Electrochemical and surface studies of the effect of naphthalene-based additives on tin electrodeposition

Aranzales Ochoa, D.M.

Citation

Aranzales Ochoa, D. M. (2021, March 17). *Electrochemical and surface studies of the effect of naphthalene-based additives on tin electrodeposition*. Retrieved from https://hdl.handle.net/1887/3151629

Author: Aranzales Ochoa, D.M.
Title: Electrochemical and surface studies of the effect of naphthalene-based additives on tin electrodeposition
Issue date: 2021-03-17

CHAPTER 1

Introduction

1.1 Electrodeposition

Electrodeposition of metals is a process that has profoundly influenced the world, allowing the improvement of properties of metals or other materials by protecting and enhancing their functionality. Electrodeposition is used in many diverse industries, including home appliances, jewellery, automotive, aircraft and airspace, batteries and electronics, both for decorative and engineering applications. Electrodeposition has a strong technological and economic significance, which has evolved over the years. Nowadays, decorative applications have diminished, primarily due to added expenses and problems associated with plant effluent control and waste treatment; on the other hand, applications in engineering, electroforming and electronics are continuously increasing.

Electroplating as a process started in 1772 with Giovanni Beccaria, who decomposed metal salts using the charge of a Leyden jar to supply a pulse of current[1]. Later, in 1803, Luigi Brugnatelli officially invented the electroplating process by successfully plating a thin layer of gold onto a silver coin[2]. Initially, the development of electroplating was slow because of the limitations of electricity sources. Alessandro Volta's invention of the "Volta's pile" in 1796 did not prove to be an appropriate source of energy for commercial electroplating[3]. However, shortly afterwards, in 1836, the understanding of electricity allowed the development of the first electricity generators, and subsequently it led J.F Daniell to invent the self-polarizing cell, a more reliable source of electricity. Finally in 1840, George Elkington patented an improved method of gilding copper, brass and other metals or alloys of metals[1].

1.2 Tin plating

Multiple metals are currently used in electroplating processes. However, there is a metal that stands out as one of the earliest metals to be known and used since the earliest periods of urban civilization: Tin[4]. It is a soft metal, ductile, with a low melting point. Tin finds application as a metal and in chemical compounds. As a metal, it is mainly used as an alloy or coating, and its chemical compounds are of high relevance in agricultural, plastics and pharmaceutical products. Currently, tin plays an important role in daily life, being used in food packaging, jewellery, also in modern technology in electric vehicles, aerospace, batteries, photovoltaics cells, among others[5]. Tin coatings are used to protect from air oxidation, to enhance corrosion resistance, to improve solderability, for decorative purposes and as anode material for Li-ion batteries[6, 7].

1.2 Tin plating

The development of tin plating was independent on the electrodeposition process during the early stages. The origin of tinplate can be traced to the tinning of hammered iron sheet in Bavaria in the 14th century. Later on, the tinplate industry spread to Dresden (Germany), and tinplate articles were exported to many countries, including England. In 1720, a tinplate factory was set up in South Wales - UK, where the incorporation of mechanical tinning machines allowed to extend and increase the productivity. Subsequently, tinplate reached the United States, and later on Asia. During the first half of the 20th century continuous advancements in the tinplate process were achieved, from hot-dipping to electrotinning.

Electrotinning became popular giving the advantages of producing thinner, more uniform tin coatings and lower manufacturing cost than the hot-dipping process. However, it was not until World War II, when tin supplies were scarce, that electrotinning process was widely implemented. Currently, the majority of tin electroplating is done over steel sheets (thin mild steel)[8].

Three electroplating processes were developed according to the type of electrolyte and design of the processing units: alkaline tin (IV) oxide hydrate salts, ferrostan (phenolsulfonic acid or 4-Hydroxybenzenesulfonic Acid), and halogen (fluoride and chloride). Most commercial tin electroplating lines in the world use the ferrostan process, which is based on a sulfonic acid electrolyte[9]. Figure 1 shows the schematic arrangement of the handling and processing units of the three types of electrotinning lines.

