Bulletin of Electrochemistry 1 (2) Mar-Apr 1985 pp. 129-130

STUDIES ON POST-TREATMENT OF GOLD PLATED SILVER

S JOHN, MRS MALATHY PUSHPAVANAM AND (LATE) B A SHENOI
Central Electrochemical Research Institute, Karaikudi 623 006

ABSTRACT

Silver articles like jewellery, silverwares, cosmetic containers, novelties, presentation items etc. are usually plated with gold in very thin deposits to give good appearance and to protect silver from tarnishing. A very thin deposit of gold is often porous, and the silver tarnishes through the pores. This tarnishing will spread laterally over the gold and the whole component will turn black. This is often thought to indicate that the gold has tarnished, but this is not true. Thick layers of gold is useful in preventing tarnish films. However, it is very expensive. Other methods of reducing the tendency of silver to tarnish are to coat the surface with a special lacquer, grease, oil or wax or to apply special oxide or chromate films. Electrolytic treatment of gold-plated silver in an electrolyte containing 40 g/l potassium chromate, 40 g/l potassium carbonate at pH 8.8 at a cathodic current density of 2.5 A/dm^2 for 1-3 minutes significantly improves the tarnish resistance as revealed by the accelerated stain proofing test.

INTRODUCTION

Gold has found applications as a tarnish and corrosion resistant barrier for decorative and industrial applications. Among the technical uses for electrodeposited gold, pride of place goes to printed circuits and electric and electronic assemblies such as connectors, commutators, relays, friction contacts, wave guides and communication assemblies, radar components, steady state systems and hybrid circuits [1,2]. Electrodeposits of gold are also used on jewellery, scientific apparatus, silver wares, cosmetic containers, watches, pen nibs etc. [3,7]. In the application of gold as a protective coating, it should be remembered that it acts as a protective sheath rather than as a galvanic protection such as that provided by zinc and cadmium [8,10].

When the coating of gold is broken, galvanic action between the gold and the less noble base metal causes very rapid pitting of the base metal. For this reason plating should be performed under closely controlled conditions so that the deposit is free from imperfections in the form of pores, pits and cracks. Silver is often plated with gold in very thin deposits to protect the silver from tarnishing, to give good appearance and to offer low contact resistance. However, a very thin deposit of gold (<3 µm) is often porous and the silver underlayer tarnishes through the pores. This tarnish film will spread laterally over the gold and the whole component will turn black. This is often thought to indicate that the gold has tarnished, but this is not true. Hence this is a problem of tarnishing of silver.

The formation of tarnish films on silver varies in colour from light brown to black. With pure silver the composition of the film consists mainly of silver sulphide and silver sulphate formed by the reaction of the metal with gaseous sulphur compounds present in the air. Industrial atmosphere usually has higher percentages of such impurities, in particular hydrogen sulphide and sulphur dioxide. Apart from the poor appearance of the tarnish film, the practical usefulness of gold-plated silver is reduced because contact resistance rises and soldering becomes difficult. For many years considerable attention has been devoted to preventing the tarnishing of gold-plated silver by methods of surface treatment of the metal in order to form protective films by passivation [11-17].

Protection against tarnishing by means of a very thin invisible layer has given rise to extensive research. For example, dipping in a solution containing halogen produces a silver halide surface layer which protects the underlying metal against tarnishing by sulphides. In another method silver surface is cathodically treated in a solution by beryllium salts to deposit a thin adherent layer of beryllium hydroxide. Silver can also be protected by means of a thin tin oxide layer which is formed by dipping it in a solution of stannous chloride. Chemical or electrochemical passivation treatments by means of solutions containing hexavalent chromium have been proposed for protecting silver against tarnishing [11,12,15,18]. This is of special interest because of its economic significance in man's constant attempts to preserve the metals.

An improved post-treatment process for gold-plated silver has been worked out in this laboratory and this paper gives a comparative study of various post-treating solutions.

EXPERIMENTAL

Brass and copper panels of size 75 × 50 mm were mechanically polished and buffed to a smooth finish, degreased with trichloroethylene, cathodically cleaned in alkaline solution, washed, pickled in dilute acid, washed and silver plated using the strike solution of the composition given in Table I. After strike silver plating the panels were silver plated using the conventional solution of the composition given in Table I. After silver plating to the required thickness gold plating was carried out using the solution of composition given in Table I. After gold plating the panels were washed and post-treatment was carried out in solutions given in Table II.

