

(19)



(11)

EP 3 626 862 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
10.03.2021 Bulletin 2021/10

(51) Int Cl.:
C25D 5/48 (2006.01) **C25D 9/08 (2006.01)**
C25D 7/06 (2006.01)

(21) Application number: **19198876.5**

(22) Date of filing: **23.09.2019**

(54) PASSIVATION PROCESS OF A STEEL TINPLATE

PASSIVIERUNGSVERFAHREN EINER STAHLZINNPLATTE

PROCÉDÉ DE PASSIVATION DE FER BLANC D'ACIER

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

(30) Priority: **24.09.2018 IT 201800008861**

(43) Date of publication of application:
25.03.2020 Bulletin 2020/13

(73) Proprietor: **Tenova S.p.A.**
20149 Milano (IT)

(72) Inventors:
• **MARTINES, Stefano**
16138 Genova (IT)

• **ASTENGO, Giovanni**
16156 Genova (IT)
• **GIANNETTI, Armando**
00071 Pomezia (RM) (IT)

(74) Representative: **Maturano, Pasqualino**
Barzanò & Zanardo Milano S.p.A.
Via Borgonuovo, 10
20121 Milano (IT)

(56) References cited:
EP-A1- 0 732 425 EP-A1- 2 180 084
JP-A- 2018 012 858 US-A1- 2010 119 867

EP 3 626 862 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] The present invention concerns a passivation process of a steel tinplate. In particular, the present invention concerns an electrolytic passivation process, with a low environmental impact, which allows obtaining a passivated steel tinplate, on which it is possible to make adhere a further coating, such as a paint layer, an ink or a polymeric film, with an excellent degree of adhesion.

[0002] The passivated steel tinplate obtained with the passivation process according to the present invention can be advantageously used to produce steel packaging, such as for example containers for packaging food products, chemical and cosmetic products.

[0003] The steel tinplate (hereinafter "tinplate") is a steel sheet obtained by cold rolling, generally of a thickness up to a maximum of about 0.5 mm, coated on both faces with a thin tin layer, which has the function of protecting steel from corrosion. The tin coating is generally made by electrolytic deposition of metallic tin on the steel sheet. Due to the exposure to air, a thin oxide layer is present on the surface of the tin coating.

[0004] The tinplate is mainly used to produce packaging, in particular cans for food products intended for human and animal consumption, packaging for chemical products, containers for aerosol, beverage cans and to produce parts of said packaging, such as closures, lids, bottoms, etc.

[0005] In general, the tinplate has a high resistance to corrosion and stability against acids and a good processability. For some applications, for example for the production of packaging for food products, the surface of the tinplate is also provided with an additional coating, for example a paint layer (e.g. epoxy, acrylic paints, etc.) or a laminated polymeric film (e.g. polyethylene terephthalate (PET), polypropylene (PP) film, etc.), to ensure greater protection of the surface of the container from corrosion with respect to the tin coating only.

[0006] Paints, inks and coating polymeric films are generally applied to the tinplate at the end of the production process thereof and before its use in the production of packaging. In the production process of packaging, therefore, these coatings undergo mechanical processings (e.g. drawing and stretching), which can cause the deterioration or the detachment (*peel-off*) from the surface of the tinplate, if there is no good adhesion to the latter. Furthermore, in some applications, the packaging, after being filled with the contents, is subjected to heat treatments (e.g. pasteurization, sterilization), which can damage the coating, for example by forming bubbles (*blistering*), or cause its detachment.

[0007] In order to improve the resistance to attacks by aggressive chemicals and the adhesion of the coating to the tinplate, in the prior art it is known to subject the tinplate to a chromium passivation treatment, generally of the electrolytic type, by means of which a thin chromium layer is deposited on the surface of the tinplate.

[0008] In recent years, however, due to the growing demands for limiting the use of environmentally hazardous substances, such as chromium and cadmium, the need is strongly felt to have treatment processes with a low environmental impact as an alternative to the chromium passivation processes, which still guarantees an adequate degree of adhesion of the coating to the tinplate.

[0009] In the state of the art some passivation processes are known which do not use chromium compounds, the so-called "Cr-free" processes. For example, EP 2180084 A1 and EP 2557202 A1 describe Cr-free passivation processes with which a surface coating layer containing zirconium is deposited on the tinplate, which guarantees excellent adhesion of subsequent coatings, such as paints and polymeric films.

[0010] EP 2180084 A1, in particular, describes a passivation process which comprises a first step of treatment to partially remove the tin oxide layer originally present on the surface of the tinplate, until reducing it to a thickness layer in the range 0 - 3.5 mC/cm² (thickness measured by means of an electrolytic stripping method), by means of a cathodic electrolytic treatment in an aqueous solution of sodium hydrogen carbonate, followed by a second step of passivation treatment, in which the tinplate is subjected to a cathodic electrolytic treatment in an aqueous solution of zirconium sulphate to form a coating layer containing zirconium mainly in the form of oxide and hydroxide (passivation layer). In a third step, the zirconium-passivated tinplate is then subjected to washing in hot water to reduce the amount of sulphate ions present on the surface of the layer containing zirconium, preferably up to a value of weight per unit of area of sulphate ions lower than 7 mg/m², since the presence of sulphate ions in relatively high amounts negatively affects the adhesion of the coatings to the passivation layer containing zirconium.

