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Magnesium Alloys, Anodic Treatment of

RATIONALE

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1. SCOPE:

1.1 Scope:

This specification covers the requirements for equipment, materials and procedures to be used in anodic treatments for magnesium base alloys for the purpose of increasing their corrosion resistance or producing surfaces suitable for the application of a protective organic finish.

1.2 Classification:

The types, classes, and grades of anodic finishes covered by this specification are as follows:

Type I - Light coating.

Class A - Tan coating (HAE).

Grade 1 - Without post treatment (dyed).

Grade 2 - With bifluoride-dichromate post treatment.

Class C - Light green coating (Dow 17).

Type II - Heavy coating.

Class A - Hard brown coating (HAE).

Grade 1 - Without post treatment.

Grade 3 - With bifluoride-dichromate post treatment.

Grade 4 - With bifluoride-dichromate post treatment including moist heat aging.

Grade 5 - With double application of bifluoride-dichromate post treatment including moist heat aging.

Class D - Dark green coating (Dow 17).

2. APPLICABLE DOCUMENTS:

The following publications, of the issue in effect on date of invitation for bids or request for proposal, form a part of this specification to the extent specified herein.

2.1 U.S. Government Publications:

Available from DODSSP, Subscription Services Desk, Building 4D, 700 Robbins Avenue, Philadelphia, PA 19111-5094.

QQ-A-250/8 Aluminum Alloy, 5052, Plate and Sheet

MIL-M-3171 Magnesium Alloy, Processes for Pretreatment and Prevention of Corrosion on

MIL-STD-105 Sampling Procedures and Tables for Inspection by Attributes

MIL-STD-649 Aluminum and Magnesium Products Preparation for Shipment and Storage

MIL-HDBK-132 Protective Finishes

2.2 ASTM Publications:

Available from ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959.

ASTM B 244 Measurement of Thickness of Anodic Coatings on Aluminum and Other Non-conductive Coatings on Nonmagnetic Basis Metals with Eddy-Current Instruments

ASTM B 487 Measurement of Metal and Oxide Coating Thicknesses by Microscopical Examination of a Cross Section

3. REQUIREMENTS:

3.1 Materials:

3.1.1 Preparation of parts: All parts shall be free from broken edges before anodizing and unless otherwise specified, shall have all machining, drilling or other metal removal done prior to anodizing.

3.1.2 Cleaning and treatment materials: All materials used in cleaning and treating magnesium base alloys shall be free from salts of heavy metals and suitable for the purpose intended.

3.2 Equipment:

3.2.1 Materials of construction: All tanks and all pipes, valves, pumps, and other items of equipment which come in contact with the processing bath shall comply with table I, with respect to material construction.

3.2.2 Processing tanks:

3.2.2.1 Dimensions: The effective dimensions of tanks shall allow a minimum distance of two inches (51 millimeters) between the sides (including cooling coils) of the tank and the articles being treated, making due allowance for any position in which the work must be suspended.

TABLE I. Materials for construction of equipment

Classification	Recommended	To be avoided
Type I, class A and type II class A (HAE)		
Anodize tank	Black iron	Galvanized iron, brass,
Valves	Black iron or copper	bronze, tin, zinc,
Bifluoride-dichromate tank	Tank lined with polyethylene or similar inert material	rubber, all oxidizable materials
Racks and clamps	Magnesium or magnesium alloy	
Bus bars	Copper	
Type I, class C and type II class D (Dow 17)		
Tank	Unlined steel tanks or tanks lined with synthetic rubber or vinyl base materials	Copper, nickel, lead chromium, zinc, aluminum, monel
Racks and clamps	Magnesium, magnesium alloys or 5052 and 5056 aluminum alloys	

- 3.2.2.2 Heating and cooling equipment: Tanks shall be equipped, when required, with adequate facilities for heating or cooling in order to maintain the contents within the temperature limits specified for the type of coating being applied. This may be accomplished by pumping the electrolyte through an external heat exchanger or by means of coils or plates suitably located within the tank, through which cold water, steam, refrigerant or any suitable heating or cooling medium may be passed.
- 3.2.2.3 Lubrication of moving parts: Grease and other lubricants shall not be used in valves, pumps or other moving parts which are in contact with the bath since they may contaminate or chemically reduce the electrolyte.
- 3.2.3 Racks and clamps: Racks and clamps for holding magnesium articles during anodizing shall be made of materials recommended in table I. They shall be protected at the liquid-air interface with vinyl type electroplater's tape which resists the action of the electrolyte.
- 3.2.3.1 Stripping racks: The coating which forms on the magnesium racks during anodizing may be removed with a 20 percent chromic acid solution. However, the anodic coating need not be thus removed after each use provided that the points of contact are filed to provide sufficient contact area. There is usually no necessity for cleaning aluminum contacts.

3.3 Preparation for anodizing:

3.3.1 Cleaning: Cleaning prior to anodizing shall be accomplished by an alkaline cleaning solution as specified in 3.3.1.2. Before alkaline cleaning, excessive amounts of grease or oil shall be removed by a solvent method described in 3.3.1.1.

