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(71) Applicant: **TATA STEEL IJMUIDEN BV** [NL/NL]; P.O. Box 10000, NL-1970 CA IJmuiden (NL).

(72) Inventors: **PENNING, Jan, Paul**; Tata Steel Nederland Technology B.V., Group Intellectual Property Services - 3G.37, P.O. Box 10000, NL-1970 CA IJmuiden (NL). **SCHNETZ, Kokkie**; Tata Steel Nederland Technology B.V., Group Intellectual Property Services - 3G.37, P.O. Box 10000, NL-1970 CA IJmuiden (NL).

(74) Agent: **BODIN, Andre**; Tata Steel Nederland Technology B.V., Group Intellectual Property Services - 3G.37, P.O. Box 10000, NL-1970 CA IJmuiden (NL).

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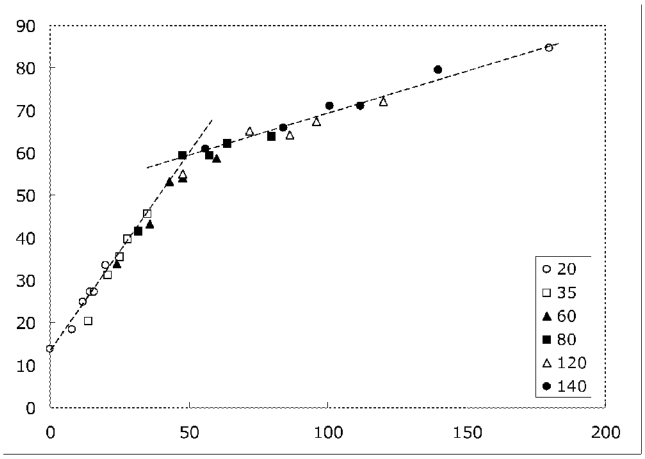

Figure 3

(57) Abstract: The invention relates to a method for forming a passivation layer on a strip of packaging steel for producing a packaging container or a can, said strip having at least one tinplated surface having excellent sulphide staining resistance. The method comprises the steps of: (i) subjecting said tin-plated surface to an anodic treatment at a pH of from 8 to 12 in a suitable aqueous electrolyte, wherein the suitable electrolyte is a phosphate solution, borate solution, sulphate solution or a carbonate solution, wherein the electrolyte for the anodic treatment does not contain mono-atomic halogen anions (Group 17) such as Cl-, F-, wherein the thickness of the tin oxide layer (D), expressed in Coulomb/m2 and representing the total charge needed to reduce the layer to metallic tin is related to anodic treatment time (t), current density (A) by D = E x A x t, where E is the efficiency of the electrochemical reaction, and wherein D is at least 30 C/m2; wherein the electrolyte comprises monoatomic cations from Group 1 or 2 from the periodic table or polyatomic cations, and polyatomic anions; (ii) optionally rinsing and drying the anodically treated tin-plated surface - subjecting the anodically treated tin-plated surface to a chemical passivation treatment free from using hexavalent chromium compounds; (iii) drying of the passivated anodically treated tin-plated surface; (iv) final processing such as oiling, winding, cutting etc.

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METHOD FOR PRODUCING TINPLATE AND PRODUCT PRODUCED THEREWITH

The invention relates to a method for forming a passivation layer on an article having at least one tinplated surface having excellent sulphur staining resistance and to an article produced by said method.

Tin is used to protect the steel base from corrosion both externally (aerobic conditions) and internally when in contact with foods (anaerobic). Under the anaerobic conditions expected inside an internally plain processed food can, tin will normally behave as the sacrificial anode, dissolving very slowly whilst protecting the steel base from corrosion and creating a reducing environment in the can. It is this mechanism that has enabled the plain tinplate can to maintain its long history and proven track record of providing wholesome food on a year round basis and safe storage for long periods of time.

Some foods, especially protein rich meat and fish and, to a lesser extent, vegetables (e.g. peas, beans, corn etc.) contain naturally occurring sulphur compounds. These can react with a plain tinplate surface to give a purple-black stain of tin sulphide. Although the stain is harmless, it may serve to change the passivation of the tinplate surface, which, in turn, could alter the rate of tin uptake. Whilst an overall increase in passivation is more likely to slow tin uptake, localised areas of staining can have a detrimental effect, especially if a corrosion accelerator such as oxygen is also present. Degree of sulphide staining is also influenced by pH, process time and temperature and the presence of certain cations.

Passivation refers to the chemical treatment applied after tin deposition which stabilises the surface characteristics of tinplate by controlling tin oxide formation and growth. Passivation treatments can be electro-chemical or chemical. Electrochemical treatments involve the use of an external electric current. At present, cathodic dichromate (CDC) treatments are usually applied. A CDC treatment is an electrochemical passivation treatment. Chromates are based on hexavalent chromium and these are nowadays considered to be hazardous substances being potentially harmful to the environment and a risk in terms of worker safety. Consequently, intensive research efforts are being made towards developing passivation treatments free from hexavalent chromium, also denoted as Cr(VI)-free passivation treatments.

Recent developments of Cr(VI)-free passivation treatments have resulted in renewed attention to combatting sulphide staining because these newly developed alternatives to cathodic dichromate treatments struggle to deliver the same performance in terms of sulphide staining resistance.

The most common method to improve the sulphide staining resistance of Cr(VI)-free passivated tinplate is to increase the thickness of the passivation layer itself (e.g. by using process conditions leading to thicker applied wet films, or by using more concentrated treatment solutions, or by employing longer treatment time, etc.) This leads to enhanced barrier properties, thus suppressing the formation of sulphide stains. However, passivation layers are mechanically weak and the risk of cohesive failure within the passivation layer increases with thickness. Cohesive failure of the passivation layer (in particular during heavy deformation that is encountered in e.g. canmaking) leads to loss of adhesion and delamination of organic coatings that are applied over the passivation layer.

