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The black-anodising of aluminium with inorganic dyes

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ABSTRACT

This specification defines the processes for black anodising aluminium with cobalt sulphide and nickel sulphide inorganic dyes. The processes are suitable for use on ESA spacecraft and associated equipment where surfaces require high solar absorptance, high emittance, high optical blackness or a combination of these properties.

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1. SCOPE

This specification defines the processes for black anodising aluminium with cobalt sulphide and nickel sulphide inorganic dyes. The processes are suitable for use in ESA spacecraft and associated equipment where surfaces require high solar absorptance, high emittance, high optical blackness or a combination of these properties.

2. GENERAL

2.1 INTRODUCTION

It should be noted that the two dyes used in these processes show some differences. Cobalt sulphide is extremely stable in a space environment, but it has a higher initial reflectance in the near infrared. Nickel sulphide shows some instability in reflectance in the region above 10μm, but has a lower reflectance in the near infrared. Also parts made of wrought aluminium alloys are usually easier to treat by these processes than castings.

These treatments can also be applied to aluminium alloys normally used for coloured surfaces. In general only alloys with less than 5% copper, 6-8% zinc and 5% silicon are suitable for anodising by this method.

2.2 RELATED DOCUMENTS

Some or all of the content of the documents listed below is directly related to this specification. The applicability of these documents is defined in the contract.

ESA PSS-01-20	Quality Assurance of ESA Spacecraft and Associated Equipment
ESA PSS-01-70	Material and Process Selection and Quality Control for ESA Spacecraft and Associated Equipment
ESA PSS-01-704	A Thermal Cycling Test for the Screening of Space Materials and Processes
ESA PSS-01-706	The Particle and Ultraviolet Radiation Testing of Space Materials
ESA PSS-01-709	Measurement of Thermo-optical Properties of Thermal Control Materials

ESA PSS-01-713	Measurement of the Peel and Pull-off Strength of Coatings and Finishes with Pressure Sensitive Tapes
ESA PSS-01-716	The Listing and Approval Procedure for Materials and Processes

2.3 DEFINITIONS

The definitions listed in Annex A shall apply.

3. PREPARATORY CONDITIONS

3.1 HAZARDS/SAFETY PRECAUTIONS

The details of the type of hazard for each material used in the process is given in Table 1. Moreover, the precautions listed below should be observed.

ITEM NO.	DESCRIPTION	TYPE OF HAZARD
1	TRICHLORO-ETHYLENE	HARMFUL
2	TRISODIUM PHOSPHATE $Na_3PO_4 12H_2O$	-
3	SODIUM CARBONATE Na_2CO_3	-
4	NITRIC ACID HNO_3	CORROSIVE, OXIDISING
5	SULPHURIC ACID H_2SO_4	CORROSIVE
6	DEIONISED WATER	-
7	COBALT ACETATE (REAGENT GRADE)	-
8	AMMONIUM HYDROSULPHIDE (REAGENT GRADE)	CORROSIVE
9	NICKEL ACETATE (REAGENT GRADE)	HARMFUL
10	BORIC ACID	-

TABLE 1 - MATERIAL LIST AND HAZARDS

(a) **Harmful.** Substances may have limited effects on health and should not be inhaled, swallowed or absorbed through the skin.

(b) **Corrosive.** Substances can destroy living tissue and contact with the skin must be avoided.

(c) **Oxidising.** Substances produce highly exothermic reactions in contact with other substances, especially flammable or combustible materials. Separation from other hazardous substances and use in no-smoking zones should be observed.

(d) **Hazard Reduction.** Unavoidable hazards to personnel, equipment and materials are to be controlled and reduced to a minimum.

(e) **Location of Hazards.** Items and controls are to be so located that personnel are not exposed to hazards such as chemical burns, electric shock, cutting edges, sharp points or toxic atmospheres.

(f) **Warning Notes.** Suitable warning and caution notes are to be provided in operations, storage, transport, testing, assembly, maintenance and repair instructions and distinctive markings on hazardous items, equipment or facilities for personnel protection.