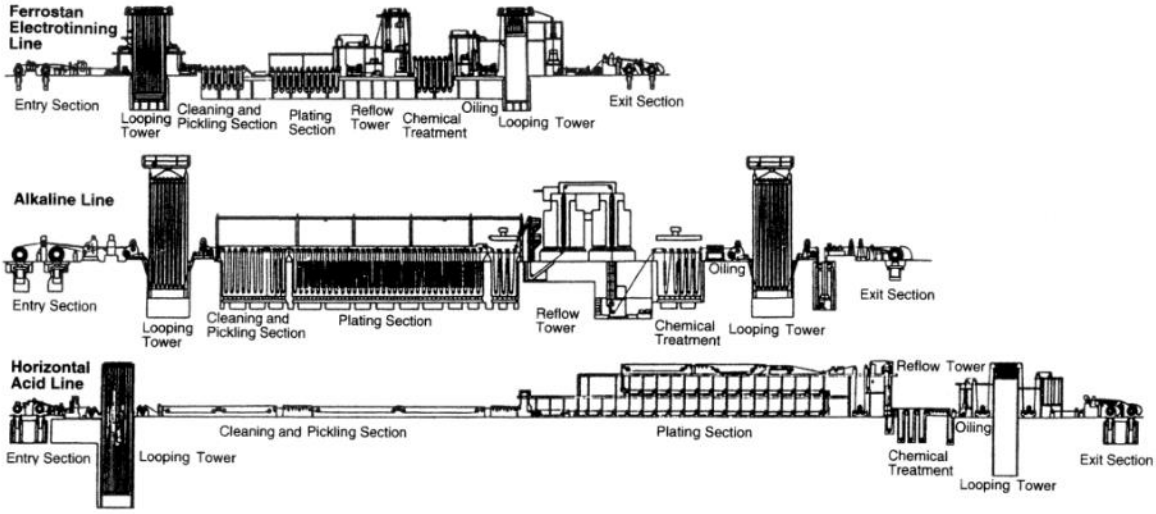


Figure 1. Schematic arrangement of handling and processing units of three types of electrotinning lines[9]

Regardless of the different electrolytes and design of the electrotinning lines, a series of common steps are present in the electroplating processes:

- Cleaning and pickling:

The strips are thoroughly cleaned by oxidation of the surface in acidic media and subsequent washing. This process is followed by pickling that removes oxides and rust layers. It also etches the surface for better deposition of tin.

- Electroplating:

Tin is electrodeposited usually via galvanostatic method. This process can be made from different electrolytes, using different tin salts and additives. This topic will be discussed in detail in the following section.

- Thermal treatment:

The tin coated strip is flow-melted by resistance heating to a temperature just above the melting point of tin and followed by a water quenching. This procedure generates a reflective surface and creates iron-tin intermetallic compounds, which play an important role in the stability of the material.

- Passivation:

The tin coated strip is passivated by immersion in dichromate solution which deposits a very thin chromate film of chromium on the surface.

- Organic coating:

A thin film of oil is applied to the surface in order to preserve the surface from attack and also to enhance the lubrication properties.

1.3 Tin electroplating baths

Although the composition of electroplating baths used in tin electrodeposition process is quite diverse, almost every single bath consists of: electrolyte, tin salts, and additives. Physical and chemical properties of the tin deposits are strongly dependent on the electrolytes, tin salts, and additives used during the process.

1.3.1 Electrolytes

Electrolytes for tin deposition can be acidic or alkaline. Currently, most of the tin electrodeposition in the industry is carried out under acidic conditions.

Alkaline baths are usually hydroxides, they do not require additives and they are known as not corrosive to steel (due to the passivation of the Fe). Alkaline baths are composed by a tin (IV) oxide hydrate which must be heated above 65 ^{0}C during the deposition, because at lower temperatures Sn (IV) precipitates as a SnO_2. Tin electrodeposition from alkaline tin (IV) oxide hydrate solution leads to low maximum current density[5] and requires twice as much electric charge necessary to deposit the same mass of tin from tin (II) salt solutions[10]. Currently, this type of bath is obsolete.

