# THE CORROSION CHARACTERISTICS OF PRINTED CIRCUIT BOARD TIN COATINGS

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*Abstract*

Immersion tin coatings are one of lead free surface finishings which are used in the printed circuit boards technology. The tin coating prevents the underlying copper from corrosion and preserves the solderability during lead-free assembly processes and for a long storage life of boards. These coatings are used more often than another surface finishings (electroless nickel/immersion gold, immersion silver, organic solderability preservatives OSP) because of its relatively low cost. The immersion tin is deposited directly on the copper surface by a chemical displacement reaction from acidic bath containing complex compounds. However, under unfavorable conditions intermetallic phases with copper ($Cu_6Sn_5$ and $Cu_3Sn$) can form, which worsen the solderability of tin coating. To guarantee the good solderability, corrosion protection and correct solder joint formation it must be applied enough thickness of the pure tin layer over the Sn-Cu intermetallic phase. Therefore thickness of immersion tin coating should be strictly controlled for its use as corrosion resistant coating in printed circuit boards technology.

In this paper the investigations of corrosion resistance of immersion tin coatings of different thickness are presented. These tin layers were deposited on electrolytic copper foil from thiourea-type bath at temperature 70°C. The thickness of Sn coating was determined by coulometry. The corrosion behavior in 0,5 M NaCl solution was determined using electrochemical methods (potentiodynamic polarization and impedance spectroscopy). The tin coatings were investigated as received and after ageing (4 h at 155ºC- it represents storage over 12 month [12]). It was found, that corrosion resistance of thicker tin layers decreases slightly after ageing. However, corrosion resistance of thinner tin layers increases after ageing. These changes were related to intermetallic phases formation.

*Keywords*: immersion tin, corrosion, anodic polarization, impedance

## *Introduction*

Immersion tin, electroless nickel/immersion gold, immersion silver and organic solderability preservatives (OSP) as well as lead-free HASL (Hot Air Solder Leveling) coatings are available on the surface finishing market for printed circuit boards (PCB) technology. All of those coatings prevent the underlying copper from corrosion and preserves the solderability during lead-free assembly processes and for a long storage life of boards. Except of HASL, they are deposited on copper in electroless (immersion) process and are characterized by proper corrosion resistance, very good solderability as well as flatness of surface. The immersion tin coating is more and more often used at present because of very low deposition costs. Modern generation of immersion tin coatings have higher densities, smaller grain with a much lower propensity towards oxidation, dendritic growth and whiskering [1,2].

Immersion tin can be deposited on the copper surface in two ways: from an alkaline bath by the process disproportionation of Sn(II) or from acidic bath, containing complex compound, by a chemical displacement reaction [1,2]. Alkaline baths are not used in PSB technology because their have destructive influence on photoresists. Acidic baths contain complex compounds which additional improve bath stability and modify structure of obtained tin film. Quality and thickness tin layer are fundamental parameters which determine its protective character. Unfortunately, tin forms intermetallic phases with copper ($Cu_6Sn_5$ and $Cu_3Sn$) which worsen the protective properties (copper oxidation) and solderability of tin coating. The interdiffusion of tin and copper also occurs if even no soldering is applied. Diffusion is very slow during storage at room temperature and very fast at higher temperatures during soldering processes. In practical the assembling of PCB is carried on in

multiple steps. Some printed boards will go through all foregoing storage and heat processes before they are finally soldered. To guarantee the good solderability, corrosion protection and proper solder joint formation it must be applied enough thickness of the pure tin layer over the Sn-Cu intermetallic phases. Thin layers even as received, have bad solderability [2-4]. Thicker tin layers lost their good solderability after ageing that is after decreased poor tin layer on surface [5,6]. For solderability measurement of PCBs the wetting balance method was used (meniscograph MENISCO ST60). The wetting force $P_{max}$, wetting time $\tau_z$ and wetting angle θ after 3 s were measured and the solderability was evaluated according to Standard's J - STD 003 [7, 8] and NF A 89400 P [9] requirements for electronics: $\iota_z < 2$ s, $P_{max} > 150$ mN/m, $\theta_3 < 55°$. The measurements were performed in air, at temperature of 260°C using SnAg3.5Cu0.7 alloy. The standard flux ROL1 according to J-STD-004 [8] was applied. The example dates are presented in Table1.

