

Rhodium Plating to Specification

By R. R. Benham, F.R.I.C.

Johnson, Matthey & Co., Limited

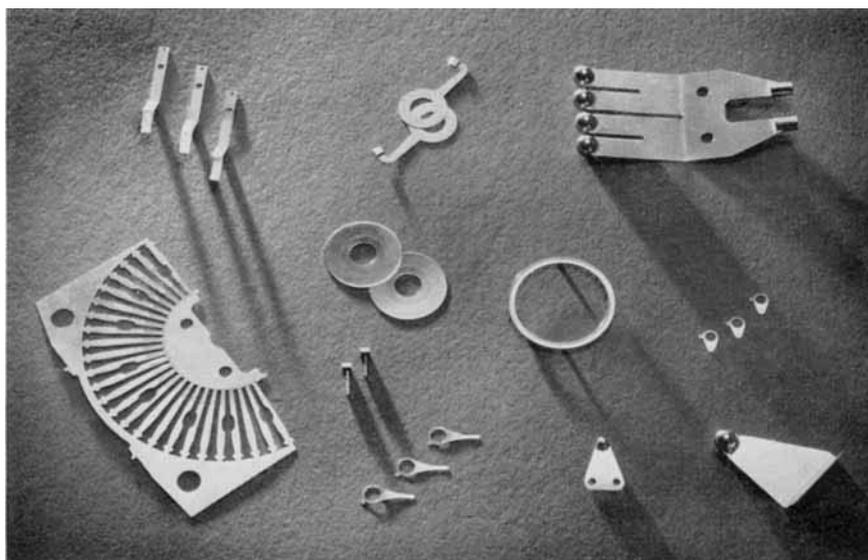
The Ministry of Aviation has recently issued Process Specification DTD 931, covering the rhodium plating of silver, copper, steel and aluminium components primarily for electrical and electronic applications. This article reviews the specification and outlines recommended procedures for the successful preparation of rhodium electrodeposits.

The electrodeposition of rhodium is conducted on normal plating lines and, at least for the thinner deposits, there are no special difficulties. It is some twenty-five years since the process was first carried out on a commercial scale. Originally it was chiefly used on jewellery to provide a white non-tarnishing surface of high reflectivity; for this purpose deposits of only 0.000005 to 0.000010 inch were adequate, and fortunately were relatively free from porosity. In addition the great hardness of electrodeposited rhodium gave an excellent resistance to wear.

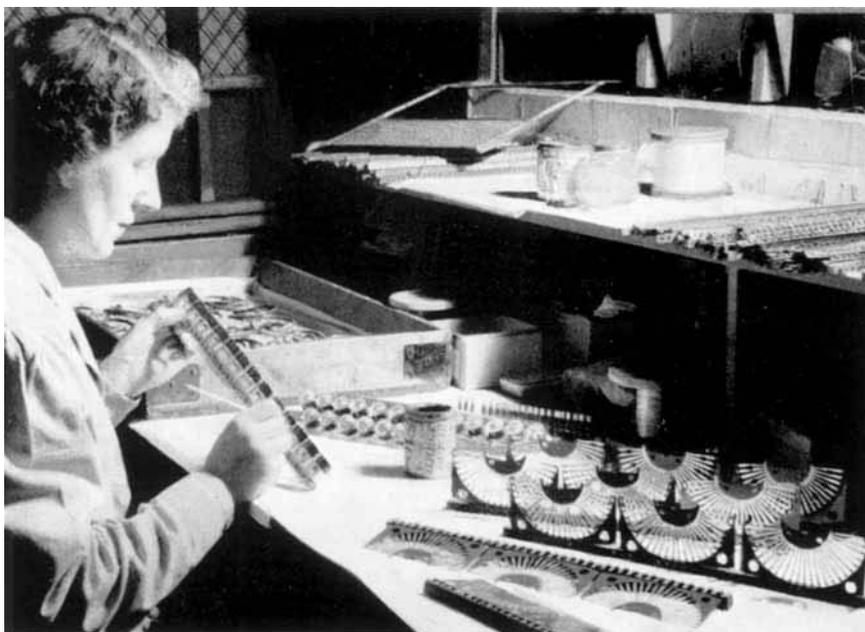
Within a few years it was found that the complete freedom from tarnish characteristic

of rhodium, coupled with its excellent resistance to abrasion, provided just the right combination of properties required in certain types of sliding or rubbing contacts in electronic equipment, and a demand arose for thicker deposits than had formerly been needed. The Second World War, with its rapid development of radio communication and radar, led to an enormous increase in the amount of rhodium used for this type of application and to the appearance on many engineering drawings and individual specifications of a note calling for such-and-such a thickness of electrodeposit.