The object of the invention is to provide a method to improve the sulphide staining resistance of tinplate that has been passivated using Cr(VI)-free passivation systems.

Another object of the invention is to provide a method to improve the sulphide staining resistance of tinplate that has been passivated using Cr(VI)-free passivation systems that can be integrated into existing electolytic tinning lines.

Still another object of the invention is to provide a tinplated article having excellent sulphide staining resistance that is at least similar to that of a cathodic dichromate passivation treatment.

One or more of the objects of the invention are reached by a method according to claim 1 and the product according to claim 9. Preferred embodiments are provided in the dependent claims.

The invention solves the problem of poor sulphide staining resistance of tinplate by subjecting the tinplate to an anodic treatment in a suitable aqueous electrolyte which is carried out within certain boundaries of treatment time, current density and total charge passed, in order to be effective in achieving the required sulphur staining resistance. A very thin layer of tin oxide on the tinplate surface is formed by the electrochemical anodic treatment. This tin oxide layer provides the improvement in sulphide staining resistance and together with the subsequent chemical Cr(VI)-free passivation treatment provides a tinplate which delivers the same, or a better performance than the known CDC-treated tinplate.

An essential element of the invention is the thickness of the tin oxide layer (D), which is expressed in Coulomb/m^2 and represents the total charge needed to reduce the layer to metallic tin. The thickness of the tin oxide layer is related to the anodic treatment time (t) and current density (A) by $D = E \times A \times t$, where E is the efficiency of the electrochemical reaction, and wherein D is at least 30 C/m^2. The efficiency thus represents the ratio of the thickness D of the produced oxide layer to the applied charge density (A x t), and can be estimated by plotting D as a function of (A x t). Initially, at values of anodic charge passed below 50 C/m^2 the curve is more or less linear, but with increasing anodic charge passed, the efficiency E decreases leading to a slower growth rate of the tin oxide layer, and thus in a slower increase in D. If $D < 30$ C/m^2, then the tin oxide layer is too thin and is not effective in achieving the desired sulphide staining resistance. A minimum thickness of 30 C/m^2 is therefore required.

The tin oxide layer thickness is determined using a coulometric method. The tin oxide layer is reduced by a controlled small cathodic current in a 0.1% solution of hydrobromic acid (HBr) that is freed from oxygen by scrubbing with nitrogen. The progress of the reduction of the oxide is monitored by measuring the reduction potential, and the charge passed (A*t) for the complete reduction serves as a measure of the tin oxide layer thickness. For the test, a cylindrical electrolysis cell is used having a circular aperture of ca. 4 cm diameter on one end. The other end of the cell contains a platinum counter electrode and an Ag/AgCl reference electrode. The test specimen covers the aperture, which is sealed using an O-ring to make a water-tight connection of well defined area (13.69 cm^2 in this case), and is tightened into place using an air-pressure cylinder. The cell is connected to the electrolyte solution by a flexible tube so that it can be filled and emptied under nitrogen atmosphere. A cathodic current density of -0.40 A/m^2 is applied to the sample using a potentiostat-galvanostat, and the potential is measured until the reduction is complete. A typical potential-time curve is shown in Fig. 1, from which the tin oxide layer thickness is determined based on the inflection point of the potential drop at time t_i. The tin oxide layer thickness D, expressed in C/m^2, is obtained from $D\ [C/m^2] = t_i\ [s] * 0.4\ [A/m^2]$.

The sole purpose of the electrolyte is to enable the anodic treatment, not to deposit foreign species contained in the electrolyte onto the substrate surface. The pH of the electrolyte may not be too low, not lower than pH = 8, otherwise the efficiency of the electrochemical reaction becomes too low and then the process cannot be incorporated into existing high productivity process lines. Also, the pH of the electrolyte may not be too high, i.e. not higher than pH = 12, because that will cause the dissolution of the tin layer in the electrolyte. Preferably the pH is not lower than 8.5 and/or not higher than 11.5. A suitable maximum pH value is 11 or even 10.5.

According to the invention the electrolyte comprises monoatomic cations from Group 1 or 2 from the periodic table or polyatomic cations, and poly-atomic anions. Group 1 and Group 2 elements, according to the new IUPAC numbering comprise the alkali metals and the alkali earth metals. It is important that the electrolyte does not contain mono-atomic halogen anions (Group 17) such as Cl^-, F^- because these anions prevent the tin-oxide layer from forming.

After the anodic treatment the article is optionally rinsed and dried before it is passed on to the subsequent step, i.e. the Cr(VI)-free passivation treatment. The need to rinse the anodically treated tinplate depends on the exact nature of the Cr(VI)-free passivation system, certain systems will be more susceptible than others to contamination of electrolyte being present on the tinplate surface.

Finally, the Cr(VI)-free passivation system is applied to the anodically treated tinplate surface by application techniques that are common for such passivation systems. Suitable application techniques include: dipping, dipping with squeegee rolls, rotor-spray application, rotor-spray application supported by the use of a smoothing roll, spray application, spray-squeegee application, application by means of a roll coater systems, application by slot coating, slot curtain coating, etc. After the passivation step, the strip is dried and passed on for final processing steps such as oiling, winding, cutting, etc.

