METHOD FOR PASSIVATING TINPLATE

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ABSTRACT

The invention relates to a method for passivating the surface of a tinned steel strip which is moved through a coating system at a strip speed of at least 200 m/min. After the steel strip is tinned, the surface is anodically oxidized, and a liquid solution of a chromium-free aftertreatment agent is applied onto the oxide layer. The invention further relates to a tinned steel strip or sheet with a support layer made of a fine or ultrafine sheet of steel, a tin layer which is deposited thereon, and a surface layer of a chromium-free aftertreatment agent. An oxide layer is formed between the tin layer and the surface layer of the aftertreatment agent, said oxide layer substantially consisting of tetravalent tin oxide (SnO₂).
METHOD FOR PASSIVATING TINPLATE

[0001] The invention pertains to a method for passivating the surface of tinned steel strips, which are moving at a strip speed through a coating system, by anodic oxidation and post-treatment of the tinned steel strip with a chromium-free post-treatment agent. The invention further concerns the use of agents with complexly bound transition metals or organic additives, which are normally used for dispersion or improvement of wetting, as chromium-free post-treatment agents in the production of tinned steel strips. A further object of the invention is a tinned steel strip or sheet with a support layer made of a fine or ultrafine sheet of steel, a tin layer deposited thereon, and a surface layer of a chromium-free post-treatment agent.

[0002] Tinplate is a versatile, economical and ecologically advantageous material, which is used first of all in the packaging industry. Tinplate is a cold-rolled steel sheet with a thickness up to 0.5 millimeters, which is coated with a thin tin layer in order to protect the steel sheet from corrosion. The tin layer is deposited electrolytically, for example, on the sheet.

[0003] In the production of tinned steel sheet, especially in electrolytic strip coating systems, the coated steel sheet is chemically or electrochemically passivated and then coated with lubricant in order to make the tinned steel sheet resistant to oxidation and in order to reduce the coefficient of friction so that the tinned steel sheet can be more readily worked in the subsequent processing, for example in the manufacture of tin packaging for food. Solutions containing Cr(VI) are usually used in the passivation. The use of chromium-containing agents in the treatment of metal products is environmentally harmful and therefore should be regulated by law, especially in the case of metal products that are intended for the food industry.

PRIOR ART

[0004] For this reason Cr(VI)-free passivation solutions were proposed in the prior art. For example, DE4205819A discloses a water-free composition for production of corrosion protection layers on metal surfaces, which is based on silane compounds and compounds of tetravalent titanium or zirconium.


[0006] For the most part, these publications concern the passivation of aluminum-containing and zinc-containing surfaces of hot-dip galvanized fine sheet material and other hot-dip galvanized steel parts for use in the automobile industry. On the other hand, there is not yet a method that can be used in practice for chromate-free passivation of tinplate that affords satisfactory results.

[0007] EP1270764A discloses a surface-treated tinplate comprising an alloy layer on a surface of a steel sheet, a tin layer that has been deposited on the alloy layer so that the alloy layer is exposed over a surface area of 3.0% or more and a film comprising P and Si with a film weight of 0.5 to 100 mg/m² or 250 mg/m², is deposited on the exposed alloy layer and the tin layer.


[0009] When coated steel sheet is used to make food containers (tin cans), different requirements on the resistance to oxidation and thus the passivation of the coated metal surface are imposed by comparison with the requirements on said materials when intended for use in the automobile industry. In particular, the passivation in this case has to prevent too strong a growth of the tin oxide layer during the storage of the coated steel sheet or the food container made therefrom until it is coated with a protective enamel and furthermore until the preserved food is consumed. In addition, the passivation should prevent discolorations of the coated metal surface. Such discolorations arise, for example, when tin cans that contain sulfur-containing substances are sterilized, since the sulfur reacts with the tin in the coated steel surface if it is not sufficiently passivated. Because of the matte discoloration (marbling) or gold discoloration of the surface of the packaging, the consumer may get the idea that the contents are tainted. Enamel adhesion problems may also arise due to reaction with sulfur and these can be avoided by passivation of the coated steel sheet. The passivation moreover must guarantee the resistance of the enameled metal container, after being filled with foods, to the acids contained in the foods, such as mercaptoaminocarboxylic acid anions, for example cysteine and methionine. If passivation is not sufficient, such acid anions in the can contents can give rise to delamination of the inner coating of the container.

