

Chemical and electrochemical behaviour of Cu(II) and Cu(I) sulfamate baths, and of copper against sulfamic solutions. II.

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RIASSUNTO - COMPORFAMENTO CHIMICO ED ELETTROCHIMICO DELLE SOLUZIONI DI SOLFAMMATI DI Cu(I) E Cu(II) E DEL RAME IN PRESENZA DI BAGNI SOLFAMMICI. II. - Ulteriori notizie sui metodi di preparazione, la composizione chimica ed alcune proprietà dei solfammati di Cu(I) ed Na (o K) cristallini, in parziale contrasto con i risultati di un'analogia ricerca di Raub et al.

ABSTRACT - Further information on the preparation methods, chemical composition and some properties of crystalline Cu(I) and Na (or K) sulfamates, partially in contrast with the results of an analogous research work by Raub et al.

Although thirty years have elapsed since the first studies by Cambi-Piontelli (1) and Piontelli-Giulotto (2) on Cu-deposition from sulfamate baths, and although subsequently several authors: Cupery (3), Ades (4), Poli et al. (5), Sammour (6), Venkatachalam and Rama Char (7) (8), Bockris et al. (9), Peraldo-Bicelli et al. (10), Kikuchi et al. (11) have been interested in various aspects of the deposition itself; researchers have never made a thorough study of the peculiar characteristic of the behaviour of Cu-sulfamate solutions—that is, the high percentage which the cuprous form may reach in them, in the presence of metallic copper.

With the recently renewed interest in sulfamate baths, which was confirmed in a special Symposium held in Milan in May, 1966 (12), two research studies have been made, almost contemporaneously and independently, in which the above aspect was particularly studied.

The first of the two researches was carried out by the authors of this paper at the Istituto di Elettrochimica del Politecnico di Milano, and its results were the subject of patents (13) and of publications (14) (15).

The other research was conducted by Raub and Elser at the Forschungsinstitut für Edelmetalle und Metallchemie di Schwäbisch Gmünd, and the results the-

reef appeared in the review «Metalloberfläche» (16).

In both these works the chemical and electrochemical behaviour of Cu(I) and Cu(II) sulfamate solutions was studied, in the absence and in the presence of metallic copper, with particular respect: to the so-called hydrolysis of the solutions reaction; to the formation in solution of high Cu(I) contents and to the separation of crystalline cuprous compounds; to the anodic and cathodic current efficiencies of copper electrodes; to the electrode voltages; to the throwing power; to the structure of the deposits, etc.

In a wide section of these aspects the results agree.

We have, however, noted some differences between the results which we obtained and those of the German researchers, concerning which we believe it opportune to make some observations, even if these differences concern above all secondary aspects, with respect to the essentially galvanotechnic objects, of the work of Raub and Elser.

The differences noted concern particularly:

1. the formulas of cuprous compounds which separate from the Cu(I) sulfamate solutions in the presence of Na⁺ or K⁺ ions;

II. the occurrence of the separation of a cuprous compound, even in the absence of Na^+ or K^+ ions.

New cuprous compounds

I) The preparation of crystalline sulfamates containing Cu(I) and Na or K was accomplished by the authors of this paper in various ways:

a) by chemical reduction of cupric-sulfamate solutions in the presence of Na^+ or K^+ , with reducing agents: metallic (copper, tin, etc.) or dissolved, such as sodium or potassium hypophosphite, ferrous sulfamate, etc.;

b) by electrochemical reduction of cuprous-sulfamate solutions, associated with partial conversion of metallic copper to Cu(I) , which can be effected with either direct or alternating current, in the presence of or with successive addition of Na^+ or K^+ ;

c) starting with Na or K -sulfamate solutions, in the presence of sulfamic acid (pH in the range 2/2.5), and adding Cu_2O .

The Na^+ or K^+ ions were added as a rule in the form of sulfamates, but the operation is possible also with the addition of sulphates.

Work conditions: temperature, composition of the solutions (with regard to: $[\text{Cu}^{2+}]$, $[\text{Cu}^+]$, $[\text{Na}^+]$ or $[\text{K}^+]$, pH, $[\text{NH}_2\text{SO}_3^-]$, the eventual presence and percentages of other cations and anions), current density, can be quite widely varied.

The compounds obtained by the various methods and under varying conditions were characterized by means of chemical analysis and X-ray spectrum, and they always resulted as identical and corresponding to the same empirical formula.

