

# ELECTROLESS TIN DEPOSITION FOR PRINTED CIRCUIT BOARDS

A. Arażna<sup>a</sup>, E. Kurpisz<sup>b</sup>, J. Bieliński<sup>b</sup>

<sup>a</sup> Tele and Radio Research Institute, Ratuszowa 11, 03-450 Warsaw, Poland

<sup>b</sup> Department of Inorganic Chemistry and Solid State Technology, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland  
e-mail: araznetka@itr.org.pl (corresponding author)

## Abstract

Development of the contemporary electronics and particularly in semiconductor industry gives rise to need for high density and precision of printed circuit boards (PCB) and for new techniques of PCB mounting, as surface mounting technology (SMT). In the last 10 years the *increase of environment protection pressure* LED to eliminatION OF Pb use in industry (EU regulation by January 2007). The electroless deposition of tin (so called „immersion tin“) is one of the mostly used alternatives to Pb-Sn COATINGS (hot air solder leveling) of surfaces for flat mounting of electronic components. The main type of electroless tin deposition process in PCB technology is displacement of copper by tin in thiourea-complexed, acidic bath [1-3].

The purpose of this work was the investigation of the thiourea-type electroless tin bath for different parameters of deposition process. The role of baths basic composition (Sn(II)-salt, thiourea TU and HCl concentration) as well as the influence of Cu(I), Sn(IV), benzotriazol and rokafenol additives were investigated. The time of deposition and temperature were also examined as the process parameters. Special investigation was devoted to explain the reason for the stepwise decrease of the coating rate with the deposition time. The thickness (coulometry) and surface morphology of Sn coatings (microscopy) were determined. Additionally the soldering wettability of tinned samples was measured for as-deposited and after annealing.

The experiments results confirmed the dominating influence of the TU and HCl concentration and bath temperature on the Sn deposition rate. Process stops at low TU and HCl concentration because the unsatisfied Cu(I) complexation and Cu passivation effects. To high concentration of HCl and TU stops process as result of Sn dissolution and TU decomposition. The final thickness of deposited Sn (up to 2 μm) is determined by deposition time, when the Cu surface is almost completely covered by tin. The additives of Sn(IV) and Cu(I) salts decreased considerably the tin deposition rate and could response for observed decrease of the coating rate with the longer deposition time. Applied surface active agents did not influence the deposition process in visible manner.

*Keywords:* immersion tin, deposition rate, coulometry, solderability

## Introduction

In the last 20 years a true revolution in the printed circuit boards (PCB) technology was observed. New techniques of PCB assembly, as surface mounting technology (SMT) as well as development of the contemporary electronics and particularly in semiconductor industry, gives rise to need for high density and precision of PCB. Conventional solderable materials (mainly Sn-Pb, coated in hot air solder leveling process), applied as final coatings for the PCB's conductive patterns, are not able to meet new high requirements in SMT. The new metallic coatings, as Au/Ni-P systems, thin electroless palladium, silver or tin layers are stepwise introduced in industry [1,2]. In the last 10 years additionally the growing environment protection pressure on legislation lead to elimination of Pb use in industry (EU regulation by January 2007). The electroless coatings of tin (known in electronics as „immersion tin“) is one of the frequently used alternatives to Sn-Pb coatings in PCB technology. The main type of electroless tin deposition process in PCB technology is displacement of copper by tin in thiourea-complexed, acidic bath, applied after 1985 by IBM in computer production [3].

After 20 years there are still many problems not dissolved in immersion tin process applied in PCB technologies. The optimal coating structure preventing changes in solderability for short – and long-time use and storage is the object of new investigations. Unfortunately the particular details of deposition process are described only in few publications [3-7], limited to data on main bath components and process parameters.

The purpose of this work was the investigation of the thiourea-type electroless tin bath for different parameters of deposition process. The role of baths basic composition (Sn(II)-

salt, thiourea (TU) and HCl concentration) as well as the influence of some other additives were investigated. The time of deposition and temperature were also examined as the process parameters. Special investigation was devoted to explain the reason for the stepwise decrease of the coating rate with the deposition time. The thickness and surface morphology of Sn coatings were determined. Additionally the soldering wettability of tinned samples was measured for as-deposited and after annealing.

