compatible with water (compatible in organic phase) it is especially possible to cite those marketed by Dupont de Nemours under the name TYZOR® AA (titanium acetylactonate) or TYZOR® DC (dipropoxyl bisethylactoacetate titanate).

The titanates compatible in aqueous phase are advantageously chelated titanates, which can be represented by the following general formula (II):

\[
\begin{align*}
R & \quad O \\
X & \quad O \\
Y & \quad O \\
\end{align*}
\]

in which \( R \) and \( R' \) independently of one another represent an optionally substituted \( \text{C}_1-\text{C}_{10} \) alkyl radical, \( X \) and \( X' \) independently represent a functional group comprising an oxygen or nitrogen atom, and \( Y \) and \( Y' \) independently represent a hydrocarbon chain having 1 to 4 carbon atoms. \( X \) and \( X' \) advantageously represent an amino or lactate radical.

The organic titanate in chelated form compatible in aqueous phase is advantageously chosen from the group constituted by the triethanolamine titanates (TYZOR® TE and TEP marketed by Dupont de Nemours). As an example of organic titanates in chelated form compatible in aqueous phase, it is likewise possible to cite those marketed by Dupont de Nemours under the name TYZOR® LAZ (chelate of zirconate and lactic acid).

The particulate metal of the coating composition can be chosen from the group constituted by the metallic pigments such as aluminium, manganese, nickel, titanium,
stainless steel, zinc, their alloys, as well as their mixtures. The particulate metal is advantageously chosen from zinc and aluminium, as well as their alloys and their mixtures or their alloys with manganese, magnesium, tin or Galfan. The particulate metal present in the composition is advantageously in powder form, different homogeneous or heterogeneous geometric structures, especially spherical, lamellae, lenticular forms or other specific forms. The particulate metal advantageously has a particle size of less than 100 µm, even more advantageously less than 40 µm. When the particulate metal is an alloy or a mixture of zinc and aluminium, the aluminium can optionally be present in very small quantities, for example 1 to 5% by weight of the particulate metal, while at the same time nevertheless providing a coating of shiny appearance. Customarily, the aluminium represents at least 10% by weight of the particulate metal, thus the weight ratio of the aluminium to the zinc is of the order of 1:9. On the other hand, for reasons of economy, the aluminium does not represent more than approximately 50% by weight of the total zinc and aluminium, so that the weight ratio of the aluminium to the zinc can reach 1:1. The content of particulate metal of the coating composition will not exceed approximately 40% by weight of the total weight of the composition in order to maintain the best coating appearance and will customarily represent at least 10% by weight in order to obtain a shiny coating appearance.

The metal can contain in minor quantity one or more solvents, for example dipropylene glycol and/or white spirit, especially when the metal has been prepared in lamellar form. The particulate metals containing solvents are customarily used in the form of pastes, which can be used directly with other ingredients of the composition.

3 However, the particulate metals can likewise be used in a dry form in the coating composition.

The said silane-based binder advantageously comprises a silane carrying at least one hydrolysable function in hydroxyl function chosen from a C₁-C₄, preferably C₁-C₂, alkoxy radical. The silane advantageously carries three hydrolysable functions in hydroxyl function, preferably identical. The silane can additionally carry an epoxy (oxirane) function, which favours the reticulation and adhesion to the substrate. “Hydrolysable function in hydroxyl function” is understood as meaning any chemical function capable of reacting with water in order to be converted into a hydroxyl function —OH.

The silanes, in the compositions of the present invention, serve as binding agents. They likewise allow the coating bath to be stabilized against a harmful autogenous reaction. The silane seems to bind and passivate the particulate metal, so that the stability of the bath of the coating composition is improved. In addition, it allows the adhesion of the coating and its resistance to corrosion to be improved. The silane advantageously represents 3 to 20% by weight of the total weight of the composition.

The silane is advantageously easily dispersed in the aqueous medium and is, preferably, soluble in such a medium. The silane used is advantageously a silane with an epoxy function chosen from di- or trimethoxysilane with an epoxy function and di- or triethoxysilane with an epoxy function, as well as their mixtures, in particular like beta-

(3,4-epoxycyclohexyl)ethyl-trimethoxysilane, 4-(trimethoxysilyl)butane-1,2-epoxide or gamma-glycidoxypropyltrimethoxysilane.

If the organic titanate and/or zirconate used is an organic titanate and/or zirconate compatible in aqueous phase, the silane is advantageously introduced in quantities such that the proportions by mass, in the final composition, of organic titanate and/or zirconate compatible in aqueous phase:silane are between 95:5 and 5:95.

The anticorrosion composition can be prepared by mixing an organic phase, especially comprising the silane and the particulate metal, with an aqueous phase, especially comprising water and the silane. The organic titanate and/or zirconate compatible in aqueous phase can be introduced either into the aqueous phase or into the organic phase.

When the organic titanate and/or zirconate compatible in aqueous phase is introduced into the organic phase, it is possible to substitute the silane, normally present in the organic phase, by this organic titanate and/or zirconate.

The proportions by mass, expressed in dry parts, of organic titanate and/or zirconate and of silane are advantageously between 1:19 and 2:1, more advantageously between 1:16 and 1:8.

When the organic titanate and/or zirconate compatible in aqueous phase is introduced into the aqueous phase, it is advantageously first co-hydrolysed with the silane, normally present in the aqueous phase. The mass proportions of organic titanate and/or zirconate and of silane during the co-hydrolysis are advantageously between 0.12 and 0.36, expressed in dry parts. The optimal conditions for the co-hydrolysis are obtained for a ratio by mass of 0.24 titanate and/or zirconate for 1 silane, the ratios being expressed in dry parts.

In order to co-hydrolyse the organic titanate and/or zirconate and the silane, the organic titanate and/or zirconate is introduced into the silane, in an appropriate ratio, then the are co-hydrolysed by addition of 200 to 500% of water. It would appear that the duration of the co-hydrolysis reaction, that is to say the waiting time which follows the addition of the water, for example 30 or 90 min, does not have any influence on the properties of the co-hydrolysate obtained. If, instead of co-hydrolysing the silane and the organic titanate and/or zirconate compatible in aqueous phase, they are each hydrolysed separately, less satisfactory results are obtained in terms of product stability.

