Electrodeposition of Tin-Based Alloys As Functional Coatings

By V.N. Kudryavtsev, K.M. Tyutina, A.N. Popov, S.A. Maksimenko and V.A. Zonin

Tin-based alloy coatings (tin-lead, tin-bismuth, tin-cobalt, tin-nickel) are widely used instead of precious metals in preparing electronic devices, printed circuit boards, etc., for soldering. These coatings provide diverse functional properties for the metal surface, such as good solderability, electroconductivity, corrosion resistance and, to a large extent, determine the reliability and service life of the electronic devices. These requirements are met by a tin-lead alloy (61 percent Sn).[a]

At the Moscow Mendeleev Institute of Chemical Technology (MChTI) a series of investigations was made of the kinetics of bright-tin-based alloy coatings electrodeposited from baths containing brightener systems, and of the properties of the coatings. In recent years, new brightener systems based on aliphatic carbonyl compounds have been synthesized from readily available materials. Fluoboric acid baths based on them have been formulated with a low content of fluoboric acid (as little as 100 g/L). Fluoboric and sulfamate baths are the most widely used baths in the (former) USSR for tin-lead alloy coating. The main purpose was to determine the effects of components of the brightener systems developed at MChTI on kinetics of alloys electrodeposited from acid baths.

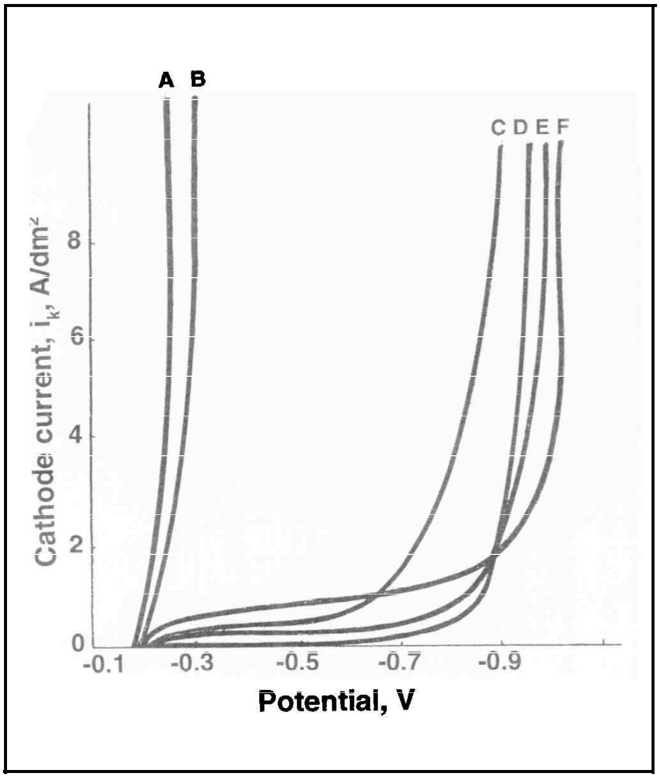

Fig. 1—Polarization curves for tin-bismuth alloy electrodeposition from a sulfuric acid bath; A: 20 g/L $SnSO_4$, 100 g/L H_2SO_4; B: Solution A +20 mL/L HCHO (37-percent solution in water); C: Solution B + 20 g/L nonionic (c) + 10 mL/L N1 brightener; D: Solution A + 10 mL/L N1 brightener; E: So/n D +20 g/L nonionic (c); F: Soln A + 20 g/L nonionic (c).

Without brighteners, the rate of electrodeposition and the throwing power are low in these baths. The deposits are dull and do not retain solderability for long; after 10 to 14 days, soldering, using acid-free fluxes, is impossible. To overcome this difficulty, the coating must be reflowed. In many cases, such an operation is undesirable, even inadmissible, because heat treatment may cause copper to scale off a printed-circuit board, solder to flow into holes, or may lead to other problems. Bright alloy coatings have a number of advantages compared to dull coatings. They retain solderability after long storage, are harder, more corrosion-resistant and less porous. The deposition rate without agitation is three to four times that for dull coatings, and throwing power is better for a bath with a brightener.