[0010] In the traditional production of tinplate in strip coating systems, the cold rolled fine or ultrafine sheet after coating is first fused by heating to temperatures above the melting point of tin and then quenched in a water bath. This is followed by passivation by treating the tin coated sheet with a chromate solution and finally rinsing it with demineralized water and drying it under heat. This is followed by electrostatic lubrication with dioctyl sebacate (DOS) or acetyl tributyl citrate (ATBC). The chromate adsorbed on the surface is reduced to Cr(III) by a reaction with the —Sn—O and —Sn—OH groups on the tin surface and also in some cases to chromium metal in the case of electrochemical cathodic passivation. The Cr(III) precipitates as Cr(OH)₃ hydroxide. After rinsing and drying the tinplate surface, the passivation layer no longer contains any Cr(VI) ions.

PROBLEM OF THE INVENTION

[0011] Based on this, the invention has the problem of making available a method for chromium-free passivation of the surface of steel strips that have been coated with a tin coating, which are moving at a strip speed through a coating system, said method enabling efficient passivation of the steel strip surface even at high strip speeds. Moreover, at the same time improved enamel coat adhesion and resistance to acids in foods, especially to amino acids that contain sulfur, should be achieved.

SOLUTION OF THE PROBLEM OF THE INVENTION

[0012] These problems are solved with a method that has the features of claim 1 and with a tinned steel sheet or strip
that has the features of claim 17. Preferred embodiments are defined in the dependent claims.

[0013] In the method in accordance with the invention, after the fusion and quenching of the tinned steel strip and before the treatment with a chromium-free post-treatment agent, the conduction of an anodic oxidation of the tin surface is provided. The invention proceeds from the knowledge that passivation of the tinned surface of the steel strip by post-treatment with a chromium-free post-treatment agent is not by itself sufficient to protect the surface completely and permanently against corrosion and discolorations (marbling). In particular, it has been shown that chromium-free post-treatment agents do not protect the tinned steel strip surface against a reaction with sulfur everywhere. It has now been surprisingly established that the resistance of the tinned steel strip surface to corrosion and reaction with sulfur can be considerably increased if a deactivation of the tinned steel strip surface by an anodic oxidation takes place first before the post-treatment with a chromium-free post-treatment agent. An oxide layer with a layer thickness in the nanometer range is produced on the tinned steel strip surface by the anodic oxidation. The oxide layer is substantially a layer of tetravalent tin oxide (SnO₂), which is considerably more inert than divalent tin oxide (SnO). If now a thin surface layer of a chromium-free post-treatment agent is deposited on said oxide layer, the surface of the tinned steel strip will become completely and effectively protected against corrosion and against a reaction with sulfur.

[0014] The method in accordance with the invention will be described below in more detail by means of an embodiment example:

Step 1

[0015] In the first step of the method in accordance with the invention, an electrochemical tinning of a cold rolled steel strip (line or ultrafine sheet) takes place in a strip tinning system. The steel strip is moved through an electrolysis bath at a strip speed that usually lies in the range of 200 m/min to 750 m/min and is electrolytically coated with tin. Then the steel strip is heated to temperatures above the melting point of tin (232°C) conductively or inductively (or even conductively and inductively) in order to fuse the tin coating onto it. Then the moved strip is quenched in a water bath. The tinned steel strip arrives with this fresh surface at the second step of the method, namely anodic oxidation of the tin surface.

Step 2

[0016] In the second step of the method in accordance with the invention, an anodic oxidation takes place in a soda solution, i.e., in a sodium carbonate solution. The tinned steel strip is moved along at the strip speed and is connected as the anode in the soda electrolyte bath. An aqueous soda solution serves as the electrolyte. The concentration of sodium carbonate in the soda solution is preferably 1 wt % to 10 wt %, particularly 2 wt % to 8 wt %, preferably 3 wt % to 7 wt %, above all 4 wt % to 6 wt %, especially about 5 wt %.

[0017] The device for electrolytic anodic oxidation expediently comprises an electrolysis immersion bath with a vertical tank. Near the bottom in the vertical tank is a reversing roller over which the tinned steel strip reverses travel. The vertical tank is filled with the electrolyte. A potential is applied between the tinned steel strip and the counter electrode (for example a steel cathode) in the vertical tank. The charge Q is expeditiously between 0.2 C and 2 C, preferably between 0.2 C and 0.6 C at a current density of 1-3 A/dm².

