Characterization of Passivated Tinplate For Food Can Applications

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INTRODUCTION

Tinplate specimens for food can applications, passivated by cathodic treatment in a sodium dichromate solution, were studied. Three experimental methods: coulometric, spectrophotometric, and atomic absorption spectrophotometry (AAS), were used to quantify the chromium content in the passive coating as total chromium, metallic chromium, and chromium oxide. Morphological and chemical analyses using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) were performed. The study was completed by conducting X-ray photoelectron spectroscopy (XPS) experiments in order to elucidate the passive layer chemical composition.

Tinplate is a nonhomogeneous material with a stratified structure, basically consisting of a thin sheet of carbon steel coated with pure tin on both faces and usually lacquered. Despite the increasing use of new alternative materials such as aluminum and chromate steel sheet in the canning industry, tinplate continues to be used in more than 80% of cases.

In order to stabilize the tinplate surface it is important to apply a passivation treatment during its manufacturing and before lacquering. The general purpose of the passivation treatment is: (a) to prevent tin oxide growth on the surface, as excessive oxide can produce discoloration during prolonged storage and in stoving operations associated with lacquering and printing, especially in the curing of the lacquer; (b) to prevent the appearance of sulfide staining by sulfur contained in certain canned foods; (c) to improve lacquer adhesion to the metal substrate; and (d) to improve corrosion resistance after lacquering.[1]

Chromium salts are one of the most effective aqueous corrosion inhibitors for tinplate. However, it has been recognized that chromium is highly toxic. For instance, oral ingestion of one to two grams of chromic acid causes blood disorders, liver damage, and kidney failure.[2] The concentration levels of chromium allowed in the workplace are becoming regulated by authorities, and users of chromium containing materials are being warned of the possible health risks. Several options have been considered: Cr(VI) reduction to Cr(III), which is 100 times less toxic; elimination of chromium containing waste; and utilization of chromium alternatives such as molybdates, vanadates, rare earth metal salts, etc.[3] Yet, at the present time, this metal continues to be a problem.

In a recent paper it has been found that the adhesive properties of lacquer coatings based on epoxyphenolic resins applied on tinplate improve with the metallic chromium (CrM) content and worsen as the total chromium (CrT) content increases, with an important role being played by the CrO_x/CrT relationship, where CrO_x is chromium oxide content.[4] A linear relationship was obtained between adhesion measured as T-peel strength and the different species of chromium present in the passive layer:

$$\text{Adhesion} = \text{CrM} + 10(\text{CrO}_x/\text{CrT}) \quad (1)$$

In accordance with equation (1), the factors controlling adhesion are CrM and the CrO_x/CrT relationship. Lacquer detachment took place due to the fracturing of the CrO_x layer between the tin surface and the chromium surface layer.[5] From a practical viewpoint, the canning industry is in need of new studies to establish the composition and structure of the passive layer formed on a tinplate surface.

The aim of this paper is to characterize the passive layer formed by chromium passivation treatment on tinplate for food can applications and compare it with unpassivated tinplate. The experimental techniques used were coulometric, spectrophotometry, diphenylcarbazide (DPC), atomic absorption spectrophotometry (AAS), scan-

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ning electron microscopy (SEM), energy dispersive X-ray (EDX), and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Tinplate (E 2.8/2.8) with a tin coating of 2.8 g/m² on each face was passivated in a manufacturing line using a code 311 passivation treatment: cathodic treatment in a sodium dichromate solution. Tinplates labeled A and B were tested. For comparative purposes, an unpassivated tinplate was also analyzed.

