

**Ministry of Defence
Defence Procurement Agency, ADRP2
Abbey Wood
Bristol
BS34 8JH**

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
TIN-ZINC ALLOY PLATING**

Note. — Marginal lines indicate modifications since previous issue.

1. Definition

Tin-zinc plate is defined, for the purpose of this specification, as an electrodeposited coating containing $75 \pm \frac{5}{10}$ per cent of tin and the remainder zinc.

2. Scope

This specification covers the requirements for tin-zinc alloy coatings applied primarily to ferrous parts for protection against corrosion or to facilitate soldering.*

NOTE. - Sweating or soldering of high tensile steels should be avoided.

3. Preparation

The surfaces to be plated shall be cleaned and prepared for plating in accordance with Specification D.T.D.901 (latest issue).

4. Electrolyte

The electrolyte for still baths shall have the following composition when determined by the methods given in Appendix I:-

Tin	25 - 30 g per litre (4.0 - 4.8 oz/gal)
Zinc	2.5 - 3.5 g per litre (0.40 - 0.56 oz/gal)
Total cyanide (expressed as sodium cyanide)	27 - 30 g per litre (4.3 - 4.8 oz/gal)
Free sodium hydroxide	4.0 - 6.0 g per litre (0.64 - 0.96 oz/gal)

The tin shall be added as sodium stannate to BS 1468 (sodium stannate to this standard is required to contain not less than 38 per cent of soluble tin). The zinc shall be added as zinc cyanide (this contains approximately 55 per cent of zinc). The amounts required will depend on the exact composition of the salts used.

Mercury or mercury compounds shall not be used at any stage of the preparation or finishing, nor shall they be present in any of the materials used (see Appendix II for detection of mercury).

Frequent additions of sodium cyanide will be required, as this salt is slowly decomposed when the electrolyte is hot. Less frequently it may be necessary to make small additions of sodium stannate and sodium hydroxide. The zinc content of the bath remains fairly constant. Sodium carbonate accumulates in the bath with use, and the carbonate content should not be allowed to exceed the saturation value at room temperature (about 120 g per litre). Suspended solids should be removed periodically.

If stannite is present (see Clause 5.5) sodium peroxide, sodium percarbonate or hydrogen peroxide shall be added. An addition of 1/2 oz of sodium peroxide per 100 gal (3 g per 100 litres) of electrolyte will normally be sufficient to correct the condition. The presence of stannite will cause the deposit to be rough.

NOTE. - Sodium peroxide reacts violently with the electrolyte, and should hence be added with caution.

For barrel plating some modification of the above electrolyte is necessary, as the movement of the electrolyte affects the composition of the coating, tending to reduce its zinc content. The amounts of zinc, total cyanide and free sodium hydroxide in the solution will have to be increased by amounts that will depend on the plating equipment used. The exact composition of the electrolyte will have to be determined by trial, but a solution of the following concentration should give a deposit fairly close to the required composition:-

Tin	30 g per litre (4.8 oz/gal)
Zinc	7 g per litre (1.1 oz/gal)
Total cyanide (expressed as sodium cyanide)	40 g per litre (6.4 oz/gal)
Free sodium hydroxide	10 g per litre (1.6 oz/gal)

Cleanness, both of the bath and the plating room, is an important factor in obtaining good results.

5. Plating

5.1 Vats and barrels. - Vats should be of welded mild steel lined with alkali-resistant rubber or replaceable sheets of reinforced glass. Barrels should be of materials resistant to alkali, and should preferably be of the horizontal-immersed type.

5.2 Temperature. - The temperature shall be maintained at 65° ± 2°C (149° ± 4°F). Thermostatic control is desirable.

*This process was developed by Tin Research Institute, Perivale, Middlesex, who will be pleased to advise on its operation.

5.3 *Cathode current density.* - The cathode current density for still baths shall be 10-30 amp per sq ft.

5.4 *Anodes.* - The anodes shall be of tin-zinc alloy containing 75 ± 2 per cent of tin; the lead content shall not exceed 0.075 per cent and total impurities 0.25 per cent; extruded anodes are often preferred to cast anodes. Auxiliary anodes shall be of mild steel or tin (filmed). The anode hooks shall be of mild steel, and shall make positive electrical contact with the anodes and anode bars at all times.

The working anode current density range shall be 7.5 - 15 amp per sq ft. The total anode area shall be such as to comply with this requirement.

To ensure proper filming (see Clause 5.5) the anodes shall be not more than 4 inches wide, nor less than 1 inch apart, nor less than 3 inches from the sides of the vat.

