

**Ministry of Defence
Defence Procurement Agency, ADRP2
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OBSOLESCENCE NOTICE

All DTD specifications were declared obsolescent from 1st April 1999. All DTD 900 series approvals also lapsed at that time. The standards will no longer be updated but will be retained as obsolescent documents to provide for the servicing of existing equipment.

Further Guidance

The aim in declaring the specifications obsolescent is to recognise that the documents are not being updated and thus should be used with care by both purchaser and supplier. For example, a specification could contain valid technical information but may also contain type approval clauses that contradict procurement policy and/or use materials that do not comply with environmental legislation. The obsolescent specification can still be used as a basis for a purchase provided that the supplier and purchaser agree suitable changes to the specification within the purchase order/contract.

For the DTD 900 system, each specification has provided an MoD approved material and process. For these items, the declaration of obsolescence will constitute the termination of both the extant MoD approval and the continuing MoD assessment that had underpinned those approvals. Again, the technical content of the document remains valid and can be used by both purchaser and supplier as a basis for a contract but an acceptable (to the parties) approval/assessment procedure would be required.

Process Specification

RHODIUM PLATING

1. General

1.1 Rhodium plating is used primarily in electrical and electronic equipment where its resistance to tarnishing permits the maintenance of low contact resistance and its resistance to wear provides long life for sliding contacts, particularly if these are free from arcing and sparking. The high reflectivity in the visible and infra-red ranges and the resistance to tarnishing of polished rhodium make rhodium plating particularly suitable for reflectors.

1.2 Mercury or mercury compounds shall not be present in any of the materials used at any stage of the process (see Appendix VI). Care should be taken to avoid accidental contamination of the materials with mercury.

2. Areas to be plated

The rhodium deposit, but not necessarily the undercoats (see Clause 5), shall, when practicable, be confined to the "significant surfaces", i.e., the areas on which rhodium is essential for satisfactory functioning of the part. These areas should be agreed between the Design Authority and the plater, and shall be indicated on the drawing or order.

3. Materials to be plated

3.1 *Instructions to plater.* The plater shall be given such information about composition, condition and strength of the material to be plated as is necessary to enable him to select the appropriate treatments under Clauses 5 and 8; alternatively, the plater shall be given precise instructions regarding the treatments to be applied under these clauses.

3.2 *Silver-rich materials.* These will normally comprise silver and silver-copper alloys.

3.3 *Copper-rich materials.* These will most commonly be copper, brass, copper-nickel-zinc alloy ("nickel silver"), phosphor bronze and beryllium copper.

3.4 *Steels.* These shall be of minimum specified tensile strength not exceeding 90 tonf/in² or of minimum specified hardness not exceeding 405 HB or 430 HV.

3.5 *Aluminium-rich materials.* These will normally be in wrought form.

4. Polishing

When a polish is required on the final rhodium plating, the part and / or any undercoat (see Clause 5) shall be polished to the necessary extent.

5. Undercoats

5.1 *Preparation.* Silver-rich materials may be rhodium plated directly as described in Clauses 6 and 7; other materials shall be cleaned and prepared in accordance with Specification D.T.D. 901 and then plated as described below before rhodium plating.

5.1.1 *Copper-rich materials.* If no intermediate deposit of silver or nickel is required (see Clauses 5.2 and 5.3), these materials should receive a flash coating of copper by the procedure described in Appendix I or by other suitable means.

5.1.2 *Steels and aluminium-rich materials.* These materials shall be plated with a dense, non-porous deposit of silver or nickel according to the requirements of Specification D.T.D. 919; alternatively, deposits of the same thickness consisting wholly or partly of copper may be applied (see also Clauses 5.2 and 5.3). Unless there is any reason to the contrary (see Clause 5.3), a silver undercoat is generally preferred when the rhodium deposit required is 0.0001 in or more thick (Classes Rh 100, Rh 200, Rh 400 and Rh 800 of Clause 9).

5.1.3 *Soldered areas.* The requirements of Clause 5.1.2 for steels also apply when areas of soft solder form part of the surface to be rhodium plated. Certain special soft solders, viz., 95/5 lead/silver or 93.5/5/1.5 lead/tin/silver, however, will permit of direct rhodium plating or the use of thin, say 0.0001 in, silver undercoating.