Table 1. The wetting balance measurement results for PCBs with Sn coating at different thickness [5].

| Thickness of tin layer [μm] | Type of PCB | τz (θ=90°) [s] | Pmax [mN/m] | $\theta_3$ [°] | Solderability valuation |
|---|---|---|---|---|---|
| 1,07 | Sn – as received | 1.19±0.15 | 83±14 | 54±6 | acceptable |
| 0,26 | Sn - after 4h at 155°C | >10 | 0 | 101±6 | bad |
| 0,99 | Sn - as received | 1.16±0.15 | 89±5 | 53±2 | acceptable |
| 0,18 | Sn - after 4h at 155°C | >10 | 0 | 180±0 | very bad |
| 0,80 | Sn - as received | 0.93±0.18 | 102±25 | 49±5 | good |
| 0,01 | Sn - after 4h at 155°C | >10 | 0 | 180±0 | very bad |

The question stands up in that situation: the corrosion resistance of thin tin layer is the factor determining the solderability and decreased for annealed tin coatings? There is no answer for this question in the literature concerning the immersion tin coating process and technology.

In this paper the investigation of corrosion resistance of immersion tin coating, witch have different thickness, are presented, as continuation of preliminary paper [10].

*Experimental*

Immersion tin layers were deposited on electrolytic copper foil from thiourea-type bath. The surface of copper was degreased and microetched before deposition process [1,6]. The tin layers deposition was carried on at 70°C. The composition of bath was: 0,1M $SnCl_2$, 0,6M thiourea and 0,3M HCl.

The thickness of Sn coatings was determined by coulometry in 2M HCl with controlled potential change of Cu/Sn electrode relative to saturated calomel electrode (SCE). The coulometry method gives the information about layer thickness and also about possibility of existence of intermetallic phases. The thickness of Sn coatings which were used for corrosion test was: 0,2; 0,5; 0,9 and 1,4 μm.

The corrosion properties of tin coatings were determined on the basis of potentiodynamic polarization and impedance spectroscopy experiments in 0,5 M NaCl solution. The scanning rate during potentiodynamic polarization measurements was 5 mV/s. The impedance spectroscopy measurements were made at corrosion potential applying AC signal of ±10 mV in the frequency range 1 kHz to 5 mHz. The AUTOLAB set with GPES 4.4 and FRA 2.3 software respectively was used [11]. The investigation was made in three electrodes cell with platinum counter electrode. The working electrode was testing sample with surface area of 1,1 $cm^2$ and SCE was used as reference electrode. The impedance measurements was made after 0,5 and 2,5 h exposition of samples in solution and the polarization curves after 2,5 hours exposition of samples in solution.

Tin coatings were investigated as received and after ageing (4 h at 155ºC in air, what is comparable with 12 months storage [12]).

*Results and discussion*

The thick (1,4 μm) and thin (0,2μm) immersion tin layers have similar values of corrosion potential as received: -0,52 and -0,53 V/SCE, respectively. The value of corrosion potential of thinner tin layer increases after ageing from -0,53 V to -0,25 V/SCE. This change in $E_{corr}$ can be related to the formation of Sn-Cu intermetallic compounds. In the contrary, the corrosion potential of thicker tin layer remains on the same level and is equal to -0,52 and -0,51 V/ SCE for as received and annealed samples, respectively (see tables 3 and 4). This finding indicates that Sn-Cu intermetallic compounds are formed at the copper–tin interface and they are absent at the surface of thicker Sn coatings. Figures 1 and 2 show polarization curves obtained for testing samples in 0,5M NaCl solution. There are small differences between curves obtained for 1,4 μm thick tin layers in as received and annealed states. They have similar course (fig.1). However, the polarization curves obtained for 0,2 μm thick tin layer in as received and annealed states are different in their courses. The curve obtained for annealed tin layer is similar to that one for copper (fig.2).

