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(54) **Titre** : PROCEDE POUR LA PASSIVATION DE LA SURFACE DE FER NOIR OU DE FER BLANC ET SYSTEME D`ELECTROLYSE POUR LE RENDEMENT DUDIT PROCEDE

(54) **Title:** METHOD FOR PASSIVATION OF THE SURFACE OF BLACKPLATE OR TINPLATE AND ELECTROLYSIS SYSTEM FOR PERFORMANCE OF THE METHOD

(57) **Abrégé/Abstract:**

The invention concerns a method for passivation of the surface of blackplate or tinplate by electrolytic deposition of a chromium oxide-containing passivation layer on the surface, wherein the electrolytic deposition of the chromium-containing passivation layer occurs from an electrolyte solution (E) that contains a trivalent chromium compound as well as at least one salt to increase the conductivity and at least one acid or a base to adjust a desired pH value, wherein the electrolyte solution (E) contains no additional components apart from the trivalent chromium compound as well as the at least one salt and the at least one acid or base and is especially free of organic complexing agents and free of buffering agents.

Abstract

The invention concerns a method for passivation of the surface of blackplate or tinplate by electrolytic deposition of a chromium oxide-containing passivation layer on the surface, wherein the electrolytic deposition of the chromium-containing passivation layer occurs from an electrolyte solution (E) that contains a trivalent chromium compound as well as at least one salt to increase the conductivity and at least one acid or a base to adjust a desired pH value, wherein the electrolyte solution (E) contains no additional components apart from the trivalent chromium compound as well as the at least one salt and the at least one acid or base and is especially free of organic complexing agents and free of buffering agents.

Method for Passivation of the Surface of Blackplate or Tinplate and Electrolysis System for Performance of the Method

The invention concerns a method for passivation of the surface of a blackplate or a tinplate by electrolytic deposition of a chromium oxide-containing passivation layer on the surface, as well as an electrolysis system for electrolytic deposition of a chromium- and chromium oxide-containing passivation layer on the surface of a blackplate or a tinplate.

Steel sheets electrolytically coated with a passivation layer of chromium and chromium oxide/chromium hydroxide are known from the prior art for the production of packaging, which are referred to as Tin-Free Steel (TFS) or as Electrolytic Chromium Coated Steel (ECCS) and represent an alternative to tinplate. These tin-free steel sheets are characterized in particular by good adhesiveness for paints or organic coatings (such as PP or PET polymer coatings). Despite the limited thickness of the passivation layer from chromium and chromium oxide/chromium hydroxide, which is generally less than 20 nm, these chromium-coated steel sheets exhibit good corrosion resistance and good workability in deformation processes used in the production of packaging materials, for example, in deep drawing and ironing processes.

Tinplate is generally provided with a passivation layer after electrolytic tin plating in order to suppress oxidation of the tin surface in atmospheric oxygen. Chromium-containing layers have proven suitable as passivation layers, which can be deposited electrolytically from a chromium(VI)-containing electrolyte on the tin surface of tinplate. These chromium-containing passivation layers consist of metallic chromium and chromium oxides. Chromium oxide is understood to mean all compounds of chromium and oxygen, including chromium hydroxides.

Electrolytic coating methods are known from the prior art for the production of chromium-plated steel sheets (ECCS) and for the passivation of tinplate surfaces, with which a passivation layer containing metallic chromium and chromium oxide/chromium hydroxide can be applied to a sheet-like substrate (uncoated steel sheet or tinplate) in a strip coating line, using a chromium(VI)-containing electrolyte. However, these coating methods have serious drawbacks due to the environmentally harmful and health-threatening properties of the chromium(VI)-containing electrolytes used in the electrolytic process and will have to be replaced with alternative coating methods in the not too distant future, since the use of chromium(VI)-containing materials will soon be prohibited.

For this reason, electrolytic coating methods have already been developed in the prior art which obviate the use of chromium(VI)-containing electrolytes. For example, WO 2015/177314-A1 and WO 2015/177315-A1 disclose a method for the electrolytic passivation of a strip-shaped sheet steel, especially blackplate or tinplate, with a chromium metal/chromium oxide (Cr-CrOx) layer, in which the steel sheet in a strip coating line is connected as cathode and passed at high sheet speeds of more than 100 m/min through a single electrolyte solution that contains a trivalent chromium compound (Cr(III)) as well as a complexing agent and a salt that increases conductivity and is free of chlorides and buffering agents such as boric acid.

Organic substances, especially formates and preferably sodium or potassium formate, are then used as complexing agents. The electrolyte solution can contain sulfuric acid to adjust a preferred pH value in the range of 2.5 to 3.5. The passivation layer from chromium metal or chromium oxide can then be deposited in layers in successive electrolysis tanks or in strip coating systems arranged one after the other, each electrolysis tank being filled with the same electrolyte solution.

It was then observed that the electrolytically deposited passivation layer also can contain chromium sulfates and chromium carbides, in addition to the components chromium metal and chromium oxide/chromium hydroxide, and that the fractions of these components in the total coating weight of the passivation layer depends significantly on the current densities used in the electrolysis tanks. It was established that three regions (regime I, regime II and regime III) are formed as a function of the current density, in which no chromium-containing deposition on the steel substrate occurs in a first region with low current density up to a first current density threshold (regime I), a linear relation exists between current density and coating weight of the deposited passivation layer in a second region with medium current density (regime II) and partial decomposition of the applied passivation layer occurs at current densities above a second current threshold (regime III), so that the coating weight of chromium of the passivation layer in this regime initially diminishes with increasing current density and is then set at an equal value at higher current densities. In the region with medium current density (regime II) essentially metallic chromium is deposited on the steel substrate with a weight fraction of up to 80% (referred to the total weight of the passivation layer) and above the second current density threshold (regime III), the passivation layer contains a higher fraction of chromium oxide, which accounts for between 1/4 and 1/3 of the total coating weight of the passivation layer in the region of higher current densities. The values of the current density thresholds that delimit the regions (regime I to regime III) from each other are then dependent on the sheet speed with which the steel sheet is moved through the electrolyte solution.

