

A UNIQUE ANTI-TARNISH FILM BY RHODIUM PLATING

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Paper presented at the
All India Seminar on : PRECIOUS METAL PLATING
held in Bombay on : 18.8.1979

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INTRODUCTION

Of the metals of the platinum group, rhodium plating has the widest applications owing to several of its desirable and unique properties. It has been found of immense value when a permanent, hard, nontarnishable deposit of pleasing colour is needed. The rhodium deposit is extremely inert or stable chemically. It is insoluble even in aqua regia and is difficult to polish or strip. Further, rhodium has good electrical conductivity and low contact resistance.

Rhodium is the only metal the automakers can use to meet certain air pollution standards set for the model year (1981) in U.S.A. It is reported to have the unique ability to absorb on its surface the nitrogen oxides and give off harmless nitrogen gas. Rhodium is also used in Fibre glass industry, where it is used to make the templates through which the glass fibres are drawn.

Rhodium is too hard a metal to be worked by craftsmen. However, in the electro deposited form, the properties of the noble metal are of practical value to science and industry at relatively lower costs. Rhodium plating is now an established commercial process and several proprietary solutions are currently available. All standard texts and reviews cover various aspects of rhodium plating²⁻¹⁰. The objective of this paper is to introduce this technology with the specific aim of focussing a 'commercial need' for its use.

THE PROCESS

a) Plating Baths : The only commercial baths for rhodium plating are fairly strong acid solutions of sulphate, phosphate or mixed phosphate-sulphate type. The purity of the electrolyte is extremely important. Bath filtration over activated carbon is normally recommended for this purpose. Majority of solutions are prepared from concentrates sold by supply houses (like Technic Inc., Engelhard, Sel-Rex, U.S.A., Nippon Mining Co., Japan, Johnson-Matthey, U.K.) which specialise in the refining and treatment of platinum group of metals.

Rhodium plating baths produce coatings mostly in the range of 0.0005 to 0.005 mm thick. The thinner coatings are used mainly on silver for tarnish resistance; for increased wear and/or corrosion resistance, thicker coatings are specified. Rhodium plating can be done in barrels also.

Table I gives details of some typical rhodium plating baths and their operating conditions.

Several additions have been employed to obtain beneficial effects like low stress, brightness. Mention may be made of the addition of Indium², selenic acid additive⁵, aluminium or magnesium as sulphate (6 g/l)⁵, aluminium ions and polycarboxylic acid¹², copper ions and sulphamic acid¹³ and hexametaphosphate¹⁴ to get low stress rhodium deposits. A rhodium alloy deposit with 3-5% platinum has also been reported¹⁵ as an antitarnish coating for silver and having the same colour as silver.

b) Basis Metal : Rhodium is usually deposited on to silver, nickel, nickle-tin, or nickle-silver, though it can be directly plated over copper, brass, bronze, phosphor-bronze, beryllium copper as well as gold and platinum. Because of the fairly strong acid contents of the bath and position of rhodium in the electrochemical

TABLE - I

OPERATING CONDITIONS OF RHODIUM PLATING BATHS

Sl. No.	C O M P O S I T I O N	Temp. in °C	C.d. in Amp/dm ²	R E M A R K S	REFERENCES
1)	Rhodium (as sulphate concentrate) 5-8 g/l Sulphuric acid -----100-300 ml/l (95-96%)	35-50	2-10	Voltage 3-6 volts, anode platinum and agitation optional, but agitation is preferred for heavy deposits.	2
2)	Rhodium (as phosphate concentrate) ----- 8 g/l Phosphoric acid (C.P, 85%) -----150-300 ml/l	35-50	2-15	Anode platinum	2
3)	Rhodium (as phosphate concentrate) ----- 8 g/l Sulphuric acid (C.P. 95-96%) ----- 100-300 g/l	35-50	2-15	Anode platinum	2
4)	Rhodium (from phosphate concentrate) ----- 2 g/l	40-50	1-8	Mild agitation, platinum anode, bath voltage 2.5 - 5 V, Cathode efficiency 10-20%, Usual thickness, 0.1 - 0.06 mil.	8
5)	Rhodium (sulphate concentrate) ----- 1.8 - 2.2 g/l Sulphuric acid --- 40-50 g/l	40-50	1-3	Proper agitation, platinum sheet or platinum plated titanium sheet as anode.	11
6)	Rhodium (sulphate concentrate) ----- 4.5 - 5.5 g/l Sulphuric acid ---- 70 - 90 g/l	30-60	1-15	Strong agitation, for 10 b thick film, rest as above.	11

