Throwing power of sulfamate baths

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RIASSUNTO - *POTERE PENETRANTE DEI BAGNI SOLFAMMICI* - Si è determinata la distribuzione della deposizione catodica da bagni solfammici per i seguenti metalli: Pb, Cd, Zn, Ag, In, Rh, Fe, Ni e Co.
   Il potere penetrante è risultato praticamente nullo tranne che per Rh ed In.

ABSTRACT - The distribution of the cathodic deposition from sulfamate baths has been determined for the metals: Pb, Cd, Zn, Ag, In, Rh, Fe, Ni and Co.
   Throwing power is very low except for Rh and In.

The problem of the determination of the « throwing power » of galvanic baths has been already investigated in this Laboratory (1).

As is well known, throwing power whatever defined, depends, in practice, upon the ensemble of the electrolysis conditions, i.e. geometry of the cell and electrodes, bath composition, nature of the electrodes, current intensity, duration of the electrolysis, temperature, eventual agitation and its characteristics. It may be considered, therefore, as a bath characteristic only in a quite conventional way.

The experimental methods and the cells here studied found application in a group of systematic researches on copper plating both in acid and alkaline baths and on nickel and chromium plating (2).

These methods have now been applied to the most interesting sulfamate baths, such as those of: Pb, Cd, Zn, Ag, In, Rh, Fe, Ni, Co.

The case of copper is not dealt with here. It is in fact a particularly complex one because in order to determine the actual distribution of the cathodic deposit, the reduction process of Cu^{2+} to Cu^+, concurrent with the ones to metallic copper of the ions above, must be taken into account *.

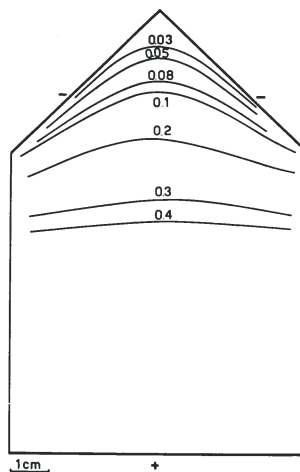On this subject we shall return more specifically in a paper on the chemical and electrochemical behaviour of the copper sulfamate baths **.

Experimental and Results

Tests were carried out in a Hull symmetrical cell (fig. 1) with cathode bent to

Fig. 1 Hull symmetrical cell for the study of the throwing power of galvanic baths. The equipotential surfaces have been drawn for the system: Pb electrodes in $Pb\sigma_2$ 0.5 M aqueous solution at: 25 °C, I = 0.38 A, anodic c.d. $\simeq$ 100 A/m², average cathodic c.d. $\simeq$ 75 A/m². The numbers give the voltages (V) of the tensiometric cell formed by the cathode and the reference electrode (see fig. 2).

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* Owing to the particular relationships between the sulfamic ion and the cuprous one.
** See p. 81.

TABLE I
Conditions for the throwing power determinations.

$M\sigma_r$	Additions	pH	Average c.d. (A/m²)	T (°C)	Additives
Pb σ_2 0.5 M	—	4.5	100	25	celpex (6 g/l), glue (1/2 g/l), phenol (2 g/l)
Cd σ_2 (1.5/2.1) M	NH$_4\sigma$ 1 M	0.9/3.7	800/3500	25	dextrin (2 g/l), licorice (6 g/l), caffein (2 g/l)
Zn σ_2 (1/2) M	NH$_4\sigma$ 1 M	2.7/5.5	800/3500	25	dextrin (2 g/l), licorice (12 g/l),
Ag σ (24 g/l Ag)	—	1.3	40/100	25	tartaric acid (1 g/l)
AgHNSO$_3$K · H$_2$O (20 g/l Ag)	NH$_3$ (70 g/l)	—	70	25	—
In σ_3 0.6 N	—	1.6	5	25	—
In σ_3 0.6 N	KCl 0.6 N	1.6	5	25	—
Fe σ_2 1 M	H$_3$BO$_3$ (30 g/l)	1.8	800/4000	60	—
Co σ_2 1 M	H$_3$BO$_3$ (30 g/l)	1.8	800/4000	60	—
Ni σ_2 1.8 M	H$_3$BO$_3$ (30 g/l)	1.7/2.3	800/4000	60	—
Rh σ_3 (10 g/l Rh)	H σ (50 g/l)	—	750	25	—

93 deg. and with three values of the average distance (d_a) between anode and cathode, i.e. 35,57 and 98 mm (width, 80 mm; liquid height, 20 to 50 mm).