Results and Discussion

Many brightener systems employ alcohol solutions of surface-active substances that contain carbonyl compounds and their derivatives. The baths often contain formaldehyde and non-ionic ethoxylated surface-active substances. They are the monoesters of various alcohols with ethylene oxide. Their formulas are:

$C_{20}H_{41}\text{-}O\text{-}(C_2H_4O)_{20}H$[c] (Ref. 1)

$C_{10}H_{21}\text{-}O\text{-}(C_2H_4O)_{10}H$[d] (Ref. 2)

$C_6H_4(R)\text{-}O\text{-}(C_2H_4O)_{12}H$[e] (Ref. 3)

According to various investigations, bright tin alloy coatings incorporate organic impurities which occasionally cause faults in solderability and some difficulties in reflowing. According to operational instructions of some companies: tin-based alloys must not contain more than 0.3 mass percent of carbon to have good solderability. Because of this problem, concomitant with well-known advantages of bright tin-lead alloys, carbon contamination in coatings deposited from our original baths was also studied. Simultaneously with control of incorporated carbon, the solderability of our coatings, stability in aging (storage) and the feasibility of reflowing were investigated.

We recorded potentiodynamic cathode polarization curves for electrodeposition of tin and tin-bismuth alloys (employed as model coatings), baths with various surface active compounds of N1 brightener (a solution of cinnamic aldehyde in alcohol), o-anisidine, a Schiff's base, and amine-cinnamic aldehyde copolymerization products[g] (Fig. 1). The first curve of Fig. 1 is from

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[a] *POS-61*

[b] *MChTI-M4, ALSOC, COSLA, STANEX, etc., mfd. by the chemical plant of the Moscow Mendeleyev Institute. BOS-MChTI mfd. by Voikov Chemical Plant, Moscow. Surfactants listed in subsequent footnotes supplied by the Ministry of Chemical Industries of Russia.*

[c] OS-20

[d] *Syntanol DS-10*

[e] *Neonol 0912*

[f] *0XY (Sel-Rex Div., Enthone-OMI, Nutley, NJ.)*

[g] *STANEX-2H3 (for tin-bismuth alloy), STANEX-3H3 (for tin-lead alloy)*

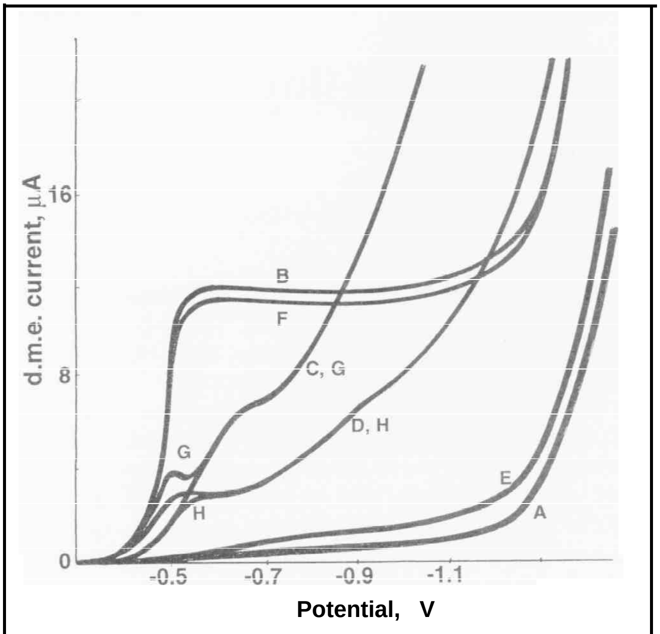


Fig. 2—Polarograms for the following solutions; A: 1M sulfuric acid; B: Solution + 4X10 M tin sulfate; C: Solution A + 1.25 g/L cinnamic aldehyde; D. Solution + 2.5 g/L N 1 brightener; E: Solution A + 1.25 g/L o-anisidine; F: Solution B + 25 g/L o-anisidine; G: Solution B + 1.25 g/L cinnamic aldehyde; H: Solution B + 2.50 g/L N 1 brightener.

a bath without addition agents. Other curves show that all the additives employed inhibit electrodeposition of the alloy. This reduction of electrodeposition rate was accompanied by an increase of cathodic polarization.

