

A SIMPLE METHOD FOR THE PREPARATION OF RUTHENIUM PLATING SOLUTION

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Ruthenium is the least expensive of the platinum group metals, and is an attractive alternative to both rhodium and gold in contact finish applications, as in electronics. Ruthenium in sealed-reed contacts to resist contact sticking, is a noteworthy application. However much ruthenium can be applied for a particular purpose, the availability of satisfactory electroplating processes demands an extensive investigation for the establishment of the same. Hence there is a need to get a standard basic electrolyte which can help getting a good uniform and smooth deposit of ruthenium continuously, without any deterioration of the electrolyte. Till today there has been no citation in literature regarding the same. The present paper focuses on the method of preparation of ruthenium plating concentrate, its stability with time, and some of its performance characteristics.

Keywords: Ruthenium, electrodeposition, concentrate.

INTRODUCTION

Ruthenium is commercially reported to be used to harden alloys of palladium and platinum [1]. The alloys are used as electrical contacts (12% Ruthenium in platinum) and in jewellery, and in fountain pen tips. It is also used for industrial catalysis (hydrogenation of alkenes and ketones) and for automobile emission control. In the last decade of this century, following the development of Ruthenium as an alternative deposit to cheaper rhodium in electrical contact applications, preparation of ruthenium plating concentrates based upon nitrosyl sulphamate was reported in [2]. From the comparative performance studies of the alloys of Ruthenium and Platinum, it was reported [3] that Ruthenium deposits behave technically superior. In spite of the numerous applications of Ruthenium as a deposit, numerous solutions have also been proposed in the past. However, all these were either unstable in operation or it gets plated [4,5] externally at low cathode current efficiencies.

In view of the non availability of a good method for the preparation of a stable Ruthenium plating electrolyte the present work was undertaken to arrive at a standard method for the preparation of the Ruthenium plating concentrate and to study its stability and also some of the characteristic properties of the solution as well as of the deposits obtained therefrom.

EXPERIMENTAL

Standard information available from literature indicated the convenient starting material for preparation of the plating complex to be Ruthenium chloride in HCl at a concentration level 350-400 g of Ruthenium per litre. Based upon the report [4], various means of preparing ruthenium sulphamate concentrate have been explored. Among the various methods studied, the treatment of the Ruthenium chloride salt ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$), hydrochloric acid and sulphamic acid in the appropriate manner only (as given under) proved to be the worthy method of preparing quite a stable ruthenium plating complex.

Method of preparation of the ruthenium plating complex

As reported elsewhere, the authors wanted to prepare 25 gpl ruthenium concentrate and investigate further. Accordingly, from the available basic AR grade Ruthenium chloride trihydrate salt (available only as 1 g ampules, of SISCO Research Laboratory, Mumbai) was considered and further preparations were carried out as follows:

A known amount of Ruthenium chloride salt was treated with the required quantity of AR conc. hydrochloric acid and the required quantity of AR sulphamic acid, and the mixture was boiled under reflux for thirty hours to get the ruthenium chloride sulphamate complex with proper digestion. When the volume of the solution became 20 ml (after cooling) it was made upto a known volume in a standard volumetric flask,

eg. to 50 ml or 100 ml etc....., so that the concentration of ruthenium could be fixed exactly.

For example, 5 g, of the salt ruthenium chloride containing 2 g of ruthenium may require 10 ml HCl and 1.5 g sulphamic acid. All in total after the above evaporation and reflux the plating complex separated in 60% yield as dark red crystals. Further evaporation of the filtrate and cooling yielded 30% more of the product. When the solution is made upto 50 ml, the conc. of ruthenium shall be 40 g/l. Such a solution concentrate is always preferable for further preparation of plating electrolytes. Dilute solutions of this concentrate (4 ml made upto 50 ml) were used for plating operations.

Experiments with different concentrations of ruthenium

Various plating electrolytes were prepared with different ruthenium concentrations for the volume of 50 ml, and various studies on the current efficiency, temperature, pH were carried out with different substrates like copper, Nickel plated on copper, Nickel and then gold plated on copper. The size of the specimen was 1" x 5". A 1 x Sq" area of copper was exposed for plating.

Effect of bath composition

Different bath compositions were used for plating under conditions, as to optimise the bath for further studies.

Effect of current density

Numerous investigations were carried out with the standardised bath under different current densities so as to optimise it for obtaining a good deposit with higher current efficiency. The current densities used were 0.5 A/dm², 0.75 A/dm² and 1 A/dm² respectively.

Effect of temperature

Investigations were also carried out in the standardised bath at various current densities for different temperatures like 313, 323 and 333 K so as to identify the suitable temperature for further studies.

Effect of pH

The effect of pH on the characteristics of the plating solutions was studied with the standardised bath for different pH values of 1, 2, 3, 7, 8, and 9 under other standard conditions.

Effect of substrate on deposition

To see the effect of substrate on deposition experiments were carried out on different substrates like copper, nickel plated copper, gold plated copper (2 µm gold) so as to observe the change in the nature of the deposit on the various substrates.

RESULTS AND DISCUSSION

Characterisation of the ruthenium plating electrolyte

The concentrate of Ruthenium complex, prepared as per the method described earlier in the experimental part, was made upto a known volume and the concentration of ruthenium in the above made up solution was 12 g/l.