The total D as specified above can be achieved by any combination of A and t, but a combination of a high current density ($A > 0.1$ A/dm^2, preferably $A > 1.0$ A/dm^2) in combination with a short treatment time ($t < 1$ sec) is preferred in view of its processability on a high-speed tinning line. The interchangeability of A and t in the anodic treatment, which is further demonstrated in Example 1 and Figures 2 and 3, implies that the process can be operated at short treatment times, by adjusting the applied current density accordingly. Thus, the method according to the invention can be employed in industrial tinning lines running at line speeds in excess of 300 m/min to speeds of up to 1000 m/min. Furthermore, the treatment time t is determined not only by line speed v but also by the effective length or 'anode length' L of the treatment section, according to $t = L / v$, meaning that the processing window can be further extended by the proper choice of the anode length L. For instance, to deposit a layer having a thickness of 50 C/m^2 (assuming $E=1$) on a line running at 600 m/min (10 m/s) a current density A of 1000 A/m^2 and a treatment length of 0.5 m would be required. It could also be done at a current density of 100 A/m^2 if the treatment length is 5 m. This design and process flexibility is a great advantage of this method.

In an embodiment of the invention the anodic treatment is performed in-line with or immediately after electrolytic tinning, and wherein the anodic treatment time (t) is at most 5 seconds, preferably at most 2 seconds, more preferably between 0.05 seconds and 1.5 seconds. This range and the more preferable ranges are consistent with high speeds processing lines. In an embodiment the anodic treatment is performed in-line with an industrial electrolytic tinning line, and wherein the current density during the anodic treatment (A) is at least 10 A/m^2, preferably at least 50 A/m^2 and more preferably at least 100 A/m^2, and/or at most 4000 A/m^2, preferably at most 2000 A/m^2 or more preferably at most 1000 A/m^2. This range and the more preferable ranges are consistent with high speeds processing lines.

The electrolyte to be employed can be an aqueous solution of an acid, a base or a salt. The main function of the electrolyte is to support the electrochemical reaction intended by the anodic treatment while the ionic species present in the electrolyte do not take part in the electrochemical modification of the tinplate surface. Although there is considerable freedom in selecting a suitable electrolyte, use the following ionic species must be avoided:

- monoatomic anions such as fluorides, chlorides, bromides, etc. since these are detrimental to forming a suitable tin oxide layer
- cations from or containing inner-transition metals, transition metals and post-transition metals; such elements typically exhibit multiple valency states and therefore can easily take part in electrochemical reactions, and may negatively affect the stability of the electrolyte by forming insoluble salts with the available anions, or by forming insoluble oxides

Based on the above considerations, the preferred electrolyte contains cations from Group 1 (e.g. Na^+, K^+) or Group 2 (e.g. Mg^{2+}, Ca^{2+}) from the Periodic Table or polyatomic cations (e.g. NH_4^+), and polyatomic anions (phosphates, borates, sulphates, carbonates and the like). Also, the anion may be the conjugate base of an organic acid (e.g. acetates, citrates). Since it is of importance that the pH be maintained within certain boundaries, a buffered solution could be used. Furthermore the electrolyte may contain other chemical additives, such as surfactants, wetting agents, anti-foaming agents etc. to support the electrochemical treatment, provided these additives do not adversely affect the formation of the tin oxide.

The anodic treatment of the tin-plated surface converts the extreme outer layer of the tin surface from metallic tin into tin oxide by electrochemical oxidation. The tin oxide layer produced as such (within a certain range of thickness) provides a barrier against sulphide staining. The tin oxide layer is, however, not sufficiently stable and/or passive in itself and will, during prolonged storage under ambient and/or humid conditions, or during heat treatments such as baking and stoving, continue to grow into a thicker tin oxide layer with undesirable properties (poor wettability, yellowish appearance, poor lacquer adhesion).

If we consider the Cr(VI)-free passivation system on its own, it usually will provide a stable passivation layer protecting the tinplate against uncontrolled growth of tin oxides and furthermore providing good adhesion of organic coatings. However, the Cr(VI)-free passivation layer in almost all investigated cases has a poor resistance against sulphide staining.

By applying the present invention, a favourable combination of properties is achieved. First, a tin oxide layer of the correct thickness is applied by employing the anodic treatment under proper process conditions, and then the tin oxide layer is passivated and/or stabilised against further uncontrolled growth, by applying a Cr(VI)-free passivation system on top of it, by using a non-electrolytic application method.

The anodic treatment of the present invention must take place after tinning and/or flow melting and before the application of a Cr(VI)-free passivation system.

The Cr(VI)-free passivation system before which the anodic treatment is applied must be a chemical passivation treatment, preferably a so-called no-rinse process, for the application of a no-rinse, dry-in-place passivation system. The anodic pre-treatment is not expected to work in combination with a Cr(VI)-free passivation system that itself is applied electrolytically. In particular, the anodic pre-treatment is not expected to work in combination with a Cr(VI)-free passivation system that is applied by a cathodic electrochemical process, since such a process will remove the anodic treatment layer through electrochemical reduction.

Suitable no-rinse Cr(VI)-free passivation systems that can be used in combination with the anodic treatment of this invention are e.g.:

- all organic systems such as organic acids (oleic acid, abietic acid);
- all organic systems such as acrylates, polyurethane dispersions and other types of thin organic coatings;
- organic/inorganic coupling agents, such as one-component and two-component siloxane systems;
- inorganic systems such as silicate-based systems;
- inorganic systems in an organic matrix such as fluoro-titanates and zirconium-titanates in combination with an organic polymer matrix.