Formaldehyde (curve B) is the weakest inhibitor of the electrodeposition process. The main brightener, N1 (curve D), is the strongest inhibitor, as it gives the lowest value of the limiting adsorption current. With the N1 brightener additive alone, inhibition is so strong that the alloy is not deposited at all and only hydrogen is evolved. When the ethoxylated substance is added to a bath containing the main N1 brightener (curve E), the limiting adsorption current is somewhat higher and this is associated with deposition of dull alloy coatings.

Addition of formaldehyde to a bath containing ethoxylated compound and N1 brightener (curve C), produces a small increase in alloy electrodeposition. It has been reported that the uninhibiting effect of formaldehyde can be attributed to the fact that when a carbonyl group is adsorbed on the cathode, in the same way as cinnamic aldehyde, it binds a certain number of active centers.[4] In contrast to cinnamic aldehyde, shielding by formaldehyde is weak, inasmuch as it contains hydrogen instead of a bulky aryl radical. Therefore, overall inhibition by the surface-active organic compounds decreases. In the presence of these addition agents (curve C) mirror-bright coatings of the alloy are deposited. The leveling agent in the N1 brightener composition is cinnamic aldehyde,[5] the inhibiting action of which, just as that of the N1 brightener additive as a whole, increases as agitation increases. According to the adsorption-diffusion theory of leveling, such behavior may be considered proof of its leveling properties.[6]

Figure 2 shows polarograms that characterize the effect of the brightener additive and its components on reduction of tin ions on a dropping mercury electrode (d.m.e.). It is evident that cinnamic aldehyde is reduced on the d.m.e. (curve C) at a potential of -0.45 V (vs. n.h.e.). For the solution containing cinnamic aldehyde and the tin salt at more positive potentials, where reduction of cinnamic aldehyde begins, curves G and H exhibit a rise, which indicates reduction of the tin. At potentials more negative than -0.45V, the additive yields a "wave" that is a result of reduction of the cinnamic aldehyde (curves D and H); the height of the waves is much smaller than for the same concentration of pure cinnamic aldehyde (curves C and G). This may be because of a decrease in its concentration in the N1 brightener additive by the reaction:

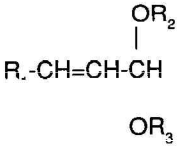
$$\mathrm{Ar^{*}\text{-}\ CH = CH - CHO + H_2N - Ar - OCH_3} \rightarrow$$

$$\mathrm{Ar - CH = CH - CH = N - Ar - OCH_3 + H_2O}$$

In the region of potentials more negative than -0.45V, cinnamic aldehyde and the N1 brightener additive (curves D and H) reduce the rate of tin ion reduction practically to zero; this follows from a comparison of curves G and H with curves C and D. Because the heights of the waves that correspond to reduction of cinnamic aldehyde (curve C) and of cinnamic aldehyde in the presence of tin (curve G) are the same, it can be concluded that the current density fraction associated with tin in curve G corresponds to "zero" current density. It means that the rate of reduction at potentials more negative than the potential at which cinnamic aldehyde reduction begins is negligibly small. From these results, it follows that the inhibiting effect of the cinnamic aldehyde and the N1 brightener additive is a result not mainly of cinnamic aldehyde proper in the molecular form, but of the products of its reduction at the cathode. The same effect was found in refs. 7 and 8.

During electrodeposition of tin or its alloys, the inhibiting effect of the brightener system gradually decreases. It maybe assumed that products of cinnamic aldehyde reduction that inhibit the cathode process more strongly than its molecular form are continuously removed from the zone of the electrochemical reaction, either by reduction to a weak-inhibitor modification or by mechanical incorporation into the alloy deposit. Ortho-anisidine is electrochemically inactive, and catalyzes hydrogen discharge to some degree (curve E), and slightly inhibits reduction of tin (curve F).

The newly developed brightener N2, based on an aliphatic aldehyde type of brightener system[h] also consists of an ethoxylated nonionic surface active substance, a brightener and formaldehyde.[9] The composition of the N2 additive was investigated by NMR and PMR spectroscopy and other physiochemical analytical methods.[10] The main inhibiting component of the N2 brightener system was determined; the component in question (component 1) has the following structural formula:



$$\mathrm{R_1\text{-}CH{=}CH\text{-}CH(OR_2)(OR_3)}$$

where R_1 is an alkyl or aryl group (such as CH_3, or C_6H_5).

