

**A critical assessment of the current
understanding of chromium passivation
treatments on tinfoil**

By

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A dissertation submitted in partial fulfilment of the requirements of the degree of

Magister Scientiae
(Applied Sciences: Corrosion)

in the

**Faculty of Engineering, Built Environment and Information Technology,
University of Pretoria,
Pretoria**

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1 August 2005

Acknowledgments

To Elmarie, Charné and Luske for their love, understanding and support during this work.

To my colleagues at IMMRI, the University of Pretoria and Mittal Steel for the fruitful discussions, ideas, and supply of experimental material.

To Dr. Elsabe Cloete for her contribution, at a time it was needed the most.

To my supervisor, Professor Sandenbergh, who nearly drove me to insanity with the quest for a “story”.

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Abstract

Chromium passivation treatment on tinplate is important in stabilising the active tin surface in terms of oxidation resistance, sulphide stain resistance and ensuring good lacquer adhesion properties. Through this research, the reason was explored why dip passivation treatment, in sodium dichromate, provides superior lacquer adhesion properties on tinplate compared to electrolytic sodium dichromate (CDC) treatments. A critical assessment of the current knowledge of chromium passivation treatments on tinplate formed the basis of the experimental work. Through electrochemical and surface analytical techniques (X-Ray Photoelectron Spectroscopy and Auger Electron Spectroscopy) both dip and CDC treated tinplate surfaces were characterised in terms of surface species. It was shown through XPS, using angle resolved techniques, that no metallic chromium forms on the tinplate surface during CDC treatments. Furthermore, a difference in chromium surface species was established for the dip and CDC processes showing additional SnO and $\text{Cr(OH)}_3 \cdot n\text{H}_2\text{O}$ species for the latter. Complementary to these findings, it was verified that the formation of additional chromium hydroxide species is a function of pH, governed by the applied cathodic current during the CDC process itself. The inferior adhesion properties of CDC treated tinplate were shown to be related to the difference in the respective surface species formed during dip and CDC applications.

Samevatting

Chroompassivering op tinplaat is belangrik ten einde die aktiewe tin oppervlak te stabiliseer met betrekking tot oksidasievorming, sulfiedvlekvorming asook om goeie lakhegtingseienskappe te verseker. Gedurende hierdie navorsing, is die rede ondersoek waarom doop-passivering, in natriumdichromaatoplossings, beter lakadhesie toon as elektrolitiese natriumdichromaat behandelings. 'n Kritiese evaluering van die bestaande kennis op die gebied van chroompassivering op tinplaat het die basis gevorm waarop eksperimentele werk beplan is. Deur middel van elektrochemiese- en oppervlaksensitiewetegnieke, (X-straal foto-elektronspiekstroskopies - XPS en Auger elektronspiekstroskopies - AES is beide die doop- en elektrolitiesbehandelde tinplaatoppervlakke gekarakteriseer in terme van oppervlaksies. Daar is gevind met behulp van XPS – hoekafhanklike tegnieke, dat geen metaliese chroom tydens die elektrolitiese behandelings deponeer nie. Verdere verskille in chroomsies met betrekking tot doop- en elektrolitiese behandelings is ook aangetoon. Behalwe vir SnO_2 en Cr_2O_3 wat in beide behandelings voorkom, is SnO and $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ in die elektrolitiese behandeling addisioneel waargeneem. Komplimenterend tot die bevindinge, is daar ook bewys dat die addisionele chroomhidroksied spesies 'n funksie van pH is en bepaal word deur die toegepaste katodiese stroom tydens die elektrolitieseproses. Die swakke lak-adhesie eienskappe van die elektrolitiesgepassiveerde tinplaat is herlei na die verskillende oppervlaksies wat tydens die twee prosesse vorm.

Chapter 1.
Research Proposal

1.1 Introduction

Electrolytic tinplate, *i.e.* steel electrolytically coated with a thin layer of tin, was introduced for the first time during the 1940's and has since grown into being one of the major packaging materials used in the food industry. An estimated 32 billion food cans are annually produced in the USA alone, of which 80% is manufactured from tinplate. The value of tinplate as packaging material arose from a combination of advantages unmatched in any other product; it is relatively cheap, light, strong and can easily be formed into many intricate shapes. It has an attractive appearance and unique electrochemical properties, which makes it remarkably corrosion resistant to conditions obtained inside the can.

In order to keep up with the demand for tinplate, continuous high-speed tin-plating lines, capable of strip speeds up to 450 m/min were developed. Hoare et al. (1965) described electrolytic tinplating as an intricate process, involving pre-treatment of the steel strip by means of alkaline cleaning and acid pickling, to ensure adequate plating properties. Electroplating is performed separately on each side of the steel strip to allow for differential tin coatings. The electrochemically deposited tin coating is then flow melted to form an iron-tin alloy layer and to give the tinplate its characteristic bright appearance.

However, the tinplate cannot be left in this state as tin is relatively active and oxidises readily. The oxidation products result in discolouration of the surface, which is aesthetically unacceptable. Some form of stabilisation of the tin surface is therefore necessary and is achieved by depositing a rather thin, but very protective chromium passivation layer onto the freshly produced tinplate.

The passivation process therefore forms an integral part of the high-speed continuous tinfoil production process. In its simplest form it involves merely dipping of the strip in a diluted sodium dichromate solution, followed by a hot water or steam rinse to remove any remaining hexavalent chromium residues. This type of treatment would typically result in 1-3 mg/m² of chromium being deposited on the tin surface. When required, higher chromium levels (between 5 and 10 mg/m²) can be obtained through electrolytic application, called cathodic sodium dichromate treatment, or CDC treatment.

Throughout the literature on tinfoil passivation, it is evident that the function of tinfoil passivation is threefold. Apart from protecting the tin surface from oxidation, it also has to prevent corrosion and staining of the tin in the presence of sulphur bearing food and finally plays an important role in the adhesion of lacquers to tinfoil.

Improving oxidation resistance

Tinfoil is quite susceptible to oxidation during long-term storage, especially in humid conditions, and during the high temperature curing of lacquers. The success of chromium passivation treatment on tinfoil is mainly due to the inhibition of tin oxidation.

Although chromium passivation is effective in retarding tin oxide growth at the low levels obtained by dip treatments, oxidation resistance improves considerably with higher levels of chromium (Pattiasina et al., 1992). They indicated that CDC passivation treatments with chromium levels, in the order of 8 mg/m², did not only

contain much less tin oxides when compared to dip treated tinplate, but also showed considerably less tin oxide growth after the stoving process. Stoving is normally performed during the curing of lacquers when tin plate is typically heated to 210 °C for 15 minutes.

Improving staining resistance

Another important function of passivation is preventing stain formation inside the can when sulphur-bearing food such as green peas and meat products are packed. These stains are a result of sulphide corrosion products forming on the tin surface and do not pose any health risk (Rauch and Steinbicker, 1975). However, for the consumer the aesthetical appearance of the can relates directly to the freshness of the contents of the can and would therefore be unacceptable. Castrillo et al. (2002) indicated that the success of preventing sulphide stain formation is directly related to the amount of chromium being deposited on the tin surface. It was shown that higher chromium levels, typically as achieved with CDC treatments, perform better.

Improving lacquer adhesion

Chromium passivation treatment works well in preventing tin oxide growth and sulphide staining and the higher the chromium levels the better the protection. But lacquer adhesion on tinplate is unfortunately not necessarily better with these higher chromium levels.

Servais et al. (1979) pointed out that dip treatment results in less surface chromium and more tin oxides than CDC treatments, with the former displaying better lacquer adhesion properties. In addition, Pattiasina et al. (1992) showed that under film

corrosion is related to the type of chromium treatment applied. Their results also indicated that the dip treatment performed better than the CDC treatment with regard to under film attack. As suspected, undercutting and detinning were also more pronounced with higher chromium levels. Castrillo et al. (2002) confirmed these findings by showing that lower levels of chromium improved lacquer adhesion performance after sterilisation in acid media, while higher total chromium levels in the passivation film resulted in poorer acid resistance. Dry adhesion performance of the lacquer was better when the total chromium was lower than 6 mg/m^2 , therefore implicating that dip passivation treatments perform better.

This implies an important functional concern for tinfoil, *i.e.* to obtain good lacquer adhesion dip treatments should be employed. These however, don't afford the same oxidation and staining resistance as the CDC treatments. Some workers (Carter, 1961; Servais, 1979; Helwig, 1996) considered that high levels of surface chromium might not alone be responsible for the poor adhesion performance. In the review by Helwig (1996), factors such as the thin oil film applied to the tin to prevent fretting, wetting characteristics of the tinfoil and tin oxides, have also been indicated to affect lacquer adhesion performance.

It is accepted that there are multiple factors that should be taken into account when considering adhesion properties of organic coatings on tinfoil, but there is still a paucity of information regarding specific reasons why tinfoil treated by means of dip and CDC treatments respectively, behave different when it comes to lacquer adhesion.

1.2 Problem statement

Given the marked difference in lacquer adhesion behaviour between dip passivated tinplate and those with CDC treatments, it could be expected that characterisation and comparison of these tinplate surfaces would provide some answers. Although surface species on CDC treatments have been investigated extensively in the past, as lacquering was mostly done on CDC treated material, not much attention has however been given to the composition of dip treatments.

The question therefore still remains as to why dip passivation treatment provides superior lacquer adhesion on tinplate compared to CDC passivation?

1.3 Solution approach

The purpose of this study is to compare dip and CDC passivation treatments on tinplate in terms of surface species. This is done in order to explain the superior lacquer adhesion properties presented by dip passivation treatments.

A combination of research techniques was used in this study namely, a literature review, constructing arguments and propositions, experimentation, verification and contextual evaluation of the results.

In the context of this research, a literature study was conducted on the existing literature regarding chromium passivation on tinplate, with specific reference to chromium and tin surface species. Through this survey, essential information was extracted to identify the existing gaps in the knowledge and understanding of chromium passivation layers on tinplate.

Based on current knowledge, propositions were made regarding the deposition of chromium during both dip and CDC treatments. These propositions were then evaluated through planned experimentation using relevant electrochemical and surface analytical techniques.

Finally, verification of the experimental findings was made through conventional lacquer adhesion tests and the results evaluated in terms of available literature.

1.4 Research context

Currently, most of the tinplate manufactured in South Africa is supplied with CDC passivation treatments. This is more costly due to the additional sodium dichromate consumption and especially the higher energy (electricity) input of the CDC process.

The present research aimed to add to the existing knowledge, regarding the two types of chromium passivation, in terms of their functional properties. This would allow both the tinplate producer and consumer (can-maker) to make more informed decisions regarding process parameters and choice of passivation treatments.

1.5 Scope of study

The following issues were not considered in this research:

- Variables, apart from the chromium and tin surface species, which could influence the functional properties of tinplate with respect to lacquer adhesion properties.

- Deriving mechanisms for chromium deposition on tinplate. The propositions stated were merely to obtain a better understanding of passivation treatments and to assist with the interpretation of experimental results.

1.6 Presentation of the work

Chapter 2 provides the background and current knowledge on tinplate passivation treatments. The two types of treatments namely dip and CDC are considered with the focus on the formation and differences between surface species formed on tinplate as a result of these treatments. *Chapter 3* provides suggestions on the deposition of chromium on tinplate, based on the current understanding, and basic chemical reactions. These propositions, as well as the gaps identified in the literature, form the basis of the experimental work. *Chapter 4* provides the experimental plan, layout and background information regarding the techniques used during the study as well as detailed experimental parameters. *Chapter 5* presents the experimental results and the discussion of these. *Chapter 6* provides the conclusions based on the findings of this study.

Chapter 2.

Literature survey - The current understanding of tinplate passivation

2.1 Introduction

The search for a way of stabilising tin surfaces date back to the days when hot-dip tinfoil was still produced. The oxide film normally present on tin was protective to some extent, but grew readily, resulting in discolouration of the tinned surface. It was, however, not only the appearance of the material that was objectionable, but the oxide growth also affected the adherence of lacquers. These and related problems, such as stain formation when sulphur bearing food was packed, led to extensive investigations concerning suitable passivation treatments for tinfoil.

Mason (1931) patented a process in which metallic surfaces were treated with sodium dichromate or chromic acid. This process was, however, relatively unknown to the tinfoil industry until World War II when the increasing demand for tinfoil sparked the production of electrolytic tinfoil on high-speed continuous lines. However, the oxide stability and lacquering properties of untreated electrolytic tinfoil was considered inferior to that of hot dip tinfoil and the most convenient way of stabilising the tin surface at that point in time, was considered to be the chromic acid treatment.

Later, Neish and Donelson (1960) reviewed the patents and previous work on tinfoil passivation and through laboratory experiments concluded that sodium dichromate treatments were very effective and the most practical for commercial use. They also found that the oxidation protection obtained was limited if the oxidation film on tin formed prior to this treatment, was not removed. The easiest way to remove this film was by cathodic reduction in the sodium dichromate solution, followed by chemical or electrochemical oxidation in the passivation solution. These findings led

to the introduction of the so-called cathodic sodium dichromate (CDC) treatment of tinplate.

2.2 Application of chromium on the tinplate surface

The introduction of sodium dichromate treatments was so successful that it is still used today despite concerns regarding the toxic nature of Cr(VI).

The stabilisation of the tinplate surface by means of chromium is achieved either through dipping, or with applied cathodic polarisation, using sodium dichromate as reagent. Tinplate simply dipped in the dichromate solution is called passivation treatment 300 (refer to nomenclature, table 2.1) and typically has a total chromium coating weight of 1-3 mg/m².

In order to obtain higher levels of surface chromium (5-10 mg/m²) it is necessary to apply a cathodic current during the dip process. These procedures, called 311 to 314 passivation treatments, are also referred to as cathodic dichromate passivation (CDC) treatments (Hoare et al. 1965).

Table 2.1 - Nomenclature of different passivation treatments as devised by United States Steel Corporation (Hoare et al. 1965).

First digit	Second digit	Third digit
Chromic acid = 1	Non electrolytic = 0	Refers to the coulomb level employed. (Typically from 0 - 4)
Chromate phosphate = 2	Cathodic = 1	
Sodium dichromate = 3	Cathodic / anodic = 2	
Sodium carbonate = 4		

2.2.1 Passivation process outlay

An illustration of a typical passivation unit is shown in figure 2.1. The reflowed tinplate passes between a deflector and a chrome plated conductor roll at the entry side of the passivation unit. The function of the conductor roll is to polarise the strip negatively in the case of CDC passivation treatments. The strip then enters a tank filled with a sodium dichromate solution as electrolyte. The cathodic treatment is achieved by applying a direct current between two sets of (anodically polarised) grid plates and the tinplate strip. At the exit side of the tank the strip is again in contact with a conductor roll to ensure good electrical contact.

For dip treatments, however, the strip is passed through the tank without the application of current. Squeegee rolls prevent drag-out and the strip is subsequently rinsed by a high-pressure hot water system to remove the excess sodium dichromate solution.

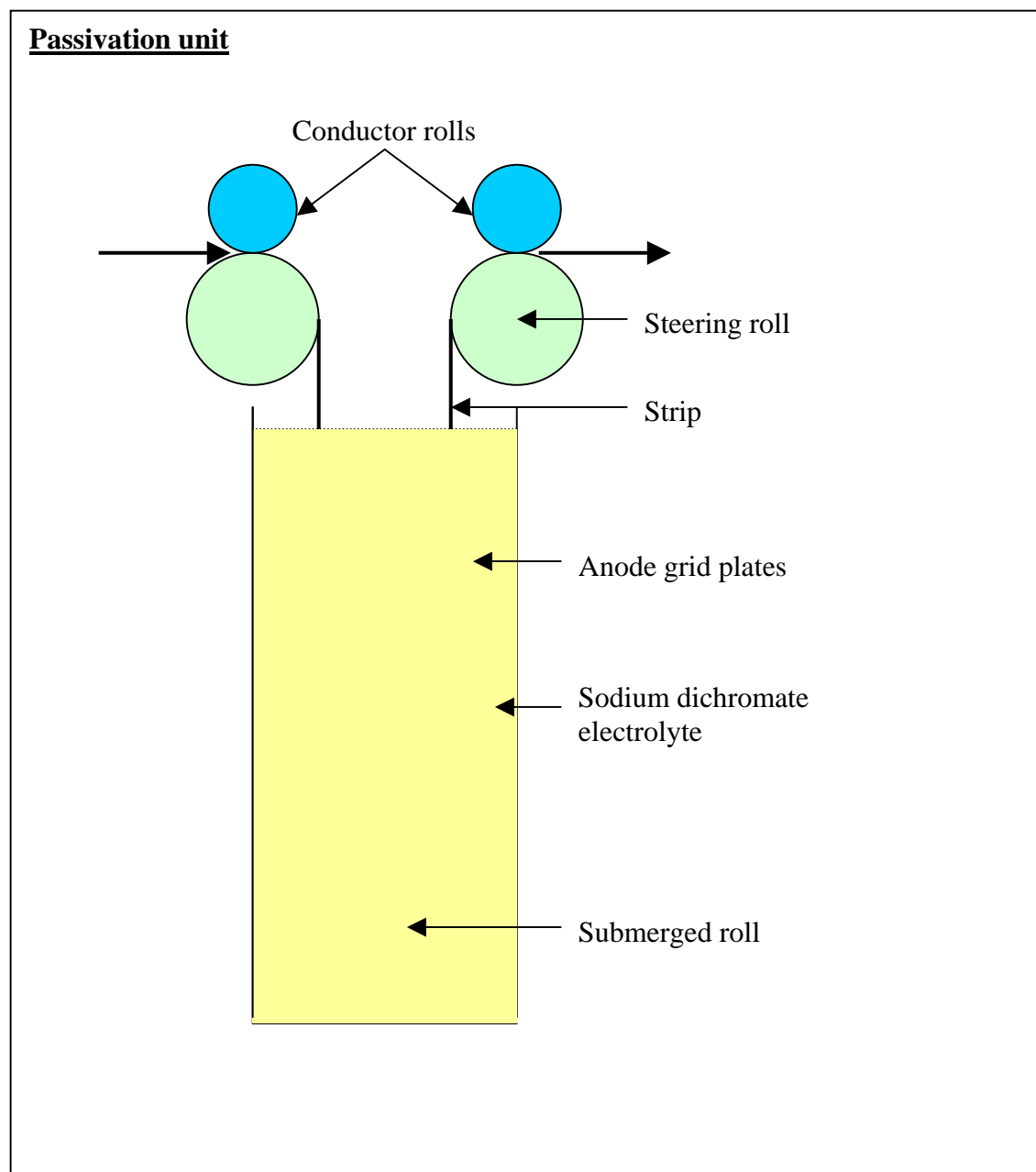


Figure 2.1 - Simplified illustration of a typical passivation unit in the tinline at Mittal Steel South Africa.

2.2.2 Passivation process parameters

Typical parameters used at a local tinplate producer (Mittal Steel - South Africa) are indicated in table 2.2.

Important to note from these parameters are the high line speeds the continuous tinplating line is operated at, resulting in short exposure times during the passivation treatment. The line speed is determined to a great extent by the tin coating mass required and the number of plating cells available. With lighter coating weights, faster line speeds are possible, which implies that increased deposition rates will be required at the passivation unit, to achieve the desired passivation level during CDC treatments. This may be achieved by increasing the applied current density, provided that the rate of the deposition process is not mass transfer limited.

For dip treatments, higher line speeds result in less time available for the passivation treatment and therefore less chromium is deposited onto the tin surface.

Another important process parameter is the pH of the bulk electrolyte solution, which rises gradually as CDC treatments are performed and can be corrected by chromic acid additions, Hoare and Hedges (1965), although this is not typically done.

Table 2.2 - Passivation processing parameters as at Mittal Steel - South Africa.

Process parameter	Range
Sodium dichromate concentration	20 - 25 g/l
Sodium dichromate solution, temperature	70 - 75°C
Average strip speed	400 - 450 m/minute
Applied current	2.5 kA
Anode grid dimensions	Length = 2.667m Width = 1.372m
Calculated current density (applied to the tinplate surface)	6.8 A/dm ²
Depth of passivation tank	5m
pH	4 - 5.0
Calculated charge density	4.8 C/dm ²
Calculated strip contact time during the dip process assuming a strip speed of 450 m/min.	1.3 seconds
Calculated time, at a strip speed of 450 m/min, that the strip is exposed to a cathodic current.	0.7 seconds

The theoretical amount of chromium deposited on the tinplate from Cr(VI) solution can be calculated using Faraday's law.

$$m = \frac{Ita}{nF}$$

Where:

m = Mass of chromium deposited (g/m²)

I = Current density (A/m²)

F = Faraday's constant (96500) (C/mole electrons)

n = Number of equivalents per mole

a = Atomic weight (g/mole)

t = Time (seconds)

When for example a charge of 400 C/m^2 is used during a CDC passivation treatment, the theoretical amount of chromium deposited should be 71.8 mg/m^2 as Cr(III) or 23.9 mg/m^2 as Cr^0 . However employing charge densities in this range, CDC treatments yield only between and 5 and 10 mg/m^2 chromium indicating that the current efficiency of chromium deposition is low.

This is in agreement with the calculations of Carter (1961) who also found a ten-times higher theoretical value. He proposed that the reduction of tin oxides and the evolution of hydrogen, of which the latter accounts for the biggest fraction of the charge used during CDC treatments, could explain the difference between calculated and actual values.

There are therefore, apart from the reduction of chromium, also other reactions that play an important role in the deposition of chromium during CDC treatments. However, before considering the postulations of previous investigators regarding the deposition of chromium on tinplate, it is necessary to briefly look at the analytical techniques used, as the interpretation of results depends largely on the selectivity of the methods for certain chromium species.

2.3 A brief overview of characterisation techniques for chromium

Analysis of the passivation layer, either in terms of the amount of chromium or speciation of chromium species, forms the basis of the work performed in literature. A wide variety of techniques are used to assess the passivation layer, which include chemical, electrochemical and surface analytical techniques. Each of these techniques has unique capabilities to address certain aspects of the chromium

passivation layer. Some background information on the different techniques is discussed in order to give a clearer understanding of the findings reported in the literature.

2.3.1 Chemical analysis

The chemical test method, ASTM (1979), for determination of chromium on tinplate is based on the spectrophotometrical determination of chromium in an acidic solution using diphenylcarbazide.

A tinplate sample of total surface area, 52 cm^2 , is specified for the test. The method involves the removal of chromium from the tinplate surface in two separate steps, the reason being that part of the passivation layer is soluble in a caustic solution. Rauch and Steinbicker (1975) referred to the soluble part as chromium hydroxide species, while the insoluble part was considered to be metallic chromium. Only later on, through surface analytical studies, the contribution of chromium oxides to the insoluble part was recognised by Servais et al (1979).

The first step for removal of chromium therefore facilitates the partial dissolution of chromium in a boiling 1N sodium hydroxide - 5% trisodium phosphate solution. But it must be kept in mind that while chromium is stripped from a tin substrate, tin readily oxidises in aerated solutions and that the tin oxidation products are soluble when the pH is high enough (Pourbaix, 1974). For this reason it is important to use a boiling (or nitrogen purged) caustic solution to minimize the dissolution of tin. The remaining chromium can then be removed through a separate step by means of boiling 25% sulphuric acid.

The stripping solutions are added together and the chromium in solution is oxidised with KMnO_4 while boiling. The excess oxidising agent (KMnO_4) has a pink colour that would interfere with photometric analysis and is removed by the addition of hydrochloric acid. After the solution has cooled down and made up to volume, diphenylcarbazide reagent is added, and then analysed against chromium calibration standards, with the aid of a spectrophotometer. The amount of chromium is calculated and expressed as chromium mass per surface area of tinplate.

2.3.2 *Electrochemical analysis*

Electrochemical analysis of chromium on tinplate involves the anodic oxidation of chromium species from a trivalent state to a soluble hexavalent state. The method (based on galvanostatic principles) was originally described by Britton (1965), and involved the oxidation of chromium on the tinplate surface, by means of an applied current, to soluble hexavalent chromium in a phosphate buffer solution. During the course of the test the potential follows the typical potential vs. time curve as illustrated figure 2.2. An initial sharp rise in potential is followed by a potential arrest (point A) during which chromium is oxidised, usually in the region of +700 mV vs. Ag/AgCl, or +922 mV vs. SHE. As the oxidation of tin begins (point B), the potential again increases up to point C where, oxygen evolution starts.

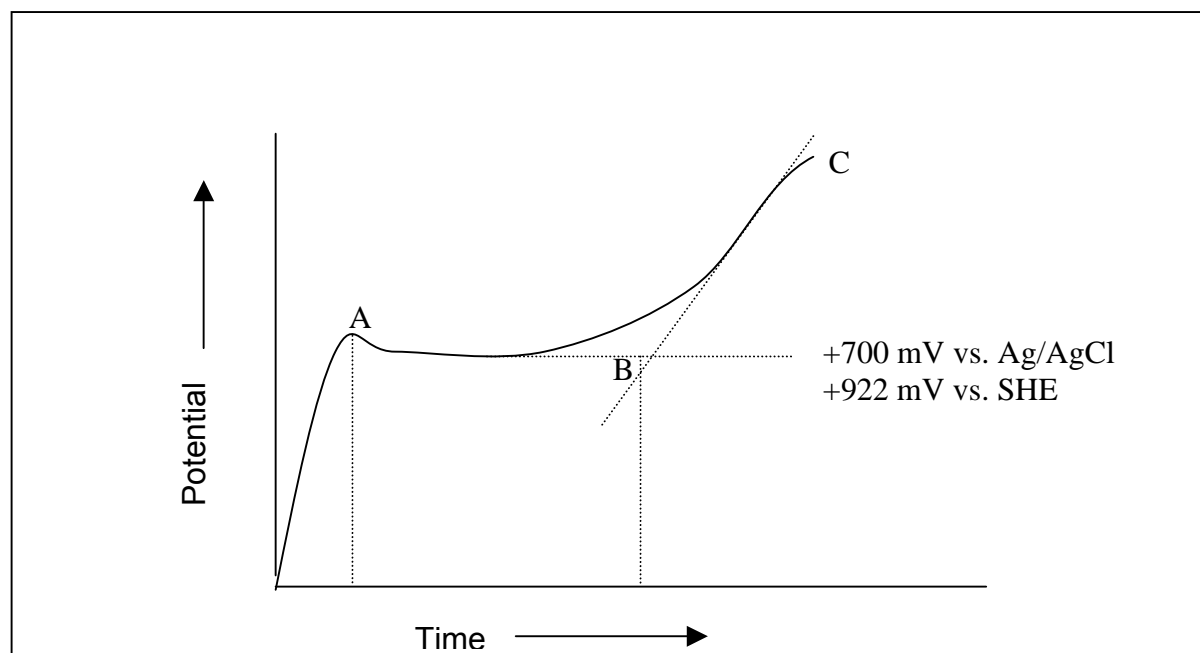


Figure 2.2- Schematic potential vs. time curve for chromium oxidation on CDC tinplate during galvanostatic polarisation.

