www.sphinxsai.com

ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.9, No.09 pp 563-570, 2016

Influence of the concentration of tin in the plating tank. Defects and behavior towards the corrosion of tin

Ali Kissoum[1,3], Abdenabi Abidi[2*] , Mohamed Labaiz[3], Omar Assala[3] and Noureddine Gherraf [4]

[1]Technical Direction, Arcelor Mittal Annaba, 23000, Algeria
[2]Laboratoire de Synthèse Organique, Modélisation et Optimisation des Procédés Chimiques.(LOMOP) Université Badji-Mokhtar d e Annaba, BP 12 ~EL Hadjar - Annaba ~ Algérie
[3]Laboratory of metallurgy and engineering of materials (LMGM) Badji Mokhtar University, Annaba 23000, Algeria.
[4]Laboratoire des Ressources Naturelles et Aménagement des milieux sensibles, Université Larbi ben M'hidi, Oum Elbouaghi, Algeria

Abstract : The main objective of the present work is to study the influence of the concentration of tin in the plating tank, the electrochemical behavior of tin in contact with aggressive media if fabric surface defects generated during the manufacturing process. Surface defects of tinned steel are causing the degradation of the coating whose role is essential with respect to corrosion resistance. Aggressive media most commonly in contact in tin boxes are chlorides that promote corrosion by pitting, sulfates where the acidity of the medium acting on the pores that exist inevitably is the starting point for corrosion and nitrates that disrupt the cell formed by the combination of iron and tin.

We try to determine the causes of appearance of these defects to reduce the risk of developing in the final product.

Keywords: tin, defect, corrosion, environment, electrochemical test, salt spray, micrograph.

1. Introduction

Tinplate coatings confer to the steel a good protection against corrosion through the formation of a tin-iron battery and thus enhancing the substrate resistance against the attack of aggressive media[1]. If the alloy layer FeSn2 is continuous (reflow well conducted), the corrosion rate is slowed. Exfoliations designate the dairy-based inclusions mold, which are effectively exfoliated and inclusion lines Original of deoxidation or reoxidation inclusions, this is to say of alumina clusters. These cause surface defects (black line before coating which are not exfoliated.

The term "slivers" refers to the original defects scale encrusted during rolling operations and which are not differentiated from inclusion lines by all control systems[2].

The approach to distinguish the different types of exfoliation and better identify training mechanisms was also reported by Kobe Steel[3]: exfoliation of dairy origin, alumina clusters and calamine origin (therefore formed in reheating furnace and to the rolling direction).

The mold of dairy origin slag inclusions are droplets entrained in the meniscus by vortex or shear.

The formation of droplets is a function of the viscosity of the slag, optionally in thickness, and of metal-slag interface voltages. The interfacial tension is primarily a function of the sulfur and oxygen activity of the metal. However, the oxygen activity remains low for killed steel to aluminum and sulfur levels vary little from casting to another[4].

Cracks can cause pitting corrosion or lack of coating also are serious defects in tinplate[5]. Defects formed during the electrodeposition of tin may be caused during the tin reflow or an electrodeposition problem (e.g. tar formation suspended in the electrolyte are deposited in places and prevent the formation of the tin deposit). These defects have a direct impact on the quality of the tin deposited film having an influence on the continuity and homogeneity of the film.

We have found defects and have studied the electrochemical behavior of the tin film having defects in 03 different media (NaCl Sodium chloride, 3.5% sulfuric acid H2SO4 0.1N and potassium nitrate KNO_3 10 mg / l). We used the test potential as a function of time.