Acidic baths are often composed of sulfate or sulfonate electrolytes using tin (II) salts. Acidic solutions offer faster deposition rates at ambient temperature. However, Sn (II) easily oxidizes and produces SnO_2 that precipitates in the plating tanks. To avoid Sn (II) oxidation and to stabilize the acidic bath, inorganic and organic additives have to be added in the solution. The most used acidic electrolytes are:

- Phenol sulfonic acid (PSA) electrolyte:

The PSA electrolyte consists of a solution of PSA, tin (II) salts solutions and additive agents that ensure the quality of the deposits over a wide current density range[11]. This bath was one of the first to be developed, and it is still present in some parts of the world; nonetheless, it has been gradually substituted due to environmental regulations.

- Halogen electrolyte:

The halogen electrolyte consists of a solution of tin chloride, sodium and potassium fluoride, chloride salts and organic additives. It is a widely employed electrolyte bath; it has the distinction that it operates with a different type or design of electroplating line, having horizontal rather than vertical plating tanks, which enables lines to be run faster. It was developed by E. I. du Pont de Nemours, Weirton Steel and Wean Engineering.

- Flouroboric acid electrolyte:

The fluoroboric acid electrolyte contains tin fluoroborate, fluoroboric acid and boric acid. Boric acid is known to prevent hydrolysis of the fluoroborate ions. It was developed by Rasselstein in the late 1940's; this bath did not become popular due to commercial restrictions.

- Methane sulfonic acid electrolyte:

The use of methane sulfonic acid as electrolyte in the electroplating of tin and tin alloys started in the early 1980's. MSA easily gained an important market and spread in the electroplating industry with wide acceptance, owing to its many advantages, which include: high conductivity, biodegradability, less Sn (II) oxidation and high current density. The wide approval of MSA generated additional developments for applications in mass scale process. In 1989, the first commercial tinplate production line using a patented MSA process (Ronastan) was implemented in IJmuiden, The Netherlands.

Studies of tin electrodeposition using deep eutectic solvents have also been performed[12, 13]. Deep eutectic electrolytes offer advantages such as high metal salt solubility and the ability to tailor redox properties of the metal ions through choice of the anion. This type of bath has been used for tin alloys, where it is very difficult to control alloy composition because of the large differences in the redox potentials for the metal ions, or because of other effects, such as different kinetics of deposition of the two metals with respect to each other and the substrate[13]. Deep eutectic solvents are formed between a variety of quaternary ammonium salts and carboxylic acids.

Recent years have shown constant improvements of the tin electroplating process from MSA electrolyte and other electrolytes, allowing to get thinner thickness in the tin deposits, tailoring morphology and decreasing the amount of sludge formed during the process. However, many questions remain unsolved about the effect of the electrolyte at the electrode-electrolyte interface and in the solution, as well.

1.3.2 Additives

Tin electrodeposition in acidic conditions require the use of organic additives, as tin coatings plated without additives in the electrolyte are non-adherent, coarse, porous, and exhibit dendrites[14]. The use of additives in the electroplating baths allows to tailor and improve properties of the deposits, fulfilling the required characteristics for the different uses of tin electroplated surfaces. Some studies have also reported adverse effect of additives by organic co-deposition on the coatings[15, 16].

The chemical structure of the organic additives employed in tin electrodeposition is quite diverse and complex including aromatic sulfonates, amine derivatives, phenol derivatives, unsaturated carbonyl compounds, polyoxyethylene and polyoxypropylene, glue, gelatin, wood tar, resins, among others. The development of these organic additives has been mainly empirical and their mechanism of action remains not fully understood. In contrast to what is seen for copper electrodeposition, where a widely accepted classification of the additives has been established (i.e., accelerator, suppressor, leveler), the classification of additives used in tin electrodeposition based on their effect is still under discussion. Nonetheless, one of the classifications for additives used in tin and tin-lead alloy plating baths is given by Jordan[17].

Jordan classified the organic additives as surface active agents, oxidation inhibitors, grain refiners and brighteners[17].