5.5 *Anode filming.* - The anodes shall at all times be operated in the filmed condition, to ensure the tin in them dissolving wholly as stannate and not as stannite (see Appendix I for detection of stannite).

To establish the film a current density of about 30 amp per sq ft shall be employed for a short time at the outset. This is best done by placing all the anodes in the bath without any current passing and then applying about 6 volts for 15-30 seconds, after which the voltage is reduced to give the normal working current density. Prolonging the time of application beyond 30 seconds will cause the anodes to become passive. When properly filmed the anodes present a clean appearance and tend to a greenish-yellow colour.

When electrolysis stops the anodes remain filmed for a time, but ultimately the film is lost and thereafter tin will enter the solution as stannite. The anodes shall therefore be removed if the bath is likely to be out of use for any considerable time. No precise figures can be given for the time that the anodes may be allowed to remain in the bath after the cessation of electrolysis, but experience indicates that the time increases with the volume of the bath. In baths of over 500 gallons (2,250 litres) the anodes can usually remain idle for an hour or even longer without much risk of stannite formation, provided they were filmed at the moment electrolysis ceased. *In no circumstances shall unfilmed anodes be allowed to remain in the bath.*

5.6 *Voltage.* - The working voltage is normally about 4 volts. An appreciable drop in the voltage usually indicates the loss of the film from one or more anodes.

6. Treatment after plating

6.1 *Washing.* - The plated parts shall be thoroughly washed in clean running water and then treated as detailed in Clause 6.2, except that plated parts requiring heat treatment in accordance with Clause 6.3 shall be so heat treated before the chromate dip treatment or passivation specified in Clause 6.2.

6.2 *Chromate dip.* - The parts shall be immersed for 10-15 seconds at a temperature of 50-60°C in an aqueous solution containing 2 per cent of chromic acid. The parts shall then be washed in cold running water, followed by a rinse in clean hot water and drying.

This treatment does not normally produce any marked change in the appearance of the coating, but prolonging the time of immersion produces a yellowish film.

Alternatively the plated parts may be treated in accordance with Specification DEF-130. This treatment produces a yellowish film.

6.3 *Removal of embrittlement.* - Plated parts in steel, other than springs, whose specified minimum ultimate tensile strength is 65 tons per square inch or greater, shall be heated for not less than four hours at 100-150°C. Steel springs shall be immersed in boiling water for two hours. (The spring rating may be affected at a higher temperature.)

7. Inspection

7.1 *Visual.* - The coating shall be smooth and of a uniform metallic white colour. The coating shall be free from pores and blisters, and shall appear to be continuous.

7.2 *Thickness.* - The Inspector shall select at his discretion any parts, usually not more than 2 per cent of production (minimum of one part), for the determination of thickness of coating. He shall be satisfied that the thickness, determined by local and/or average thickness tests (see Clauses 7.3 and 7.4), is in accordance with Table 1.

7.3 *Local thickness.* - The local thickness shall be determined by the B.N.F. Jet Test (see Appendix III), an approved magnetic test or other local thickness test approved by the Inspecting Authority.

The tests on any one part shall be not less than four in number, depending on the size of the part, and shall be made at those areas which would be expected to be comparatively thinly coated. Unless otherwise specified, the points selected shall be capable of being touched by a sphere of 1 inch diameter but shall be not less than $\frac{1}{4}$ inch from an edge.

7.4 *Average thickness.* - The average thickness shall be determined by the stripping and weighing method described in Appendix IV; alternatively, the average thickness may be determined by any other method approved by the Inspecting Authority.

7.5 *Retests.* - If the thickness requirements are not satisfied, then additional parts to the extent of not less than 2 per cent in number shall be selected from the batch or consignment represented by the samples that failed, and the test repeated. If 10 per cent or more of these further samples fail to meet the thickness requirement the batch or consignment shall be rejected.

7.6 *Composition.* - Once weekly the composition of the plate shall be determined on a small percentage of the articles plated, the actual percentage being decided by the Inspecting Authority. The plate shall contain not less than 20 per cent and not more than 35 per cent of zinc when analysed as described in Appendix V.

Table 1 - Thickness requirements

	Local thickness, inch Minimum	Average thickness, inch Minimum
1. Normal requirement for steel parts	0.0003	0.0005
2. Threaded parts		
Bolts, screws, etc. of sizes :-		
(a) up to and including 0.112 inch diameter	—	0.00015
(b) greater than (a) up to and including ¼ inch diameter	—	0.0002
(c) greater than (b), up to and including ⅜ inch diameter	—	0.0003
(d) greater than (c)	—	0.0004

Approved for issue,

E. W. RUSSELL,

Director of Materials Research and Development/Aviation.