In using a high-cost metal such as rhodium



A group of typical electrical and electronic components with rhodium plated contact surfaces



Masking of surfaces not required to be plated is carried out with a chlorinated rubber paint

a good deal of discrimination naturally needs to be used in deciding on the appropriate thickness of deposit to meet any particular set of design requirements, and in the earlier days of its employment there was sometimes a tendency for users to settle upon one arbitrary thickness to meet a variety of conditions. Much more information is nowadays available on the thickness of rhodium suitable for a particular application, and it is well understood that thicknesses may range from a minimum of, say, 0.00001 inch for the protection of a silver surface from tarnish up to something over 0.001 inch where heavy mechanical wear is to be met with.

This variation in optimum thickness was recognised to some extent in the Ministry of Supply Inter-Service Specification RCS/1000 (now replaced by Defence Specification DEF-5000), "General Requirements for Service Telecommunication Equipment", which called for a rhodium thickness of 0.00015 inch over a silver undercoating, but added that special requirements might be demanded where unusually heavy wear was to be encountered. Where an untarnishable

surface was required without wear-resisting qualities, the thickness of rhodium was specified as a minimum of 0.00001 inch. This specification made no reference, however, to the methods or procedures to be adopted in producing rhodium electrodeposits.

The recent issue by the Ministry of Aviation of Process Specification DTD 931, "Rhodium Plating" fills this gap and provides both users and electroplaters with a comprehensive guide to the factors involved in the successful use of rhodium.

Basis Metals and Undercoats

Most of the metals and alloys commonly used may readily be rhodium plated directly, although for reasons of skin conductivity, exposure to high temperatures or other special requirements it is more usual to deposit first an undercoating of silver or less frequently of nickel.

The exceptions to this include steel and aluminium, which are readily attacked by the strongly acid plating bath unless a dense non-porous undercoating of silver or nickel is first applied. Masking materials such as lacquers

or chlorinated rubber paints are not sufficiently protective when the rhodium plating time is more than a few minutes. For the deposition of say 0.00025 inch of rhodium this may be of the order of 1 to 1½ hours, and much damage could result in this time unless the steel or aluminium were completely protected. The specification therefore calls for a deposit of silver, copper or nickel not less than 0.001 inch in thickness for steel or 0.0015 inch for aluminium after polishing.

Tin-lead solders also present a problem in that unless they are completely covered with a non-porous undercoat before immersion in the rhodium bath a dense black stain is produced on the solder and over an appreciable area around the joint. A similar requirement of a minimum deposit of silver, copper or nickel is therefore specified on all areas of soft solder.

As soldered joints are frequently located on the inside corners of assemblies to be rhodium plated, it is essential that allowance be made for the fact that less silver will deposit in such areas by comparison with the average thickness over the whole component. It would appear to be the tin content of the solder that gives rise to the problem, and where possible the use of a tin-silver-lead solder containing no more than 5 per cent tin is to be preferred.

The writer has found that only 0.0001 inch of silver is adequate before rhodium plating over joints made with this alloy, while they may even be plated directly with no more than a very slight yellowing of the rhodium over the soldered area. A straight 5 per cent silver-lead solder is completely satisfactory for direct rhodium plating but is rather more difficult to use.

The choice of undercoat for rhodium is often dictated by the application. Thus, as already mentioned, silver is specified when the plated component is to be used in a high-frequency circuit. Here, particularly at very high frequencies, the "skin effect" is pronounced, the current being concentrated more in the outer skin of the conductor as the frequency increases. In certain very high frequency circuits the thickness of rhodium may therefore have to be restricted because of its inferior conductivity compared with that of silver (35 per cent IACS against 106 per cent). The choice of rhodium thickness then becomes a compromise between the conflicting requirements of long life and conductivity.