It has been shown that the highest possible fraction of chromium oxide should be contained in the chromium-containing passivation layer for good passivation of a blackplate or tinplate surface against oxidation in an oxygen-containing environment and to form a good adhesive base for organic coatings, such as paints or thermoplastics, especially for lamination of PET, PP, PE plastic films or their mixtures.

The problem of the present invention therefore consists of providing the most efficient and cost effective-possible electrolysis method that is environmentally safe and non-hazardous to health for passivation of the surface of a blackplate or tinplate with a passivation layer containing chromium oxide/chromium hydroxide based on an electrolyte solution with a trivalent chromium compound. In each case, the use of chromium(VI)-containing substances, even as intermediates of the electrolysis process, is to be avoided, in order to fully satisfy the legal requirements with respect to the prohibition on chromium(VI)-containing substances. In addition, the blackplate or tinplate coated according to the method should have the highest possible resistance against oxidation in an oxygen-containing environment, especially in atmospheric oxygen, and form a good adhesive base for organic coatings, such as organic paints and for polymer layers, especially for PET, PE or PP polymer films.

This problem is solved by a method with the features of claim 1 and by an electrolysis system with the features of claim 16 and by a blackplate or tinplate according to claim 18. Preferred embodiments of the method and the electrolysis system are apparent from the dependent claims.

In the method according to the invention, a chromium oxide-containing passivation layer is electrolytically applied from an electrolyte solution that contains a trivalent chromium compound, as well as at least one salt to increase conductivity and at least one acid or base to adjust a desired pH value, to an uncoated or tin-plated steel sheet (blackplate or tinplate sheet), wherein the electrolyte solution contains no additional components beyond the trivalent chromium compound and the at least one salt or the at least one acid or base and is particularly free of organic complexing agents and free of buffering agents. No chromium(VI)-containing substances are then used, not even as intermediates, so that the method is entirely free of chromium(VI)-containing substances and is therefore environmentally safe and non-hazardous to health during performance of the method.

It was then surprisingly shown that it is possible to deposit a chromium oxide-containing layer on the surface of a blackplate or tinplate electrolytically, even without using organic complexing agents, such as formates, as components of the electrolyte solution, in which case the deposited layer consists at least essentially of just chromium oxide, during use of an electrolyte solution without organic complexing agents.

It has also been shown that a layer of pure chromium oxide/chromium hydroxide forming the surface of the passivation layer is advantageous with respect to oxidation resistance and adhesion effect of organic coatings, such as paints or polymer layers. It is therefore prescribed in the method according to the invention that (organic) complexing agents, especially formates, such as sodium or potassium formate, be left out of the electrolyte solution. The passivation layer electrolytically deposited on the surface of the blackplate or tinplate with such an electrolyte consists at least essentially of pure chromium oxide and/or chromium hydroxide.

In referencing chromium oxide, all oxide forms of chromium (CrOx), including chromium hydroxides, especially chromium(III) hydroxide and chromium(III) oxide hydrate, as well as their mixtures, are meant. The compounds of chromium and oxygen in which the chromium is present in trivalent form, especially as dichromium trioxide (Cr_2O_3) are then preferred. The coating therefore contains (in addition to metallic chromium) preferably just trivalent chromium compounds and especially only trivalent chromium oxides and/or chromium hydroxide.

The electrolytically deposited passivation layer then preferably has the highest possible weight fraction of chromium oxide, including chromium hydroxides. The weight fraction of chromium oxide and/or chromium hydroxides is then preferably more than 90% and especially preferably more than 95%. On the one hand, this ensures good passivation against oxidation of the surface of the blackplate or tinplate and, on the other hand, offers a good adhesive base with good adhesion capability for organic coatings, such as paints or polymer layers from thermoplastics, such as PET or PP.

For the electrolytic deposition of the passivation layer, the blackplate or tinplate is connected as cathode and brought into contact with the electrolyte solution for a prescribed electrolysis time in at least one electrolysis tank. The electrolysis time is then preferably in the range of 0.3 to 5.0 seconds and with particular preference between 0.6 and 1.5 seconds. For this purpose, the blackplate or tinplate sheet is passed at a prescribed sheet speed through at least one electrolysis tank or in succession through several electrolysis tanks arranged one behind the other in the sheet travel direction, in which case the sheet speed is preferably at least 100 m/min and especially between 200 m/min and 750 m/min. High efficiency of the process can be ensured by the high sheet speeds.

The thickness and coating weight of the passivation layer of chromium oxide can be controlled by the electrolysis time and therefore the sheet speed. The electrolysis time is preferably chosen so that the deposited chromium oxide has a coating weight of at least 3 mg/m^2 and preferably 7 mg/m^2 to 10 mg/m^2. To achieve an oxidation and corrosion resistance sufficient for packaging applications, a coating weight of chromium oxide in the passivation layer of at least 5 mg/m^2, preferably more than 7 mg/m^2, is preferred. These coating weights of chromium oxide ensure sufficient resistance to oxidation and corrosion of the blackplate or tinplate surface and also offer a good adhesive base for organic coatings, such as paints or thermoplastic films.

To improve the corrosion resistance and to form a barrier against sulfur-containing materials, especially against sulfate- or sulfite-containing fillers of packaging, after electrolytic application of the passivation layer, a coating that adheres well to the chromium oxide layer of the passivation layer from an organic material, especially a paint or a thermoplastic, especially a PET, PE, PP polymer film or their mixture, can be readily applied without problem by coating the surface of the passivation layer with an organic paint or providing a plastic layer from a thermoplastic such as PET, PE and/or PE.