[0018] The anodization time corresponds to the residence time of the tinned steel strip in the electrochemical oxidation bath (electrolyte bath). This is determined by the length of the electrolyte bath or its fill level and the anode length and the strip speed and for typical strip speeds it expediently lies in the range of 0.1 s to 1 s, especially between 0.1 s and 0.7 s, preferably in the range of 0.15 s to 0.5 s, and ideally around 0.2 s. The anodization time, in dependence on the strip speed, can be set via the fill level to values that are suitable in accordance with the invention.

[0019] The spacing between the steel strip and the counter electrode in the electrolyte bath is set in dependence on the system. It lies, for example, in the range of 3 to 15 cm, preferably in the range of 5 to 10 cm, and especially around 10 cm.

[0020] The temperature of the electrochemical oxidation bath preferably lies in the range of 30 to 60°C, more preferably in the range of 35 to 50°C, and especially around 45°C.

[0021] The current density is set in the range of 1.0 to 3 A/dm², preferably 1.3 to 2.8 A/dm², more preferably 2 to 2.6 A/dm², especially around 2.4 A/dm². The total charge in this case varies between 0.2 C and 0.6 C and is preferably, for example, 0.48 C. The corresponding charge densities (with respect to the area of the strip being treated) lie in the range of 0.2 C/dm² to 0.6 C/dm².

Step 3

[0022] In the third step of the method, there takes place a thorough rinsing of the tinned and oxidized steel strip with distilled or fully demineralized water and a subsequent drying, which can take place, for example, with hot air. However, other drying means are also suitable for this, such as drying with water-absorbing solvents followed by drying with a cold or hot air blower, hot air being preferred, drying with convective air-free drying systems like IR radiators, inductive heating, or resistance heating, or drying only with a cold or hot air blower, preferably a hot air blower.

Step 4

[0023] In the fourth step of the method, a coating of the tinned and oxidized steel strip surface with a post-treatment agent takes place.

[0024] For this, a solution of the post-treatment agent, preferably a solution in water or an organic solvent or a ready to use preparation of the post-treatment agent, is sprayed onto the steel strip, which is moving at the strip speed. 1.5 to 10% aqueous solutions of the post-treatment agent proved to be expedient. Preferably the solution of the post-treatment agent is then stripped off by squeeze rollers and dried. A thin film of the post-treatment agent still remains on the surface of the coated metal strip after the squeezing and drying, where the weight of said thin film as a rule is between 2 and 30 mg/m².

[0025] The post-treatment agent is sprayed, for example via tubes that are arranged at a distance from the coated metal strip surface and transverse to the direction of strip travel and have holes or nozzles through which the post-treatment agent reaches the coated steel strip surface. Preferably at least one tube with such holes is arranged on each side of the steel strip in order to splatter or spray both sides of the metal strip with the post-treatment agent. Preferably, the distance between the
tubes and the tinned and anodically oxidized steel strip is adjusted and the position of the holes or nozzles with respect to the direction of travel of the steel strip selected so that the exiting liquid treatment agent strikes the steel strip perpendicularly to its surface or at least within an angle range of ±4.5°, preferably within an angle range of ±15° about the normal (perpendicular) to the surface of the steel strip.

[0026] As an alternative to spraying the post-treatment agent onto the surface of the tinned steel strip, an application in an immersion process is also possible.

[0027] To strip off the sprayed treatment agent, expeditiously two squeeze roller pairs are arranged after the tubes in the direction of strip travel. The spacing of the first squeeze roller pair from the tubes in the direction of strip travel is, for instance, between 20 and 100 cm. After the stripping, only a few molecular layers of the post-treatment solution remains on the tinned steel strip surface, possibly only one monomolecular layer of solution.

[0028] The solution stripped off by the squeeze rollers is collected in a supply tank, from which the excess post-treatment solution is optionally sent by pump to a preparation step and reused.

[0029] The agents defined below can be used as post-treatment agents. The application of a Ti/Zr-containing post-treatment agent is described as representative of this. The substance obtainable from Henkel KGaA under the trade name Granodine® 1456, for example, is used as a Ti/Zr containing post-treatment agent. It is applied to the tinned and oxidized steel strip surface as a solution with a dry layer weight in the range of 0.5 to 2 mg Ti/m², preferably 0.8 to 1.5 mg Ti/m², especially around 1 mg Ti/m².