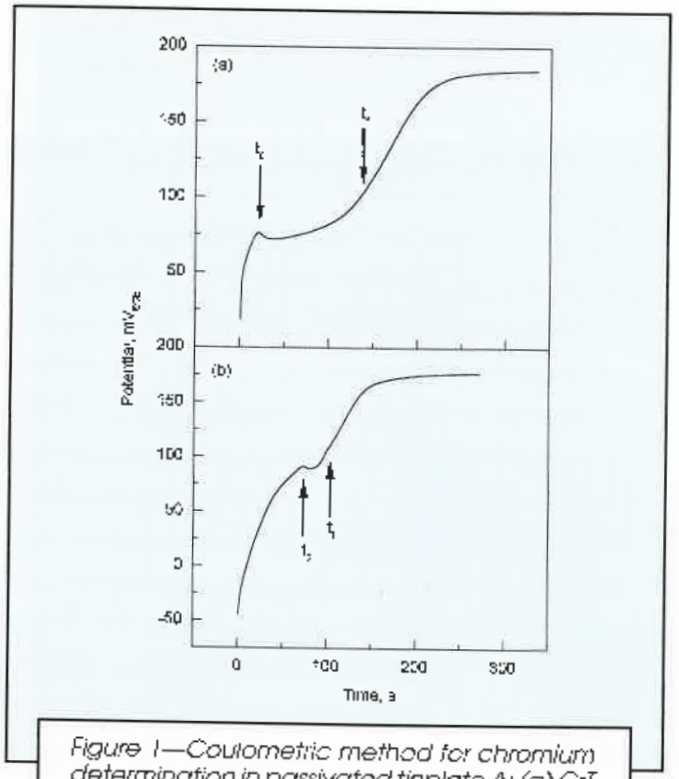

Figure 1—Coulometric method for chromium determination in passivated tinplate A: (a) CrT and (b) CrM; t_0 is the start and t is the end of the oxidation process: Cr^0 to Cr^{3+}.

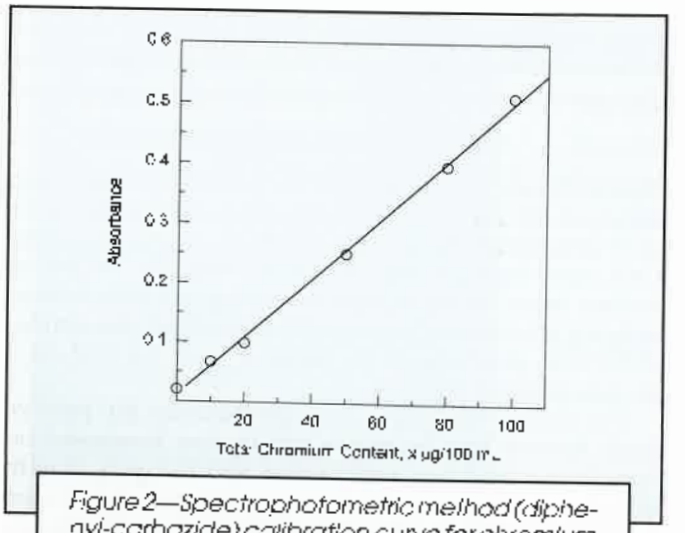

Figure 2—Spectrophotometric method (diphenyl-carbazide) calibration curve for chromium determination in passivated tinplate B.

The CrT content in the passive layer on tinplate A was determined using a coulometric method.[6,7] A current density, i, of 50 µA/cm² was applied anodically to the specimen in a phosphate buffer solution at pH 7.4: 200 mL of 8 g/L sodium dihydrogen phosphate dihydrate [$NaH_2PO_4{\cdot}2H_2O$] and 800 mL of 9.5 g/L disodium hydrogen phosphate anhydrous [Na_2HPO_4], and, using equation (2), the CrT was determined:

$$CrT = \frac{0.1 \times i \times t}{5 \times 10^{-4}} \qquad (2)$$

where t is the time for detinning (difference between t_f and t_0) (see *Figure* 1a).

The CrM content in tinplate A was determined after washing the specimens in a boiling 1.0 M sodium hydroxide [NaOH] solution for one minute. The analysis was carried out using a coulometric method. A current density, i, of 50 µA/cm² was applied in a 50 g/L of $NaH_2PO_4{\cdot}2H_2O$ test solution, which was brought to pH

