

Preparation of metal powders from sulfamate baths. I)

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RIASSUNTO - PREPARAZIONE DI POLVERI METALLICHE PER ELETTRODEPOSIZIONE DA BAGNI SOLFAMMICI. I) - E' stato effettuato uno studio sperimentale sistematico sulla preparazione, per elettrodeposizione da bagni solfammici, di polveri o spugne di: Cu, Ag, Zn, Cd, Ni, Co, Pb, Sn, In, precisando le condizioni optimum per quanto riguarda: composizione dei bagni, temperatura e densità di corrente, e le principali caratteristiche morfologiche.

ABSTRACT - A systematic experimental study of the preparation conditions by electrolysis from sulfamate baths of powdery or spongy deposits of Cu, Ag, Zn, Cd, Ni, Co, Pb, Sn, In has been carried out, determining the optimum conditions as far as: bath composition, temperature and current density are concerned, and the main morphological properties.

A significant part of the production of metal powders is carried out, at present, by electrolysis. Thus about half of the Cu and a large part of the Ni, Fe, Mn — powders are obtained electrolytically.

It is well known that the methods of producing metal powders by external electrolysis are:

1. the direct method, by which powdery deposits are obtained;
2. the indirect method, by which brittle deposits are separated, suitable for a successive grinding;
3. the indirect method, by which amalgams are obtained and then the mercury distilled off.

Among the electrochemical methods, one may consider also:

4. the powder production, by displacement of the metal, to be obtained in powdery form: by means of a less noble one (eventually by « internal electrolysis » in diaphragm cells).

Each one of these methods is characterized by its own peculiarities; but the methods: 1), 4), present the common requirement that the metal is obtained in powdery form, thank to: the high ratio of

the nucleation rate in respect to the growth rate of the existing nuclea; and to the cooperation of circumstances, hindering the agglomeration of the coarse crystals to form a compact metallic phase.

In the case of the indirect method 2), the practical success of the preparation rests on the possibility of imparting to the deposits the suitable brittleness, arising from a status of mechanical stress of the plated metal.

In the case of the method 3), it is just required the preparation of suitable amalgams, with the minimum costs arising from the power and materials consumption.

Applications of the sulfamate baths

1. Early work

In the early research work of Piontelli and Giulotto (1) on the electrodeposition from sulfamate baths, the formation of deposits: either powdery or spongy, or brittle and thus suitable to give metal powders by grinding, has been recognized for various metals and conditions. Thus, powdery deposits were obtained: from

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baths of $\text{Cu}\sigma_2$; $\text{Ag}\sigma$ (for instance: 0.2 M, at 160 A/m²); $\text{Cd}\sigma_2$ (1 M, over 1,000 A/m²); and for other metals (Pb, Zn) and conditions. Brittle deposits were observed with Fe, Ni, Mn, Co; for instance: for Fe, with $\text{Fe}\sigma_2$ 1 M, $\text{H}\sigma$ 20 g/l, at 36°C, 500 A/m²; for Ni, with $\text{Ni}\sigma_2$ 1 M, $\text{H}\sigma$ 5 g/l, glue 0.2 g/l, at 15°C, 50/200 A/m²; for Co, with $\text{Co}\sigma_2$ 1 M, $\text{NH}_4\sigma$ 50 g/l, at 20°C, 200 A/m².

The only successively published paper on this matter appears to be the short one by Kikuchi, Takiguchi, Yanagisawa (2). The Authors obtained the Cu powder by electrolysis of acid sulfamate baths: $[\text{Cu}^{2+}]$ 0.25 M, $\text{H}\sigma$ 0.13 to 0.5 M, pH from 1 to 4, at 1,000 A/m². The powder from sulfamate bath was mainly formed by typical flat dendrites; while the one, obtained in analogous conditions from the sulphate bath, contained particles of different shape. The oxygen content of the sulfamate powder was lower than the one of the sulphate powder.

This interesting characteristic of the sulfamate baths of giving deposits uncontaminated by basic compounds, together with other peculiarities of the baths themselves (e.g. the fact that some salts of the sulfamic acid — as the one of Pb — are soluble, while the corresponding ones of the most common acids — e.g. sulphuric, hydrochloric — are practically insoluble, etc.), suggested us to accomplish a new research work on the direct powder production by electrolysis from sulfamate baths.