series, it cannot be plated on iron, steel, zinc, aluminium, lead or tin. For decorative purposes, bright nickel² is used as a base plate for rhodium to increase brightness or gloss and prevent attack on the softer, more malleable basis metals used for jewelry. Superior wear qualities are reported¹⁶ from rhodium deposits if applied over a tink-nickle underplate.

c) Immersion Plating : Rhodium can be plated simply by immersion, particularly on copper, in a solution of 5 g/l rhodium (concentrate) and 250 ml/l of concentrated hydrochloric acid and can be sealed after plating. This process is especially applicable to the printed circuits since it eliminates the need for electrical connections to isolated parts of the printed pattern⁵.

S Similarly a non-magnetic rhodium-nickel alloy has been claimed¹⁷ to be chemically deposited.

A CASE HISTORY

In some commercial malpractices, bright nickel plating itself is passed off for rhodium plating, as was revealed in a case referred to our laboratory. This can easily be tested by the usual spot tests with dimethylglyoxime.

APPLICATIONS

Though rhodium plating was earlier used only as a decorative or tarnish resistant film on silver and silver-ware, its industrial use has increased enormously in the last decade.

The major applications of rhodium plating are in the following fields:

1. Decorative : Since rhodium has high reflectivity (approximately 78%), it is extensively used for decorative purposes in

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jewelry, for silver, silver-ware and novelties. Rhodium plated silver mountings for diamonds have a potential export market.

2. Protective : Rhodium plating produces a film of practically permanent protection against corrosion. Even a thin coating is sufficient to give a tarnish resistant film on silver and silverware. The value of rhodium deposit for preventing bimetallic corrosion for phosphor-bronze has been demonstrated⁵. Rhodium plating is also used in the industrial finishing of wiper blades⁵ etc.

3. Reflectors : The hardness, high reflectivity and wear resistance have been used to great advantage on search light reflectors - the first commercial application of rhodium plating. It is particularly useful for the manufacture of reflectors, e.g. cinematograph reflectors where the conditions are severe.

4. Electrical and Electronics Industry : Rhodium plating has been commercially successful because of good electrical conductivity and low contact resistance of its film for long life, efficiency and reducing noise in electrical contacts, switch gears, armature/slip rings. The use of electrodeposited rhodium in coaxial radio frequency circuits has been described in detail⁵. Rhodium deposits suppress secondary electron emissivity and are finding ever-increasing acceptance in semi-conductor applications³.

5. Watch and Clock Industry : Rhodium plating is used for special parts in the watch and clock industry, e.g. the movement of the watch¹⁸, and watch cases.

6. Cutlery and Utensils : Rhodium plating imparts an aesthetic and permanent touch to cutlery and utensils. It may replace stainless steel cutlery in sophisticated places.

CONCLUSION

Rhodium plating should be used only when no other metal can replace it, because rhodium is very costly (nearly \$ 600 per-ounce¹). It is concluded that rhodium plating should be encouraged in India for special applications like electrical contacts, electronic components, switch gears, cinematograph reflectors and for jewelry and novelties like silver-mountings for diamonds for export purposes only.

ACKNOWLEDGEMENT

The author wishes to thank Prof. V.A. Altekar, Director, National Metallurgical Laboratory, for his suggestions and keen interest.

The author also thanks his colleagues, especially Sh. S.K. Ray, for their cooperation.

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