The way in which the structure of component 1 influences the kinetics of the cathodic process during electrodeposition of tin

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* Aryl

[h] MChTI-M4

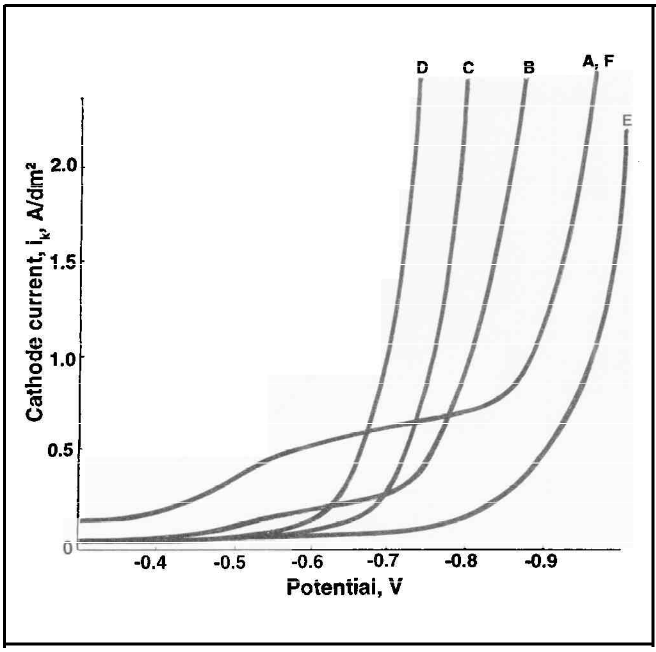

Fig. 3-Polarization curves for tin electrodeposition in the presence of N2 brightener; A: 1MH_2SO_4,10g/L monionic (d); B: Solution A + 1mL/L brightener NS ($R_1$is CH_3); C: Solution B + 5 mL/L brightener NS (R_1 is CH_3); D: Solution C +2 mL/l HCHO (37 percent solution in water); E: Solution A + 5 mL/L Compound 1 (R_1- is C_6H_5); F: Solution A +2 mL/L HCHO.

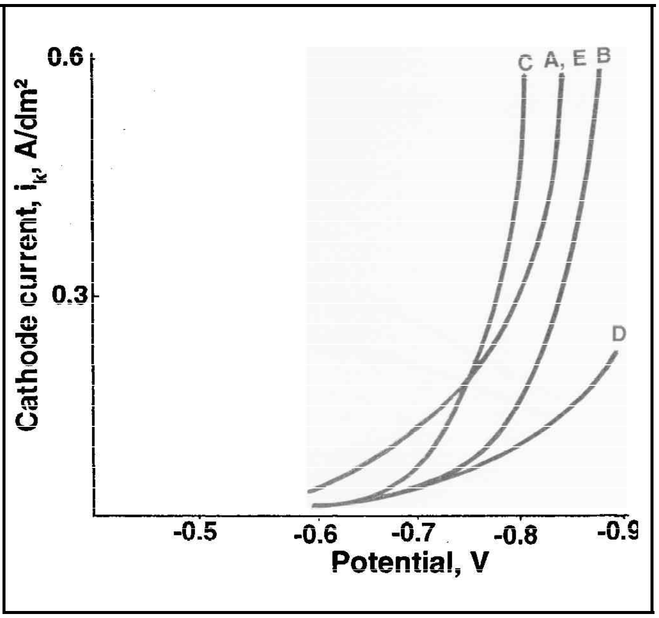

Fig. 4-Polarization curves for hydrogen discharge on a tin electrode in the presence of brightener N2 system components; A: 1M H_2SO_4; B: Solution A + 10 g/L nonionic (d); C: Solution B + 5 mL/L brightener N2 ($R_1$is CH_3); D: Solution B+ 5 mL/L Compound 1 ($R_1$is C_6H_5; E: Solution A + 2 mL/L HCHO (37-percent solution in water).

from an acid bath may now be considered. Figure 3 shows the potentiodynamic cathodic polarization curves for tin electrodeposition from a bath with and without brightener additive N2 (curve A). As can be seen from curves B and C, when the radical RI is a CH_3 group, increasing the concentration of additive results in inhibition of the cathode process over the potential range -0.35 to -0.75V. At more negative potentials (i.e., where hydrogen can be discharged), increasing the concentration of the additive results in depolarization of the overall cathodic process. When the radical R_1 is a C_6H_5 group (curve E), the additive inhibits the cathode process at all potentials.