Step 5

[0030] As the fifth step, a drying step again takes place, where the drying temperature (strip temperature) lies in the range of 30 to 95° C and preferably between 35 and 60° C. The drying time is matched to the strip speed. The drying devices indicated in step 3 can be used in this case.

[0031] The described method yields a tinned steel sheet with a layer structure composed as follows: at the bottom there is, as support, a cold rolled steel sheet, in particular a fine or ultrafine sheet with a thickness of 0.5 mm to 3 mm (fine sheet) or less than 0.5 mm (ultrafine sheet). The tin layer, for example electrolytically deposited, follows as the next layer on the sheet sheet. The amount of tin as a rule is 0.1 to 11.2 g/m², but in individual cases it can even be less than 0.1 g/m² or more than 11.2 g/m². Any alloy layers of support material and tin are ignored here as special intermediate layers. On the tin layer there then follows the oxide layer produced by anodic oxidation with a thickness of a few nm, which substantially consists of tetaevatrel tin oxide. The thickness of the tin oxide layer varies roughly in the range of 2 to 10 nm. The post-treatment agent layer, which was deposited on the thin oxide layer by the post-treatment and subsequent drying, follows on the oxide layer as the surface layer. The weight of the post-treatment agent in the dry state (dry film weight) is expediently between 2 and 30 mg/m².

[0032] The sheet produced and post-treated in accordance with the invention will either be cut into sheet panels or rolled up as a coil. The end user, for example the maker of tin cans, will as a rule then provide the sheet with an enamel layer, for example with a protective can enamel or an epoxide resin enamel. By comparison with the known tinplate materials, the enameled sheet will then be processed by deep drawing into molded objects, for example tin cans. The layer structure produced through the treatment in accordance with the invention contributes to an improved enamel adhesion and reduced flaking of the enamel, for example because of the presence of mercapto group-containing amino acids.

[0033] The substances that are suitable for use in the method in accordance with the invention for post-treatment of the surface of anodically oxidized tinplate must have properties such that they can adhere to the tin surface and at the same time allow wetting of the enamel layer that is to be applied in the subsequent enameling of the tin surface. The bonding between the functional group on the anodically oxidized tin surface and the functional groups of the enamel surface with their adhesion mediating molecules must be strong enough after drying the enamel film that they are [sic; it is] not disrupted in the cystine test (sterilization of the enameled tinplate for 90 min at 121° C in a solution of 3.65 g/L KH₂PO₄ with 7.22 g/L Na₂HPO₄·2H₂O and 1 g/L cystine).

In addition, the substances used for post-treatment should be chromium free and usable without the addition of organic solvents, or be soluble in distilled water, since the use of dissolving aids produces high concentrations of solvent in the exhaust air and thus would necessitate expensive purification systems to remove the solvent.

[0034] Substances that in practice are preferably used as additives for better dispersion of pigments in enamels or to improve the wetting and/or adhesion of enamels to metal surfaces, for example, prove to be especially suitable substances as post-treatment agents. Such agents are chosen from copolymers of acrylates, polyethyleneoxanes with polyether side chains, acid polyethers, and polymers with heterocyclic groups. However, substances that are used as corrosion protection agents for sheet metal, for example in the automotive industry, for example bonderizing or Parkerizing agents can also be advantageously used. Such substances are chosen from acidic, aqueous, liquid compositions that contain complex metal-fluoride anions with di- to tetravalent cations and polymer substances.

[0035] Besides copolymers of acrylates, the following substances proved to be especially suitable as post-treatment agents for the method in accordance with the invention:

[0036] a) an organically modified polysiloxane with a refractive index of 1.456 to 1.466 per DIN 53491 and a density at 20° C of 1.09-1.13 g/cm³ per DIN 51757 (commercially available under the name “EFKA 3580”),

[0037] b1) a polymer with a chemical composition of an acid polyether with a density of 1.20-1.30 g/cm³ per DIN 51757 and an acid value of 270-310 mg KOH/g per DIN 53402 [EFKA 8512],