[0011] EP 2557202 A1 describes a passivation process which comprises a first step of treatment to partially remove the tin oxide layer present on the surface of the tinplate, until reducing it to a thickness layer in the range 0 - 3.5 mC/cm², by means of a cathodic electrolytic treatment in an aqueous solution of sodium carbonate or sodium hydrogen carbonate or by immersion in an aqueous solution of sulphuric acid, followed by a second step, in which the tinplate is subjected to a cathodic electrolytic treatment in an aqueous solution of a sulphate of an alkali metal containing a zirconium compound to form a passivation layer containing zirconium. In a third step, the tinplate is then subjected to washing in hot water to reduce the amount of sulphate ions present on the surface of the passivation layer containing zirconium, preferably up to a value of weight per unit of area of sulphate ions lower than 7 mg/m².

[0012] In consideration of the aforesaid state of the art, the Applicant set out to solve the primary objective of providing a passivation process of the tinplate that is of the Cr-free type, namely that does not use chromium compounds, but that

nevertheless guarantees a high adhesion of the coatings, such as paints, inks or laminated polymer films.

[0013] In the course of their own research, the Applicant has observed that the degree of adhesion of the coatings to a passivated tinplate with zirconium compounds, as obtainable for example with the known processes described above, is influenced by the possible presence of carbonate ions on the surface of the passivation layer containing zirconium, as well as the presence of sulphate ions as already known in the state of the art.

[0014] Therefore, the passivation processes known in the art which envisage electrolytic pre-treatments in aqueous solutions containing carbonate and hydrogen carbonate ions (hereinafter generally referred to as carbonate ions), have the disadvantage of involving problems of adhesion of the coating in the final product, if the concentration of carbonate ions is not carefully controlled.

[0015] Furthermore, in the known passivation processes which envisage a preliminary step of reduction of the thickness of the tin oxide layer by immersion in aqueous solutions of sulphuric acid, there is the drawback of not being able to adequately control the process of reduction of the thickness. With respect to the electrolytic treatments, in fact, in the immersion pre-treatments substantially only the duration of immersion and the concentration of sulphuric acid in the bath can be regulated: if the concentration of sulphuric acid is too high, there is the risk that the tin layer, after treatment, is deteriorated and does not have a uniform thickness over the entire surface with consequent problems of adhesion of the coatings; if the concentration of sulphuric acid is too low, instead, the time necessary for the treatment becomes excessively long. Furthermore, the pre-treatments by immersion in aqueous solutions of sulphuric acid require a subsequent step of very accurate washing of the tinplate with water, with consequent increase in the consumption of energy and raw materials and the use of more bulky plants.

[0016] The Applicant has now found that the aforesaid and other drawbacks of the state of the art, which will appear more evident in the following description, can be overcome, at least in part, by a Cr-free passivation process of a tinplate which allows obtaining a tinplate coated with a passivation layer containing zirconium, in which the preliminary treatment for reducing the thickness of the tin oxide layer present on the non-passivated tinplate is carried out by means of a cathodic electrolytic treatment in an aqueous solution of at least one sulphate of an alkali metal, in substantial absence of carbonate ions; in a subsequent step, the so-treated tinplate is subjected to a second cathodic electrolytic treatment in an aqueous solution containing at least sulphate ions and zirconium ions to form a passivation layer containing zirconium.

[0017] Using an electrolytic solution based on sulphate ions in the electrolytic treatment for reducing the initial tin oxide layer avoids introducing an excessive amount of carbonate ions in the passivation process; this makes it easier to control the amount of carbonate ions on the final passivated tinplate.

[0018] Furthermore, the treatment for reducing the tin oxide layer, being carried out electrolytically in an aqueous solution of a sulphate of an alkali metal, in addition to being more rapid and easily controllable than the treatment by immersion in a solution of sulphuric acid, is simple to make and does not require the adoption of particular safety systems for the operators or anticorrosive materials for the equipment, as is the case in the case of processes that use aqueous solutions of sulphuric acid.

[0019] According to a first aspect, the present invention therefore concerns a passivation process of a tinplate comprising the following steps in sequence:

- a. subjecting said tinplate to at least one cathodic electrolytic treatment in an aqueous solution containing at least one alkali metal sulphate to obtain a tin oxide surface layer having thickness lower than 6 mC/cm^2 ;
- b. subjecting said tinplate to at least one cathodic electrolytic treatment in an aqueous solution containing at least sulphate ions and zirconium ions to form a passivation layer containing zirconium on said tin oxide surface layer.

[0020] According to a second aspect, the present invention concerns a process for producing a coated tinplate which comprises the following steps in sequence:

- providing a passivated tinplate comprising a passivation layer containing zirconium obtained with the aforesaid passivation process;
- applying at least one coating on said passivation layer containing zirconium selected from: paint layer, lacquer layer, enamel layer, ink layer and polymeric material film.

[0021] For the purpose of the present description and appended claims, the verb "comprise" and all the terms deriving therefrom also include the meaning of the verb "consist" and of the terms deriving therefrom.

[0022] The limits and numeric ranges expressed in the present description and appended claims also include the numeric value or numeric values mentioned. Furthermore, all the values and sub-ranges of a limit or numeric range must be considered to be specifically included as if they had been explicitly mentioned.

[0023] The passivated tinplate in accordance with the process according to the present invention is a substrate on which organic coatings, such as paints, lacquers, enamels, inks or polymeric films adhere very well. The degree of

adhesion is comparable to that of the chrome-passivated tinplates of the known art.

[0024] The process according to the present invention, not using compounds containing chromium (Cr-free), is a process with a low environmental impact. Furthermore, at least in one embodiment, the process does not even use fluorinated or nitrogen-based compounds which can give rise to nitrate compounds which, as is known, represent a problem from the point of view of the environmental impact.

