

Plating with precious metals from sulfamate containing baths

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RIASSUNTO - *ELETTRODEPOSIZIONE DI METALLI PREZIOSI DA BAGNI SOLFAMICI* - E' anzitutto svolta una rassegna della letteratura e dei principali brevetti relativi alla elettrodeposizione di metalli preziosi (argento, rodio, rutenio, palladio e platino) da bagni solfamici. Inoltre, per quanto concerne la elettrodeposizione di argento e rodio, sono presentati anche nuovi risultati ottenuti in questo Istituto.

ABSTRACT - A review of literature and patents concerning the plating of precious metals (silver, rhodium, ruthenium, palladium and platinum) from sulfamate containing baths is presented. Furthermore, some new results obtained in this Laboratory in the plating of silver and rhodium are given.

A fruitful field of application of sulfamate containing baths is the plating of precious metals. In fact, besides the characteristics of other satisfactory plating baths (e.g. easy preparation and handling, smoothness and brightness of deposits, etc.), sulfamate baths present some advantages ensuing from the very peculiar characteristics of the anion. Thus, in comparison with other baths, the sulfamate ones give good deposits in a wider range of current density (c.d.) and concentration, often with higher current efficiencies.

The internal stresses of deposits are lowered (as in the case of Ni) and the protective value of coatings is sometimes enhanced.

In some cases, as in the one of silver, the sulfamate baths present the behaviour of complex baths. Thus, even in the case of metals, as just the one of silver, characterized by low ion-exchange overvoltages and therefore by large-grained deposits with treeing, the silver complex sulfamate baths can give fine-grained deposits, without treeing.

The « throwing power » is relatively good in the case of rhodium, which is rather exceptional for sulfamate baths.

Finally, the relatively small conductivity of sulfamate baths is not a serious disadvantage in the field of the plating of

precious metals, as it could be for instance in the case of the metal refining.

1. Silver

Silver plating from sulfamate baths has been firstly carried out by Piontelli and Giulotto (1).

The solutions have been prepared either by reaction of the acid and Ag-carbonate, or by double exchange between Ag-sulfate and Ba σ .*

The electrolysis was carried out with theoretical efficiencies (at both the anode and cathode) from solutions of Ag σ ([Ag $^{+}$] 20 to 25 g/l), at 20/60 °C, the c.d. being in the range: 40 to over 100 A/m 2 .

In the absence of additives, the deposits are large-grained with treeing for c.d. \geq 50 A/m 2 .

Temperature increments and the addition of free acid (20 g/l) do not exert beneficial influence.

The study of additives among those indicated as efficient in nitrate baths (2) has given the following results: H acid (0.8 g/l); β naphthol (sat.); triethanolamine (0.4 g/l); CH $_3$ COOK (1 g/l); aloin (0.2 g/l); hydroxylamine-chlorhydrate (1 g/l); lactic

* For brevity sake, we indicate the group NH $_2$ SO $_3$ with σ .

acid (1.5 cm³ of acid 1.21 sp. gr./l), do not improve appreciably the deposits structure.

On the contrary the addition of tartaric acid (1 g/l) * definitely improves the deposits structure also for long range depositions at 50 A/m² (see last reference in (4)).

Results of some interest have been obtained (4) in the Ag deposition from ammonia containing solutions of the complex salt: AgHNSO₃K · H₂O ** (silver-sulfamate of potassium) isolated in 1912 by: Hofmann-Biesalski-Söderlund (5), who obtained it by adding a solution of AgNO₃ to one of K₂CO₃, made strongly alkaline by free KOH.

The complex may be obtained anhydrous by simple vacuum drying.

In water with alkali excess, it forms unstable solutions containing colloidal matter.

The electrolysis of these baths leads to plates having quite good structural characteristics; but the baths are too unstable, however, to present practical interest.

By dissolving the separated complex in ammonia solutions (25/200 g/l NH₃, against 10 to 50 g/l Ag) we obtain baths which, at rather low temperature (10/15°C), with c.d. till about 70 A/m², give deposits, with structural characteristics comparable with those of Ag complex cyanides, the cathodic current efficiency being theoretical.

