



# Standard Practices for Preparation of Magnesium Alloy Surfaces for Painting<sup>1</sup>

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*This standard has been approved for use by agencies of the U.S. Department of Defense.*

## 1. Scope

1.1 These practices cover two classes of treatment for preparation of magnesium alloy surfaces for painting, as follows:

*Class I—Chemical Treatments.*

*Class II—Anodic Treatments.*

In general, the latter treatments are the more protective of the two classes. Mechanical (abrasive) treatments, solvent cleaning, alkaline solution treatments, and acid pickles not resulting in protective conversion coatings are suitable preliminary treatments only for metal to be exposed under mildly corrosive (indoor) exposures. When a high degree of corrosion protection and paint adhesion are desired, as in many outdoor environments, surface preparation by one of the above conversion-coat classes is necessary. The hexavalent chromium based methods given are not recommended as hexavalent chromium is a known carcinogen.

NOTE 1—*Testing of Coatings*—Quality control tests of coatings are frequently desirable, and these generally consist of exposures, with or without paint, to salt spray, humidity, or natural environments, with suitable procedures for assessing the degree of breakdown suffered after fixed time intervals. It is recommended that quality control tests of coatings shall be made as far as possible with high-purity material (for example AZ31A alloy),<sup>2</sup> the inherent corrosion rate of which is relatively consistent from batch to batch) and that precautions shall be taken to remove surface contamination before coatings are applied. Such contamination shall be removed by acid pickling to a depth of at least 0.001 in. (25  $\mu$ m) per side.

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to*

*establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. (See Note 11.)*

## PRELIMINARY TREATMENT OF SURFACES

### 2. Procedure

2.1 Certain anodic treatments simultaneously produce conversion coatings on, and remove contamination from, magnesium alloy surfaces. In general, however, apply conversion coatings only to surfaces previously freed from all contamination, including oxide, rolling-scale, corrosion product, burned-on drawing and forming lubricant, and the contamination introduced by blast cleaning and fabrication operations. Contamination in or under surface conversion coatings seriously reduces their protective values (Note 2). For the removal of tenacious surface contamination, such as rolling-scale or casting skin, an acid pickle to dissolve some of the actual surface is essential. When organic contamination, such as grease or oil, is also present, an initial degreasing operation in solvent or in an alkaline degreasing solution is usually necessary to allow the subsequent acid to wet the surface. These matters are discussed in more detail under the headings of the specific cleaners or treatments (Note 3), as follows:

2.2 *Alkaline Cleaners*—Oil, grease, and old (but not baked) chrome-pickle coatings are readily removed by most commercially available heavy-duty alkaline cleaners; but such cleaners are not suitable for removing oxide and the like, for which purpose use acid pickles, preceded by alkaline cleaners. Remove graphite lubricant and also baked chrome-pickle coatings by a solution conforming to the following composition:

Caustic soda (NaOH)	12 oz (90 g)
Wetting agent	0.1 oz (0.74 g)
Water (Note 4)	1 gal (1 litre)

Soak the parts in the above cleaner for 10 to 20 min at boiling-point, and a treatment shall follow either in the chromic acid-nitrate pickle described under 2.3.3 or, for parts machined to fine tolerances, in the chromium trioxide solution described under 2.3.1. After alkaline cleaning, rinse in water very thoroughly. Alkaline cleaners may be held in plain steel tanks.

<sup>1</sup> These practices are under the jurisdiction of ASTM Committee B08 on Metallic and Inorganic Coatings and is the direct responsibility of Subcommittee B08.07 on Conversion Coatings.

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<sup>2</sup> For information concerning magnesium and aluminum alloys, see ASTM Specification B80, B90, B91, B93, B107, and B209 covering these alloys, in the section on Aluminum and Magnesium and Their Alloys, *Annual Book of ASTM Standards*, Vol 02.02. See also ASTM Practice B275, for Codification of Certain Nonferrous Metals and Alloys, Cast and Wrought.

2.3 *Acid Cleaners (Note 1)*—Acid picking removes mill-scale, oxide, corrosion product, and the like. Use as a preliminary treatment for surface conversion coatings when the highest degrees of surface uniformity and protective values are required. Acid cleaners are as follows:

2.3.1 *For Sand and Permanent Mold Castings:*

2.3.1.1 *Nitric-Sulfuric Acid Solution*—Use a solution of 8 volume % of concentrated nitric acid (HNO<sub>3</sub>) plus 2 volume % of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) in water (see **Note 1(a)**) at 70 to 90°F (21 to 32°C) as a preliminary treatment for new sand castings and to remove the surface-contaminating effects of blast cleaning. Immerse for about 10 to 15 s, or until 0.002 in. (51 μm) per surface is removed. The solution may be held in ceramic, rubber, synthetic rubber, or vinyl-lined tanks.