[0025] Further characteristics and advantages of the present invention will become clear from the following detailed description of the invention in which reference will also be made to the appended figure 1, which schematically shows the trend of the detachment strength (T-peel strength) of a coating as a function of the amount of carbonate ions present on the surface of the passivated tinplate.

[0026] The tinplate that can be treated with the passivation process according to the present invention does not present particular restrictions in terms of composition. In general, the tinplate can be a conventional tinplate, for example of the type used to produce packaging, such as containers (so-called cans) for food products intended for human and animal consumption, chemical products, containers for aerosol and to produce parts of said packaging, such as closures, lids, bottoms, etc.

[0027] The tin layer of the tinplate is preferably present in a weight per unit of area in the range 0.5-15.2 g/m² (expressed as metallic Sn; weight per unit of area referred to each face of the tinplate).

[0028] The coating layer of metallic tin is coated superficially by a tin oxide layer, which inevitably forms following the exposure of the tinplate to air.

[0029] In the first step (step a) the tinplate is subjected to at least one cathodic electrolytic treatment (that is, an electrolytic treatment in which the tinplate acts as a cathode) using as an electrolytic solution an aqueous solution containing at least one alkali metal sulphate. The purpose of the electrolytic treatment of step a is to reduce the thickness of the tin oxide layer on the non-passivated tinplate. The Applicant has observed that thickness values of the tin oxide layer lower than 6 mC/cm² promote the adhesion of the passivation layer containing zirconium applied in step b.

[0030] Preferably, the thickness of the tin oxide surface layer obtained at the end of the treatment of step a is lower than or equal to 5.0 mC/cm², more preferably it is comprised in the range 0.1-3.0 mC/cm². In fact, it has been observed that a thickness of the tin oxide layer in the aforesaid range promotes a more uniform and reproducible deposition of the passivation layer containing zirconium.

[0031] For the purposes of the present invention, the thickness values of the tin oxide layer expressed in mC/cm² (before or after step a) are considered to be determined by the method described in the Examples.

[0032] The aforesaid thickness values of the tin oxide can be obtained in step a by selecting the ion concentration in the electrolytic solution, the pH, the temperature and the current density applied in relatively wide ranges of values.

[0033] Preferably, the sulphate of an alkali metal of the electrolytic bath of step a is selected from sodium sulphate, potassium sulphate or mixtures thereof.

[0034] Preferably, the concentration of the alkali metal sulphate in the bath is in the range 30-150 g/l, more preferably in the range 40 - 100 g/l.

[0035] Preferably, the cathodic electrolytic treatment is carried out in the aforesaid solution in substantial absence of carbonate ions, that is in the absence of carbonate and bicarbonate ions added on purpose.

[0036] Preferably, the cathodic electrolytic treatment is carried out with an electric current density in the range 2-50 A/dm², more preferably in the range 5 - 30 A/dm².

[0037] Preferably, the temperature of the electrolytic solution is in the range 20-80°C, more preferably in the range 40 - 60°C.

[0038] Preferably, the pH of the electrolytic solution used in step b is in the range 6-8.

[0039] Preferably, the duration of the cathodic electrolytic treatment is in the range 0.3-2.0 seconds, more preferably in the range 0.4-1.4 seconds.

[0040] The cathodic electrolytic treatment is carried out with a continuous electric current.

[0041] At the end of step a, the tinplate can be subjected to a washing with water to eliminate any electrolyte residues or other impurities present on the surface. However, considering that in the process according to the present invention also the electrolytic solution used in step b is based on sulphate anions, the possible entrainment of these anions from step a to step b does not represent a criticality.

[0042] In step b the tinplate treated in step a is submitted to at least one cathodic electrolytic treatment in a bath formed by an aqueous solution containing at least sulphate ions and zirconium ions. The purpose of step b is to form a passivation layer containing zirconium on the tin oxide surface layer present on the tinplate after step a. The treatment of step b allows the deposition of a passivation layer containing zirconium mainly in the form of oxide or hydroxide.

[0043] Preferably, after step b the amount of zirconium in the passivation layer containing zirconium is in the range 5-15 mg/m². For the purposes of the present invention, the weight per unit of area of the passivation layer containing zirconium is meant to be determined by X-ray fluorescence absorption spectroscopy.

[0044] In a first embodiment the electrolytic solution used in step b is an aqueous solution of zirconium sulphate.

[0045] In a second embodiment, the electrolytic solution used in step b is an aqueous solution containing zirconium

sulphate and alkali metal sulphate, preferably sodium.

[0046] In both of the aforesaid embodiments, the concentration of zirconium ions in the electrolytic solution is preferably in the range 0.1-10.0 g/l, more preferably in the range 0.5-2.0 g/l.

[0047] Preferably, the concentration of alkali metal sulphate in the electrolytic solution, where present, is in the range 5-60 g/l, more preferably in the range 10-50 g/l.

[0048] It has been observed that the presence of sodium sulphate in the electrolytic solution of step b in addition to zirconium sulphate promotes the control of the zirconium deposition, thus being obtainable a more uniform passivation layer, even in the presence of possible variations in the density of the electric current.

[0049] Preferably, the pH of the electrolytic solution used in step b is in the range 0.5-2.5, more preferably in the range 1.5-2.4. The pH of the solution can be adjusted, for example, by adding an aqueous solution of sulphuric acid.

[0050] Preferably, the temperature of the electrolytic solution used in step a is in the range 20-80°C, more preferably in the range 40 - 60°C.