In order to ensure a process that is completely free of chromium(VI)-containing substances, an appropriate anode is expediently selected during the electrolytic deposition of the passivation layer and arranged in the electrolysis tank, which prevents the oxidation of chromium(III) from the trivalent chromium compound of the electrolyte solution to chromium(VI). For this purpose, anodes with an outer surface or a passivation layer made from a metal oxide, particularly iridium oxide, or from a mixed metal oxide, particularly iridium-tantalum oxide, have proven to be especially suitable. The anode preferably contains neither stainless steel nor platinum. By using such anodes, coatings that contain exclusively trivalent chromium oxide and/or chromium hydroxides, especially Cr_2O_3 and/or $Cr(OH)_3$, can be deposited on the blackplate or tinplate.

As in any galvanic process, during galvanic chrome plating from a chromium(III) electrolyte, at least one anodic oxidation is present simultaneously in addition to cathodic reduction. During galvanic chrome plating from a chromium(III) electrolyte, anodic oxidation consists of oxidation of chromium(III) to chromium(VI) on the one hand, and of oxidation of water to oxygen, on the other. Both potentials lie close together in the electrochemical series:

(1) Chromium (Cr) $Cr^{6+} + 3\ e^- \rightleftharpoons Cr^{3+}\ \ + 1.33\ V$

(2) Oxygen (O) $O_2 + 4\ H^+ + 4\ e^- \rightleftharpoons 2H_2O + 1.23\ V$

Measurement in the corresponding Daniell element serves as basis for the potentials. The potential of the redox equation then depends on the anode material employed. The choice of anode material therefore decidedly dictates whether reaction (1) is suppressed and reaction (2) occurs exclusively. In order to prevent the formation of Cr^{6+} in the method according to the invention, anodes based on metal oxides, particularly iridium oxide, or mixed metal oxides can be used to suppress reaction (1), such as mixed metal oxides that consist mostly of multiple layers of tantalum oxide and iridium oxide. The anodes can then have an outer surface or an outer passivation layer from a mixed metal oxide. Anodes with a core of titanium and an outer passivation layer from a tantalum oxide-iridium oxide have proven to be particularly suitable. During use of such anodes, it could be demonstrated by polarography measurements (mercury dropping electrode) that no Cr(VI) is formed.

When anodes made of stainless steel are used, oxidation of Cr(III) to Cr(VI) (reaction 1) is not (sufficiently) suppressed. Comparative measurements with stainless steel anodes show a distinctly detectable Cr(VI) concentration after an electrolysis time of just a few seconds. Stainless steel as anode material therefore does not at least fully suppress oxidation of Cr(III) to Cr(VI). This leads to enrichment of Cr(VI) in Cr(III) electrolytes and therefore to a different deposition mechanism. Consequently, anodes that are free of stainless steel are preferably used in the method according to the invention. This can ensure that no Cr(VI) forms as an intermediate during electrolysis and that the deposited passivation layer contains exclusively Cr(III) compounds and metallic chromium. In addition, final treatment, for example, with thiosulfate, can be omitted, which would otherwise be necessary during the use of stainless-steel anodes for reduction of deposited Cr(VI) to Cr(III).

The electrolyte solution preferably has a temperature in the range of 20°C to 65°C, and more preferably in the range of 30°C to 55°C, and especially between 35°C and 45°C. Electrolytic deposition of the chromium oxide-containing passivation layer is very efficient at these temperatures. When alluding to the temperature of the electrolyte solution or temperature in an electrolysis tank, the average temperature is meant, which is the average over the entire volume of the electrolysis tank. A temperature gradient with a temperature increase from the top down is generally present in the electrolysis tank.

In addition to the trivalent chromium compound, the electrolyte solution contains at least one salt that increases conductivity and at least one acid or base to adjust an appropriate pH value and is preferably free of chloride ions and free of buffering agents, particularly free of a boric acid buffer.

The trivalent chromium compound of the electrolyte solution is preferably chosen from the group including basic Cr(III) sulfate ($Cr_2(SO_4)_3$), Cr(III) nitrate ($Cr(NO_3)_3$), Cr(III) oxalate (CrC_2O_4), Cr(III) acetate ($C_{12}H_{36}ClCr_3O_{22}$), Cr(III) formate ($Cr(OOCH)_3$) or their mixture. The concentration of trivalent chromium compound in the electrolyte solution then preferably lies at at least 10 g/L and especially at more than 15 g/L and in particular at 20 g/L or more.

To increase conductivity, the electrolyte solution contains at least one salt that is preferably an alkali metal sulfate, especially potassium or sodium sulfate.

A very efficient deposition of a passivation layer containing chromium oxide is achieved if the pH value (measured at a temperature of 20°C) of the electrolyte solution lies in a range of 2.3 to 5.0 and preferably between 2.5 and 2.9. The desired pH value can be set by adding an acid or base to the electrolyte solution. When basic Cr(III) sulfate is used as trivalent chromium compound, sulfuric acid or an acid mixture containing sulfuric acid is particularly suitable for adjustment of the desired pH value.

Particularly preferred compositions of the electrolyte solution include basic Cr(III) sulfate ($Cr_2(SO_4)_3$) as trivalent chromium compound, as well as sodium sulfate as conductivity-increasing salt and sulfuric acid to adjust the preferred pH value in the range of 2.3 to 5.0.

The electrolyte solution then contains no additional components in addition to the trivalent chromium-containing substance, the at least one salt to increase conductivity, and the at least one acid or base to adjust the pH value. This ensures simple and cost-effective production of the electrolyte solution.

To produce the electrolyte solution, the trivalent chromium compound, which was initially freed largely of organic residues, as well as the at least one salt and the at least one acid or base to adjust the desired pH value, are dissolved in water. Since the electrolyte solution contains no complexing agent, the solution thus obtained should expediently be allowed to stand for complexation for at least 5 days, preferably at least 7 days (in atmospheric oxygen). A fine adjustment of the desired pH value can then be conducted by adding an acid or base.

Blackplate or tinplate with a chromium oxide-containing passivation layer can be produced with the method according to the invention, in which the passivation layer consists at least essentially of just chromium oxide and/or chromium hydroxide, preferably just trivalent chromium oxide and/or chromium hydroxide and preferably has a weight fraction of chromium oxide and/or chromium hydroxide of more than 90%, especially preferably more than 95%. Such blackplate or tinplate according to the invention is characterized by a high corrosion resistance and good adhesion capacity for organic coatings such as paints or polymer layers. The passivation layer preferably contains at least essentially only compounds of chromium and oxygen in which the chromium is present in trivalent form, especially as Cr_2O_3 and/or $Cr(OH)_3$.