[0038] b2) a polyacrylate modified with fluorocarbon residues, which has been neutralized with dimethylthanolamine, where an aqueous solution containing 59 to 61 wt % active substances has a density at 20° C of 1.04 to 1.06 g/cm³ per DIN 51757, a refractive index of 1.420 to 1.440 per DIN 53491, and an acid value of 50-70 mg KOH/g per DIN 53402 [EFKA 3570],

[0039] b3) a modified polyacrylate that has, for a content of 38-42 wt % active substance in water, a density of 1.02 to 1.06 g/cm³ per DIN 51757 and an amine number of 22 to 28 mg KOH/g per DIN 16945 [EFKA 4560],
c) a polymer that contains:

i) 0-80 mol % of one or more polymers of the formula

\[
R_1 - R_2 - R_3 - R_4
\]

where \( R_1, R_2, R_3, \) and \( R_4 \) can be the same or different and represent \( H \) or an alkyl,

ii) 0-70 mol % of one or more monomers of the formula

\[
R_5 \bigg( O - R_6 \bigg) - R_7 - R_8
\]

in which \( R_5, R_6, \) and \( R_7 \) can be the same or different and represent \( H \) or an alkyl, and \( R_8 \) represents an alkyl or a substituted alkyl, and the alkyl group \( R_8 \) can be interrupted by ---O--- groups,

iii) 5-50 mol % of one or more monomers containing a heterocyclic group with at least one basic ring nitrogen atom, or in which such a heterocyclic group is present after a polymerization,

iv) 0-10 mol % of one or more monomers containing one or more groups that are reactive for crosslinking or coupling, and

v) 0-20 mol % of one or more monomers that do not fall into the preceding groups i) iv), where the amount of the monomer of group i) together with monomers that contain an acrylate group is at least 20 mol %, and organic salts thereof, or

d) an acidic, aqueous, liquid composition that contains, besides water and optional solvents, the following components:

(A) fluorometallate anions with titanium, zirconium, hafnium, silicon, aluminum, and/or boron as central atoms; and optionally ionizable hydrogen atoms, and/or optionally one or more oxygen atoms;

(B) one or more divalent or tetravalent, especially divalent and/or tetravalent cations of cobalt, magnesium, manganese, zinc, nickel, tin, copper, zirconium, iron, and/or strontium;

(C) phosphorus-containing inorganic oxyanions and/or phosphonate anions, and

(D) one or more water-soluble and/or water-dispersible organic polymers and/or polymer-forming resins.

Preferably, the substance (d) is an acidic, aqueous, liquid composition that contains the following components in addition to water:

(A) fluorometallate anions that each consist of: (i) at least four fluorine atoms and (ii) at least 1 atom of a metallic element that is chosen from the group consisting of titanium, zirconium, hafnium, silicon, aluminum, and boron; and optionally (iii) ionizable hydrogen atoms, and/or optionally (iv) one or more oxygen atoms;

(B) an amount of one or more divalent, especially divalent and/or tetravalent cation(s) of cobalt, magnesium, manganese, zinc, nickel, tin, copper, zirconium, iron, and/or strontium, so that the ratio of the total number of cation (cations) to the number of anions in the component (A) is at least 1:5, but no more than 3:1;

(C) phosphorus-containing inorganic oxyanions and/or phosphonate anions, and

(D) one or more water-soluble and/or water-dispersible organic polymers and/or polymer-forming resins,

where the amount of these components is such that the ratio of the solids content of organic polymer and polymer-forming resin in the composition to the solids content of the component (A) lies in the range of 1:2 to 3:1.

In particular, the substance (d) is an acidic, aqueous, liquid composition that is substantially free of hexavalent chromium and/or ferricyanide, for treatment of metal surfaces, which contains no more than 1.0% and preferably no more than 0.0002% of both hexavalent chromium and ferricyanide and that otherwise contains the following components in addition to water:

(A) at least 0.010 M/kg [sic] fluorometallate anions, where said anions respectively consist of: (i) at least four fluorine atoms and (ii) at least 1 atom of a metallic element that is chosen from the group that consists of titanium, zirconium, hafnium, silicon, aluminum, and boron; and optionally (iii) ionizable hydrogen atoms, and/or optionally (iv) one or more oxygen atoms;

(B) an amount of di- to tetravalent, especially one or more divalent and/or tetravalent cation(s) of cobalt, magnesium, manganese, zinc, nickel, tin, copper, zirconium, iron, and/or strontium, so that the ratio of the total number of cation (cations) to the number of anions in the component (A) is at least 1:5, but no more than 3:1;