2. New experiments on the direct* powder production from sulfamate baths

The deposition was carried out in small parallelepiped ($9 \times 5 \times 4$ cm) glass cells, in which a rectangular plate cathode (of the metal to be deposited, or also of: graphite, stainless steel, Al, Cu) was placed between two symmetrically arranged anodes of the metal to be deposited. No stirring was provided.

The investigation concerned the characteristics of the deposits, in the explored range of conditions (bath composition, current density (c.d.), temperature) and the power consumption, through the two factors (current efficiency and cell voltage) involved.

The total circulated charge was measured by means of a copper voltameter, arranged in series with the circulating current.

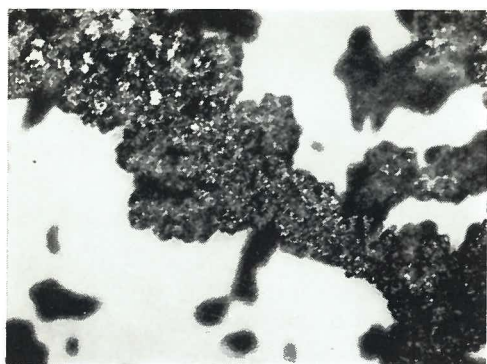
Tables 1 to 5 and figures 1 to 3 summarize the results of the new research work accomplished on the direct production of powder, by cathodic deposition of the metals: Cu, Ag, Zn, Cd, Ni, Co, Pb, Sn**.

* The experiments summarized here did not concern the preparation of brittle compact deposits.

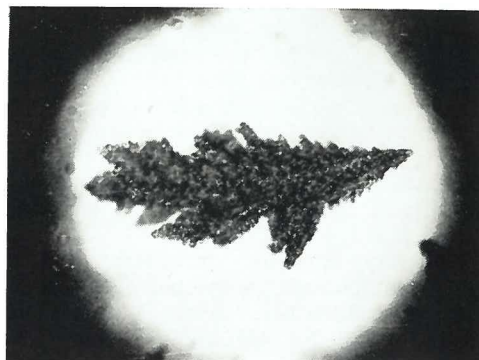
** The production of spongy deposits, suitable to give powders, is also easy for such metals as Tl, whose behaviour was not systematically investigated, however, like the one of the platinum group metals, readily obtained in the form of « blacks ».

TABLE 1
Conditions for Cu-powder deposition

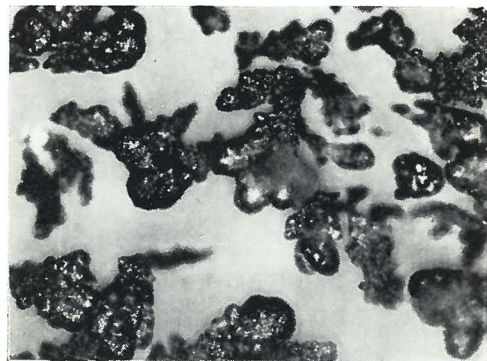
bath			T (°C)	c.d. (A/m ²)	cell voltage (V)	η_c (%)	observ.
$[\text{Cu}^{2+}]$ M	$[\text{H}\sigma]$ M	pH					
0.1	1.5	—	20	100	1.1	77	—
0.1	—	4.0	20	200	7.8	—	dark, basic comp.
0.2	1.5	—	20	100	1.2	80	—
0.2	1.5	—	20	500	3.1	60	—
0.2	1.5	—	20	1,000	5.0	55	—
0.2	—	1.4	20	500	5.2	95	—
0.2	—	1.4	25	1,000	8.2	85	—
0.25	1.5	—	20	100	1.1	90	—
0.25	1.5	—	20	500	3.0	70	—
0.35	1.5	—	20	500	3.2	95	—
0.35	1.5	—	20	1,000	6.0	93	—
0.35	—	1.3	30	1,000	10	96	—
0.5	—	1.3	25	1,000	7.5	96	—