Surface active species are known to have strong polarizing effects on tin deposition. They also act as emulsifying agents for brighteners, meaning that they facilitate their dissolution. Some of the most characteristic compounds are: polyethylene glycol, polypropylene glycol, fatty acid ethoxylates, alkylphenol ethoxylates, α or β naphthol ethoxylates, poly alcohols, among others. The most characteristic effect of surface-active species is to produce tin deposits free of dendrites, with smaller grain size that generates matt to satin-bright deposits.

Oxidation inhibitors or stabilizers are added to the acidic baths in order to avoid or minimize the oxidation rate of Sn^{2+} to Sn^{4+}. Sn (IV) ions easily form SnO_2 that precipitates and forms sludge in the plating tanks, generating technical and economic problems. Some of the molecules that are used as oxidation stabilizers are hydroquinone, hydrazine, ascorbic acid and sulfonic acid. 2-hydroxy-6-methylbenzenesulfonic acid (cresol sulfonic acid) seems to be one of the first compounds to be used as an oxidation stabilizer in tin electrodeposition[18] .

Grain refiners are compounds that generates a decrease of the size of the metal features. Some of the typical grain refiners are aromatics such phenol sulfonic acid, 2–naphthol based compounds, also alkyl sulfonic acids, among others.

Brighteners lead also to a significant grain refining and increase the reflectivity of the metal deposit surface. Reflective surfaces are characterized by crystallite sizes at the surface of less than 0.3 μm^2. Kanani[19] describes two types of brighteners. The first group generates a decrease in the grain size but it does not generate mirror-finish deposits; sulfonamides, alkyl sulfonic acids are in this group. The second group of brighteners impart a near mirror finish deposit, even at very low concentrations; thiourea, thiocarbazone mercaptoalkylsulfonic belong to this group[19].

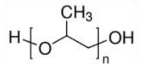
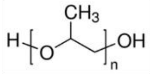
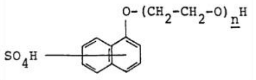
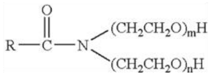
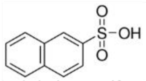
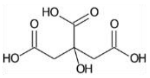
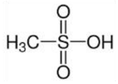
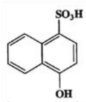
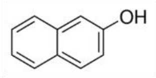
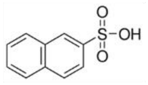
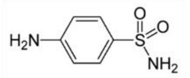
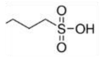
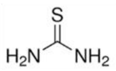
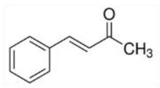
4-phenylbut-3-ene-2-one (an alpha beta unsaturated ketone) is also known as a model brightener reagent that generates very smooth and bright tin deposits by inhibiting the metal growth by its strong adsorption or the adsorption of its reaction products on the substrate[17]. Other compounds are also broadly used as brighteners, such as aromatic amines and aliphatic aldehydes.

The broad variety of current applications of tin coatings in technological and daily life products and its potential future uses has triggered an important increase of tin electrodeposition studies in the last 25 years. Multiple studies about the influence of the electrolytes, tin salts and additives have been performed; these studies have been mainly focused on the characteristics of the tin deposits, therefore properties such as smoothness, brightness, adhesion, grain size, crystalline orientation, wear resistance have been meticulously considered for tin electrodeposition on different substrates and in the presence of different electrolytes and mixes of additives. On the other hand, the studies that consider single additives and their role in the initial stages of the tin electrodeposition process are much fewer.

The development in the composition of the plating baths has been mostly empirical and ad hoc, which explains why there are fewer studies that consider baths with single additives and their influence in the initial stages of the deposition process. Further, a considerable percentage of plating baths composition remains undisclosed by the companies.

A proper understanding of the initial stages of tin electrodeposition process and the influence of the electrolyte and additives would allow an extension of the current applications and an improvement of the process. Nonetheless, many questions remain unsolved, such as the influence of the electrolyte and additives on the metal ions species in solution, the mechanisms of interaction of the electrolyte and additives with the substrate, on the kinetics of nucleation and growth, the evolution of the morphology during the nucleation and growth, the chemical composition of the deposit, among others.