Other methods to apply a tin oxide layer, and potentially to achieve the same technological effect, include chemical oxidation by strong oxidising agents such as permanganates or peroxides and thermal oxidation. The former is not preferred because strong oxidising agents are unpleasant for human beings and the environment and the latter method turns out to be very time-consuming and it may take several minutes at very high temperatures to achieve a tin oxide layer of suitable thickness

The anodic treatment of the present invention is capable of applying the suitable tin oxide layer on a very short time scale (down to 0.1 sec), using environmentally friendly chemical solutions, and with a very low energy consumption.

Although the method according to the invention also works with a thickness of the tin oxide layer of e.g. 150 or 200 C/m^2 it is preferable for the thickness of the tin oxide layer D to be at most 100 C/m^2. A value above 100 is not possible to achieve economically in the high speed tinplating process and it also leads to a reduced adhesion of subsequently applied organic coatings. The preferred range for the tin oxide layer thickness D is therefore 30 to 100 C/m^2.

A suitable minimum value of D is 40 C/m^2. A suitable maximum value for D from a process efficiency point of view is 80 C/m^2 or even 60 C/m^2.

In a preferable embodiment the polyatomic anion in the electrolyte is a phosphate, a borate, a sulphate, or a carbonate anion. In a preferable embodiment the cation in the electrolyte is Na^+, K^+ (Group 1) and/or Ca^{2+} (Group 2) and/or polyatomic e.g. $NH4^+$.

In an embodiment the article is a strip of packaging steel provided with a tin layer on at least one side (for typical chemical compositions see e.g. EN10202-2001 or ASTM 623M). This strip is produced in a known way, e.g. by cold rolling and annealing and optionally temper rolling a steel strip of suitable composition, followed by electrolytic tinplating.

In an embodiment the article is further provided with an organic coating layer such as epoxy-phenolic gold lacquers, epoxy-anhydride white lacquers, PVC or vinyl organosol coatings, polyester lacquers, epoxy-amino or epoxy-acrylic-amino waterborne coatings. The excellent adhesion of organic coating layers to the passivated tinplate enables to provide this product as a replacement for CDC treated and subsequently polymer coated systems, thereby avoiding the use of chromates altogether.

The invention is now explained by means of the following, non-limitative Examples and Figures.

Example 1

This Example describes various lab-scale trials that are aimed to demonstrate the anodic treatment using various electrolytes and process conditions regarding current density A and treatment time t.

For all experimental results presented here flow melted, non-passivated tinplate was used. The material was produced on an industrial electrolytic tinning line (ETL). The applied tin coating weight is about 2.8 g/m^2. After flow melting, the amount of free tin is about 1.9 g/m^2 and the amount of $FeSn_2$ alloy is about 1.1

g/m^2, corresponding to about 0.9 g/m^2 of tin in the alloy layer. After tinning and flow melting, the tinplate strip was passed on the coiler while by-passing the chromate passivation section. In this way, non-passivated tinplate without contamination with chromium-residues is obtained.

Two electrolytes were used:

- Phosphate solution, containing 3.56 g/l KH_2PO_4 and 7.22 g/l $Na_2HPO_4.2H_2O$ in deionised water, pH = 7.1;
- Sodium carbonate decahydrate solution, containing ca. 1 g/l $Na_2CO_3.10H_2O$ in deionised water, pH = 10.3.

Obviously, whereas sodium carbonate decahydrate was used in these experiments, the results would equally be achievable by using anhydrous sodium carbonate or a sodium carbonate hydrate with a different number of water molecules than 10, provided the appropriate pH is obtained. Prior to the study the 'natural' tin oxide layer was removed in a so-called cathodic soda treatment. The sample was placed in the pH = 10.3 sodium carbonate solution described above, at a solution temperature of 50°C. The tinplate sample was then connected as cathode to a galvanostat, and a current density of - 1.0 A/dm^2 was applied during 1 second. The sample was then rinsed with deionised water and used immediately for the anodic treatment experiment ('wet-in-wet' application).

In the anodic treatment experiments, the tinplate sample was placed in the electrolyte at 50°C, and connected as the anode to a galvanostat. Various current densities (in the range 0.2 - 1.4 A/dm^2) and treatment times (in the range 0.4 - 9.0 sec) were employed. After the treatment, the sample was removed from the electrolyte, rinsed with deionised water and dried at ambient temperature. The tin oxide layer thickness was then determined as described above.

Figure 1 gives a typical curve of reduction potential (V) as a function of time (t) in a tin oxide reduction experiment.

Figure 2 gives the tin oxide layer thickness (in C/m^2) as a function of the charge passed (A*t) in the anodic treatment using the phosphate solution for different current densities (see legend) and time combinations. The dashed line serves as a guide to the eye.

Figure 3 gives the tin oxide layer thickness (in C/m^2) as a function of the charge passed (A*t) in the anodic treatment using the sodium carbonate solution for different current densities and time combinations. For instance, a current density of 120 A/m^2 for 0.4 seconds resulted in the same layer thickness as a current density of 60 A/m^2 for 0.8 seconds. The dashed lines serve as guide to the eye. From the different current densities (see legend) and the associated differences in treatment time it is clearly visible that the different combinations of time (t) and current density (A) result in the same tin layer thickness.

For a given electrolyte, the amount of tin oxide produced in the anodic treatment is a unique function of the charge passed. For a given charge, it does not matter whether this was achieved by e.g. a low current density and a long treatment time or by a high current density and a correspondingly short treatment time. Thus, the process of tin oxidation can be very easily controlled over the total charge passed and, in an industrial process can be made independent of e.g. line speed. For the sodium carbonate electrolyte with pH = 10.3 (Fig. 3), the relationship between tin oxide layer thickness and total charge passed shows two distinct regimes. When the charge passed is low, i.e. lower than ca. 50 C/m^2, a steep, linear relationship is observed. The slope of the regression line in this regime is 0.92, meaning that the efficiency (E) of the oxidation process is 92%. At higher total charge passed, i.e. higher than 50 C/m^2, the oxidation process still progresses with increasing charge, but at a much slower rate.