3.2 MATERIALS

Handling of the materials used in the treatment process requires protective gloves. However, finished workpieces shall only be handled as stated in paragraph 4.5. The materials should be stored in a cleanliness-controlled area, ambient temperature 20 ± 3°C and relative humidity of 55 ± 10%. Limited-life materials shall be labelled with their shelf lives and date of manufacture, or date of delivery if date of manufacture is not known.

3.3 FACILITIES

3.3.1 Cleanliness

The work area shall be clean and free of dust. Air used for ventilation shall be filtered to prevent contamination of the workpieces by moisture, oil or dust.

3.3.2 Environmental Conditions

The ambient conditions for the process and work area shall be 22 ± 3°C with a relative humidity of 55 ± 10% unless otherwise stated.

3.3.3 Special Utilities

(a) **Chemical Bath(s).** Capable of meeting the following criteria:-

i) Containing the corrosive solutions used in the processes;

ii) Accommodating the workpiece;

iii) Maintaining the solutions at the following temperatures:-

24 ± 2°C;

25 ± 2°C;

45 ± 2°C;

93 ± 2°C;

99 ± 1°C.

iv) Air agitation of the solution.

(b) **Ultrasonic Bath.** Capable of accommodating the workpiece (if used).

3.4 EQUIPMENT

(a) For acceptance tests the test equipment listed in the following test specificatons will be needed. Further test equipment may be required if additional tests are required by project etc.

ESA PSS-01-709	Thermo-optical Properties
ESA PSS-01-704	Thermal cycling
ESA PSS-01-713	Adhesion Properties
ANNEX B	Thickness Measurement

(b) Suitable measuring equipment to fulfil the monitoring requirements of the process:-

Temperature	10 - 110°C	Current	0 - 3 A
Humidity	40 - 70%	pH Value	5 - 6

4. PROCEDURE (SEE CHART 1)

4.1 PRETREATMENT

4.1.1 Before anodising, all parts shall be cleaned in the sequence given. These treatments shall immediately precede anodising.

(a) Vapour degreasing in TRICHLORO-ETHYLENE for 30 minutes.

(b) Etching is to be carried out in a solution of:-
TRISODIUM PHOSPHATE $Na_3PO_412H_2O$ 12.5 g/l
SODIUM CARBONATE Na_2CO_3 6.2 g/l
The temperature of the solution should be held at 93 ± 2°C with a part-immersion time of 5 minutes.

N.B. Other degreasing and etching systems are possible. These should be evaluated to determine their suitability before being incorporated in this process.

(c) Rinsing with water.

(d) Deoxidising for 3 minutes at room temperature in a 50 volume percent solution of nitric acid in water.

(e) Rinsing with water.

(f) Removal of all residue before anodising by scrubbing and /or ultrasonic cleaning.

(g) Rinsing in deionised or distilled water.

4.2 ANODISING

4.2.1 The anodising electrolyte shall consist of a solution of sulphuric acid, 150 g/l in deionised or distilled water. During the lifetime of the electrolyte, it must be kept within the following limits:

H_2SO_4 concentration:	120 to 180 g/l
Chloride content:	should not exceed the equivalent of 0.2 g NaCl/l
Aluminium content:	maximum 3 g/l
Fluoride content:	maximum 0.001 g/l

4.2.2 Parts shall be suspended in such a way that good electrical contact is maintained throughout the treatment. Any metallic part of a suspension device which makes contact with the electrolyte shall be of aluminium or titanium.

4.2.3 Cathode materials should be either lead or aluminium.

4.2.4 The temperature during anodising shall be kept at 25° ± 1°C. Air agitation of the electrolyte must be sufficient to keep the specimen to electrolyte difference below 0.5°C.