In addition to chromium oxides and/or chromium hydroxides, residual components of chromium sulfate (as the initial chromium compound of the electrolytic deposition process) can be contained in the passivation layer in addition to unavoidable contaminants.

The passivation layer preferably consists of a first layer facing the surface of the blackplate or tinplate and a second layer forming the surface of the passivated blackplate or tinplate, in which the first layer contains metallic chromium and the second layer consists of pure chromium oxide and/or chromium hydroxide except for the mentioned residual components of chromium sulfate and unavoidable contaminants.

A particularly good corrosion resistance of the blackplate or tinplate according to the invention can be achieved if the passivation layer has a total coating weight of chromium oxide and/or chromium hydroxide of at least 3 mg/m^2, preferably 5 mg/m^2 to 15 mg/m^2.

The invention is further explained below by means of embodiment examples with reference to the accompanying drawings, where the aforementioned embodiment examples explain the invention only in exemplary terms and do not restrict it with reference to the scope of protection defined in the subsequent claims. The drawings show:

Figure 1:	schematic depiction of a strip coating line for performance of the method according to the invention;
Figure 2:	schematic sectional view of a blackplate or tinplate sheet coated with the strip coating line of Figure 1 in a method according to the invention;
Figure 3:	GDOES spectrum of a layer deposited electrolytically, using electrolyte solution from a trivalent chromium substance (basic Cr(III) sulfate) and an organic complexing agent (sodium formate) on a steel sheet, which contains chromium metal, chromium oxide and chromium carbides;
Figure 4:	GDOES spectrum of a layer deposited on a steel sheet electrolytically, using electrolyte solution from a trivalent chromium substance (basic Cr(III) sulfate) without organic complexing agent, which consists essentially of pure chromium oxide.

A strip coating line for performance of the method according to the invention is shown schematically in Figure 1. The strip coating line includes three electrolysis tanks 1a, 1b, 1c arranged one next to or behind the other, each of which is filled with an electrolyte solution E. An initially uncoated blackplate sheet or tinplate sheet (subsequently referred to as sheet B) is passed through electrolysis tanks 1a-1c in succession. Sheet B is pulled for this purpose by a transport device (not shown here) in a sheet travel direction v at a prescribed sheet speed through the electrolysis tanks 1a-1c. Current rolls S are arranged above the electrolysis tanks 1a-1c, through which the sheet B is connected as cathode. A deflection roll U is also arranged in each electrolysis tank around which the sheet B is guided and in so doing directed into or from the corresponding electrolysis tank.

At least one anode pair AP is arranged within each electrolysis tank 1a-1c beneath the liquid level of the electrolyte solution E. In the depicted embodiment example, two anode pairs AP arranged one behind the other in the sheet travel direction are provided in each electrolysis tank 1a-1c. The sheet B is then guided between the opposite anodes of an anode pair AP. In the embodiment example of Figure 1, two anode pairs AP are therefore arranged in each electrolysis tank 1a, 1b, 1c, so that the sheet B is guided through these anode pairs AP in succession. The last anode pair APc of the last electrolysis tank 1c, as viewed in the sheet travel direction v in the downstream direction, then has a shortened length in comparison to the other anode pairs AP. A higher current density can thus be generated with this last anode pair APc when an equally high electric current is applied.

For preparation of the electrolysis process, the sheet B is initially degreased, rinsed, pickled and rinsed again and passed through the electrolysis tanks 1a-1c in succession in this pretreated form, during which sheet B is connected as cathode by supplying electric current via current rolls S. The sheet speed with which the sheet B is passed through the electrolysis tanks 1a-1c is at least 100 m/min and can be as high as 900 m/min.

The electrolysis tanks 1a to 1c arranged one behind the other in the sheet travel direction are each filled with the same electrolyte solution E. The electrolyte solution E contains a trivalent chromium compound, preferably basic Cr(III) sulfate, $Cr_2(SO_4)_3$. To increase the conductivity, the electrolyte solution E also contains a salt, especially an alkali metal sulfate, for example, potassium or sodium sulfate, as well as an acid or base to adjust an appropriate pH value. The pH value of the first electrolyte solution E is adjusted by adding the acid or base to a preferred value between 2.0 and 5.0. When basic Cr(III) sulfate is used as trivalent chromium compound, sulfuric acid has proven to be an appropriate acid for pH value regulation. The concentration of trivalent chromium compound in the electrolyte solution E preferably lies at at least 10 g/L and with particular preference at 20 g/L or more.

The temperature of the electrolyte solution E is expediently equally high in electrolysis tanks 1a, 1b, 1c, and preferably lies between 25°C and 70°C. However, different temperatures of the electrolyte solution can also be set in the electrolysis tanks 1a, 1b, 1c. For example, the temperature of the electrolyte solution in the center electrolysis tank 1b can be lower than in the front electrolysis tank 1a arranged upstream. The temperature of the electrolysis solution in the center electrolysis tank 1b then lies, for example, between 25°C and 37°C and especially at 35°C and the temperature of the electrolyte solution E in the front electrolysis tank 1a lies between 40°C and 75°C and especially at 55°C.

The electrolyte solution E contains no organic components and especially no complexing agent. The electrolyte solution E is also free of halides and buffering agents, such as boric acid.

The anode pairs AP arranged in electrolysis tanks 1a-1c are exposed to electrical direct current so that a sufficiently high current density is present in the electrolysis tanks 1a, 1b, 1c in order to produce electrolytic deposition of a chromium-containing (especially a Cr(III)-containing) layer. The minimum current density required for this purpose is then dependent on the sheet speed and amounts to about 15 to 20 A/dm^2 at a (minimal) sheet speed of 100 m/min. At higher sheet speeds, the minimum current density required for electrolytic deposition of a chromium-containing layer increases.