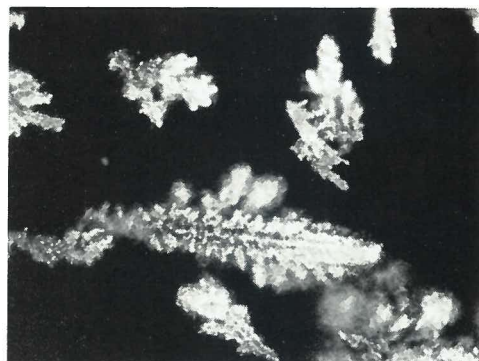
a Cu $\times 200$



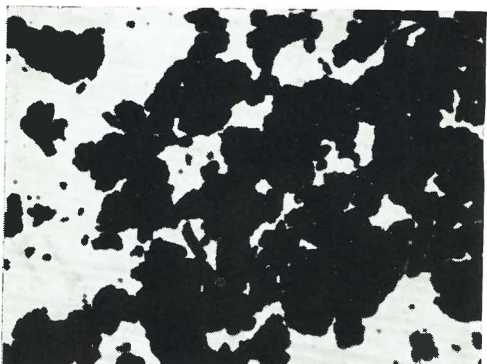
b Cu $\times 200$



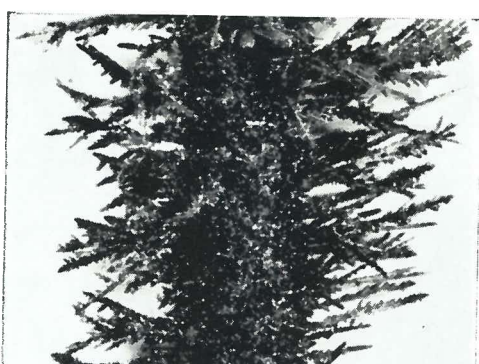
c Cu $\times 200$



d Cu $\times 200$



e Cu $\times 50$



f Cu $\times 2.5$

Fig. 1 - Cu - a): $[\text{Cu}^{2+}]$ 0.2 M, $H\sigma$ 1.5 M, 20°C , 100 A/m^2 ;
b): $[\text{Cu}^{2+}]$ 0.1 M, $H\sigma$ 1.5 M, 20°C , 500 A/m^2 ;
c): $[\text{Cu}^{2+}]$ 0.35 M, pH 1.3, 25°C , 500 A/m^2 ;
d): $[\text{Cu}^{2+}]$ 0.35 M, pH 1.3, 30°C , $1,000 \text{ A/m}^2$;
e): $[\text{Cu}^{2+}]$ 0.1 M, pH 4.0, 20°C , 200 A/m^2 ;
f): $[\text{Cu}^{2+}]$ 1 M, pH 1, 50°C , $1,000 \text{ A/m}^2$.

a. Cu-powder preparation

The conditions for Cu powder deposition from $\text{Cu}\sigma_2$ solutions have been thoroughly investigated as far as the influence of bath composition and c.d., the morphological properties of the products, the presence of basic compounds and other significant aspects of the process are concerned (see tab. 1 and fig. 1).

Powdery deposits, uncontaminated by basic compounds, may be obtained, at room temperature, from baths: $\text{Cu}\sigma_2$ (0.1/0.35 M) + $\text{H}\sigma$ (pH \leq 1.5), at 100/1,000 A/m².

Tab. 1 indicates the optimum conditions also with orientative figures on the cathodic current efficiency and cell voltage.

The current efficiency decreases by decreasing $[\text{Cu}^{2+}]$ and increasing c.d. In spite of the increment of power consumption, it is not convenient in practice to operate in a way to get current efficiency higher than 90/95%, in view of the excessive tendency to formation of compact and not easily detachable deposits.

At low pH, the deposits are clearer and exempt from basic compounds. At pH $>$ 1.5 the oxygen content of the powder becomes higher and the bath is less stable.

The size of particles increases with $[\text{Cu}^{2+}]$.

In the low c.d. range (in which the tendency to the formation of compact deposits is especially marked), the particles are tendentially rounded. By increasing c.d. the structure becomes tendentially bidimensional, especially in the form of fern leaves and other laminar notched forms.

The pH increments promote the tridimensional form of the particles.

Deposits rich in trees and needles and particles of fern leaves shape are obtained, for pH \leq 1, even with $[\text{Cu}^{2+}] = 1/1.5$ M (fig. 1 f).

b. Ag, Zn, Cd, Ni, Co, Pb, Sn, In - powder preparation

At room temperature, dilute solutions of $\text{Ag}\sigma \leq 0.2$ M, at c.d. in the range of 2,000 A/m², give crystalline powdery deposits. When the ratio c.d./ $[\text{Ag}^+]$ is furtherly increased, black silver deposits may be obtained.

At room temperature, spongy deposition of Zn is obtained* in the following conditions:

1. acid Zn salt solutions at high c.d.;
2. neutral Zn salt solutions at very low c.d.