The plating may be directly effected on ferrous materials or nickel; while for

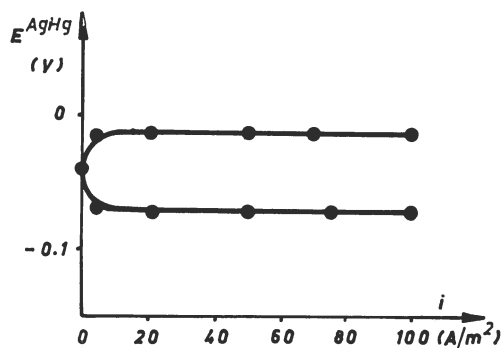


Fig. 1 Anodic (upper curve) and cathodic (lower curve) voltages (in respect of the SCE) of Ag electrodes in an ammonia solution with 200 g/l NH₃ containing 28 g/l of Ag as complex salt AgHNSO₃K · H₂O, at 9°C. The equilibrium voltage is: -0.034 V (+ 0.207 V referred to the SHE).

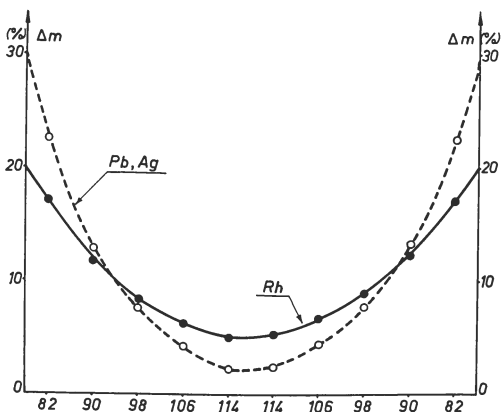


Fig. 2 Distribution of the cathode deposition of Ag and Rh from sulfamate baths in a Hull symmetrical cell. The curve for Ag is roughly superposable to that corresponding to the primary distribution (dashed line), approximated in practice by the systems: Pb electrodes in Pb₂₊ bath. In the diagram, the mass increment of each cathode streak, as per cent of the total mass increment, is plotted as a function of the distance (in mm) of the streak itself from the anode. Average distance between anode and cathode: 98 mm. Cathode bent to 92 deg. Operation conditions: 1) for Ag: Ag 24 g/l (as sulfamate), pH 1.3, average cathodic c.d. 40 A/m² for 30' and 100 A/m² for 22'; Ag 24 g/l, tartaric acid 1 g/l, pH 1.3, 40 A/m² for 30'; Ag 20 g/l (as complex salt AgHNSO₃K · H₂O), NH₃ 70 g/l, 70 A/m² for 30'; 2) for Rh: Rh 10 g/l (as sulfamate), H₂O₂ 50 g/l, 750 A/m² for 3'; 3) for Pb: Pb₂₊ 0.5 M, pH 4.5, 100 A/m² for 6'. Stirring was always provided. Temperature: 25°C. The cathodic current efficiencies were theoretical for Pb and Ag, and about 10% for Rh.

copper and copper-base alloys previous nickel plating is required.

By adding NH₄NO₃, the NH₃ content of the baths may be reduced.

A satisfactory condition is:

Ag (as complex salt)	40 g/l;
NH ₃	60 g/l;
NH ₄ NO ₃	50 g/l;

* Already suggested for other baths by F. C. Mathers et al. (3).

** The weakness of the aminic character of N due to the S-N bond makes possible, in strongly alkaline solutions the replacement of aminic hydrogen with Ag. The Ag-N bond in the complex may be compared with the one in Ag-ammonia complexes.

c.d. 50 A/m²;
temperature 15 °C.

An investigation of the electrochemical behaviour of silver in the complex sulfamate baths above has been carried out with the following results.

In the absence of current circulation, the electrode voltage of silver in these baths is distinctly more negative than in solutions of the same concentration of simple silver salts. For instance, an ammonia solution with 200 g/l NH₃ containing 28 g/l of Ag as complex salt, at 9 °C, shows an electrode voltage of + 0.207 V referred to the SHE. In comparison, the electrode voltage of silver in a solution of Ag₂O 0.2 M (21.6 g/l Ag), at 11 °C, is + 0.733 V (referred to the SHE), well corresponding to those in the other simple salt solutions.

The anodic and cathodic voltages of silver electrodes during current circulation, in the case of the complex bath, are plotted in the diagram of fig. 1 against the current densities.