4.2.5 Current density shall be between 1 and 2 A/dm^2.

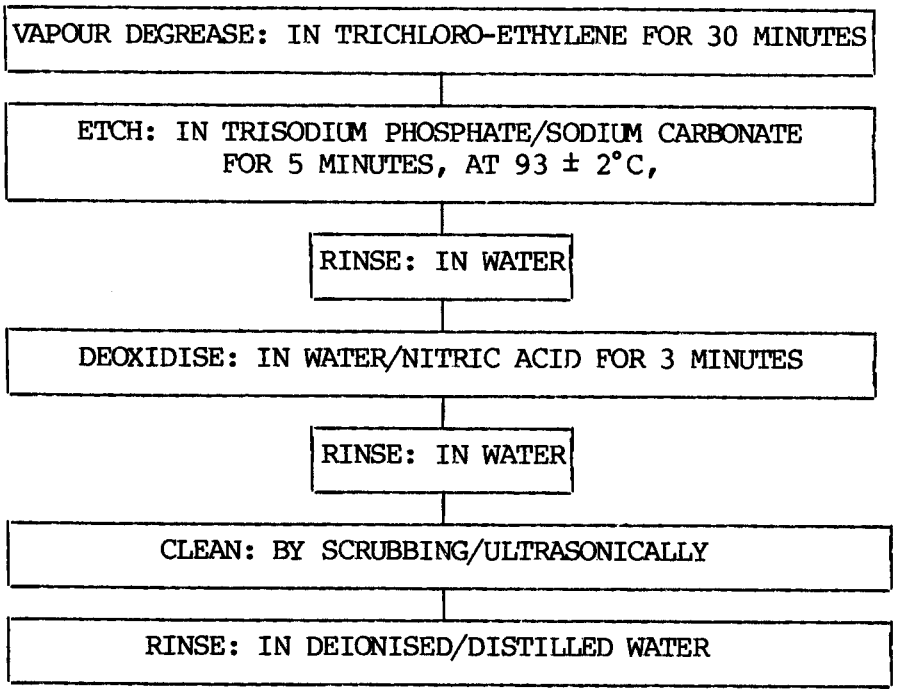
4.2.6 Anodising time must be set to give a thickness of the anodic film between 25 and 35 microns. This can be estimated from the formula:

$$\frac{\text{current density* x time min}}{3.22} = \text{thickness microns}$$

* expressed in A/dm^2

4.2.7 Immediately after removal from the bath, the parts shall be washed to remove the electrolyte, and finally rinsed with deionised water.

PRETREATMENT (SEE PARA 4.1)



PROCEDURE FLOW DIAGRAM

CHART 1

ANODISING (SEE PARA 4.2)

IMMERSE IN ELECTROLYTE, AT 25 ± 1°C, ADJUST CURRENT, SET TIME TO GIVE THICKNESS OF 25 - 35 µm, SEE PARA 4.2.4 - 4.2.6 INC.

RINSE: IN DEIONISED WATER, SEE PARA 4.2.7

DYEING PROCESS (SEE CHART 2)

PROCESS MUST COMMENCE WITHIN 1 HOUR OF ANODISING: SEE PARA 4.2.8

COBALT SULPHIDE **NICKEL SULPHIDE**

ACCEPTANCE TESTING

PROCEDURE FLOW DIAGRAM

CHART 1 (CONT'D)

4.2.8 There should normally be minimum delay between the rinsing and dyeing operations, to avoid lowering the absorptive capacity of the film. However, dyeing can be delayed up to a maximum of 1 hour, if the anodised parts are kept in cold deionised water.

4.3 COBALT SULPHIDE BLACK DYEING PROCESS (SEE CHART 2)

4.3.1 The two bath solutions shall consists of:

(a) A solution in deionised water of 200 g per litre reagent-grade cobalt acetate;

(b) A solution in deionised water of 30 g per litre reagent-grade ammonium hydrosulphide.

4.3.2 The wet parts shall be immersed in the cobalt acetate solution maintained at 45 ± 2°C for 15 minutes. They shall then be rinsed with deionised water to remove excess of cobalt acetate solution and immersed in the ammonium hydrosulphide solution maintained at 24 ± 2°C until deep black coloration is attained. This will take between 5 and 15 minutes.