(C) at least 0.015 MP/kg [sic] and preferably at least 0.030 M/kg [sic] phosphorus-containing inorganic oxyanions and/or phosphonate anions, and

(D) at least 0.10% and preferably at least 0.20% of a water-soluble (or more water-soluble) and/or water-dispersible (more dispersible in water) organic polymer (organic polymers) and/or polymer forming resin (polymer forming resins), where the amount of said component is such that the ratio of the solids content of the organic polymer (organic polymers) and the polymer forming resin (polymer forming resins) in the composition to the solids content of the component (A) lies in the range of 1:2 to 3:1.

Preferably, the component (d) comprises dihydrogen hexafluorotitanate (2-) and organic polymers. Especially preferably is the component Granodine 1456.

The polymer (D) can be a polymer compound that comprises a copolymer material, where at least a part of the copolymer has the structure
which is defined more precisely in claim 1 and the dependent claims of the European patent application with the Publication Number EP0319017 A2.

[0065] Such a polymer can be prepared, for example, as follows:

[0066] A plastic flask is filled with 400 mL. Propasol P (a propoxylated propane solvent obtainable from Union Carbide Corp., Danbury, Conn.) and 160 g resin M (a polyvinyl phenol, obtainable from Maruzen Oil, MW=5000). A slurry of 263.3 g N-methylglucamine in 400 [sic] deionized water is added and the mixture is heated to 60-75° C. while stirring. Then 100.2 mL 37% formaldehyde is added over one to one and a half hours. The mixture is then heated to 90° C. and held for 6 hours. After cooling, the mixture is diluted to 9.6 wt% solids with deionized water. The pH of the prepared solution is 9.1 and the solution comprises an N-methylammonium derivative.

[0067] Also suitable are the polyphenylene derivatives in accordance with claim 1 and the dependent claims of the European patent application with the publication number EP 0 319 016 A2:

[0068] Such a polymer can be prepared, for example, as follows:

[0069] 80 g of a resin of the above formula with an average molecular weight of about 2400, in which R₅, R₁₁, R₁₄, and W₂ are II, R₆ is —CH₂—, and Y₂ is an alkylamine residue or an alkyllammonium residue (with reference to the Formula 1 given in EP 0 319 016 A2 and its definitions), are slowly dissolved in 160 mL Propasol P (a propoxylated propanol solvent obtainable from Union Carbide Corp., Danbury, Conn.) in a 1 liter plastic flask using a high speed mixer. The plastic flask is fitted with a paddle stirrer, a reflux condenser, and a nitrogen flush device. Then 53.5 g 2-(methylamino) ethanol and 160 mL deionized water are added to the resin solution. Careful heating to 60° C. is begun. When 60° C. is reached, the addition of 50 mL 37% formaldehyde in water is begun, and this addition is continued over a time of 1 h. Another 25 mL Propasol P are added, and the reaction mixture is held at 60° C. for 1.5 h. The temperature is raised to 80° C. and held there for 1.75 h. The reaction mixture is allowed to cool to room temperature, and 21.8 g 75% H₃PO₄ followed by 960 mL deionized water are added. Optionally, an amine oxide, which does not require an additional neutralization step, is formed by adding 0.75 mol 30% H₂O₂ (85 g) to the reaction mixture. The reaction mixture is stirred overnight and then diluted with 960 mL deionized water. The result of this optional step is a water-soluble amine oxide resin, which does not require neutralization for water stability.

[0070] Suitable post-treatment agents with complex bound transition metals are, for example, products of the Granodine® series, which are aqueous solutions containing complex bound transition metals (Ti, Mn, Zr) and optionally a silane. Titanium- and/or zirconium-containing post-treatment agents proved to be especially suitable, for example products of the Granodine® series (manufacturer: Henkel) or Gardobond® series (manufacturer: Chemetall), especially the products “Granodine® 1456” and “Gardobond® X 4707.” These titanium- and zirconium-containing products are expediently metered as post-treatment agents for the method in accordance with the invention so that after the squeezing out and drying, a titanium weight (dry weight) of 0.5 g/m² to 2 mg/m² and especially about 1.0 mg/m² is present on the surface of the treated triplate. Typically for this, 1.5-10% aqueous solutions of said post-treatment agents are used, where the fraction of titanium in the aqueous solution is preferably between 0.2 and 1.2 g/L and especially preferably between 0.2 and 0.5 g/L.