5.2 *Conducting surfaces.* When the plated surface is to be used as a current-carrying part of H.F. circuits, the rhodium shall normally be applied to a silver undercoat of thickness not less than 0.0005 in.

5.3 *Reflecting surfaces.* When the rhodium plating is required to function as a reflecting surface, particularly at elevated temperatures (preferably not above 450°C), the rhodium shall be deposited on an undercoat of silver, copper or, preferably, nickel of thickness not less than 0.0005 in.

6. Preparation for rhodium plating

6.1 *Degreasing.* After treatment as described in Clause 5 the parts should be freed from grease and other foreign matter, e.g., residual polishing compounds, by one or both of the following methods :

- (a) solvent degreasing with liquid and/or vapour;
- (b) immersion in hot alkaline cleaning solution with or without an emulsifying agent

followed by bristle brushing and rinsing in running water, and a final rinse in hot water.

6.2 *"Stopping-off".* Areas in which a rhodium deposit is not required should be dried after cleaning and rinsing as in Clause 6.1 and then "stopped-off" by any suitable means. The materials used for "stopping-off" shall not contaminate the rhodium plating electrolyte.

6.3 *Electrolytic cleaning.* The parts shall be cleaned electrolytically in an alkaline solution. A suitable solution contains :

Sodium hydroxide (NaOH)	2 oz/gal
Sodium carbonate (Na ₂ CO ₃) or trisodium phosphate (Na ₃ PO ₄ .12H ₂ O)	8 oz/gal

Suitable proprietary metal cleaning solutions may be used. The current density is not critical but should produce brisk gas evolution over the metal surface. For cathodic degreasing the bath shall not be allowed to become contaminated with metals which may plate out and cause smut on the work.

6.4 *Pre-plating dips.* The cleaned parts shall be rinsed in cold running water. This may be followed, for silver plated or copper plated parts, by a dip in 1-5 per cent potassium cyanide solution and a further rinse in water. This should normally be followed by a dip in 5 per cent (vol) sulphuric acid solution and a final rinse in water before transferring the parts to the rhodium plating bath. The areas to be plated shall, on draining, remain covered with a continuous film of water, otherwise the electrolytic cleaning and subsequent steps shall be repeated.

- NOTES.* (i) The above procedure will normally suffice to give adequate adhesion of thin rhodium deposits, e.g., Classes Rh 15 and Rh 25 of Clause 9, to copper-rich materials and silver-rich materials and to silver-, copper- and nickel-plated surfaces whether produced from conventional or bright-plating electrolytes.
- (ii) For thicker rhodium deposits, e.g., Classes Rh 100, Rh 200, Rh 400 and Rh 800 of Clause 9, it is desirable, in view of the stressed nature of the rhodium, to supplement the above cleaning cycle by further pre-treatment to ensure good adhesion. Typical procedures for copper-rich materials are shown in Appendix I, and for silver-rich materials and nickel-plated surfaces in Appendix II.

7. Rhodium plating

7.1 Electrolytes

7.1.1 *General.* Rhodium is supplied for plating purposes in the form of concentrated solutions, either of rhodium sulphate or rhodium phosphate. Either phosphate-sulphate or sulphate electrolytes may be used to produce bright deposits of good colour for reflecting or protective purposes, but the sulphate type is preferred for the majority of applications, and particularly for the thicker deposits. Operational details appropriate to the sulphate electrolyte are given in Clause 7.2.

7.1.2 *Addition agents.* Addition agents which can be shown to improve the quality of the rhodium plating, e.g., by reducing the stresses in the coating and the consequent tendency to crack, may be used provided that the hardness or other required property of the rhodium is not adversely affected.

7.1.3 *Alternative electrolytes.* Electrolytes other than those of the above two types may be used for the deposition of rhodium provided that they have been approved by the Director of Materials Research and Development/Aviation.

7.2 Sulphate electrolyte

7.2.1 *Composition.* The initial make-up of a sulphate electrolyte should lie within the following ranges :

Rhodium	2-10g/l
Sulphuric acid (sp. gr. 1.84)	20-100 ml/l

The electrolyte should be made up with distilled water.