Depending on the sheet speed, the sheet B connected as cathode and passed through electrolysis tanks 1a-1c is effectively in electrolytic contact with the electrolyte solution E during an electrolysis time t1, t2 and t3 in the electrolysis tanks 1a, 1b, 1c, respectively. At sheet speeds between 100 and 700 m/min, the electrolysis time t1, t2, t3 in each of the electrolysis tanks 1a, 1b, 1c lies between 0.5 and 2.0 seconds. High sheet speeds are preferably set so that the electrolysis time in each electrolysis tank 1a, 1b, 1c is less than 2 seconds and especially between 0.6 seconds and 1.8 seconds. The entire electrolysis time $tG = t1 + t2 + t3$, in which the sheet B is electrolytically in contact with electrolyte solution E over all electrolysis tanks 1a-1c, is accordingly between 1.8 and 5.4 seconds. The electrolysis time in the individual electrolysis tanks 1a, 1b, 1c can then be adjusted, on the one hand, by the sheet speed, and, on the other hand, by dimensioning of the electrolysis tanks 1a-1c.

When a current density in the corresponding electrolysis tanks 1a-1c that is greater than the minimum current density is adjusted, a layer is deposited on at least one side of the sheet B in each electrolysis tank 1a, 1b, 1c that consists at least essentially of chromium oxide and/or chromium hydroxide and optionally contains chromium sulfates, when a sulfate-containing electrolyte solution E is used. A layer B1, B2, B3 is then produced in each of the electrolysis tanks 1a, 1b, 1c, in which the composition of layers B1, B2, B3 is at least essentially the same if the same electrolyte solution E is contained in the electrolysis tanks 1a-1c and the same electrolysis parameters, especially the same current densities and temperatures, are used.

The weight fraction of chromium oxide/chromium hydroxide in the coating weight of the layers B1, B2 and B3 and also the total coating weight of the coating that consists of these layers B1, B2 and B3 then expediently lies at at least 90%, preferably at more than 95%.

A sectional view of a sheet B electrolytically coated with the method according to the invention is schematically shown in Figure 2. A passivation layer P consisting of the individual layers B1, B2, B3 is applied to one side of sheet B. Each individually layer B1, B2, B3 is then applied to the surface in one of the electrolysis tanks 1a, 1b, 1c.

The layer structure of the layers B1, B2, B3 deposited on the sheet can be demonstrated by GDOES spectra (*Glow Discharge Optical Emission Spectroscopy*).

Comparative experiments have demonstrated that when, according to the invention, known prior-art electrolyte solutions with organic complexing agents such as formates are not used, a metallic chromium layer with a thickness of 10-15 nm can be deposited on sheet B in electrolysis tanks 1a, 1b, 1c as a function of electrolysis time. The surface of these layers oxidizes after deposition and is mostly present as chromium oxide in the form Cr_2O_3 or as a mixed oxide-hydroxide in the form $Cr_2O_2(OH)_2$. This oxide layer is a few nanometers thick. In addition, chromium-carbon and chromium sulfate compounds that are formed from reduction of the organic complexing agent or the sulfate of the electrolyte solution are formed, uniformly incorporated through the complete layer. Typical GDOES spectra of layers B1, B2, B3 deposited in the individual electrolysis tanks exhibit a strong increase in oxygen signal in the first nanometers of the layer, from which it can be concluded that the oxide layer is concentrated on the surface of the corresponding layer (Figure 3).

A GDOES spectrum of a sheet B is shown in Figure 4, which was passivated with the method according to the invention, using an electrolyte solution E, in which the electrolyte solution E did not contain organic complexing agents, such as formates. It is shown that a layer (passivation layer) is then deposited on sheet B that consists at least essentially of just chromium oxide/chromium hydroxide and contains possibly limited fractions of chromium sulfate.

The composition of the passivation layer can be determined according to the EURO standard DIN EN 10202 (Cr oxides photometric: (Euro norm) step 1: 40 mL NaOH (330 g/L), reaction at 90°C for 10 minutes, oxidation with 10 mL 6% H_2O_2, photometric @ 370 nm).

After electrolytic deposition of the passivation layer, the sheet B provided with the passivation layer can be rinsed, dried and oiled (for example, with DOS). The sheet B electrolytically coated with the passivation layer can then additionally be provided with an organic coating. The organic coating is then applied in a known manner, for example, by painting or lamination of a plastic film onto the surface of the passivation layer, i.e., onto the upper layer B3 of chromium oxide. The chromium oxide surface of layer B3 then provided a good adhesive base for the organic material with a coating. The organic coating, for example, can be an organic paint or a polymer film from thermoplastic polymers such as PET, PE, PP or their mixtures. The organic coating can be applied, for example, in a strip coating process or in a plate process in which the coated sheet in the plate process is initially divided into plates that are then painted with an organic paint or coated with a polymer film.

To achieve a resistance to oxidation and corrosion sufficient for packaging applications, the passivation layers applied by means of the method according to the invention preferably have a total coating weight of chromium oxide/chromium hydroxide of at least 3 mg/m^2, and preferably at least 5 mg/m^2. Good adhesion of organic paints or thermoplastic polymer materials on the surface of the passivation layer B could be achieved at coating weights of chromium oxide/chromium hydroxide up to 15 mg/m^2. A preferred range for the coating weight of chromium oxide/chromium hydroxide in the passivation layer therefore lies between 3 and 15 mg/m^2, and a particularly preferred range lies between 5 and 15 mg/m^2.

The thickness and the coating weight of the individual layers B1, B2, B3 can be adjusted in the depicted embodiment example of the method according to the invention by the electrolysis times t1, t2, t3 and the current density in the electrolysis tanks. As soon as a sufficiently high current density is selected for the electrolysis tanks, the thickness and coating weight of the deposited layers B1, B2, B3 will be a linear function of the current density and (at equivalent temperature of the electrolyte solution) of the electrolysis time t1, t2, t3 in the electrolysis tanks, in which the sheet B is effectively in electrolytic contact with the electrolyte solution E.

