One goal that has been pursued for a long time is to efficiently and inexpensively produce homogeneous coatings in an immersion process in order to produce thicker coatings that are essentially smooth and as closed as possible.

The object of the present invention is therefore to propose a method by which a paint formulation can be deposited easily and homogeneously on metallic surfaces with good coverage using a liquid system, which is also rinse-resistant, if necessary. Therefore, the object was also to propose the simplest possible method for accomplishing this.

Summary of Invention

In a first aspect, the present invention refers to a method for coating metallic surfaces of substrates comprising the steps or consisting of the steps:

I. Preparing a substrate with a cleaned metallic surface,

II. Contacting and coating metallic surfaces with an aqueous composition in the form of a dispersion of film-forming polymers ~~and/~~or suspension of film-forming polymers comprising inorganic particles to obtain an organic coating, and

~~VI. Optionally rinsing the organic coating and~~

~~V~~III. Drying and/or baking the organic coating, ~~or~~

~~VIII. Optionally drying the organic coating and coating with a similar or additional coating composition before drying and/or baking,~~

characterized in that ~~in step II the coating is applied with an aqueous composition in the form of dispersion and suspension, wherein~~ at least one anionic polyelectrolyte in an amount of 0.01 to 5.0 wt%, based on the total mass of the resulting mixture, is added to ~~a~~ the dispersion of film-forming polymers ~~and/~~or ~~a~~ the suspension of film-forming polymers comprising inorganic particles, wherein the suspension of film-forming polymers comprising inorganic particles has ~~with~~ a solids content of 2 to 40 wt% and an average particle size of 10 to 1000 nm, wherein the aqueous composition has a pH value in the range of 4 to 11 and forms a coating based on an ionogenic gel which binds cations dissolved out of the metallic surface, these cations originating from a pretreatment stage and/or from contacting in step II.

In a second aspect, the present invention refers to an aqueous composition containing an anionic polyelectrolyte in an amount of 0.01 to 5.0 wt%, based on the total mass of the resulting mixture, in a dispersion of film-forming polymers and/or a suspension of film-forming inorganic

particles with a solids content of 2 to 40 wt% and an average particle size of 10 to 1000 nm, wherein the aqueous composition has a pH value in the range of 4 to 11.

~~In a further aspect, the present invention refers to the use of the method of the present invention for coating substrates which have posed problems in coating with an electrodip paint.~~

Detailed description

~~The object of the present invention is achieved with~~Disclosed herein is a method for coating metallic surfaces of substrates, comprising or consisting of the steps:

I. supplying a substrate having a cleaned metallic surface,

II. contacting and coating metallic surfaces with an aqueous composition in the form of a dispersion and/or suspension,

III. optionally rinsing the organic coating and

IV. drying and/or baking the organic coating or

V. optionally drying the organic coating and also coating with a similar or additional coating composition before drying and/or baking,

such that in step II, the coating is performed using an aqueous composition in the form of a dispersion and/or suspension, wherein at least one anionic polyelectrolyte is added in an amount of 0.01 to 5.0 wt%, based on the total mass of the resulting mixture, to a dispersion of film-forming polymers and/or a suspension of film-forming inorganic particles with a solids content of 2 to 40 wt% and an average particle size of 10 to 1000 nm, such that the aqueous composition has a pH value in the range of 4 to 11 and forms a coating based on an ionogenic gel, which binds cations dissolved out of the metallic surface, so that these cations originate from a pretreatment stage and/or from contacting in step II.