The addition of organic titanate and/or zirconate compatible in aqueous phase in the aqueous phase of the anticorrosion composition improves the anticorrosion properties of this composition more than if this titanate and/or zirconate had been added in the organic phase.

If the organic titanate and/or zirconate used is a titanate and/or zirconate compatible in organic phase, advantageously a C₅₋₆ tetraalkyl titanate and/or zirconate, the silane is advantageously introduced in quantities such that the proportions by mass, in the final composition, of titanate and/or zirconate compatible in organic phase:silane are between 60/40 and 5/95, advantageously between 50/50 and 10/90.
0043. The liquid medium of the coating composition is virtually always water or a combination of water and organic solvent. Other solvents can optionally be used but, preferably, only in very small quantities. Typically, the composition comprises 28 to 65% by weight of water, with respect to the total weight of the composition.

0044. According to an advantageous embodiment of the invention, the coating composition additionally comprises 1 to 30% by weight of organic solvent or of a mixture of organic solvents, with respect to the total weight of the composition. The organic solvents are advantageously chosen from the group constituted by the glycolic solvents such as the glycol ethers, in particular diethylene glycol, triethylene glycol and dipropylene glycol, the acetates, propylene glycol, polypropylene glycol, nitropropane, the alcohols, the ketones, propylene glycol methyl ether, 2,2,4-trimethyl-1,3-pentanediol isobutyrate (texanol), white spirit, as well as their mixtures.

0045. Dipropylene glycol is particularly advantageous, especially for reasons of economy and of protection of the environment. The quantity of solvents is advantageously lower than 25% by weight, even more advantageously lower than 15% by weight, with respect to the total weight of the composition. When the metallic particles have been prepared in lamellar form in a solvent, the particulate metal resulting can be in the form of paste. It can then form a part of the organic solvent of the coating composition according to the invention.

0046. According to an advantageous embodiment of the invention, the coating composition additionally comprises 0.1 to 7% by weight of molybdenum oxide, with respect to the total weight of the composition. The presence of molybdenum oxide MoO₃ in the anticorrosion coating composition allows control of the sacrificial protection exerted by the particulate metal in suspension in the composition to be improved. The molybdenum oxide MoO₃ is preferably used in an essentially pure orthorhombic crystalline form having a content of molybdenum of greater than approximately 60% by mass. Advantageously, the molybdenum oxide MoO₃ will be used in the anticorrosion compositions in the form of particles of dimensions of between 5 and 200 μm.

0047. According to an advantageous embodiment of the invention, the coating composition additionally comprises 0.5 to 10% by weight of a reinforcing agent of the anticorrosion properties of the composition chosen from the group constituted by yttrium, zirconium, lanthanum, cerium, praseodymium, in the form of oxides or of salts. The said reinforcing agent of the anticorrosion properties of the composition is advantageously yttrium oxide Y₂O₃ or cerium chloride. The said reinforcing agent of the anticorrosion properties of the composition can advantageously be combined with the abovementioned molybdenum oxide, in a mass ratio 0.25:1 reinforcing agent of the anticorrosion properties: MoO₃≤20, advantageously 0.5:1 reinforcing agent of the anticorrosion properties: MoO₃≤16, even more advantageously 0.5:1 reinforcing agent of the anticorrosion properties: MoO₃≤14.

0048. According to an advantageous embodiment, the coating composition additionally comprises a corrosion inhibitor pigment or corrosion inhibitor pigment such as the tri- or polyphosphate of aluminum, the phosphates, the molybdates, the silicates and borates of zinc, strontium, calcium, barium and their mixtures, at levels of the order of 0.2 to 4% by weight, with respect to the total weight of the coating composition.

0049. The coating composition according to the invention can additionally comprise a thickening agent. The thickening agent is advantageously chosen from the group constituted by the cellulosic derivatives such as hydroxyethylcellulose, hydroxyethylcellulose, hydroxy-propylcellulose, cellulose acetobutyrat, xanthan gum, the associative thickeners of polyurethane or acrylic type, the silicates such as the optionally treated silicates of magnesium and/or of lithium or the organopholic clays as well as their mixtures. The content of thickening agent is advantageously lower than 7% by weight with respect to the total weight of the composition, advantageously between 0.005 and 7% by weight with respect to the total weight of the composition.

0050. The coating composition according to the invention can likewise comprise a wetting agent, in a content advantageously lower than 4% by weight, more advantageously between 0.1 and 4% by weight, with respect to the total weight of the composition.

0051. The composition according to the invention can also comprise a pH stabilizer such as boric acid, metabolic acid, tetraboric acid and boron oxide or boron salts. The composition can comprise, with respect to the total weight of the composition, 0.1 to 10% by weight, advantageously 0.2 to 5% by weight and even more advantageously 0.4 to 0.8% by weight, of pH stabilizer.

0052. The composition can likewise comprise a pH modifier, generally chosen from the oxides and the hydroxides of alkali metals, advantageously lithium and sodium, the oxides and the hydroxides of metals belonging to groups IIA and IIB of the Periodic Table, such as the compounds of strontium, calcium, barium, magnesium and zinc. The pH modifier can likewise be a carbonate or a nitrate of the abovementioned metals.

0053. The composition according to the invention can likewise comprise phosphates, substituents containing phosphorus, such as ferrophosphate (pigment), non-organic salts, in quantities lower than 2% by weight with respect to the weight of the composition.

0054. The composition according to the invention is advantageous free from chromium VI. The composition can, however, contain chromium in soluble or non-soluble form such as, for example, metallic chromium or chromium of oxidation state III.

0055. The composition has good stability on storage, confirming the protective role of the silane towards a harmful reaction of the particulate metal with other ingredients of the composition. The silane likewise allows organic titanate to be stabilized.