The coating weight of the passivation layer can therefore be adjusted by the electrolysis time and/or the current density in which sheet B is effectively in electrolytic contact with electrolyte solution E. The electrolysis time t is again dependent on the dimensioning of the electrolysis tanks and the sheet speed.

Claims

1. A method for passivation of the surface of blackplate or tinplate by electrolytic deposition of a chromium oxide-containing passivation layer on the surface, wherein electrolytic deposition of the chromium-containing passivation layer occurs from an electrolyte solution that is composed of a trivalent chromium compound, at least one salt to increase the conductivity and at least one acid or base to adjust a desired pH value and is free of organic chelating agents and free of buffering agents, wherein the blackplate or tinplate has the form of a sheet, which is passed through at least one electrolysis tank or several electrolysis tanks arranged one behind the other in a sheet travel direction at a prescribed sheet speed, which is at least 100 m/min, wherein in each electrolysis tank at least one anode is arranged and the sheet is connected as a cathode, wherein the anodes contain no stainless steel and no platinum and are exposed to electrical current so that a sufficiently high current density is present in each of the electrolysis tanks in order to produce electrolytic deposition of a chromium oxide-containing layer, wherein the current density is 15 A/dm^2 or more.

2. The method according to claim 1, wherein the passivation layer consists at least essentially of chromium oxide and/or chromium hydroxide.

3. The method according to claim 1, wherein the passivation layer has a weight fraction of chromium oxide and/or chromium hydroxide of more than 90%.

4. The method according to claim 1, wherein the blackplate or tinplate for electrolytic deposition of the passivation layer is brought into contact with the electrolyte solution during an electrolysis time, wherein the electrolysis time lies in the range of 0.1 to 2.0 seconds.

5. The method according to claim 1, wherein the blackplate or tinplate for electrolytic deposition of the passivation layer is brought into contact with the electrolyte solution during an electrolysis time, wherein the electrolysis time lies between 1.0 and 1.5 seconds.

6. The method according to claim 1, wherein the temperature of the electrolyte solution has a temperature averaged over the volume of the corresponding electrolysis tanks in the range of 20°C to 65°C.

7. The method according to claim 1, wherein the temperature of the electrolyte solution has a temperature averaged over the volume of the corresponding electrolysis tanks in the range of 30°C to 55°C.

8. The method according to claim 4, wherein the electrolysis time, in which the blackplate or tinplate is in effective electrolytic contact with the electrolyte solution, is less than 1.0 seconds in each of the hydrolysis tanks, wherein the entire electrolysis time wherein the blackplate or tinplate is in effective electrolytic contact with the electrolyte solution in all electrolysis tanks between 0.5 seconds and 2.0 seconds.

9. The method according to any one of claims 1 to 8, wherein the trivalent chromium compound is chosen from the group of basic Cr(III) sulfate ($Cr_2(SO_4)_3$), Cr(III) nitrate ($Cr(NO_3)_3$), Cr(III) oxalate (CrC_2O_4), Cr(III) acetate ($C_{12}H_{36}ClCr_3O_{22}$), Cr(III) formate ($Cr(OOCH)_3$) or a mixture thereof, and the salt of the electrolyte solution contains at least one alkali metal sulfate.

10. The method of claim 9, wherein the at least one alkali metal sulfate contains potassium or sodium sulfate.

11. The method according to any one of claims 1 to 10, wherein the electrolyte solution has a pH value in the range of 2.3 to 5.0, wherein the pH value is adjusted by adding at least one acid to the electrolyte solution.

12. The method according to any one claims 1 to 11, wherein the electrolyte solution has a pH value between 2.5 and 2.9.

13. The method according to any one of claims 1 to 12, wherein the concentration of trivalent chromium compound in the electrolyte solution is at least 10 g/L.

14. The method according to any one of claims 1 to 13, wherein the passivation layer applied from the electrolyte solution has a total coating weight of chromium oxide and/or chromium hydroxide of at least 3 mg/m^2.

15. The method according to any one of claims 1 to 14, wherein the anodes, during electrolytic deposition of the passivation layer, prevent an oxidation of chromium(III) from the trivalent chromium compound of the electrolyte solution to chromium(VI).

16. The method according to claim 1, wherein the anodes contain an outer surface or a coating of a metal oxide or of a mixed metal oxide, or the anodes consist of a metal oxide or of a mixed metal oxide.

17. The method according to any one of claims 1 to 16, wherein the electrolyte solution is produced by mixing the trivalent chromium compound, that has been freed of organic residues except for unavoidable contaminants, with the at least one salt and the at least one acid or base to adjust the desired pH value and the mixture is dissolved in water and the solution thus obtained is allowed to stand for complexation for at least 5 days or at least 7 days, and then a fine adjustment of the pH value occurs by addition of an acid or base.

18. An electrolysis system for electrolytic passivation of the surface of a blackplate or tinplate sheet by deposition of a chromium oxide containing passivation layer on the surface of the sheet, wherein the electrolysis system includes:

at least one electrolysis tank filled with an electrolyte solution, or several electrolysis tanks arranged one behind the other, each of which is filled with the same electrolyte solution, wherein in each electrolysis tank at least one anode, which contain no stainless steel and no platinum, is arranged,
wherein the electrolyte solution is composed of a trivalent chromium compound, at least one salt to increase the conductivity and at least one acid or base to adjust a desired pH value and is free of organic chelating agents and free of buffering agents, and
the blackplate or tinplate sheet for electrolytic deposition of the passivation layer can be passed through the at least one electrolysis tank or through the several electrolysis tanks in succession with a predetermined sheet speed in a sheet travel direction so that the surface of the sheet is electrolytically in effective contact with the electrolyte solution and a passivation layer consisting at least essentially or completely of chromium oxide and/or chromium hydroxide is deposited on the surface.

19. The electrolysis system according to claim 18, wherein each anode has an outer surface or a coating of a metal oxide or of a mixed metal oxide.