The rhodium content and sulphuric acid addition should be correlated with the thickness of metal to be deposited according to the following table:

Class No. (Clause 9)	Recommended minimum rhodium content g/l	Recommended minimum sulphuric acid content ml/l
Rh 15 and Rh 25	2	20
Rh 100 and Rh 200	4	20
Rh 400 and Rh 800	10	50

Rhodium plating electrolytes are sensitive to contamination, particularly by organic materials. Appropriate precautions shall be taken to minimise contamination and adequate filtration shall be employed.

7.2.2 Operating conditions. The electrolyte should normally be operated at a temperature within the range 30°C to 50°C, with a cathodic current density of 10 to 20 amp / ft². Interruption of the current may lead to exfoliation of the deposit.

Care should be taken to avoid local overheating of the electrolyte. Parts should be agitated to avoid pitting or streaking of deposits due to adhesion of hydrogen bubbles. If persistent difficulties are encountered because of this effect it may be advantageous to reduce the current density. An effective form of agitation is provided by periodic lifting and dropping of the cathode bar, either by hand or by mechanical means.

7.2.3 Anodes. Insoluble anodes, usually of platinum or platinum-rhodium alloy, are used. The rhodium content of the electrolyte shall be replenished by the addition of concentrated rhodium solution, and should not be allowed to fall by more than 10 per cent of the nominal value. A suitable method of checking the rhodium content of the electrolyte for control purposes is given in Appendix III.

7.2.4 Thickness control. The time necessary to deposit a required thickness of rhodium under particular operating conditions may be derived from the efficiency or plating rate of the process, which should be determined and periodically checked as described in Appendix IV. The average thickness of deposit on a given batch of parts can be checked by weighing either the whole or part of the batch before and after plating.

7.2.5 Rinsing. After plating, the parts should be rinsed in a "drag-out" tank of distilled water, which may, at the discretion of the plater and with appropriate precautions to maintain cleanness, be used to replace evaporation losses from the electrolyte. The parts should finally be rinsed in running water and dried.

7.2.6 Final polishing. The rhodium deposit may be polished in the normal way if required.

8. Heat treatment

Plated parts in steel or aluminium-rich material shall be heat treated in accordance with the requirements of Specification D.T.D. 919.

9. Thickness recommendations

The following table is provided for guidance in selecting suitable thicknesses of rhodium plate for different purposes. Classes Rh 100 to Rh 800 would normally be suitable for electrical contacting surfaces under increasingly severe loading and / or abrasive conditions. The thickness of rhodium required shall normally be specified by quoting the appropriate Class Number from the table; alternatively or additionally, the Design Authority may specify the thickness required on the order or drawing.

Table of recommended thicknesses of rhodium coatings

Class No.	Typical application	Minimum thickness on agreed significant surfaces, in
Rh 15	Tarnish resistance	0.000 015
Rh 25	Reflectors, anti-tarnish	0.000 025
Rh 100	Light mechanical loading, for reliability of electrical contacts after long idle periods	0.000 100
Rh 200	Medium mechanical loading — sliding contacts	0.000 200
Rh 400	Heavy mechanical loading — sliding contacts	0.000 400
Rh 800	Very heavy loading conditions — special applications only	0.000 800

10. Inspection

10.1 *Freedom from surface defects.* After rhodium plating and polishing, if any, all parts shall be examined at a magnification of $\times 10$ to verify that the significant surfaces present a smooth, uniform appearance, substantially free from pits, blisters, nodules, exfoliation or other blemishes and that no unplated areas are present. Fine hair cracks may be accepted in deposits of 0.0001 in (Class Rh 100) thickness or greater, at the discretion of the inspector.

10.2 *Sampling for test.* Unless otherwise agreed, 2 per cent of each batch of aluminium-rich parts and 1 per cent of parts in other materials, with a minimum of 2 parts from each vat or barrel load, shall, after any polishing which is to be applied, be tested for compliance with the requirements of Clauses 10.3 to 10.6 as appropriate.

10.3 *Thickness.* The thickness of the deposit shall conform to the requirements of the order or drawing, when measured by the method given in Appendix V or by any other method acceptable to the Inspecting Authority.

10.4 *Adhesion.* Adhesion of the rhodium plate shall be such that when a plated part, selected at random from the batch, is deformed or broken by sharp bending no exfoliation shall be visible at or near the bend or fracture.

NOTE. Cracking of the deposit such as will normally occur on bending should be carefully distinguished from exfoliation.