Table 1. Some of the most common additives used on tin electrodeposition process

Surface active species	Oxidation inhibitors	Grain refiners	Brighteners
 Polyethylene glycol  Propylene glycol  Ethoxylated naphthalene sulfonic acid (ENSA)  Polyoxyethylene alkylamine (POOAA)	 Hydroquinone  2- naphthalene sulfonic acid  Citric acid  Methanesulfonic acid	 Hydroxy naphthalene sulfonic acid (HNPTS)  Naphthol  2 - naphthalene sulfonic acid	 4-amino benzene sulfonamide  Alkyl sulfonates  Thiourea  4-phenylbut-3-ene-2-one

1.4 Outline of this thesis

The aim of this thesis is a fundamental approach to the understanding of the effect of electrolytes and additives on the mechanism of tin electrodeposition process, and the corresponding thermodynamics and kinetics parameters of the nucleation and growth processes. The work provides insights for the improvement of the tin electrodeposition process and also for electrodeposition of other metals.

In Chapter 2, we study tin electrodeposition on polycrystalline gold electrodes from two different supporting electrolytes: sulfuric acid (SA) and methanesulfonic acid (MSA), both of them commonly used in the industry. We show electrodeposition of tin takes place via three different mechanisms: irreversible adsorption, underpotential deposition and overpotential deposition. Our results show tin overpotential deposition is faster in the presence of sulfate than in methanesulfonate anions, presumably due to complex formation. Static and hydrodynamic measurements also show methanesulfonate anions lead to a more homogenous tin coverage than sulfate.

Subsequently, in Chapter 3 we build upon on the findings obtained in the previous chapter, and we study the effect of naphthalene derivatives: naphthalene (NPT), naphthalenesulfonate (NPTS), hydroxynaphthalenesulfonate (HNPTS), and ethoxylated napthalenesulfonic acid

(ENSA), a commonly used additive in the industry, on the tin electrodeposition process on a gold electrode. We conclude the formation of (condensed) films of NPT, NPTS, HNPTS and ENSA. We show tin electrodeposition is strongly affected by the presence of the naphthalene derivatives films. Tin bulk electrodeposition is inhibited in the presence of NPT and NPTS, but promoted in the presence of HNPTS. Tin deposits grown in the presence of NPT and NTPS seem to have the same morphology, but the tin deposit grown in the presence of HNPTS exhibits markedly smaller features. ENSA exhibits a similar behaviour to NPT and NPTS during the tin deposition process in terms of the measured voltammetry: a suppression of the bulk Sn electrodeposition, but essentially no effect on the AuSn alloy formation. Furthermore, sulfonated additives lead to some form of sulfur incorporation in the AuSn alloys.

In Chapter 4, we continue the study of the effect of naphthalene-based additives on the kinetics of tin electrodeposition on a boron doped diamond electrode. Current transients in the presence of NPT, NPTS and HNPTS are analysed with the standard Scharifker-Hills model determining the steady state nucleation rate (AN_0) and the number density of nucleation sites (N_0). In the absence of additives, the nucleation process is shown to transition from progressive to instantaneous with increasingly negative potential. A decrease in the nucleation kinetics of tin deposition on BDD is observed in the presence of naphthalene-based additives: NPT showed the smallest effect on the reduction of the kinetics, followed by NPTS, and the strongest effect is observed in the presence of HNPTS. Moreover, we show that Sn (II) is not complexed by the additives and charge transfer kinetics is not influenced by the presence of the additives. Additives only affect the nucleation process. Furthermore, the behavior of ethoxylated α-napthalenesulfonic acid (ENSA) exhibits an identical behavior that on gold, i.e., a strong inhibition of the tin deposition process.