4.3.3 The parts shall be sealed by immersion in a solution of 5 g/l nickel acetate and 5 g/l boric acid at a temperature of 98 to 100°C. The pH of the solution shall be maintained at 5.5 to 5.8 for 25 minutes.

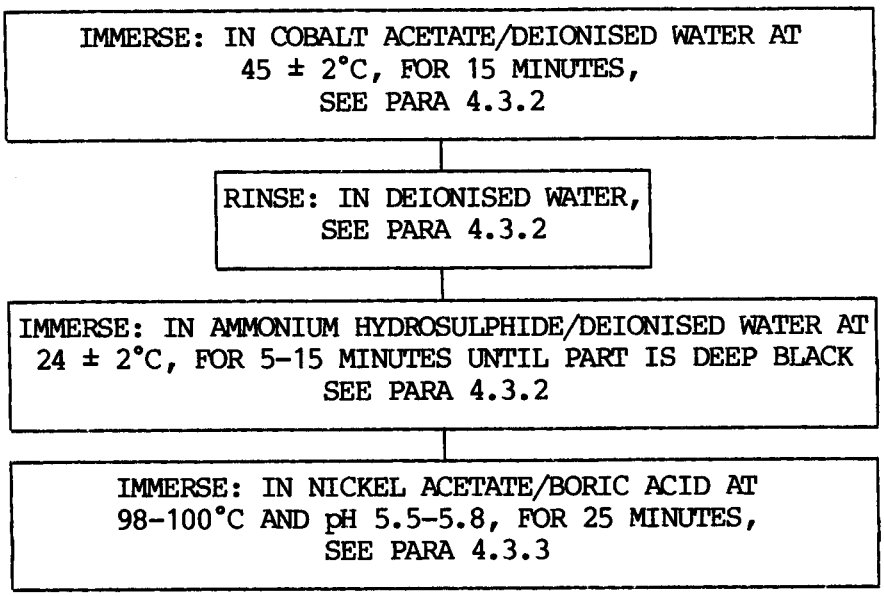
4.4 NICKEL SULPHIDE BLACK DYEING PROCESS (SEE CHART 2)

4.4.1 The two bath solutions shall consist of:

(a) A solution in deionised water of 50 g per litre reagent-grade nickel acetate;

(b) Ammonium hydrosulphide 25%.

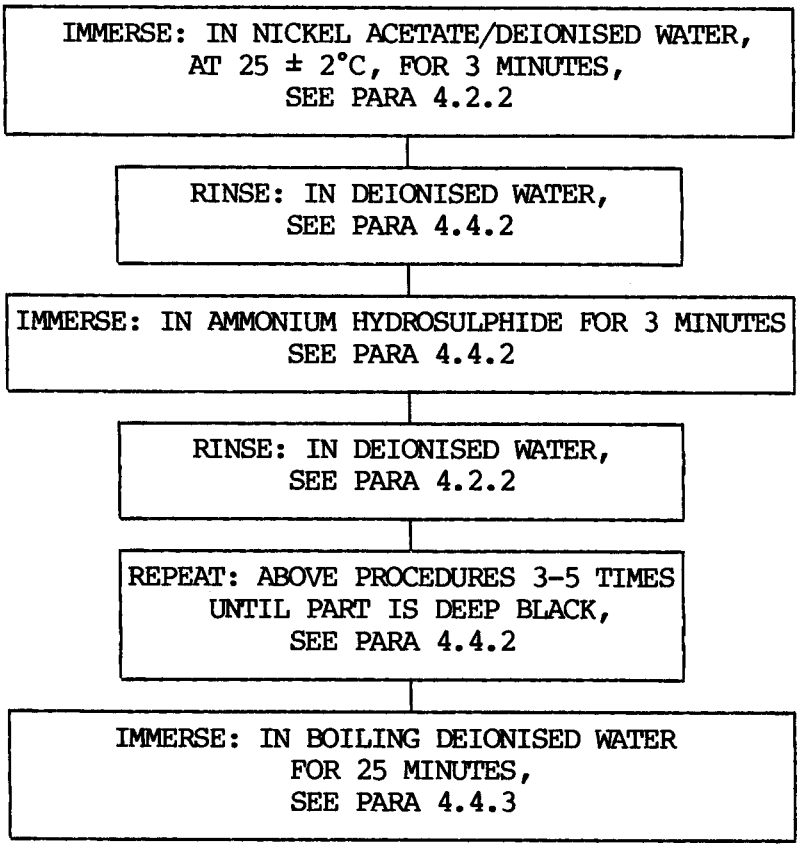
COBALT SULPHIDE (SEE PARA 4.3)