[0072] The following products from BASF SE are preferred: EFKA 3570, EFKA 3580, EFKA 4560, and EFKA 8512. EFKA 4560 is especially preferred.

[0073] Acrylate-containing agents with N-heterocyclic groups proved to be especially suitable for the post-treatment agents, for example EFKA 4560. These agents correspond to the above defined components (c).

[0074] They can be prepared, for example, as follows:

[0075] 2.84 g vinyltoluene, 4.55 g isobutyl methacrylate, 7.36 g ethylhexyl acrylate, 5.20 g hydroxyethyl methacrylate, 1.80 g polyethylene glycol monomethacrylate with a molecular weight of about 400, and 0.44 g di-tert-butyl peroxide are dissolved in 9.86 g xylene and 4.93 g methoxypyrrol acetate in a reaction flask that is suitable for polymerizations and that is equipped with a reflux condenser. The polymerization was carried out at the boiling point of the mixture with stirring and with feeding of an inert gas. At the end of the polymerization, 9.79 g isophorone disiocyanate were dissolved in 16.58 g isobutyl acetate and 16.58 g methoxypyrrol acetate, and the remaining free NCO groups were then reacted with 3.60 g
polyethylene glycol monomethacrylate with a molecular weight of about 400 and 4.51 g 1-(3-aminopropyl)imidazole.

[0076] The solids content was then adjusted to 40 wt % with butyl acetate.

[0077] Similarly, 3.54 g vinyl toluene, 5.69 g isobornyl methacrylate, 9.20 g 2-ethylhexyl methacrylate, 7.15 g hydroxyethyl methacrylate, and 1.28 g di-tert-butyl peroxide dissolved in 11.94 g xylene and 5.97 g methoxypropyl acetate were polymerized.

[0078] Then 12.23 g isophorone diisocyanate dissolved in 20.36 g butyl acetate and 20.36 g methoxypropyl acetate were added. The remaining free NCO groups were then reacted with 4.50 g polyethylene glycol monomethacrylate with a molecular weight of about 400 and 3.78 g 3-amino-1,2,4-triazole in 11.34 g N-methylpyrrolidone.

[0079] The solids content was then adjusted to 40 wt % with butyl acrylate.

[0080] In accordance with the above described method of the invention, these substances are sprayed in undiluted form or as an aqueous solution onto the tinned steel strip and optionally then squeezed off and dried. Dry film weights in the range of 2 to 15 mg/m² and preferably between 2 and 10 mg/m² are suitable as application weights for, for example, the substance EFKA 4560.

[0081] With the post-treatment agent(s), the (further) zinc oxide buildup on the coated metal strip surface during its storage before being coated with lubricant can be highly reduced. At the same time, with the treatment of the anodically oxidized, tinned steel strip surface with said post-treatment agents in accordance with the invention, there is an improvement of enamel adhesion. The tinplate surfaces treated in accordance with the invention proved to be very readily coatable with enamel.

[0082] As a result of the treatment of tinplate with an anodic oxidation and the application of a chromium-free post-treatment agent in accordance with the invention, it turned out that sulfur-containing substances, which are present in foods and derived, for example, from the amino acids cysteine or methionine, are no longer able to pass by diffusion through the subsequently applied enamel coating layer and the passivation in accordance with the invention to the tin surface and to give rise to unsightly marbling flaws there (yellow or brown discolorations), which are substantially due to the formation of tin sulfide, and which in an extreme case can lead to deterioration of the adhesion of the enamel to the tinplate or to separation of the enamel coating.

[0083] The tinplate samples treated in accordance with the invention in some cases have clearly lower sliding friction than untreated tinplate, and with individual substances it is even possible to obtain lower coefficients of friction than the traditional treatment of the tinplate with DOS.

[0084] From a thorough examination of the results of comparative experiments, it can be concluded that, with the method in accordance with the invention for passivation of the surface of tinplate by anodic oxidation and coating with the post-treatment agents used in accordance with the invention, the best results with regard to resistance to oxidation and marbling (sulfide blocking activity) and friction are obtained. The results are comparable with the quality of the passivation of tinplate with chromium-containing post-treatment agents that is known from the prior art.