0056. The present invention likewise relates to the coating obtained by application of the coating composition according to the invention to a substrate, advantageously by spraying, soaking-draining or soaking-centrifugation, the coating layer then being subjected to a baking operation, preferably at a temperature of between 180° C. and 350° C., for approximately 10 to 60 minutes, by supply of thermal energy, such as by convection or infrared, or for approximately 30 seconds to 5 minutes by induction.
[0057] According to an advantageous embodiment, the anticorrosion coating will result from an application operation involving, prior to a baking operation, a drying operation of the coated metallic parts, by supply of thermal energy, such as by convection, infra-red or induction, at a temperature of between 30 and 250°C, advantageously of the order of 70°C, in convection or in infrared for 10 to 30 minutes on line or for approximately 30 seconds to 5 minutes by induction. Before coating, it is judicious in the majority of cases to eliminate the foreign matter from the surface of the substrate, especially by cleaning and careful degreasing. Under these conditions, the thickness of the dry coating film thus applied is between 3 μm (11 g/m²) and 30 μm (110 g/m²) and preferably between 4 μm (15 g/m²) and 12 μm (45 g/m²), more particularly between 5 μm (18 g/m²) and 10 μm (40 g/m²).

[0058] The present invention also extends to the metallic substrate, preferably of steel or steel coated with zinc or with a base layer of zinc deposited by different application methods including mechanical deposition, to cast iron and aluminium, provided with an anticorrosion coating according to the invention applied with the aid of the abovementioned compositions.

[0059] The metallic substrate can be previously treated, for example by a treatment with chromate or with phosphate. Thus, the substrate can be pretreated in order to have, for example, a phosphate coating of iron in a quantity of 0.1 to 1 g/m² or a phosphate coating of zinc in a quantity of 1.5 to 4 g/m².

[0060] The present invention likewise relates to an aqueous composition of C₃₋C₆ tetraalkyl titanate and/or of C₃₋C₆ tetraalkyl zirconate, intended for the preparation of a coating composition for a metallic substrate in aqueous dispersion, prepared from a water-soluble organic solvent, a binder containing a silane carrying at least one hydrolysable function in hydroxyl function, a C₃₋C₆ tetraalkyl titanate and/or zirconate and water, in the following proportions (percentages by mass):

[0061] water-soluble organic solvent: 0 to 20%

[0062] silane-based binder: 20 to 50%

[0063] C₃₋C₆ tetraalkyl titanate and/or zirconate: 5 to 25%

[0064] water: 40 to 70%

[0065] In the context of the present invention, that is to say when the silane is found in the presence of C₃₋C₆ tetraalkyl titanate and/or zirconate, it would appear that the silane, in hydrolysable form before condensation, is capable of reacting with the abovementioned hydrated titanium oxide and/or zirconate in order to give a partially stable polymeric chain containing silicon and titanium and/or zirconium atoms. The silane then appears capable of stabilizing the C₃₋C₆ tetraalkyl titanate and/or zirconate. The chemical reactions could be written as follows:

[0066] (1) Hydrolysis of the silane:

\[ \text{R} - \text{Si(OH)}_3 + 3\text{H}_2\text{O} \rightarrow \text{R} - \text{Si(OH)}_2 + 3\text{OH} \]

[0067] (2) Conversion of the organic titanate or zirconate to hydrated titanium or zirconium oxide:

\[ \text{X} - (\text{OR})_4 + 4\text{H}_2\text{O} \rightarrow \text{X(OH)}_4 + 4\text{ROH} \]

[0068] (3) Reaction between the hydrated titanium or zirconium oxide and the hydrolysed silane:

\[ 2\text{R} - \text{Si(OH)}_2 + \text{X(OH)}_2 \rightarrow (\text{R} - \text{Si(OH)}_2)\{\text{X(OH)}_2\} \]

[0069] The silane and the organic titanate or zirconate thus associate in order to form the following partial polymeric chain:

\[ \text{X(OH)}_2 \rightarrow (\text{R} - \text{Si(OH)}_2)\{\text{X(OH)}_2\} \]

[0070] The reaction can continue and lead to the formation of a polymeric chain of the following formula (III):

\[ \text{ROH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \]

\[ \text{HO} - \text{Si} = \text{O} - \text{X} - \text{O} - \text{Si} = \text{O} - \text{OH} \quad \text{OH} \]

in which X represents Ti or Zr.

[0071] The water-soluble organic solvent is advantageously chosen from the group constituted by the glycolic solvents such as the glycol ethers, in particular diethylene glycol, triethylene glycol and dipropylene glycol, the acetates, propylene glycol, the alcohols, the ketones, propylene glycol ether, as well as their mixtures.

[0072] The silane carrying at least one hydrolysable function in hydroxyl function contained in the binder is advantageously chosen from a C₃₋C₆, even more advantageously C₃₋C₅, alkoxy radical. In addition, this silane advantageously carries an epoxy function. The said silane is preferably chosen from di- or trimethoxysilane with an epoxy function and di- or trimethoxysilane with an epoxy function, as well as their mixtures, in particular gamma-glycidoxypropyl-trimethoxysilane or beta-(3,4-epoxycyclohexyl)ethy1trimethoxysilane.

[0073] The C₃₋C₆ tetraalkyl titanate is advantageously chosen from the group comprising tert-ethyl titanate (TET), tetra-n-butyl titanate (T₄BT) and octylenglycol titanate (OGT) and the C₃₋C₆ tetraalkyl zirconate is chosen from the group comprising tert-n-propyl zirconate and tetra-n-butyl zirconate. In the aqueous composition, the ratio by mass of C₃₋C₆ tetraalkyl titanate and/or zirconate with respect to the silane is from 60/40 maximum, advantageously to 50/50 maximum, advantageously to 40/60 maximum.

[0074] The aqueous composition of C₃₋C₆ tetraalkyl titanate and/or C₃₋C₆ tetraalkyl zirconate can be prepared by mixing the silane-based binder, the said titanate or zirconate and, if necessary, the said water-soluble organic solvent, with a small quantity of water and then, by continuous progressive addition, at a low rate, of the remaining quantity of water.