Patent Claims

1. A method for coating metallic surfaces of substrates comprising the steps or consisting of the steps:
   I. Preparing a substrate with a cleaned metallic surface,
   II. Contacting and coating metallic surfaces with an aqueous composition in the form of a dispersion of film-forming polymers or suspension of film-forming polymers comprising inorganic particles to obtain an organic coating, and
   III. Drying or baking the organic coating,
   characterized in that at least one anionic polyelectrolyte in an amount of 0.01 to 5.0 wt%, based on the total mass of the resulting mixture, is added to the dispersion of film-forming polymers or the suspension of film-forming polymers comprising inorganic particles, wherein the suspension of film-forming polymers comprising inorganic particles has a solids content of 2 to 40 wt% and an average particle size of 10 to 1000 nm, wherein the aqueous composition has a pH value in the range of 4 to 11 and forms a coating based on an ionogenic gel which binds cations dissolved out of the metallic surface, these cations originating from a pretreatment stage or from contacting in step II.

2. The method of claim 1, further comprising IIa rinsing the organic coating.

3. The method of claim 1 or 2, wherein III further comprises coating with an additional coating composition before drying.

4. The method of claim 1 or 2, wherein III further comprises coating with an additional coating composition before baking.

5. The method according to claim 1, characterized in that the anionic polyelectrolyte contains or consists of any one or more of **a)** at least one polysaccharide based on glycogens, amyloses, amylopectins, calloses, agar, algines, alginates, pectins, carrageenan, celluloses, chitins, chitosans,

curdlans, dextrans, fructanes, collagens, gellan gum, gum arabic, starches, xanthans, gum tragacanth, carayans, carabean powder and glucomannans; or **b)** at least one based on polyamino acids, collagens, polypeptides, lignins or **c)** at least one synthetic anionic polyelectrolyte based on polyamino acids, polyacrylic acids, polyacrylic acid copolymers, acrylamide copolymers, lignins, polyvinyl sulfonic acid, polycarboxylic acids, polyphosphoric acids or polystyrenes.

6. The method according to any one of claims 1 to 5, characterized in that the anionic polyelectrolyte contains or consists of at least one polysaccharide based on pectins or gellan gum.

7. The method according to any one of claims 1 to 5, characterized in that the aqueous composition and/or the organic coating prepared therefrom contains a mixture of at least two different anionic polyelectrolytes.

8. The method according to claim 7, characterized in that the aqueous composition and/or the organic coating prepared therefrom contains a mixture of two pectins.

9. The method according to one or more of the preceding claims, characterized in that the aqueous composition and/or the organic coating prepared therefrom contain(s) at least one anionic polysaccharide selected from those having a degree of esterification of the carboxyl function in the range of 5 to 75%, based on the total number of alcohol and carboxyl groups.

10. The method according to one or more of the preceding claims, characterized in that the aqueous composition and/or the organic coating prepared therefrom contain(s) at least one anionic polysaccharide and/or at least one anionic polyelectrolyte selected from those having a molecular weight in the range of 500 to 1,000,000 g/mol^{-1}.

11. The method according to one or more of the preceding claims, characterized in that the aqueous composition and/or the organic coating prepared

therefrom contain(s) at least one anionic polysaccharide and/or at least one anionic polyelectrolyte selected from those having a degree of amidation of the carboxyl functions in the range of 1 to 50%, a degree of epoxidation of the carboxyl functions of up to 80%.

12. The method according to one or more of the preceding claims, characterized in that the anionic polyelectrolytes are modified with adhesion imparting adhesion groups selected from the group consisting of chemical groups of multifunctional epoxies, isocyanates, primary amines, secondary amines, tertiary amines, quaternary amines, amides, imides, imidazoles, formamides, Michael reaction products, carbodiimides, carbenes, cyclic carbenes, cyclocarbonates, multifunctional carboxylic acids, amino acids, nucleic acids, methacrylamides, polyacrylic acids, polyacrylic acid derivatives, polyvinyl alcohols, polyphenols, polyols with at least one alkyl and/or aryl group, caprolactam, phosphoric acids, phosphoric acid esters, epoxy esters, sulfonic acids, sulfonic acid esters, vinyl sulfonic acids, vinyl phosphonic acids, catechol, silanes as well as the silanols and/or siloxanes formed therefrom as well as triazines, thiazoles, thiazines, dithiazines, acetals, hemiacetals, quinones, saturated fatty acids, unsaturated fatty acids, alkyds, esters, polyesters, ethers, glycols, cyclic ethers, crown ethers, anhydrides as well as the acetyl acetones and β-diketo groups, carbonyl groups and hydroxyl groups.