All the chemicals used were of laboratory reagent (LR) grade Distilled water was used for solution preparation. Mild air agitation was employed during plating. The solutions were taken in a three-litre beaker and temperature was maintained by means of thermostat. Accelerated tarnish testing was carried out to

Table 1 : Plating conditions for silver and gold

	Silver strike	Silver plate	Gold plate
Silver nitrate g/l	2.2	25.0	—
Gold potassium cyanide g/l	—	—	2.0
Potassium cyanide g/l	36.0	100.0	15.0
Potassium carbonate g/l	14.0	15.0	10.0
Temperature °C	35.0	35.0	55.0
Current density A/dm^2	1.0	1.6	0.4
Plating time, mins.	2.0	15.0	5.0

Table II : Post-treatment of gold plated silver

	Solution one	Solution two	Solution three	Solution four
Potassium chromate g/l	20.0	20.0	50.0	40.0
Potassium cyanide g/l	2.0	—	—	—
Potassium carbonate g/l	—	—	50.0	40.0
Sodium carbonate g/l	40.0	—	—	—
Potassium hydroxide to pH	12.0	9.0	8.5	8.8
Sodium thiosulphate g/l	—	20.0	—	—
Temperature °C	90.0	90.0	35.0	35.0
Cathodic CD A/dm^2	—	—	—	2.5
Treatment time, min.	2.0	2.0	2.0	1-3

ascertain the protection afforded by various post treating solutions [19-21]. In this method, the post-treated samples were kept in a glass chamber containing concentrated ammonium polysulphide solution. The time taken for tarnishing was observed with a stop watch.

RESULTS AND DISCUSSION

Table III shows the data obtained for gold-plated silver panels after treatment in various solutions.

Table III : Results of post-treated gold plated silver

	Time for tarnishing	Protection
As plated silver	Tarnished in 30 sec	Very poor
Solution 1	2 min	Poor
Solution 2	1 min	Poor
Soluton 3	3 min	Good
Solution 4	7 min	Excellent

Immersion treatment in the solutions listed are not improving the corrosion resistance. Immersion treatment at elevated temperature (90°C) is also not helpful. Change of pH has also not improved the corrosion resistance. It is clearly evident from the results presented that electrolytic treatment alone significantly improves the corrosion resistance of gold plated silver against tarnishing. As in the case of chromating of zinc and cadmium, a passive film containing hexavalent and trivalent chromium is formed which gives adequate protection against tarnishing. Further, the post-treatment process does not change the appearance of the panel as these coatings are very thin and transparent. The panels are solderable after post-treatment without any risk of non-wetting.

CONCLUSION

Electrolytic treatment of gold-plated silver in an electrolyte containing potassium chromate 40 g/l and potassium carbonate 40 g/l at pH 8.8 and cathodically treated at a current density of 2.5 A/dm^2 for 1-3 minutes gives excellent protection against tarnishing as revealed by the accelerated stain proofing test.

REFERENCES

1. C R Draper, *Printed Circuits and Electronic Assemblies*, Robert Draper Ltd., Teddington (1969).
2. G Leonida, *Handbook of Printed Circuit Design, Manufacture, Components and Assembly*, Electrochemical Pub. Ltd. Ayr, Scotland (1981)
3. F A Lowenheim, *Modern Electroplating*, John Wiley & Sons Inc., New York (1974).
4. F A Loweheim, *Electroplating*, McGraw Hill Book Co., New York (1978).
5. J Fischer and D E Weimer, *Precious Metal Plating*, Robert Draper Ltd., Teddington (1964).
6. F H Reid and W Goldie, *Gold Plating Technology*, Electrochemical Pub. Ltd., Ayr, Scotland (1973).
7. M A Brimi and J R Luck, *Electrofinishing*, American Elsevier Pub. Co., Inc., New York (1965).
8. R M Burns and W W Bradley, *Protective Coatings for Metals* Reinhold Publishing Co., New York (1967).
9. D R Gabe, *Principles of Metal Surface Treatment and Protection*, Pergamon Press, Oxford (1972).
10. H Silman, G Isserlis and A F Averill, *Protective and Decorative Coatings for Metals*, Finishing Pub., Ltd., Teddington (1978).
11. W Goldie, *Electropla Metal Finish* ***16*** (1963) 336.
12. *Ibid*, ***17***-1 (1964) 13.
13. H Dettner, *Plating*,
13. H Dettner, *Plating*, ***48*** (1961) 283.
14. M Melse and P Baeyers, *Proc Amer Electroplat Soc*, 46 (1959) 293.
15. F W Eppensteiner and M R Jenkins, *Metal Finish* ***73***-9 (1975) 29
16. K S Rajagopalan and R Aravamudhan, *Metal Finish* ***66***-12 (1968).
17. K S Rajagopalan and R Aravamudhan, *Trans SAEST*, ***7*** (1972) 105.
18. S John, Malathy Pushpavanam and B A Shenoi, *Proc All India Precious Metal Plating Conf* Bombay (1979).
19. US Federal Agencies Specification QQ-S-365.
20. T Biestek, *Int Cong Met Corros 2nd National Assn of Corros Eng* (1963) 676.
21. S Ramachandran and R Aravamudhan, *Metal Finish*, 66-10 (1966) 78.