[0051] Preferably, the cathodic electrolytic treatment of step b is carried out with an electric current density in the range 2-50 A/dm², more preferably in the range 5- 30 A/dm².

[0052] Preferably, the cathodic electrolytic treatment has a duration in the range 0.3-5.0 seconds, more preferably in the range 0.5-2.0 seconds.

[0053] The cathodic electrolytic treatment is carried out with a continuous electric current.

[0054] At the end of step b, preferably the passivated tinplate is subjected to a washing with water to remove any sulphate ions possibly present on the surface, which negatively affect the adhesion capacity of the coatings (both in the form of paint or ink and in the form of film) or they can give rise to the appearance of stains on the surface of the tinplate. It has been observed that generally the adhesion of the coating to the passivation layer is acceptable when a residual amount of sulphate ions lower than about 20 mg/m² is present on the passivated surface.

[0055] For the purposes of the present invention, a coating has a degree of adhesion suitable for most applications if the detachment strength is greater than or equal to 60 N/10mm, determined with the T-peel strength test described in the examples.

[0056] The washing with water can be carried out by immersion of the passivated tinplate in water or with spray systems, preferably with hot water (e.g. up to 80°C). The duration of the washing is preferably in the range 0.4-5.0 seconds, preferably in the range 0.5-2.0 seconds. The washing is generally followed by a drying step, for example by exposure to ambient air or by heating.

[0057] Since the process according to the present invention does not envisage steps of treatment for the tinplate with solutions containing carbonate ions added on purpose, their concentration on the surface of the passivated tinplate is generally such as not to significantly affect the adhesion of the coating. However, in certain cases, for example when water of relatively high hardness is used in the process, the concentration of carbonate ions on the passivated tinplate could be such as to create problems of coating adhesion. The Applicant has observed that the best results of coating adhesion are obtained when the concentration of carbonate ions on the passivation layer containing zirconium is lower than or equal to about 20 mg/m² (Figure 1).

[0058] For the purposes of the present invention, the concentration of the sulphate and carbonate ions is considered to be measured by the method described in the Examples.

[0059] The tinplate passivated with the coating layer comprising zirconium obtained with the passivation process according to the present invention is a suitable support for the application of a coating, such as a paint layer, a lacquer layer, an enamel layer, an ink layer or a polymeric material film.

[0060] Examples of paints that can be applied as coatings are: epoxy paints, phenol-epoxy paints, vinyl paints, acrylic paints.

[0061] Examples of polymeric films that can be applied as a coating are: polyethylene terephthalate (PET), polypropylene (PP) film.

[0062] The passivation process according to the present invention as well as the process for applying a coating on the passivated tinplate can be made with the techniques and equipment known to the person skilled in the art.

[0063] Embodiments of the present invention are provided below solely by way of illustrative example, which must not be considered limiting of the scope of protection defined by the appended claims.

EXAMPLES

[0064] The characterization of the materials described in the present patent application was carried out with the following methods.

1. Measurement of the thickness of the tin oxide layer

[0065] The thickness of the tin oxide layer was determined by means of a coulombometric method. According to this

method, the tin oxide layer is reduced by applying a constant and controlled cathodic current, in an aqueous solution of hydrobromic acid (HBr) 0.1% which is deprived of the oxygen present therein by insufflation of gaseous nitrogen. The progress of oxide reduction is monitored by measuring the reduction potential. The delivered electric charge (current density * treatment time) to reach the complete reduction is used as a measurement of the thickness of the tin oxide layer.

[0066] The test is carried out in an electrolytic cell with a platinum counter-electrode and an Ag/AgCl reference electrode. A cathodic current density of - 0.40 A/m² is applied to the sample and the potential is measured until the potential of the metallic tin is reached, indicating that the reduction has been completed. The measured values are displayed in a graph potential v. treatment time, which typically shows a sharp decrease in the potential with a point of inflection at which the treatment time (ti) corresponding to the completed reduction of the tin oxide layer is determined. The thickness value of the tin oxide layer is calculated by means of the equation $D \text{ [mC/cm}^2\text{]} = 0.1 * ti \text{ [seconds]} * 0.40 \text{ [A/m}^2\text{]}$.

2. Quantitative determination of the carbonate and sulphate ions

[0067] The quantitative determination of the carbonate and sulphate ions on the surface of a tinplate was carried out according to the ASTM E1019, E1409 and E1806 standards. The tinplate sample (dimensions 4 mm x 100 mm) was cleaned with acetone and dried with hot air before the test. The test is based on the determination of the amount of CO₂ and SO₂ produced following the heat treatment of the sample in an induction furnace to cause the complete conversion of carbon into CO₂ and sulphur into SO₂. For each material, the test was carried out on three samples, extrapolating a final average value.

3. Test of staining with Cysteine

[0068] The resistance of a passivated (uncoated) tinplate to prolonged contact with food was evaluated by the test of staining with Cysteine.

[0069] The test provides for the immersion of square samples (40x40 mm) of passivated (uncoated) lamina in a solution containing 3 g/l of Cysteine hydrochloride neutralized at pH 7 with Na₃PO₄ 0.2 M and allowed to boil for 1 hour.

[0070] The samples, drilled with a 4 mm hole and skewered with a glass rod spacing them with 15 mm spacers, are introduced into a 1000 ml bottle, made of glass resistant to sterilization, filled with the Cysteine solution.

[0071] The bottle is introduced into a suitable pressure container which is heated at 110°C and remains at this temperature for 30 minutes.