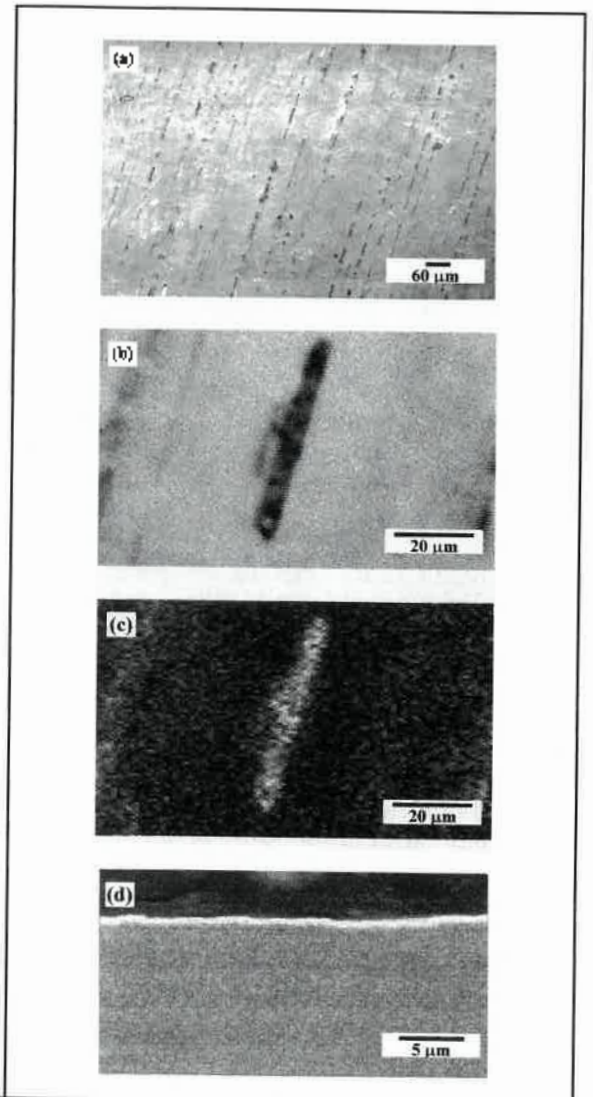

Figure 3— SEM micrographs for passivated tinplate A: (a) secondary electrons, (b) backscattered electrons, (c) Fe K_α-mapping, and (d) cross-section.

5.0 by adding NaOH,[8] and, using equation (2), the CrM was determined, where t is the difference between t_f and t_o (see *Figure* 1b).

The amount of CrO_x in tinplate A corresponds to the difference between CrT and CrM, since $CrT = CrM + CrO_x$.

The spectrophotometric method was used to determine the CrT content in tinplate B, with a lower CrT content than tinplate A and for this reason the coulometric method cannot be used. DPC $[C_6H_5(NH)_2CO(NH)_2C_6H_5]$ was used to perform absorbance measurements, using a HACH model DR/3000 spectrophotometer. *Figure* 2 shows that the absorbance measured at a wavelength value of 560 nm is proportional to the CrT content in the range from 0 μg/100 mL to 100 μg/100 mL.[9]

At the same time, and for comparative purposes, the CrT content of tinplates A and B was also determined using the stamped-out circular method. Tinplate specimens of 50 mm diameter (19.63 cm^2 surface area) predegreased with acetone were used. The chromium was extracted from passive coatings using 10 mL of 6.0 N hydrochloric [HCl] acid solution, heated at 300°C for 30 sec. The extracted chromium was analyzed by AAS using a UNICAM 9100 unit with a 5 cm burner with optical pass, and a nitrogen oxide/acetylene $[N_2O/C_2H_2]$ flame at a wavelength value of 357.9 nm.

Table 1—Chromium Content in the Passive Coating, as Total Chromium (CrT), Metallic Chromium (CrM), and Chromium Oxide (CrO_x) Using Coulometric Method (Tinplate A) and Spectrophotometric Method (Tinplate B)

Tinplate	Chromium Content, mg/m²		
	CrT	CrM	CrO_x
A	5.50	1.27	4.23
B	1.70	—	—

Table 2—Chromium Content in the Passive Coating, as Total Chromium, using Atomic Absorption Spectrophotometry Method

Tinplate	Chromium Content (CrT), mg/m²
A	5.7
B	1.5

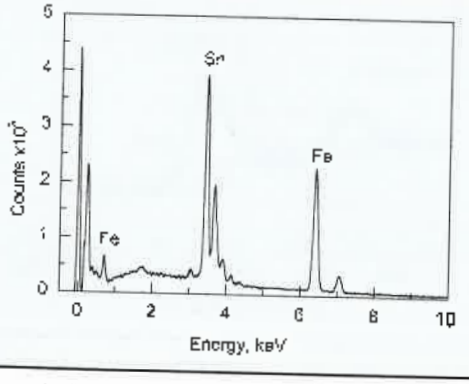

Figure 4—EDX spectrum for passivated tinplate A.