The equipotential surfaces * corresponding to the so-called « primary distribution », that is in the absence of polarization processes, have been drawn approximately (at room temperature) with Pb electrodes in Pb σ_2 0.5 M pH 4.5 solution, direct current of sufficiently low density (anodic c.d. $\simeq$ 100 A/m²; average cathodic c.d. $\simeq$ 75 A/m²), and with bath agitation.

The circuit used to draw the equipotential surfaces is shown in fig. 2.

The effective deposit distribution on the cathode having the form of ten parallel copper ** streaks, has been determined by weight and expressed by plotting the mass increment Δm of each streak, as percent of the total mass increment, as a function of the distance d between the anode and the streak itself.

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

In tab. 1 a list of the tests carried out is given together with the most significant data concerning the working conditions.

The composition of the baths and working conditions were chosen so as to carry out systematic tests and bearing in mind results previously obtained in this Laboratory as regards to achieving good quality deposits (3).

As far as indium is concerned, owing to the peculiar electrochemical behaviour of this metal (4) which presents, over certain critical values of c.d., a « cathodic passivation » ***, the throwing power has been determined also in conditions in which this anomalous phenomenon occurs.

The results of tests are summarized in fig. 3 and in what follows.

The distribution curves of the cathode deposition for most metals and for most working conditions are roughly superposable mutually and to the one corresponding to the primary distribution.

In particular, no beneficial influence on the throwing power is exerted by various additions among those indicated as efficient to improve the structure of the deposits or the properties of the baths; furthermore no significant change is due

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* Marked in volt in fig. 1.
** In the case of silver plating, previous nickel plating is required.
*** Due to the concurrent process of hydrogen development interfering with the indium discharge, thus leading to an inhibition condition by hydride formation.

to stirring * and to c.d. and pH variations **.

The only cases wich present a noticeable change from the primary distribution are those of Rh and In and they are shown in the diagrams illustrated in fig. 3.

Discussion

It is well known that the actual distribution of the current on the cathode depends on the geometrical characteristics of the cell, on the conductivity of the baths and on the rate of cange with c.d. of the overvoltages (inclusive of concentration polarization).

The actual deposit distribution can then be related to the current distribution by means of the current efficiency which is a function of c.d.

In the case of sulfamic baths, characterized by relatively low conductivities, one can foresee that, at least in the cases in which the current efficiencies are close to the unit, the throwing power is therefore bad.

The situation, furthermore, does not change in the presence of additives and does not seem to be generally susceptible of improvement.

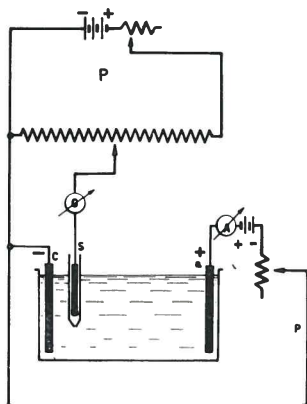The case of rhodium in an exception owing to the high increase of the overvoltage with c.d. and to the decrease of
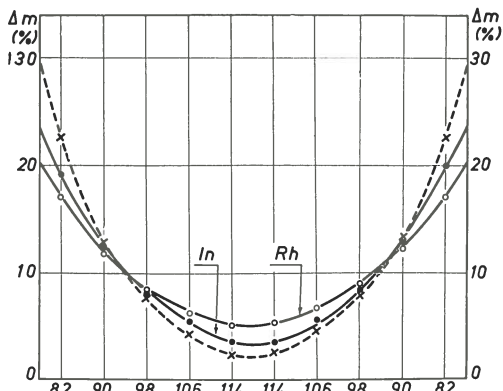
Fig. 3 **Distribution of the cathode deposition from sulfamate baths in a Hull symmetrical cell: △ m% vs. d (mm). The dashed curve corresponds to the primary distribution. The curve for In is in the absence of KCl, while with addition of KCl 0.6 N the curve is superposed to that corresponding to the primary distribution. The data concerning the working condition for In and Rh are given in tab. I. The curves for most metals and conditions correspond roughly to the primary distribution.**

current efficiency due to the concurrent process of hydrogen development.