2.3.1.2 *Chromic Acid Solution*—Use a boiling 20 weight % solution of chromic anhydride (CrO<sub>3</sub>) in water to remove old chemical and anodic treatments, corrosion product, and oxide layers, without significant dissolution of metal and hence without changing the dimensions of machined parts. Immersion time varies from 1 to 5 min, depending upon the condition of the surface. The solution may be held in lead-lined steel or ASTM alloy No. 990A or its Aluminum Association equivalent, alloy No. 1100 aluminum tanks.

2.3.2 *For Die Castings:*

2.3.2.1 *Chromium Trioxide-Nitric-Hydrofluoric Acid Solution*—This solution is used to produce a smut-free surface on die castings, without violent attack of the metal. The solution shall conform to the following composition:

Chromium trioxide (CrO <sub>3</sub> )	37.5 oz (280 g)
Hydrofluoric acid (60% HF)	1 fl oz (8 ml)
Nitric acid (70% HNO <sub>3</sub> )	3.25 fl oz (25 ml)
Water ( <b>Note 4</b> )	to 1 gal (1 litre)

Immerse the parts in the above solution at 70 to 90°F (21 to 32°C) for 30 s to 2 min, or until a bright, clean surface is obtained. The solution may be held in tanks lined with synthetic rubber or vinyl-base materials.

2.3.3 *For Wrought Products:*

2.3.3.1 *Acetic Acid-Nitrate Solution*—This solution rapidly removes surface contamination to 0.001 in. (25.4 μm). Use for wrought parts subsequently to be finished for the maximum protective value. The solution shall conform to the following composition:

Glacial acetic acid	25.5 fl oz (199 ml)
Sodium (NaNO <sub>3</sub> )	6.6 oz (49.5 g)
Water ( <b>Note 4</b> )	to 1 gal (1 litre)

Immerse the parts in the above solution at 70 to 90°F (21 to 32°C) for 30 s upwards, or until a bright, clean surface is obtained. When heavy surface contamination, such as hot-rolled mill-scale is to be removed, immersion times shall be sufficient to remove at least 0.001 in. (25 μm) per surface. The solution may be held in No. 990A aluminum, ceramic, or rubber-lined tanks.

2.3.3.2 *Chromium Trioxide-Nitrate Solution*—Use this solution following the use of the method described in 2.2 for the removal of burned-on graphite lubricants from hot-formed parts. The solution shall conform to the following composition:

Chromium trioxide (CrO <sub>3</sub> )	1.5 lb (180 g)
Sodium nitrate (NaNO <sub>3</sub> )	2 oz (15 g)
Water ( <b>Note 4</b> )	to 1 gal (1 litre)

Immerse the parts in the above solution at 70 to 90°F (21 to 32°C) for approximately 5 min, for the removal of graphite.

2.4 Abnormally slow reaction in the above solution indicates that it is depleted and that the pH has risen to 1.7 or higher. Revivify the solution by the addition of chromium trioxide to bring the pH back to 0.5 to 0.7. Attempt no more than four revivifications. The solution may be held in ceramic, No. 990A aluminum, 18-8 stainless steel, or synthetic rubber-lined tanks.

**NOTE 2—Removal of Contamination by Welding Fluxes**—When a part to be painted has been welded by an operation involving the use of flux, such flux shall be removed before the subsection of the part to any surface preparation process. Such removal shall be made immediately by immersing the part in hot water with scrubbing, and finally by immersing it for 1 h in a boiling 5 % solution of sodium dichromate, after which the part shall be well rinsed.

**NOTE 3—Suspension of Articles for Treatment**—The use of magnesium alloy suspension wires is preferred for use in acid pickles in order to avoid objectionable contamination of the solutions through dissolution of the wire materials. Heavy metal contamination, particularly of copper, may deposit on the magnesium surface and lead to seriously reduced corrosion resistance. Copper suspension wires in the hot dichromate solutions are not objectionable.

**NOTE 4—Quality of Water**—In the preparation and makeup of acid pickles, dichromate solutions, and hot-water rinses, precautions shall be taken against the use of water contaminated with heavy-metal impurities, or excessive chlorides or sulfates. No upper limits can be specified at this stage for soluble impurities in the water, but powdering of coatings and poor resistance to corrosion are known to result from the use of contaminated water. Thus, when a choice exists, water from steam condensate or ion-exchange-treated water shall be employed in preference to well water or hard tap water.

## SURFACE PREPARATION PROCEDURES— CHEMICAL

### 3. Class I, Type I (Chrome Pickle)<sup>3</sup>

3.1 *Scope*—Class I, Type I treatment is applicable to all forms and alloys of magnesium except certain special alloys containing silver, but since it may remove as much as 0.0006 in. (15 μm) of metal per surface, it shall not be used on parts machined to fine tolerances. When properly applied, the process constitutes a good paint base, but rigid control is required at each step. The treatment is applicable to magnesium alloy containing inserts of, or attached to, other metals.