20. The electrolysis system according to claim 18, wherein each anode has an outer surface or a coating of iridium oxide or iridium-tantalum oxide.

21. A blackplate or tinplate with a surface passivated by electrolytic deposition of a chromium oxide containing passivation layer, wherein the passivation layer has a total coating weight of chromium oxide and/or chromium hydroxide of at least 3 mg/m^2 and consists at least essentially or completely of chromium oxide and/or

chromium hydroxide and has a weight fraction of chromium oxide and/or chromium hydroxide of more than 90%.

22. A blackplate or tinplate with a surface passivated by electrolytic deposition of a chromium oxide containing passivation layer, wherein the passivation layer consists at least of a first layer facing the surface of the blackplate or tinplate and a second layer forming the surface of the passivated blackplate or tinplate, the first layer containing metallic chromium and a second layer consisting of pure chromium oxide and/or chromium hydroxide.

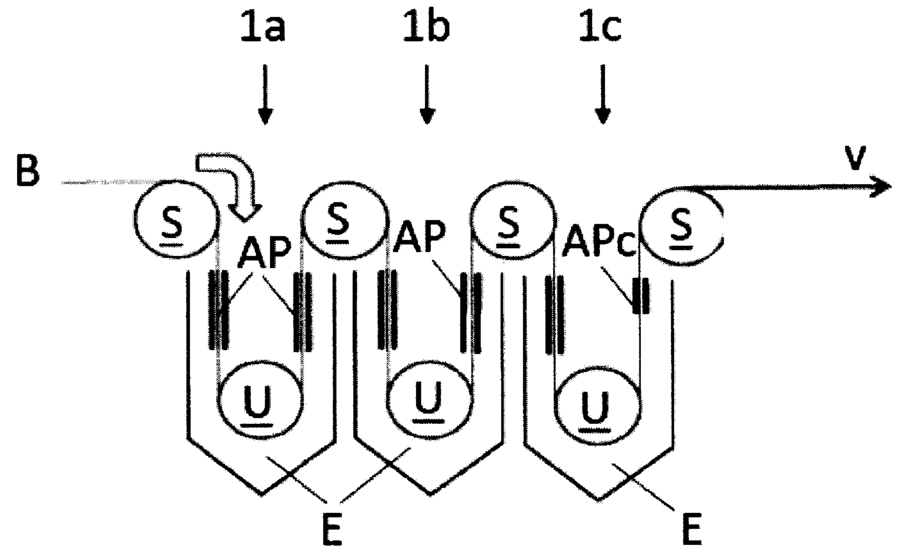

Fig. 1

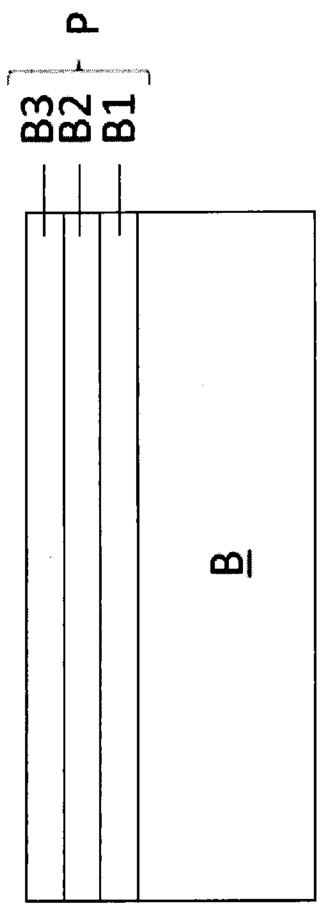

Fig. 2

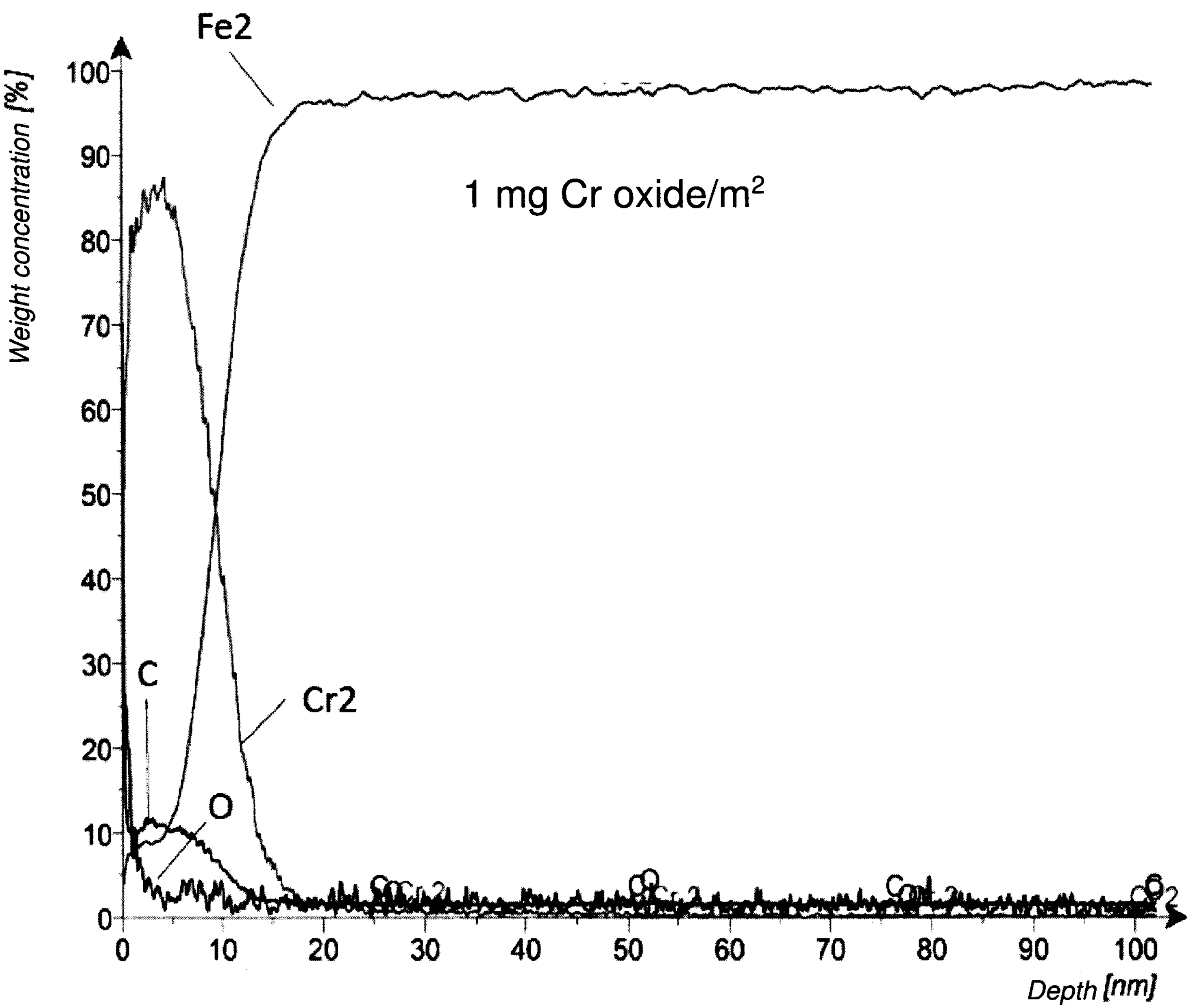
Fe2
1 mg Cr oxide/m²
Weight concentration [%]
100
90
80
70
60
50
40
30
20
10
0
C
Cr2
O
0
10
20
30
40
50
60
70
80
90
100
Depth [nm]