Moreover, rough powder is obtained with neutral Zn salt solutions at high c.d.

Cd is obtained in powdery form more easily than Zn. The conditions for Cd are therefore less drastic than for Zn: for instance, at equality of other conditions, lower c.d. are required.

Ni powders (generally having the shape of spear points: fig. 3 a, b) are obtained at room temperature from baths: $\text{Ni}\sigma_2 \approx 0.1$ M, $\text{NH}_4\sigma$ 0.4/0.5 M, $\text{NH}_4\text{Cl} \approx 0.1$ M (in order to prevent the anode passivation), pH $>$ 2.5, in the c.d. range 500/2,000 A/m². The range of conditions in which powdery Ni deposits can be obtained is very narrow**. In order to obtain powdery deposits,

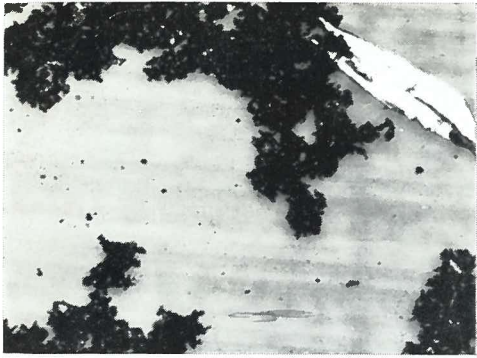
* According to Wranglen (3).

** For instance for Ni (as for Co and Fe) bright flashes can be obtained from very dilute solutions, with low pH values and at rather high c.d. (4).

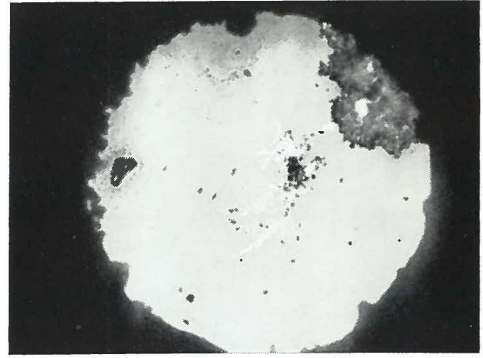
TABLE 2
Conditions for Zn-powder deposition*

bath		c.d. (A/m ²)	η_c (%)	observ.
$[\text{Zn}^{2+}]$ M	pH			
0.1	1	$\geq 2,000$	< 100	sponge rough powder rough powder sponge/rough powder
0.1	6/7	$\geq 2,000$	≈ 100	
0.5	6/7	≤ 20	≈ 100	
1	1/6	$\geq 10,000$	≤ 100	