FLOW DIAGRAM OF DYEING PROCESSES

CHART 2

NICKEL SULPHIDE (SEE PARA 4.4)



FLOW DIAGRAM OF DYEING PROCESSES

CHART 2 (CONT'D)

4.4.2 The wet parts shall be immersed in the nickel acetate solution maintained at 25 ± 2°C for 3 minutes. They shall then be rinsed with deionised water to remove excess of nickel acetate solution and immersed in ammonium hydrosulphide for 3 minutes and rinsed.

The above procedure shall be repeated until the parts are deep black. This takes normally 3 to 5 alternate dips.

4.4.3 The parts shall be sealed by immersion in boiling deionised water for 25 minutes.

4.5 HANDLING

Coated parts shall only be handled with clean nylon or lint-free gloves. The parts are to be stored in such a way as to prevent any damage or contamination by dust, moisture or grease. Coated surfaces shall be shielded from contact by using polyethylene or polypropylene bags or sheets. Mechanical damage shall be avoided by packing the polyethylene- or polypropylene-wrapped workpieces in clean, dust- and lint-free material.

5. ACCEPTANCE CRITERIA

Every bath shall be subjected to acceptance tests as listed below, and any other tests that are appropriate to mission/project requirements. Test pieces shall be prepared at the same time as the workpieces to enable destructive and other tests to be performed.

(a) **Thermo-optical Properties** to be measured according to ESA PSS-01-709. Solar absorptance (α_S) of the parts shall be at least 0.93. Normal emittance (ε_N) of the parts shall be at least 0.90.

(b) **Adhesion Properties** to be measured according to ESA PSS-01-713. There shall be no signs of anodising lifting from substrate.

(c) **Thermal Cycling.** 100 cycles in a vacuum of 10^{-5} torr from -100 to +100°C according to ESA PSS-01-704 without any loss of adhesion (See para. 5(b)).

(d) **Thickness** , to be measured in accordance with Annex B, shall not be less than 20 µm.

(e) **Additional Acceptance Tests.** Depending on the particular project or mission requirements, any of the following tests may be invoked in order to evaluate the finish of the workpiece or test piece:

- Vibration
- Radiation
- Cleaning
- Outgassing
- Humidity
- Thermal Shock
- Salt Spray
- etc.

Tests detailed in ESA PSS-01-700 Series specifications should be used whenever possible in preference to those of other documents.

6. QUALITY ASSURANCE

The quality assurance requirements are defined in ESA PSS-01-20. However, particular attention should be given to the following points:-

6.1 DATA

The logbooks shall contain, as a minimum, the following:-

(a) copy of final inspection documentation;

(b) index of limited-life articles and their use times;

(c) nonconformance reports and corrective actions;

(d) copy of the inspection and test results with reference to the relevant procedure;

(e) an event log which is a chronological history of process operations, inspection and tests;

(f) details of failure mode (if applicable).

6.2 NONCONFORMANCE

Any nonconformance which is observed in respect of the process shall be dispositioned in accordance with quality assurance requirements.