The polarization curves obtained for samples of different thickness (0,2; 0,5; 0,9 and 1,4μm) in 0,5M NaCl solution are compared in figure 3 - for as received state and in figure 4 - for tin layers after ageing. As we can see the polarization curves for as received samples have similar courses independently of layer thickness (figure 3). In the causes of samples after ageing the polarization curves for 0,2 and 0,5 μm thick layers have courses approximate to copper (figure 4). It would be supposed from polarization data analysis, that thicker tin layers do not change their protectiveness after ageing. Besides we would be supposed also that tin is totally transformed to Sn-Cu intermetallics for thin coatings.

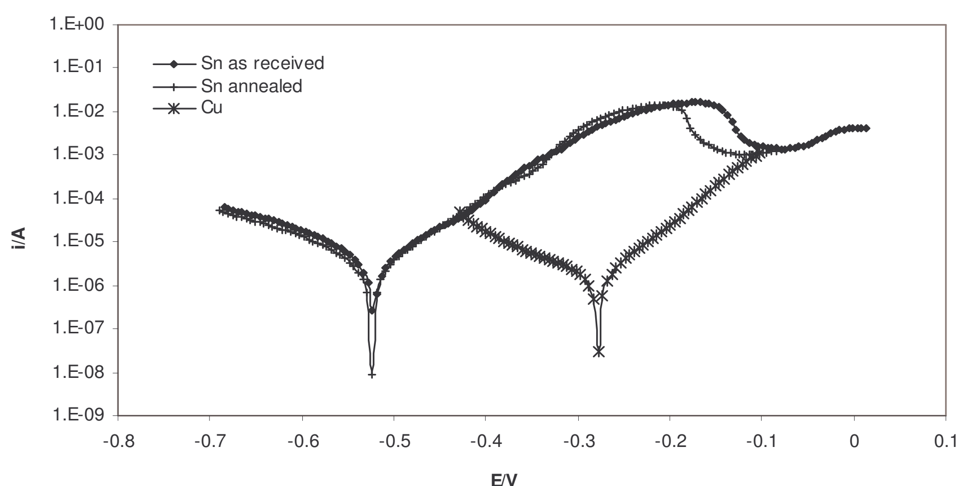


Fig. 1. Polarization studies of 1,4μm thick Sn layer as received and after ageing and for copper substrate in 0,5 M NaCl

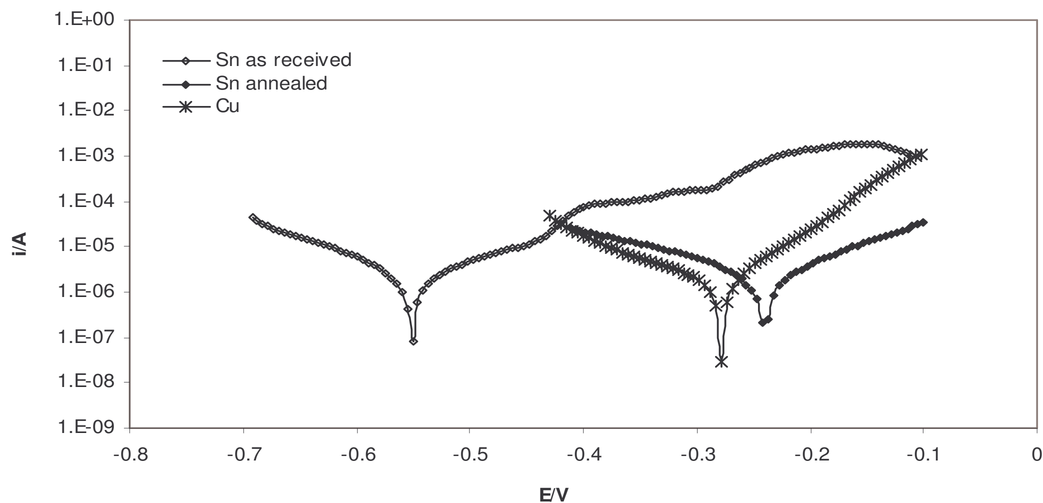


Fig. 2. Polarization studies of 0,2μm thick Sn layer as received and after ageing and for copper substrate in 0,5 M NaCl