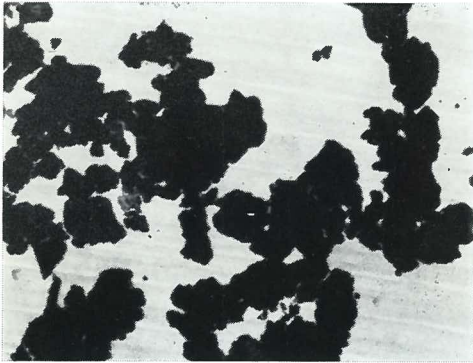
* Room temperature



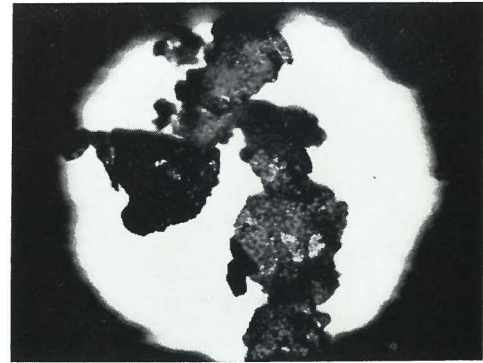
a Ag $\times 100$



b Ag $\times 200$



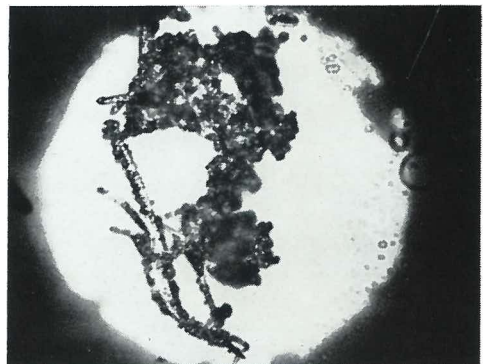
c Zn $\times 50$



d Zn $\times 100$



e Cd $\times 100$



f Cd $\times 200$

Fig. 2 - a) and b): Ag - $[\text{Ag}^+] 0.1 \text{ M}$, 25°C , $1,500 \text{ A/m}^2$;
c): Zn - $[\text{Zn}^{2+}] 0.1 \text{ M}$, pH 1, 25°C , $2,000 \text{ A/m}^2$;
d): Zn - $[\text{Zn}^{2+}] 0.1 \text{ M}$, pH 6, 25°C , $2,000 \text{ A/m}^2$;
e) and f): Cd - $[\text{Cd}^{2+}] 0.3 \text{ M}$, pH 1, 25°C , $1,500 \text{ A/m}^2$.

TABLE 3
Conditions for Cd-powder deposition*

bath		c.d. (A/m ²)	η_c (%)	observ.
[Cd ²⁺] M	pH			
0.1	1	\approx 300	< 100	sponge
0.5	1	\approx 1,500	< 100	sponge
0.5	6	\approx 10	\approx 100	rough powder
0.5	6	\approx 1,500	\approx 100	sponge

* Room temperature

TABLE 4
Conditions for Ni-powder deposition

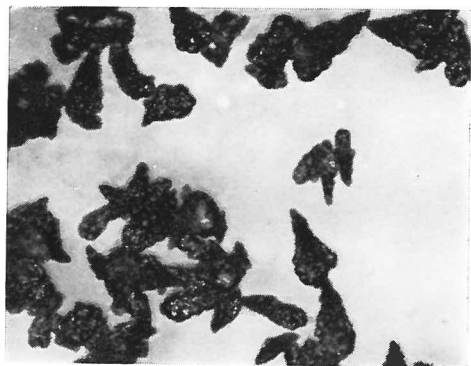
bath				T (°C)	c.d. (A/m ²)	cell voltage (V)	η_c (%)	observ.
[Ni ²⁺] M	[NH ₄ ⁺] M *	[Cl ⁻] M **	pH					
0.1	0.6	0.1	5	25	500	6	65	spear points
0.1	0.6	0.1	5	25	1,000	9	55	»
0.1	0.6	0.1	5	30	1,500	10.5	53	»
0.1	0.6	0.1	5	35	2,000	12	51	»
0.125	0.7	0.1	4.6	25	500	5.5	73	»
0.125	0.7	0.1	4.6	25	750	7.0	66	»
0.125	0.7	0.1	4.6	25	1,000	8.5	64	»
0.125	0.7	0.1	4.6	35	2,000	13.5	61	»

* From NH₄OH and NH₄Cl

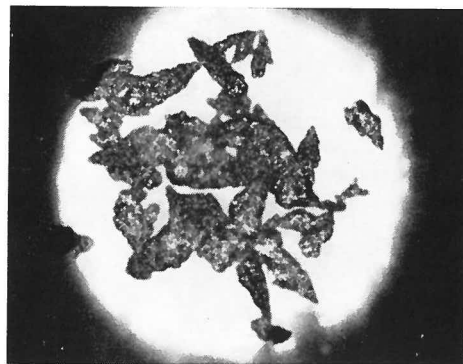
** As NH₄Cl

TABLE 5
Conditions for Co-powder deposition

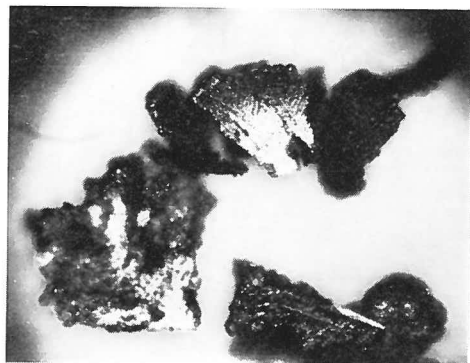
bath		T (°C)	c.d. (A/m ²)	cell voltage (V)	η_c (%)	observ.
[Co ²⁺] M	pH					
0.1	1	22	2,000	5.5	< 50	rough powder
0.1	3.0	22	500	4.5	98	»
0.1	3.0	25	1,500	7	75	»
0.2	3.5	25	1,000	5	98	»
0.2	3.5	25	2,000	7	90	»