Morphological and chemical characterization were performed by SEM and EDX, using a JEOL JSM 35C unit with a Noran Voyager spectrometer for EDX measurements. The specimens were analyzed after cleaning with ethanol, using secondary and backscattering electron images and an X-ray map (Fe K_α). An acceleration voltage of 10 kV was selected to increase sensitivity at the coating surface. For tinplate cross-section observations a Philips XL-FEG scanning electron microscope with EDX detector was utilized.

XPS analysis was performed to characterize the passive films formed. The spectra were obtained utilizing a VG microtech model MT 500 electron spectrometer, using an Mg $K\alpha_{1,2}$ anode X-ray source (hν=1253.6 eV), with a primary beam energy of 15 keV and an electron current of 20 mA. The pressure in the analysis chamber was maintained at 1×10^{-9} Torr throughout the measurements. The regions of interest were O 1s, Cr 2p, and Sn $3d_{5/2}$. The instrumentation was calibrated periodically using Ag $3d_{5/2}$ (368.3 eV) and Au $4f_{7/2}$ (84.0 eV) substrates. The concentration of each element was estimated by measuring the respective peak area in the high resolution spectrum and

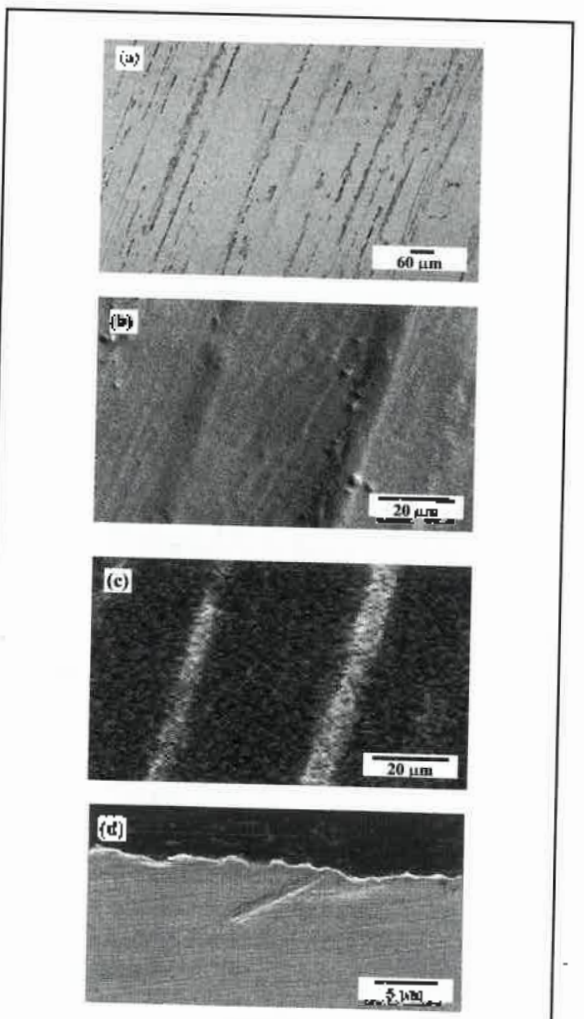

Figure 5—SEM micrographs for passivated tinplate B: (a) secondary electrons, (b) backscattered electrons, (c) Fe K_α-mapping, and (d) cross-section.

using elemental sensitivity factors. Spectral analysis was performed using peak fitting with Gaussian-Lorentzian peak shape and Shirley types background subtraction.

XPS in conjunction with Ar^+-ion sputtering was used to characterize the element composition of the surface as a function of depth. Successive sputterings were carried out up to 60 sec with a primary beam energy of 5 kV and an ion intensity of 10 mA.

RESULTS AND DISCUSSION

Table 1 shows chromium content in the passive coating, as CrT, CrM, and CrO_x, for the two types of passivated tinplates studied, tinplates A and B. Each value is the average of five tests. Similar results were yielded using coulometric and AAS methods (see *Table* 2). For passivated tinplate A, the CrO_x content corresponds to the difference between CrT and CrM. The CrO_x is the amount of Cr_2O_3 and hypothetical CrO_3, between which the coulometric method cannot distinguish (as can be seen below, when using the XPS method, CrO_3 was not observed). It should be said that for passivated tinplate B the CrM content is at the determination threshold of the coulometric method and for this reason this method was not used.