Fig. 3

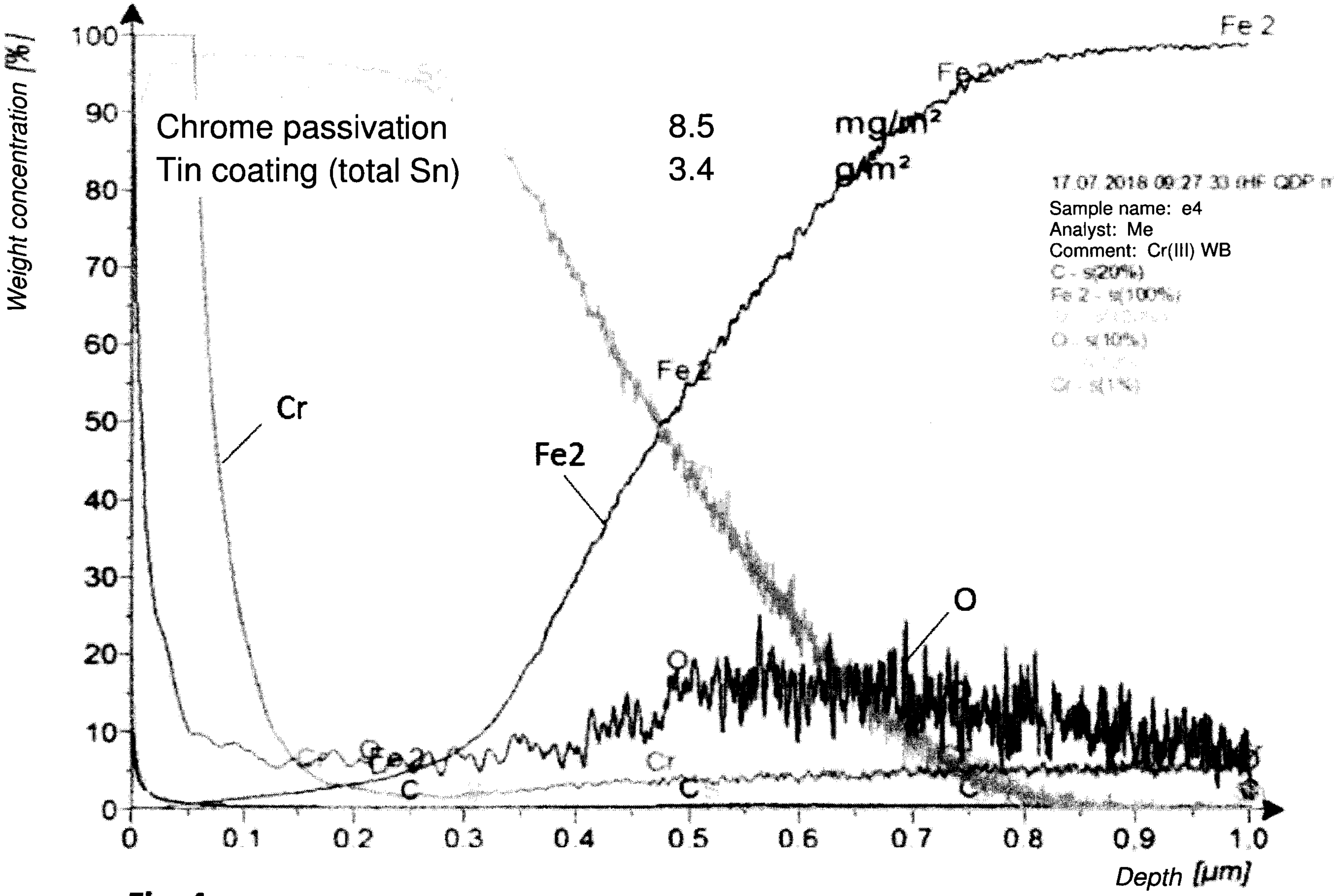
Chrome passivation 8.5 mg/m²
Tin coating (total Sn) 3.4 g/m²
17.07.2018 09:27:33 (HF QDP
Sample name: e4
Analyst: Me
Comment: Cr(III) WB
C - s(20%)
Fe 2 - s(100%)
O - s(10%)
Cr - s(1%)
Weight concentration [%]
100
90
80
70
60
50
40
30
20
10
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Depth [µm]
Cr
Fe2
O
C
Fe 2

Fig. 4