[0075] In this stabilized form, the C₃₋C₆ tetraalkyl titanate and/or zirconate can, for example, then be introduced into a coating composition for a metallic substrate in aqueous phase, especially an anticorrosion coating composition based on particulate metal in aqueous dispersion, while limiting the formation of titanium dioxide.

[0076] The present invention finally relates to the use of the aqueous composition of C₃₋C₆ tetraalkyl titanate and/or C₃₋C₆ tetraalkyl zirconate defined above in pretreatment for coatings or adhesives (polyurethane, acrylic, rubber . . . ).
This composition can also be used in posttreatment as a sealer based on metallic particles. This composition can likewise be used in passivation treatment for substrates based on steel, zinc, aluminium or steel covered with a zinc-based coating. This composition can finally be used in an additive in order to improve the adhesion of the coatings or adhesives (polyurethane, acrylic, rubber, ...) in aqueous phase.

[0077] The examples below show ways in which the present invention can be employed, but do not limit the present invention in any fashion.

Preparation of the Test Panels:

[0078] Unless indicated otherwise, the test panels are typically stainless steel panels with a low carbon content, laminated in the cold. They can be prepared first of all by immersion in a cleaning solution. Then, the panels can be wiped with a cleaning pad and then rinsed with water and again immersed in the cleaning solution. After removal of the solution, the panels are rinsed with tap water and dried.

Application of the Coating to the Test Panels and Weight of the Coating:

[0079] The clean parts are coated, in a typical fashion, by dipping then into the coating composition, by withdrawing and draining the composition in excess of this, several times with a moderate stirring action, and then by immediate baking or drying at ambient temperature or pre-hardening at a moderate temperature until the coating is dry to the touch and thus baked. The coating weights (mg/cm²) are determined by comparative weighing before and after coating.

[0080] Test of Resistance to Corrosion (ISO 9227) and Estimation:

[0081] The resistance to corrosion of coated parts is measured by means of the standard salt projection test (saline mist) for paints and varnishes ISO 9227. In this test, the parts are placed in a chamber maintained at a constant temperature where they are exposed to a fine projection (mist) of a 5% saline solution during specific periods of time, rinsed with water and dried. The extent of corrosion of the parts tested can be expressed in the form of the percentage of red rust.

EXAMPLE 1

Composition Based on Organic Titanate Compatible in Organic Phase

[0082]

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Quantity (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPG (dipropylene glycol)</td>
<td>170.60</td>
</tr>
<tr>
<td>R40</td>
<td>13.00</td>
</tr>
<tr>
<td>R95</td>
<td>14.00</td>
</tr>
<tr>
<td>Dry aluminium</td>
<td>25.00</td>
</tr>
<tr>
<td>Zinc paste</td>
<td>245.00</td>
</tr>
<tr>
<td>Silane A-187</td>
<td>90.00</td>
</tr>
<tr>
<td>Dehydran</td>
<td>5.00</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>8.00</td>
</tr>
<tr>
<td>Boric acid</td>
<td>7.50</td>
</tr>
</tbody>
</table>

TABLE 1-continued

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Quantity (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo2bcennum oxide</td>
<td>8.00</td>
</tr>
<tr>
<td>Tn-BT (tetra-n-butyl titanate)</td>
<td>40.00</td>
</tr>
<tr>
<td>Kelzan</td>
<td>0.65</td>
</tr>
<tr>
<td>Water</td>
<td>373.30</td>
</tr>
</tbody>
</table>

1 Zinc in the form of paste to approximately 92% in white spirit
2 Alu Chromal VIII powder marketed by Eckart Werke
3 1-glycidoxypropyltrimethoxysilane (Crompton)
4 Sodium silicate (Rhodia)
5 Ethoxylated nonylphenol of R40 or of R95, supplier Oxolano SA (Brazil)
6 Kelzan/Rhodolop 23 from Rhodia
7 supplier DuPont de Nemours
8 supplier Lavollie
9 supplier Cognis SA

EXAMPLE 2

Composition Based on Organic Titanate Compatible in Organic Phase

[0083]

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Quantity (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPG (dipropylene glycol)</td>
<td>175.60</td>
</tr>
<tr>
<td>R40</td>
<td>13.00</td>
</tr>
<tr>
<td>R95</td>
<td>14.00</td>
</tr>
<tr>
<td>Dry aluminium</td>
<td>10.00</td>
</tr>
<tr>
<td>Zinc paste</td>
<td>260.00</td>
</tr>
<tr>
<td>Silane A-187</td>
<td>115.00</td>
</tr>
<tr>
<td>Silicate H300</td>
<td>10.00</td>
</tr>
<tr>
<td>Boric acid</td>
<td>9.50</td>
</tr>
<tr>
<td>Mo2bcennum oxide</td>
<td>10.00</td>
</tr>
<tr>
<td>Tn-BT (tetra-n-butyl titanate)</td>
<td>60.00</td>
</tr>
<tr>
<td>Kelzan</td>
<td>0.65</td>
</tr>
<tr>
<td>Water</td>
<td>317.25</td>
</tr>
</tbody>
</table>

TABLE 3

<table>
<thead>
<tr>
<th>Duration of bath (days)</th>
<th>Density coating layer (g/m²)</th>
<th>Resistance to saline mist (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>23.6</td>
<td>2064</td>
</tr>
<tr>
<td>10</td>
<td>19.8</td>
<td>1944</td>
</tr>
<tr>
<td>15</td>
<td>20.1</td>
<td>1752</td>
</tr>
</tbody>
</table>
EXAMPLE 3
Composition Based on Organic Titanate Compatible in Organic Phase