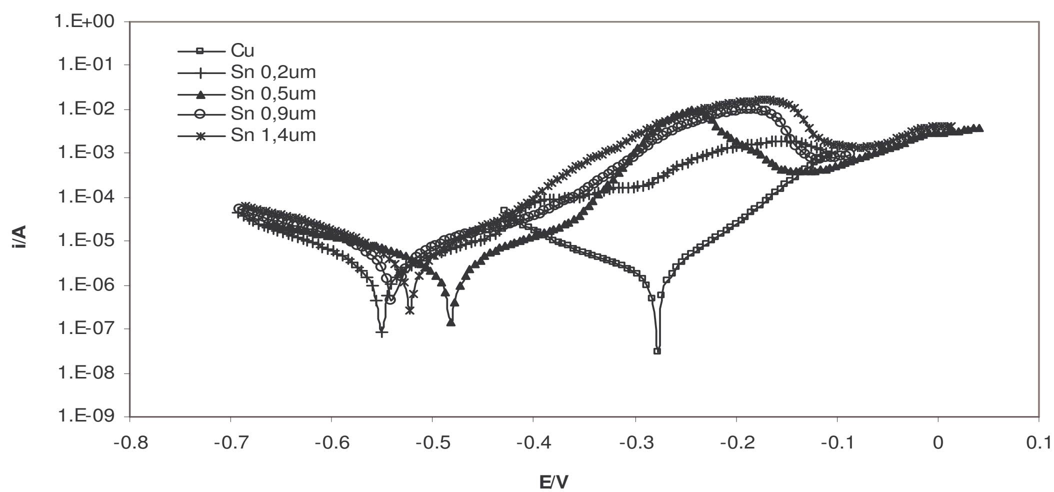


Fig. 3. Polarization curves for Sn layers of different thickness (0,2; 0,5; 0,9 and 1,4μm) as received and for copper substrate in 0,5 M NaCl.

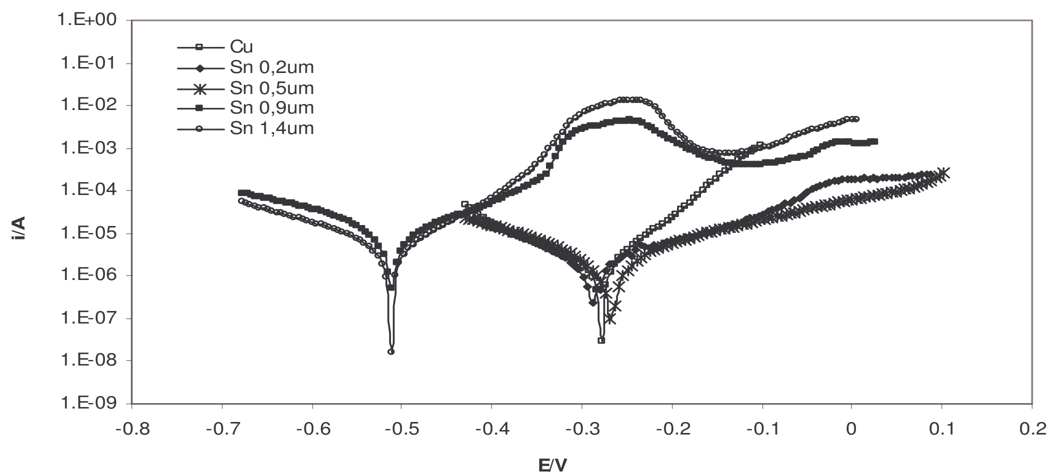


Fig. 4. Polarization curves for annealed Sn layers of difference thickness (0,2; 0,5; 0,9 and 1,4μm) and for copper substrate in 0,5 M NaCl.