### *Experimental*

Immersion tin layers were deposited on copper wires. The surface of copper was degreased and microetched before deposition process, as in earlier work [8]. Table 1 present composition of solutions and other parameters which were applied during samples preparation in aim:

- to determine of role of baths composition and temperature on deposition process;
- to estimate influence of the time of deposition on rate of tin deposition;
- for measurement of the soldering wettability.

In the experiments with time deposition changes and in series with addition of anti-oxidants or wetting agents the tin samples were deposited 30 min at 70°C basic baths: 0,1M Sn(II)-salt, 0,6M thiourea and 0,3M or 0,1M HCl.

The thickness of Sn coatings on Cu was determined by coulometry in 2M HCl. An anodic constant current was applied to the sample and a saturated calomel electrode (SCE) was used to monitor the changes in potential [8]. This method is fast and not expensive and recently used for accurate determination of coatings thickness in PCB industry [9].

Table 1. The composition of baths and process parameters for deposition of immersion tin coatings on copper

Investigation	Influence of bath composition and temperature on the deposition process	Influence of the time on the deposition process	Measurement of soldering wettability
Composition of BATH used to the deposition of tin	0,05- 0,4M SnCl <sub>2</sub> 0,2- 0,5M HCl 0,6- 0,85M TU	0,1M SnCl <sub>2</sub> , 0,3M HCl, 0,6M TU	
Temperature of deposition [°C]	60-80	70	70
Time of deposition [min]	15	15-240	10-60

### *Results and discussion*

#### *Influence of baths composition and temperature on deposition process*

The immersion tin deposition baths were consisting of three basic components (see table 1). In every from series was changed only one component of solution. Two remaining components of solution stay on the same level (SnCl<sub>2</sub>- 0,1M; HCl- 0,3M; TU- 0,6M). The influence of Sn(II) ions, thiourea and HCl concentration and temperature deposition on rate of tin deposition (tin layer thickness) was determined. The results of investigations were presented in Figure 1-3.

The experiments results confirmed the dominating influence of the TU and HCl concentration and bath temperature on the Sn deposition rate [8]. Process stops at low TU and HCl concentration because the unsatisfied Cu(I) complexation and Cu passivation effects. To high concentration of HCl and TU stops process as result of Sn dissolution (according to reaction:  $\text{Sn} + 2\text{HCl} \rightarrow \text{SnCl}_2 + \text{H}_2$ ) and TU decomposition [10]. The thickness of tin layer

grows when temperature increases (Fig. 1-3). But high temperature is disadvantage too, because occurs decomposition of the solution.

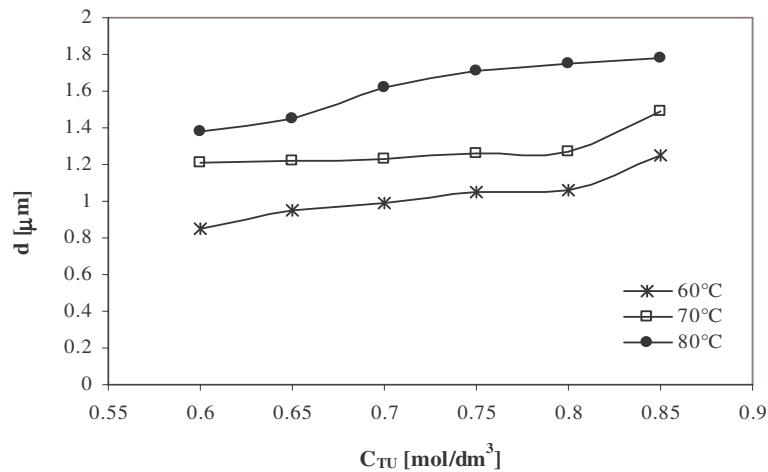


Fig. 1. Changes in thickness of immersion tin coatings deposited at different concentrations of thiourea and bath temperature.