For a phosphate buffer electrolyte with a pH of 7.4 and a current density of $25 \mu\text{A}/\text{cm}^2$, a charge of $1 \text{ mC}/\text{cm}^2$ obtained between A and B, is equivalent to $0.1 \mu\text{g}/\text{cm}^2$ of chromium on the tinplate surface (Britton 1965).

This method has the advantage of rapidly delivering quantitative results and is suitable for routine control purposes, provided that it is calibrated against the chemical method. The method and interpretation was however not generally accepted. Rauch and Steinbicker (1975) and others indicated that a considerable part of the chromium is still left on the tinplate surface after anodic oxidation. Additional investigations by Britton (1975) indicated that the passivation layer consisted of two chromium constituents. One is oxidised by means of the constant anodic current conditions of the test and can also be dissolved in sulphuric acid. The other constituent can be dissolved by alkaline solutions, but is not oxidised during the

anodic oxidation. No attempt to identify the different chromium constituents was made at the time. The practical implication of these findings was that the calibration of the anodic dissolution results against the chemical analysis (total chromium) was acceptable, provided that the ratio of the chromium constituents remained the same. Conditions that could change this ratio were however not indicated.

Although not within the scope of the present research, factors that have an effect on the formation of the different constituents within the passivation layer were identified.

2.4 The deposition of chromium during the passivation treatment

Considering the selective dissolution and oxidation behaviour of the different test methods, it is possible to interpret and synthesize previous work performed on the deposition of chromium onto the tinplate surface.

2.4.1 Factors affecting chromium deposition during the passivation treatment

The importance of process parameters during CDC passivation treatment were already recognised by Carter (1961). He established through laboratory experiments, pilot line and production trials that charge density, current density and pH significantly influence the amount of chromium deposited. As expected, the amount of chromium deposited was proportional to the current density used. For the same charge density, chromium levels remained constant or decreased with increasing current density. Furthermore, more chromium is deposited at the same charge density for sodium dichromate solutions of lower pH.

But at that stage, and even in some cases today, the influence of the method used for quantification was not realised. In his work, Carter used a modified version of an unpublished chemical method to characterise the deposited chromium.

The approach of Carter, however, interested others. Soepenberget al. (1976) studied the formation of dichromate passivation films and were amongst the first researchers to show the differences between the results of the chemical and the electrochemical techniques used to quantify surface chromium. Their work involved the study of the formation kinetics of the passive layer by measuring the surface chromium content chemically (photometrically), and also with the electrochemical method published by Britton (1965), as a function of important process parameters. The results obtained are summarised in table 2.3.

In general terms these results indicate that process parameters do influence the amount and nature of chromium deposited on the tinplate surface during CDC treatments.

Furthermore, the method employed to measure these values are equally important. There are significant differences in the chromium values indicated by the two methods, even showing conflicting trends in some cases that can be summarised as follows:

- The chemical method for total chromium, gave higher surface chromium values than the electrochemical method established by Britton (1965), as the latter only reported the acid soluble constituent.

- At low current densities the results of these tests are the same, indicating that the constituents in the passivation layer are all acid soluble.

- An increase in current density at constant treatment time resulted in higher chromium values, as determined chemically, but lower chromium values when determined electrochemically.

At that stage these trends were reported, but not fully understood. The question is, whether the different constituents (acid soluble and caustic soluble parts) can be ascribed to specific chromium species?

Table 2.3 - Influence of process parameters on the amount of chromium deposited as measured chemically and electrochemically, after Soepenberget al. (1976)

Process parameters	Chemical (Photometric determination)	Anodic Cr dissolution (Briton's method)
Surface Cr determination expressed as mg/m ² Values over 4 mg/m ²	Generally higher chromium values Much higher chromium values	Generally lower chromium values Chromium does not exceed 9 mg/m ²
Charge density of 200 C/m ² Increasing charge density (normal CDC treatment)	Equal chromium values Chromium values rises steadily	Equal chromium values Chromium hardly rises
Increasing current densities at constant treatment time	Chromium values increase	Chromium values decrease
Increase of treatment time from 1 to 5 sec. at 1200 A/m ²	Chromium values increase	Chromium values increase

Rauch and Steinbicker (1975), made a significant contribution to the understanding of the chromium passivation layer by establishing that the CDC passivation films contained species with different solubilities when exposed to NaOH (10M) at 90 °C for 10 minutes, some of which dissolved, while the other remained as residual chromium on the surface of the tinplate. However, directly after the passivation treatment all the chromium dissolved in the caustic medium, suggesting that only one species of chromium is deposited. As the tinplate was allowed to age for several weeks an increasing amount of chromium became insoluble and within three to five weeks the insoluble portion reached a maximum value as shown in figure 2.3. Noteworthy was that material produced at low current densities, showed less aging.

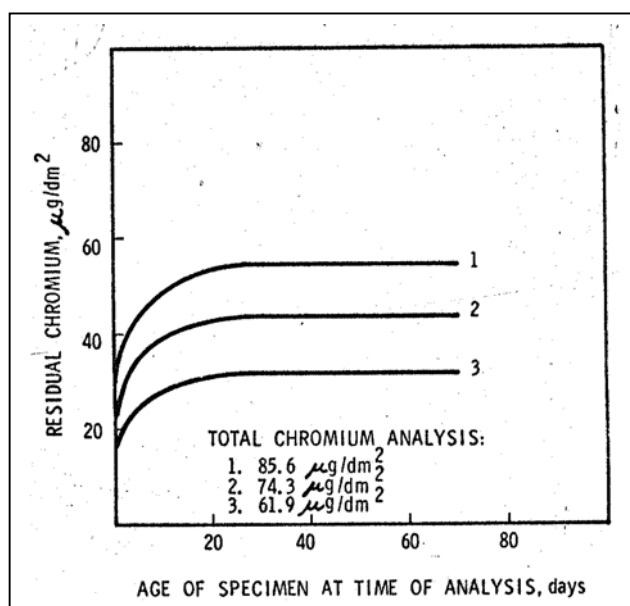


Figure 2.3 - Relationship between ageing in air and the amount of insoluble chromium during hot caustic dissolution, as indicated as residual chromium on the sample surface (Rauch & Steinbicker 1975).

In order to determine how dehydration affects the CDC passivation film, Rauch & Steinbicker (1975) stoved passivated tinplate at 210 °C for one hour. It was found that the entire film then became insoluble. Using Britton's electrochemical method they found that the entire film could now be electrochemically dissolved through anodic polarisation, whereas only 75% of the film could be dissolved prior to dehydration.

The authors suggested that two chromium species existed in the CDC passive layer, namely Cr_2O_3 , which is insoluble in the caustic medium, but can be readily oxidized electrochemically and chromium hydroxide, which is soluble in caustic, but not easily oxidized electrochemically.

Referring again to the results obtained by Soepenberget al. (1976), who showed the differences between Britton's electrochemical test (EC chromium) and the chemical test for total chromium, as shown figure 2.4, it was indicated that the EC determined surface chromium and the total surface chromium values are about equal at low charge densities, but that as the charge density increased the difference between the two became more marked. Based on the findings of Rauch & Steinbicker (1975) this would suggest that as the charge density increases, more chromium hydroxide species are formed.

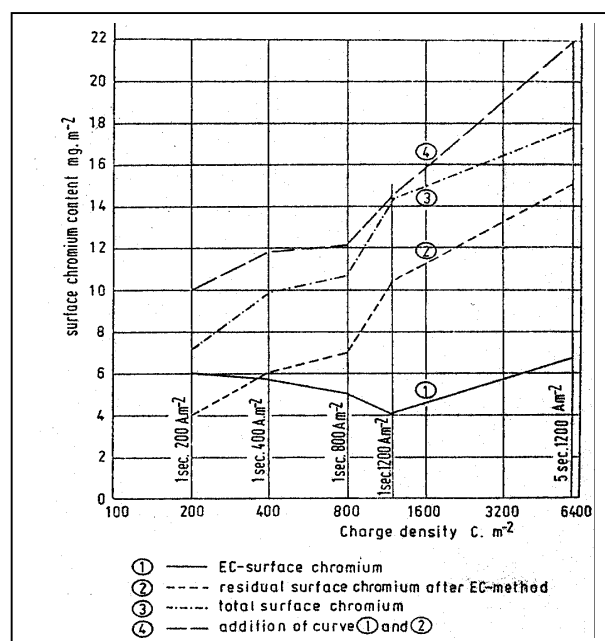


Figure 2.4 - Electrochemically determined surface chromium (EC), residual surface chromium after EC stripping and the total surface chromium as a function of charge density (Soepenberget al. 1976).

Takano and Watanabe (1980) made similar findings. They suggested that the dissolution rate of chromium in a hot alkaline solution (7.5N NaOH, 90 °C) varied with the type of chromium compound present, namely:

- Soluble chromium, $\text{Cr}(\text{OH})_3$, which is dissolved during a 1-minute immersion in NaOH.
- Sparingly soluble chromium, Cr_2O_3 , the portion dissolved during a subsequent 60-minute immersion in NaOH.
- Insoluble chromium, Cr^0 , the remaining chromium on the surface after the above treatments.

They considered two processes namely: A - (CDC treatment) and B - (cathodic sodium carbonate treatment followed by the normal CDC treatment). What is however important, is the fact that as the charge passed increased, the amount of

total chromium (as chemically determined) increased with little effect on sparingly soluble chromium and insoluble chromium as shown in figure 2.5. Based on the interpretation of these results the assumption can be made that $\text{Cr}(\text{OH})_3$ will be the species predominantly deposited during CDC treatments as indicated by the *italic* subscripts in figure 2.5.

Considering that no polarisation is applied during dip passivation treatments, none or very little chromium hydroxide is therefore expected on these surfaces compared to CDC treated tin surfaces, and could possibly explain why CDC passivation treatments behave differently from dip treatments in terms of lacquer adhesion.

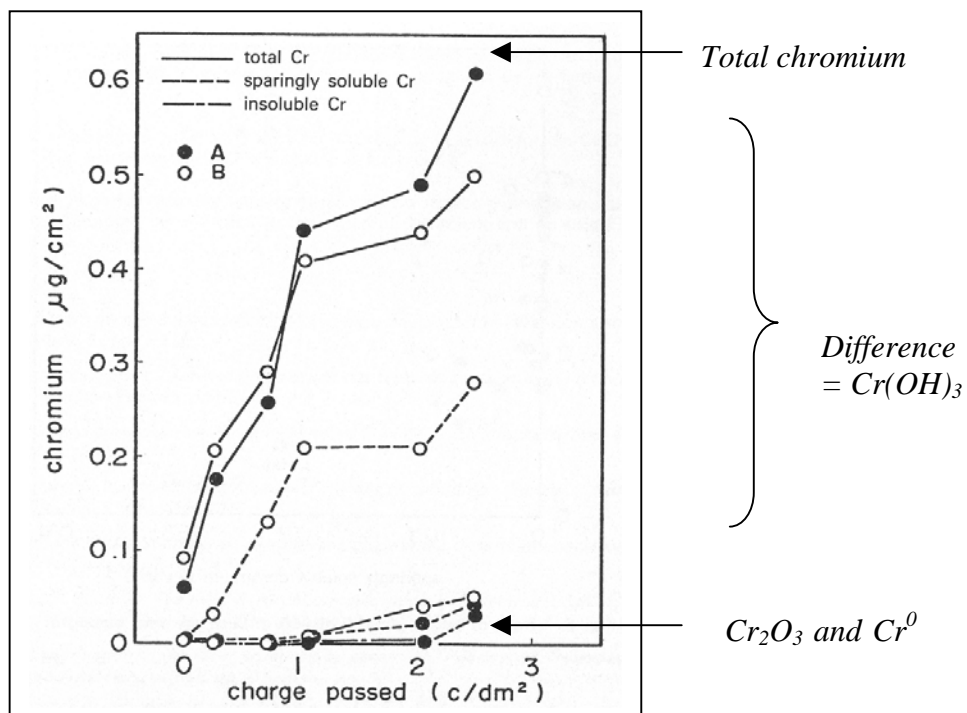


Figure 2.5 - Effect of charge passed during cathodic treatment on the amount of chromium deposited (Takano and Watanabe 1980)

2.5 Proposed mechanisms for chromium deposition

Although the different chromium species in terms of solubility and electrochemically behaviour were identified, the way in which they formed was not fully established as will be reflected in the mechanisms proposed by Carter, (1961) and Rauch and Steinbicker, (1975).

Carter (1961) proposed a tentative mechanism for chromium deposition. He suggested that existing tin oxides are reduced by cathodically produced H-atoms. The freshly reduced tin reacts with the dichromate solution to produce mixed tin and chromium oxides in the tetravalent and trivalent states respectively. The chromium content then increases with increasing charge by means of Cr (III) build-up on the existing lattice of mixed chromium and tin oxides. Finally an outer layer of hexavalent chromium is chemisorbed to the surface.

Rauch & Steinbicker (1975) suggested that the predominant reactions occurring during the passivation treatment in sodium dichromate are hydrogen evolution at the cathode (tinplate surface) and oxygen evolution at the anode. The evolution of hydrogen is normally displaced cathodically from its reversible potential and its rate depends largely on the nature and condition of the surface. For most metals the overvoltage is relatively small and such that chromium species would not typically be reduced to metallic chromium. But for tinplate they proposed that, due to the high overpotential for hydrogen evolution on tin, it would be possible for the potential to become negative enough for chromium to be reduced to metallic chromium. Metallic chromium is therefore initially deposited on the tin and as the surface becomes increasingly covered with chromium, it starts acting more like a chromium electrode.

The surface potential therefore becomes less cathodic due to the lower hydrogen overvoltage on the chromium and it becomes more and more difficult to deposit Cr^0 up to the point where no tin is exposed and Cr^0 deposition stops. They claimed to have found this in production as well as in laboratory prepared samples, with the upper limit for chromium deposited, as illustrated in figure 2.6. To test their hypothesis, Rauch & Steinbicker performed experiments by increasing the tin surface area through etching. They found that double the amount of metallic chromium was deposited on the sample containing the larger surface area.

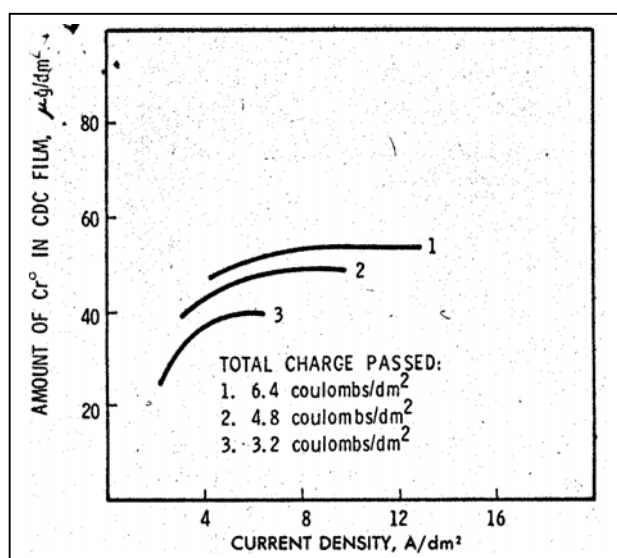


Figure 2.6 – Presumed metallic chromium, plated as a function of current density and charge passed (Rauch & Steinbicker, 1975).

The limited extent to which identification of the chromium species was possible through existing techniques and the assumption that all alkaline insoluble species are metallic chromium, resulted in high predicted values for the latter. It was only later that Servais et al. (1979) contradicted this notion by using XPS depth profiling to establish that the insoluble part consists mainly of chromium oxide species (Cr_2O_3) and with only a small portion present as metallic chromium.

2.6 Functional differences between dip and CDC treatments

Functional differences of the passivation layers on tinplate namely oxidation resistance, sulphide stain resistance and lacquer adhesion properties prompted extensive research over the years, using both conventional analytical techniques, as well as surface sensitive techniques to characterise the passivation layers. With surface analytical techniques such as X-Ray Photo-electron Spectroscopy (XPS) and Auger Spectroscopy (AES) appearing on the scene during the 1970's, more in depth studies regarding the composition of the passivation layer were possible. Due to the high degree of surface sensitivity that these techniques offer, they are suitable for studying extremely thin surface layers such as the passivation layer on tinplate. AES surveys were mainly used for characterising the passivation layer in terms of its elemental composition and thickness, while XPS studies were very useful in identifying the different tin and chromium surface species, as well as obtaining structural information of the layer through argon sputtering.

2.6.1 Oxidation resistance

Pattiasina et al. (1992) indicated that CDC chromium treatments are more effective in preventing tin oxide growth when tinplate is exposed to long-term storage and high temperature conditions. During high temperature curing (stoving) of lacquer, tinplate is typically heated for 15 minutes at temperatures of up to 210 °C. By investigating the effect of various passivation treatments on tin oxide formation during stoving, they concluded that dip passivation not only showed initially higher levels of tin oxides, but also that these tin oxides grew considerably after the stoving process compared to the CDC treated samples.

Referring to figure 2.7, samples A-C represent dip treatments with chromium levels below 2 mg/m², on which considerably more tin oxides were measured before and after stoving, compared to the CDC treated samples D-F.

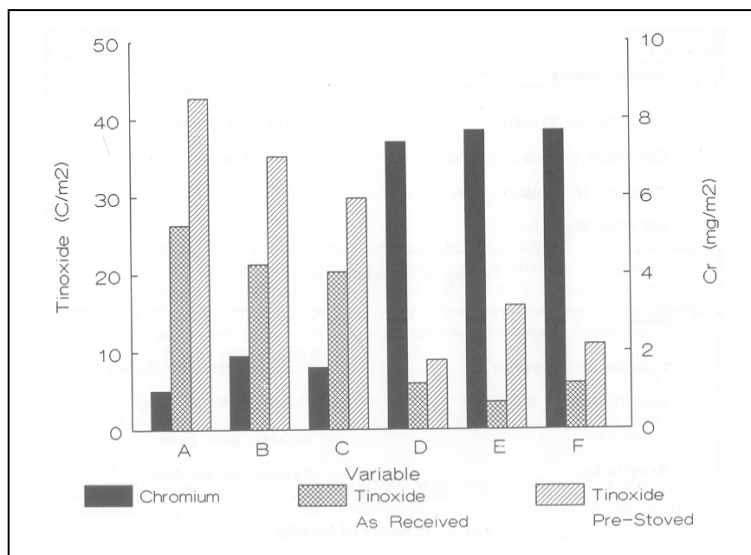


Figure 2.7 - Chromium and tin oxides in the passive film as determined by coulometric means (Pattiasina et al., 1992).

2.6.2 Staining resistance

Once the tinplate has been formed into cans, another requirement for passivation is that it has to prevent staining of the tin surface when in contact with sulphur bearing food. This includes meat and some vegetable products, for instance green peas. Britton (1975) showed that during heat processing (sterilisation), breakdown of complex sulphur compounds in the food produce free sulphides and the evolution of H₂S in the headspace of the can. The subsequent formation of tin sulphides produces an unsightly discolouration of the tinplate surface, which is harmless, but nevertheless presents an aesthetic problem (Rauch & Steinbicker, 1975). The hydrogen sulphide, which passes into the headspace, may also cause the formation of iron sulphide at defects in the coating. Shelf tests performed by Pattiasina et al.

(1992), using split green peas, showed that higher chromium levels on the tinplate surface, as achieved by electrolytic passivation treatments, are necessary to prevent sulphide staining for these conditions. According to Castrillo et al. (2002), sulphur resistance is improved by chromium coverage of more than 3 mg/m², *i.e.* CDC treated tinplate performs better.

2.6.3 *Lacquer adhesion*

Food packaging involves a vast variety of products, each with unique requirements concerning corrosion protection. Organic coatings are generally used for corrosion protection and as there are no surface preparation processes for tinplate comparable to the phosphate processes used for steel and zinc, it is imperative that the tinplate surface itself be compatible with the lacquer.

Chromium species affect adhesion of lacquers by preventing excessive tin oxide formation and by the adhesion of the lacquer on the chromium species itself. Pattiasina et al. (1992) investigated the effect of different chromium passivation treatments (dip and electrolytic) on the performance of epoxy phenolic lacquers, using shelf tests with chicken soup, which is an aggressive agent for tinplate which enhances the under film attack on tin. The results indicated that a dip passivation treatment performed better than the electrolytic treatment with regard to under film attack. As expected, undercutting or detinning was also found more pronounced with higher chromium levels on the surface. Castrillo et al. (2002) confirmed this by showing that lower levels of chromium improved lacquer adhesion performance after sterilisation in acid media, while higher total chromium levels in the passivation film

resulted in poorer acid resistance. The dry adhesion performance of the lacquer was also better when the total chromium was lower than 6 mg/m^2 .

This suggests the opposite of what is required for oxidation and staining resistance. However, a high level of surface chromium may not be, *per se*, responsible for the poor adhesion performance. Carter (1961), for instance, found that the chromium levels achieved with two different passivation processes, namely cathodic and cathodic - anodic, were the same and yet phenolic lacquers were shown to be more sensitive to chromium levels on the cathodic - anodic treatment. It is therefore also important to consider the contribution and interaction of chromium and tin species on lacquer adhesion.

2.7 Compositional differences between dip and CDC treatments

Leroy et al. (1976) used XPS to obtain information on the chemical shifts of chromium and tin in various valence states. The following standards were used: Sn^0 , Cr^0 , Cr_2O_3 , CrO , SnO , and SnO_2 . Most of the preparations of the oxides were done in the preparation chamber attached to the XPS by means of heat treatment under pure oxygen. Tinplate samples were prepared by either dip passivation or CDC passivation, of which the latter was obtained at different temperatures and current densities. Their results indicated that only Cr(III) was present for immersion (dip) treatments and that both Cr(III) and Cr^0 were present in CDC passivation films. Some indication of Cr^{6+} , albeit at low levels, was found for CDC and immersion treatments. However, the fact that metallic chromium, on the CDC treated samples was always only found after Argon sputtering, gave rise to the notion that sputtering may have

caused it. Furthermore, no interpretation of how and why the specific oxide and hydroxide species formed was attempted.

Nakakoji et al., (1988), however, indicated through XPS analyses that the Cr (III) compound (as described earlier as alkali soluble chromium) is combined with -OH (hydroxide) and that the alkali insoluble chromium compound, combined with -O (oxide). They also indicated the presence of two tin species namely SnO and SnO₂ as being part of the CDC layer on tinplate.

The compositional differences between the dip and CDC passivation layers can be summarised as indicated in figure 2.8. It is noted that less information regarding the speciation of chromium and tin species for dip treated passivation layers exist.

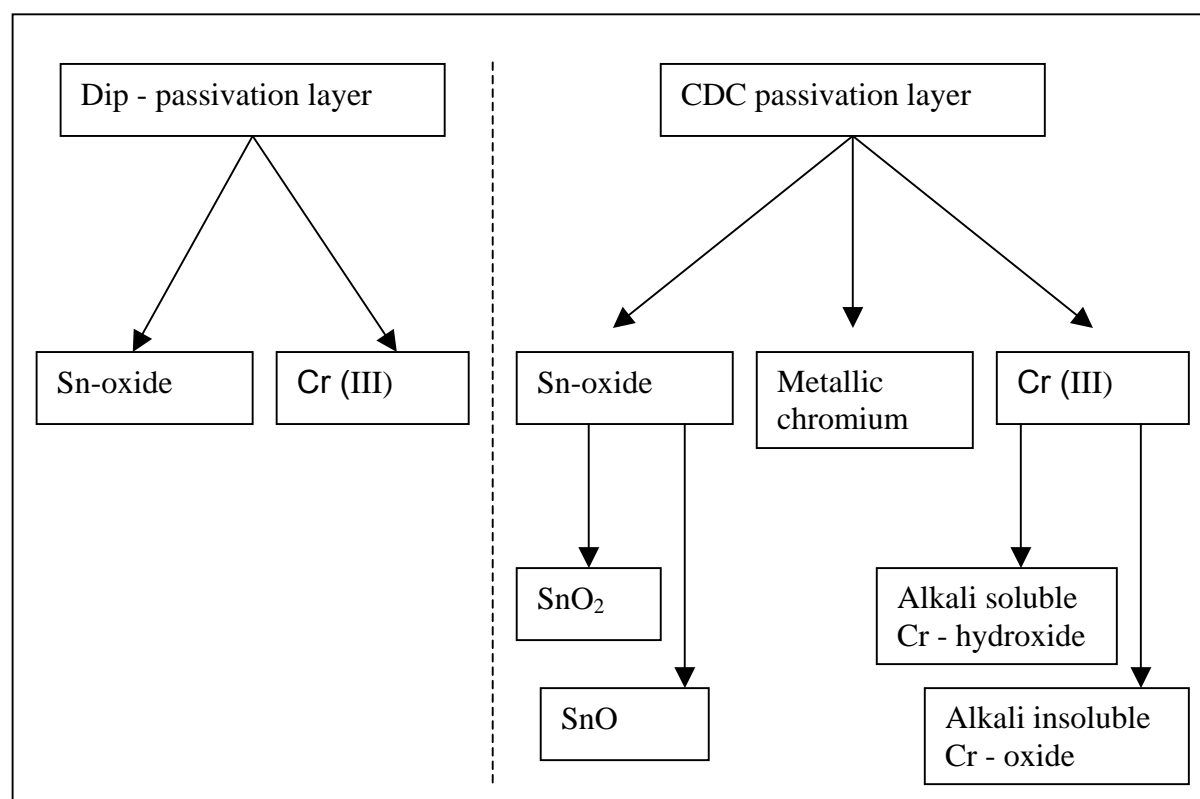


Figure 2.8 - Schematic summary of composition for dip and CDC passivation layers.

2.8 Concluding remarks

Most of the research on the chromium passivation layers on tinplate were directed at quality control, rather than the nature of the passivation layer, and also concentrated more on CDC treatments rather than on dip treatments. The mechanisms proposed for the deposition of chromium were likewise based on parametric studies.

The chemical and electrochemical results offer limited information regarding surface species, but the interpretation of the solubility characteristics suggested the presence of multiple chromium species for CDC treated tinplate. The assumptions that chromium oxide and hydroxide are present in CDC passivation layers were verified to a certain extent by surface analytical techniques. However, there is still a paucity of information on the influence of dip and CDC treatments and their related process parameters on the formation of metallic chromium, chromium oxides and chromium hydroxides.