TABLE 4

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Quantity (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPG (dipropylene glycol)</td>
<td>153.50</td>
</tr>
<tr>
<td>R40</td>
<td>13.00</td>
</tr>
<tr>
<td>R95</td>
<td>14.00</td>
</tr>
<tr>
<td>Dry aluminium</td>
<td>10.00</td>
</tr>
<tr>
<td>Zinc paste</td>
<td>260.00</td>
</tr>
<tr>
<td>Silane A-187</td>
<td>95.00</td>
</tr>
<tr>
<td>Silicate H300</td>
<td>10.00</td>
</tr>
<tr>
<td>Boric acid</td>
<td>9.50</td>
</tr>
<tr>
<td>Molybdenum oxide</td>
<td>10.00</td>
</tr>
<tr>
<td>TET (tetraethyl titanate)</td>
<td>40.00</td>
</tr>
<tr>
<td>Kelzan</td>
<td>0.65</td>
</tr>
<tr>
<td>Water</td>
<td>379.35</td>
</tr>
</tbody>
</table>

supplied by DuPont de Nemours

EXAMPLE 4
Process for Preparation of an Aqueous Composition of Tetrabutyl Titanate, Organic Titanate Compatible in Organic Phase

TABLE 5

<table>
<thead>
<tr>
<th>Duration of bath (days)</th>
<th>Density coating layer (g/m²)</th>
<th>Resistance to saline mist (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>20.8</td>
<td>456</td>
</tr>
<tr>
<td>10</td>
<td>19.7</td>
<td>360</td>
</tr>
</tbody>
</table>

EXAMPLE 5
Process for Preparation of an Aqueous Composition of Organic Titanate Compatible in Organic Phase

TABLE 6

<table>
<thead>
<tr>
<th>Composition according to the invention A (g/kg)</th>
<th>Composition of the prior art B (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPG</td>
<td>160.60</td>
</tr>
<tr>
<td>Silane A 187</td>
<td>90.00</td>
</tr>
<tr>
<td>Water</td>
<td>383.30</td>
</tr>
<tr>
<td>Tetrabutyl titanate</td>
<td>40.00</td>
</tr>
<tr>
<td>Dry aluminium lamellae</td>
<td>25.00</td>
</tr>
<tr>
<td>Zinc paste</td>
<td>245.00</td>
</tr>
<tr>
<td>Molybdenum oxide</td>
<td>8.00</td>
</tr>
<tr>
<td>R40</td>
<td>13.00</td>
</tr>
<tr>
<td>R95</td>
<td>14.00</td>
</tr>
<tr>
<td>Dehydran</td>
<td>5.00</td>
</tr>
</tbody>
</table>
The characteristics of composition A are reported in table 7 below:

**TABLE 7**

<table>
<thead>
<tr>
<th>Duration of the bath</th>
<th>Adhesion</th>
<th>Appearance</th>
<th>Density</th>
<th>% Sold</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>72 hours</td>
<td>excellent</td>
<td>very good</td>
<td>7.7</td>
<td>36.1</td>
<td>54°C (C.)</td>
</tr>
<tr>
<td>5 days</td>
<td>excellent</td>
<td>very good</td>
<td>7.9</td>
<td>37.0</td>
<td>64°C (C.)</td>
</tr>
<tr>
<td>10 days</td>
<td>excellent</td>
<td>very good</td>
<td>8.0</td>
<td>38.3</td>
<td>70°C (C.)</td>
</tr>
<tr>
<td>15 days</td>
<td>excellent</td>
<td>very good</td>
<td>7.9</td>
<td>40.0</td>
<td>83°C (C.)</td>
</tr>
<tr>
<td>20 days</td>
<td>excellent</td>
<td>very good</td>
<td>7.8</td>
<td>41.9</td>
<td>121°C (C.)</td>
</tr>
<tr>
<td>25 days</td>
<td>excellent</td>
<td>very good</td>
<td>8.1</td>
<td>39.4</td>
<td>90°C (C.)</td>
</tr>
</tbody>
</table>

The resistance of the two compositions to the saline mist is compared. The resistance values to the saline mist measured are summarized in table 8 below.

**TABLE 8**

<table>
<thead>
<tr>
<th>Composition according to the invention A</th>
<th>Composition of the prior art B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density coating layer (g/m²)</td>
<td>Resistance to saline mist (hours)</td>
</tr>
<tr>
<td>16</td>
<td>704</td>
</tr>
<tr>
<td>20</td>
<td>880</td>
</tr>
<tr>
<td>24</td>
<td>1056</td>
</tr>
<tr>
<td>28</td>
<td>1232</td>
</tr>
<tr>
<td>32</td>
<td>1408</td>
</tr>
<tr>
<td>36</td>
<td>1584</td>
</tr>
</tbody>
</table>

Satisfactory results for resistance to the saline mist are thus observed for the coating composition according to the invention. In fact, for a layer density of 24 g/m², it is possible to attain a duration of resistance to the saline mist of greater than 1000 hours whereas for a composition without organic titanate the duration of resistance to the saline mist is only 312 hours. The addition of organic titanate allows the corrosion resistance of the coating to be at least tripled under these conditions.

**EXAMPLE 9**

Composition Based on Organic Titanate Compatible in Organic Phase

The addition of small quantities of organic titanate (10, 20 or 30 g/kg) allows the quantity of silane and of molybdenum oxide to be introduced to be decreased, which allows a limitation of the costs, while conserving good anticorrosion results.

In the following examples of compositions (table 9), the quantity of silane is reduced to 44% by weight and the quantity of molybdenum oxide is reduced to 20% by weight, with respect to the quantities conventionally introduced into anticorrosion coating compositions.

**TABLE 9**

<table>
<thead>
<tr>
<th>Composition C (g/kg)</th>
<th>Composition D (g/kg)</th>
<th>Composition E (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPG</td>
<td>160.60</td>
<td>160.60</td>
</tr>
<tr>
<td>Silane A 187</td>
<td>50.00</td>
<td>50.00</td>
</tr>
<tr>
<td>Water</td>
<td>453.20</td>
<td>443.20</td>
</tr>
<tr>
<td>Tetra-n-butyl titanate</td>
<td>10.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Dry aluminium lamellae</td>
<td>25.00</td>
<td>25.00</td>
</tr>
<tr>
<td>ZnS</td>
<td>245.00</td>
<td>245.00</td>
</tr>
<tr>
<td>Molybdenum oxide</td>
<td>8.00</td>
<td>8.00</td>
</tr>
<tr>
<td>R40</td>
<td>13.00</td>
<td>13.00</td>
</tr>
<tr>
<td>R95</td>
<td>14.00</td>
<td>14.00</td>
</tr>
<tr>
<td>Dehydradix</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>8.00</td>
<td>8.00</td>
</tr>
<tr>
<td>Boric acid</td>
<td>7.50</td>
<td>7.50</td>
</tr>
<tr>
<td>Kelzan</td>
<td>0.70</td>
<td>0.70</td>
</tr>
</tbody>
</table>

The values of resistance to the saline mist measured are summarized in table 10 below.