[0072] After cooling, washing and drying, the surface appearance of the samples is compared with standards at different levels of stains:

- Level 1 = surface with no stains
- Level 2 = surface with no stains but with a faint colouring or surface with a few small dark stains
- Level 3 = surface with diffuse stains and a few areas with no stains
- Level 4 = completely stained surface (like the non-passivated tinplate).

4. Coating of the passivated tinplate

[0073] The passivated tinplate in accordance with the present invention was coated with a white epoxy enamel using a "bar coater". The applied coating layer had a thickness equal to 24 micrometres. After application, the coating was thermally treated at 200°C for 10 minutes and then allowed to cool up to room temperature by exposure to air. The completion of the curing of the coating was verified by the ASTM D 5402 method.

[0074] For comparison, the same coating was applied to a commercially available sample of a tinplate passivated with chromium ("Reference").

5. Evaluation of the adhesion strength of the coating on the passivated tinplate

[0075] The adhesion strength of the coating applied on the passivated tinplate as described in the previous point 4 was evaluated with the following tests.

5.1 Dry adhesion test

[0076] The dry adhesion strength of the coating was evaluated with the ASTM D3359 B method. The method provides

for the application of a strip of adhesive tape on the surface of the coating, on which a grid was previously engraved, and after 15 minutes of contact for its removal by a quick tear. The extent of the defects visible to the naked eye caused by the tear was evaluated using a scale of values from 0 to 5, which were assigned based on the percentage of the damaged surface area (0 = no visible defect; 5 = more than 50% of the surface area has visible defects).

5.2 Cathodic wet adhesion test

[0077] The wet adhesion strength of the coating was evaluated by submitting a sample of a passivated and coated tinplate on which a grid in an area of 4 cm x 4 cm was previously engraved, to immersion in a solution containing citric acid (0.1 M, pH = 3) with application of a cathodic polarization of -2 V, for 30 minutes, at 25°C. The sample was then washed with distilled water and dried. The adhesion strength of the coating was evaluated with the ASTM D3359 B method described at point 5.1.

5.3. Coating detachment strength ("T-peel test")

[0078] The detachment strength of the coating was determined by a comparative test derived from the ASTM D1876-08 method, which was modified as described below.

[0079] Two laminae of passivated and coated tinplate having dimensions of 100 mm x 10 mm were glued together by means of an epoxy structural adhesive (3M - EC 923 B/A). The adhesive was applied on the laminae for a length of 30 mm, so as to leave free two 70 mm long ends (bent at 90 ° with respect to each other so as to form a "T") to be fixed to the traction machine.

[0080] During the test, the tensile load applied by the machine at the two ends necessary to obtain a separation speed of the two laminae equal to 10 mm/min was recorded. The result is expressed in N/10 mm unit. For each material, the test was carried out on three samples, extrapolating a final average value that was compared with the one of a sample of an industrial chromium-passivated lamina. In addition to the load it was evaluated whether the detachment was of the "cohesive" (within the layer of structural adhesive) or "adhesive" type (between the coating and tinplate). If the break is of the cohesive type, it can be concluded that the test measured the breaking strength of the adhesive and that the adhesion of the coating is greater than this value. Considering 60 N/10mm as a threshold value for a satisfactory adhesion, an adhesive with a greater adhesion value was chosen.

6. Passivation of the tinplate

[0081] A first series of samples (no. 1-7) of a (not passivated) tinplate having a tin layer of 2.8 g/m² by weight per unit of area on both faces was passivated using the process according to the present invention. The tinplate was subjected to a cathodic electrolytic treatment to partially remove the tin oxide layer (step a). The operating conditions of step a adopted for each sample are shown in Table 1 below.

Table 1 - Removal of tin oxide (step a)

Sample no.	Na ₂ SO ₄ electrolytic bath (g/l)	Treatment duration (s)	Bath temp. (°C)	Current density (A/dm ²)	Thickness SnOx ⁽ⁱ⁾ (mC/cm ²)
1	50	0.7	50	10	1.6
2	50	0.7	50	3	5.5
3	50	0.7	60	10	1.8
4	150	0.7	50	10	1.0
5	40	0.5	50	30	2.3
6	30	0.5	40	10	4.3
7	40	1	50	3	2.1
(i): thickness of the tin oxide layer on the tinplate at the end of step a					

[0082] The results of Table 1 highlight that by varying the operating conditions of step a it is possible to obtain thicknesses of the tin oxide layer on the tinplate in a wide range of values (1.6 - 5.5 mC/cm²).

[0083] Samples 1, 3 and 5 were then subjected to a subsequent cathodic electrolytic treatment for zirconium deposition

to form the passivation layer (step b) in a bath containing zirconium sulphate and sodium sulphate. The operating conditions of step b adopted for each sample are shown in Table 2 below. At the end of step b, the passivated tinplate was subjected to washing with mains water (T = 50 °C).

Table 2 - Cathodic electrodeposition of the passivation layer comprising zirconium (step b)

Test	Na ₂ SO ₄ in the electrolytic bath (g/l)	Treatment duration (s)	Bath temp. (°C)	Current density (A/dm ²)	pH	Zr in the bath (g/l)	Deposited Zr (mg/m ²)
A (sample 1)	20	0.5	50	25	2	1.5	7.4
B (sample 1)	35	0.5	50	20	2	1	5.5
C (sample 1)	20	1.0	50	30	2	1	15.2
D (sample 3)	35	0.5	50	25	2	1	6.6
E (sample 3)	20	1	50	25	2	1.5	16.6
F (sample 3)	50	0.7	40	20	2.4	1.5	8.7
G (sample 5)	35	1	30	10	1.5	0.5	3.4
H (sample 5)	50	0.7	60	20	1.5	1	5.6
I (sample 5)	20	0.7	50	20	2.4	1.5	12.1

[0084] The results of Table 2 highlight that by varying the operating conditions of step b it is possible to obtain a passivation layer based on zirconium with weights per unit of area in a wide range of values.