10.5 *Hardness.* The hardness of rhodium deposits is normally in the range 800–900 HV. The hardness shall be measured at the discretion of the inspector or if required by the order. A micro-hardness tester acceptable to the Inspecting Authority shall be used and the loading on the diamond shall be related to the thickness of the plating. The test is not satisfactory for coatings thinner than about 0.0004 in (Class Rh 400).

10.6 *Reflectivity.* When the rhodium deposit is required primarily as a reflecting surface, its mean reflectivity over the visible spectrum shall be not less than 80 per cent of that of freshly polished silver when determined by a method agreed between the Design Authority for the equipment and the plater. The reflectivity shall be measured only if required by the order.

10.7 *Use of special test pieces.* At the discretion of the inspector the thickness and adhesion tests (Clauses 10.3 and 10.4) may alternatively be made on test pieces of similar material to the parts concerned and of acceptable form and dimensions. The test pieces shall be subjected to every operation in the plating process together with each batch of parts.

APPENDIX I

Procedures for the flash copper plating of copper-rich materials prior to rhodium plating

(a) Copper, brass, "nickel silver" and beryllium copper

(i) Degrease cathodically in any suitable alkaline cleaning solution

(ii) Rinse thoroughly

(iii) Etch anodically

Electrolyte :

Phosphoric acid (sp. gr. 1.75)	15 ml/l
Current density	7 amp/ft ² (0.7 amp / dm ²)
Time	40 sec
Temperature	room

(iv) Rinse thoroughly

(v) Copper plate

Electrolyte :

Copper sulphate (CuSO ₄ .5H ₂ O)	125 g/l
Sulphuric acid (sp. gr. 1.84)	38 ml/l
Current density	20 amp/ft ² (2 amp / dm ²)
Time	1 min
Temperature	room

(vi) Rinse thoroughly and transfer to rhodium plating bath without delay.

(b) Phosphor bronze

(i) Degrease cathodically in any suitable alkaline cleaning solution

(ii) Rinse thoroughly

(iii) Etch by immersion in solution containing:

Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$)	20 g/l
Hydrochloric acid (sp. gr. 1.16)	60 ml/l
Time	10—15 sec
Temperature	room

(iv) Rinse thoroughly

(v) Dip in 10 per cent potassium cyanide solution to remove etching stain

(vi) Rinse thoroughly

(vii) Copper plate as in (a)(v)

(viii) Rinse thoroughly and transfer to rhodium plating bath without delay.

APPENDIX II

Procedures for the etching of silver and nickel for rhodium plating

(a) *Silver*

(i) Etch anodically

Electrolyte :

Potassium cyanide	10 g/l
Current density	2 amp/ft ² (0.2 amp/dm ²)
Time	1 min
Temperature	room

It is preferable to avoid the use of mild steel either as a tank material or for cathodes.

(ii) Rinse thoroughly

(iii) Dip in 5 per cent (vol) sulphuric acid and transfer to rhodium plating bath without delay.

(b) *Nickel*

(i) Etch by immersion in solution containing :

Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$)	20 g/l
Hydrochloric acid (sp. gr. 1.16)	60 ml/l
Time	20—30 sec
Temperature	room

(ii) Rinse thoroughly and transfer to rhodium plating bath without delay.

APPENDIX III

Procedures for the determination of rhodium in rhodium plating electrolytes

(a) *By electrolysis*

Dilute a measured volume of the electrolyte calculated to contain not less than 0.1 g of rhodium to 150—200 ml, heat to and maintain at about 40°C and electrolyse between a platinum anode and a weighed copper cathode, using a current of 0.5—1.0 amp for twice the time taken to render the electrolyte colourless. It may be necessary to initiate plating by “striking” at a higher current for a few seconds. The increase in weight of the cathode gives the weight of rhodium in the sample.

(b) *By gravimetric analysis*

Where facilities are available, the rhodium content may be determined by reduction of the metal from a measured volume of electrolyte by boiling with hydrazine in alkaline solution.

Dilute the sample solution to 30—50 ml and treat with 15—20 drops of hydrazine (50 per cent) followed by an excess of 10 per cent sodium hydroxide solution. Addition of hydrazine usually produces a yellow precipitate, which may darken or dissolve on addition of the alkali. Heat to boiling in order to precipitate and coagulate the rhodium. Then cool the solution slightly, just acidify with hydrochloric acid, and filter through a coarse-textured ashless filter paper, washing thoroughly with hot water. Wrap the rhodium residue in the paper, transfer to a porcelain crucible, dry, char the paper and ignite. Remove the superficial oxide film on the rhodium by directing a gentle stream of coal gas or hydrogen on to the residue while cooling.