To determine the cause of depolarization of the overall process (when R_1 is CH_3), the effect of the brightener additive on the hydrogen discharge at the tin electrode was investigated. The polarization curves for hydrogen discharge in the bath, with and without the components of the N2 brightener systems, are shown in Fig. 4. Curve A represents the hydrogen discharge process in acid without addition agents. As can be seen from curve B, a nonionic compound[d] increases the cathode polarization during hydrogen discharge; formaldehyde (curve E) has no effect. The brightener may either enhance polarization (curve D) if radical RI is C_6H_5, or produce depolarization (curve C) if radical R, is CH_3, during hydrogen discharge. Similar measurements made on the lead electrode showed that at -0.8V, there is a limiting diffusion current proportional to the bulk concentration of the additive. From this, it follows that the additive is reduced in the operating range of the potentials under diffusion control. From these experiments, it can also be concluded that one of the causes of cathode depolarization at potentials of about -0.7V is acceleration of hydrogen discharge by component 1.

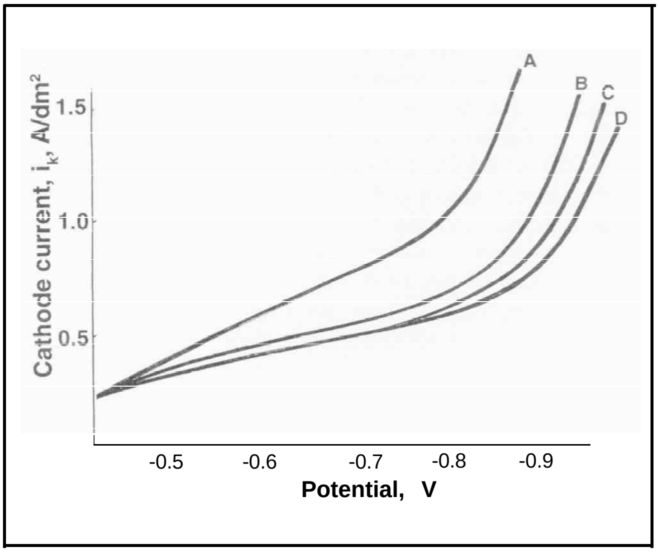

Fig. 5-Polarization curves for tin electrodeposition in the presence of nonionic (d); A: 1M H_2SO_4, 0.1M $SnSO_4$, 2.5 g/L (d); B: Solution A +2.5 g/L nonionic (d); C: Solution B + 5 g/L nonionic (d); D: Solution C + 10 g/L nonionic (d).

Accordingly, these investigations show that additives with brightener properties (or their reduction products) can not only inhibit the overall process over the entire potential range (component 1 when $R_1$is C_6H_5) but can also depolarize the overall process in the range of negative potentials (component 1 when RI is CH_3).

To determine whether it is possible to replace a nonionic surface active component with some others, we investigated the way in which the cathode process is affected by the following surface active substances:[11] Cationics,[i] nonionics,[c,d] and nonionic aromatics.” From the potentiodynamic cathode polarization curves, it is evident (Fig. 5) that “nonionic (d)” inhibits the cathode process at concentrations up to 10 g/L, (curves A-C). Further increase in concentration does not alter the polarization curves (curve D, Fig. 5).

From Fig. 6, it can be seen that addition agent “nonionic (c)” inhibits the cathode process at concentrations up to 20 g/L (curves A-C). Similar measurements made with other nonionic ethoxy surface active substances showed that the largest decrease in the limiting adsorption current occurs at concentrations proportional to the degree of ethoxylation; for instance,

