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(54) Titre : COMPOSE DE TREMPAGE POUR LE TRAITEMENT DES REVETEMENTS DE GALVANISATION
CHROMATISES OU PASSIVES

(54) Title: DIPPING COMPOSITION FOR THE TREATMENT OF CHROMATIZED OR PASSIVATED GALVANIZING
COATINGS

(57) **Abrégé/Abstract:**

A dipping composition for the treatment of a chromitized or passivated zinc or zinc alloy coating deposited on a steel substrate is disclosed. The composition comprises titanate, acid esters, titanium chelates or mixtures thereof, organo-functional polysiloxanes and a solvent selected from the group consisting of organic solvents, preferably alcohols and hydrocarbons, water and mixtures thereof. The weight ratio of titanate acid esters to polysiloxanes in the composition is from about 1:1 to about 1:4. Using the composition, a coating having thickness of, for example, 4 to 6 microns can be applied using a dipping process, which coating is subsequently dried at 80°C and burnt in at up to 250°C. The coating so obtained provides corrosion protection times at least 5 to 10 times longer than those which may be achieved without it. In particular, it can be used to improve the corrosion resistance and durability of chromitized coatings obtained using chromium III compounds, which chromitizing, normally less durable than that obtained using chromium VI compounds, is preferred because of its lesser environmental impact.



ABSTRACT

A dipping composition for the treatment of a chromatinized or passivated zinc or zinc alloy coating deposited on a steel substrate is disclosed. The composition comprises titanate acid esters, titanium chelates or mixtures thereof, organofunctional polysiloxanes and a solvent selected from the group consisting of organic solvents, preferably alcohols and hydrocarbons, water and mixtures thereof. The weight ratio of titanate acid esters to polysiloxanes in the composition is from about 1:1 to about 1:4. Using the composition, a coating having thickness of, for example, 4 to 6 microns can be applied using a dipping process, which coating is subsequently dried at 80°C and burnt in at up to 250°C. The coating so obtained provides corrosion protection times at least 5 to 10 times longer than those which may be achieved without it. In particular, it can be used to improve the corrosion resistance and durability of chromatinized coatings obtained using chromium III compounds, which chromatinizing, normally less durable than that obtained using chromium VI compounds, is preferred because of its lesser environmental impact.

The present invention relates to the use of dipping agents for the treatment of chromitized or passivated galvanizing coatings on zinc alloy coatings used on steel parts.

Such dipping agents are known in the prior art. The dipping agents are used, in particular, for parts that are not to be subsequently lacquered and are galvanized electrolytically or coated mechanically with zinc. Zinc is understood to include not only the pure metal, but also zinc alloys.

10 Parts of this kind are, for example, nuts, bolts, fasteners, fittings, or the like.

In particular, organic dipping agents are known in the prior art. These are, for example, aqueous organic resin dispersions with corrosion protection inhibitors. Even though such materials may be used, they cannot prevent corrosion of the galvanizing coatings over a sufficiently long period of time.

Inorganic dipping agents are also known, and these contain chromic acid. However, such dipping agents are undesirable for environmental reasons.

20 Proceeding from this state of the art, it is the object of the present invention to create a dipping agent based essentially on inorganic components and which, using simple processing, ensures long-lasting protection against corrosion of the zinc coating, and which is relatively environmentally friendly.

This object may be achieved by the use of a combination of binding agents made up to titanate acid esters and organofunctional polysiloxanes dissolved in a solvent, wherein organic

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solvents, in particular alcohols and hydrocarbons, are used as the solvent. It is also possible to use a combination of binding agents comprising titanitic acid esters, titanium chelating agents and organo-functional polysiloxanes, where
5 alcohols and/or hydrocarbons, either alone or mixed with water, are used as the solvent, or a combination of binding agents consisting of titanium chelates and organo-functional polysiloxanes, where water or alcohols or hydrocarbons or a mixture thereof are used as the solvent.

10 Under certain circumstances, it is also possible that zirconium form a component of the combination of binding agents in place of titanium.

In one aspect the present invention provides a dipping composition for the treatment of a chromitized or
15 passivated zinc or zinc alloy coating deposited on a steel substrate, which composition comprises titanitic acid esters, titanium chelates, zirconium acid esters, zirconium chelates or mixtures thereof, organo-functional polysiloxanes and a solvent.

20 In another aspect the present invention provides a dipping composition for the treatment of a chromitized or passivated zinc or zinc alloy coating deposited on a steel substrate, which composition comprises titanitic acid esters, titanium chelates or mixtures thereof, organo-functional
25 polysiloxanes and a solvent.

The dipping agent is prepared in the form of a solution ready for processing, which solution can be transparent or tinted and can be applied to electrolytically galvanized, phosphated or passivated substrates, where the
30 passivation can be free of chromium VI. Coatings having thicknesses of, for example, 4 to 6 μ can be applied in a

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dipping process or in an accelerated dipping process. The applied coating may be subsequently forced dried at 80°C, or may be burnt in at up to 250°C.

The dipping agent is essentially inorganic. The main advantage of this material is that for extremely thin coatings it is possible to achieve at least 5 to 10 times longer corrosion protection times, without any base metal corrosion. In this manner the usual corrosion protection methods can be significantly improved by subsequent coating with the dipping agent in the form of a thin, accurately dimensioned layer.