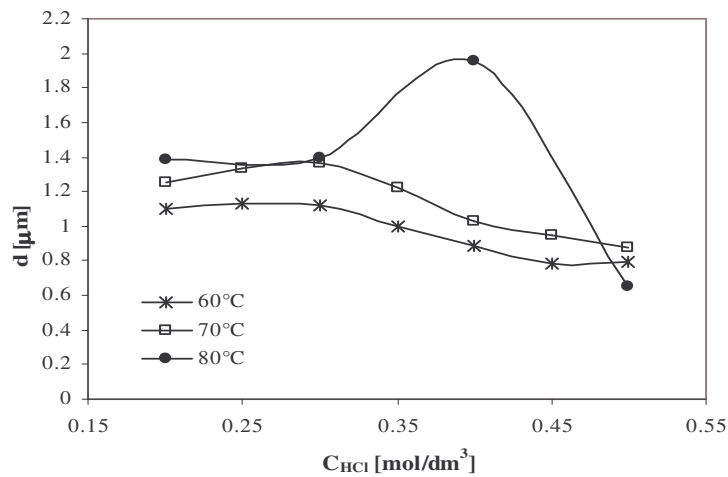


Fig. 2. Changes in thickness of immersion tin coatings deposited at different concentrations of HCl and bath temperature.

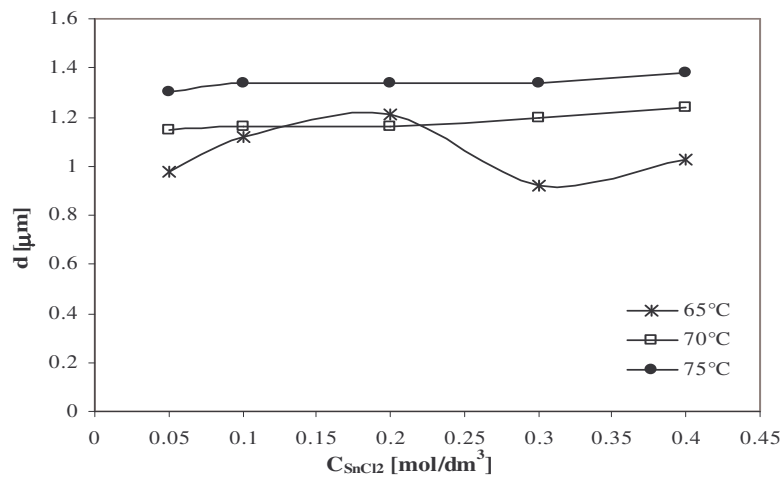


Fig. 3. changes in thickness of immersion tin coatings deposited at different concentrations of SnCl<sub>2</sub> and bath temperature.

### *Influence of the time of deposition on tin layer thickness*

The thickness of immersion tin deposited on copper was determined for deposition time ranged from 15 min to 4 hours (other process parameters according to tab.1). The obtained dependence is presented in fig.4 as a change in tin deposition rate.

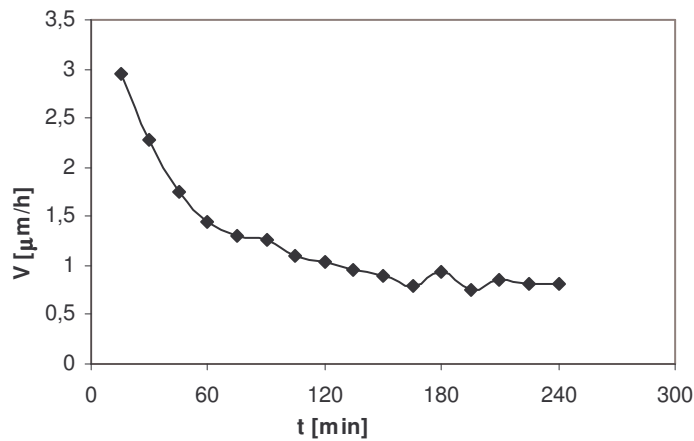


Fig. 4. Changes in deposition rate of tin layer with increased time of immersion.

The deposition rate of tin coatings decreases with extension of tinning time. That is not linear dependence. The deposition rate is higher on the beginning of the process and successively diminishes to the some final level. After about 2 hours the deposition rate starts stay on the same level. The deposition of tin on the copper from thiourea type bath is displacement reaction:  $\text{Sn}^{2+} + 2\text{Cu} \rightarrow \text{Sn} + 2\text{Cu}^+$  (figure 5). In acidic medium follow the dissolution of copper. The thiourea creates strong complexes with copper ions. That keeps concentration of copper ions on the very low level and makes deposition of tin layer on the copper surface possible. On the start deposition the displacement process runs quickly. But when thickness of tin layer increase the displacement Cu for Sn is limited and the deposition rate decreases. That is the main for decrease of the rate the of immersion process with the deposition time - growth of the layer of the tin what can slow down displacement process.