In the phosphate electrolyte with pH = 7.1 (Fig. 2), also a linear relationship between tin oxide layer thickness and total charge passed (irrespective of current density) is observed, but it takes much more charge compared to the pH = 10.3 sodium carbonate electrolyte to achieve the same tin oxide layer thickness. The slope of the regression line for the phosphate electrolyte corresponds to 0.19, showing the much lower efficiency of the oxidation reaction in this case.

In the following Examples, flow melted, non-passivated tinplate material as described above was subjected to various treatments on a coil-to-coil process line. The line consists of the following sections: uncoiler, electrochemical treatment tank, rinsing tank, hot air drying unit, spray-squeegee application section, second hot air drying unit and coiler. All experiments were conducted at 50 m/min line speed using a tinplate coil of 300 mm in width. In all experiments, the electrolyte was the sodium carbonate solution having a pH of 10.3 as described above which was maintained at 60°C.

In some of the Examples, a Cr(VI)-free passivation treatment was applied to the tinplate using a spray-and-squeegee application unit. The passivation solution was a commercial product, denoted Granodine™ 1456, from Henkel AG & Co. KGaA (Düsseldorf, Germany) containing, among other things, fluoro-titanates, fluoro-zirconates and organic polymers. A passivation solution containing 150 g/l of Granodine™ 1456 in deionised water was used in the experiments. The passivation solution was sprayed onto one side of the strip using an Ahlbrandt IQ-140 Rotorspray system. The strip was then passed through a (non-driven) pair of rollers consisting of a stainless steel coater roll and a polyurethane-coated backing roll, in which the applied wet film is homogenised and the excess liquid is squeezed off from the strip. After passing through the squeegee rolls, the strip is heated to 70°C using an inductive heater and subsequently passed through an air dryer operated at 90°C air temperature.

The as-received, non-passivated tinplate coils were first passed through the line and were given a cathodic treatment in sodium carbonate using the electrochemical treatment tank. This is done to remove the 'natural' tin oxide layer that has developed on the non-passivated tinplate material during storage. A total cathodic current density of 1.11 A/dm^2 was employed during 0.72 sec, giving a total charge density of 80 C/m^2. Then, the treated coil was placed back on the uncoiler and subjected to the following treatments:

A (Comparative Example 1) - The coil was passed through the line, including the electrochemical treatment tank, but no current was applied. No passivation treatment was applied.

B (Comparative Example 2) - The coil was passed through the electrochemical treatment tank, but no current was applied in the electrochemical treatment tank. In the passivation section, ca. 5 ml/m^2 of the passivation solution was applied to the strip. After passing through the set of squeegee rollers and drying unit, the strip was coiled. The homogeneity and thickness of the applied passivation layer was determined using X-Ray Fluorescence by measuring the surface concentration of the element Ti.

C (Comparative Example 3) - The coil was passed through the electrochemical treatment tank, filled with the sodium carbonate solution as described above, and an anodic current density of 0.83 A/dm^2 was employed during 0.72 sec, giving a total charge density of 60 C/m^2. No passivation treatment was applied.

D (Inventive Example 1) - The coil was passed through the electrochemical treatment tank, filled with the sodium carbonate solution as described above, and an anodic current density of 0.28 A/dm^2 was employed during 0.72 sec, giving a total charge density of 20 C/m^2. The Granodine 1456 passivation was applied as described above.

E (Inventive Example 2) - As Inventive Example 1 but using an anodic current density of 0.83 A/dm^2 during 0.72 sec, giving a total charge density of 60 C/m^2.

F (Inventive Example 3) - As Inventive Example 1 but using an anodic current density of 1.39 A/dm^2 during 0.72 sec, giving a total charge density of 100 C/m^2.

The conditions of the various treatments are summarised in Table 1.

Table 1. Condition of various treatments employed.

Treatment		Anodic Pre-treatment	Anodic Charge density (C/m^2)	D (C/m^2)	Passivation Treatment	Passivation Layer Thickness (mg Ti/m^2)
A	Comp.Ex. 1	No	-	28	No	-
B	Comp.Ex. 2	No	-	27	Yes	1.3
C	Comp.Ex. 3	Yes	60	54	No	-
D	Inv. Ex. 1	Yes	20	31	Yes	1.4
E	Inv. Ex. 2	Yes	60	44	Yes	1.3
F	Inv. Ex. 3	Yes	100	50	Yes	1.3

The performance of various treated tinplate samples was tested with respect to three properties with are of utmost importance regarding the end use of tinplate, such as food cans, can ends etc:

- Oxidation of the tin surface under ambient conditions
- Resistance toward sulphide staining
- Adhesion of lacquers after sterilisation in food media

To determine the rate of oxidation of the tin surface, the amount of tin oxide present on the treated surface was measured directly after preparing the samples, using the coulometric method described above. Then, the samples were stored at ambient temperature in dry air during 14 weeks, after which the tin oxide layer thickness was determined again. If the increase in tin oxide layer thickness during this period is 10 C/m^2 or less, the stability of the tin oxide layer is considered to be adequate.