Finally, in Chapter 5 we use the gathered knowledge of the effect of naphthalene-based additives on tin electrodeposition on more stable substrates, i.e., gold and boron doped diamond electrodes, to provide insights of the interaction of the additives with iron and their effect on the overall tin deposition process on an iron electrode. We showed the effect of NPT and NPTS on tin electrodeposition remains mainly independent of the substrate. HNPTS shows a stronger decrease of tin deposition, in agreement with has been previously observed on tin deposition on a BDD electrode. Furthermore, we showed that transport of Sn (II) ions from the bulk to the electrode surface is not affected by NPT, NPTS and HNPTS. We verified that ENSA-6 forms a thick film on the iron surface, a behavior correlated with the results on the gold and BDD surfaces. Lastly, ENSA-6 also exhibits the strongest inhibition of tin deposition on iron.

1.5 References

(1) Raub, C. The History of Electroplating. In *Metal Plating and Patination*; Elsevier, 1993; pp 284–290.

(2) Hunt, L. B. The Early History of Gold Plating - A Tangled Tale of Disputed Priorities. *Gold Bull.* 1973, *6* (1), 16–27.

(3) de Santillana, G. Alessandro Volta. *Sci. Am.* 1965, *212* (1), 82–91.

(4) Barry, B. T. K. Tin Processing. *Encyclopeadia Britannica*; Encyclopaedia Britannica, inc., 2017.

(5) Walsh, F. C.; Low, C. T. J. A Review of Developments in the Electrodeposition of Tin. *Surf. Coatings Technol.* 2016, *288*, 79–94.

(6) Hassoun, J.; Scrosati, B. A High-Performance Polymer Tin Sulfur Lithium Ion Battery. *Angew. Chemie - Int. Ed.* 2010, *49* (13), 2371–2374.

(7) Zhou, X.; Bao, J.; Dai, Z.; Guo, Y.-G. Tin Nanoparticles Impregnated in Nitrogen-Doped Graphene for Lithium-Ion Battery Anodes. *J. Phys. Chem. C* 2013, *117* (48), 25367–25373.

(8) ITRA Ltda. Guide to Tinplate. 2001, pp 1–124.

(9) Schlesinger, M. Paunovic, M. *Modern Electroplating*, 5th editio.; Wiley: New Jersey, 2014.

(10) He, A.; Liu, Q.; Ivey, D. G. Electrodeposition of Tin: A Simple Approach. *J. Mater. Sci. Mater. Electron.* 2008, *19* (6), 553–562.

(11) Morgan, E. Tinplate and Modern Canmaking Technology; Pergamon: Oxford, 1985; pp 5–73.

(12) Abbott, A. P.; Capper, G.; McKenzie, K. J.; Ryder, K. S. Electrodeposition of Zinc-Tin Alloys from Deep Eutectic Solvents Based on Choline Chloride. *J. Electroanal. Chem.* 2007, *599* (2), 288–294.

(13) Abbott, A. P.; Alhaji, A. I.; Ryder, K. S.; Horne, M.; Rodopoulos, T. Electrodeposition of Copper-Tin Alloys Using Deep Eutectic Solvents. *Trans. Inst. Met. Finish.* 2016, *94* (2), 104–113.

(14) Aragón, A.; Figueroa, M. G.; Gana, R. E.; Zagal, J. H. Effect of a Polyethoxylate Surfactant on the Electrodeposition of Tin. *J. Appl. Electrochem.* 1992, *22* (6), 558–562.

(15) Hill, J. S.; MacLachlan, D. F. A.; Stoddart, C. T. H. The Structure and Superconductive Properties of Electrodeposited Tin Films. *Br. J. Appl. Phys.* 1966, *17* (4), 513–520.

(16) Jaén, J.; Vértes, A.; Tjutina, K. M.; Kasmodamianskaya, L. V.; Kiss, L.; Shepeleva, E. V. Mössbauer Studies on Electrodeposited Tin-Copper Alloys. *Electrochim. Acta* 1985, *30* (4), 535–539.

(17) Jordan, M. *The Electrodeposition of Tin and Its Alloys*; ASM International, 1999.

(18) Hothersall, A. W.; Bradshaw, W. N. The Electrodeposition of Tin from Acid Sulfate Solutions. *Trans. IMF* 1936, *12* (1), 113–128.

(19) Kanani, N. *Electroplating: Basic Principles, Processes and Practice*, 1st editio.; Elsevier science: Berlin, 2004.