APPENDIX I

Analysis of the electrolyte

1. Tin

1.1 *Volumetric method.* - A piece of apparatus required comprises a 1,000 ml wide-necked conical flask fitted with a 3-hole bung. One hole carries a tube connected to a supply of carbon dioxide from an apparatus of Kipps type, the second a tap funnel of about 400 ml capacity. The third hole is used to insert a burette, and is closed by a glass rod when not in use. A nickel coil is also required, made from a piece of pure nickel strip about 12 in x 2 in. A new coil should be etched before use by boiling for 10 minutes in a mixture of equal parts of 1 : 1 hydrochloric acid and 20 per cent sodium chloride solution.

Heat 5 ml of the electrolyte with hydrogen peroxide to decompose cyanide, add 10 ml of concentrated sulphuric acid, and evaporate the solution to fumes of sulphur trioxide. Transfer the solution to the flask of the apparatus described above, with 200 ml of water, and add 75 ml of concentrated hydrochloric acid. Place the nickel coil in the solution, and pass a rapid current of carbon dioxide through the flask for a few minutes to expel all air. Reduce the gas flow to a slow stream, and boil the solution vigorously for 40-45 minutes. Increase the gas flow, close the tap of the funnel, and allow the flask to cool without closing the tap of the Kipps apparatus. When the flask has cooled add 2 ml of 1 per cent starch solution through the tap funnel, insert the burette and titrate with N/10 iodine to a permanent blue colour.

Millilitres of N/10 iodine x 1.19 = tin content in grammes per litre.

1.2 *Gravimetric method.* - To a 2 ml sample of the electrolyte add 5 ml of nitric acid and 5 ml of sulphuric acid, and evaporate to fumes of sulphur trioxide. Cool, add 50 ml of water, 1 ml of 15 per cent ferric nitrate solution and 25 ml of saturated ammonium chloride solution. Make alkaline with ammonia, heat to boiling to coagulate the precipitate, and filter through a rapid paper (Whatman No. 41). Wash with hot water, and dissolve the precipitate through the paper into the original beaker with 50 ml of a boiling solution of 10 per cent hydrochloric acid (by volume) containing 3 g ammonium oxalate, washing the paper thoroughly with hot water. Add 25 ml of saturated ammonium chloride solution, dilute to 200 ml, heat to boiling, and add 1 g of tannin dissolved in a little water. Nearly neutralise by adding 30-40 ml of 5 per cent ammonia (by volume) to the boiling solution (the dark colour of the iron-tannin must be avoided). Allow to settle, and filter through a rapid paper (Whatman No. 41), washing thoroughly with 2 per cent ammonium nitrate solution to remove all iron. Ignite in a silica crucible, and weigh as stannic oxide.

Grammes of stannic oxide x 394 = tin content in grammes per litre.

2. Zinc

Acidity 50 ml of the electrolyte with nitric acid, add 30 ml of sulphuric acid, and evaporate the solution to fumes of sulphur trioxide. After cooling dilute with 50 ml of water, and add 50 ml of 50 per cent citric acid and 10 ml of 15 per cent ferric nitrate solution (the ferric nitrate solution should contain a few ml of nitric acid to prevent hydrolysis). Make the solution just alkaline to litmus with ammonia (1 : 1) dilute to about 200 ml and heat to boiling point. Titrate the hot solution with standard potassium ferrocyanide solution using 50 per cent acetic acid as an external indicator, the colour change being from yellow, through green, to blue. The ferrocyanide solution, containing 20 g per litre approximately, should be standardised against a known zinc solution. From the titration the percentage of zinc in the electrolyte can be calculated.

3. Total cyanide (estimated as sodium cyanide)

To 5 ml of the electrolyte add 10 ml of 10 per cent potassium iodide solution, 3 to 5 g of sodium hydroxide and 50 ml of water. Titrate the solution with N/10 silver nitrate solution until a faint permanent turbidity is obtained.

Millilitres of N/10 silver nitrate x 2 = total cyanide as NaCN in grammes per litre.

4. Free sodium hydroxide

To a 5 ml sample of the electrolyte add twice the volume of N/10 silver nitrate solution used in the titration for total cyanide and 50 ml of 10 per cent barium chloride solution. Titrate the solution with N/10 hydrochloric acid using thymolphthalein as indicator.

Millilitres of N/10 hydrochloric acid x 0.8 = free sodium hydroxide content in grammes per litre.