We also realized corrosion tests: determination of the corrosion current, polarization resistance and salt spray according to the concentration of tin in the tinning tank. The trials on samples shiny appearance

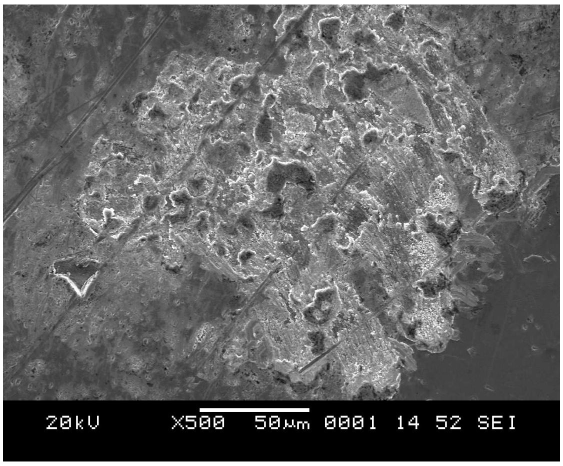
2. Micrographic observations

The samples were examined with a stereomicroscope at 10-65 times magnification.A few representative features were identified on each sample with scribe marks for more detailed examination with the scanning electron microscope.

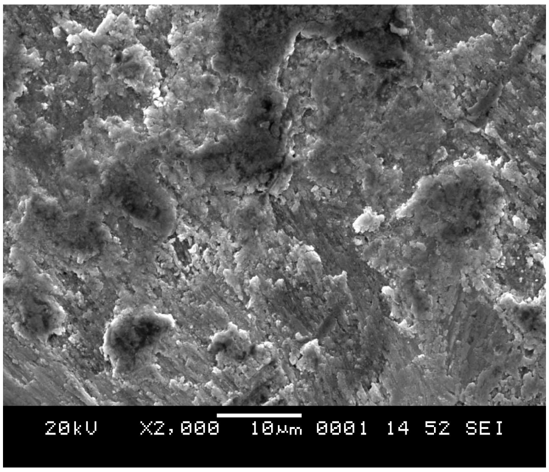
The sample labeled No. 1 had a few areas that appeared different from the surrounding reflowed tinplate. An example of such an area approximately 200 microns in diameter is shown in Figure 1 with the corresponding EDS spectrum that shows the presence of both tin and iron. The relatively large iron peak indicates that the tin coating is very thin in these areas. The tin coating in the high magnification SEM photo, does not appear to be abraded or reflowed, but more like dendrite crystals. No contaminants were identified with the EDS spectrum. Also, no obvious bare spots were identified on sample No. 1.

The sample labeled No. 2, non-reflowed, had numerous bare spots up to 1 mm in size on both sides of the sample. Examples of the appearance of the bare spots are presented in Figure 2 along with an EDS spectrum obtained from within the bare spot. There was some spotty tin deposits within the area of the bare spots. EDS spectra did not detect the presence of a contaminant on the bare steel surface. It may be possible that the contaminant that prevented the uniform tin deposition was washed off in the final rinse or the contaminant is extremely thin carbon or oxide layer was not detected by EDS analysis.

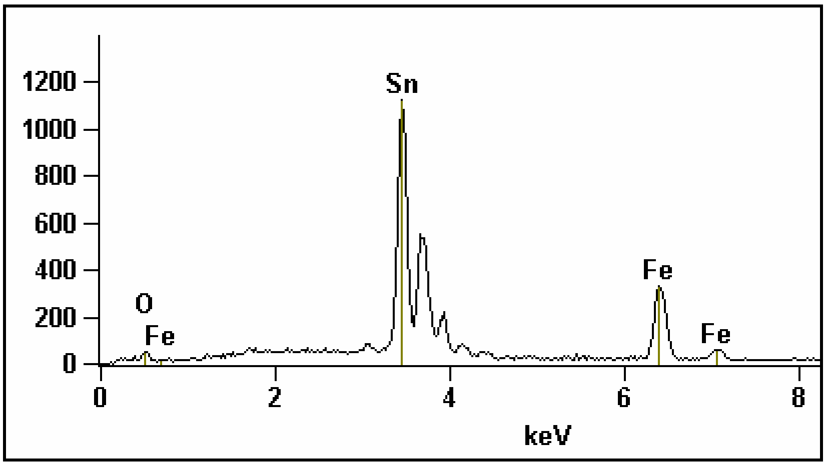
Other than these features discussed above the tin deposits appeared continuous and adherent to the steel as observed in cross-section.