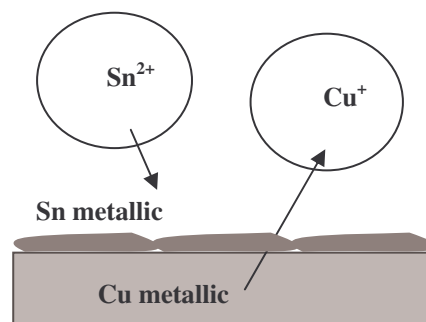


Fig. 5. The immersion deposition of tin on the copper

### *Other factors for decrease of tin deposition rate with the time*

The second probable cause of immersion process slow down is accumulation of the  $\text{Cu}^+$  ions in solution. In this cause the potential of  $\text{Cu(I)}/\text{Cu}$  half-cell is approaching to the values of  $\text{Sn(II)}/\text{Sn}$  half-cell, especially in surface area of copper dissolution, where the alloys Cu-Sn are created likely. The polarization between anodic and cathodic parts of cu substrates

diminishes critically. Another cause for decrease of deposition rate is decrease of Sn(II) concentration as a result of oxidation to Sn(IV) by oxygen dissolving in bath.

To verify the Cu-accumulation and tin oxidation detrimental action, the deposition series were carried out from the basic bath with  $\text{Cu}^+$  (0,05M) or  $\text{SnCl}_4$  (0,1M) additives (Fig.6 and 7). In experiment with Cu(I) additive, 10 successive Cu samples (foil,  $1,88 \text{ cm}^2$ ) were tinned in the same bath. For bath with Sn(IV) additive only 6 samples were immersed successively. The first tinning was made from solution:  $\text{SnCl}_2$  0,1M, HCl 0,3M, TU 0,6M. The second to sixth tinning was made from solution witch contain 0,1M of  $\text{SnCl}_4$  instead of  $\text{SnCl}_2$ .

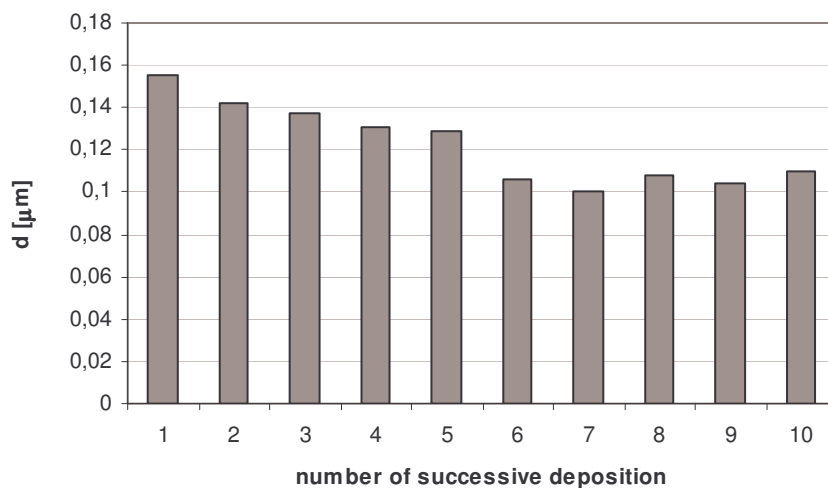


Fig. 6. The change of thickness of tin layer in successive tinning from bath with Cu(I) additive.

The tin layers obtained from solution witch contain  $\text{Cu}^+$  ions are thin (the thickest layer from first deposition has thickness about  $0,15\mu\text{m}$ ). In the next depositions thickness of tin layer slowly decreased. The formation of Cu(I) is then the main cause for decreasing of tin deposition rate after many turnovers of cu substrate without regeneration of bath.