3.3.1.1 Solvent cleaning: Solvent cleaning may be accomplished by soaking, spraying, vapor degreasing, or ultrasonic cleaning, using organic solvents or an emulsion consisting of a mineral oil distillate, water, and an emulsifying agent. Petroleum spirits, naphtha, chlorinated hydrocarbons, lacquer thinners and similar grease solvents, which do not attack magnesium, may be used. Methyl (wood) alcohol should not be used in cleaning formulations.

3.3.1.2 Alkaline cleaning: Alkaline cleaning shall be accomplished by soaking, preferably accompanied by some form of agitation, in an alkaline cleaner recommended for steel or in a cleaning solution which has a pH above 8. The cleaning solution may be a proprietary type, in which case the operation shall be performed according to the vendor's instructions. A cleaner of the following formulation may be used under the indicated operating conditions.

Solution Make-up

	oz/gal	g/L
Sodium hydroxide	2-8 oz	15-60 g
Sodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$)	1.3 oz	10 g
Soluble soap or wetting agent	0.1 oz	0.8 g
Water to make	1 gal	1 L

Operating conditions

Tank construction	Steel
Temperature	190-212 F (88-100 C)
Time	3 to 10 minutes

NOTE: Alkaline cleaners containing more than 2 percent caustic (sodium hydroxide) will etch ZK60A, ZK60B, and some magnesium-lithium alloys with resultant change in dimensions.

3.3.1.2.1 Cathodic cleaning: If available, direct current (dc) may be used with the alkaline cleaning solution to reduce the time required for cleaning. The parts are made cathodic in the bath and a current density of 10 to 40 amperes per square foot A/ft^2 at 6 volts is applied (current density in amperes per square decimeter is 1.1 to 4.3 A/dm^2).

3.3.1.2.2 Rinsing: After alkaline cleaning, the parts shall be given a thorough rinse in cold running water.

3.3.2 Acid pickling:

- 3.3.2.1 Type I, class A and type II, class A anodizing: Acid pickling is not required for these coatings. Acid pickling is recommended for type I, class A, where maximum corrosion resistance is required.
- 3.3.2.2 Type I, class C: The magnesium base alloy shall be pickled using the appropriate procedure as described in MIL-M-3171.
- 3.3.2.3 Type II, class D: The magnesium base alloy shall be pickled when necessary using the appropriate procedure as described in MIL-M-3171.
- 3.4 Anodizing procedures:
- 3.4.1 Process conditions: The composition of processing baths and the operating conditions shall be as stated in tables II to III, inclusive.

TABLE II. Process conditions for type I, class A and type II, class A anodizing (HAE).

Cleaning (see 3.3.1)		
Bath composition	Solution make-up	
	oz/gal	g/L
Potassium hydroxide	22 oz	165 g
Aluminum hydroxide (see 3.5.1)	4.5 oz	34 g
Potassium fluoride, anhydrous	4.5 oz	34 g
Trisodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$)	4.5 oz	34 g
Potassium manganate (or permanganate, see 7.1)	2.5 oz	19 g
Water to make	1 gal	1 L
For preparation and replenishment of bath, see para. 3.5.1		
Anodizing conditions	Type I, class A	Type II, class A
Temperature	Room temp.	Room temp. (cooling required)
Current density	18-20 A/ft ²	18-25 A/ft ²
Voltage	0-60 ac	0-85 ac
Time (approx)	8 min.	60 min.
Tank	See table I	

TABLE II A. Operating data for type 1, class A post treatments.

Solution	<u>Grade 1</u>	<u>Grade 2</u>
	No post treatment; dye this coating as indicated below.	Bifluoride-dichromate solution
		oz/gal g/L Ammonium bi 10.8 oz 81 g fluoride (NH₄HF₂)
		Sodium dichro 2.7 oz 20 g mate (Na₂Cr₂O₇·2H₂O)
Conditions -		
Temperature	----	Room temperature
Time	----	1 Minute
Rinse	After tan coating is applied, rinse thoroughly in cold then hot water	No rinse
Dye solutions	Sandoz Aluminum Black 3 B or equal	
Strength	1.3 to 1.6 oz/gal (10 to 12 g/L)	
Temperature	150 F (66 C)	
Time	5 Minutes	
Sealing	Rohm and Haas Acryloid B66 or equal ^{1/}	

^{1/}When specified, the dyed coating shall be sprayed lightly with an acrylic ester resin lacquer in order to seal the pores.

TABLE II B. Operating data for type II, class A, post-treatment

	Grade 1	Grade 3	Grade 4	Grade 5 ^{1/}
Solution	No post treatment	Bifluoride-dichromate solution 10.8 oz/gal (8 g/L) ammonium bifluoride (NH ₄ HF ₂) 2.7 oz/gal (20 g/L) Sodium dichromate (Na ₂ Cr ₂ O ₇ ·2H ₂ O)	Same as grade 3	Same as grade 3
Condition				
Temp.	---	Room Temperature	Same as grade 3	Same as grade 3
Time	---	1 Minute	"	"
Rinse	---	No Rinse	"	"
Aging conditions				
Temp.	---	---	Approx. 185 F (85 C)	Approx. 185 F (85 C)
rh ^{2/}	---	---	85 ± 5% rh	85 ± 5% rh
Time	---	---	6 hrs to overnight	3 to 4 hrs

^{1/} Repeat entire post-treatment including aging.

^{2/} Relative humidity (rh) - Moisture condensation on parts shall be avoided.