13. The method according to one or more of the preceding claims, characterized in that the aqueous composition and/or the organic coating prepared therefrom contain(s) at least one complexing agent for metal cations or a polymer modified by complexing with metal cations.

14. The method according to claim 13, characterized in that the aqueous composition and/or the organic coating prepared therefrom contain(s) at least one complexing agent selected from those based on maleic acid, alendronic acid, itaconic acid, citriconic acid or mesaconic acid or the anhydrides or hemiesters of these carboxylic acids

15. The method according to one or more of the preceding claims, characterized in that the aqueous composition and/or the organic coating prepared therefrom contain(s) at least one type of cations selected from those based on salts having a cationic effect selected from the group consisting of melamine salts, nitroso salts, oxonium salts, ammonium salts, salts with quaternary nitrogen cations, salts of ammonium derivatives and metal salts of Al, B, Ba, Ca, Cr, Co, Cu, Fe, Hf, In, K, Li, Mg, Mn, Mo, Na, Nb, Ni, Pb, Sn, Ta, Ti, V, W, Zn and/or Zr.

16. The method according to claim 15, characterized in that Al, Cu, Fe and/or Zn are selected as the cations that are or have been dissolved out of the metallic surface and/or are/have been added to the aqueous composition.

17. The method according to one or more of the preceding claims, characterized in that the aqueous composition and/or the organic coating prepared therefrom contain(s) an amount of organic particles based on polyacrylates, polyurethanes, polyepoxies and/or the hybrids thereof.

18. The method according to one or more of the preceding claims, characterized in that the aqueous composition and/or the organic coating prepared therefrom contain(s) at least one emulsifier.

19. The method according to claim 18, characterized in that the aqueous composition and/or the organic coating produced therefrom contain(s) at least one emulsifier selected from those based on anionic emulsifiers.

20. The method according to one or more of the preceding claims, characterized in that the aqueous composition and/or the organic coating prepared therefrom contain(s) at least one additive selected from additives from the group of biocides, dispersant aids, film-forming aids, acidic and/or basic aids for adjusting the pH value and thickeners and flow control agents.

21. The method according to one or more of the preceding claims, characterized in that before contacting and coating the metallic surfaces with an aqueous

composition in process step II, the metallic surfaces are cleaned, pickled and/or preprocessed.

22. The method according to one or more of the preceding claims, characterized in that the aqueous composition forms a coating based on an ionogenic gel, and the dry film formed then or later has a thickness of at least 1 µm.

23. The method according to one or more of the preceding claims, characterized in that the organic coating is formed in 0.05 to 20 minutes in an immersion bath and after drying has a dry film thickness in the range of 5 to 100 µm.

24. An aqueous composition containing an anionic polyelectrolyte in an amount of 0.01 to 5.0 wt%, based on the total mass of the resulting mixture, in a dispersion of film-forming polymers and/or a suspension of film-forming inorganic particles with a solids content of 2 to 40 wt% and an average particle size of 10 to 1000 nm, wherein the aqueous composition has a pH value in the range of 4 to 11.

25. The aqueous composition claim 24, characterized in that the dispersion of film-forming polymers has an organic particle content based on polyacrylates, polyurethanes, polyepoxies and/or their hybrids, an amount of at least one complexing agent selected from those based on maleic acid, alendronic acid, itaconic acid, citriconic acid or mesaconic acid or anhydrides or hemiesters of these carboxylic acids and at least one anionic polyelectrolyte based on pectins or gellan gum.