**TABLE 10**

<table>
<thead>
<tr>
<th>Composition C</th>
<th>Composition D</th>
<th>Composition E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of layer (g/m²)</td>
<td>21</td>
<td>22.5</td>
</tr>
<tr>
<td>Red rust (number of hours)</td>
<td>170</td>
<td>310</td>
</tr>
</tbody>
</table>

**EXAMPLE 10**

Process of Introduction of Chelated Organic Titanates or Zirconates, Compatible in Aqueous Phase, into an Aqueous Phase—Co-Hydrolysis with the Silane

**[0109]** a) Titanates

**[0110]** i) Preparation of the Aqueous Phase:

10 parts by weight of TYZOR® TEP (supplied by DuPont de Nemours, 60% dry extract) and 25 parts by weight of silane A-187 are mixed with magnetic stirring for one hour. 113 parts by weight of water are then added rapidly and the magnetic stirring is maintained for one hour.

**[0112]** This mixture is then introduced into an aqueous composition constituted of 550 parts by weight of water, 8.8 parts by weight of sodium silicate, 8.2 parts by weight of boric acid and 9 parts by weight of molybdenum oxide.

**[0113]** ii) Composition of the Organic Phase:

The organic phase contains:

- dipropyleneglycol 75 parts by weight
- Remycal N4 100¹³ 14 parts by weight
- Remycal N9 100¹³ 15.5 parts by weight
The organic phase contains:

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight (parts by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silane A 187</td>
<td>70</td>
</tr>
<tr>
<td>Zinc paste</td>
<td>235</td>
</tr>
<tr>
<td>Aluminium Stapa 14</td>
<td>30</td>
</tr>
<tr>
<td>Schwego foam 832512</td>
<td>5.5</td>
</tr>
<tr>
<td>Yttrium oxide 18</td>
<td>30</td>
</tr>
<tr>
<td>Aerosil 3800</td>
<td>0.4</td>
</tr>
</tbody>
</table>

1. Wetting agent of ethoxylated nonylphenol type (CECA)
2. Wetting agent of ethoxylated nonylphenol type (CECA)
3. 80% Chromal VIII in dipropylene glycol, marketed by Eckart Werke
4. Hydrocarbon-type anti-foam (Schwegman)
5. $\gamma\text{Al}_2\text{O}_3$ of purity equal to 99.99%
6. Anti-sedimentation agent of silica type (Degussa)

**iii) Results of the Saline Mist Tests:**

[0114] Bath according to the invention: anticorrosion coating composition according to the invention: the organic and aqueous phases obtained (steps ii) and i), respectively) are mixed.

[0115] Reference bath: reference composition:

[0116] The aqueous phase of the reference composition contains:

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight (parts by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>463</td>
</tr>
<tr>
<td>Sodium silicate 20 N 32</td>
<td>8.8</td>
</tr>
<tr>
<td>Boric acid</td>
<td>8.2</td>
</tr>
<tr>
<td>Molybdenum oxide</td>
<td>9.0</td>
</tr>
<tr>
<td>Silane A 187</td>
<td>31</td>
</tr>
</tbody>
</table>

[0117] The organic phase of the reference composition has the same composition as the organic phase of the bath according to the invention (step ii).

[0118] The saline mist tests are carried out after an ageing of the baths, according to the invention and reference, of the order of 48 hours. The results obtained are given in table 11 below:

<table>
<thead>
<tr>
<th></th>
<th>Results on screws</th>
<th>Results on steel support</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(5% / 8%) € V + CM $^a$</td>
<td>€ 2 x G$^b$ protection</td>
</tr>
<tr>
<td><strong>Reference bath</strong></td>
<td>672 / 672</td>
<td>456 / 440</td>
</tr>
<tr>
<td><strong>Bath according to</strong></td>
<td>€1150</td>
<td>840 / 912</td>
</tr>
<tr>
<td><strong>the invention</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$: V + CM: saline mist results after the screws had been subjected to the mechanical shocks of vibrations and falls.

$^b$: 2 x G: saline mist results after the screws or the plates had been subjected twice to chipping, that is to say, a scattering of impacts.

$^c$: Sacrificial protection: number of hours of exposure to the saline mist, without red rust after incision of the coating to the metal.

$^d$: Notation 5: results corresponding to less than 1% of red rust on surface.

$^e$: Notation 4.8: results corresponding to less than 5% of red rust on surface.

Table 11 makes it appear clear that the introduction of chelated organic titanate, compatible in aqueous phase, co-hydrolysed with the silane in the coating compositions increases the good behaviour to saline mist of the samples treated by these compositions.

1. An anticorrosion coating composition of metallic parts based on particulate metal in aqueous dispersion comprising, in the following proportions (percentages by weight):

   - at least one of an organic titanate and an organic zirconate in an amount from 0.3 to 24%;
   - a particulate metal or a mixture of particulate metals in an amount from 10 to 40%;
   - a silane-based binder in an amount from 1 to 25%; and water in an amount sufficient to produce 100%;

   wherein the sum of the organic titanate and/or zirconate and of the silane-based binder is between 5 and 25%.

2. The composition according to claim 1, characterized in that wherein (i) the organic titanate is selected from the group consisting of titanates compatible in organic phase, compatible in aqueous phase, and combinations thereof, and (ii) the organic zirconate is selected from the group consisting of zirconates compatible in organic phase, zirconates compatible in aqueous phase, and combinations thereof.