Silver is also the preferred undercoat to minimise the possibility of cracking in thick rhodium deposits. Where the application involves conditions of exposure to high temperatures, however, such as in reflectors of various kinds, a nickel undercoat is to be preferred.



Rhodium plating a batch of electrical contact springs

Preparation for Plating

The degreasing and alkaline cleaning procedures given in the DTD specification follow the normally accepted practice for these operations, but with rhodium plating very great care must be exercised to ensure thorough cleaning, or poor adhesion of the deposit may result. When thick deposits of rhodium are to be applied an additional etching step may well be incorporated, such as the anodic etch in cyanide for silver and the immersion in a ferric chloride-hydrochloric acid solution for nickel described in an appendix to the specification. Activation of nickel by cathodic treatment in sulphuric acid (say 10 per cent by volume) at 20 to 25 amperes per square foot for half a minute is also beneficial. Work so treated should be transferred without rinsing with as little delay as possible into the rhodium solution. It is the writer's experience, however, that adhesion on nickel is inferior to that to be obtained on silver even when these etching treatments have been used.

For stopping-off materials, either chlorinated rubber paints or special cellulose lacquers are to be recommended, but wax is not satisfactory. The edge of the stopping-off

paint should never be immediately adjacent to the essential contact area, but should be brought to within about one-sixteenth inch of this area. Rhodium deposits adjacent to stopping-off materials are sometimes found to be defective and this small margin is helpful in reducing the possibility of failure on this score. When using chlorinated rubber paint, stoving for two or three hours at 160°F effectively removes solvents in the paint film and also reduces the possibility of failure. When parts are stopped-off it is also advisable to use a cold cleaner to prevent the paint or lacquer from "frilling" at the edges.

Plating Procedure

The concentration of rhodium in the plating bath, its temperature, and the current density at which it is operated may be varied over quite a wide range. For the production of thick deposits, a high metal content and a low current density are to be preferred, especially when pinholes in the deposit must be avoided. This particular defect is also minimised by regular tapping of the work bar to dislodge hydrogen bubbles adhering to the surface. Alternatively, it is possible to fit a cam, operated by a fractional H.P. motor, to

Recommendations for Rhodium Thickness and Electrolyte Composition				
Class No.	General Type of Application	Minimum Thickness on Agreed Significant Surfaces (inch)	Recommended Rhodium Content, gm/litre	Recommended Minimum Sulphuric Acid Content, ml/litre
Rh 15	Tarnish protection	0.000015	2	20
Rh 25	Reflectors	0.000025		
Rh 100	Light mechanical loading and infrequent use	0.0001	4	20
Rh 200	Medium mechanical loading ..	0.0002		
Rh 400	Heavy mechanical loading ..	0.0004	10	50
Rh 800	Very heavy loading conditions in special applications only	0.0008		

lift the work bar say one inch and then drop it back on to the top of the vat at intervals of about 20 or 30 seconds.

Thin deposits may be obtained from a more dilute solution, thus economising in the amount of metal tied up, and higher current densities are satisfactory. The specification recognises these variables, and to some extent correlates recommended electrolyte compositions with thickness of metal to be deposited. The table on page 16 combines the suggested rhodium and sulphuric acid concentrations appropriate to the thicknesses of deposit set out in the specification.

The electrolyte is recommended to be operated between 30 and 50°C, with a cathode current density of 10 to 20 amp./sq.ft., although in special cases a reduction to 5 amp./sq.ft. is preferable.

Rhodium plating is an insoluble anode process, the anodes normally being of platinum or rhodium-platinum, and the metal deposited from solution must therefore be replaced by the addition of rhodium sulphate concentrate. The specification calls for this replenishment to be made before the rhodium content of the bath has fallen by 10 per cent of its nominal value. Attention to this is most important, as if proper replenishment is not carried out the cathode efficiency of the bath will fall and less rhodium will be deposited, other things being equal. The best practice is to add the necessary quantity of concentrate immediately after the completion of each batch of work. Periodic chemical analyses of the solution should be made to ensure that the correct rate of replenishment has been achieved, and reliable methods for the determination of rhodium are given in an appendix to the specification.