It can also be concluded that passivation treatments are crucial to ensure acceptable tinplate properties with regard to oxidation resistance, sulphide staining and lacquer adhesion. It is evident, however, that not all three requirements can be optimised by a single treatment. Higher chromium levels in the passivation layer enhance oxidation and sulphide-staining resistance, but affects lacquer adhesion adversely.

Finally, the specific tin and chromium species formed during the dip and electrolytic application, most probably define the difference in these properties. The processes used for chromium passivation will now be reviewed in view of the available knowledge of the passivation layers.

Chapter 3.

Propositions for explaining the deposition of chromium during Dip and CDC passivation treatments

3.1 Introduction

The nature and quantity of chromium species deposited onto the tinplate surface during dip and CDC passivation treatments are most probably different due to differences in the driving force for the reduction of chromium and different chemical conditions close to the tinplate surface. In the dip process the reduction of chromium is governed by the presence of oxidisable species on the tinplate surface, while in the CDC process the polarisation is externally applied, with a resultant more negative potential, that would also support hydrogen evolution on the tinplate surface. The influence of these factors on the chromium species deposited will be explored in the following sections.

3.2 Dip passivation treatment

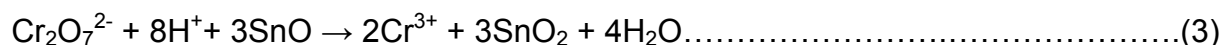
During a dip passivation treatment, the same bath configuration as for CDC passivation treatment is used, but without the application of cathodic polarisation. Sodium dichromate solutions used for passivation treatments of tinplate are slightly acidic (pH 4) and strongly oxidising. The half-cell reaction for reduction of dichromate ions can be written as:



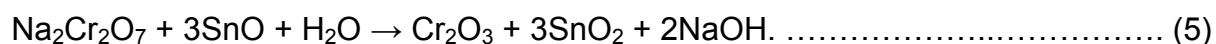
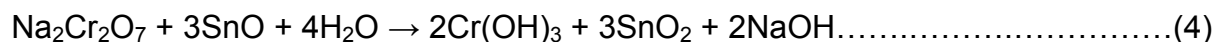
In order for the reduction of dichromate to take place, a reductant such as Sn(II) needs to be oxidised:



The reason for considering only Sn(II) is because tetravalent tin Sn(IV) is already in its highest oxidation state and would not contribute to the reduction of chromium. It is also important to keep in mind that tinfoil is subjected to a flow brightening process prior to the passivation treatment. During the melting and subsequent water quench, tin oxides are formed on the tin surface (Castell-Evans and Wach, 1973). For this reason the oxidation of metallic tin is unlikely during the dip process. The redox reaction occurring on the tinfoil surface during dip passivation treatment in a dichromate solution can therefore be written as:



However, more than one possibility exists for the formation of chromium species as indicated by reactions 4 and 5.



In terms of the suggested reactions for dip treatments, two aspects are pertinent:

- The oxidation state of the tin on the tinfoil surface prior to dip passivation treatment is important, as it will determine the amount of chromium deposited.
- An upper limit for chromium deposition will be reached once the readily available tin species are converted to Sn(IV) as it is unlikely that the tin beneath an already formed chromium oxide layer will be significantly oxidised.

3.3 Cathodic dichromate treatment

During CDC passivation treatments, tinplate is negatively polarised in a sodium dichromate solution. What makes this process more complex than the dip treatment is that reduction of species at the tinplate surface are driven by the applied cathodic polarisation rather than by the presence of oxidisable species. Apart from reactions 1 and 2, which were possible during dip treatments, reactions 6 and 8 may also contribute to the deposition of chromium during CDC process and will therefore be discussed in greater detail.



3.3.1 Reduction of tin oxides

Agreement exists in terms of the mechanisms proposed by (Carter, 1961; Rauch and Steinbicker, 1975; Soepenberget al. 1976) that during the CDC process, tin oxides could be reduced due to the cathodic polarisation of the tin surface following reactions 8 and 9.



3.3.2 Hydrogen evolution reaction

Hydrogen evolution through the reduction of water typically occurs at the applied negative potentials. As OH^- species are formed during this reaction, an increase in pH will occur at the surface of the tinfoil indicated in figure 3.1.

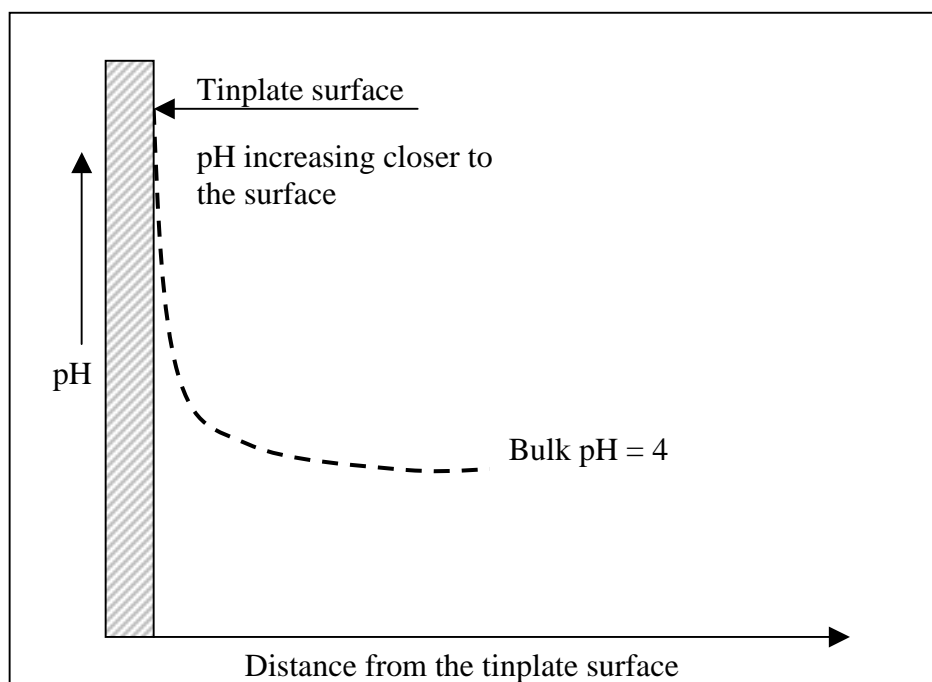


Figure 3.1 – Schematic representation of pH profile likely to develop at the surface of the tinplate during CDC passivation treatments.

The increase of pH could have an important effect on the species forming at the tinplate surface. During CDC passivation treatment, the chromium species formed at a pH 4 or lower, and could therefore be different from those formed at higher pH values, as indicated in figure 3.2.

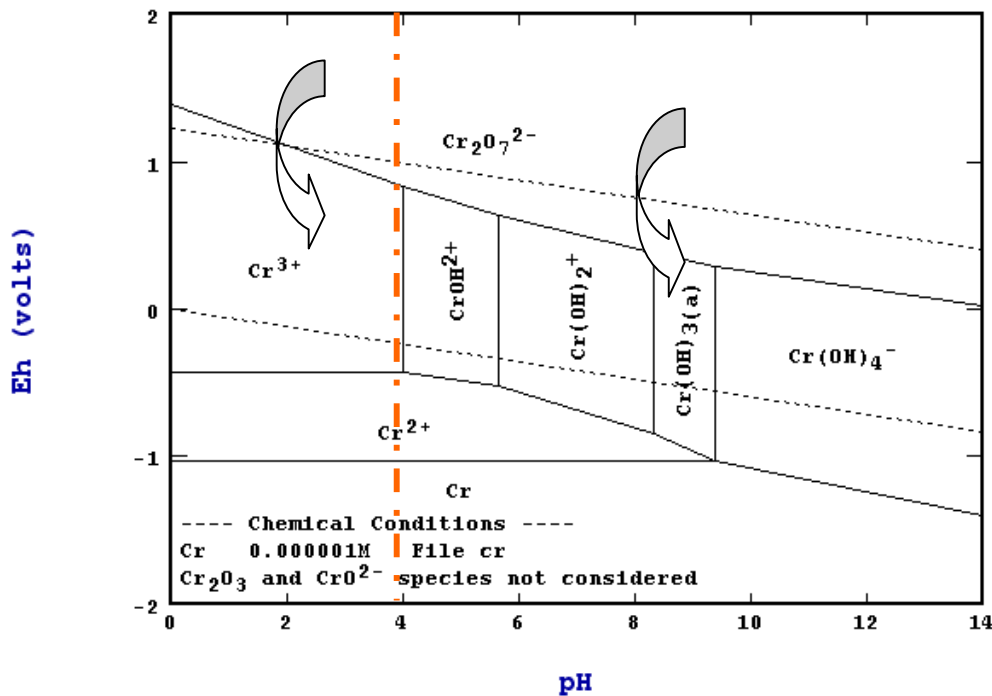


Figure 3.2 - Pourbaix diagram for the system Cr-H₂O at 25 °C (Stabcal –software)

Baes and Mesmer (1986), stated that when a base is added to Cr(III), Cr₂O₃ precipitates in a state of undefined hydration. As the pH near the sample surface increases, more chromium hydroxide species are therefore likely to be deposited.

3.3.3 Deposition of metallic chromium

Another reaction that is possible and also the reason for a considerable amount of research and controversy, is the deposition of metallic chromium through reaction 7. Rauch & Steinbicker (1975) suggested in their proposed mechanism that metallic chromium forms during CDC treatments. The levels of metallic chromium reported by them, (2 - 5.5 mg/m²) in proportion to the non-metallic chromium (3 - 4.5 mg/m²), seem high when compared to those of later publications. They assumed that the residual chromium left on the surface after exposure to a 90 °C 10M NaOH solution

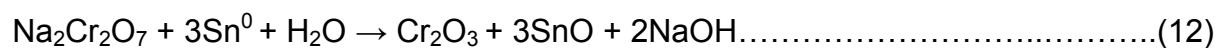
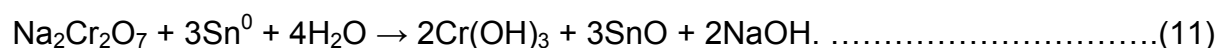
for 10 minutes was metallic chromium. Servais (1979) showed through XPS analysis that this specific portion was mainly chromium oxide (Cr_2O_3) and that only a small part (0.5 mg/m^2) consisted of metallic chromium.

The existence of metallic chromium, as detected by means of XPS analysis, however, led to much debate. A number of researchers (Leroy et al., 1976; Servais et al., 1979; Maeda et al., 1980; Azzeri and Cerboncini, 1984; Warwick et al., 1984) have identified the presence of metallic chromium in the passivation film through XPS techniques. Metallic chromium was however always found only after argon sputtering. Coad et al. (1976), however, argued that sputtering would not reduce Cr_2O_3 , since it is more stable than the compounds generally found to decompose under ion bombardment, and also that passivation films containing no metallic chromium (dip passivation) showed no signs of chrome reduction during ion bombardment. Servais et al. (1979) also agreed that ionic bombardment did not reduce trivalent chromium or tetravalent tin, although they found that hexavalent chromium might be reduced to trivalent chromium and bivalent tin be reduced to metallic tin.

Nogueira et al. (1988), however, indicated that earlier work performed by Grundner and Hanwritter (1980) and Sanz and Hofmann (1983) showed that ion sputtering could reduce metal species to lower valence states. There is therefore no unequivocal evidence for the existence of metallic chromium in CDC passivation films, although it may be present after argon etching of overlaying species.

3.3.4 Possible redox reactions during CDC treatment

Apart from reactions 4 and 5, the following reactions are also possible considering the arguments presented for the reduction of tin, the formation of chromium oxides and hydroxides, due to the drift of the potential on the tinplate to more positive values during the later stages of the CDC treatment, when hydrogen reduction is depolarised by the deposition of chromium oxides.



3.4 Concluding remarks

The literature indicates that chromium may be deposited on the tinplate in the form of Cr^0 , Cr_2O_3 or $\text{Cr}(\text{OH})_3$ depending on the method of application. For dip passivation Cr_2O_3 is most probably formed, while for CDC treatments, the more negative potential makes reduction of chromium to Cr^0 possible, although it has not been unequivocally identified. Also, the higher pH conditions close to the surface, generated by hydrogen reduction, may facilitate the formation of $\text{Cr}(\text{OH})_3$, rather than Cr_2O_3 .

In order to verify these propositions the following issues were addressed during the experimental investigations:

- The influence of the oxidation state of tin, prior to the passivation treatment, on the deposition of chromium.

- The oxidation state of the tin species in the surface layer, once an upper limit for dip passivation has been reached.
- The reduction of tin oxides under cathodic polarisation during CDC treatments.
- The preferential formation of chromium hydroxide species during CDC treatments.
- The possible deposition of metallic chromium during CDC treatments.
- Verification of chromium and tin species formed during dip and CDC treatments.

Chapter 4.

Experimental approach and description of techniques

4.1 Introduction

During the course of this study, focus remained on the problem associated with the type of passivation treatment employed vs. the functionality of chromium passivation on tinplate with specific reference to the lacquer adhesion properties. As indicated, there are still unresolved issues that require experimental verification. The selection of techniques, suitable for the characterisation of chromium passivation on tinplate, was therefore necessary.

Scanning Auger Spectroscopy (AES) and X-ray Photo Electron Spectroscopy (XPS) were chosen as surface analytical techniques during this study due to the high degree of surface sensitivity they offer. AES surveys were mainly used for characterising the passivation layer in terms of its elemental composition and thickness. XPS studies were very useful in identifying the different tin and chromium surface species, as well as obtaining structural information of the layer through angle resolved analysis. Complimentary to the surface sensitive techniques, galvanostatic and potentiodynamic electrochemical techniques were used to verify findings obtained through earlier research work, and acted as basis for interpreting the surface analytical results.

Table 4.1 summarises the investigations undertaken and techniques used during this study.

Table 4.1- Experimental outlay

Investigation	Purpose	Technique
Characterisation of surface species on tinplate.	To establish the difference in surface species produced during dip and CDC passivation treatments.	Electro-chemical and XPS
The formation of metallic chromium during CDC treatment.	To use a surface sensitive technique different from that employed in literature but still capable of detecting metallic chromium.	Angle resolved XPS
Reduction of tin oxides	To establish the influence of tin oxides prior to passivation treatment on the deposition of chromium during dip and CDC treatments.	AES + XPS
Deposition of chromium species during CDC treatment as a function of pH	To investigate the influence of pH on the amount and type of chromium species deposited.	Electro-chemical.

4.2 Scanning Auger Spectroscopy

The surface sensitivity of Scanning Auger Spectroscopy (AES) renders this technique ideal for studying passivation layers on tinplate. The kinetic energy of the main constituencies in the passivation layer on tinplate, namely tin and chromium, are detected at 432 eV and 531 eV respectively (Childs et al. 1995). Briggs and Seah (1983) showed that a high degree of surface sensitivity is achieved in this range. AES surface analysis of tinplate would typically include approximately 4 atomic layers as can be deduced from figure 4.1.

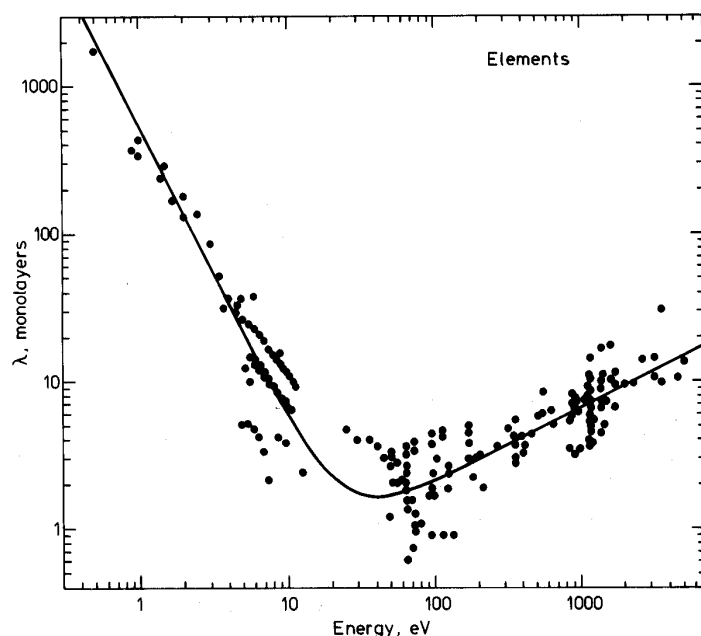


Figure 4.1 - The dependence of escape depth on the electron energy (Briggs and Seah 1983).

4.2.1 Instrumentation and experimental parameters used during analysis

A Perkin Elmer PHI 600 instrument was used throughout this study with vacuum conditions better than 1×10^{-9} Torr during point analysis and better than 1×10^{-8} Torr during depth profiling. Surveys were performed at a primary beam energy of 3 keV and a current of 1×10^{-6} A.

A lanthanum hexaboride (LaB_6) electron source was used to produce the electron beam, which was focussed on the sample by two electromagnetic lenses. Under the impact of electrons the surface atoms were excited and lost their energy through emitting Auger electrons of which the energy distribution $N(E)$ was measured by means of a cylindrical mirror analyser. The results are presented as the variation of $dN(E) / dE$ with respect to the energy E which are presented in the form of spectrum lines characterising the nature of the elements present on the surface as shown in figure 4.2. Taking into account the sensitivity factors for each element, the peak-to-peak amplitude of a line is proportional to the atomic concentration, Childs et al. (1995), using the following general expression:

$$X_a = (I_a / S_a) / (\sum I_{abc..} / S_{abc..})$$

Where: X_a = Atomic concentration of element (a)

I_a = Auger peak intensity for element (a)

S_a = Sensitivity factor for element (a)

$I_{abc..}$ = Auger peak intensities for all the elements (abc..)

$S_{abc..}$ = Sensitivity factors for elements (abc..)

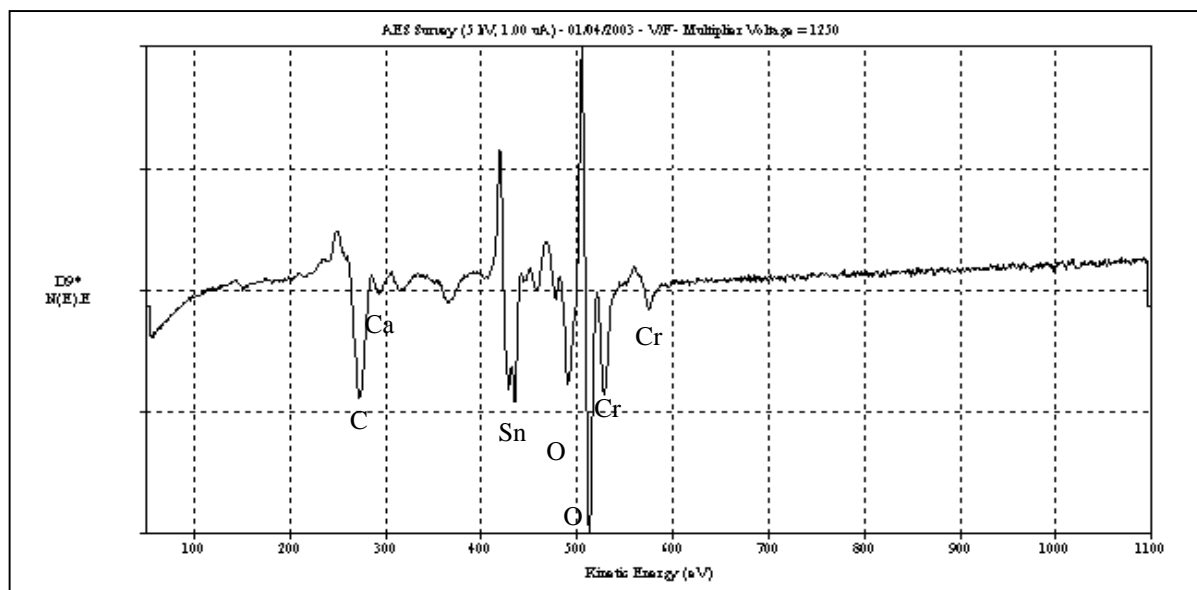


Figure 4.2 - Typical Auger spectrum of a chromium passivated tinplate surface. (Production material with CDC passivation treatment)

4.3 Description of X-ray Photoelectron Spectroscopy

The x-ray photoelectron spectrometer used was a Physical Electronics model 5400 equipped with both an Al/Mg dual x-ray source and an Al monochromator. The instrument was operated at a base pressure of less than 4×10^{-9} Torr with a lateral resolution of 10mm.

X-ray Photoelectron Spectroscopy (XPS) involved irradiating the tinplate surface under ultra high vacuum with mono-energetic soft x-rays and analysing the energy of the emitted electrons. Characteristic of the x-rays, Mg K α (1253.6 eV) or Al K α (1486.6 eV), used in this technique are that they have limited penetrating capabilities therefore only interacting with atoms in the surface region of approximately 1-4 monolayers. This characteristic renders the XPS technique useful for analysing passivation layers on tinplate.

4.3.1 Survey analysis

By using the binding energy of the atomic orbital from which the electron originates, identification of the different elements is possible. A typical survey analysis of a tinplate surface is given in figure 4.3 indicating the assignment of peaks.

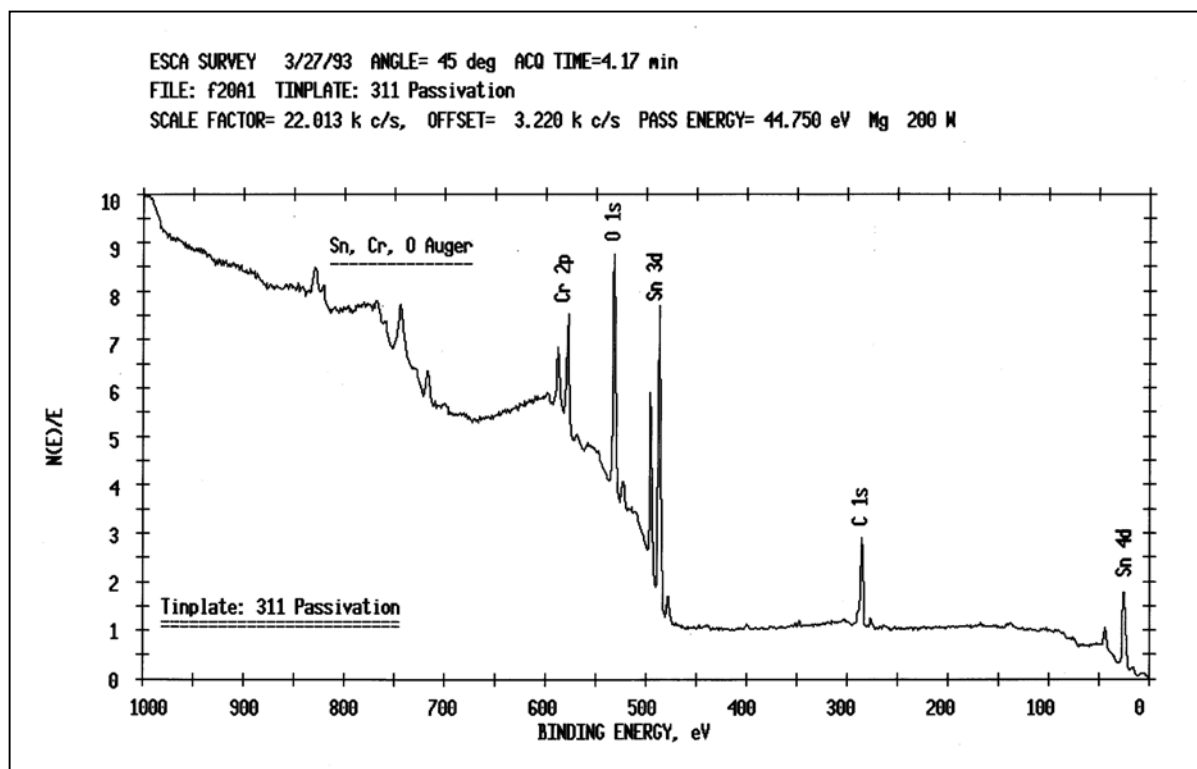


Figure 4.3 - XPS survey of CDC treated tinplate

To ensure the correct measurement of binding energy the instrument was calibrated using argon etched pure gold and pure silver samples. The hydrocarbon peak at 285eV was used as calibration during the day-to-day analysis.

Carbon is accepted as a standard to provide a universal binding energy scale. The multiplex analysis of the carbon peak, obtained on the tin sample, is shown in figure 4.4. Three carbon peaks can be fitted to the acquired peak and these are identified as species containing (-C-H-), (-C-O-) and (-C=O-) bonds. The highest peak,

originating from (-C-H-) is normalised to a binding energy of 285eV and the energy shift is accordingly recorded in order to normalise the remaining peaks. This binding energy is in agreement with the National Institute of Standards and Technology, NIST (1989) data.

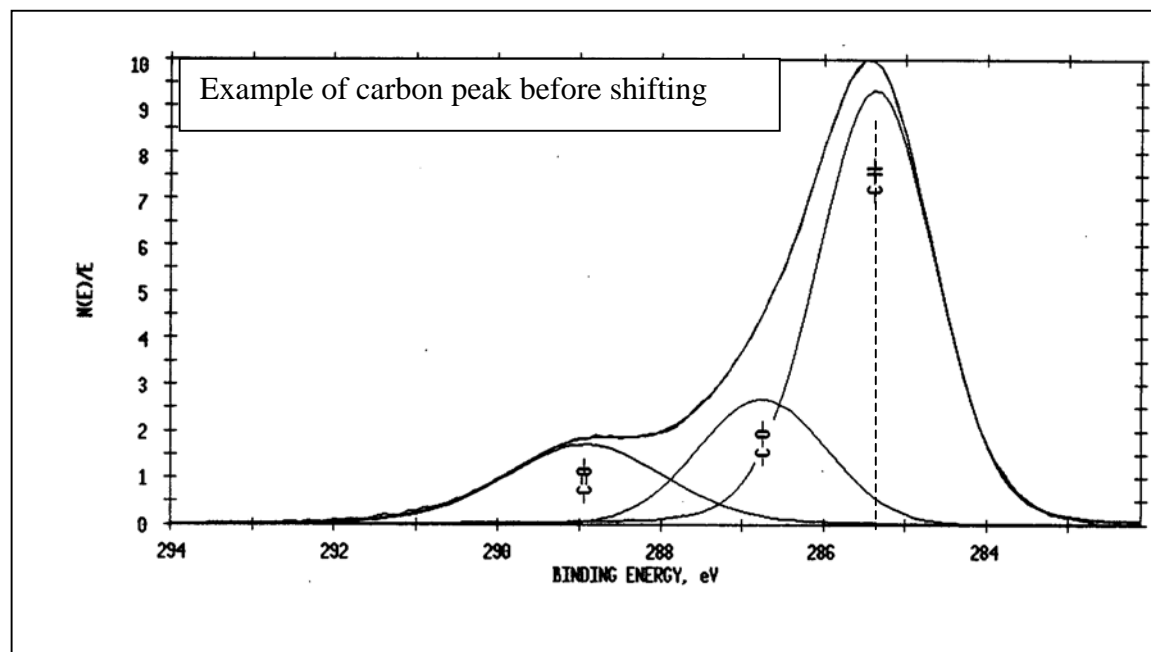


Figure 4.4 - High-energy resolution analysis of the 1s XPS carbon peak.