Various concentrations of ruthenium for plating experiments were obtained by appropriate dilutions of the concentrate so as to get the concentration of ruthenium of 0.5, 0.8 and 1.0 g/l respectively, and then other necessary additions were made for further use.

Results on the effect of concentration on current efficiency

Table I contains the results of various experiments carried out using different electrolytes, with different concentrations of Ruthenium. From the table it may be observed that the bath having the Ruthenium concentration of 0.8 g/l was able to produce a good, adherent, semi bright deposit with a considerable current efficiency of 51.0%, at 0.5 A/dm² current density, at 333 K.

Though the current efficiency of bath A, which contained 1 g/l of Ruthenium has as high a current efficiency as 76.4% under the same operating conditions, the nature of the deposit was not satisfactory (Table I).

Similarly, the ruthenium deposit from bath C, (which contained 0.5 g/l of Ruthenium, the nature of the deposit was not desirable and the current efficiency of 25% was also the lowest.

TABLE I: Effect of bath composition on the nature of deposit
Current density = 0.5 A/dm² Temperature = 333 K
pH = 1.8 Time = 15 mins

Bath	Weight gain (g)	C.E. (%)	Nature of deposit
Bath A			
'Ru' as Ruthenium Chloride	1 g/l		
HCl	100 g/l		
Sulphamic acid	147 g/l	0.0154	76.4 Grey & rough
Bath B			
'Ru' as Ruthenium Chloride	0.8 g/l		
HCl	100 g/l		
Sulphamic acid	147 g/l	0.0154	51.1 Semi bright
Bath C			
'Ru' as Ruthenium Chloride	0.5 g/l		
HCl	100 g/l		
Sulphamic acid	147 g/l	0.0132	25.0 Patchy

TABLE IV: Effect of time on the nature of deposit
 Temperature = 333 K C.D. = 0.5 A/dm² pH = 1.8

Bath	Time (mins)	Current (%)	Nature of deposit
'Ru' as Ruthenium Chloride 0.8 g/l HCl 100 g/l Sulphamic acid 147 g/l	15	51.1	A
	30	54.1	A
	45	51.1	A
	60	43.4	A
	75	41.4	A
	90	37.5	B
	105	25.0	B
	120	18.7	B

A = Semi bright; B = Matte white

like 1.8 or 2.0 may produce low current efficiencies of about 51% the semi bright nature of the deposit is obtained, whereas at higher pH of 7 and beyond, it becomes black and powdery. Moreover, at high pH the solution tends to decompose. From the above observations, it is clear that a pH of 1.8 appears to be most favourable for obtaining good deposits.

Effect of substrate on the nature of the deposit

Table VI shows the results of the above studies. From the table it may be observed that the current efficiency is more or less not affected by the change of substrate but it has influence on the nature of the deposit.

On a copper substrate with first nickel and then gold overcoatings the nature of the deposit obtained was very good, viz, it was semibright. On a copper substrate the

TABLE V: Effect of pH on the nature of deposit
 Temp = 333 K C.D. = 0.5 A/dm² Time = 15 mins

Bath	pH	C.E. (%)	Nature of deposit
'Ru' as Ruthenium Chloride 0.8 g/l HCl 100 g/l Sulphamic acid 147 g/l	1.6	43.80	A
	1.8	51.10	B
	2.0-	47.80	B
	2.2	44.50	B
	7.0	99.00	C
	8.0	99.25	C
	9.0	99.50	C

A = Patchy; B = Semi bright; C = Black, powdery

TABLE VI: Effect of substrate on the nature of deposit
 Bath = 'Ru' as ruthenium chloride = 0.8 g/l
 HCl = 100 g/l and sulphamic acid = 147 g/l
 Time = 15 mins Temp = 333 K pH = 1.8

Substrate	Current efficiency (%)	Further buildup (g)	Deposit nature
Copper	54.1	Nil	A
Copper with nickel flash	43.8	0.0016	Grey
Copper with nickel and gold flash	51.1	0.0016	Semi bright
Mild steel	-----	-----	Pitting

A = Non adherent, blackish

deposit was not adherent, and on the mild steel pitting was observed.

CONCLUSION

From all the above preliminary studies the following conclusions were drawn:

1. It is possible to prepare a Ruthenium electroplating bath concentrate from the basic salts like ruthenium chloride (RuCl₃ · 3H₂O), HCl, and sulphamic acid.
2. The concentration of ruthenium in this bath is 12 grams per litre.
3. This concentrate can be stored for more than six months without any decomposition and can be used for preparing plating baths with different concentrations.
4. The plating bath was found to be stable for minimum 6 months with the efficiency of producing good deposits and maintaining the current efficiency.
5. The following electrolyte composition may be used for obtaining a semibright of ruthenium on gold super coated copper substrate, with the current efficiency of 51%. The method of preparation is also not hazardous.
6. The same plating electrolyte can be revived for use by fresh additions of the concentrate.

REFERENCES

1. American Society of Metals, *Metals Handbook Desk Edition*, (1985)
2. F H Reid and J C Blake, *Trans Inst Metal Finishing*, (1961)
3. H C Angus, *Trans Inst Metal Finishing*, 43 (1965) 135
4. G S Reddy and P Taimsalu, *Trans Inst Metal Finishing*, 47 (1969) 187
5. M J Cleare and W P Griffith, *Chem Comm*, (1968) 1302