A) Sample 1, Area 1

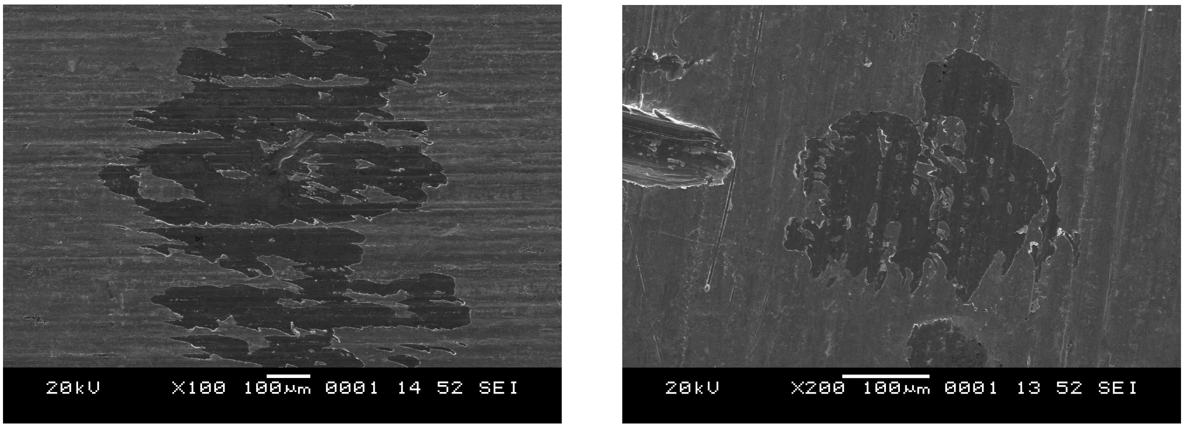


(B) Sample 1, Area 2

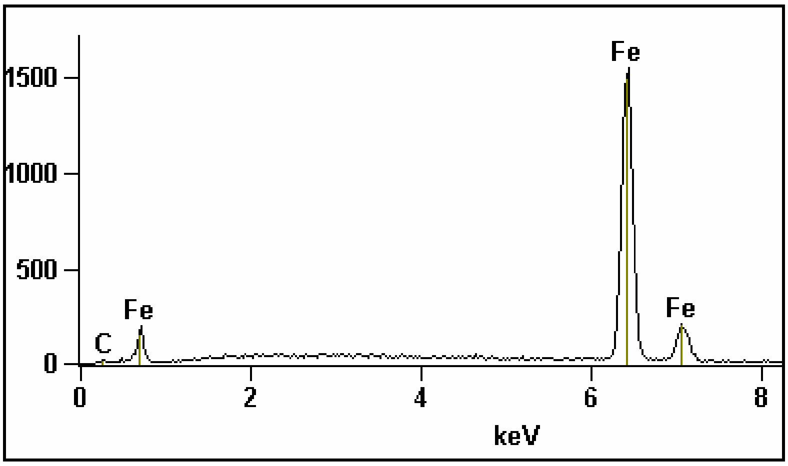


(C) EDS spectrum obtained from Sample 1, Area 1, Spot 1

Figure 1. SEM photos and EDS spectrum obtained from sample 1, area 1 and 2, spot 1 indicating that the coating is thin and non-reflowed.



Sample 2, Area 1 **Sample 2, Area 2**



Representative EDS spectrum in all 2 areas

Figure 2. SEM photos and representative EDS spectrum indicating the presence of bare spots on sample No. 2.