4.3.2 Multiplex analysis

During multiplex analysis, high-resolution peaks of the selected elements were obtained, figure 4.5. The improved accuracy of the binding energies obtained, allowed the assignment of different chemical species to the peaks.

For the assignment of the different species the following databases were employed:

- NIST database (National Institute of Standards and Technologies, 1989);
- The PSI Database included in the instrument's software;
- Values obtained from relevant literature.

It was however also important to take the history of the sample in account in order to obtain positive identification of the various species.

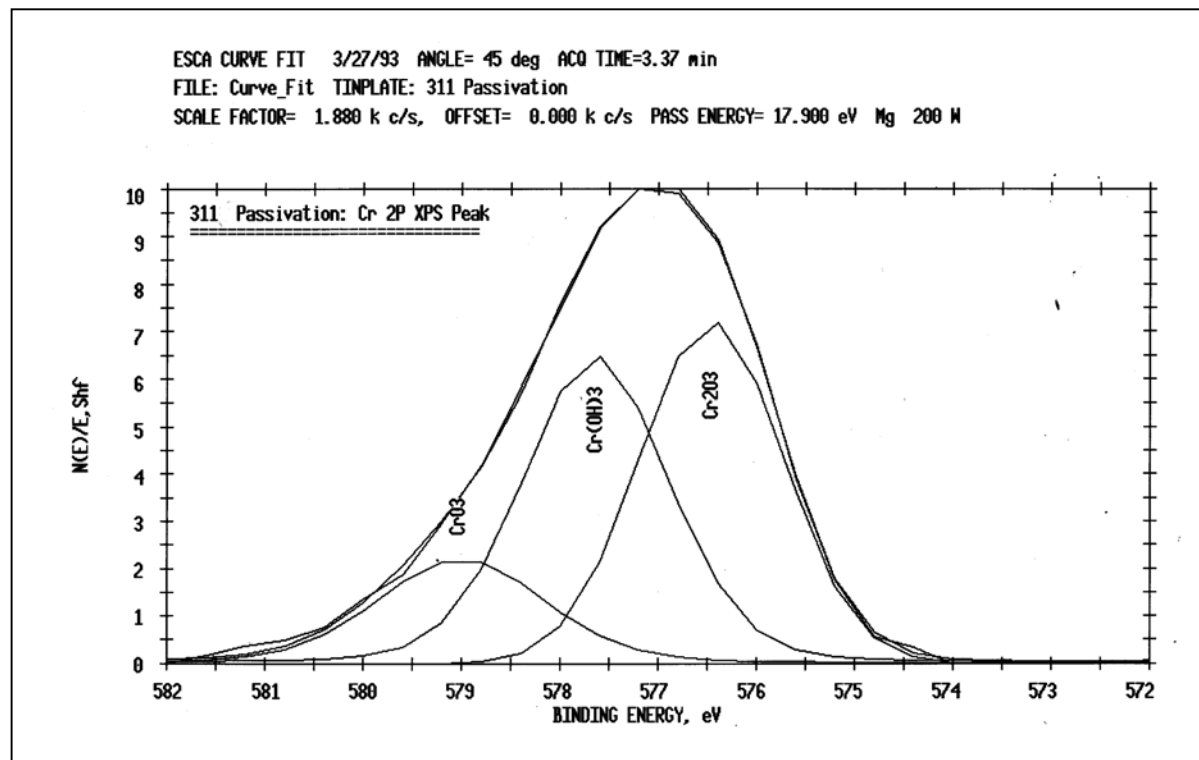


Figure 4.5 - Multiplex analysis of the Cr 2P peak indicated in figure 6.3. The presence of CrO_3 is indicative of sodium dichromate drag-out from the passivation unit.

4.3.3 Angle resolved analysis

The angle resolved analysis technique is based on the principle that a low (shallow) take-off angle, at which the photoelectron is detected in relation to the sample, accentuates the spectrum of elements closer to the surface of the sample. At the other extreme, for a sample mounted at an angle normal to the analyser (high take off angle), the contribution of the above-mentioned elements is minimised (Moulder, et al. 1992). The angle resolved technique is illustrated in figure 4.6 for low take off angles and figure 3.6 for high take off angles (Von Moltke, 1992).

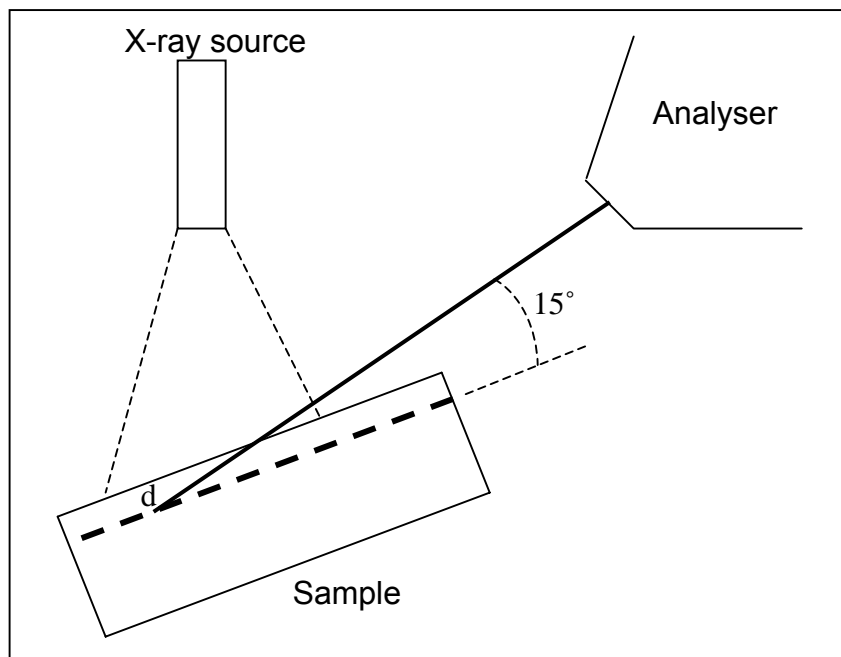


Figure 4.6 - Analysis obtained at low take off angles (15°), contains a high proportion of photoelectrons originating near the surface (Von Moltke, 1992).

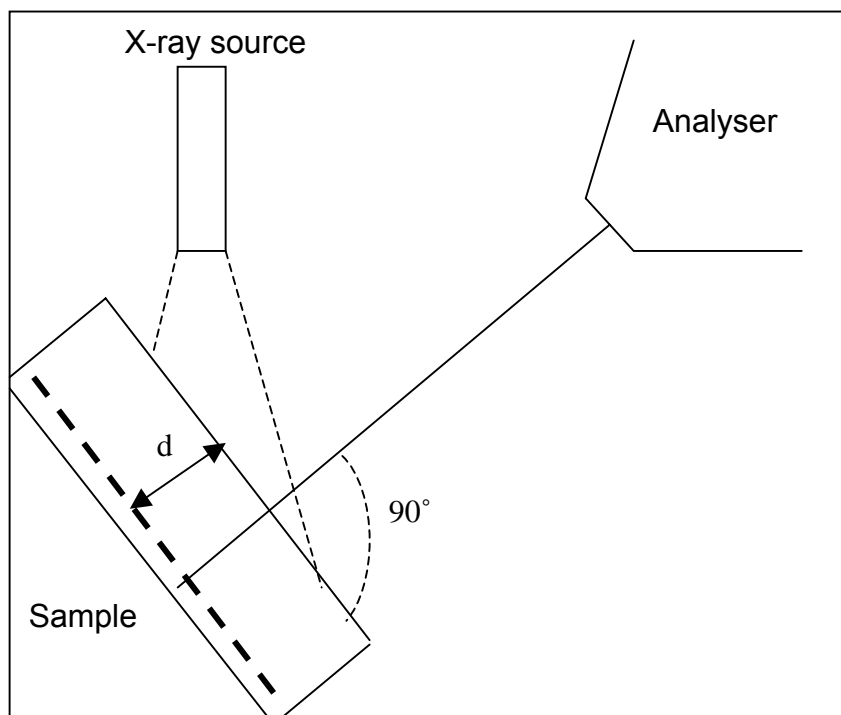


Figure 4.7 - Analysis obtained at high take off angles (90°), contains photoelectrons originating at the maximum escape depth for the technique (Von Moltke, 1992)

This technique is extremely useful in studying passivation layers because depth-profiling information can be obtained without possibly altering the oxidation state of species by ion sputtering. This would rule out the probability that chromium species are reduced during analysis.

Figure 4.8 shows a montage of tin, oxygen and chromium analysed with take off angles ranging from 15° through to 90° for a CDC passivated tinplate sample. Note how the peak of the metallic tin increases, as the angle is increased. This indicates that the passivation layer is in the order of 4 monolayers and as the angle increases more of the tin substrate is detected. It should also be noted that chromium did not show this behaviour. Proper interpretation of these spectra will, however, only be done later during discussion of the experimental results.

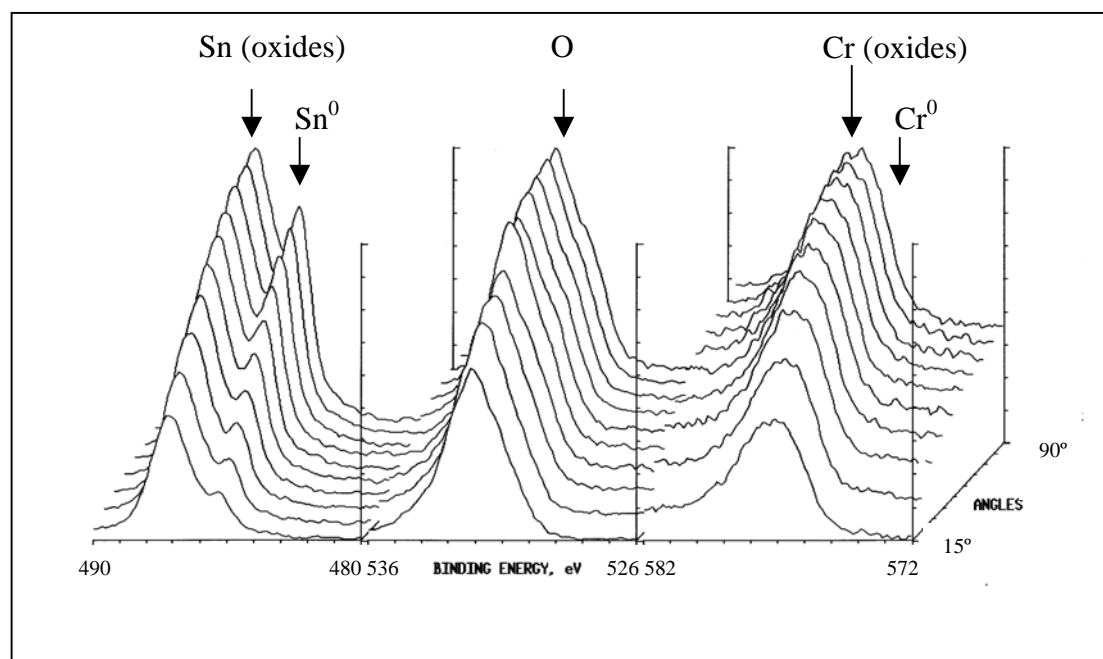


Figure 4.8 - Typical angle resolved XPS results for tin, oxygen and chromium on a CDC tinplate sample

4.4 Samples and preparation

Due to the risk and cost implications of production line trials, manipulation of process parameters during the passivation treatment were performed on a laboratory scale. Typical parameters for the laboratory prepared samples are given in table 4.2. Pure tin was used to simulate both the dip and CDC treatments and the effect of varying process parameters on the latter. Scanning Electron Microscope analysis performed on reflowed tin coatings indicated complete coverage of the steel substrate with tin. The depth resolution of surface analysis AES and XPS have been indicated as only a few monolayers and tin was therefore the only substrate detected by these techniques. It was therefore considered acceptable to use pure tin as substrate for laboratory prepared samples. Apart from the ease of preparation and re-usability of samples, an additional benefit of using pure tin is that a standard surface finish can be obtained for analysis. AES, having a spatial resolution of less than one micrometer, can be affected by surface roughness. In cases where possible, the laboratory analyses were, however, verified through analyses of production samples.

Table 4.2 - Typical parameters used during laboratory passivation treatments

Parameter	Dip treatment	CDC treatments
Cell dimensions	1 litre, glass beaker, Diameter =100mm Height = 150mm	1 litre, glass beaker, Diameter =100mm Height = 150mm
Distance between sample and the anode	--	90mm
Anode material	--	Carbon
Electrolyte concentration	25g/l $\text{Na}_2\text{Cr}_2\text{O}_7$	25g/l $\text{Na}_2\text{Cr}_2\text{O}_7$
Electrolyte volume	800ml	800ml
Temperature of the electrolyte	70°C	70°C
Magnetic stirring	Yes	Yes
Applied cathodic current	--	10A/dm ²
Treatment time	1 second	1 second

Deviations from these parameters are indicated during the discussion of the results in chapter 5.

4.5 Electrochemical analysis

The electrochemical analysis of chromium on tinplate involves two methods of which the method of Britton (1965) was described in chapter 2. In addition, potentiodynamic measurements of chromium-passivated tinplate are useful in studying the passivation layer because it is sensitive enough to distinguish between chromium species soluble in alkaline solutions and those that are not. The anodic potentiodynamic polarisation curve for chromium-passivated tinplate shows a single current-peak at $E_{(max)}$, which is typically positioned at (+700 mV vs. Ag/AgCl or +922 mV vs. SHE), figure 4.9.

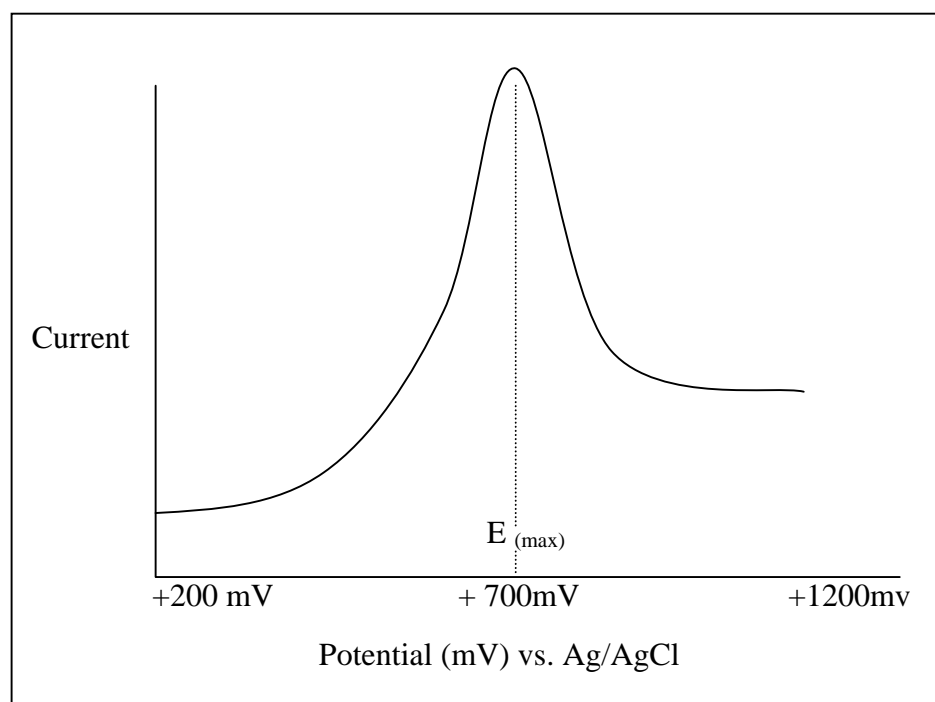


Figure 4.9 - Illustration of a typical potentiodynamic plot for the determination chromium on tinplate surface.

As indicated through chemical dissolution, part of the passivation layer is soluble in sodium hydroxide and can be removed while leaving the insoluble part on the surface. A shift for $E_{(max)}$ towards more positive potentials, figure 4.10, is observed

when a CDC passivated sample was exposed to boiling sodium hydroxide prior to the potentiodynamic test, (Aubrun and Pennera, 1976).

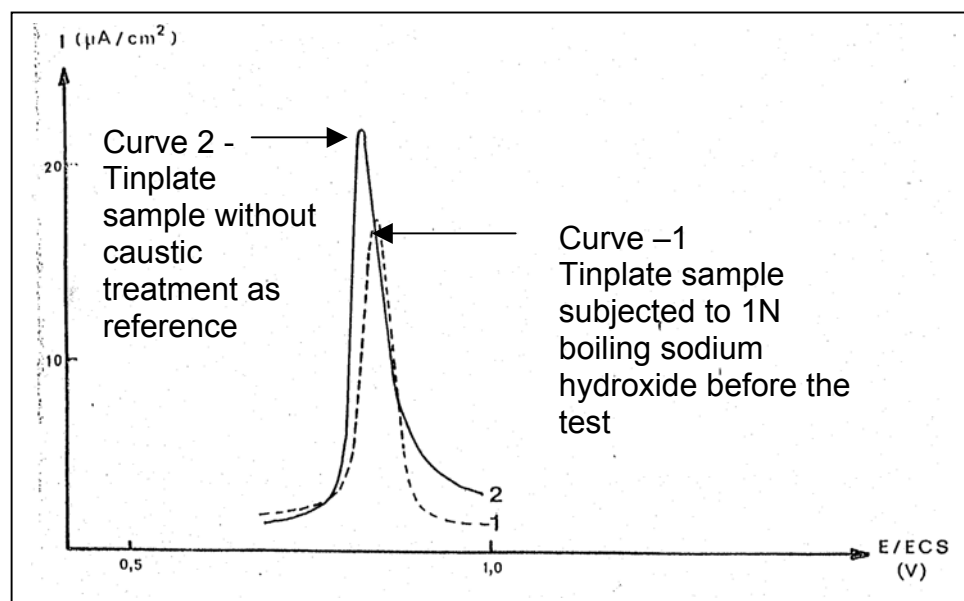


Figure 4.10 – Influence of sodium hydroxide pre-treatment on the anodic potentiodynamic polarisation curve (Aubrun and Pennera, 1976).

Salm et al. (1984) also found a positive shift for $E_{(max)}$, and in some cases a change in shape of the current peaks, when CDC passivated tinplate samples were aged. The same occurred when CDC samples were heated for different times at 40 °C or when it was stoved at temperatures ranging from 100°C to 200 °C for 10 minutes. The shift in $E_{(max)}$ and changes in the shape of the current peaks are illustrated in figure 4.11. The authors believed that these changes could be explained by the dehydration of the chromium species.

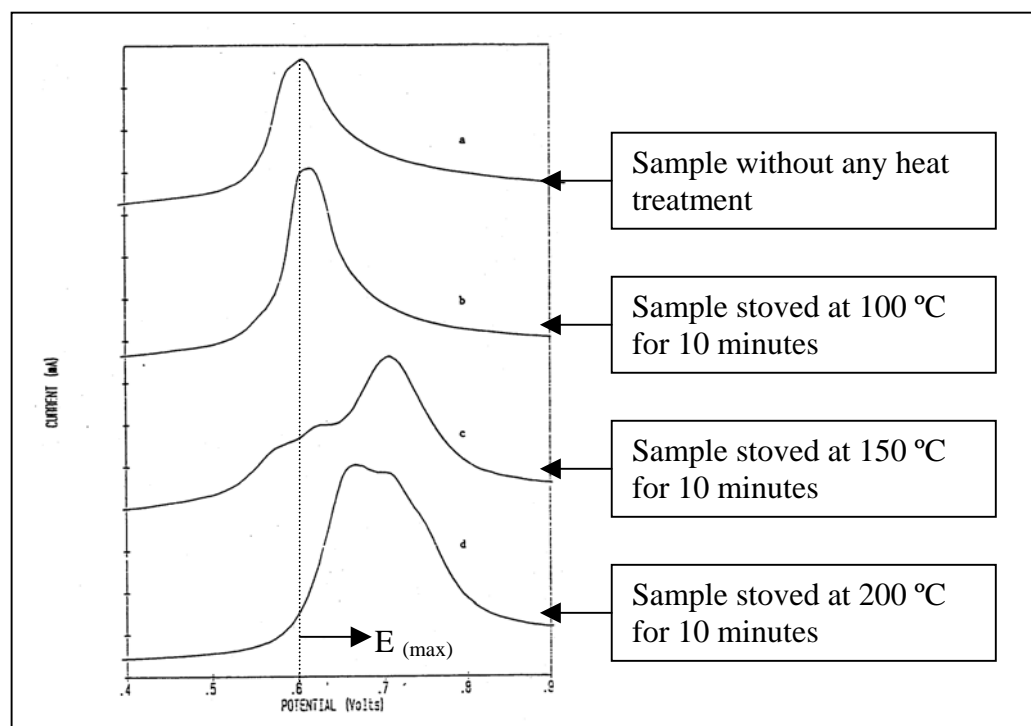


Figure 4.11 – Effect of temperature on the position and shape of anodic potentiodynamic polarisation current peaks obtained on CDC treated tinplate samples (Salm et al. 1984)

These observations would therefore render this technique very useful for studying differences in chromium passivation layers, provided the observed changes are calibrated with a technique such as XPS.

4.6 Experimental parameters used during electrochemical measurements

Electrochemical tests were performed with the aid of a Solartron electrochemical interface, model 1286. The following parameters, table 4.3, were used during the electrochemical testing of the passivation layers. Deviations from these parameters are indicated in the discussions of the results, chapter 5.

Table 4.3 - Typical parameters used during electrochemical testing

Parameters	Galvanostatic measurements	Potentiodynamic measurements
Cell dimensions	Perspex cell, 100 x 100mm	Perspex cell, 100 x 100mm
Working electrode size, (Sample size)	5 cm ²	5 cm ²
Counter electrode	Platinum wire	Platinum wire
Reference electrode	Silver / silver chloride electrode in a luggin tube filled with saturated potassium chloride	Silver / silver chloride electrode in a luggin tube filled with saturated potassium chloride
Distance between sample and luggin tip.	3mm	3mm
Electrolyte	200ml (8g/l sodium di-hydrogen phosphate) mixed with 800ml (9.5g/l di-sodium hydrogen phosphate)	200ml (8g/l sodium di-hydrogen phosphate) mixed with 800ml (9.5g/l di-sodium hydrogen phosphate)
Electrolyte pH	7.4	7.4
Temperature of the electrolyte	Ambient	Ambient
Applied anodic current	25μA/cm ²	--

Chapter 5.
Results and discussion

5.1 Introduction

Considering the propositions made regarding the deposition of chromium in chapter 3, the surface species listed in table 5.1 were the most likely to be present on the surface of dip and CDC treated tinplate samples. Detailed analyses of various tinplate samples were performed, to establish if the difference in lacquer adhesion, indicated for dip and CDC treated tinplate, was related to the nature of surface species.

Table 5.1 – Surface species expected on passivated tinplate following a specific application method

Surface species	Dip treatment	CDC treatment
Tin	SnO_2	Sn^0 SnO SnO_2
Chromium	Cr_2O_3	Cr^0 Cr_2O_3 $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$

5.2 Electrochemical analysis of dip and CDC treated samples

Production samples obtained from the tinning line were used during the analysis. The process parameters at the passivation unit at the time the material was processed are listed in table 5.2. The parameters were the same for both dip and CDC treatments except that during the dip treatment no current was applied.

Table 5.2 - Passivation treatment parameters used on the tin line for the preparation of dip and CDC passivated tinplate.

Parameter	Value
Line Speed	425 m/minute
Passivation unit temperature	59.5 °C
Current used at the time	3.8 kA
Electrolyte concentration	25 g/l
Electrolyte pH	5.2
Calculated contact time	0.4s
Calculated current density	10.5 A/dm ²
Calculated charge density	3.99 C/dm ²
Process-laboratory values for surface chromium during CDC treatment.	Top surface = 4.8 mg/m ² Bottom surface = 5.2 mg/m ²

The process-laboratory values for surface chromium were obtained by means of an electrochemical test. The test parameters used during this test, deviated however quite significantly from those proposed by Briton (1965). The results of repeated tests using Briton's original method are shown in figure 5.1.

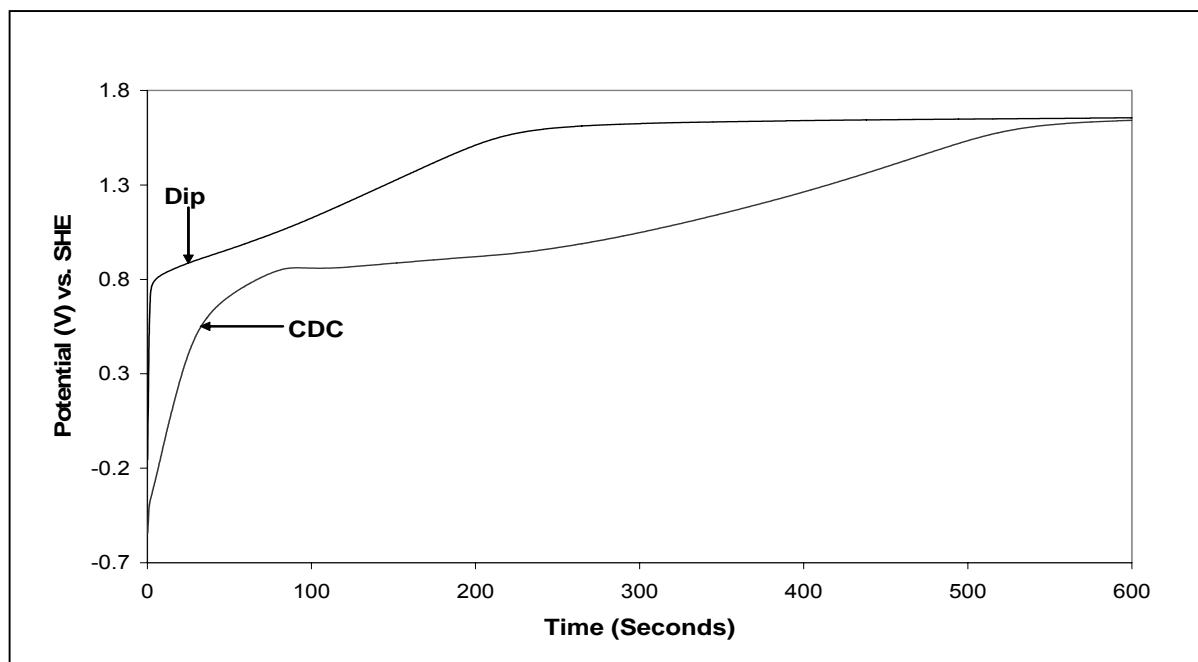


Figure 5.1 - Potential vs. time curves, obtained in a pH 7.4 phosphate buffer, during galvanostatic measurements of dip and CDC passivated tinplate.