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[i] Catamin-B

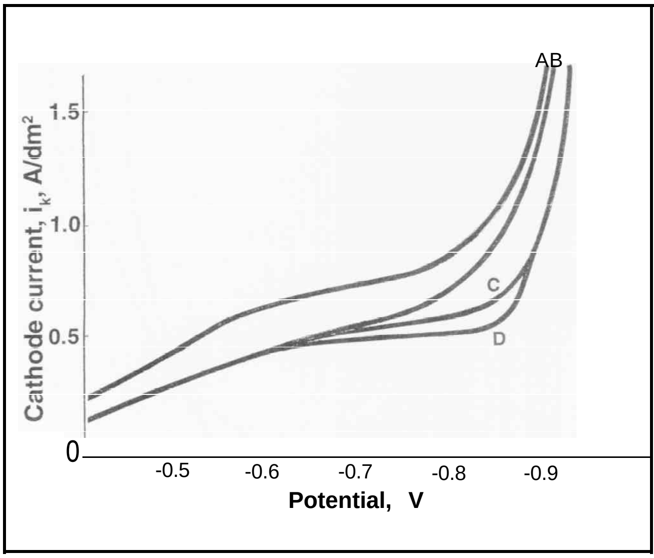

Fig. 6—Polarization curves for tin electrodeposition in the presence of nonionic (c); A: 1M H_2SO_4, O.1M $SnSO_4$, nonionic (c) 5g/L; B: Solution A + 5 g/L nonion (c); C: Solution B + 10 g/L nonionic (c); D: Solution C + 10 g/L nonionic (c).

for “nonionic (c)” at 20 g/L, for "nonionic (d)” at 10 g/L, and for “nonionic aromatic (e)” at 12 g/L, without any significant effect resulting from the nature and length of the hydrocarbon radical. It follows that all nonionic ethoxylated surface active substances, being wetting agents, can be used in aliphatic brightener N2 and other systems at concentrations above the necessary minimum, which is proportional to their degree of ethoxylation.

Conclusions

A number of general conclusions can be drawn concerning the mechanism of the effect of the brighteners as a result of these investigations. The Schiff's base and acetal (component N1), which are constituents of the additives in question are hydrolyzed according to the following schemes in acid solutions:

$$R_1\text{-}CH=CH\text{-}CH=NR_2 \rightarrow$$

$$R_1\text{-}CH=CH\text{-}CH=OH^+ + H_2NR_2$$

$$R_1\text{-}CH=CH\text{-}CH\underset{OR_3}{\overset{OR_2}{\rightarrow}}$$

$$R_1\text{-}CH=CH\text{-}CH=OH^+ + R_2OH + R_3OH$$

In both cases, despite the different initial substances, the same protonated form of the aldehyde is produced, and this determines the effect on the kinetics of the electrocrystallization of bright deposits of tin and its alloys.

We have also studied carbon incorporation in the alloy by electrostatic accelerator (Van de Graaf), according to proton emission of nuclear reaction

$$C^{12} + d \rightarrow C^{13} + p^+$$

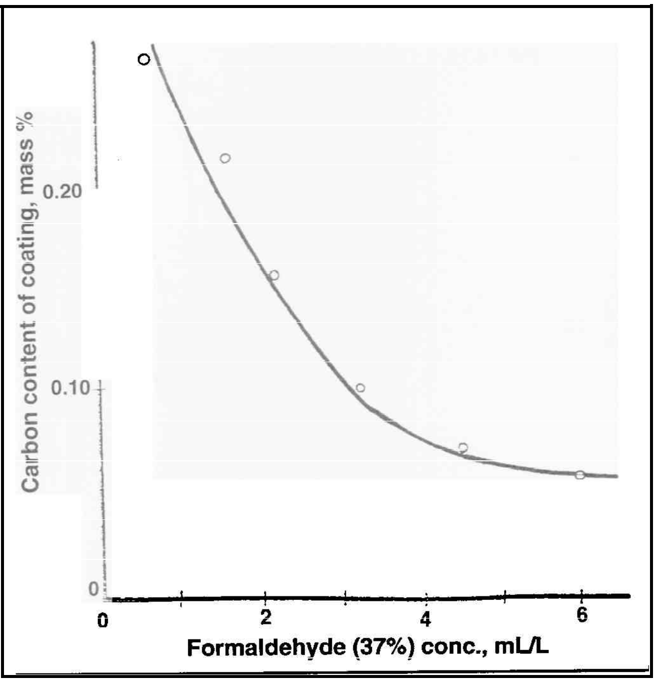

Fig. 7—Carbon Concentration in coating obtained from the bath with brightener N3 as a function of formaldehyde volume concentration in the bath.