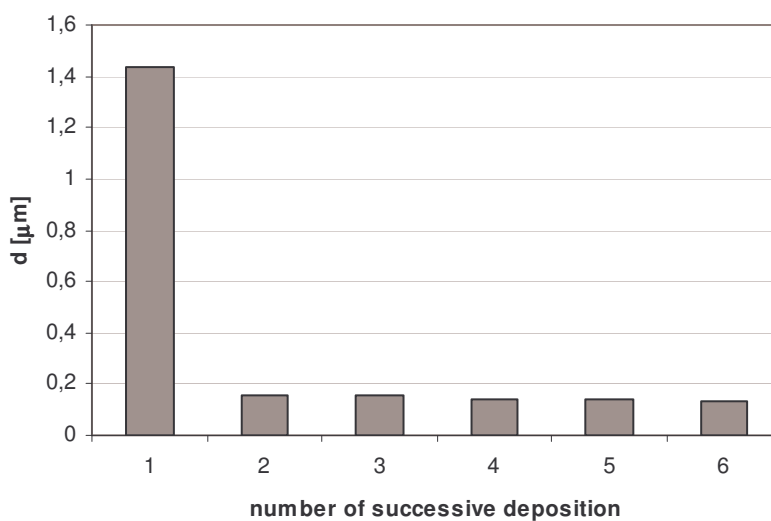


Fig. 7. The change of thickness of tin layer in successive tinning from bath with Sn(IV) additive. 1- Basic bath; 2-6- Bath with Sn(IV) 0,1m.

After addition to the solution  $\text{Sn}^{4+}$  ions the thickness of tin layer drastically decrease. Presence of the  $\text{Sn}^{4+}$  ions in the bath practically stops the deposition. Nevertheless the tin oxidation in bath is less harmful than the Cu(I) accumulation.

#### *Influence of surface active agents on deposition process*

The influence of the 2 surface active compounds on immersion tin deposition process was investigated. Benzotriazol was added to basic bath in aim to complex additionally Cu(I) species [10]. Rokafenol n-8 (analog of tritox n-100, wetting agent) was added in aim to regulate the tin deposition process [11]. In both cases the decrease of immersion tin deposition rate was observed (fig.8). There was no improving in uniformity of tin coatings.

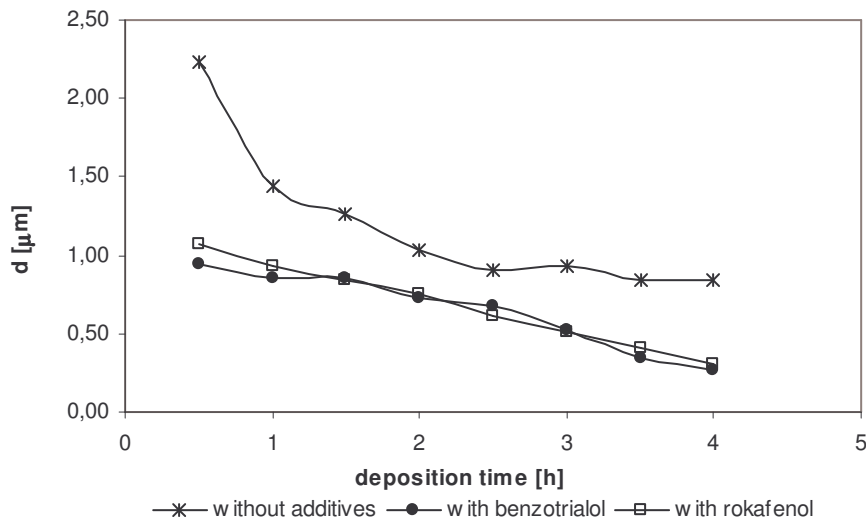


Fig. 8. The influence of the benzotriazol (0,01 M) and rokafenol (0,01 M) additives on the thickness of deposited tin layers.

#### *The soldering wettability*

Measurement of tin coating solderability was performed for samples of different tin thickness. Tin coatings were investigated as received and after ageing (4 h annealing at 155°C in air condition; it is equal to PCB storage over 12 month [12]).

For solderability measurement of PCBs the wetting balance method was used (meniscograph MENISCO ST60). The wetting force  $F_2$ , wetting time  $\tau_z$  and wetting angle  $\theta$  after 3 s were measured and the solderability was evaluated according to Standard's J - STD 003 and J-STD-004 [13,14] and NF A 89400 P [15] requirements for electronics:  $\tau_z < 2$  s,  $F_2 \geq 2/3 F_{\text{max theoretical}}$  [mN],  $\theta_3 < 55^\circ$ . 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 [14] was applied. The solderability results for tin layers of different thickness are presented in table 2.

All investigated samples of immersion tin coatings with thickness above 0,7μm meet solderability requirements in as received state and after aging. However, tin coatings below 0,7μm of thickness have bad or very bad solderability independently on the state of coating.