3. The composition according to claim 2, wherein the titanates compatible in organic phase are C$_{12}$-C$_{18}$ tetraalkyl titanates, and the zirconates compatible in organic phase are C$_{12}$-C$_{18}$ tetraalkyl zirconates.

4. The composition according to claim 2, wherein the titanates compatible in aqueous phase are chelated organic titanates, and the zirconates compatible in aqueous phase are chelated organic zirconates.

5. The composition according to claim 1 wherein the particulate metal is selected from the group consisting of zinc, aluminium, zinc alloys, aluminium alloys, zinc and aluminium alloys, and combinations thereof.

6. The composition according to claim 1 wherein the silane-based binder comprises a silane having at least one hydrolysable function.

7. The composition according to claim 1 wherein the silane includes an epoxy function.

8. The composition according to claim 7, wherein the silane is selected from the group consisting of di- or tri-methoxysilane with an epoxy function, di- or triethoxysilane with an epoxy function, and mixtures thereof.

9. The composition according to claim 1, further comprising 1 to 30% by weight of organic solvent or a mixture of organic solvents, with respect to the total weight of the composition.

10. The composition according to claim 9, wherein the organic solvent is selected from the group consisting of glycolic solvents, acetates, nitropropane, alcohols, ketones, white spirit, and mixtures thereof.

11. The composition according to claim 1 further comprising 0.1 to 7% by weight of molybdenum oxide, with respect to the total weight of the composition.

12. The composition according to claim 1 further comprising 0.5 to 10% by weight, with respect to the total weight of the composition, of an anticorrosion reinforcing agent selected from the group consisting of yttrium, zirconium, lanthanum, cerium, praseodymium, in the form of oxides or of salts thereof.

13. The composition according to claim 1 further comprising at least one of a thickening agent.
14. A method for forming an anticorrosion coating of metallic parts, the method comprising:

- obtaining a coating composition comprising, in the following proportions (percentages by weight): at least one of an organic titanate and an organic zirconate in an amount from 0.3 to 24%, a particulate metal or a mixture of particulate metals in an amount from 10 to 40%, a silane-based binder in an amount from 1 to 25%, and water in an amount sufficient to produce 100%, wherein the sum of the organic titanate and/or zirconate and of the silane-based binder is between 5 and 25%;

- forming a coating layer by spraying, soaking-draining or soaking-centrifugation; and

- subjecting the coating layer to a baking operation by supply of thermal energy to thereby form the anticorrosion coating.

15. The method according to claim 14, further comprising, prior to the baking operation, the coated metallic parts are subjected to a drying operation by supply of thermal energy.

16. The method according to claim 14, wherein the anticorrosion coating has a thickness of the dry film of between 3 µm (11 g/m²) and 30 µm (110 g/m²).

17. A coated metallic substrate comprising an anticorrosion coating formed from a coating composition including in the following proportions (percentages by weight): at least one of an organic titanate and an organic zirconate in an amount from 0.3 to 24%, a particulate metal or a mixture of particulate metals in an amount from 10 to 40%, a silane-based binder in an amount from 1 to 25%, and water in an amount sufficient to produce 100%, wherein the sum of the organic titanate and/or zirconate and of the silane-based binder is between 5 and 25%.

18. An aqueous composition of C₄-C₆ tetraalkyl titanate, adapted for use in a coating composition for a metallic substrate in aqueous dispersion, in the following proportions (percentages by weight):

- water-soluble organic solvent in an amount from 0 to 20%;

- silane-based binder in an amount from 20 to 50%, the silane having at least one hydrolysable hydroxyl function;

- at least one of C₁-C₈ tetraalkyl titanate and zirconate in an amount from 5 to 25%, compatible in organic phase; and

- water in an amount sufficient to produce 100%.

19. The composition according to claim 18, wherein the water-soluble organic solvent is selected from the group consisting of glycolic solvents, alcohols, ketones, and mixtures thereof.

20. The composition according to claim 18, wherein the hydrolysable hydroxyl function is a C₁-C₄ alkoxy radical.

21. The composition according to claim 18, wherein the silane includes an epoxy function.

22. The composition according to claim 21, wherein the silane is selected from the group consisting of di- or trimethoxysilane with an epoxy function, di- or trimethoxysilane with an epoxy function, and mixtures thereof.

23. The composition according to claim 18, wherein the C₁-C₈ tetraalkyl titanate is selected from the group consisting of tetraethyl titanate, tetra-n-butyl titanate, octylene glycol titanate and mixtures thereof.

24. (canceled)

25. The composition according to claim 3 wherein the C₄-C₆ tetraalkyl titanates are selected from the group consisting of tetraethyl titanate, tetra-n-butyl titanate, octylene glycol titanate, and combinations thereof.

26. The composition according to claim 3 wherein the C₄-C₆ tetraalkyl zirconates are selected from the group consisting of tetra-n-propyl zirconate, tetra-n-butyl zirconate, and combinations thereof.

27. The composition according to claim 4 wherein the chelated organic titanates are triethanolamine titanates.

28. The composition according to claim 4 wherein the chelated organic zirconates are triethanolamine zirconates.

29. The composition according to claim 5 wherein the alloys include metals selected from the group consisting of manganese, magnesium, tin, and combinations thereof.

30. The composition according to claim 5 wherein the alloys include a eutectic alloy of zinc and aluminium and a trace of rare earth elements.

31. The composition according to claim 6 wherein the hydrolysable hydroxyl function is a C₁-C₄ alkoxy radical.

32. The composition according to claim 8 wherein the trimethoxysilane is selected from the group consisting of gamma-glycidoxypropyltrimethoxysilane, beta-(3,4-epoxy-cyclohexyl)ethyltrimethoxysilane, and mixtures thereof.

33. The composition according to claim 10 wherein the glycolic solvents are glycol ethers.

34. The composition according to claim 33 wherein the glycol ethers are selected from the group consisting of diethylene glycol, triethylene glycol, dipropylene glycol, propylene glycol methyl ether, and mixtures thereof.