Figure 3 shows four SEM micrographs for passivated tinplate A: (a) secondary electrons, (b) backscattered electrons, (c) Fe-mapping, and (d) cross-section. In general, SEM results present a compact passive layer, some iron-rich and tin-rich zones can be observed (see *Figure* 3a). Thus, careful observation of the SEM results shows that the surface presents a striated structure, which is more evident in the observation of backscattering electrons (*Figure* 3b) and on the Fe-mapping micrograph. The cross-section micrograph (*Figure* 3d) presents a uniform tin layer.

Figure 4 shows, as an example, a typical EDX spectrum for tinplate A. The spectrum was obtained from an iron-rich (dark) zone of the specimen (see *Figure* 3a). The signal elements are tin and iron.

Figure 5 shows four SEM micrographs for passivated tinplate B: (a) secondary electrons, (b) backscattered electrons, (c) Fe-mapping, and (d) cross-section. As in tinplate A (*Figure* 3), some iron-rich and tin-rich zones can be observed on the passivated surface.

Figure 6 shows high resolution O 1s XPS spectra for unpassivated tinplate and passivated tinplates A and B. In general, the three types of tinplate surfaces studied present similar features. A deconvolution of the spectra shows three components: at ~530 eV binding energy (BE), corresponding to oxygen in metallic oxides [O–M]; at 531.5 eV BE, corresponding to metallic hydroxides [OH–M] and C=O from surface contamination; and at 533.0 eV BE corresponding to water [H_2O].

Figure 7 shows Cr 2p core level XPS results for passivated tinplates A and B. Two wide components can be observed: at 576.5 eV BE, corresponding to Cr(III)-oxide,

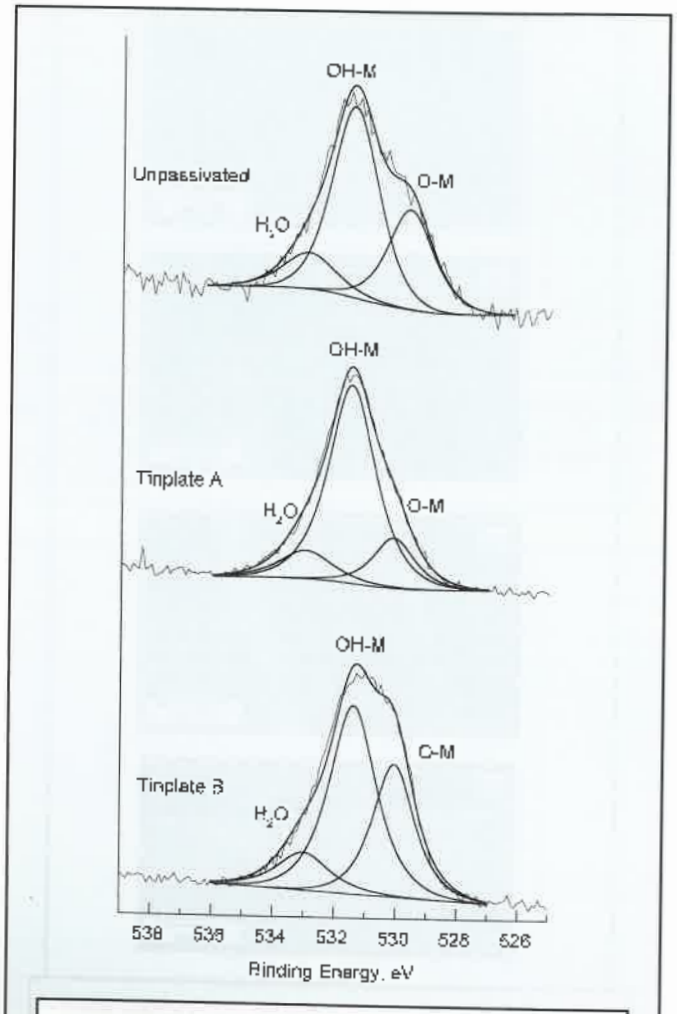

Figure 6—High resolution XPS spectra for O 1s for unpassivated tinplate and passivated tinplates A and B.