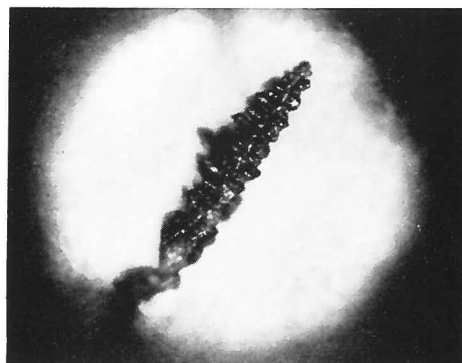
a Ni $\times 200$



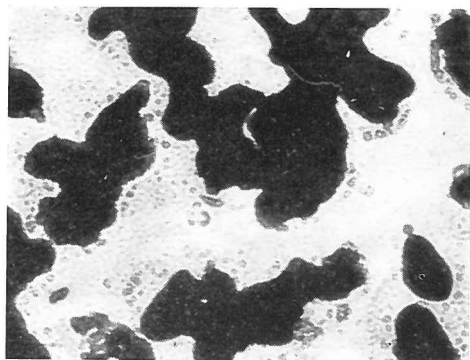
b Ni $\times 200$



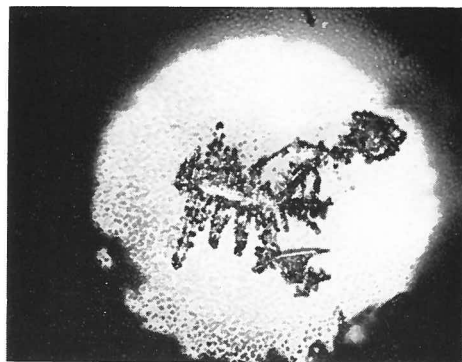
c Co $\times 200$



d Pb $\times 200$



e Pb $\times 100$



f Sn $\times 200$

Fig. 3 - a) and b): Ni - $[\text{Ni}^{2+}]$ 0.125 M, $[\text{NH}_4^+]$ 0.7 (from $\text{NH}_4\sigma$ and NH_4Cl), $[\text{Cl}^-]$ 0.1 M (as NH_4Cl), pH 4.6, 25 °C, 750 A/m²;
 c): Co - $[\text{Co}^{2+}]$ 0.1 M, pH 3, 22 °C, 500 A/m²;
 d): Pb - $[\text{Pb}^{2+}]$ 0.1 M, pH 1, 25 °C, 1,000 A/m²;
 e): Pb - $[\text{Pb}^{2+}]$ 0.1 M, pH 1, 25 °C, 2,000 A/m²;
 f): Sn - $[\text{Sn}^{2+}]$ 0.1 M, pH 1, 25 °C, 1,000 A/m².

the most critical factors are: the ratio $[\text{NH}_4^+]/[\text{Ni}^{2+}]$, that must be in the range 4 to 6; and pH, that cannot be lowered under 2.5.

Suitable conditions for obtaining Co powders at room temperature are: $[\text{Co}^{2+}]$ 0.1/0.2 M, pH 1/3 (the cathodic current efficiency being less than 50% at the lowest values), c.d. 500/2,000 A/m².

In acid dilute (0.1/0.2 M) solutions of $\text{Sn}\sigma_2$, or $\text{Pb}\sigma_2$, by adequately high values of the ratio: c.d./ $[\text{M}^{2+}]$, for instance: 3,000/1,000 A/m² and ≤ 0.2 M baths, at room temperature, Sn or Pb spongy deposits are obtained.

In the case of Pb deposition, by increasing the c.d., in relation to $[\text{Pb}^{2+}]$, needles, laminar forms, sponges and blacks are successively obtained.

It presents good compact deposits up to c.d. values (in the order of hundred A/m², depending upon the In content of the baths, in the range 0.3/0.6 N), at which other « normal » metals, such as Pb, Sn, Cd, Tl, Ag give dendritic deposition. By c.d. increasing (in the order of thousand A/m²), deposits present relatively rough

crystalline structure and copious trees at the boundaries. Finally, spongy deposits are obtained in very drastic conditions: for instance, at room temperature, from solutions of $\text{In}\sigma_3$ 0.1 N, pH 1.8, in the c.d. range 2,000/3,000 A/m², or $\text{In}\sigma_3$ 0.05 N, pH ≈ 2 , at 1,000 A/m². Current efficiencies are always very low in relation to the concurrent and interfering hydrogen discharge (5).

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