Following Britton's guideline that a charge of $1\text{mC}/\text{cm}^2$ results from $0.1\mu\text{gCr}/\text{cm}^2$, the calculated chromium mass on the dip treated tinplate equals $1\text{ mg}/\text{m}^2$ while the chromium mass on the CDC treated tinplate equals $4\text{ mg}/\text{m}^2$ chromium. The chromium value for the latter is significantly less than the specified $5\text{-}10\text{ mg}/\text{m}^2$ chromium for CDC treatments. As has been indicated in chapter 2, chromium oxide species are readily oxidised while chromium hydroxide species are not. It was therefore decided to investigate this aspect in more depth.

Anodic potentiodynamic polarisation curves were also determined for the dip and CDC treated tinplate samples as shown in figure 5.2. The dip treated tinplate yielded less chromium than the CDC treated tinplate as indicated by the difference in the areas beneath the current peaks. Furthermore a potential shift of approximately 0.1V

in the peak positions is indicated, with the tin passivated by the dip process showing a higher breakdown potential than that for the CDC sample.

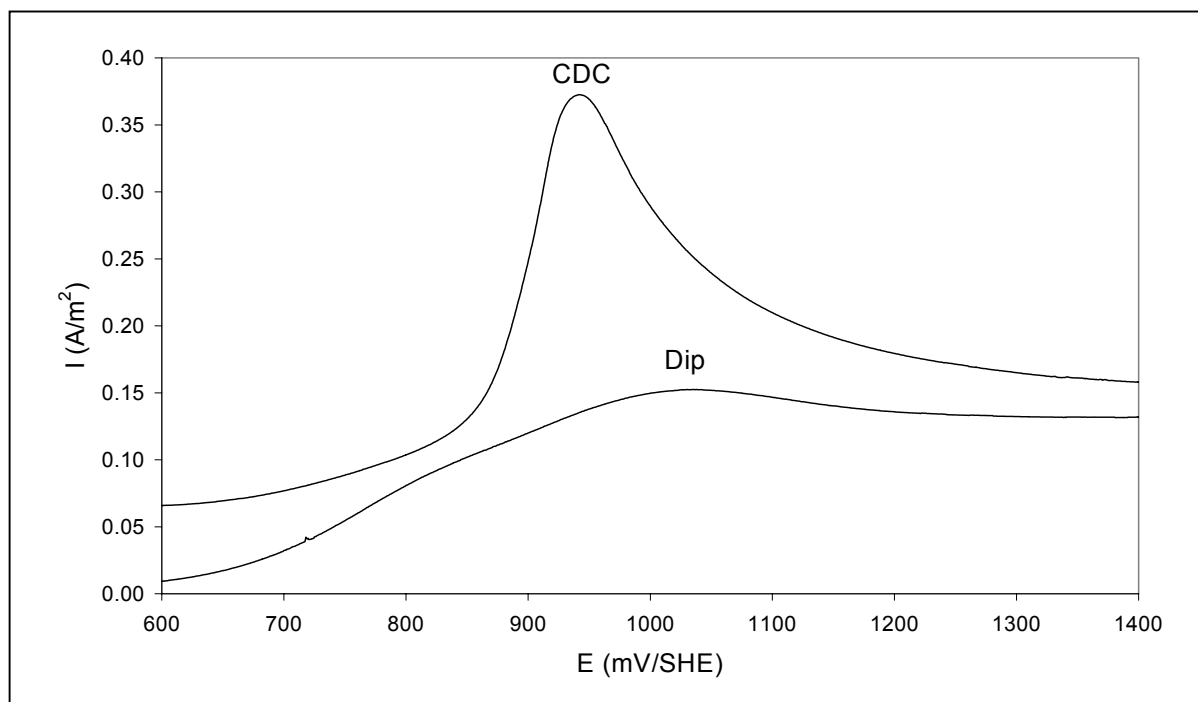


Figure 5.2 – Potentiodynamic polarisation curves, determined in a pH 7.4 phosphate buffer, of tinplate after dip and CDC treatments.

Considering the species as proposed in table 5.1, the potential shift obtained between dip and CDC treated samples might be due to the presence of hydrated chromium species on the latter. In order to evaluate this, chromium hydroxide was chemically removed from the surface of a CDC treated sample by immersing the passivated tin sample in boiling 1N NaOH for 1 minute followed by rinsing and drying before testing. The potentiodynamic scan, shown in figure 5.3, indicates that some chromium was removed from the CDC material by this treatment, leaving only the insoluble species (Cr_2O_3 and Cr^0) on the surface.

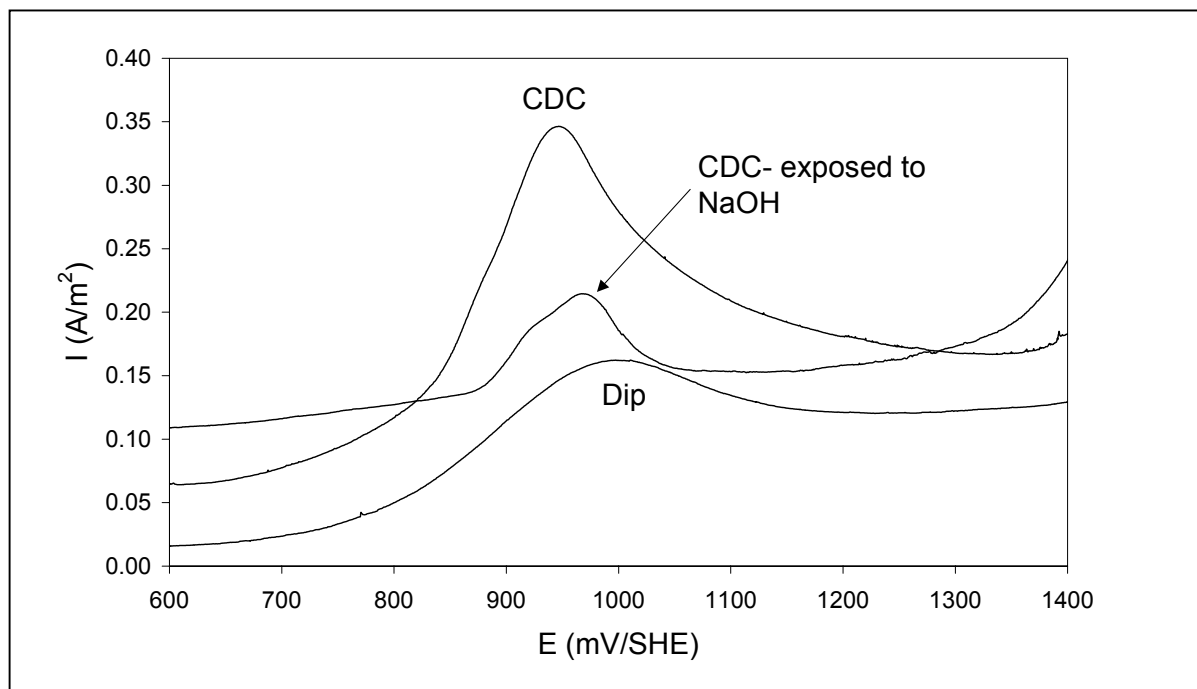


Figure 5.3 – Potentiodynamic polarisation curves, determined in a pH 7.4 phosphate buffer, of tinplate after dip passivation, CDC passivation and CDC passivation leached in NaOH.

In addition to the chemical removal of chromium hydroxides, thermal treatment by heating the sample could also dehydrate the surface species. When the CDC treated sample was subjected to a thermal treatment of heating it to 200 °C for 30 minutes, behaviour similar to that of the caustic treated CDC samples was found in terms of the chemical shift toward the potentials for dip treatment. Furthermore, a duplet peak was also observed for the stoved sample as shown in figure 5.4. The occurrence of a duplet peak is probably due to the different temperatures at which the chromium species are dehydrated. Vucich (1974) identified at least four stages of chromium dehydration occurring at temperatures between 177°C to 510°C, as shown in figure 5.5. At 200°C only partial dehydration of $2\text{Cr}(\text{OH})_3 \cdot \text{H}_2\text{O}$ to $\text{Cr}(\text{OH})_3$ is therefore expected.

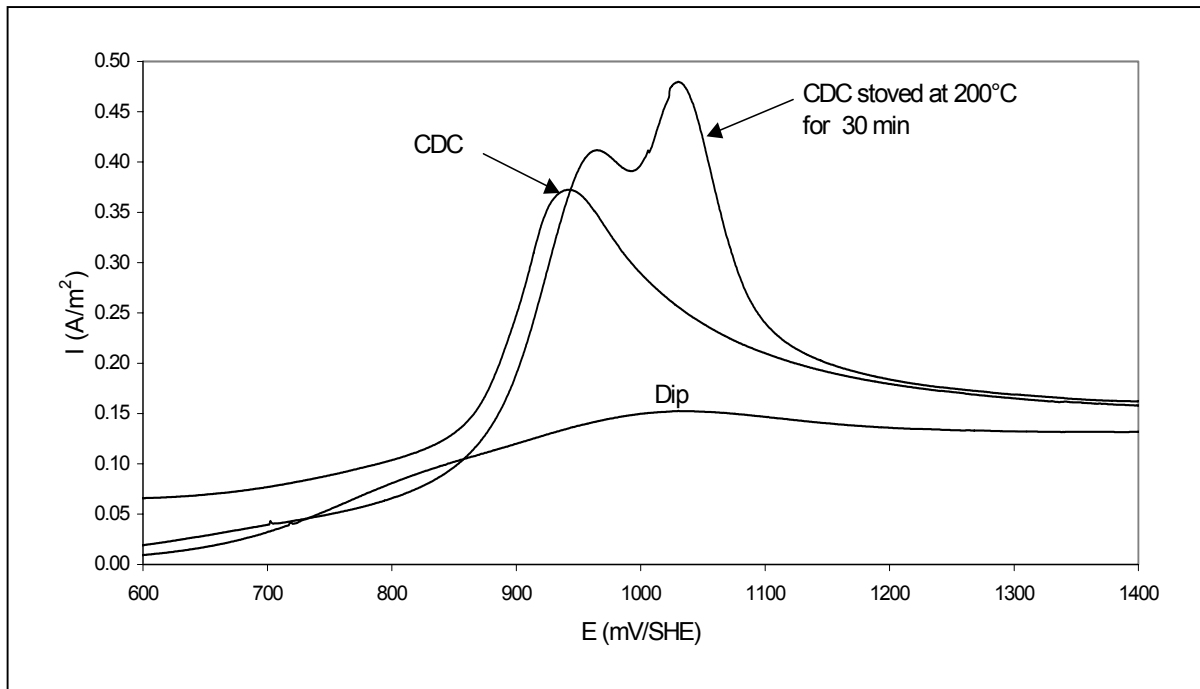


Figure 5.4 - Potentiodynamic polarisation curves, obtained in a pH 7.4 phosphate buffer, of tinplate after dip passivation, CDC passivation, CDC passivation stored at 200°C.

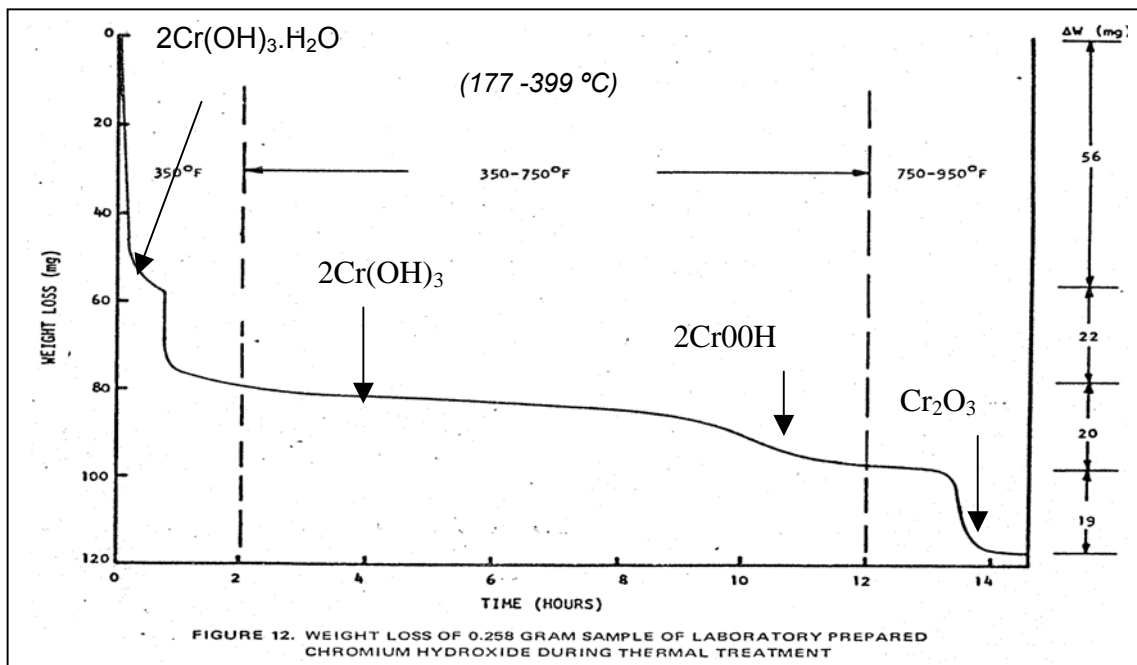


Figure 5.5 – Temperature dependence for the dehydration of chromium (Vucich 1974)

The galvanostatic polarisation curves on the unstoved and stoved CDC samples revealed a bigger overall potential arrest for the latter as indicated in figure 5.6. Two potential arrests can be identified for the stoved tinplate, corresponding to the potentials of the peaks identified on the potentiodynamic polarisation curve (figure 5.4). Recalculation of the amount of chromium present on the surface, based on the longer potential arrest obtained for the stoved CDC samples, revealed that the chromium increased from 4 to 5.9 mgCr/m² due to stoving. This indicates that Briton's method did not detect the hydrated chromium hydroxide present on the surface, which suggest that the electrochemical results for chromium determination is a function of the nature of chromium species present on the surface. This was further investigated using XPS characterisation of the surface species.

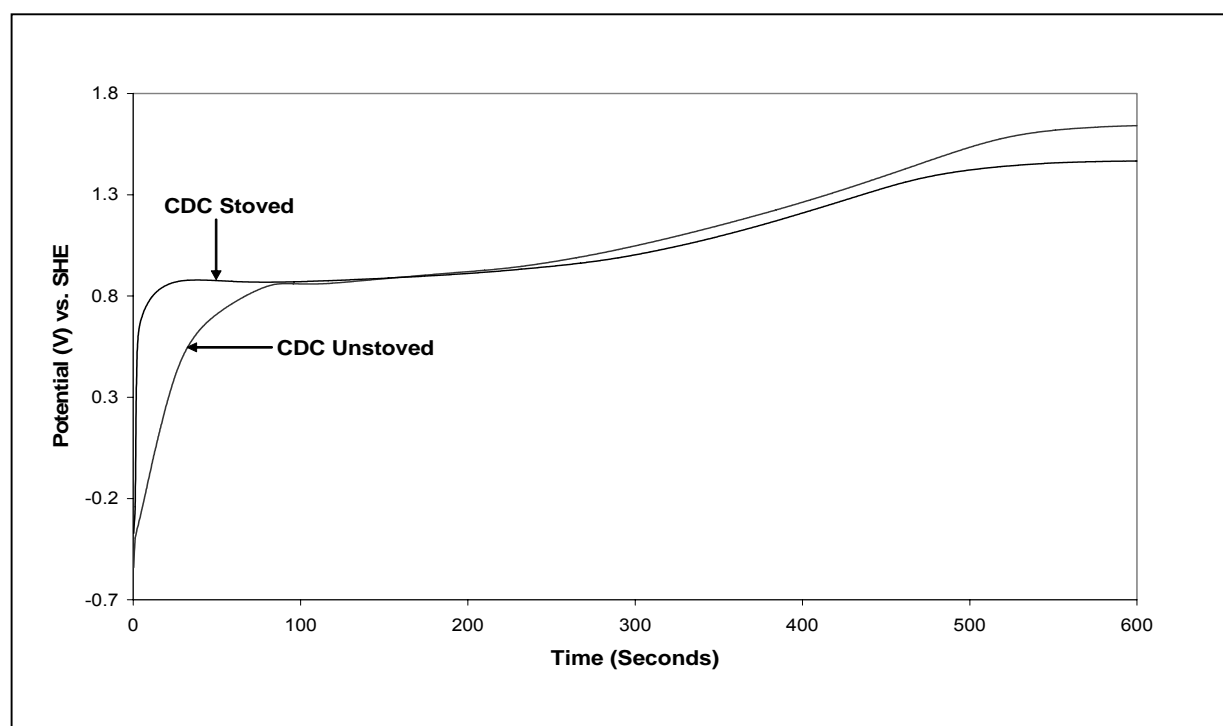


Figure 5.6 – Galvanostatic polarisation behaviour of unstoved and stoved and CDC treated tinplate.

5.3 XPS characterisation of dip and CDC passivation layers

XPS spectra obtained on dip and CDC tinplate samples, shown in figures 5.7 and 5.8, indicate the presence of less chromium and more tin species for dip treatments than for CDC treatments, as expected. No other contaminants, apart from carbon, were detected on these production sample surfaces.

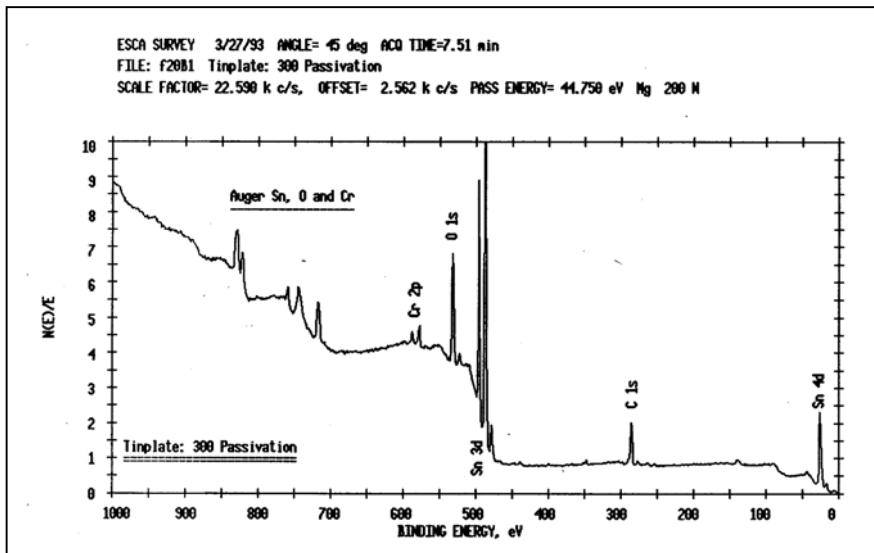


Figure 5.7 - XPS survey analysis for tinplate, passivated with a sodium dichromate dip treatment.

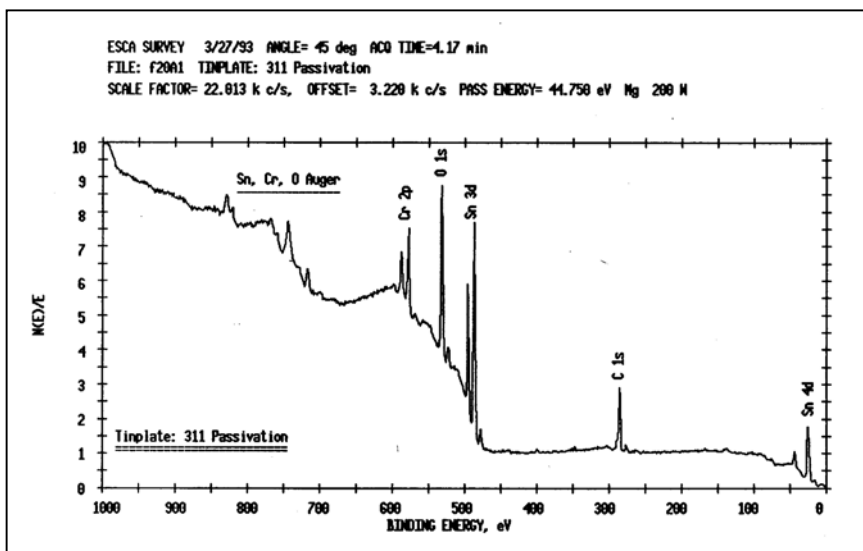


Figure 5.8 - XPS survey analysis for tinplate, passivated with a CDC treatment.

The carbon peaks, for both the dip treated and CDC treated tinplate samples, have the same shape indicating a predominance of (C-H) species as well as no charging of the samples (figure 5.9). The survey analyses can therefore be normalised to a binding energy of 285 eV.

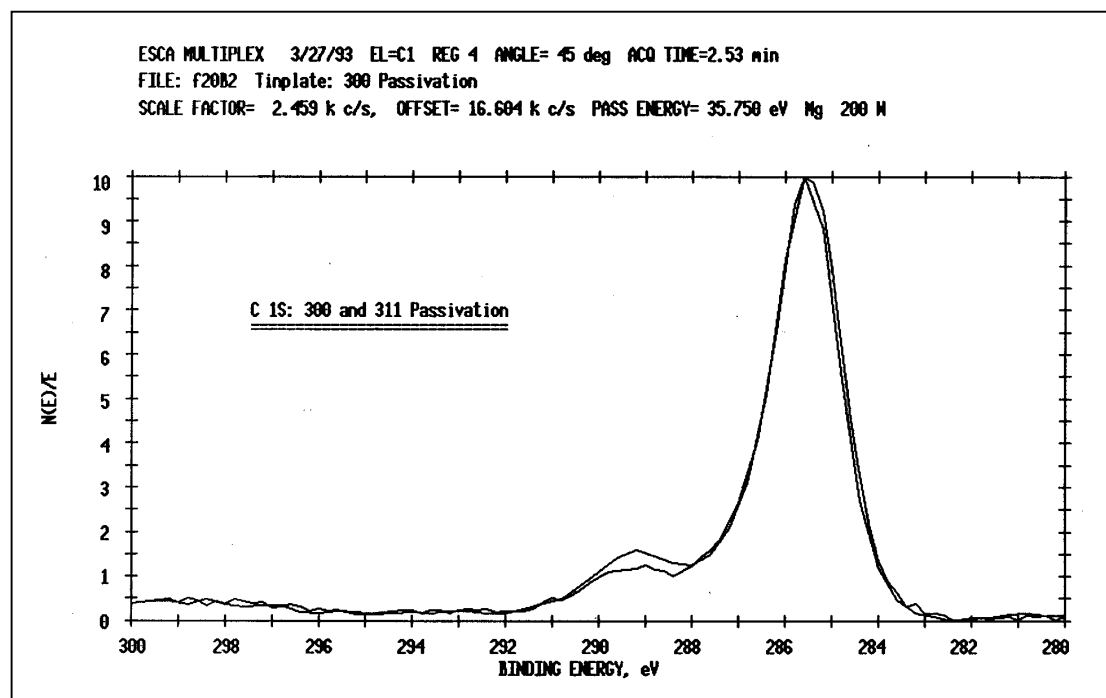


Figure 5.9 – Comparison of carbon XPS peaks for the dip- and CDC treated samples before normalisation.

This normalisation procedure allows the comparison of dip and CDC samples in terms of their tin and chromium peaks, shown in figure 5.10. The shapes of the Cr 2p and Sn 3d peaks, for dip and CDC treated samples, are not significantly different apart from the slightly bigger shoulder on the CDC spectrum for the latter. However, the O 1s peaks as shown in figure 5.11 reveal a significant increase in the binding energy, at the maximum of the peak, for the CDC tinplate.

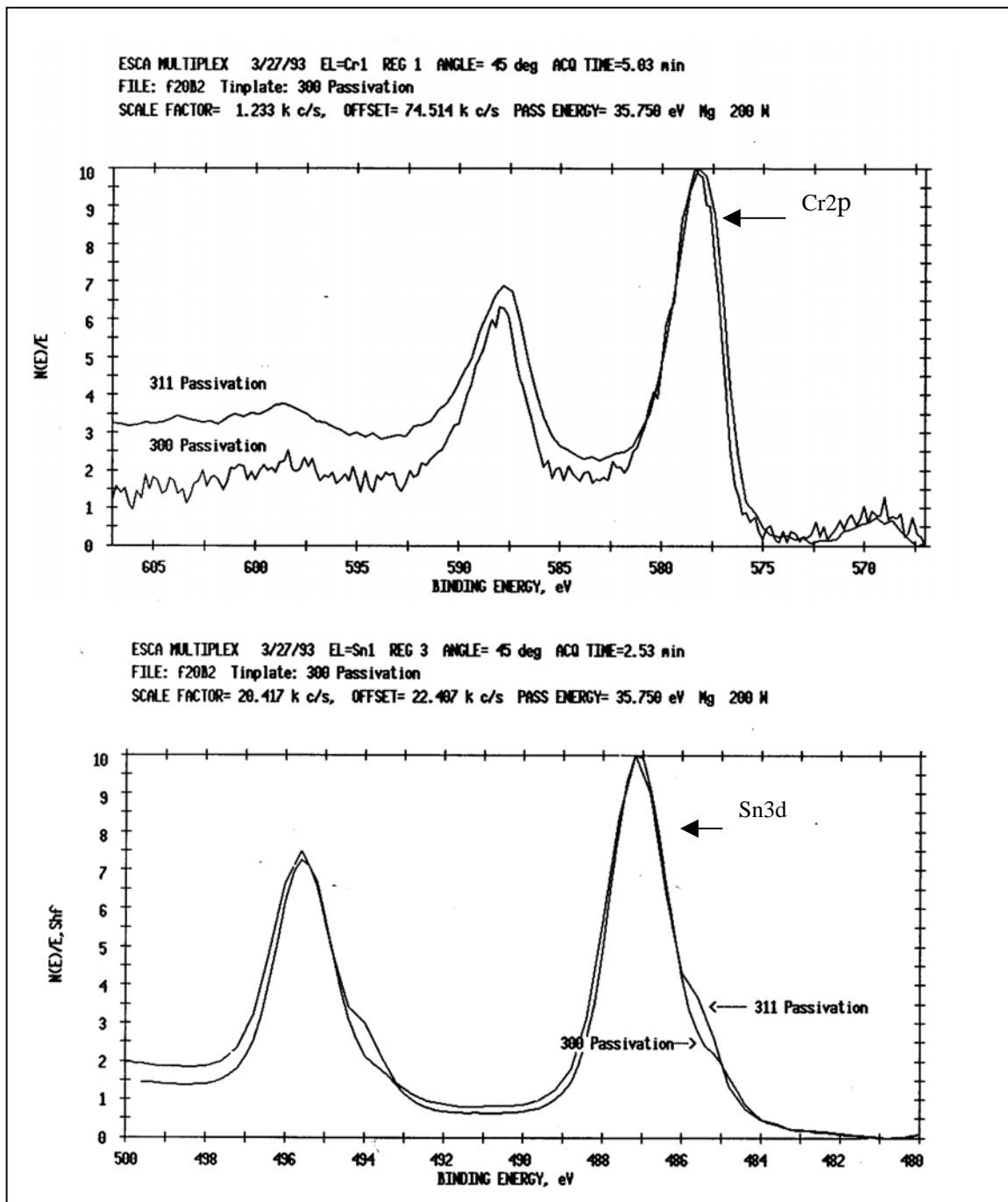


Figure 5.10 – Comparison of Cr 2p (top) and Sn 3d (bottom) for the dip- and CDC treated samples.