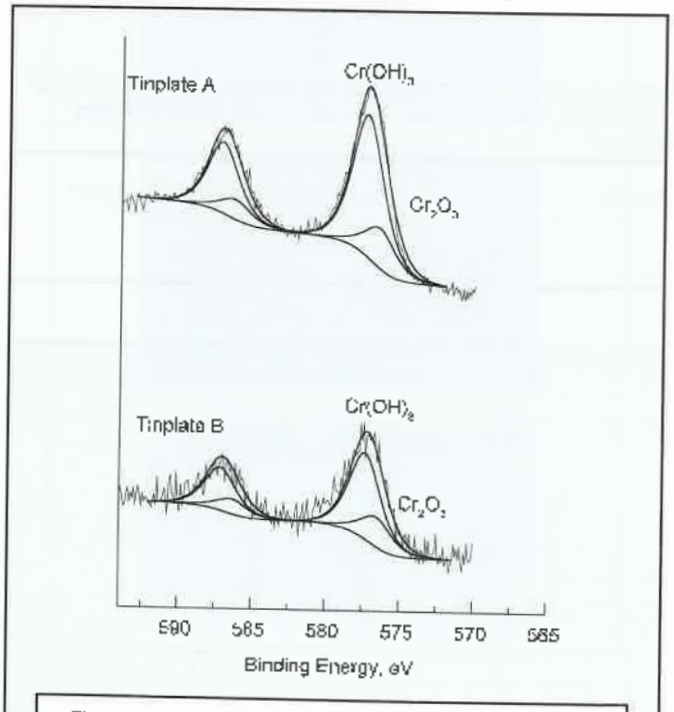

Figure 7—High resolution XPS spectra for Cr 2p for passivated tinplates A and B.

as Cr_2O_3, and at 577.3 eV BE corresponding to Cr(III)-hydroxide, as $Cr(OH)_3$. The Cr(VI) oxide [CrO_3], which presents a peak located at 580.1 eV BE, cannot be observed in the two passivated tinplates A and B studied (*Figure* 7). Furthermore, XPS results do not show a metallic chromium (CrM or Cr^0) peak at 574.3 eV BE, previously found using coulometric methods (see *Table* 1). This discrepancy between the surface analysis technique (XPS) and coulometric methods may indicate that Cr^0 is found deeper in the passive layer than is analyzed by XPS method (~2-3 nm).

Figure 8 shows curve fitting of the high resolution XPS spectra for Sn $3d_{5/2}$ core level for the unpassivated tinplate and passivated tinplates A and B. It is possible to distinguish a peak located at 485.8 eV BE, corresponding to tin oxides, and an insurgence at 484.5 eV BE due to metallic tin (Sn^0). Tin has a large difference in BE between its metallic state (Sn^0) and its oxides: SnO and SnO_2 in the Sn $3d_{5/2}$ core region, but only a small difference in BE between SnO and SnO_2. Thus, high-resolution XPS measurements do not permit a distinction between SnO_2 and SnO oxide forms because both have very similar BE: 486.6 eV and 486.9 eV, respectively.[10]

To study the depth profile of the outermost layers of the three types of tinplates tested, Ar^+-ion sputtering was performed for up to 60 sec. *Figure* 9 shows oxides, hydroxides, and water components in the O 1s peak versus sputtering time. The main feature observed in all the specimens is a decrease in hydroxides and an increase in oxide compounds with sputtering time, suggesting a stratified structure where hydroxides are located externally and oxides internally.

Figures 10 and 11 show that the hydroxide is $Cr(OH)_3$, while the oxides are a mix of Cr_2O_3, SnO, and/or SnO_2. *Figure* 10 shows a big difference in chromium content between passivated tinplates A and B. In tinplate A, not only is the total chromium content higher, but the hydroxide layer is also thicker: after 60 sec of Ar^+-ion sputtering there is a significant hydroxide signal, while in tinplate B the hydroxides almost disappear after 30 sec of Ar^+-ion sputtering. Consistently, the tin content in tinplate B is higher (*Figure* 11) than in tinplate A. *Figure* 11 also shows that in tinplate B, tin is mainly an oxide (SnO and/or SnO_2) while in tinplate A around half of the tin is in the metallic state (Sn^0). Comparing the results for tinplates A and B (*Figure* 11), the amount of tin oxides decreases as the chromium content in the passive layer increases. The high tin oxide content may be attributed to the short sputtering time (60 sec) and the superficial character of the XPS method (~2-3 nm). Finally, in the unpassivated tinplate, the oxide layer is very thin and after 60 sec of Ar^+-ion sputtering the main component is Sn^0.