As a rule in the case of the sulfamate baths, the « throwing power » is very low for both the simple salt (even with additives) and the complex sulfamate solutions (see fig. 2, where the distribution curve of the cathode deposition for silver in a Hull symmetrical cell is shown, superposed to that for lead, corresponding to the « primary distribution »).

A structural investigation on silver deposits on single-crystal cathodes from the complex sulfamate baths, with a comparison between the structure of the deposits obtained from these baths and that from other complex silver baths (cyanides, thiocyanates, iodides), has been accomplished in this Laboratory by Poli and Rivolta (6).

2. Rhodium

The rhodium plating from sulfamate baths has been firstly effected by Piontelli (7). The baths were prepared from freshly precipitated hydroxide, dissolved in H₂O and the electrolysis carried with Pt anodes and Pt, Cu, Ag, Ni cathodes.

The composition range was: 2/12 g/l Rh; free acid: 10/50 g/l; at 15/40 °C, with c.d. varied in the range: 20 to 1,000 A/m² (the higher values being only compatible with Rh contents \geq 10 g/l). The deposits pre-

sent excellent characteristics. Also the « throwing power » of the baths appears to be good and comparable with that of the sulphate ones. In fig. 2, the distribution of the cathode deposition from sulfamate baths is reported, as a function of the distance from the anode in a Hull symmetrical cell.

Rhodium was also plated on titanium, previously treated with a method studied in this Laboratory*. The composition of the plating bath and the operation conditions were:

Rh	12 g/l;
H ₂ O	95 g/l;
c.d.	100 A/m ² ;
temperature	20/25 °C.

The deposits up to 0.005 mm thick are smooth and bright and their adhesion is excellent: they are not detached after reiterated bending tests.

Reid (8) has compared the heavy Rh-plating from sulfamate bath with those from sulphate and fluoborate. The last was similar to the sulphate one.

The sulfamate baths did not exhibit the characteristic colour change from orange to green in operation.

The current efficiency is relatively low, but increases: with increasing temperature, with high Rh, and low free acid concentrations. The deposits were only slightly cracked**.

The sulfamate electrolyte offers a greater range of conditions over which smoothness of deposits could be maintained.

Reid proposed a variant of the sulfamate solution, obtained by reacting NH₄⁺rhodinitrite, (NH₄)₂Rh(NO₂)₆, with a solution of H₂O in the ratio: 6 M H₂O to 1 of salt***, with 5 g/l Rh, at c.d. of 200/400 A/m², at 70 °C. Very bright plates are obtainable (with very little H₂ evolution, despite low cathode current efficiency). The deposits are free from cracks at 0.0025/0.005 mm.

According to patent literature (9), deposits of low residual stress may be obtained from baths based on rather large

* Patent pending.

** As opposed to the severely fissured deposits from sulphate, fluoborate, and phosphate baths, under corresponding conditions.

*** By the volume of N₂ evolved, it appears that only 3 of the 6 nitrito groups are affected on heating the solution to 100 °C.

additions of Mg as sulphate or sulfamate, or mixtures, to a Rh-sulphate electrolyte.

A typical bath (operated at 20/50 °C, in the c.d. range 40/200 A/m²) is:

Rh	5 g/l;
H ₂ SO ₄	10 g/l;
Mgσ ₂	30 g/l;
MgSO ₄	10 g/l*.

3. Ruthenium

Volterra (12) developed and patented the sulfamate bath for the plating of electrical contacts.

Good quality plates 0.0025 mm thick are obtained, which are said to withstand high intensity arcs.

Reid and Blake (11. 13) carried out tests on three sulfamic baths:

1. ruthenium nitrosyl sulfamate bath;
2. simple ruthenium sulfamate bath;
3. a bath obtained by reaction of sodium-tetranitro-nitrosyl-ruthenate (Na₂[RuNO(NO₂)₄OH]) with Hσ.

The first bath emerges as the most immediately useful to furnish smooth, bright deposits up to 0.005 mm thick over a fairly wide range of operation conditions:

Ru	2.5/50 g/l;
Hσ	10/50 g/l;
c.d.	200/800 A/m ² ;
temperature	20/90 °C.