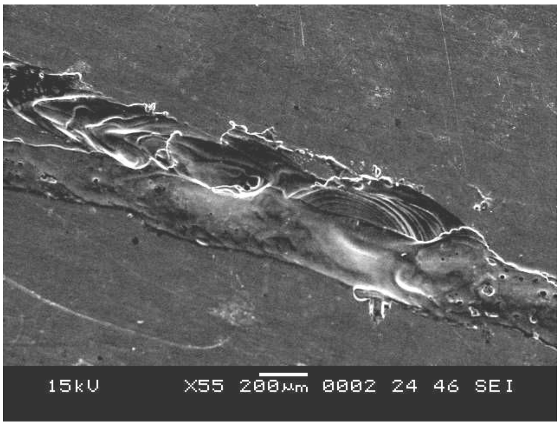


Figure3a Side 1–Stripe of non-uniform melted porosity in non-uniform melted tin

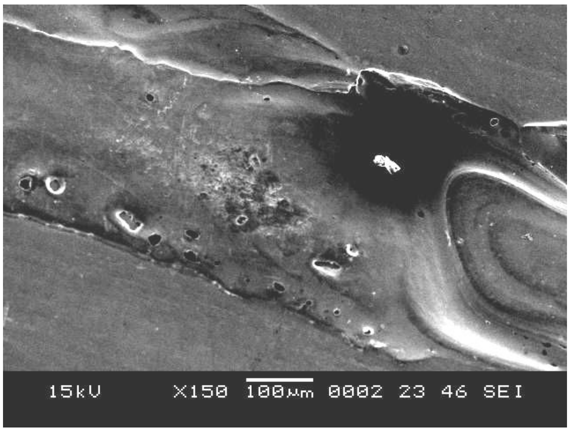


Figure3b Side 1 – Close up of stripe showing tin

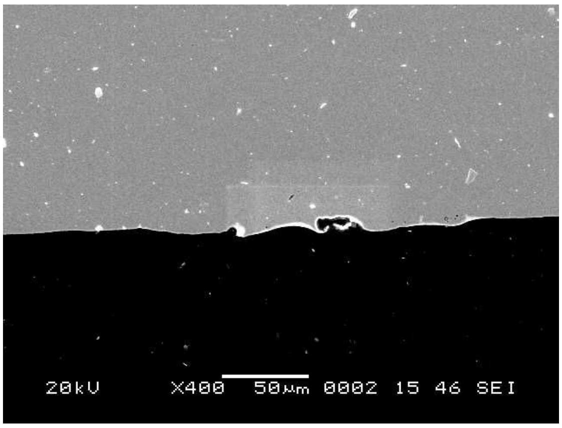


Figure 4a Cross-section through stripe, area 1 indicate approximate width of surface defect

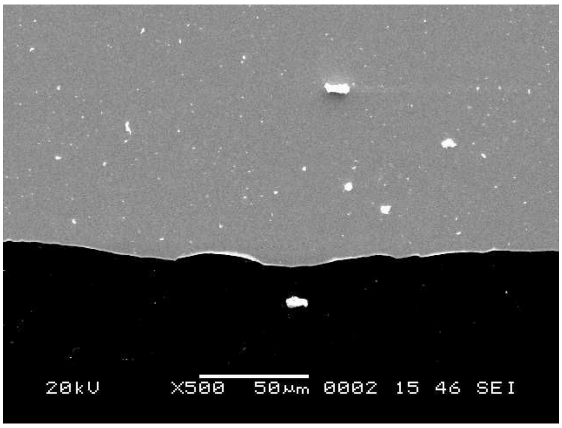


Figure 4b Cross-section through stripe, area 2 arrow arrow indicate approximate width of surface defect

The SEM photos indicate that defect was likely the result of an electrical arc that caused the tin to melt and splatter. The SEM photos (figures3a and 3b) of the stripe also indicate that it may have been caused by premature tin melting. The stripe has the appearance of a weld bead. Cross-sections (figures 4a and 4b) through the stripe in two locations did not reveal a steel defect. Build up on the re-flow conductor rolls is the likely cause of these defects.