Table 2. The wetting balance measurement results for Sn coatings of different thickness

Time of deposition of tin coating	Type of tin coating	Thickness of tin coating	$\tau_z$ ( $\theta=90^\circ$ ) [s]	$F_{\max}^{2/3}$ theoretical [mN]	F2 [mN]	$\theta_3$ [°]	Mark
10	Sn – as received	0,74	0,46	0,58	$1,07 \pm 0,01$	$0 \pm 0$	very good
	Sn - 4h at 155°C	0,16	> 10		< 0	$141 \pm 18$	very bad
15	Sn - as received	0,77	0,45		$1,08 \pm 0,01$	$0 \pm 0$	very good
	Sn - 4h at 155°C	0,36	> 10		< 0	$121 \pm 17$	very bad
20	Sn - as received	0,95	0,46		$0,99 \pm 0,18$	$19 \pm 3$	very good
	Sn - 4h at 155°C	0,36	> 10		< 0	$116 \pm 9$	very bad
30	Sn - as received	1,24	0,56		$1,02 \pm 0,02$	$0 \pm 0$	very good
	Sn - 4h at 155°C	0,68	0,77		$0,38 \pm 0,39$	$58 \pm 23$	bad
45	Sn - as received	1,48	0,45		$1,06 \pm 0,07$	$4 \pm 1$	very good
	Sn - 4h at 155°C	0,79	0,62		$0,90 \pm 0,05$	$15 \pm 11$	very good
60	Sn - as received	1,74	0,44		$1,06 \pm 0,04$	$7 \pm 2$	very good
	Sn - 4h at 155°C	1,19	0,66		$0,90 \pm 0,06$	$18 \pm 14$	very good

### Conclusions

The present study reports observations of influence the different parameters of deposition process on immersion tin coating on copper. The following conclusions can be drawn on the basis of the study:

- Dominating influence on the Sn deposition rate have the TU and HCl concentration and bath temperature. Process stops at low TU and HCl concentration because the unsatisfied Cu(I) complexation and Cu passivation effects. To high concentration of HCl and TU stops process as result of Sn dissolution and TU decomposition.
- The deposition rate of tin coatings decreases with extension of tinning time. That can be due by cover of Cu by the tin layer and limited displacement process.
- The additives of Sn(IV) and Cu(I) salts decreased seriously the tin deposition rate. The applied surface-active agents (rokafenol, benzotriazol) decreased tinning process in not large extent.
- The immersion tin coatings deposited from basic bath passed the requirements of good solderability at the tin thickness over  $0,7\mu\text{m}$ .

The authors gratefully acknowledge financial support from the Warsaw University of Technology and Institute of Tele- and Radio Research.

### References

- [1] Bieliński J., Bielińska A., Koziół G. (2001) Elektronika 52:22
- [2] Milad G., Orduz M. (2007) Metal Finishing 105:25
- [3] Kovac Z., Tu K.N. (1984) IBM J.Res.Develop. 28: 726
- [4] Rozovskij G., Petretyte L., Gavrilov G., Karagiozova Z. (1990) Plating Surf.Finish. 77: 60
- [5] Dobрева Ek., Petrova M., Petrov Chr. (2003) Oberflaechen Polysurfaces 44:18; 44: 25

- [6] Huttunen-Saarivirta, E. (2002) Surface and Coating Technology 160:288
- [7] Meeh P. (2003) PLUS 4: 1030; 4: 1346
- [8] Bieliński J., Arażna A., Rzepka A. (2006) Inżynieria Powierzchni 11:32
- [9] Lamprecht S. (2005) Circuit World 31: 15
- [10] Farndon E.E., Walsh F.C., Campbell S.A., J.Appl.Electrochem. (1995) 25: 574.
- [11] Jordan M. Eugen G.Leutze Verlag, Saulgau 1995.
- [12] IEC 60068-2-2 "Environmental testing- Part 2-2: Tests- Test B: Dray heat", 2007
- [13] ANSI/J-STD-003 „Solderability Test for Printed Boards” April 1992, update February 2003
- [14] J-STD-004 "Requirements for Soldering Fluxes", January 1995
- [15] NF A 89400 P "Brasage tendre, Mesure de brasabilité au méniscographe", November 1991