On the other hand, with the conditions for obtaining the compounds, the aspect of these compounds varies. For example, in the absence of imposed current, through slow growth on copper, coatings are obtained which are: adherent, compact and fibrous; and instead, with imposed current, coatings which become easily detached from the electrodes and which are characterized by high porosity*; while, when Na^+ or K^+ are added to solutions containing Cu(I) , no matter how produced, crystals separate in the solutions themselves. These crystals, under the micro-



a)

× 270



b)

× 90

Fig. 1 - Needle-shaped crystals of the new cuprous compounds: a) $\text{CuNH}_4\text{SO}_4 \cdot 2 \text{NaNH}_2\text{SO}_3$ and b) $\text{CuNH}_4\text{SO}_4 \cdot 2 \text{KNH}_2\text{SO}_3$.

scope, always have a needlelike aspect and, under equal conditions, potassium compound crystals always have greater size than those of sodium compound; Fig. 1.

Obviously, under varying work conditions, the yield of compounds obtained also varies, as has been thoroughly covered in a previous paper (11).

Under vacuum, the thermal decomposition of these sulfamates occurs starting from 180°C , with formation of variously

* The protective power of the separate coatings is particularly influenced by the preparation conditions of the compounds themselves.

This power generally is scarce, especially when thick coatings are formed.

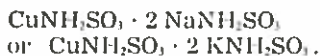
colored compounds, to which we shall return.

Cuprous compounds analogous to those obtained with Na or K are not obtained by the addition of other alkaline metal sulfamates (Li, Rb, Cs), of ammonium sulfamate or sulfamates of alkaline-earth metals (Ca, Mg, Sr, Ba) or of other metals (Pb, Sn, Fe, Co, Ni, etc.).

Chemical analysis of Cu(I) and Na or K containing compounds gives the following values of the gram-atom ratios:



so that the empirical formulas can be proposed:



Chemical analysis has repeatedly carried out in the following way*.

The compounds precipitated as previously indicated were dissolved in HNO_3 and heated in water-bath for long time.

Then the solution was dried and the residue dissolved in H_2O .

On a portion of the obtained solution the sulphates were determined as BaSO_4 , by adding BaCl_2 .

On another portion copper was determined electrolytically.

The electrolyzed solution was dried and the residue treated several times with H_2SO_4 to remove HNO_3 completely.

The solution obtained by adding H_2O was treated with an anion-exchanging resin and from the collected solution NH_3 was removed by boiling. The total alkali-content was titrated with 0.1 N HCl.

Raub and Elser, on the other hand, attribute to the compound obtained in the presence of sodium added as sulphate the formula $\text{CuNH}_2\text{SO}_3 \cdot \text{NaNH}_2\text{SO}_3 \cdot \text{H}_2\text{SO}_4$ supplying as the results of their analysis the gram-atom ratios:



The proposed formula is not consistent with the following facts:

- during the precipitation of the compounds there is no variation of the pH value of the solutions, even at $\text{pH} \approx 3$;
- when the compounds are dissolved in H_2O they hydrolyze, giving a solution with $\text{pH} \approx 6$ and separating Cu_2O .

* It was also recently confirmed by Prof. Giuffrè at the Analysis Laboratory of the Istituto di Chimica Industriale del Politecnico di Milano.

Therefore, independently of the validity of the Cu:Na ratio supplied by Raub and Elser, the presence of H_2SO_4 in the compounds themselves is to be excluded.

11) Raub and Elser also hint at the possibility of reaching conditions of saturation of Cu(I) in solution in the absence of Na^+ and K^+ by precipitation of a cuprous sulfamate.

The authors of this paper have often encountered the separation of small quantities of a compound, under analogous conditions.

Nevertheless, both chemical analysis as well as X-ray spectrum have shown that this is essentially the same compound $\text{CuNH}_2\text{SO}_3 \cdot 2 \text{NaNH}_2\text{SO}_3$ (much less soluble than the analogous potassium compound) due to the presence of sodium impurities in the solutions.

As a matter of fact, the elimination of sodium impurities from the solutions allows in the solutions themselves percentages of Cu(I) which are no longer limited by the separation of the compound above, but correspond to the Cu/Cu(I)/Cu(II) equilibrium.

We did not succeed in obtaining crystalline cuprous sulfamate in the absence of Na^+ or K^+ , even by sudden cooling of solutions having a high percentage of Cu(I) produced at high temperature, since in these conditions the dismutation of Cu(I) with the separation of metallic Cu occurs.

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Continued on p. 100

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