3. Corrosion tests

3.1 Determination of corrosion current and the polarization resistance according to the concentration of the tin bath.

Tin samples at different concentrations of the tinning bath line were subjected to electrochemical characterization (determination of corrosion current and the polarization resistance). the selected medium is a solution of potassium nitrate KNO_3 10 mg /L. The results are shown in Table 1.

The tin concentration recommended in the tinning bath is in the range (28-32 g /L), however the presence of high chloride content in the quality of water used for the preparation of the bath reacts with tin to form precipitates at the bottom of the tank. this was confirmed by the chemical characterization of the precipitate yielded grades of 50% of tin chlorides.

We used the electrochemical cell that corresponds to a conventional electrode assembly 03 (Figure 5). The tests were carried out on the shiny tin; scan speed was 60 mV/min

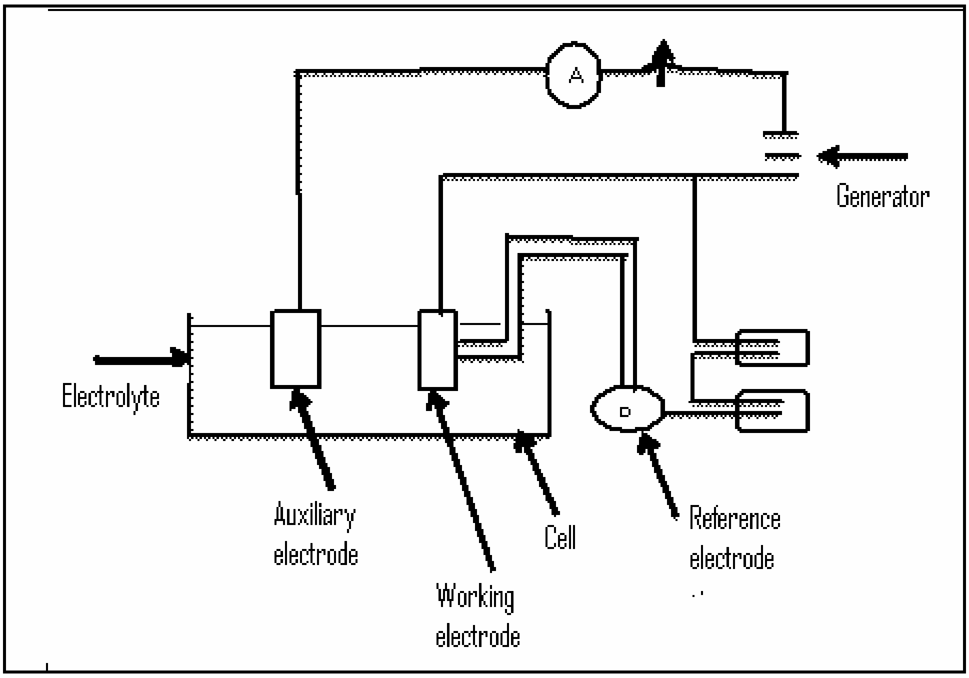


Figure 5: Electrode system 3

Table 1: Results of electrochemical tests: Corrosion current and Rp with respect to the concentration of the tin bath

Material	**1**	**2**	**3**	**4**	**5**
Concentration of tin Sn^{++} (g/L)	30	25	23	21	18
Rp (kΩ.cm^2)	194.5	162.2	142.8	106.0	72.35
Corrosion current (uA/ cm^2)	98.96	111.6	142.2	152.9	300.2

The corrosion current increases gradually with decreasing the concentration of tin in tin tray. It is opposite to the polarization resistance. tin-plated steel is more resistant to corrosion when the bath is rich with tin salts.