The Bode plots obtained for 0,2 and 1,4μm thick tin coatings are shown in figures 5 and 6, respectively. In the case of 0,2 μm coating the highest absolute impedance has annealed coating- figure 5. However, for 1,4 μm coating, the highest absolute impedance has as received tin layer (see figure 6). These findings indicate that after ageing the corrosion occurs slower on thinner coating, but faster on thicker coating. That confirms results obtained from polarization measurements.

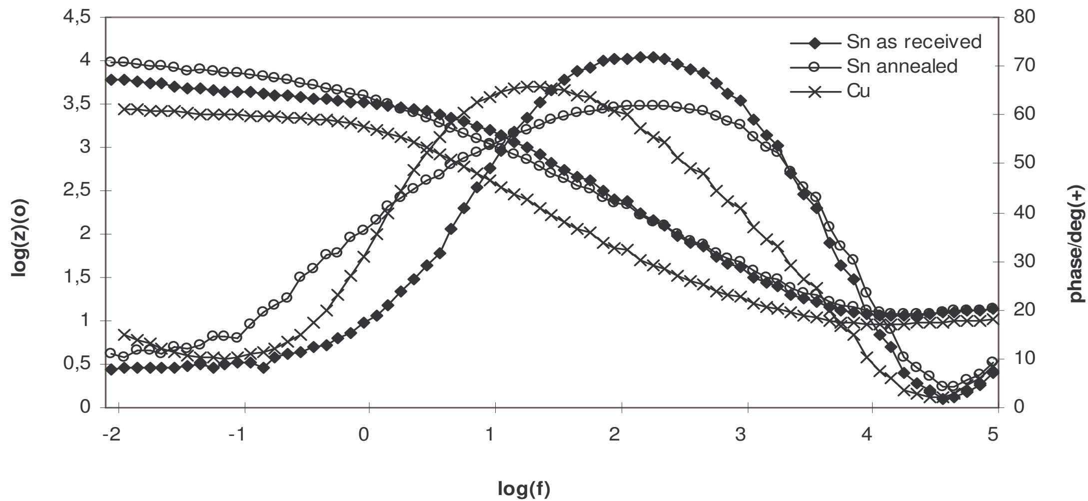


Fig. 5. Bode plots for 0,2μm thick tin layers as received and after ageing as well as for Cu in 0,5 M NaCl