[0085] The substances EFKA 3580, EFKA 4560, EFKA 8512, and EFKA 3570 produce very good results with regard to the properties low coefficients of friction, resistance to oxidation (low tin oxide buildup), and resistance to marbling (sulfide blocking activity). In this regard EFKA 4560 turned out to be the preferred post-treatment agent. With regard to resistance to marbling and enamel adhesion, the titanium-containing post-treatment agents of the Granodine® series (especially Granodine® 1456) and Gardobond® series (especially Gardobond® X 4707) show very advantageous results. However, other chromium-free post-treatment agents, in some cases already known from the prior art, are also suitable for conducting the method in accordance with the invention. The method in accordance with the invention can be employed both in the case of tinplate with a fused-on tin layer as well as in the case of a tinplate in which the tin layer has not been fused on.

1. Method for passivating the surface of a tinned steel strip, which is moving at a strip speed of at least 200 m/min through a coating system, wherein after tinning the steel strip the surface is first anodically oxidized in order to form an oxide layer, which substantially consists of tetravalent tin oxide (SnO₂), and then a liquid solution of a chromium-free post-treatment agent is applied to the oxide layer.

2. Method of claim 1, wherein the anodic oxidation is conducted with a basic electrolyte and at a current density of 1.0 A/dm² to 3.0 A/dm² by passing the tinned steel strip through an electrolysis bath.

3. Method of claim 2, wherein the basic electrolyte is chosen from an alkali metal or alkaline earth metal hydroxide or carbonate, a basic alkali metal phosphate, and a basic organic alkali metal or alkaline earth metal salt.

4. Method of claim 2, wherein the electrolyte contains sodium carbonate.

5. Method of claim 2, wherein the electrolysis bath is adjusted so that a charge of at least 0.2 C is achieved.

6. Method of claim 1, wherein the post-treatment agent is chosen from copolymers of acrylates, polymethylsiloxanes with polyether side chains, acid polyethers, polymers with heterocyclic groups, and acidic, aqueous, liquid compositions that contain complex metal fluoride anions with di- to tetravalent cations and polymer substances.

7. Method of claim 1, wherein the post-treatment agent contains titanium and/or zirconium.

8. Method claim 1, wherein after the anodic oxidation, an aqueous solution of the post-treatment agent or a ready to use solution of the post-treatment agent is applied by a passage through a bath containing the post-treatment agent.

9. Method claim 1, wherein the post-treatment agent is sprayed through at least one tube, which is arranged at a distance from the coated metal strip surface and has at least one hole or nozzle through which the post-treatment agent is sprayed onto one or each coated surface of the steel strip.

10. Method claim 1, wherein the solution of the post-treatment agent is applied to both sides of the steel strip.

11. Method of claim 9, wherein the post-treatment agent is sprayed onto the tinned steel strip surface(s) in the form of liquid jets, where the liquid jets strike the surface in an angle range of between +45° and −45° to the normal to the surface.

12. Method of claim 1, wherein the solution of the post-treatment agent, after being applied to the tinned and oxidized surface of the steel strip, is squeezed off by means of squeeze rollers.

13. Method of claim 12, wherein the tinned steel strip is dried after squeezing off the post-treatment agent.

14. Method as in claim 13, wherein after squeezing off the post-treatment agent and drying, a thin film of the post-treat-
ment agent with a weight between 2 mg/m² and 30 mg/m² is present on the tinned steel strip.

15. Method as in claim 13, wherein the post-treatment agent is titanium-containing and that after squeezing off the titanium-containing post-treatment agent and after drying, a thin film of the post-treatment agent with a titanium weight between 0.5 mg/m² and 2 mg/m² is present on the surface of the tinned steel strip.

16. Method of claim 1, wherein the anodic oxidation of the tinned surface of the steel strip takes place within an anodization time of 0.1 to 1.0 second and preferably within an anodization time between 0.2 and 0.7 second.

17. Tinned steel strip or sheet with a support layer of a fine or ultrafine sheet of steel, a tin layer deposited thereon, and a surface layer of a chromium-free post-treatment agent, characterized in that between the tin layer and the surface layer of the post-treatment agent, an oxide layer is formed, which substantially consists of tetravalent tin oxide (SnO₂).