To determine the resistance of the treated tinplate towards sulphide staining, the as-prepared samples were subjected to immersion in a sulphide-containing solution. Based on extensive research within our laboratories, we have found that the chemical process leading to the formation of sulphide stains on tinplate proceeds as follows. Organically-bound sulphur, such as present in e.g. proteins, can be converted by e.g. sterilisation processes to inorganic sulphides, such as the S^{2-} anion. Inorganic sulphides can destabilise the tin oxide surface and accelerate the dissolution of tin oxides in food media. Once the tin oxide layer is dissolved from the surface and metallic tin is exposed to the sulphide-containing medium, the chemical reaction between tin and the sulphide, leading to the formation of tin-sulphide, can take place. Also, if the reaction proceeds further, a chemical reaction between the sulphide and exposed iron from the underlying steel substrate can take place leading to the formation of iron-sulphide. Tin-sulphides and possibly iron-sulphides present on the tinplate surface are observed as unsightly dark stains known as sulphide stains.

Our test method to determine sulphide staining resistance is based on measuring the dissolution rate of tin oxide during exposure to a sulphide solution. It is found that the rate of dissolution of tin oxides correlated strongly with the development of sulphide staining in real-life testing. The advantage of our method is that the results can be easily quantified, and offers a better and faster way to investigate sulphide staining as compared to the more commonly used visual observation. A particularly convenient method employs a solution containing 5 g/l NaOH and 5 g/l Na_2S*3H_2O maintained at 30°C. An (unlacquered) test specimen is immersed in this solution during 6 minutes, and subsequently the tin oxide layer thickness is determined using the coulometric test method described above. If the thickness of the tin oxide layer after the above-mentioned exposure test is higher than 30 C/m^2, the sulphide staining resistance is adequate.

To determine the lacquer adhesion performance in various food simulant media, the samples were lacquered with a white-coloured, epoxy-anhydride internal food can lacquer. This lacquer is critical regarding adhesion and very discriminating in sterilisation tests and is commonly used in stringent product evaluation. The lacquer was applied at 10 - 12 g/m^2 dry coating weight. The lacquered panels were sterilised at 121°C during 60 minutes, in the following media:

1) deionised water
2) solution containing 22.5 g/l lactic acid in deionised water
3) solution containing 18.7 g/l sodium chloride and 30 g/l acetic acid in deionised water

After sterilisation, the panels were allowed to cool and dry, after which the lacquer adhesion was immediately tested in a so-called cross-hatch and tape test according to ASTM D3359 - 09e2 "Standard Test Methods for Measuring Adhesion by Tape Test". This test gives a ranking on a scale from 0 (excellent adhesion) to 5 (very poor adhesion) and was performed using Scotch No. 610 adhesive tape.

The results of the performance tests described above are given in Tables 2 and 3.

Table 2. Tin oxide stability and sulphide staining resistance

Treatment		Tin oxide thickness at t = 0 wks (C/m^2)	Tin oxide thickness at t = 14 wks (C/m^2)	Increase in thickness (C/m^2)	Tin oxide thickness after sulphide exposure test (C/m2)
A	Comp.Ex. 1	28	47	19 (poor)	20 (poor)
B	Comp.Ex. 2	27	25	-2 (good)	19 (poor)
C	Comp.Ex. 3	54	68	14 (poor)	59 (good)
D	Inv. Ex. 1	31	39	8 (good)	38 (good)
E	Inv. Ex. 2	45	47	2 (good)	43 (good)
F	Inv. Ex. 3	50	57	7 (good)	58 (good)

Table 3. Lacquer adhesion after sterilisation in various media.

Treatment		Solution 1 (D.I. water)	Solution 2 (Lactic Acid)	Solution 3 (Salt and Acid)
A	Comp.Ex. 1	5	4	3
B	Comp.Ex. 2	1	1	1
C	Comp.Ex. 3	5	2	4
D	Inv. Ex. 1	1	1	1
E	Inv. Ex. 2	3	2	1
F	Inv. Ex. 3	1	1	1

Comp.Ex. 1 shows that no treatment at all of the tinplate surface leads to poor tin oxide stability, poor sulphide staining resistance and poor lacquer adhesion. Comp.Ex. 2 shows that a Cr(VI)-free passivation treatment stabilises the tin oxide surface, provides excellent lacquer adhesion, but has a poor resistance to sulphide staining. Comp.Ex. 3 shows that the anodic treatment of the present invention provides much improved sulphide staining resistance, but since it is applied without further passivation treatment, the tin oxide layer is not stable and lacquer adhesion is poor.

Inventive Examples 1 - 3 show that the combination of anodic treatment in combination with a Cr(VI)-free passivation treatment leads to the desired <u>combination</u> of improved sulphide staining resistance, a stable tin oxide layer and good lacquer adhesion.

CLAIMS

1. A method for forming a passivation layer on a strip of packaging steel provided with a at least one tin-plated surface for forming a tin-oxide layer on said tin-plated surface to provide excellent sulphide staining resistance of the strip of packaging steel, for producing a packaging container or a can for packaging food, said method comprising the steps of:
   - subjecting said tin-plated surface to an anodic treatment at a pH of from 8 to 12 in a suitable aqueous electrolyte, wherein the suitable electrolyte is a phosphate solution, borate solution, sulphate solution or a carbonate solution, wherein the electrolyte for the anodic treatment does not contain mono-atomic halogen anions (Group 17) such as Cl^-, F^-,

     wherein the thickness of the tin oxide layer (D), expressed in Coulomb/m^2 and representing the total charge needed to reduce the layer to metallic tin is related to anodic treatment time (t), current density (A) by $D = E \times A \times t$, where E is the efficiency of the electrochemical reaction, and wherein D is at least 30 C/m^2;
   - wherein the electrolyte comprises monoatomic cations from Group 1 or 2 from the periodic table or polyatomic cations, and polyatomic anions;
   - optionally rinsing and drying the anodically treated tin-plated surface
   - subjecting the anodically treated tin-plated surface to a chemical passivation treatment free from using hexavalent chromium compounds
   - drying of the passivated anodically treated tin-plated surface
   - final processing such as oiling, winding, cutting etc.