Figure 7 shows the amount of carbon contained in tin-bismuth coatings electrodeposited from the baths with brightener N3 and depending on formaldehyde volume concentration in a bath. Formaldehyde concentration significantly influences the amount of incorporated carbon in a coating. In the absence of formaldehyde, a bright coating contains a large amount of carbon, about 0.3 mass percent. An addition of formaldehyde to the bath in concentrations up to 6 mL/L (37 percent aq. solution) decreases the amount of incorporated carbon from 0.3 to 0.07 mass percent. Dull coatings obtained from the same brightener-free bath usually contain from 0.0001 to 0.01 mass percent of carbon.[12] Solderability investigations have shown that in spite of rather high carbon impurities in bright coatings, the speed of soldering is ten times higher than the speed of soldering for dull coatings.

The information on mechanisms of brighteners studied, obtained from kinetics and other fundamental investigations, allowed us to influence the quality (visual), solderability and some other special characteristics of Sn-Pb alloy coatings. The investigations of the nature of brightener systems and how they influence electrodeposition of tin and its alloys, led to development of optimal compositions of brightener additives and systems based on them. Employment of these systems resulted in development of a set of up-to-date baths for the deposition of bright tin-based alloy coatings, widely used in (former Soviet) electroplating shops, as described in the table.

All these baths yield mirror-bright coatings with Sn(61%)-Pb alloy that retain their solderability, without reflowing, over a period of more than 18 months, and which are stable with respect to cupro-ammonium and other special etching agents employed in the subtractive technology of manufacturing printed circuit boards. The baths are stable (up to 1000 A. hrs/L), possess high throwing power and a small positive leveling power (+0.4 to 0.5). Exactly such a leveling power provides optimal distribution of the coating in the mouths of through-holes in printed circuit boards.

Baths 1 and 2 permit deposition of Sn(61%)-Pb alloy on multi-layer printed circuit boards (MLPCB) with a ratio of board

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Bath Compositions for Deposition Of Bright Tin-Lead Alloy Coatings

Bath components	Bath no.				
g/L	1	2	3	4	5*
$Sn(BF_4)_2$	60	49	120	120	—
$Pb(BF_4)_2$	25	25	50	50	—
HBF_2	300	150	150	300	—
$Sn(SO_3NH_2)_2$	—	—	—	—	120
$Pb(SO_3NH_2)_2$	—	—	—	—	25
HSO_3NH_2	—	—	—	—	150
nonionic[c]	25	—	—	25	—
nonionic[n]	—	25	30	—	20
Brightener N1	5	—	—	12	—
Brightener N2	—	15	—	—	—
Brightener N3	—	—	25	—	—
Brightener N4**	—	—	—	—	30
I (A/dm²)	2-8	5-12	8-25	8-25	8-40
Leveling Power	0.4-0.5	0.4-0.5	—	0.4-0.5	—
Throwing Power (at I = 5 A/dm²)	54%	54%	—	—	—

*Bath MChTI-C

**BOVI

thickness to through-hole diameters of 5:1 and 8:1, providing, respectively, 75 and 80 percent thickness (Bath 2) and 65-75% thickness (Bath 1) at the center of the through-hole. By decreasing the concentration of the bath, distribution of the alloy in the through-holes of a MLPCB can be made even more uniform. This is an effect of the high throwing power of Baths 1 and 2.

Bath 4 is used for deposition of the Sn(61%)-Pb alloy on ribbons, wire blanks of integrated circuit leads at deposition rates of 15 m/min and higher, without agitation. Therefore, with respect to its operating properties, Bath 4 is comparable to well-known western commercial baths[f] and is being used in countries outside the (former) USSR. Baths 1 and 2 have been introduced into commercial practice for production of printed circuit boards in existing plating lines[k,l,m] in the (former) USSR and Baths 3 and 5 are used for continuous wire coating processes.

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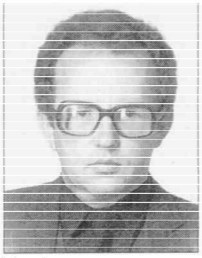
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[k] Sts Plating Line

[l] Dina-plus Plating Line, Schering AG Galvanotechnik, Berlin

[m] OXY Modul-R Plating Line, Enthone-OMI, Nutley, NJ.

[n] Syntanol ALM-10