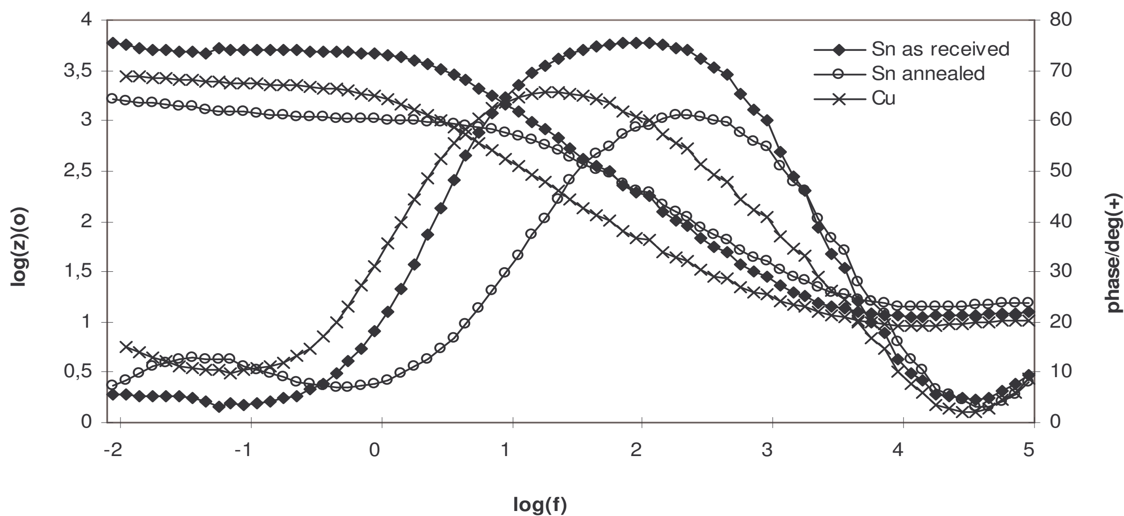


Fig. 6. Bode plots for 1,4μm thick tin layers as received and after ageing as well as for Cu in 0,5 M NaCl.

The values of corrosion current density ($j_{corr}$), charge transfer resistance ($R_{ct}$) and polarization resistance ($R_p$) were calculated from analysis of polarization and impedance curves. Obtained results are shown in tables 2 and 3.

Table 2. Corrosion parameters of as received Sn coatings

| Sample | $E_{corr}$ | $j_{corr}$ | $R_p$ | $R_{ct}$ |
|---|---|---|---|---|
| | V | μA/cm² | kΩcm² | kΩcm² |
| Cu substrate | -0,29±0,01 | 3,8±0,5 | 10±1 | 4,8±0,9 |
| Sn coating - 0,2 μm | -0,53±0,02 | 5,9±2,0 | 10±2 | 6,3±1,0 |
| Sn coating - 0,5 μm | -0,50±0,02 | 4,1±1,6 | 9,4±1,3 | 7,7±1,2 |
| Sn coating - 0,9 μm | -0,54±0,01 | 7,3±0,8 | 6,5±2,6 | 3,8±1,1 |
| Sn coating - 1,4 μm | -0,52±0,01 | 4,6±1,4 | 6,1±0,2 | 5,3±1,4 |

Table 3. Corrosion parameters of Sn coatings after ageing

| Sample | $E_{corr}$ | $j_{corr}$ | $R_p$ | $R_{ct}$ |
|---|---|---|---|---|
| | V | μA/cm$^2$ | kΩcm$^2$ | kΩcm$^2$ |
| Cu substrate | -0,29±0,01 | 3,8±0,5 | 10±1 | 4,8±0,9 |
| Sn coating - 0,2 μm | -0,25±0,03 | 2,3±0,8 | 13±2 | 12±4 |
| Sn coating - 0,5 μm | -0,25±0,02 | 1,5±0,3 | 21±5 | 16±6 |
| Sn coating - 0,9 μm | -0,51±0,01 | 16±2 | 4,5±2,1 | 2,9±0,9 |
| Sn coating - 1,4 μm | -0,51±0,01 | 6±3 | 7,0±1,3 | 1,7±0,8 |

Higher values of $R_{ct}$ as well as $R_p$ were obtained for as received 0,2 and 0,5 μm thick tin layers. This finding can result from a particular structure of such thin coatings. From values of corrosion density current it can be seen that for tin coatings of 0,2 and 0,5 μm in thickness the corrosion is slower for samples after ageing. This effect can be related with the formation of stable intermetallic Sn-Cu compounds throughout the entire coating thickness till the surface. Coatings consisting of intermetallic SnCu compounds exhibit lower corrosion rate in 3,5% NaCl than pure Sn or pure Cu deposits [13]. However, in the case tin coatings of 0,9 and 1,4μm in thickness the rate of corrosion is higher for annealed samples than for as received ones. Such a behaviour can be related to thermally induced structural modifications of Sn coatings.

*Conclusion*

In this work the corrosion resistance of immersion tin coatings of different thickness (0,2; 0,5; 0,9 and 1,4μm) and in the different state (as received and annealed) was investigated. Authors tried to answer the question: Is there any relation between the decay in the solderability and changes in the corrosion resistance of immersion tin coatings? The corrosion tests of studied Sn coatings were performed in as received state and after ageing simulating long-term storage conditions. It was found, that ageing of very thin Sn coatings (below 0,5 μm) leads to an increase in their corrosion resistance in NaCl solution. After ageing these coatings showed a decrease in the corrosion current density and an increase in the polarization / charge transfer resistance- figure 7.