It is also of utmost importance to carry out regular checks to determine the rate of deposition, or in other words to control the thickness being deposited in a particular set of operating conditions. Failure to observe this requirement can lead either to the deposition of more rhodium than is necessary and so to needless cost, or of course to less—and

failure to meet specification. The simplest means of control is to weigh a piece of copper foil before and after plating for a known time at a given current density, and a further appendix gives the simple formula to be applied.

Thickness Recommendations

The thickness of rhodium deposit called for by the user should naturally bear a relation to the application or service duty involved. Too often the phrase “rhodium flash” has been employed to cover requirements ranging from the thinnest plate for tarnish prevention to a heavy deposit needed to withstand heavy mechanical wear. The specification adopts six classes of deposit to give guidance to engineers and designers in selecting an appropriate thickness. These recommendations, reproduced in the table, will undoubtedly be of value to users and potential users of electrodeposited rhodium.

Naturally the thicker deposits are normally restricted to the areas where they are actually required, but in many cases it is usual to apply a thin tarnish-preventive deposit over the remainder of the part.

It should also be said that the heavier deposits, from say 0.00025 inch upwards, require considerable care and experience to produce sound plates free from fine hair cracks. Rhodium as deposited is normally in a state of considerable mechanical stress. Where excessive cracking is due to organic contamination, either from stopping-off paints or other sources, treatment of the solution with activated charcoal is usually effective.

Inspection Requirements

The inspection clauses of the specification cover freedom from surface defects, reflectivity, adhesion, hardness and thickness of the deposit.

The question of surface appearance is usually a matter of opinion, and it is often found advisable for the plater to discuss requirements with the user and to agree on an acceptance test. The present specification

allows the presence of fine hair cracks, particularly in deposits thicker than 0.0001 inch.

A bend test is laid down for the assessment of adhesion, but the specification draws attention to the fact that the rhodium deposit may well crack on bending and that a distinction must be made between such cracking and actual exfoliation.

The hardness of electrodeposited rhodium is extremely high—of the order of 800 to 900 Vickers—but it is naturally extremely difficult to determine hardness values on very thin

electrodeposits. The specification accepts this difficulty for deposits less than 0.0004 inch in thickness, but for thicker deposits states that the hardness, as determined by a suitable micro-hardness tester, may be checked at the discretion of the inspector.

Owing to the chemical stability of rhodium the only means of measuring the thickness of a deposit is by a destructive method. Mounting and sectioning, followed by measurement with an eyepiece graticule or direct measurement of a photomicrograph, is the specified method.

A History of Platinum

PLATINUM, by comparison with metals such as copper, silver and gold, has a relatively short history, but there is none the less a fascinating story to unfold in tracing the beginnings of an understanding of its character and in outlining its commercial exploitation.

It was not until the Spanish conquest of South America that rumours were heard of a new metal that could not readily be melted, the first published reference occurring in 1557 in the writings of the Italian scholar and poet Julius Caesar Scaliger. Only in the middle of the eighteenth century were specimens of this metal received in Europe and subjected to proper scientific examination, first by the Englishman Brownrigg and then in quick succession by chemists in France, Germany, Spain and Sweden.

Much effort was then directed towards the refining, melting and working of platinum, culminating in the well-known work of Wollaston, early in the nineteenth century, in producing malleable platinum by the technique nowadays known as powder metallurgy.

From then on the pace quickened and the commercial development of platinum, its sister metals and its alloys really began; the discovery of catalysis by Döbereiner, the introduction of the melting of glass in platinum vessels by Faraday, the design and manufacture of enormous platinum boilers for the concentration of sulphuric acid by Johnson and Matthey are but a few of the outstanding features along the way.

In **A History of Platinum**, published by Johnson, Matthey & Co., Limited (35s or \$5.50), Donald McDonald has, by diligent research into both published literature and private archives, succeeded in putting together a clear and readable account of these developments that has never before been given as a continuous story.



Two illustrations from Donald McDonald's "A History of Platinum". Above, Julius Caesar Scaliger, the Italian scholar whose writings included the first reference to platinum, published in 1557. Below, the press used by Wollaston to compress platinum powder into cakes before forging