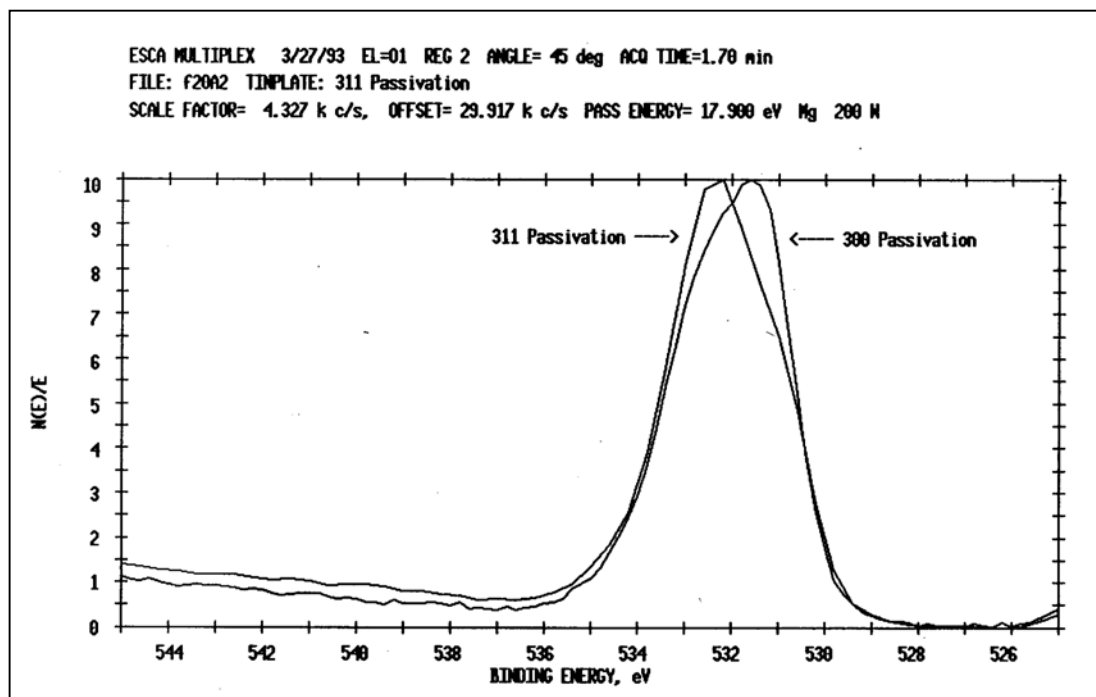


Figure 5.11 - Comparison of the O 1s peaks for the dip- and CDC treated tinplate samples.

In order to explain these apparent differences, XPS multiplex analyses would assist in identifying the different species contributing to the shape of the peaks. However, multiplex analyses of the oxygen peaks are extremely complex due to the large number of species, especially on CDC treated material that needs to be fitted under the peaks. Multiplex analyses of the Sn 3d and Cr 2p peaks are therefore more appropriate, as fewer species need to be fitted.

Multiplex analyses of the Sn3d peaks as shown in figure 5.12, indicate the presence of SnO₂ and Sn⁰ on the dip treated tinplate while the CDC treated tinplate surface also contains SnO.

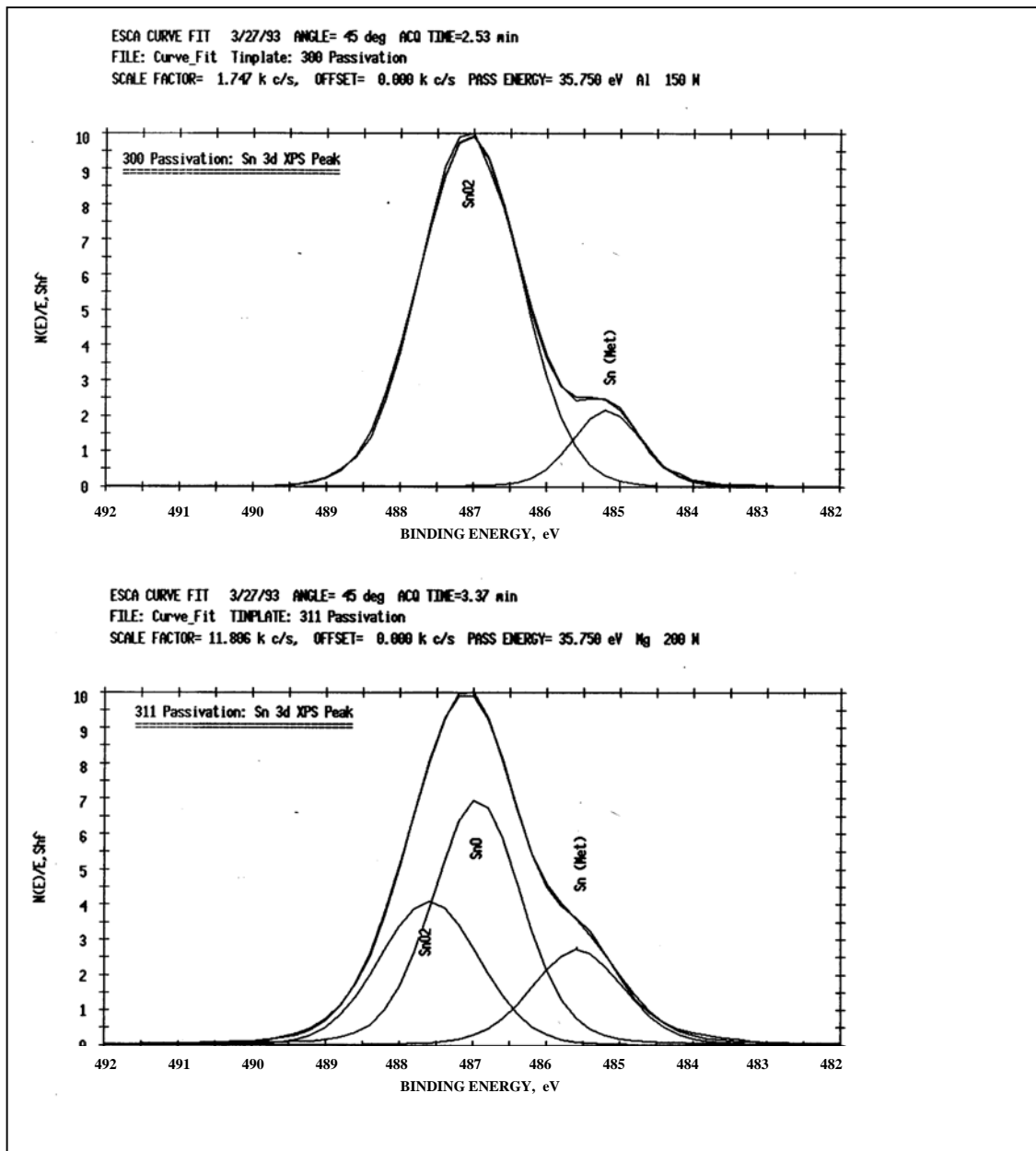


Figure 5.12 – XPS multiplex analysis of the Sn 3d peak dip treated tinplate (top) and CDC treated tinplate (bottom).

Metallic tin is however not necessarily part of the passivation layer as the contribution of the substrate to the signal, especially for dip treated layers, could account for this. As the depth resolution of XPS is only 1-4 monolayers for tin and chromium, angle resolved analysis might be used to determine the position of the species relative to

the substrate, provided that the layer is continuous. Transmission Electron Microscopy was used to confirm that the passivation layer is indeed amorphous and continuous on a nanometre scale (Tuling et al., 2004). As shown in figure 5.13, the increase in the Sn^0 peak obtained at the higher take off angle, where the depth penetration was higher, indicates that it is indeed the Sn^0 in the substrate that is detected.

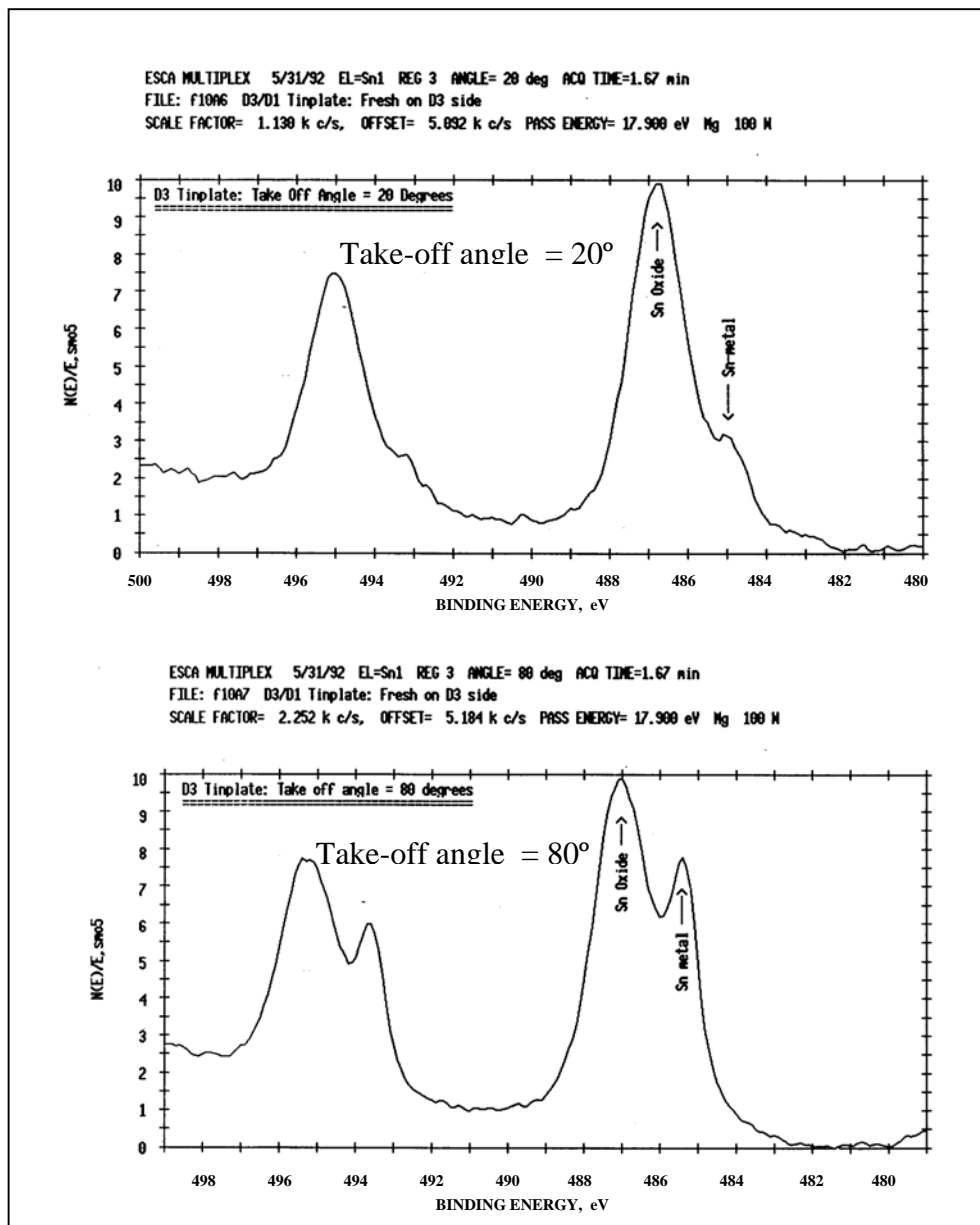


Figure 5.13 – XPS angle resolved analysis of a CDC treated sample.

The multiplex analyses of the Cr 2p peaks for dip and CDC treated tinplate, shown in figure 5.14, indicate the presence of Cr_2O_3 on both samples, but $\text{Cr}(\text{OH})_3$ on only the CDC treated samples. In addition, dichromate residues were also identified in both cases. Also note that no metallic chromium was detected.

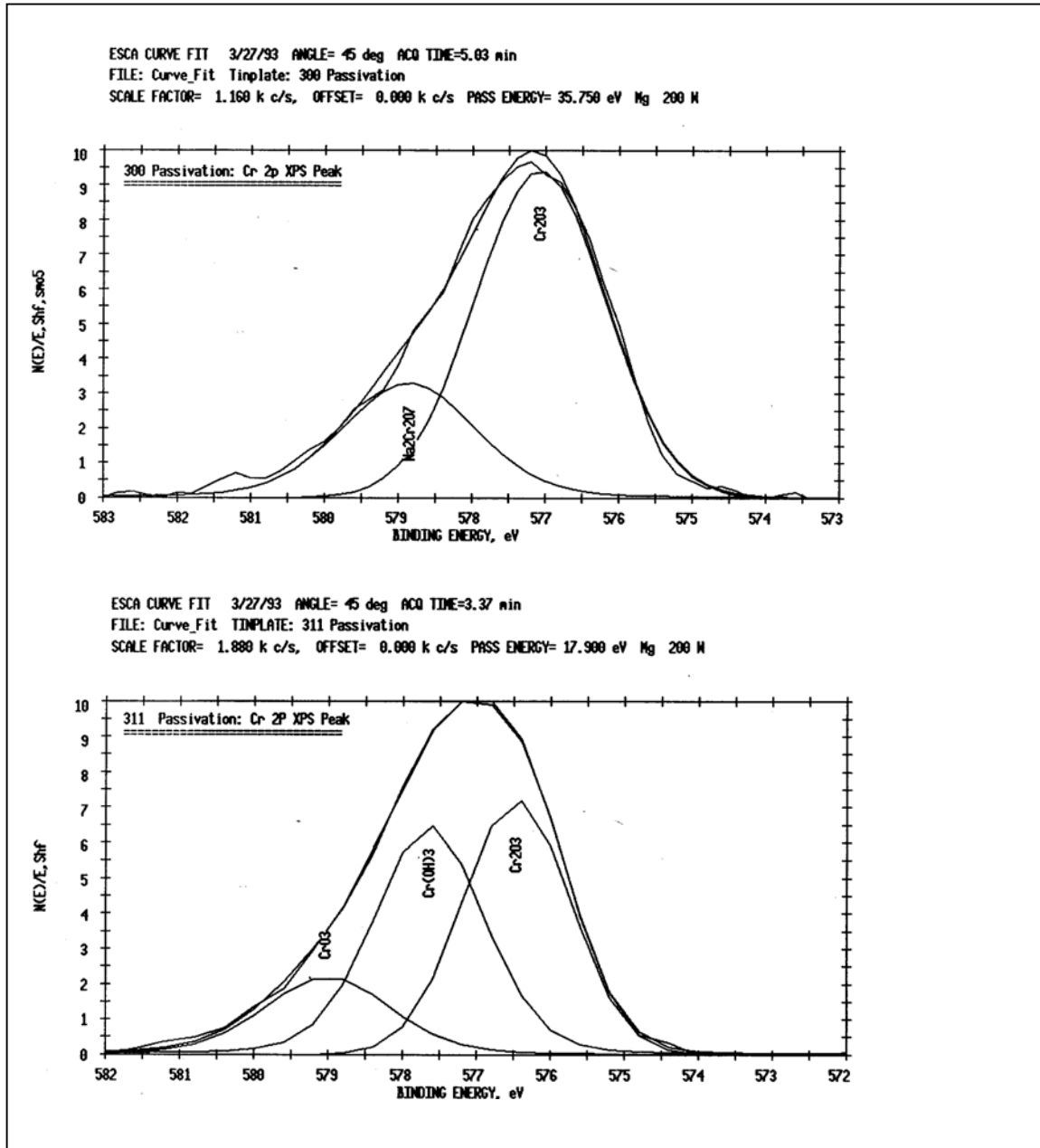


Figure 5.14 – XPS multiplex analysis of the Cr 2p peak dip treated sample (top) and CDC treated sample (bottom).

In view of the uncertainty regarding the presence or not of Cr^0 on CDC passivated tinplate and especially on the possible reduction of chromium species by argon sputtering, XPS angle resolved analyses were used in an effort to resolve this issue.

For reference a pure chromium specimen was used. The sample preparation involved abrading the sample surface in water to remove existing oxides just prior to analysis. Only the extremely thin surface oxide film that formed after the surface preparation was therefore expected. The survey analysis of this sample indicating no external contamination is shown in figure 5.15.

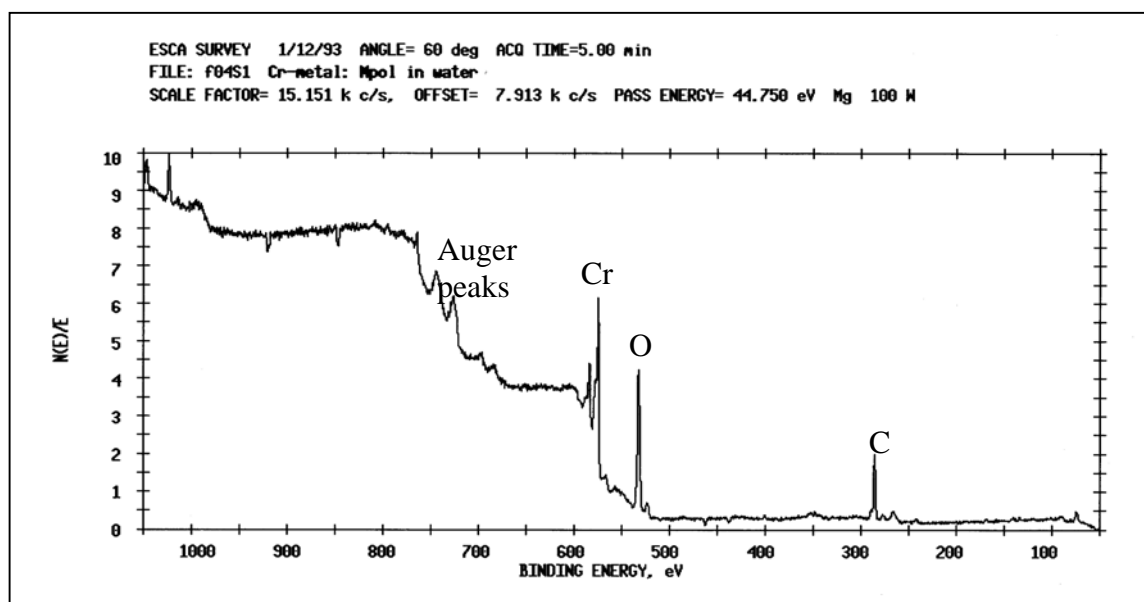


Figure 5.15 - XPS survey analysis of the mechanically polished chrome standard.

Angle resolved XPS analyses, shown in figure 5.16, indicate an increase of metallic chromium detected from the substrate as the take-off angle is increased as would be expected for such a thin layer. The position of metallic chromium XPS peak was therefore established to be at a binding energy of 575 eV.

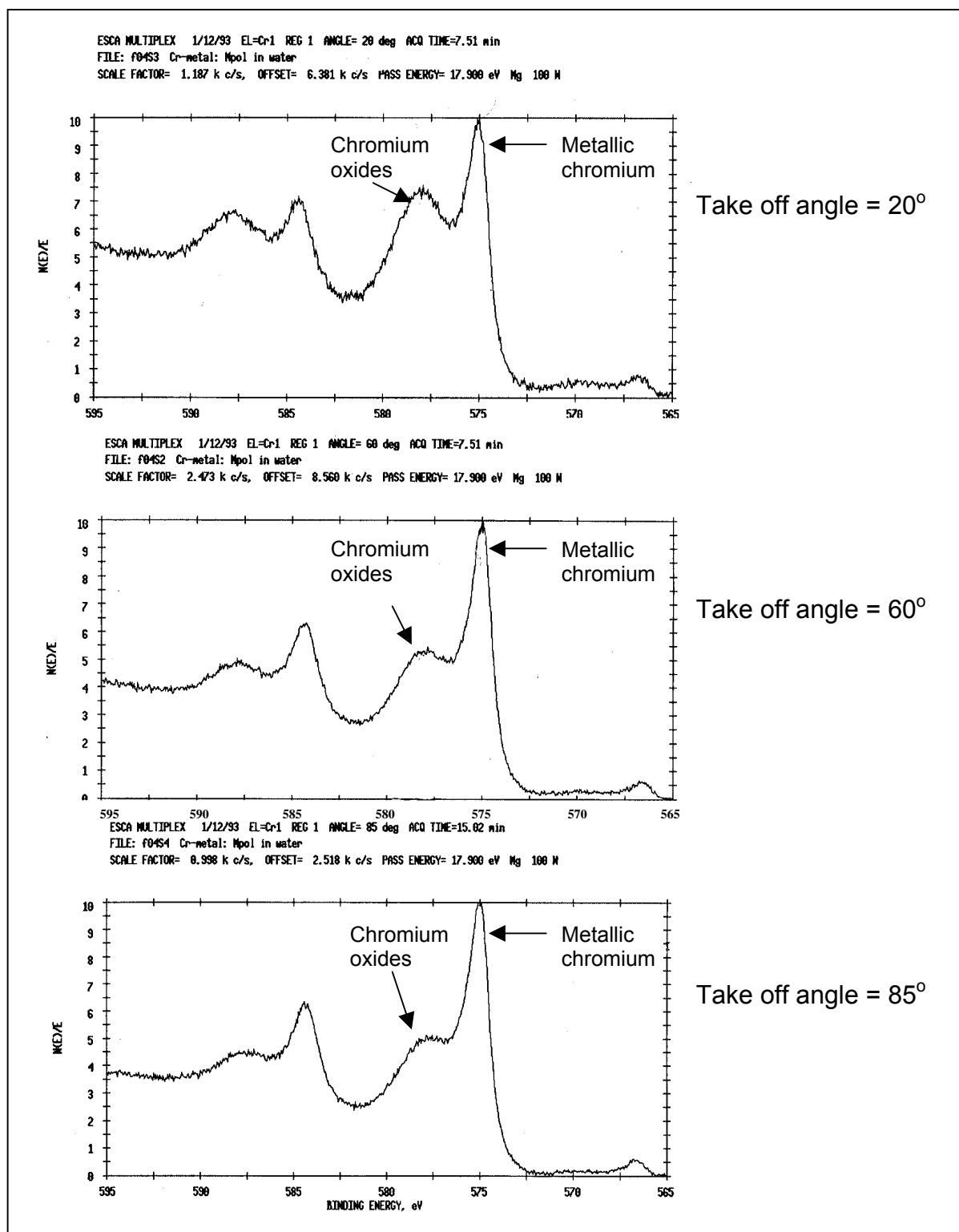


Figure 5.16 - Angle resolved XPS survey analysis of a pure chromium sample.

Angle resolved XPS analyses of the Sn 3d and Cr 2p peaks on CDC passivated tinplate, as shown in figure 5.17 (left) and 5.17 (right) respectively, indicated that the Sn⁰ peak becomes more prominent at higher take off angles, as would be expected, but that the chromium peak is not significantly dependant on the take off angle. It is also noted that the Cr⁰ peak does not appear at any stage. This is therefore a clear indication that metallic chromium is not present in CDC passivated tinplate.

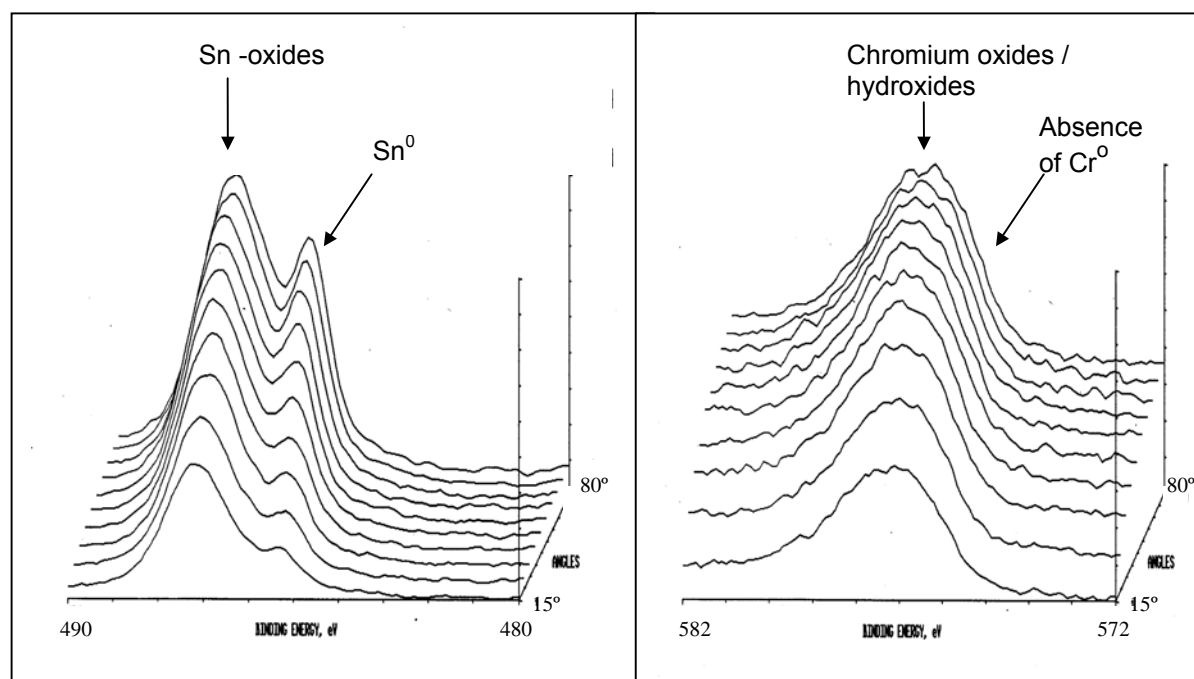


Figure 5.17 - Montage Sn 3d (Left) Montage Cr 2p (Right)

While it may not be possible to do multiplex analysis of the O 1s XPS peaks, some useful information may still be gained by following the influence of various treatments on these peaks. For convenience, the oxygen containing species making a contribution to the peaks, are summarised in figure 5.18. Apart from the chromium and tin species, tinplate would also contain some adsorbed surface water due to atmospheric exposure.