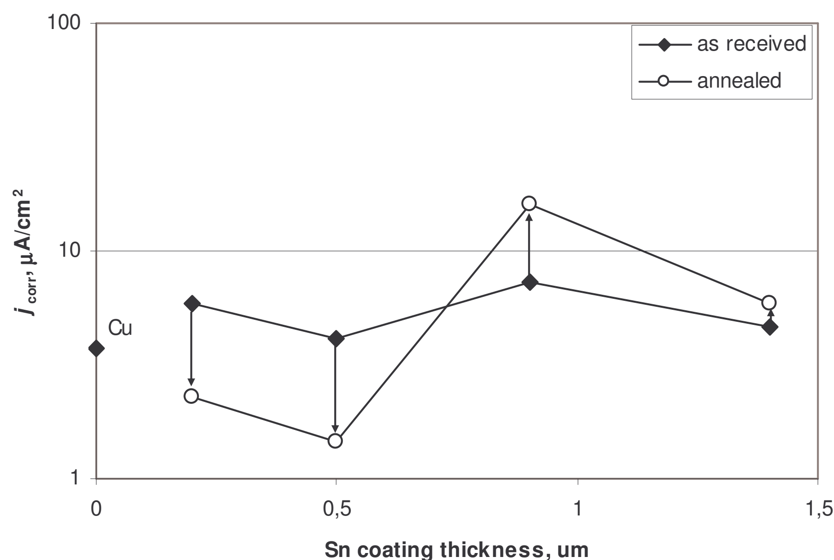


Fig. 7. The ageing effect on the corrosion current density of Sn coatings with different thickness.

Their corrosion potential was shifted in positive direction to the value typical of Cu- figure 8. This effect can be related to the formation of stable Sn-Cu intermetallics throughout the entire coating thickness till its surface. In the contrast to this, thicker Sn coatings (above

0,9 μm) showed slight increase in the corrosion rate in annealed state. An increase in their corrosion rate and small changes in the polarization / charge transfer resistance were observed. Their corrosion potential remained very similar to those in as received state- figure 8.

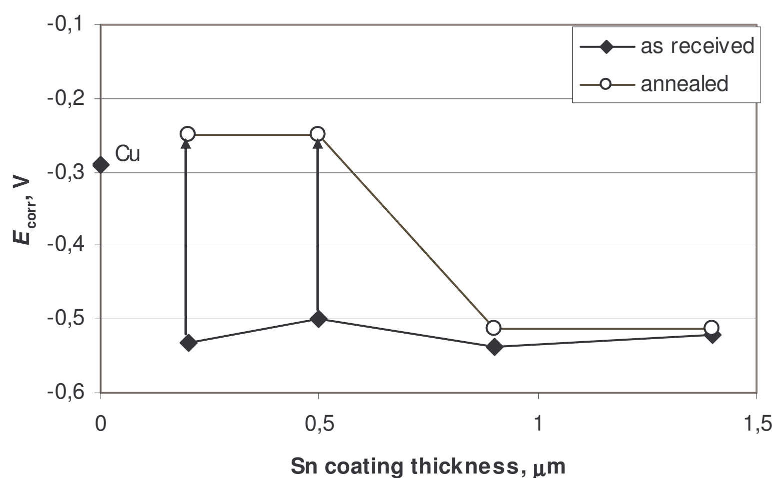


Fig. 8. The ageing effect on the corrosion potential of Sn coatings of different thickness (the $E_{corr}$ value for Cu is indicated on vertical axis)

Probably for thicker Sn coatings the thermally induced formation of Sn-Cu intermetallics occurred only in the inner part of the coatings and their surface was free of these compounds. This can correspond with the ability of thick Sn coatings to preserve good sorderability after longer storage.


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