The case of indium is rather interesting because, also when determining the throwing power, the singularity of its electrochemical behaviour on the cathodic side is evident.

Before the phenomena of cathodic passivation appear ***, one finds a deposit distribution practically identical to that of lead and corresponding to the primary distribution.

The occurrence of these phenomena where critical c.d. values are reached, involving:

1. local inhibition, with an abrupt increase of overvoltage, which makes the current lines deviate towards areas less favoured from the geometrical point of view;

2. a fall in the current efficiency, finally makes the deposit distribution more uniform.

Fig. 2 **Circuit used to draw the equipotential surfaces corresponding to the primary distribution.**
a **and** c, **anode and cathode.**
s, **capillary probe, with Pb reference electrode.**
A, **ammeter - G, galvanometer.**
p, **polarization circuit.**
P, **potentiometer.**

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* Stirring in certain cases (Ni, Co, Zn) involves a lowering of the average cathodic current efficiency.
** For Ni, by increasing pH the distribution becomes somewhat more uniform.
*** In particular, their occurrence is strongly displaced towards the high c.d. range in the case of chloride additions (4).

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Discussion

G. Bianchi - *Comparison of the information supplied on the penetrating power of the various sulfamate baths of Pb, Ni, Fe, Co, Zn and Cd indicates that the distribution of the deposit is practically not influenced by the nature of the bath; this seems to indicate that the relationship: polarization/ohmic decrease, in the case of sulfamic baths is so slight that polarizations do not have means of making their influence felt and the ohmic decrease is always preponderant in determining the distribution of the deposit.*

Now, it seems to me that from a practical point of view this is an unfavorable conclusion. Sometimes an attempt is made to increase the penetrating power of galvanic baths by increasing the conductivity; but if this is the situation for sulfamate baths, there is no hope of being able to increase the penetrating power by increasing the conductivity of the bath. I wanted to know if some other tests have been made with baths having greater conductivity in order to see if this forecast is confirmed or if something can be gained.

R. Piontelli - *No doubt, the situation concerning the throwing power is a very bad one for sulfamate baths. Of course there is some possibility of improvement; perhaps by influencing the conductivity and the rate of increase of the polarization with c.d. For instance for Cd, Zn and so on only the applications in which no need of a good throwing power is requested may be of practical interest; that is for instance the plating of wires, sheets and so on.*

G. Bianchi - *Is it possible to operate in sulfamate bath under diffusion control in order to avoid too high deposits?*

R. Piontelli - *We studied baths for powder production, for instance, working at high c.d., for Zn we have worked at 100,000 A/m^2. With an adequate relative movement of the bath in respect to electrode very good deposits may be obtained.*

G. Bianchi - *What are the characteristics of metallic deposits, when hydrogen is discharged at the electrode? Is it possible to obtain good in these conditions or not?*

R. Piontelli - *The hydrogen interference depends as a rule, upon a quite large number of factors: nobility of the metal, absolute value of the overvoltages in the reduction of both the ions of the metal itself and in the one of the hydrogen ions, and rate of increment of these overvoltages with c.d., structural sensitiveness of the metal in respect to hydrogen adsorption and occlusion and so on. In the plating from sulfamate baths no special problems appear to subsist in cases as those of Cd, Pb, perhaps Zn, and also Ni and Co. For precious metals for instance we have Rh, plated at 45% current efficiency having excellent characteristics, and other precious metals may be deposited at very low current efficiency without having bad characteristics.*

G. Bianchi - *Plating Rh with diffusion control is an example of very good throwing power of sulfamate bath, but the conclusion is not so general.*

R. Piontelli - *In the case of the plating of precious metals (silver excluded) the throwing power situation is better than before mentioned; the increase of the overvoltage with c.d. appears to be high, and the hydrogen discharge predominates as concurrent process.*