5. Detection of stannite

Prepare a suspension of bismuth hydroxide by dissolving 5 g of the oxide or carbonate in 100 ml of 25 per cent (by vol.) hydrochloric acid, make just alkaline with sodium hydroxide, and dilute to 250 ml. Filter 5 ml of this suspension through a loose filter paper (9 cm), and then pour 10 ml of the hot electrolyte on to the paper. If the precipitate on the paper shows no darkening in colour, stannite is absent. Large amounts of stannite turn the precipitate black, whilst traces produce a distinct grey colour and indicate the necessity for oxidising the electrolyte.

Alternatively, the presence of stannite may be detected by using special test papers available for the purpose.

APPENDIX II Detection of mercury

1. Mercury in salts

Make up as required an alkaline stannous chloride solution by dissolving 1.2 g of stannous chloride in 20 ml of water, disregarding the precipitate formed by hydrolysis. Pour whilst stirring into 20 ml of 20 per cent sodium hydroxide solution, and continue stirring until the precipitate is dissolved. Filter before use.

Using the salts to be tested, dissolve in water 10 g of sodium cyanide, 2 g of sodium hydroxide, 10 g of sodium stannate and 1 g of zinc cyanide in the order given, and dilute to 100 ml in a Nessler cylinder. Add 2 ml of the alkaline stannous chloride, and mix. A turbidity indicates the presence of mercury, and is visible if 0.0002 g is present.

2. Mercury in electrolyte

100 ml of solution are tested with alkaline stannous chloride as described in (1).

3. Mercury in anodes

Attack 5 g of the anode with 50 ml of concentrated nitric acid. Dilute the solution with about 40 ml of water, boil to remove oxides of nitrogen, and cool. Dilute the solution further to 100 ml in a Nessler cylinder. Immerse a straight piece of bright clean copper wire in the solution for 3 inches of its length, and allow it to remain for 15 minutes. A deposit on the copper wire indicates the presence of mercury and will be seen if 0.004 per cent is present in the anode.

4. Mercury in electrodeposited coatings

Cut a piece of clean steel sheet, 4½ in x 4½ in, which has been electro-plated to produce a coating 0.0002 in thick, into 9 pieces 1½ in square, and place the pieces in a 250 ml beaker. Pour 25 ml of hot nitric acid over the specimens, completely covering them, and swirl the beaker until effervescence has ceased. Transfer the liquid to another beaker, rinse the specimens with cold distilled water, and add the rinsings to the main solution. Boil the solution to remove oxides of nitrogen, cool and dilute to 100 ml in a Nessler cylinder, and test as in (3). A deposit will be visible on the copper wire if the test solution contains 0.0002 g of mercury. This is equivalent to 0.000025 g of mercury/0.001 in thickness/sq in or 0.02 per cent mercury in the coating.

APPENDIX III Determination of local thickness of coating by B.N.F. Jet Test

1. Apparatus

The standard B.N.F. Jet Test apparatus is used.

2. Jet test solution

The solution used consists of 50 g of trichloroacetic acid per litre in distilled water. Since trichloroacetic acid is very deliquescent, the solution is made stronger than required, titrated with N/2 sodium hydroxide solution using thymol blue indicator and adjusted to the required strength. The trichloroacetic acid solution is adjusted until 25 ml require 15.3 ml of N/2 sodium hydroxide for titration.

3. Method

3.1 *Cleaning.* - Treat the parts to be tested as follows:-

- (i) degrease in hot acetone or other suitable organic solvent;
- (ii) remove the chromate film by immersion for a few seconds in a cold 5 per cent solution of acetic acid, with subsequent rinsing in distilled water;
- (iii) treat as cathode in 5 per cent sodium carbonate solution at room temperature for 15 seconds at a current density of about 25 amp per sq ft;
- (iv) rinse in distilled water;
- (v) rub for 3 minutes with a paste of light magnesium oxide in water and
- (vi) rinse in distilled water, then in alcohol (industrial methylated spirit), and allow to dry.

3.2 *Jet test.* - Carry out the test strictly in accordance with the instructions issued by the suppliers of the apparatus.

4. Calculation of thickness

The thickness of coating is calculated using the factor (seconds to penetrate 0.0001 in of coating) for the temperature of the solution at the time of testing taken from Fig. 1.