7. Characterization

[0085] The passivated samples A - I of Table 2 and the "Reference" sample (industrial chromium-passivated) were submitted to the test with cysteine.

[0086] After being coated with epoxy enamel as described at point 4, the same samples were subjected to the dry adhesion test, to the cathodic wet adhesion test and to the T-peel test.

[0087] The results of the characterization tests performed on the A - I samples are shown in Table 3 below.

Table 3 - Test with cysteine and coating adhesion test

Sample	Deposited Zr (mg/m ²)	Cysteine test (no coating)	Dry adhesion	Cathodic wet adhesion	T-peel test (N/10 mm)	Type of detachment
Reference (Cr passivation)	-	2	0	4	69.3	C (1)

(continued)

Sample	Deposited Zr (mg/m ²)	Cysteine test (no coating)	Dry adhesion	Cathodicwet adhesion	T-peel test (N/10 mm)	Type of detachment
A	7.4	1	0	2	65.7	C (1)
B	5.5	3	0	3	62.1	C (1)
c	15.2	1	0	1	68.7	C (1)
D	6.6	2	0	2	63.9	C (1)
E	16.6	1	0	3	33.9	A (2)
F	8.7	1	0	2	67.5	C (1)
G	3.4	4	0	5	50.7	A (2)
H	5.6	3	0	3	60.9	C (1)
I	12.1	1	0	1	68.4	C (1)
(1) C = cohesive detachment (2) A = adhesive detachment						

[0088] The data of Table 3 show that the coating applied on the passivated materials in accordance with the present invention has an optimal adhesion for most tinplate applications, the values of the T-peel test being greater than 60 N/10mm. The adhesion is also comparable to that of the traditional chrome tinplates.

[0089] The materials passivated in accordance with the process according to the present invention also have a greater resistance to the detachment of the coating with respect to the reference sample when subjected to the cathodic wet adhesion test and a resistance comparable to the reference sample in the case of the dry adhesion test.

8. Adhesion of the coating in the presence of carbonate ions on the surface of the passivated tinplate

[0090] A second series of samples (no. C1 - C7) was prepared by submitting the material of the sample no. 1 of Table 1 to an electrolytic treatment for zirconium deposition (step b) under the same conditions as in sample C of Table 2. To obtain a passivated surface containing variable amounts of carbonate ions, step b was carried out in an electrolytic bath of zirconium sulphate and sodium sulphate added with an amount of sodium carbonate that was different for each sample. In some cases also the water used for the subsequent washing was added with amounts of sodium carbonate that were different for each sample.

[0091] The C1-C7 samples and the reference sample ("Reference") were coated with epoxy enamel as described in point 4 and then submitted to the T-peel test, after quantitative determination of the carbonate ions on the passivated tinplate. The results of this test (numerical values) are shown in Table 4 below and in the graph of the appended Figure 1, in which the X-abcissa shows the concentration of carbonate ions expressed in mg/m² and the Y-ordinate shows the detachment strength expressed in N/10mm.

Table 4 - T-peel adhesion test on surfaces containing different amounts of carbonate ions

Sample	Residual ions CO ₃ ²⁻ (mg/m ²)	T-peel test (N/10 mm)
Reference	1.0	69.3
C1	1.8	68.7
C2	3.2	66.9
C3	6.8	67.5
C4	18.0	65.1
C5	25.8	31.8
C6	35.8	21.6
C7	57.1	7.5

[0092] The results of the T-peel test show that the adhesion strength of the coating decreases suddenly when the coating is applied on surfaces having residual carbonate ions in an amount greater than about 20 mg/m².

Claims

1. A passivation process of a tinplate comprising the following steps in sequence:

- a. submitting said tinplate to at least one cathodic electrolytic treatment in an aqueous solution containing at least one sulphate of an alkali metal to obtain a tin oxide surface layer having thickness lower than 6 mC/cm²;
- b. subjecting said tinplate to at least one cathodic electrolytic treatment in an aqueous solution containing at least sulphate ions and zirconium ions to form a passivation layer containing zirconium on said tin oxide surface layer.

2. The process according to claim 1, wherein said tin oxide layer has a thickness lower than 5 mC/cm², preferably in the range 0.5 - 3.0 mC/cm².

3. The process according to claim 1, wherein the overall amount of carbonate ions and hydrogen carbonate ions on the surface of said coating layer containing zirconium is equal to or lower than 20 mg/m².

4. The process according to claim 1, wherein the amount of sulphate ions on the surface of said coating layer containing zirconium is equal to or lower than 20 mg/m².

5. The process according to claim 1, wherein the amount of zirconium in said passivation layer containing zirconium is in the range 5-15 mg/m².

6. The process according to claim 1, wherein the concentration of the alkali metal sulphate in the aqueous solution of step a is in the range 30-150 g/l, preferably in the range 40 - 100 g/l.

7. The process according to claim 1, wherein the aqueous solution of step b contains zirconium sulphate and alkali metal sulphate.

8. The process according to the preceding claim, wherein the concentration of the alkali metal sulphate in the aqueous solution of step b is in the range 5.0-60 g/l, preferably in the range 10 - 50 g/l.