2. Method according to claim 1 wherein D is at most 100 C/m^2.

3. Method according to any one the preceding claims wherein the pH value of the electrolyte for the anodic treatment is not lower than 8.5 and/or not higher than 11.5.

4. Method according to any one the preceding claims wherein the pH value of the electrolyte for the anodic treatment is not higher than 11.0, preferably not higher than 10.5.

5. Method according to any one the preceding claims wherein the electrolyte for the anodic treatment contains one or more of Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+.

6. Method according to any one the preceding claims wherein the electrolyte for the anodic treatment contains no
   - monoatomic anions such as fluorides, chlorides, bromides, and/or no
   - cations from or containing inner-transition metals, transition metals and post-transition metals.

7. Method according to any one the preceding claims wherein the electrolyte for the anodic treatment mainly consists of an aqueous solution of sodium carbonate, preferably at a pH value of between 10 and 11.5.

8. Method according to any one the preceding claims wherein the anodic treatment is performed in-line with or immediately after electrolytic tinning, and wherein the anodic treatment time (t) is at most 5 seconds, preferably at most 2 seconds, more preferably between 0.05 seconds and 1.5 seconds.

9. Method according to any one the preceding claims wherein the anodic treatment is performed in-line with an industrial electrolytic tinning line, and wherein the current density during the anodic treatment (A) is at least 10 A/m^2, preferably at least 50 A/m^2 and more preferably at least 100 A/m^2, and/or at most 4000 A/m^2, preferably at most 2000 A/m^2 or more preferably at most 1000 A/m^2.

10. A strip of packaging steel having at least one tin-plated surface provided on the or each tin-plated surface with a tin-oxide layer having a thickness of 30 to 100 C/m^2 and a passive layer on top of the said tin-oxide layer provided thereupon by means of a chemical passivation process, preferably a no-rinse chemical passivation process.

11. A strip of packaging steel according to claim 10 wherein the or each tin-oxide layer has a thickness of at least 40 C/m^2.

12. A blank for producing a packaging container or a can, or a packaging container or a can produced thereof produced from the strip according to any one of claim 10 or 11.