3.2 Determination of salt spray tests

We conducted tests of climate by exposing samples at the same concentrations in salt spray according to the NF X 41-002. the results are shown in Table .2:

Table.2 : Results of salt spray testing according to the NF X 41-002

Material	**1**	**2**	**3**	**4**	**5**
Concentration of tin Sn^{++} (g/L)	30	25	23	21	18
Salt spray (Hours)	24	20	18	16	10

The salt spray tests confirm the electrochemical tests, namely the corrosion resistance depends on the concentration of tin bath. As the current density plating is determined by the concentration of the tin bath, this will have a negative influence on the quality of the deposit deposited

3.3 Corrosion tests in different environments

Among the most important factors of corrosion are nitrates in plants or in water, in association with the use of fertilizer and sulfur compounds: sulfur dioxide or its derivatives or thiocarbamates of additives that give rise to hydrogen sulfide corrosion factor transmitting an unpleasant smell to food preparation and chlorides.[6]

3.3.1 Corrosion test in NaCl

Corrosion of tin in the case of metal packaging is of the same nature as that affecting steel works of art. in both cases, it is the transition from a metallic state to an oxidized state. Inside the tinplate box, corrosion is focused on tin in most cases. This element is sacrificed to protect the base steel. Otherwise, tin is covered with a roughly passivity covering that inverts the polarity of Sn and Fe generating a risk of perforation of the film. Outside the box, the classic mode is rust formed in the presence of moisture or the presence of chloride ions which promote pitting

The tests (potential drop over time) were performed in a solution of 3% NaCl. The reference electrode is a saturated calomel electrode, the counter-electrode is a platinum electrode.

The test lasted 02 hours.

At t = 0, the drop potential is - 540 mV / SCE. the potential decreases to negative values to reach - 640 mV / SCE, which shows that there is a corrosion of the tin layer and not protection in NaCl. (figure 6)

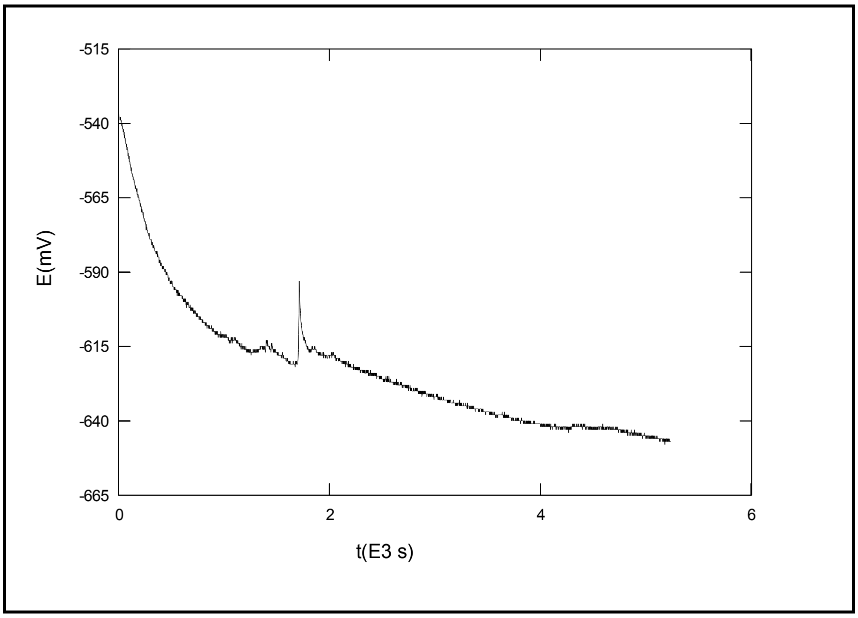


Figure 6 : Potential curve as a function of time in NaCl

3.3.2 Corrosion test in H_2SO_4

The action of acids causes a slow corrosion. The can stack is considered where two metals (iron and tin) are in contact, forming a closed circuit on an electrolyte within which an electric current passes from the anode (-) to cathode (+) through the electrolyte. Dissolution or corrosion of iron must be accelerated by the tin. The tin salts formed are inhibitors of iron corrosion even if there is no more tin to protect electrolytic iron.