NOTE. The rhodium residue obtained by either of these procedures may be contaminated by certain base metal impurities, e.g., copper and nickel. If such impurities are present in the electrolyte they will be wholly or partly co-deposited or co-precipitated during the test, but in normal operation the degree of contamination of the electrolyte should not be sufficient to render the methods inapplicable for control purposes.

APPENDIX IV

Procedure for determining rate of deposition of rhodium

Prepare a piece of copper sheet of known area for plating and weigh. A piece measuring 3.5 in x 1 in x 24 S.W.G. gives a total surface area of 7.2 in² (1/20 ft²) and is usually of convenient and suitable size.

Plate the test piece for a given time under the operating conditions which are to be used in subsequent deposition, then wash, dry and re-weigh. The thickness of the rhodium plating, from which the rate of plating under these conditions may be calculated, is given by the equation:

$$\text{Rhodium thickness (in)} = \frac{\text{Gain in weight (g)}}{\text{Area (in}^2\text{) x 200}}$$

A similar procedure may be used in batch control of thickness, in which case a suitable test piece shall be plated in the bath at the same time as the parts represented.

APPENDIX V

Determination of thickness of plating by direct measurement

(a) *Preparation of micro-sections*

Cut sections at right-angles to the plated surface. Before mounting, plate the sections with at least 0.005 in of copper to maintain the sharpness of the outer edge of the plated coating during polishing. Mount these sections in a suitable medium and prepare them by grinding the cut face on abrasive paper in the usual manner and finally polishing on a pad of suitable cloth impregnated with diamond dust of particle size up to 1 micron and a suitable lubricant. Take care throughout this preparation to ensure that the prepared face is at right angles to the plated surface, otherwise erroneous results may be obtained.

NOTE. If desired the specimen may be etched with a suitable reagent in order to increase the visual contrast between the deposit and the base metal.

(b) *Measurement of thickness*

Examine the sample so prepared under a microscope at a magnification such that the rhodium layer to be measured appears to be not less than 1 mm (0.040 in) thick.

Check the exact magnification at which the measurement is made by the use of a suitable stage micrometer. Use a measuring device for the measurement of thickness capable of reading to an accuracy of ± 5 per cent of the thickness measured.

APPENDIX VI

Procedures for detecting mercury in plating electrolytes

(a) *Reagents required*

(i) Concentrated hydrochloric acid (A.R.)

(ii) Stannous chloride solution, (5g stannous chloride (A.R.) dissolved in 5 ml concentrated hydrochloric acid (A.R.), warmed to effect solution, cooled and diluted to 100 ml with distilled water.)

(b) *Methods*

(i) *For copper, nickel and rhodium electrolytes*

Take two 10 ml samples from the electrolyte, using a measuring cylinder, and filter. Put the samples into similar test-tubes. Add 5 drops of the stannous chloride reagent to one tube only and mix thoroughly. Stand for 15 minutes and compare the two solutions. A slight turbidity in the solution to which stannous chloride was added indicates the presence of mercury.

(ii) *For cyanide silver electrolytes*

Take a 20 ml sample from the electrolyte, using a measuring cylinder, and filter into a small beaker. Place in fume cupboard, add 6 ml concentrated hydrochloric acid (A.R.), boil for a few minutes and cool. Centrifuge to remove silver chloride and place one half of the solution into each of two test-tubes. Add 5 drops of stannous chloride to one tube only and mix thoroughly. Stand for 15 minutes and compare the two solutions. A slight turbidity in the solution to which stannous chloride was added indicates the presence of mercury.

(iii) *For cyanide brass electrolytes*

Proceed as in (ii) but boil until the precipitate which forms after the addition of hydrochloric acid is redissolved.

(c) Limits of detection

The minimum concentration of mercury which can be detected by these methods is equivalent to 40 mg/l for nickel electrolytes and 20 mg/l for the remaining electrolytes.

Approved for issue,

E. W. RUSSELL,

Director of Materials Research and Development/Aviation.

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