Cathode efficiency is always low, and under preferred operating conditions is in the range of 10/20%. Deposits show internal tensile stresses in the order of 30/50 kg/mm² and fine cracks may be present at thicknesses greater than 0.0025 mm. Cracking is reduced by addition of aluminium sulphate to the electrolyte.

The simple sulfamate solution gives better performance but is less stable than the nitrosyl sulfamate one during operation, as manifested by considerable evolution of tetroxide at the anode after a short life. This inconvenience could be avoided by the use of a diaphragm cell with separate anode and cathode compartments.

Also the electrolyte based on reaction of sodium-tetranitro-nitrosyl ruthenate with Hσ is unstable in operation.

Duva in Metal Finishing Guidebook

Directory for 1965 recommends the following formulation:

Ru (as sulfamate)	5 g/l;
Hσ	5 g/l;
c.d.	100/300 A/m ² ;
temperature	30/50 °C;
agitation	moderate.

Johnson (14) utilized a sulfamate containing bath (5 g/l Ru and 250 cm³/l HCl) for the immersion plating of ruthenium, and he obtained excellent replacement deposits on copper up to 0.0025 mm thick, operating at a temperature of 95 °C, with an immersion time of 30'.

The patent literature (15) reports a method by which Au deposits are advantageously immersion-plated on to Cu substrates by a first immersion-plating of a thin layer of Ru (or Rh, Pt, Pd) using a solution containing a halide or sulfamate of the metal and then immersion-plating an Au film by using a standard KAu(CN)₂ plating solution.

4. Palladium

The Automatic Telephone and Electric Co. (A.T.E.) of Liverpool (16) developed a palladium plating process based on sulfamic bath for the plating of printed circuitry.

Sulfamate complexes of the metal were prepared by reaction of palladium « P » salt (diammino-dinitrito palladium: Pd(NH₃)₂(NO₂)₂) with Hσ or NH₄σ.

The exact nature of the compounds which are present in the plating bath is not yet established. Operating temperature is from 20 to 40 °C with a palladium content of 10/15 g/l, pH 7/8. The cathode efficiencies are from 70 to 100%. The deposits are normally bright.

Advantages over the other existing formulations are claimed in respect of a high cathode efficiency at low temperature, enhanced protective value of coatings and, in particular, successful application as a barrelling process.

A bath based on sulfamic acid solutions of palladium sulfamate complexes is also utilized in the A.T.E. electroless palladium plating process (that consists in an auto-catalytic reduction process). Thin, tarnish-resistant coatings are readily obtained on a variety of metal surfaces by simple immersion.

* For further references see (10, 11).

5. Platinum

Recently the patent literature (17) has described electrolytes based on solutions of diammino-dinitrito-platinum ($\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$, « P » salt) in sulfamic acid.

The recommended solution and operating conditions are:

Pt (as « P » salt)	6/20 g/l;
H σ	20/100 g/l;

c.d.	200/1,000 A/m ² ;
temperature	65/100 °C;
agitation	moderate.

This sulfamate-base bath produce low-stressed, ductile, dense coatings that have been electroplated to thicknesses of 1.25 mm and more without disintegration. High and costant efficiency characterizes the easy operation of this system.

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Discussion

G. BIANCHI - *We have obtained the deposition of iridium from chloroiridic acid baths in the presence of $\text{NH}_2\text{SO}_3\text{H}$, and we have compared this iridium deposit obtained from chloroiridic acid baths plus H_2SO_4 . These tests seem to show a very special role of $\text{NH}_2\text{SO}_3\text{H}$ in the deposition of noble metals, particularly iridium, or that $\text{NH}_2\text{SO}_3\text{H}$ acts as an additioning agent, conditioning the surface of the metal where iridium is deposited. These are the results of the experiments: with extremely low c.d., on the order of a few A/m², and with a bath of chloroiridic acid*

plus H_2SO_4 , compact deposits with a good appearance, whose current yield is however only 1-2%, are obtained. With chloroiridic acid of the same strength plus $\text{NH}_2\text{SO}_3\text{H}$, the c.d. can be 30-40 times greater (therefore on the order of 30-40 A/m²) and the current yields rise to 10%. Also in this case the deposit is very compact and continuous in appearance, with satisfactory mechanical characteristics.

V. SPRETER - *Did you try to prepare the gold salt of the sulfamic acid?*

B. MAZZA - *No, we didn't.*