6.3 CALIBRATION

Each standard and piece of measuring equipment shall be calibrated. Any suspected or actual equipment failure must be notified to ESA so that previous results may be examined to ascertain whether or not re-inspection/re-testing is needed.

6.4 TRACEABILITY

Traceability shall be maintained throughout the process from incoming inspection to final test, including details of test equipment serial numbers and personnel employed in performing the task.

ANNEX A

DEFINITIONS

ANODISING
Placing a protective film/coating on a metal surface by electrolytic or chemical action.

HAZARD
Any real or potential condition that can cause injury or death to personnel or damage to or loss of equipment or property.

NONCONFORMANCE
An apparent or proven condition of any item or documentation that does not conform to specified requirements or which could lead to incorrect operation or performance of the item or mission.
The term nonconformance is also used for failure, discrepancy, defect, anomaly, malfunction, deficiency, etc.

NORMAL EMITTANCE (ε_N)
Refers to the emissivity normal to the surface of the emitting body.

SOLAR ABSORPTANCE (α_S)
The relationship between the absorptance of a test item irradiated with a solar simulator to the absorptance the test item would experience from the sun.

TRACEABILITY
The ability to trace the history, application, use and location of an item through the use of recorded identification numbers.

ANNEX B

THICKNESS MEASUREMENT

B.1. ANODIC FILM THICKNESS BY EDDY-CURRENT METHOD

B.1.1 INTRODUCTION

i) The procedure detailed below is based on ASTM document D1400-67, Method 'C' and utilises a non-destructive eddy-current technique to measure the dry film thickness of organic/non-metallic coatings (i.e. paint and similar products) applied on a non-magnetic base.

ii) Thickness of an organic coating is determined by means of an electromagnetic instrument designed to measure changes in the apparent impedance of a probe coil that produces eddy currents in the base metal. The construction of the instrument is such that changes in the current flow in the coil, as produced by various spacings of it from the base metal, are calibrated to indicate the thickness of the organic coating interposed between the probe coil and the metal base. In order to ensure high accuracy, the equipment manufacturer's instructions should be closely followed.

B.1.2 TEST APPARATUS

(a) Various instruments of the eddy-current type are satisfactory, but their accuracy is dependent upon the flatness and thickness of the base metal of the specimen and the nearness of the probe to the edge.
With some instruments it is possible to measure thickness on curved surfaces with certain probes and holding jigs.

ANNEX B (CONT'D)

(b) Typical instruments mentioned in the ASTM document are listed below:
- Boonton, Film Gauge Type 255A
- Dermitron, (with Probe 'D')
- Elcotector, Non-ferrous Thickness Gauge
- Permascope, Type, ECT.

B.1.3 TEST PROCEDURE

Test Procedure shall be in accordance with the instrument maker's instructions. Before measurement, however, the instrument shall be calibrated (at the frequency specified by the manufacturer) as follows:

First, the zero reading is adjusted with a piece of bare metal of the same kind, temper and thickness as the specimen to be measured or upon the bare side of the specimen. Then the probe or search unit is placed on a standard finished panel or on a plastic film of known thickness which is laid on the surface of the bare piece. Finally, depending upon the particular make of the instrument, either a calibration curve is constructed or the instrument dial is adjusted to the known thickness of the calibration standard.

B.1.4 ACCEPTANCE CRITERIA

In order to obtain a 95% confidence level the following constraints shall be observed:

Repeatability — Duplicate results by a single operator using one instrument should be considered suspect if they differ by more than 0.15 mils (0.0038 mm).

ANNEX B (CONT'D)

Reproducibility	Results obtained with eddy-current instruments by operators in different laboratories should be considered suspect if they differ by more than 0.35 mils (0.0089 mm).

NOTE: Practicable 'standard deviations' normally obtained for the measurements are:

- Within one laboratory: 0.055 mils (0.0014 mm)
- Between laboratories : 0.11 mils (0.0028 mm)

Where possible, film measurements shall be made only with a clean, polymer sheet between the probe and the anodised surface.