35. The composition according to claim 10 wherein the glycolic solvents are selected from the group consisting of propylene glycol, polypropylene glycol, and mixtures thereof.

36. The composition according to claim 9 wherein the organic solvent is 2,2,4-trimethyl-1, 3-pentanediol isobutyrate (texanol).

37. The composition according to claim 12 wherein the reinforcing agent is yttrium oxide Y₂O₃.

38. The composition according to claim 1 further comprising 0.2 to 4% by weight, with respect to the total weight of the composition, of a corrosion inhibitor pigment.

39. The composition according to claim 38 wherein the corrosion inhibitor pigment is aluminium triphosphate.

40. The composition according to claim 13 wherein the thickening agent is present in an amount of 0.005 to 7% by weight with respect to the total weight of the composition.

41. The composition according to claim 13 wherein the wetting agent is present in an amount of 0.1 to 4% by weight with respect to the total weight of the composition.

42. The method according to claim 14 wherein the baking operation by supply of thermal energy includes at least one of convection, infrared, and induction.

43. The method according to claim 14 wherein the baking operation is performed at a temperature between 180°C and 350°C.

44. The method according to claim 43 wherein the baking operation is performed for approximately 10 to 60 minutes by convection or infrared.
45. The method according to claim 43 wherein the baking operation is performed for 30 seconds to 5 minutes by induction.

46. The anticorrosion coating formed by the method according to claim 14.

47. The method according to claim 15 wherein the drying operation by supply of thermal energy includes at least one of convection, infrared, and induction.

48. The method according to claim 47 wherein the drying operation is performed at a temperature between 30°C and 250°C by convection.

49. The method according to claim 47 wherein the drying operation is performed for approximately 10 to 30 minutes on a line.

50. The method according to claim 47 wherein the drying operation is performed for 30 seconds to 5 minutes by induction.

51. The anticorrosion coating formed by the method according to claim 15.

52. The method according to claim 16 wherein the thickness is between 4 μm (15 g/m²) and 12 μm (45 g/m²).

53. The method according to claim 52 wherein the thickness is between 5 μm (18 g/m²) and 10 μm (40 g/m²).

54. The anticorrosion coating formed by the method of claim 16.

55. The method according to claim 15 wherein the anticorrosion coating has a thickness of the dry film of between 3 μm (11 g/m²) and 30 μm (110 g/m²).

56. The method according to claim 55 wherein the thickness is between 4 μm (15 g/m²) and 12 μm (45 g/m²).

57. The method according to claim 56 wherein the thickness is between 5 μm (18 g/m²) and 10 μm (40 g/m²).

58. The anticorrosion coating formed by the method of claim 55.

59. The metallic substrate of claim 17 wherein the metallic substrate is selected from the group consisting of steel, cast-iron, and aluminium.

60. The metallic substrate of claim 59 wherein the steel is zinc coated.

61. The composition of claim 19 wherein the glycolic solvents include glycol ethers.

62. The composition of claim 61 wherein the glycol ethers are selected from the group consisting of diethylene glycol, triethylene glycol, dipropylene glycol, and mixtures thereof.

63. The composition of claim 19 wherein the glycolic solvents include propylene glycol, propylene glycol methyl ether, and mixtures thereof.

64. The composition according to claim 19 wherein the hydrolysable hydroxyl function is a C₃₋₄ alkoxy radical.

65. The composition according to claim 22 wherein the trimethoxysilane is selected from the group consisting of gamma-glycidoxypropyltrimethoxysilane, beta-(3,4-epoxy-cyclohexyl)ethyltrimethoxysilane, and mixtures thereof.

66. The composition according to claim 18 wherein the C₃₋₄ tetraalkyl zirconate is selected from the group consisting of tetra-n-propyl zirconate, tetra-n-buty1 zirconate, and mixtures thereof.

67. A method for pretreating a substrate prior to receiving an adhesive or coating, the method comprising:

- providing a composition comprising in the following proportions (percentages by weight): water-soluble organic solvent in an amount from 0 to 20%, silane-based binder in an amount from 20 to 50% the silane having at least one hydrolysable hydroxyl function, at least one of C₃₋₄ tetraalkyl titanate and zirconate in an amount from 5 to 25% compatible in organic phase, and water in an amount sufficient to produce 100%;

- applying a coating of the composition to the substrate, thereby pretreating the substrate.

68. A method for sealing a substrate or coated substrate, the method comprising:

- providing a composition comprising in the following proportions (percentages by weight): water-soluble organic solvent in an amount from 0 to 20%, silane-based binder in an amount from 20 to 50% the silane having at least one hydrolysable hydroxyl function, at least one of C₃₋₄ tetraalkyl titanate and zirconate in an amount from 5 to 25% compatible in organic phase, and water in an amount sufficient to produce 100%;

- applying a coating of the composition to the substrate, thereby sealing the substrate or coated substrate.

69. A method for passivating a substrate of steel, zinc, aluminium, or steel having a zinc-based coating, the method comprising:

- providing a substrate selected from the group consisting of steel, zinc, aluminium, and steel having a zinc-based coating;

- providing a composition comprising in the following proportions (percentages by weight): water-soluble organic solvent in an amount from 0 to 20%, silane-based binder in an amount from 20 to 50% the silane having at least one hydrolysable hydroxyl function, at least one of C₃₋₄ tetraalkyl titanate and zirconate in an amount from 5 to 25% compatible in organic phase, and water in an amount sufficient to produce 100%;

- applying a coating of the composition on the substrate, thereby passivating the substrate.

70. A method for improving the adhesion of coatings or adhesives in aqueous phase, the method comprising:

- forming a composition comprising in the following proportions (percentages by weight): water-soluble organic solvent in an amount from 0 to 20%, silane-based binder in an amount from 20 to 50% the silane having at least one hydrolysable hydroxyl function, at least one of C₃₋₄ tetraalkyl titanate and zirconate in an amount from 5 to 25% compatible in organic phase, and water in an amount sufficient to produce 100%;

- adding the composition to a coating or adhesive to thereby improve the resulting adhesion of the coating or adhesive.

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