9. The process according to claim 1, wherein the concentration of zirconium ions in the aqueous solution of step b is in the range 0.1-10 g/l, preferably in the range 0.5- 2.0 g/l.

10. The process according to claim 1, wherein the pH of the aqueous solution of step a is in the range 6-8.

11. The process according to claim 1, wherein the pH of the aqueous solution of step b is in the range 0.5-2.5, preferably in the range 1.5-2.4.

12. The process according to claim 1, wherein the cathodic electrolytic treatment of step a and/or step b is carried out with an electric current density in the range 2-50 A/dm², preferably in the range 5 - 30 A/dm².

13. The process for producing a coated tinplate which comprises the following steps in sequence:

- providing a passivated tinplate comprising a passivation layer containing zirconium obtained with the passivation process according to claim 1;
- applying at least one coating on said passivation layer containing zirconium selected from: paint layer, lacquer layer, enamel layer, ink layer and polymeric material film.

Patentansprüche

1. Verfahren zur Passivierung eines Weißblechs, das die folgenden Schritte in Abfolge umfasst:

- a. Unterziehen des Weißblechs mindestens einer kathodischen elektrolytischen Behandlung in einer wässrigen Lösung, die mindestens ein Sulfat eines Alkalimetalls enthält, um eine Zinnoxid-Oberflächenschicht mit einer Dicke von weniger als 6 mC/cm² zu erhalten;
 b. Unterziehen des Weißblechs mindestens einer kathodischen elektrolytischen Behandlung in einer wässrigen Lösung, die mindestens Sulfationen und Zirkoniumionen enthält, um eine zirkoniumhaltige Passivierungsschicht auf der Zinnoxid-Oberflächenschicht zu bilden.

2. Verfahren nach Anspruch 1, wobei die Zinnoxidschicht eine Dicke von weniger als 5 mC/cm², vorzugsweise im Bereich von 0,5 - 3,0 mC/cm², aufweist.
3. Verfahren nach Anspruch 1, wobei die Gesamtmenge an Carbonationen und Hydrogencarbonationen auf der Oberfläche der zirkoniumhaltigen Überzugsschicht gleich oder kleiner als 20 mg/m².
4. Verfahren nach Anspruch 1, wobei die Menge an Sulfationen auf der Oberfläche der zirkoniumhaltigen Überzugsschicht gleich oder kleiner als 20 mg/m² ist.
5. Verfahren nach Anspruch 1, wobei die Menge an Zirkonium in der zirkoniumhaltigen Passivierungsschicht im Bereich von 5-15 mg/m² liegt.
6. Verfahren nach Anspruch 1, wobei die Konzentration des Alkalimetallsulfats in der wässrigen Lösung von Schritt a im Bereich von 30-150 g/l, vorzugsweise im Bereich von 40 - 100 g/l liegt.
7. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die wässrige Lösung von Schritt b Zirkoniumsulfat und Alkalimetallsulfat enthält.
8. Verfahren nach dem vorhergehenden Anspruch, wobei die Konzentration des Alkalimetallsulfats in der wässrigen Lösung von Schritt b im Bereich von 5,0-60 g/l, vorzugsweise im Bereich von 10 - 50 g/l liegt.
9. Verfahren nach Anspruch 1, wobei die Konzentration an Zirkoniumionen in der wässrigen Lösung von Schritt b im Bereich von 0,1-10 g/l, vorzugsweise im Bereich von 0,5-2,0 g/l liegt.
10. Verfahren nach Anspruch 1, wobei der pH-Wert der wässrigen Lösung von Schritt a im Bereich von 6-8 liegt.
11. Verfahren nach Anspruch 1, wobei der pH-Wert der wässrigen Lösung von Schritt b im Bereich von 0,5-2,5, vorzugsweise im Bereich von 1,5-2,4 liegt.
12. Verfahren nach Anspruch 1, wobei die kathodische elektrolytische Behandlung von Schritt a und/oder Schritt b mit einer elektrischen Stromdichte im Bereich von 2-50 A/dm², vorzugsweise im Bereich von 5-30 A/dm², durchgeführt wird.
13. Verfahren zur Herstellung eines beschichteten Weißblechs, das die folgenden Schritte nacheinander umfasst:
 - Bereitstellen eines passivierten Weißblechs, umfassend eine Passivierungsschicht, die Zirkonium enthält, erhalten mit dem Optimierungsverfahren nach Anspruch 1;
 - Aufbringen mindestens einer Beschichtung auf die zirkoniumhaltige Passivierungsschicht, die ausgewählt wird aus: Farbschicht, Lackschicht, Emaille-Schicht, Tintenschicht und Film aus polymerem Material.