APPENDIX IV

Determination of average thickness of coating

Clean a plated part of known area, e.g. with trichlorethylene vapour, accurately weigh and then totally immerse in a solution prepared by dissolving 20 g of antimony trioxide in one litre of cold concentrated hydrochloric acid. Allow the sample to remain in the solution for a period of one minute after gas evolution has ceased, turning it so that all surfaces are exposed during solution of the coating. Then remove the sample, wash thoroughly with cold water, and wipe to remove the loose coating of antimony. Then wash it again, dry and reweigh. The difference between the weights represents the weight of tin-zinc coating, and the thickness is calculated from the formula:-

$$\text{Thickness (inch)} = \frac{\text{Loss in weight (g)}}{\text{Area (sq in)} \times 118}$$

APPENDIX V

Determination of composition of coating

To determine the composition of a deposit of average thickness 0.0005 in use an area of plated surface of 10-15 sq in.

Determine the weight of coating on the article(s) as in Appendix IV, using 50 ml of stripping solution and combining the washings with the stripping solution. Add 10 ml of nitric acid to the solution, and heat it to dissolve the antimony powder present. Add 25 ml of 50 per cent citric acid and 10 ml of 15 per cent ferric nitrate solutions, and make the solution just alkaline to litmus with 1 : 1 ammonia. Heat the solution to boiling, and determine the zinc content by titration with standard ferrocyanide solution as described in Appendix I.

$$\text{Zinc in coating, per cent} = \frac{\text{zinc determined (g)} \times 100}{\text{weight of deposit (g)}}$$

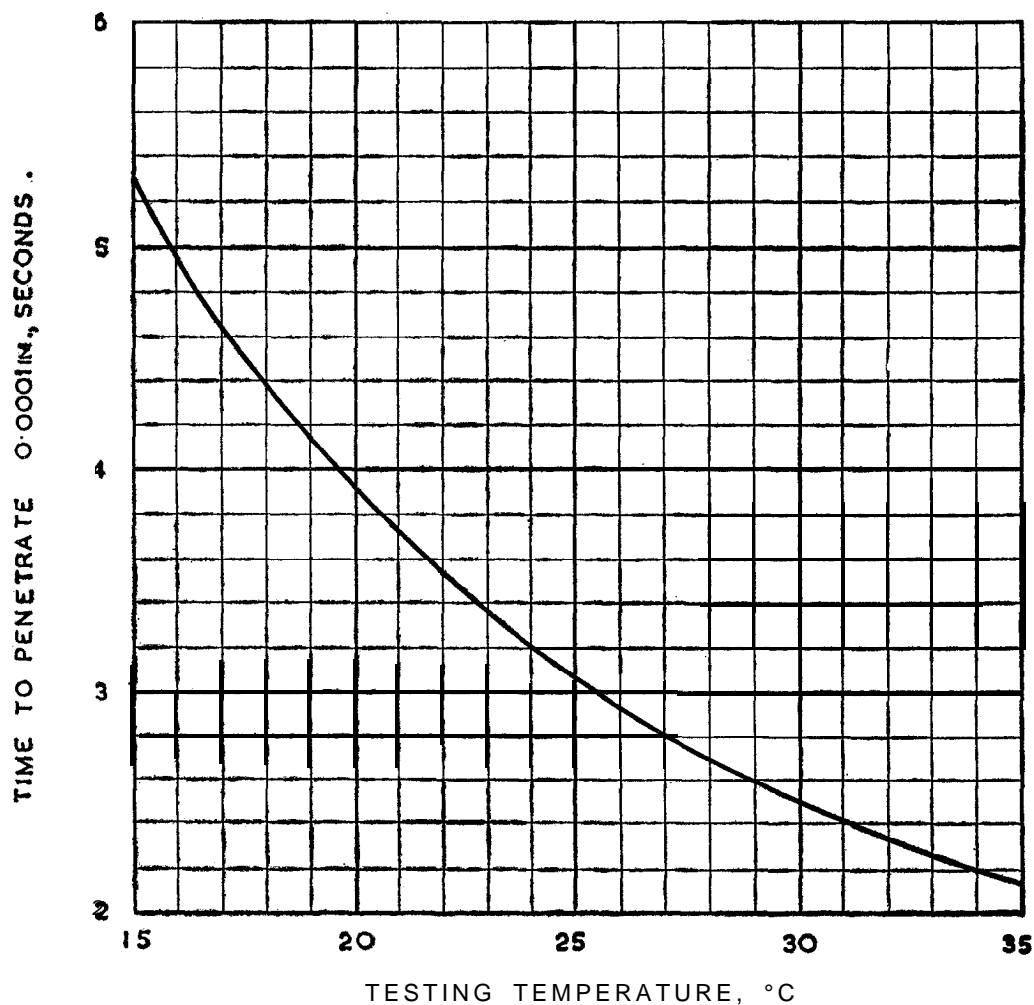


Fig.1 STANDARD CALIBRATION CURVE FOR B.N.F JET TEST.

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