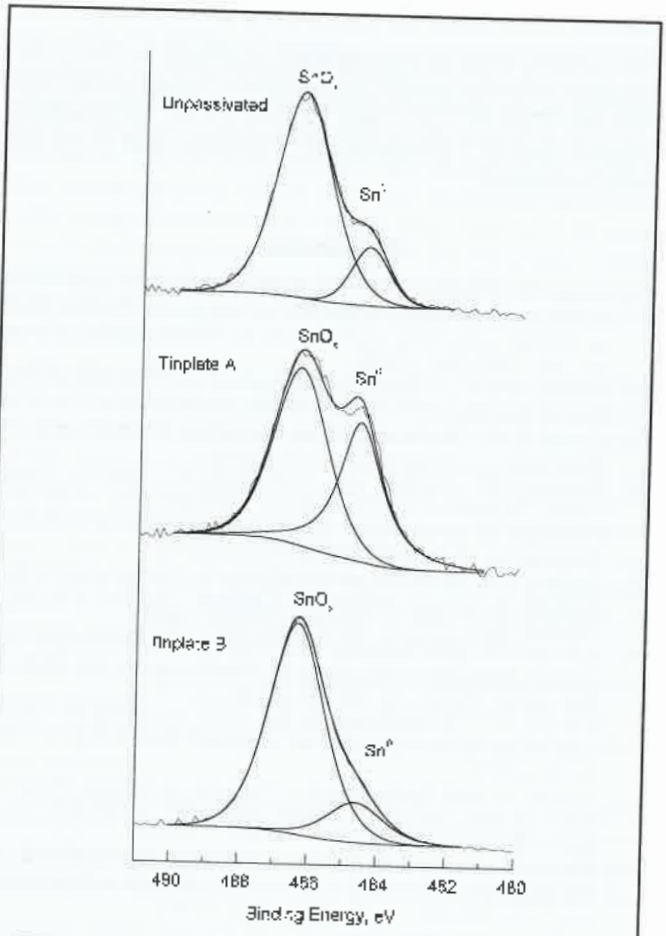

Figure 8—High resolution XPS spectra for Sn $3d_{5/2}$ for unpassivated tinplate and passivated tinplates A and B.

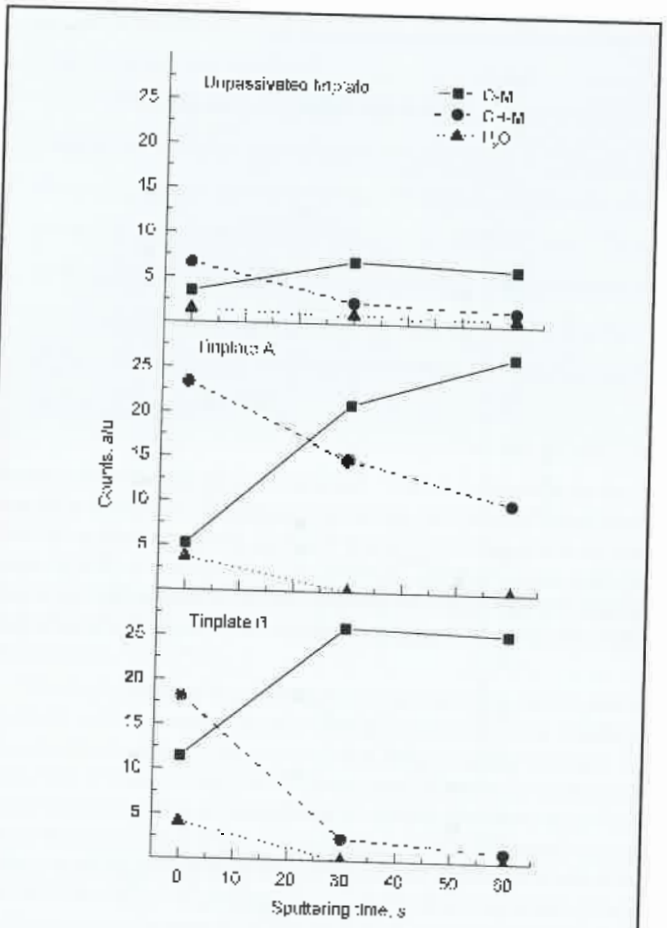

Figure 9—XPS depth profiles for oxygen for unpassivated tinplate and passivated tinplates A and B.