Patent Claims

1. A method for coating metallic surfaces of substrates comprising the steps or consisting of the steps:
   I. Preparing a substrate with a cleaned metallic surface,
   II. Contacting and coating metallic surfaces with an aqueous composition in the form of a dispersion and/or suspension,
   VI. Optionally rinsing the organic coating and
   VII. Drying and/or baking the organic coating or
   VIII. Optionally drying the organic coating and coating with a similar or additional coating composition before drying and/or baking,

   characterized in that in step II the coating is applied with an aqueous composition in the form of dispersion and suspension, wherein at least one anionic polyelectrolyte in an amount of 0.01 to 5.0 wt%, based on the total mass of the resulting mixture, is added to a dispersion of film-forming polymers and/or a suspension of film-forming inorganic particles with a solids content of 2 to 40 wt% and an average particle size of 10 to 1000 nm, wherein the aqueous composition has a pH value in the range of 4 to 11 and forms a coating based on an ionogenic gel which binds cations dissolved out of the metallic surface, these cations originating from a pretreatment stage and/or from contacting in step II.

2. The method according to claim 1, characterized in that the anionic polyelectrolyte contains or consists of **a)** at least one polysaccharide based on glycogens, amyloses, amylopectins, calloses, agar, algines, alginates, pectins, carrageenan, celluloses, chitins, chitosans, curdlans, dextrans, fructanes, collagens, gellan gum, gum arabic, starches, xanthans, gum tragacanth, carayans, carabean powder and glucomannans; **b)** at least one anionic polyelectrolyte of natural origin based on polyamino acids, collagens, polypeptides, lignins and/or **c)** at least one synthetic anionic polyelectrolyte based on polyamino acids, polyacrylic acids, polyacrylic acid copolymers, acrylamide copolymers, lignins, polyvinyl sulfonic acid, polycarboxylic acids, polyphosphoric acids or polystyrenes.

3. The method according to claim 1 or 2, characterized in that the anionic polyelectrolyte contains or consists of at least one polysaccharide based on pectins or gellan gum.

4. The method according to claim 1 or 2, characterized in that the aqueous composition and/or the organic coating prepared therefrom contains a mixture of at least two different anionic polyelectrolytes.

5. The method according to claim 4, characterized in that the aqueous composition and/or the organic coating prepared therefrom contains a mixture of two pectins.

6. The method according to one or more of the preceding claims, characterized in that the aqueous composition and/or the organic coating prepared therefrom contain(s) at least one anionic polysaccharide selected from those having a degree of esterification of the carboxyl function in the range of 5 to 75%, based on the total number of alcohol and carboxyl groups.

7. The method according to one or more of the preceding claims, characterized in that the aqueous composition and/or the organic coating prepared therefrom contain(s) at least one anionic polysaccharide and/or at least one anionic polyelectrolyte selected from those having a molecular weight in the range of 500 to 1,000,000 g/mol^{-1}.

8. The method according to one or more of the preceding claims, characterized in that the aqueous composition and/or the organic coating prepared therefrom contain(s) at least one anionic polysaccharide and/or at least one anionic polyelectrolyte selected from those having a degree of amidation of the carboxyl functions in the range of 1 to 50%, a degree of epoxidation of the carboxyl functions of up to 80%.

9. The method according to one or more of the preceding claims, characterized in that the anionic polyelectrolytes are modified with adhesion imparting adhesion groups selected from the group consisting of chemical groups of multifunctional epoxies, isocyanates, primary amines, secondary amines, tertiary amines, quaternary amines, amides, imides, imidazoles, formamides, Michael reaction products, carbodiimides, carbenes, cyclic carbenes, cyclocarbonates, multifunctional carboxylic acids, amino acids, nucleic acids, methacrylamides, polyacrylic acids, polyacrylic acid derivatives, polyvinyl alcohols, polyphenols, polyols with at least one alkyl and/or aryl group, caprolactam, phosphoric acids, phosphoric acid esters, epoxy esters, sulfonic acids, sulfonic acid esters, vinyl sulfonic acids, vinyl phosphonic acids, catechol, silanes as well as the silanols and/or siloxanes formed therefrom as well as triazines, thiazoles, thiazines, dithiazines, acetals, hemiacetals, quinones, saturated fatty acids, unsaturated fatty acids, alkyds, esters, polyesters, ethers, glycols, cyclic ethers, crown ethers, anhydrides as well as the acetyl acetones and β-diketo groups, carbonyl groups and hydroxyl groups.