The application of the material can be effected in an additional bath of a conventional electrolytic galvanizing plant

or at the end of a chromatizing production line, without the need to remove any of the parts from the corresponding transportation frames in order to achieve the coating. Drying can be effected in conventional ovens at the usual temperatures. An additional advantage is seen in the simple removal of the coatings, for example from the frames that are submerged at the same time. These can be cleaned very simply in a degreasing or etching bath. A residue of inorganic salts can be removed during detoxification of the waste water.

10 When this dipping agent is used, chromatizing with chromium III can be effected in place of the former chromatizing with chromium VI, which is preferred because chromium VI is more toxic. The usually inadequate durability of chromatizing effected with chromium III is so improved by the secondary dip coating, that better results can be achieved in this case than with the former customary chromatizing effected with chromium VI. Because of the inorganic components of the dipping agent, there is a reaction between the chromium III chromatizing and the dipping solution, which results in excellent adhesion and prevents the

20 formation of blisters. The reason for this is presumably that the dipping solution with free OH groups, COOH groups, and nitrogen adheres to the molecular water (water of crystallization) contained in the chromatizing. In place of chromatizing, it is also possible to use phosphating of the galvanizing coating, where again, after application of the dipping agent, appropriate bonding to the molecular water of the phosphate layer (hydrate

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bridge formation) is effected.

The first variant of the dipping agent, as disclosed above can be used, although it is extremely sensitive to moisture. The second variant can also be used to good effect and, for all practical purposes, is no longer sensitive to moisture, whereas the third variant is even less sensitive to moisture and is an extremely stable compound.

It is particularly preferred that polysiloxanes with epoxy end groups form a component of the combination of binding agents.

In the latter case, the best reaction is achieved with the titanates (chelates and esters), leading to particularly effective corrosion protection.

On the basis of practice, it is also regarded as advantageous if isopropanol is used as the solvent.

In a particularly preferred embodiment, a lubricant in the form of polyvalent polyalcohols with free OH group is incorporated in the dipping agent. According to the prior art, it is usual to apply a lubricant, for example, to the threads of nuts and bolts, after galvanizing and chromating. However, this lubricant can be washed off very easily, and this can cause environmental damages. In addition, when this happens, the lubricating effect can no longer be achieved.

According to the present invention, the lubricant may be a component of the dipping solution. The lubricant is therefore incorporated chemically into this solution, so that a high level of retention is ensured and, in addition, no negative environmental effects are expected. In addition, friction coefficients are considerably improved in this manner.

10 It is preferred that in the dipping agent the ratio of weight percentages of titanium acid ester:polysiloxanes is approximately 1:2 or 1:3 or 1:4. The mixture ratio of 1:2 is preferred. Furthermore, it is also preferred that the ratio of weight percentages of titanate acid ester:titane chelates is 1:1 and the ratio of this mixture:polysiloxanes is 1:2 or 1:3. The ratio of 1:1 is preferred.

In the composition according to the invention, the organic polysiloxanes serve, in particular, as an adhesive agent. Additional advantages of the dipping agent according to the present invention are that the chromatizing becomes more stable, even at a higher temperature of, for example, 200°C and that a decreased tendency to the formation of white rust is observed.

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CLAIMS:

1. A dipping composition for the treatment of a chromatized or passivated zinc or zinc alloy coating deposited on a steel substrate, which composition comprises
5 titanic acid esters, titanium chelates, zirconium acid esters, or zirconium chelates or mixtures thereof, organo-functional polysiloxanes and a solvent.
2. A dipping composition for the treatment of a chromatized or passivated zinc or zinc alloy coating
10 deposited on a steel substrate, which composition comprises titanic acid esters, or titanium chelates or mixtures thereof, organo-functional polysiloxanes and a solvent.
3. A composition according to claim 1 or 2, wherein the solvent is selected from the group consisting of organic
15 solvents, water and mixtures thereof.
4. A composition according to claim 2, which comprises titanic acid esters, organo-functional polysiloxanes and an organic solvent.
5. A composition according to claim 2, which
20 comprises titanic acid esters, titanium chelates, organo-functional polysiloxanes and an organic solvent or a mixture thereof with water.
6. A composition according to claim 2, which comprises titanium chelates, organo-functional polysiloxanes
25 and a solvent selected from the group consisting of organic solvents, water and mixtures thereof.
7. A composition according to any one of claims 1 to 6, wherein the organic solvents are selected from the group consisting of alcohols and hydrocarbons.

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8. A composition according to claim 7, wherein the alcohol is isopropanol.

9. A composition according to claim 1 or 2, wherein the organo-functional polysiloxanes contain epoxy end
5 groups.

10. A composition according to claim 1 or 2, further comprising a lubricant.

11. A composition according to claim 10, wherein the lubricant is a polyvalent polyalcohol with free OH groups.

10 12. A composition according to claim 2, wherein the weight ratio of titanitic acid esters to polysiloxanes is from about 1:2 to about 1:4.

13. A composition according to claim 12, wherein the weight ratio of titanitic acid esters to polysiloxanes is
15 about 1:2.

14. A composition according to claim 2, wherein the weight ratio of titanitic acid esters to titanium chelates is about 1:1 and the weight ratio of this mixture to polysiloxanes is from about 1:1 to about 1:3.

20 15. A composition according to claim 14, wherein the weight ratio of the mixture to polysiloxanes is about 1:1.

16. A method for the treatment of a chromatized or passivated zinc or zinc alloy coating deposited on a steel substrate, which method comprises covering the coating with
25 a layer of a composition according to any one of claims 1 to 15.

17. The use of a composition according to any one of

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claims 1 to 15 for the after treatment of a chromitized or passivated zinc or zinc alloy coating deposited on a steel substrate.

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