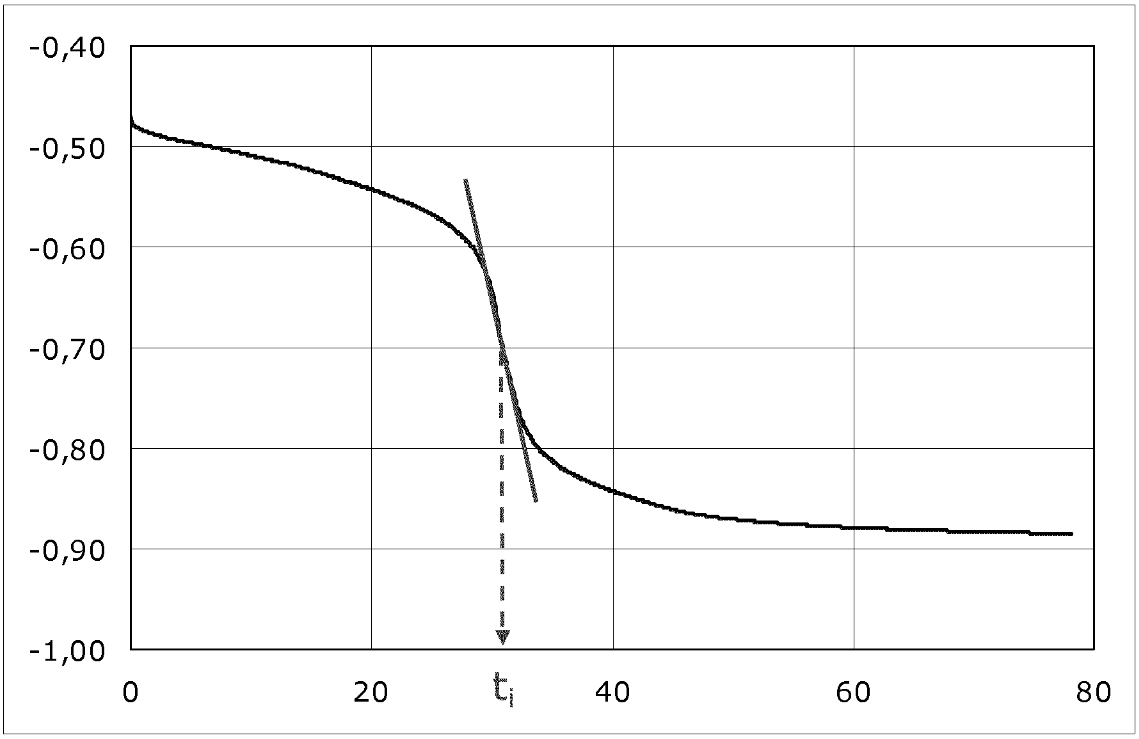

Figure 1

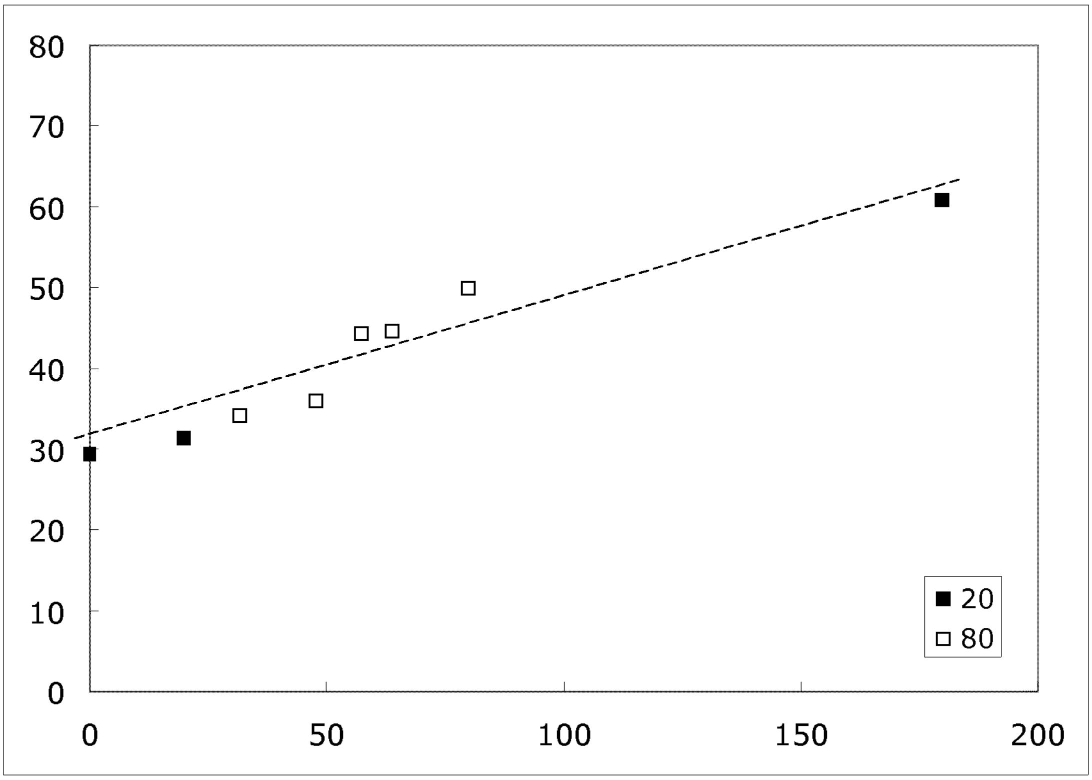

Figure 2

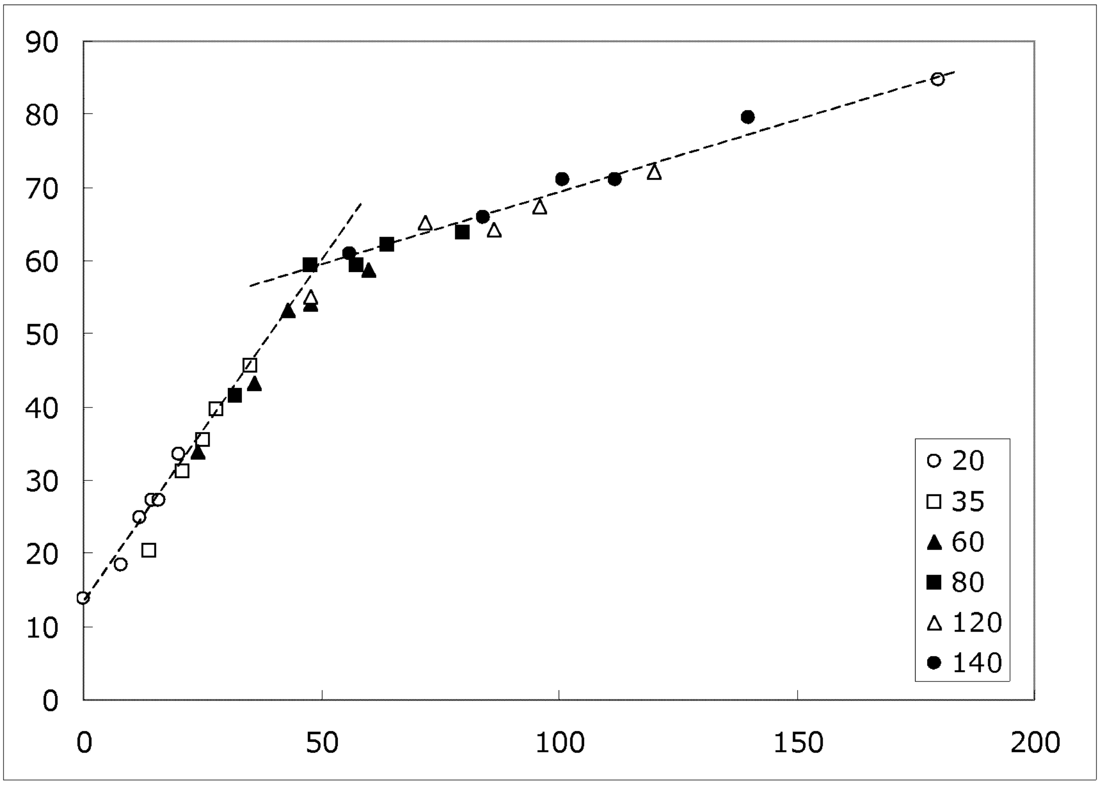

Figure 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/063912

A. CLASSIFICATION OF SUBJECT MATTER
INV. C25D5/48 C25D11/34
ADD. C25D3/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C25D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2012/097926 A1 (HENKEL AG & CO KGAA [DE]; SUNDERMEIER UTA [DE]; WOLPERS MICHAEL [DE];) 26 July 2012 (2012-07-26) abstract page 13; table 1 claims 1-15 -----	1-12
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 18 October 2013	Date of mailing of the international search report 28/10/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Haering, Christian

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International application No
PCT/EP2013/063912

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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