The acidity of the medium acting on the pores that exist inevitably is the starting point of corrosion, but it is influenced by many factors that affect its speed. These factors adsorb stannous ions are corrosion inhibitors. it is the case of a sulfuric acid solution:

The test (potential drop over time) were performed in a solution of sulfuric acid 0.1 N. The reference electrode is an electrode in saturated sulfate. Counter-electrode is a platinum electrode. The test lasted 02 hours.

At t = 0, the potential is - 635 mV / SSE, ennobled to - 580 mV / ESS then decreases to - 610 mV / SSE, which shows that there is a beginning and a protective corrosion. (Figure 7)

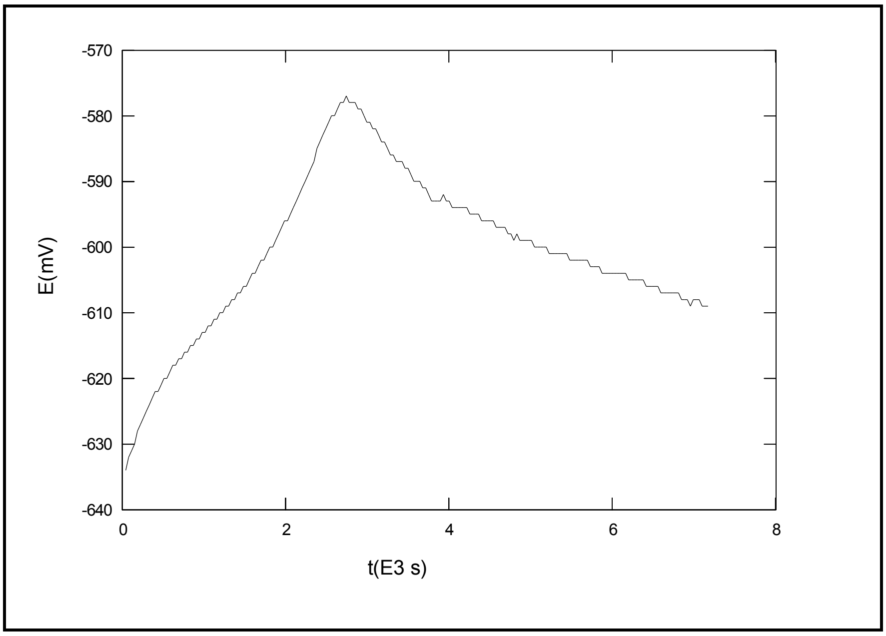


Figure 7: Potential curve as a function of time in H_2SO_4

3.3.3 Corrosion test in KNO_3

During storage, the coating of a tin-white dissolves slowly in the food product. Detinning depends on a number of factors: the nature of the stored product, the type of tin, the possible presence of a protective varnish, the temperature and time of storage. In general, the combined result of all these factors leads to a slow corrosion allowing the tin box to protect the contents for a long time. For electrochemical reasons, tin undergoes preferentially in the vast majority of cases the aggressiveness of the food and the iron holder is thereby protected catholically.

The battery consists of the combination of iron and tin sometimes disturbed by certain substances made by the food industry. Among these substances, there is the nitrate ion.

The tests (potential drop over time) were performed in a solution of KNO_3 at 50 mg / L. The reference electrode is an electrode in saturated sulfate. The counter-electrode is a platinum electrode. The test lasted 02 hours.

The dropout potential begins to - 580 mV / SSE, ennobled up - 570 mV / SSE after about a quarter of an hour and then the destruction of the passive layer and the decrease to less noble values to stabilize at - 605 mV / ESS after 02 hours. Figure 8

The potential drop versus time showed the bad behavior of material with surface defects. Tests performed on the imported tin having no surface defects give better results[7].