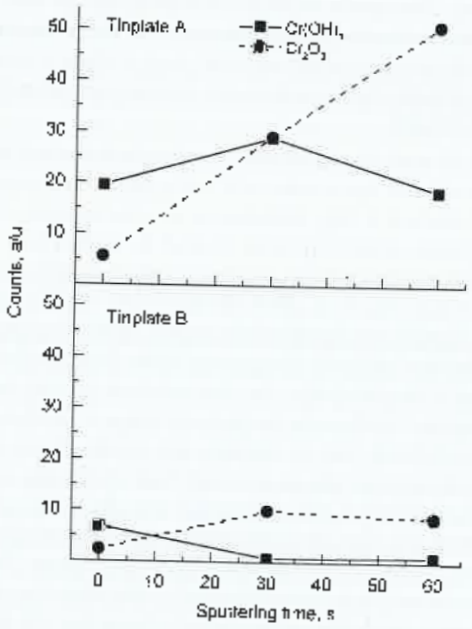

Figure 10—XPS depth profiles for chromium for passivated tinplates A and B.

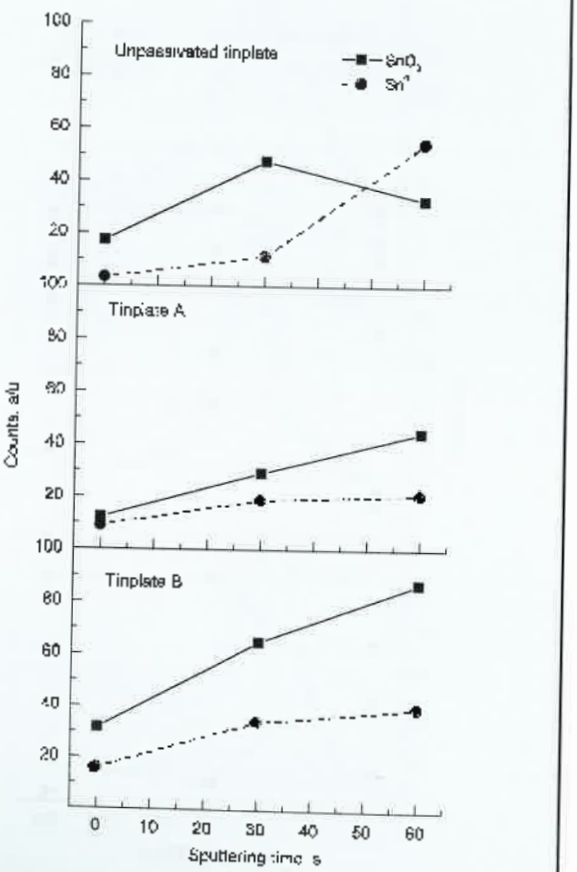

Figure 11—XPS depth profiles for tin for unpassivated tinplate and passivated tinplates A and B.

CONCLUSIONS

The chromium content in the passive layer for tinplate A was 5.5 mg/m² of CrT, 1.27 mg/m² of CrM, and 4.23 mg/m² of CrO_x. On tinplate B it was only possible to determine the CrT content: 1.70 mg/m². These results were similar for the three experimental methods used: coulometry, spectrophotometry, and atomic absorption spectrophotometry.

The SEM results show a striated structure where some iron-rich and tin-rich zones can be observed.

The XPS results show that metallic oxides, hydroxides, and adsorbed water were present on the surface. Chromium was in the form of oxide as Cr_2O_3 and hydroxide [$Cr(OH)_3$]. Hexavalent chromium, Cr(VI), was not observed in the XPS spectra and neither was metallic chromium, (Cr^0). This discrepancy among the coulometry, spectrophotometry, and AAS results was attributed to the superficial character of the XPS technique. Metallic tin and tin oxides SnO and/or SnO_2 were observed. Depth profile results performed using Ar^+-ion sputtering for up to 60 sec show a stratified structure of passivated tinplates A and B with the hydroxides located externally and oxides internally. In unpassivated tinplate after 60 sec of Ar^+-ion sputtering the main component is metallic tin.

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