Revendications

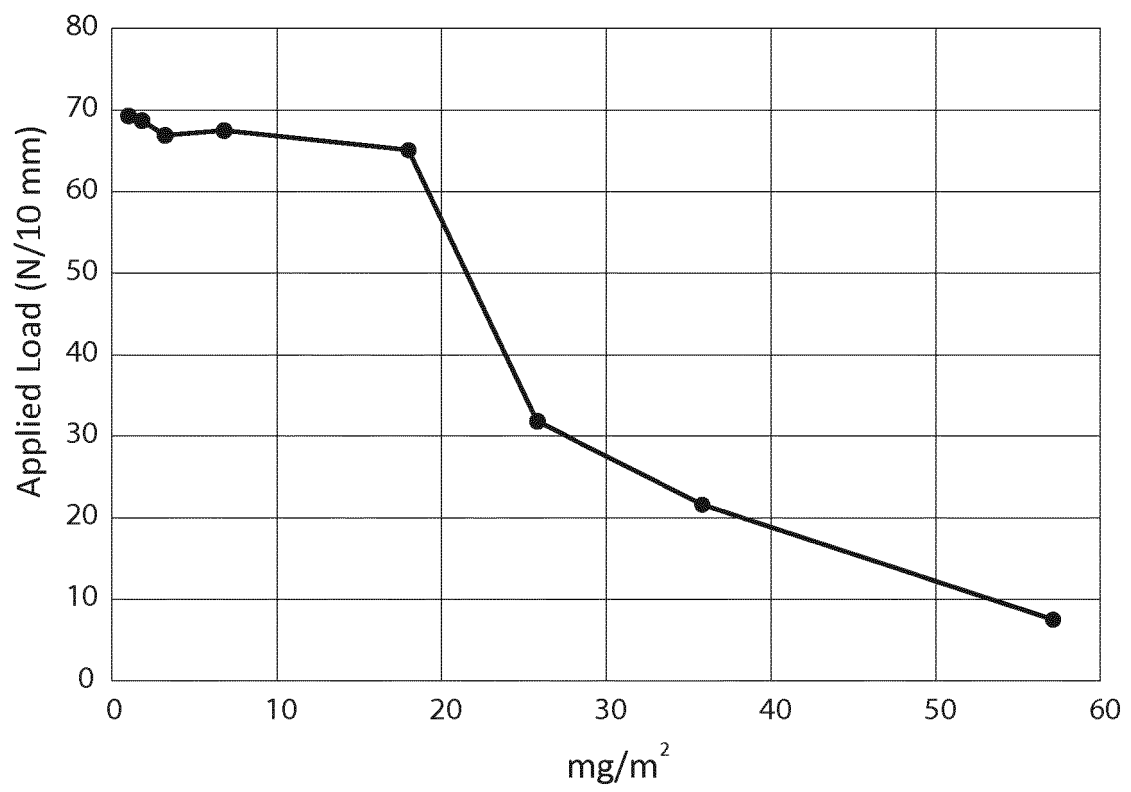
1. Procédé de passivation d'un fer-blanc comprenant les étapes suivantes en séquence :

- a. soumettre ledit fer-blanc à au moins un traitement électrolytique cathodique dans une solution aqueuse contenant au moins un sulfate d'un métal alcalin pour obtenir une couche superficielle d'oxyde d'étain ayant une épaisseur inférieure à 6 mC/cm² ;
 b. assujettir ledit fer-blanc à au moins un traitement électrolytique cathodique dans une solution aqueuse contenant au moins des ions sulfate et des ions zirconium pour former une couche de passivation contenant du zirconium sur ladite couche superficielle d'oxyde d'étain.

EP 3 626 862 B1

2. Procédé selon la revendication 1, dans lequel ladite couche d'oxyde d'étain a une épaisseur inférieure à 5 mC/cm², de préférence dans la plage 0,5 - 3,0 mC/cm².
3. Procédé selon la revendication 1, dans lequel la quantité totale d'ions carbonate et ions hydrogénocarbonate sur la surface de ladite couche de revêtement contenant du zirconium est égale ou inférieure à 20 mg/m².
4. Procédé selon la revendication 1, dans lequel la quantité d'ions sulfate sur la surface de ladite couche de revêtement contenant du zirconium est égale ou inférieure à 20 mg/m².
5. Procédé selon la revendication 1, dans lequel la quantité de zirconium dans ladite couche de passivation contenant du zirconium est dans la plage 5-15 mg/m².
6. Procédé selon la revendication 1, dans lequel la concentration de sulfate de métal alcalin dans la solution aqueuse de l'étape a est dans la plage 30-150 g/l, de préférence dans la plage 40 - 100 g/l.
7. Procédé selon la revendication 1, dans lequel la solution aqueuse de l'étape b contient du sulfate de zirconium et du sulfate de métal alcalin.
8. Procédé selon la revendication précédente, dans lequel la concentration du sulfate de métal alcalin dans la solution aqueuse de l'étape b est dans la plage 5.0-60 g/l, de préférence dans la plage 10 - 50 g/l.
9. Procédé selon la revendication 1, dans lequel la concentration d'ions zirconium dans la solution aqueuse de l'étape b est dans la plage 0,1-10 g/l, de préférence dans la plage 0,5-2,0 g/l.
10. Procédé selon la revendication 1, dans lequel le pH de la solution aqueuse de l'étape a est dans la plage 6-8.
11. Procédé selon la revendication 1, dans lequel le pH de la solution aqueuse de l'étape b est dans la plage 0,5-2,5, de préférence dans la plage 1,5-2,4.
12. Procédé selon la revendication 1, dans lequel le traitement électrolytique cathodique de l'étape a et/ou étape b est effectué avec une densité de courant électrique dans la plage 2-50 A/dm², de préférence dans la plage 5-30 A/dm².
13. Procédé pour produire un fer-blanc revêtu qui comprend les étapes suivantes en séquence :
 - fournir un fer-blanc passivé comprenant une couche de passivation contenant du zirconium obtenu avec le procédé de passivation selon la revendication 1 ;
 - appliquer au moins un revêtement sur ladite couche de passivation contenant du zirconium sélectionné parmi : couche de peinture, couche de laque, couche d'émail, couche d'encre et film de matériau polymère.

Fig. 1



REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 2180084 A1 [0009] [0010]
- EP 2557202 A1 [0009] [0011]