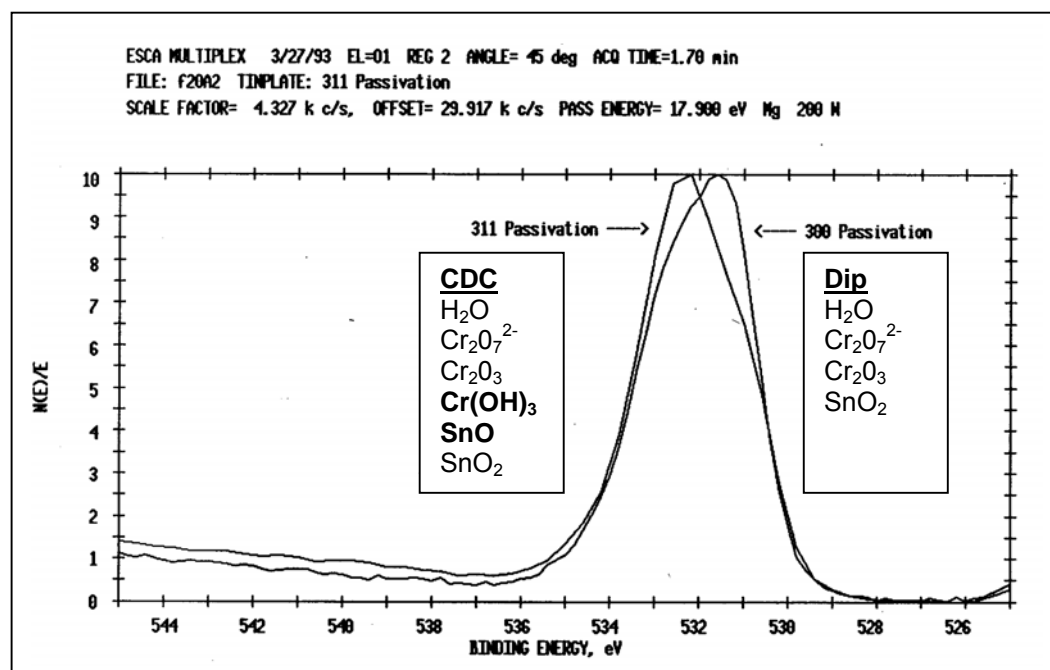


Figure 5.18 - Comparison of the O 1s peaks for the dip- and CDC treated samples

It is, however, not clear whether the Cr(OH)₃ or the SnO species makes the major contribution to the difference in the peaks. To further investigate this, stoving experiments at 200°C for 10 minutes in a nitrogen atmosphere were done; the inert environment was used to limit further oxidation of either species, while allowing dehydration. Both the sample and introductory chamber of the XPS were kept under a nitrogen atmosphere until pump down for the ultra high vacuum started. This ensured that the sample was not exposed to the atmosphere during heat treatment, cooling down and transfer to the instrument.

As quality measure to verify that no oxidation of tin had occurred, the shape of the Sn peaks before and after nitrogen stoving, as shown in figure 5.19, were compared and indicated that neither oxidation nor reduction of the tin occurred during the heat treatment.

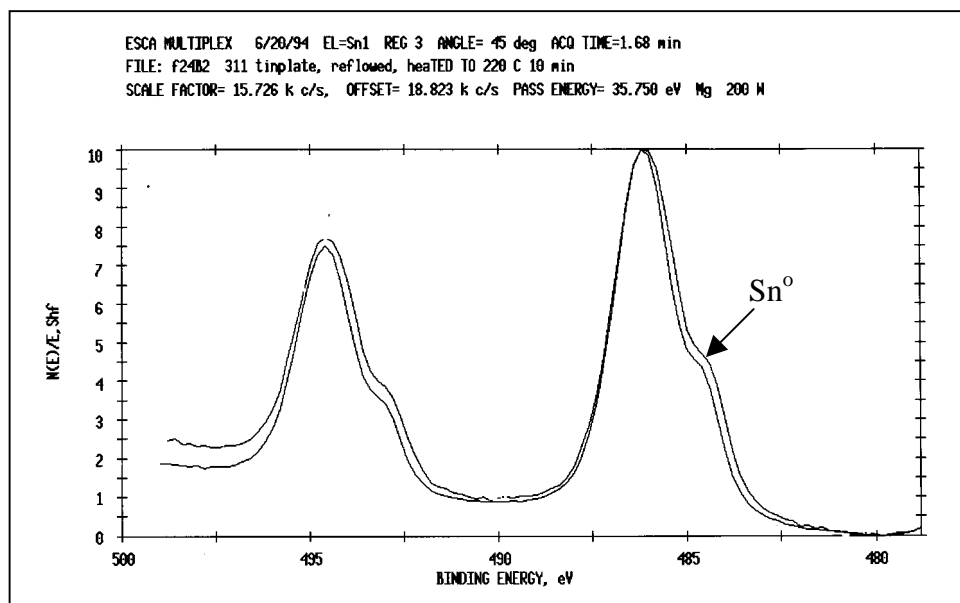


Figure 5.19 – XPS Sn peaks for the CDC treated sample before stoving as well as after stoving under nitrogen.

However, the heat treatment caused a shift of the O 1s peak's maximum to a lower binding energy, as indicated in figure 5.20. This indicates that the speciation on the CDC tinplate became more like that of dip-passivated tinplate during the heat treatment, which most probably only dehydrated the more-hydrated chromium species, which formed during CDC passivation.

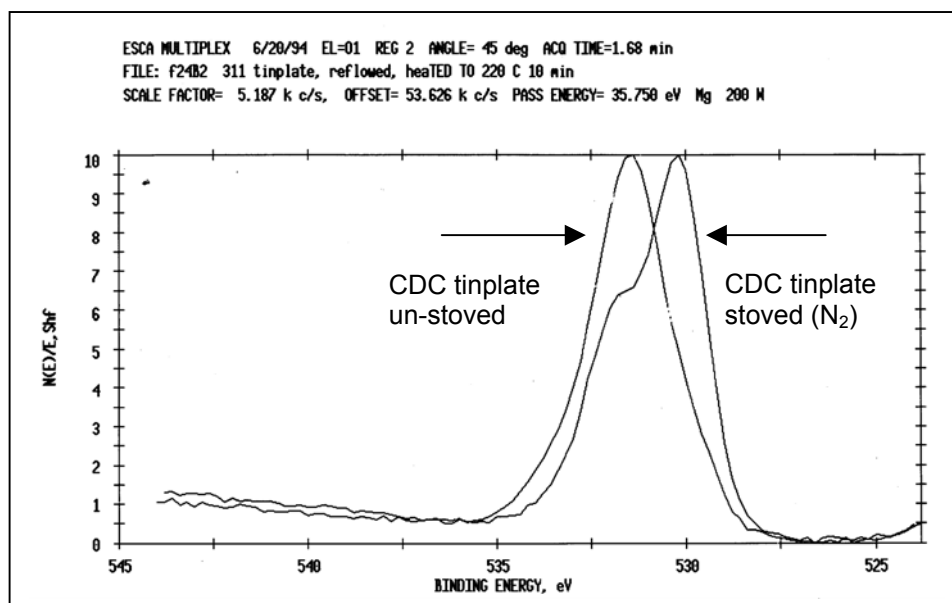


Figure 5.20 – XPS O 1s peaks for CDC passivated tinplate showing the effect of stoving under a nitrogen atmosphere.

5.4 Influence of operational parameters on chromium passivation

The results obtained indicate that during dip passivation, chromium deposition results from the reduction of chromium (VI) species in solution by oxidation of tin surface species present on the tinplate surface. It thus follows that the degree of prior oxidation of the tin could determine the quantity of chromium deposited and thus the quality of the passivation layer produced. In the case of the CDC passivation treatment the dependence of oxidisable species on the surface is circumvented by the application on cathodic polarisation. However, although the thicker chromium layers so achieved generally provide better corrosion protection, poorer lacquer adhesion may result as a result of the formation of more highly hydrated chromium species, formed at higher pH conditions resulting from the co-precipitation of hydrogen gas. The pH change at the surface could possibly be reduced by the

addition of a buffer to the passivation solution or more careful control of the polarisation applied. These aspects are investigated in the following sections.

5.4.1 Influence of tin species on the deposition of chromium during dip passivation

The influence of tin oxidation, prior to dip passivation treatments, on a tin metal sample was investigated by using a tin metal sample that was mechanically polished to a surface finish of 1200 grit, followed by an ethanol rinse and drying, and then oxidised at 212 °C in air for 60 minutes. A thick oxide layer formed on the sample as indicated by a significant yellowing of the surface, shown in figure 5.21.

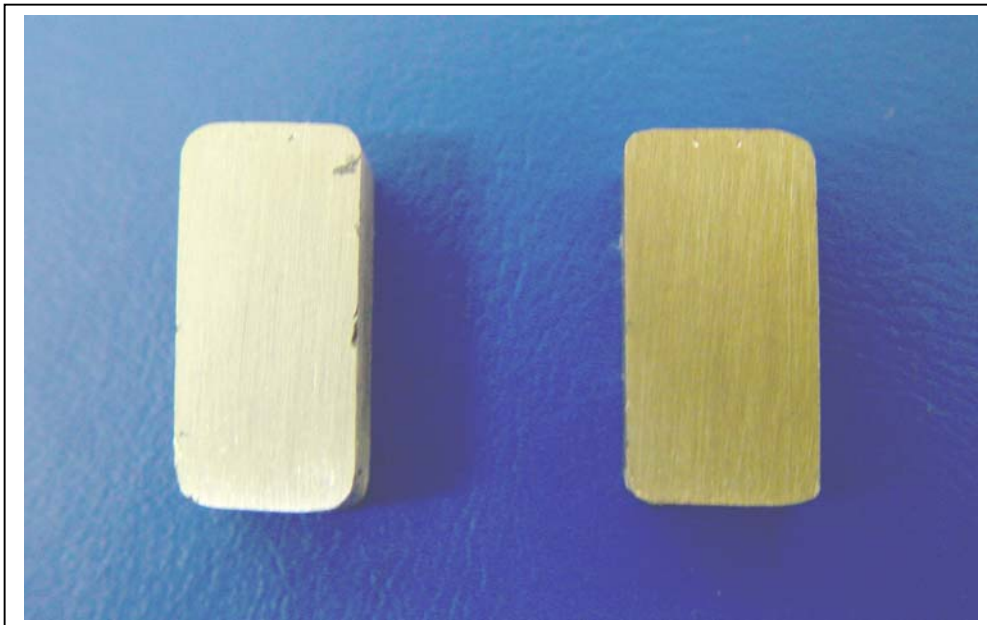


Figure 5.21 - Influence of air oxidation on the surface appearance of tin metal, (left) as abraded and (right) after oxidation.

XPS survey analysis of the oxidised tin sample is shown in figure 5.22 and indicates that apart from carbon, no other contaminants were present on the surface.

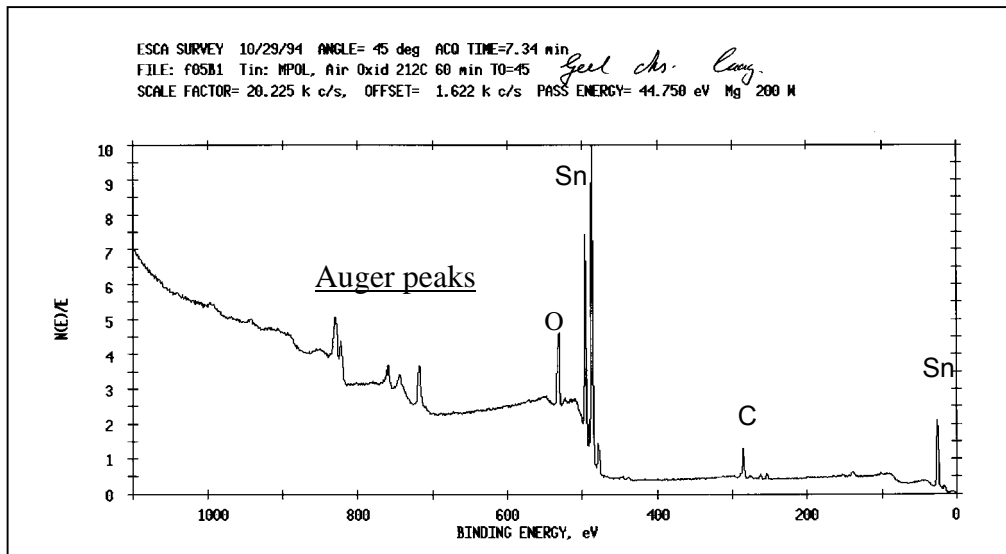


Figure 5.22 - XPS survey of air oxidised tin metal at a take off angle of 45°.

Inspection of the Sn3d peak shown in figure 5.23 indicated no metallic tin peak suggesting the presence of a thick oxide film of more than 4 monolayers.

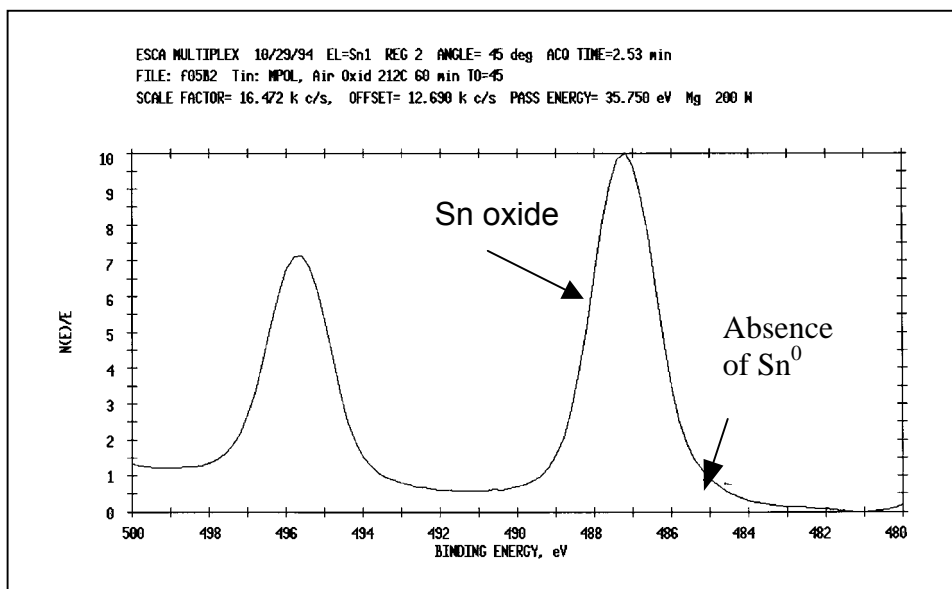


Figure 5.23 – XPS Sn 3d peak obtained on the oxidised tin metal surface at a take off angle of 45°.

The oxidised tin sample was then passivated by means of a dip treatment in 25g/l sodium dichromate at 60°C for 4 seconds. The XPS survey analysis taken after the passivation treatment is shown in figure 5.24 and indicates that no chromium was deposited on this sample. This confirms that when tin is in its highest oxidation state, no reduction of chromium could take place during dip treatments, and that the adsorption of chromium does not occur to any significant extent. This confirms that tin species with lower oxidation states are required for chromium deposition during a dip passivation treatment.

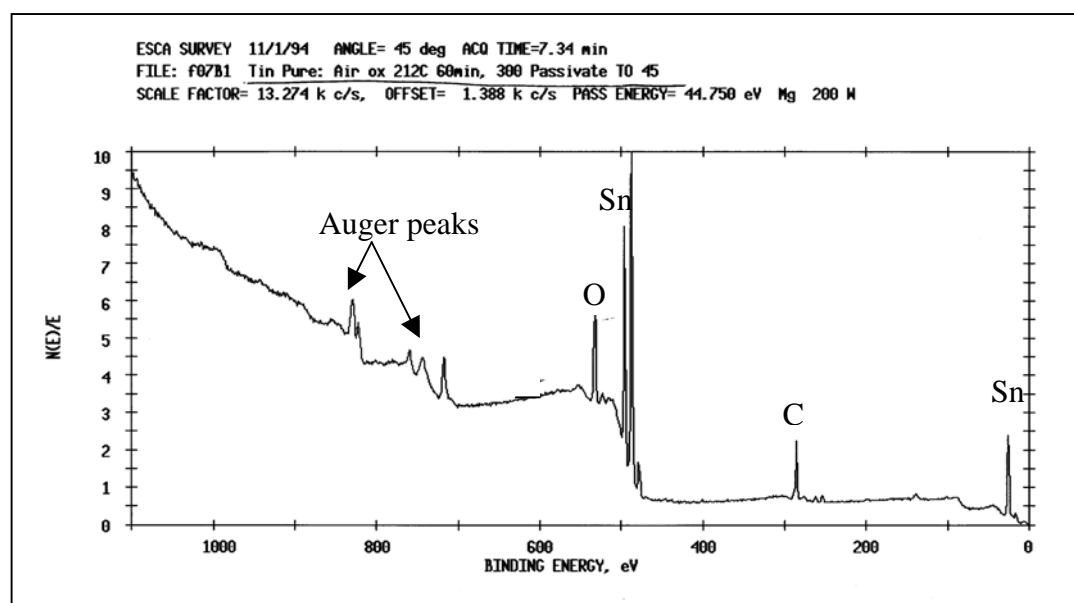


Figure 5.24 - XPS survey of oxidised tin metal, passivated with a sodium dichromate dip treatment. Note the absence of chromium peaks at a binding energy of approximately 580 eV

5.4.2 Influence of tin species on the deposition of chromium during CDC passivation

Although the deposition of chromium species during CDC passivation is not dependant on the oxidation of tin species, the properties of the surface layers might be a function of the oxidation state of the tin species. Observation of the oxidised tin

metal sample during CDC treatment, suggested that the tin oxides are quickly reduced as indicated by the disappearance of the discolouration of the surface during the initial stages of cathodic polarisation.

However, the time available for the CDC passivation treatment is typically very short and the presence of tin oxides on the surface may still reduce the deposition of chromium species. To further evaluate this, tin samples were prepared, of which the oxides were removed by means of a cathodic sodium carbonate (CSC) treatment, followed by an immediate CDC treatment. The other samples used during the test were just wet grinded, rinsed and then CDC passivated.

During the CSC treatment, the oxides on the tin samples were cathodically reduced in a 1% Na_2CO_3 aqueous solution at 50 °C to a charge density of $1\text{C}/\text{cm}^2$. The CDC passivation treatment followed immediately and was done in a 2.5% $\text{Na}_2\text{Cr}_2\text{O}_7$ solution at 70°C at a current density of $10\text{ A}/\text{dm}^2$ for a range of times. The exposure times were controlled by a timing device that automatically switched the current on as the sample was immersed and switched it off as the set time elapsed. The exposure times were varied from 0.5 – 5 seconds.

The Auger survey analyses of two of the samples are presented in figures 5.25 and 5.26. Due to the low carbon contamination and the absence of other contaminants on the surface, these spectra can be used for comparative purposes regarding the amount of chromium present on the surface.

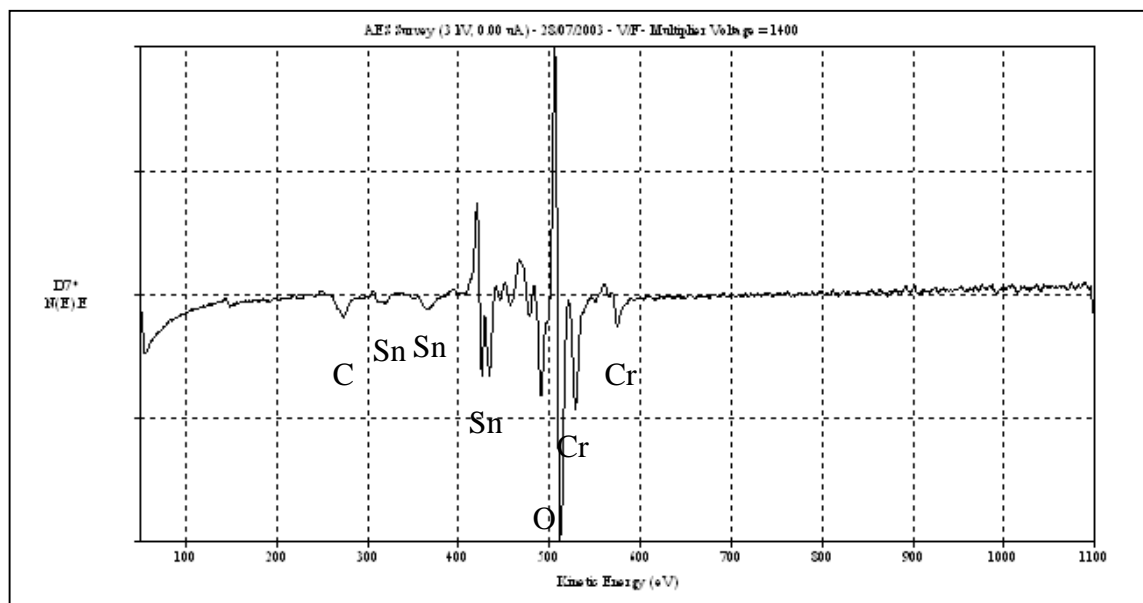


Figure 5.25 – Auger spectrum for the CSC – CDC treated sample. CDC treatment time = 0.5 seconds.

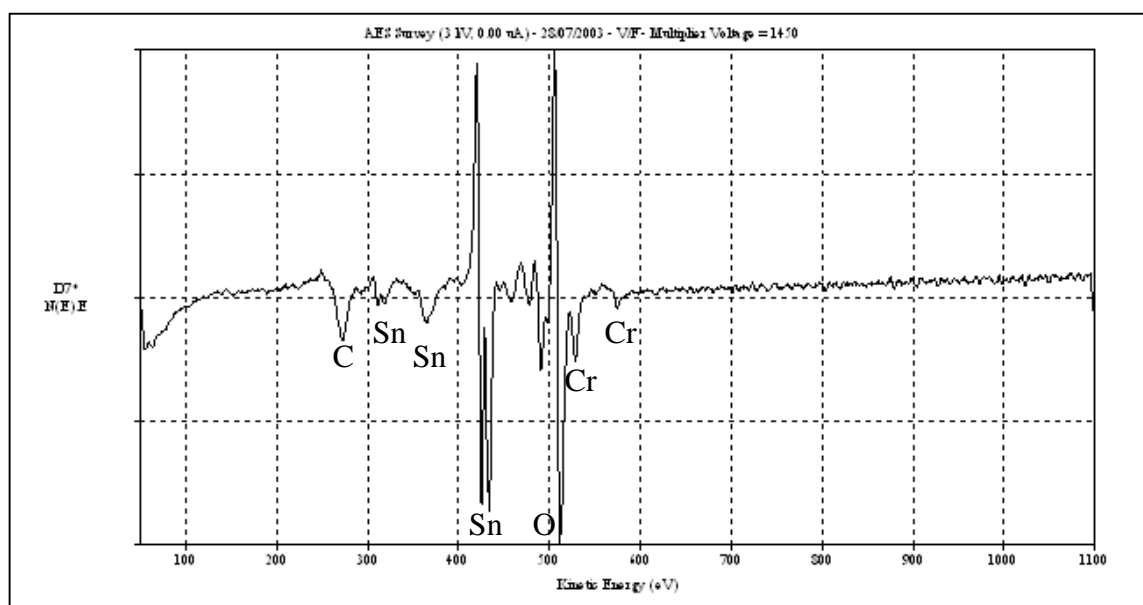


Figure 5.26 – Auger spectrum for the CDC treated sample. CDC treatment time = 0.5 seconds.

From the spectra it can be inferred that more tin and less chromium was present on the sample of which the tin oxides were not removed prior to the passivation treatment. As the passivation time was extended the chromium levels increased, as shown by the ratio of Cr / Sn peak heights, obtained from the Auger spectra, shown in figure 5.27.

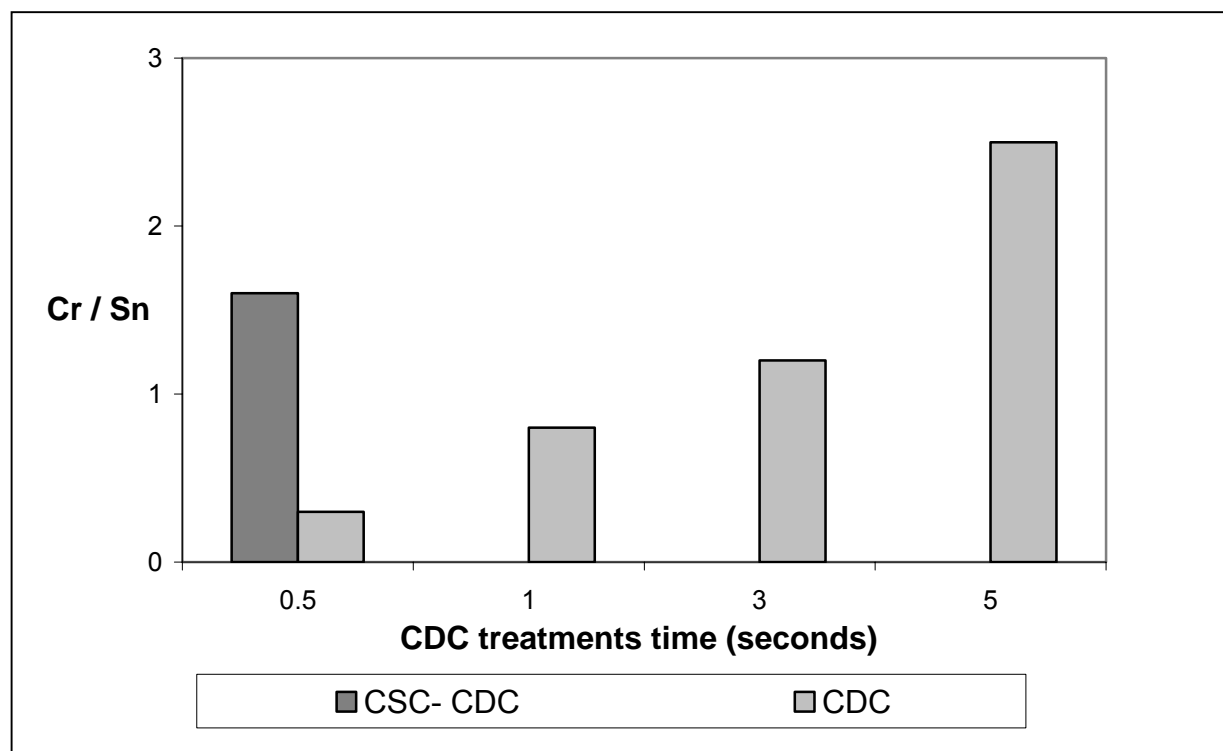


Figure 5.27 - Chromium / tin peak height ratio comparing a CSC-CDC treatment with normal CDC treatments.