10. The method according to one or more of the preceding claims, characterized in that the aqueous composition and/or the organic coating prepared therefrom contain(s) at least one complexing agent for metal cations or a polymer modified by complexing with metal cations.

11. The method according to claim 10, characterized in that the aqueous composition and/or the organic coating prepared therefrom contain(s) at least one complexing agent selected from those based on maleic acid, alendronic acid, itaconic acid, citriconic acid or mesaconic acid or the anhydrides or hemiesters of these carboxylic acids

12. The method according to one or more of the preceding claims, characterized in that the aqueous composition and/or the organic coating prepared therefrom contain(s) at least one type of cations selected from those based on salts having

a cationic effect selected from the group consisting of melamine salts, nitroso salts, oxonium salts, ammonium salts, salts with quaternary nitrogen cations, salts of ammonium derivatives and metal salts of Al, B, Ba, Ca, Cr, Co, Cu, Fe, Hf, In, K, Li, Mg, Mn, Mo, Na, Nb, Ni, Pb, Sn, Ta, Ti, V, W, Zn and/or Zr.

13. The method according to claim 12, characterized in that Al, Cu, Fe and/or Zn are selected as the cations that are or have been dissolved out of the metallic surface and/or are/have been added to the aqueous composition.

14. The method according to one or more of the preceding claims, characterized in that the aqueous composition and/or the organic coating prepared therefrom contain(s) an amount of organic particles based on polyacrylates, polyurethanes, polyepoxies and/or the hybrids thereof.

15. The method according to one or more of the preceding claims, characterized in that the aqueous composition and/or the organic coating prepared therefrom contain(s) at least one emulsifier.

16. The method according to claim 15, characterized in that the aqueous composition and/or the organic coating produced therefrom contain(s) at least one emulsifier selected from those based on anionic emulsifiers.

17. The method according to one or more of the preceding claims, characterized in that the aqueous composition and/or the organic coating prepared therefrom contain(s) at least one additive selected from additives from the group of biocides, dispersant aids, film-forming aids, acidic and/or basic aids for adjusting the pH value and thickeners and flow control agents.

18. The method according to one or more of the preceding claims, characterized in that before contacting and coating the metallic surfaces with an aqueous

composition in process step II, the metallic surfaces are cleaned, pickled and/or preprocessed.

19. The method according to one or more of the preceding claims, characterized in that the aqueous composition forms a coating based on an ionogenic gel, and the dry film formed then or later has a thickness of at least 1 µm.

20. The method according to one or more of the preceding claims, characterized in that the organic coating is formed in 0.05 to 20 minutes in an immersion bath and after drying has a dry film thickness in the range of 5 to 100 µm.

21. An aqueous composition containing an anionic polyelectrolyte in an amount of 0.01 to 5.0 wt%, based on the total mass of the resulting mixture, in a dispersion of film-forming polymers and/or a suspension of film-forming inorganic particles with a solids content of 2 to 40 wt% and an average particle size of 10 to 1000 nm, wherein the aqueous composition has a pH value in the range of 4 to 11.

22. The aqueous composition claim 21, characterized in that the dispersion of film-forming polymers has an organic particle content based on polyacrylates, polyurethanes, polyepoxies and/or their hybrids, an amount of at least one complexing agent selected from those based on maleic acid, alendronic acid, itaconic acid, citriconic acid or mesaconic acid or anhydrides or hemiesters of these carboxylic acids and at least one anionic polyelectrolyte based on pectins or gellan gum.

23. A use of the method according to one of claims 1 to 22 for coating substrates which have posed problems in coating with an electrodip paint.