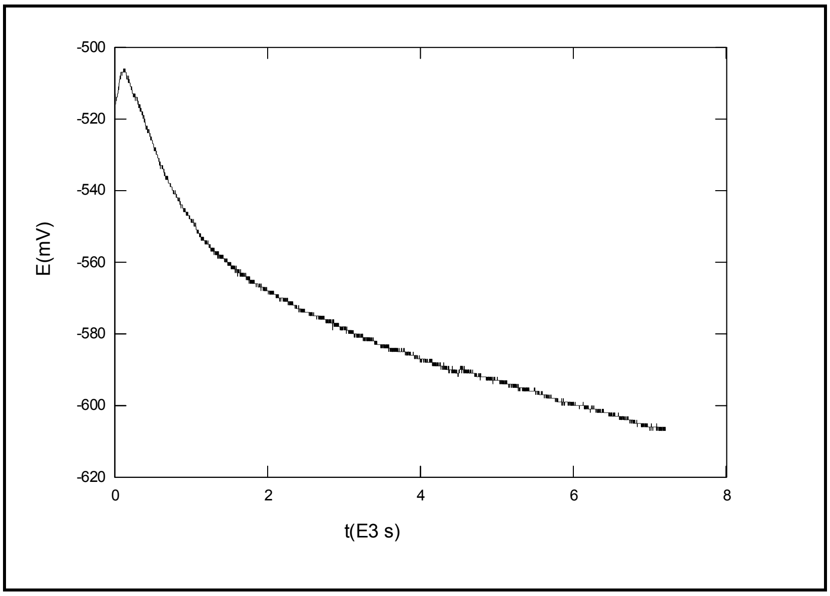


Figure 8: Potential curve as a function of time in KNO_3

4. **Conclusion**

The quality of a coating that is to say its ability to resist to corrosion (loosening, porosity, oxidation…etc) is conditioned by the processes of development and preparation of the substrate area to be coated, and the plating treatment.

The study showed that the concentration of tin has a great effect on the corrosion resistance of the plated steel and the water used to prepare the power tinning bath solution must be of good quality.

The behavior of tin is greatly influenced when there is the presence of defects in the deposited film. These defects originated either at the development stage (steel) or at the tinning line (during plating), especially when the formation of the alloy layer $FeSn_2$ was not properly made, or the result of an electrical arc that caused the tin to melt and splatter, must be detected in time and treated in order to improve the quality of the film filed for a better resistance to corrosion when the coating is in contact with different media.

It should also be noted the importance of washing and bleaching of fruit or fitted with a good quality water, to avoid the inconvenience associated with nitrates vegetables.

5. References

1. Landolt D., Corrosion and Surface Chemistry of Metals, Vol 12 treated materials, ed, Polytechnic and University, Press Romandes, 1993
2. Zeze M., Tanaka A., Tsujino A., Formation Mechanism of Surface Defect Silver type oxide scale with one sheet and coil, Tetsu to Hagan, 2001, 87 (2), 15-22.
3. Galpin J.M, Synthesis Report watchdog technique No. 30, continuous casting solidification, RI 00.11, 2000.
4. Gaye H., Lucas L.D, Olette M., Rioud P.V, Metal-slag interfacial properties: equilibrium values and "dynamic phenomena, Canadian Metallurgical Quatertely, 1984, 23 (2), 179-191
5. Canadian Food Inspection Agency. Characterization and classification of defects, April 1989
6. Bioscience and Technology, Technology and Regulatory Aspects, Regional Committee for Educational Documentation of Aquitaine, 3rd edition, 2008
7. Kissoum A., Labaiz M., Characterization of a tinplate imported from abroad by the techniques of electrochemical impedance and cyclic polarization, potential vs time, Laboratory of metallurgy and engineering of materials (LMGM) Badji Mokhtar University, Annaba, 2013.

*****