Similarly, the presence of a rather thick tin oxide, produced by air oxidation at 212 °C for 15 minutes, reduced the amount of chromium deposited during a 1 second CDC treatment, as shown by the small Auger peaks for chromium in figure 5.28. Removal of oxides by a CSC treatment significantly increased chromium deposition during the CDC passivation, as shown in figure 5.29.

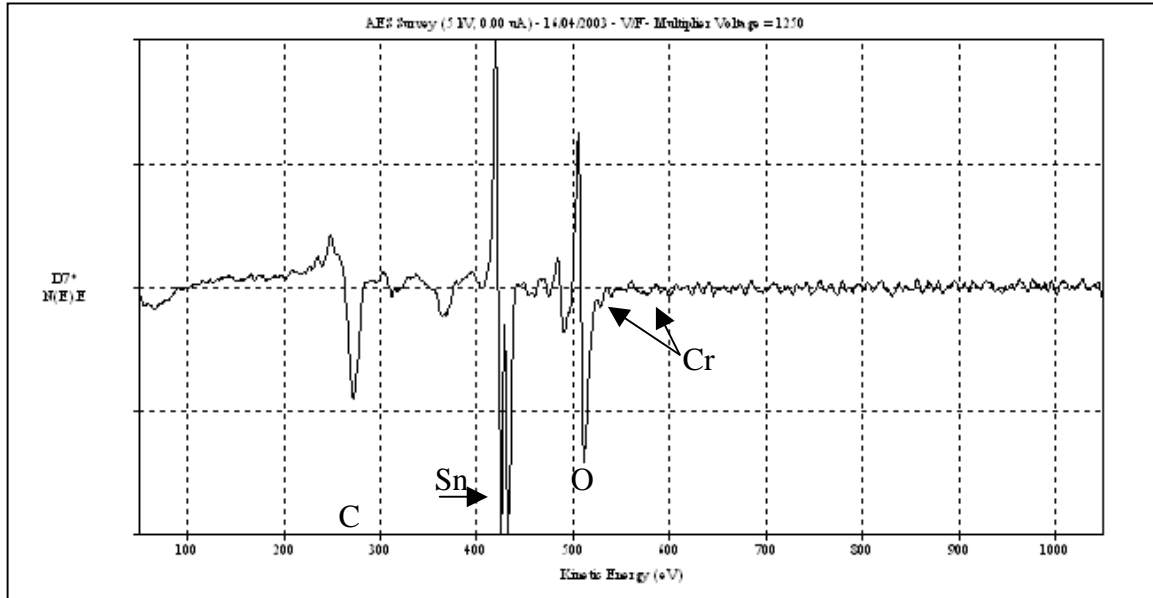


Figure 5.28 - Auger spectrum for the sample oxidised at 212 °C and then CDC treated for 1 second.

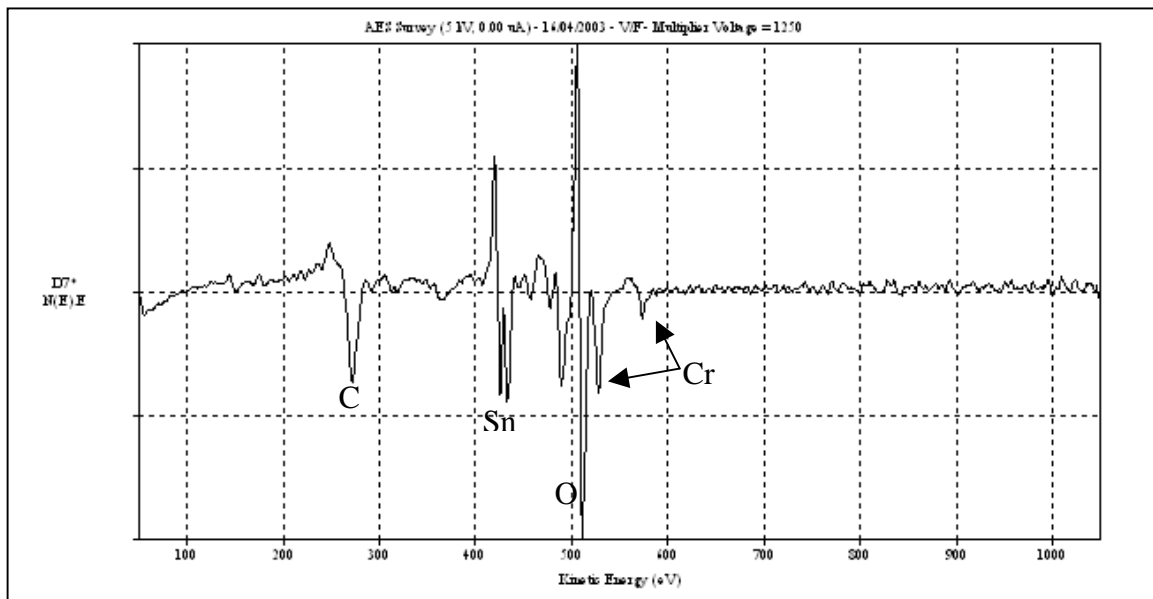


Figure 5.29 - Auger spectrum for the CSC – CDC treated sample. CDC treatment time for 1 second.

5.4.3 Influence of pH on the deposition of chromium species

The influence of the pH of the sodium dichromate solutions used during CDC passivation treatment was evaluated using tin metal samples passivated in unbuffered as well as buffered solutions at a temperature of 60 °C and an applied current density of 10 A/dm² for 4 seconds. The tin metal was wet abraded to a 1200 grit surface finish, rinsed in ethanol and dried in hot air just prior to passivation. Electrolytes containing 25 g/l chromium, as sodium dichromate, but with different pH values, were made up using only sodium dichromate to give a pH of 3.84, sodium dichromate and chromic acid to give a pH of 1.43, and sodium dichromate and caustic soda to give a pH of 6.43. Buffering of the solution was done using 0.2 and 0.5M acetic acid solutions prepared in the ratio of 80 acetic acid to 20 sodium acetate. Potentiodynamic polarisation in a phosphate buffer solution with a pH of 7.4 at 20 °C was done, in an anodic direction at a scan rate of 2 mV/s, to characterise the passive layers obtained.

The results shown in figure 5.30, indicate that significantly more chromium deposited at a lower pH, and that the potential of the peak was slightly more positive, but not as positive as that obtained for the dip treatments. The results for the buffered solutions shown in figure 5.31, indicate that moderate buffering increases the amount of chromium, but that still much less chromium than that obtained at a pH of 1.43, was deposited. Stronger buffering not only increased the chromium deposited, but also moved the anodic peak to more positive potentials, such as achieved with dip treatments. This indicates that the high pH conditions, generated at the metal surface during the CDC passivation, favour the formation of more highly hydrated chromium species.

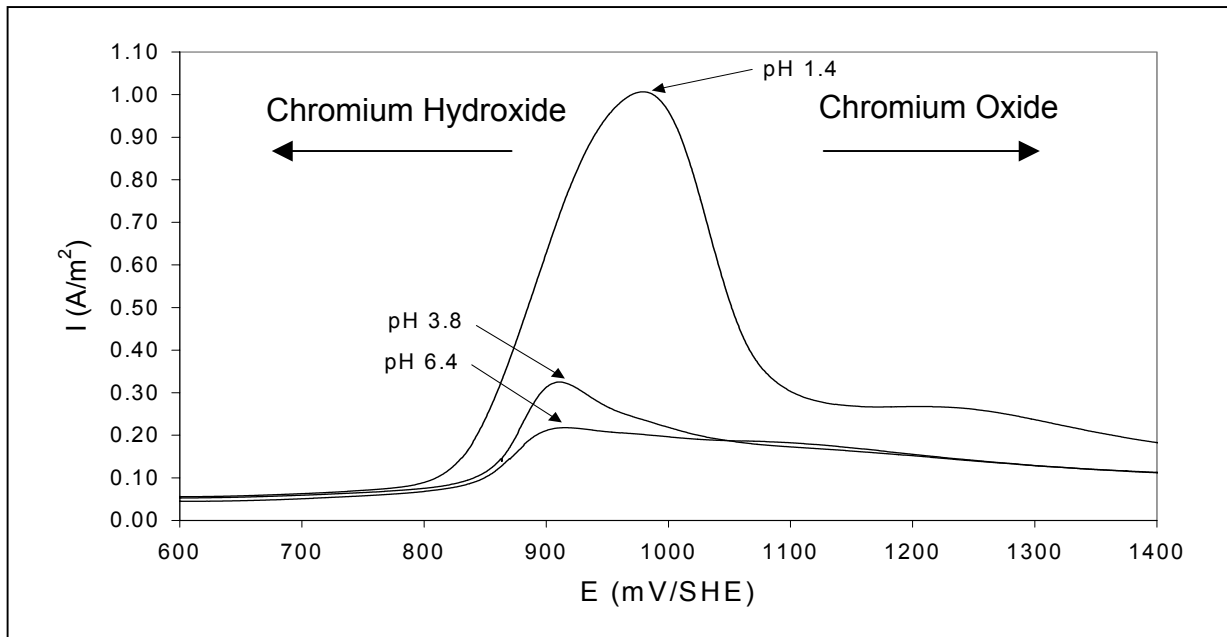


Figure 5.30 – Potentiodynamic polarisation curves, determined in a pH 7.4 phosphate buffer, of tin metal after CDC passivation in dichromate solutions with different pH values.

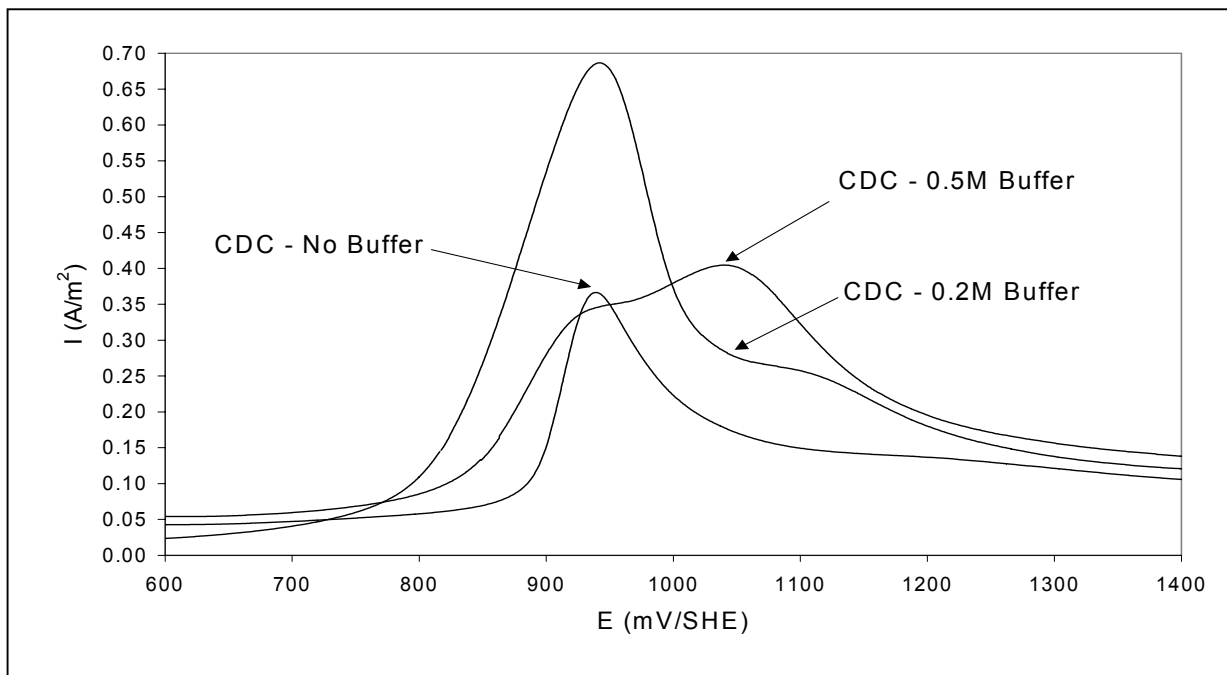


Figure 5.31 – Potentiodynamic polarisation curves, determined in a pH 7.4 phosphate buffer, of tin metal after CDC passivation in buffered dichromate solutions with a pH of 4.

5.5 Lacquer adhesion vs. surface species

The influence of the passivation treatment used on tinplate, and thus the surface species, was evaluated using industrially produced tinplate of the same lot, with either dip or CDC passivation. However, as it was not practical to change the pH of the solution in the industrial plant, tinplate with a heavy tin coating of 18.2 g/m² of tin, from which the passivation was removed by light abrasion using 600 grit paper, was passivated in the laboratory. Lacquer adhesion tests confirmed that the lacquer adhesion on the tinplate was not significantly changed by this treatment. The passivation was done as previously described in table 4.2.

An epoxy phenolic lacquer (Valspar, MBCN 5445), typically used for the inside of three-piece cans, and regarded as most sensitive to the type of passivation treatment (Helwig, 1996), was used. The lacquer was applied with a bar coater (RDS-08) to a coating mass of 30 to 60 mg / m², followed by curing for 10 minutes at 210 °C. The lacquer cured to a golden yellow colour.

The adhesion of the lacquer to the tinplate was then evaluated by gluing two different specimens together, using Henkel Macroplast[®] E6105N, and curing it for 30 minutes at 180°, and then pulling the specimens apart at a rate of at least 200 mm/sec, as shown in figure 5.34.

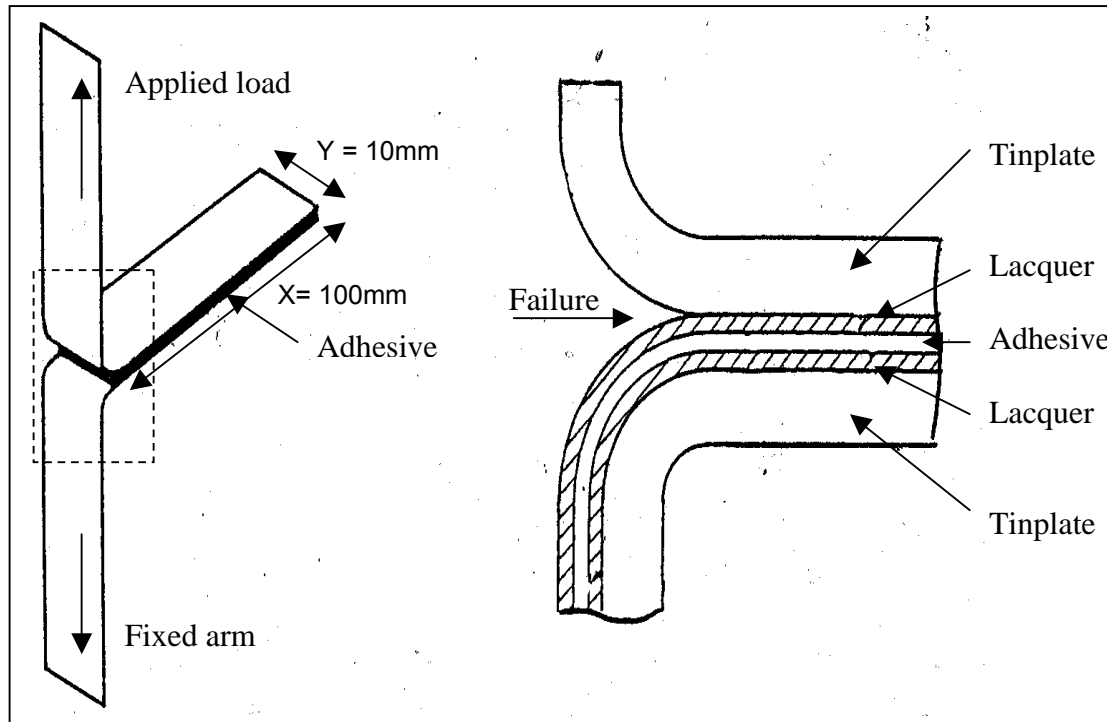


Figure 5.32 - Schematic outlay of the lacquer adhesion tests indicating two tinplate samples (with different passivation treatments) lacquer layers and adhesive between the two samples.

The position of the failure of the bond could easily be identified, as the black adhesive and the golden- yellow lacquer could easily be distinguished from the bare tinplate surface. Adhesion failure between the tinplate and the lacquer was classified as indicated in table 5.3.

Table 5.3 – Criteria for lacquer adhesion failure to tinplate

Scale	Adhesion loss
1	Total adhesion loss
2	75% adhesion loss
3	50% adhesion loss
4	25% adhesion loss
5	No adhesion loss

The results of the adhesion tests as shown in tables 5.4 to 5.8 and figures 5.35 to 5.39 indicate that:

- The lacquer adhesion on the dip-passivated tinplate was better than on any of the CDC passivated samples.
- Buffering of the passivation solution did not significantly improve lacquer adhesion.
- Lowering of the pH of the passivation solution did improve lacquer adhesion, but not to the level achieved with dip treatment.
- The repeatability of the tests was good and the industrial and laboratory samples behaved similarly.

Table 5.4 - Relative lacquer adhesion on tinplate for dip and CDC passivated production samples.

Dip	CDC
5	1
5	1
5	1
5	1
5	1
5	1
Average = 5	Average = 1

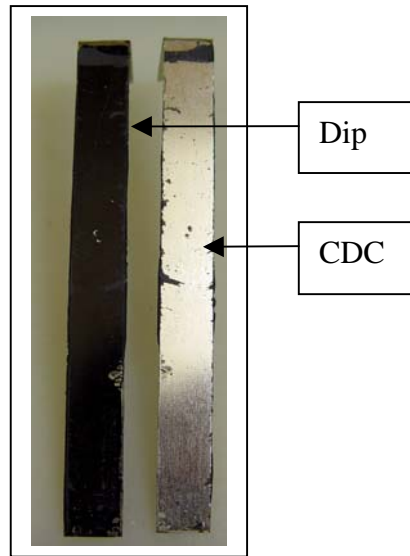


Figure 5.33 – Surface appearance of lacquered and bonded tinplate with dip and CDC passivation respectively, after the pull off test.

Table 5.5 - Relative lacquer adhesion on tinplate for dip and CDC passivated laboratory prepared samples.

Dip	CDC
5	1
5	1
5	1
5	1
5	1
5	1
Average = 5	Average = 1

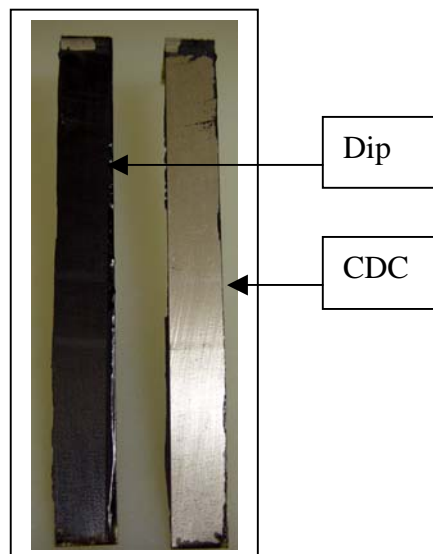


Figure 5.34 – Surface appearance of lacquered and bonded (laboratory) prepared tinplate samples with dip and CDC passivation respectively, after the pull off test.

Table 5.6 - Relative lacquer adhesion on tinplate for CDC vs. CDC passivated (buffered at pH 4)

CDC	CDC - Buffered
5	1
1	5
3	3
3	3
Average = 3	Average = 3

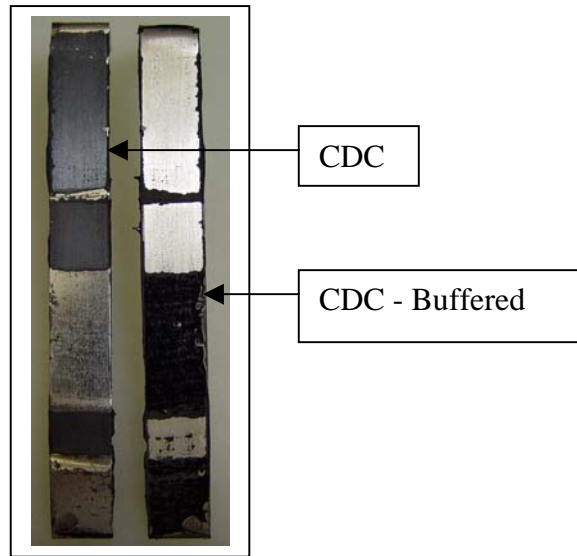


Figure 5.35 – Surface appearance of lacquered and bonded (laboratory) prepared tinplate samples with CDC and CDC (buffered at pH 4) passivation respectively, after the pull off test.

Table 5.7 - Relative lacquer adhesion on tinplate for CDC vs. CDC passivated (pH lowered to 1.5).

CDC (pH 3.8)	CDC (pH1.5)
2	4
1	5
1	5
2	4
Average = 1.5	Average = 4.5

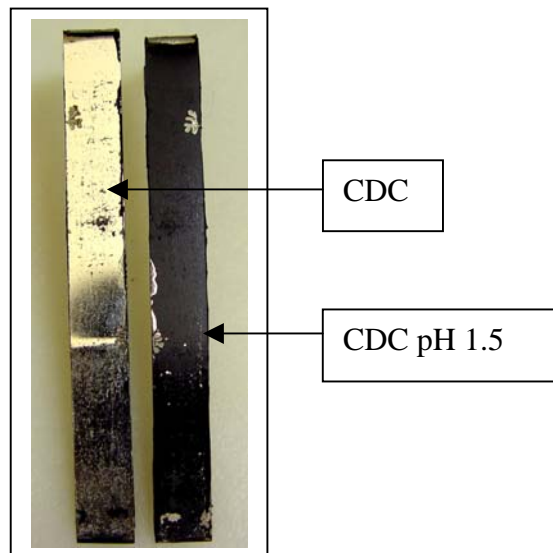


Figure 5.36 – Surface appearance of lacquered and bonded (laboratory) prepared tinplate samples with CDC and CDC (pH lowered to 1.5) passivation respectively, after the pull off test.

Table 5.8 - Relative lacquer adhesion on tinplate for dip vs. CDC passivated (pH lowered to 1.5).

Dip	CDC (pH 1.5)
5	1
5	1
5	1
5	1
Average = 5	Average = 1

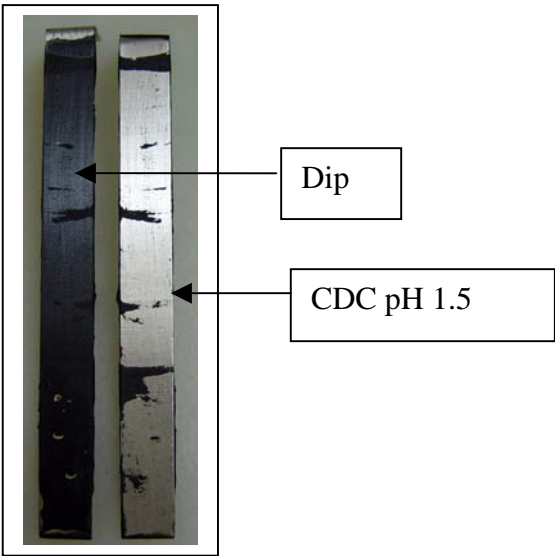


Figure 5.37 – Surface appearance of lacquered and bonded (laboratory) prepared tinplate samples with dip and CDC (pH lowered to 1.5) passivation respectively, after the pull off test.

The reasons for CDC treatments displaying inferior lacquer adhesion properties to dip are therefore related to the additional hydrated chromium oxide present on CDC layers. This supports the work of English et al. (1988) who confirmed, amongst others (Servais, 1979), that lacquer adhesion failure on tinplate takes place at the bond below the passivation layer at the tin metal / tin oxide interface. By analysing both the detached lacquer layer on the cellotape[®] as well as the tinplate surface using angle resolved XPS, a tin oxide layer was identified beneath the passivation layer. This was confirmed by depth profiling analysis. However, when subjecting the tinplate to the same stoving process without the presence of lacquer, the same extent of oxide growth was not observed.

To account for this it was proposed by English et al. (1988) that the chromium oxide, being in the form of a hydroxide, loses its water during the stoving process. In the case of the un-lacquered material the water may evaporate unhindered, but when covered by lacquer, water loss is partially prevented and is therefore available for reaction with the tin coating. The amount of tin oxide should therefore depend on time and temperature of stoving, as well as the moisture content of the chromium hydroxide.

This proposal fits in well with the findings of the present work. The main difference between dip and CDC treatments were indicated as additional SnO and $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ species in CDC treatments which leaves room for oxidation of tin below the lacquer through dehydration of the chromium species. Dip treatments, on the other hand, do not contain chromium hydroxides and tin is already in its highest oxidation state, and therefore no further oxidation below the lacquer layer is expected.

Chapter 6.
Conclusions

6.1 Concluding remarks

The present study clarified the following regarding chromium passivation on tinplate:

- The formation of an insoluble chromium passivation layer on tinplate with a dip treatment requires the presence of an oxidisable tin species such as tin metal or tin (II) oxide. Chromium deposition does not occur if the tin is already oxidised to tin (IV) oxide. After the passivation treatment the tin associating with the passivation layer is present as tin (IV) oxide.
- During CDC passivation the formation of insoluble chromium species is retarded by the presence of tin oxides on the surface, as the reduction of these probably buffers the potential at a value more positive than that required for the formation of the reduced chromium species. During the later stages of the process the potential is buffered by the evolution of hydrogen, to such an extent that metallic chromium does not form. The increase in pH close to the metal surface resulting from hydrogen evolution, favours the formation of hydrated chromium species, which is an inferior substrate for lacquer adhesion. Buffering of the solution did not improve the adhesion significantly, although the chromium species were less hydrated. Reducing the pH of the solution to low values improved the lacquer adhesion of CDC passivated tinplate, but only to a level that was still inferior to that obtained with a dip treatment.
- Characterisation of the chromium species formed during passivation treatments provided a basis for explaining the discrepancy noted between chromium analysis using electrochemical and chemical techniques, and

indicated that a calibration of the electrochemical technique will only be valid, if the degree of hydration of chromium species stays constant.

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