3.2 *Procedure*—For wrought parts the bath shall conform to the following composition:

Sodium dichromate (Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O)	1.5 lb (180 g)
Nitric acid (HNO <sub>3</sub> ) (sp gr 1.42)	1.5 pt (187 ml)
Water ( <b>Note 4</b> )	to 1 gal (1 litre)

3.2.1 For die-, sand- and permanent-mold castings the solution shall conform to the following composition:

Sodium dichromate (Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O)	1.5 lb (180 g)
Nitric acid (HNO <sub>3</sub> ) (sp gr 1.42)	1.5 pt (187 ml)
Sodium potassium, or ammonium acid fluoride (NaHF <sub>2</sub> , KHF <sub>3</sub> , or NH <sub>4</sub> HF <sub>2</sub> )	2 oz (15 g)
Water ( <b>Note 4</b> )	to 1 gal (1.0 litres)

For wrought products, sand, and permanent-mold castings the above solutions operate at 70 to 90°F (21 to 32°C). The

<sup>3</sup> Conforming to Class I, Type I treatments are the Dow No. 1 process, the AMC "A" process, and the Type I process of Military Specification MIL-M-3171A.

immersion times shall be from 1 to 2 min, the necessary time increasing with use of the solution. For die-castings give the parts a 15 to 30 s dip in water at 160 to 180°F (71 to 82°C), followed immediately by a 10-s dip in the second of the above baths, operated at 120 to 140°F (49 to 60°C). Failure to preheat the castings results in no coating in 10 s.

3.2.2 Following immersion remove the parts, allow to drain for not less than 5 s nor more than 30 s, then wash thoroughly in cold running water, followed by a dip in hot water at 160 to 180°F (71 to 82°C) to facilitate drying. Do not allow the parts to drain following the chromate treatment for more than the specified 30 s; excessive drainage times result in powdery coatings of poor value as paint bases. Such coatings also result from the use of hot-water rinses, the temperatures of which are in excess of 180°F (82°C). Paint the parts preferably immediately after they are dry. The solution may be held in Type 316 stainless steel, or ceramic tanks or in steel tanks lined with synthetic rubber or vinyl-base materials. Tanks of ASTM alloy No. 990 A, or its Aluminum Association equivalent, Alloy No. 1100 aluminum are satisfactory for the nonfluoride-containing pickle.

3.3 *Revivification of Solutions*—Sluggish reaction with the metal, associated with pale yellow, lustrous coatings, indicates that the solution is depleted. Revivification is accomplished by the addition of dichromate and nitric acid, to raise the dichromate again to 1.5 lb (180 g)/gal (1 litre) and the free nitric acid to levels indicated in the table below. Revivify when the free nitric acid content of the solution is depleted to 0.5 pt/gal (62.3 ml/litre) (see Section 11 for analytical procedure) and shall take place once only for M1 and ZK60A alloys,<sup>3</sup> and not more than six times for other alloys if good paint-base properties are desired. Excessive use of the solution or too many revivifications result in smooth, lustrous coatings not possessing the degree of etch necessary for the best paint adhesion with conventional primers. Revivify in accordance with the following table:

Revivification Number	Adjust Concentration of HNO <sub>3</sub> to:
1	1.3 pt/gal (162 ml/litre)
2	1.1 pt/gal (137 ml/litre)
3 to 6	0.9 pt/gal (113 ml/litre)

#### 4. Class I, Type II (Sealed Chrome Pickle)<sup>4</sup>

4.1 *Scope*—Class I, Type II treatment is applicable to all types and forms of magnesium-base alloys, subject only to the limitations of the Class I, Type I treatment, since it is essentially the same process as the latter, followed by sealing. In protective qualities and as a paint base, this treatment is somewhat superior to that of Class I, Type I treatment under severe exposure conditions (Note 5).

4.2 *Procedure*—Following chrome pickling as specified under Section 3 and rinsing in cold water, transfer the parts immediately to a boiling solution conforming to the following composition:

Sodium dichromate (Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O)	1.5 lb (180 g)
Calcium or magnesium fluoride (CaF <sub>2</sub> or MgF <sub>2</sub> )	½ oz (2.5 g)
Water (Note 4)	to 1 gal (1.0 litre)

Boil the parts in the above solution for 30 min, after which rinse them in cold running water, followed by a rinse in hot water at a temperature of not less than 160°F (71°C) nor more than 180°F (82°C) to facilitate drying. Preferably apply the paint coating immediately after the parts are dry. The solution may be held in a steel tank.

NOTE 5—*Causes of Defective Coatings*—The following information is intended to provide guidance on the causes of the most usual defects arising in the application of either Class I, Type I or Class I, Type II coatings:

(a) *Spotted Coatings* are caused by ineffective preliminary degreasing or by the presence of excessive surface contamination not removed prior to or during the chrome pickling treatment, or both.

(b) *Nonadherent Powdery Coatings* are caused by:

(1) Too long an interval between removal from the chrome pickle and rinsing,

(2) Ratio of acid to sodium dichromate too high,

(3) Temperature of the solution or of the hot-water rinse too high.

(4) Metal improperly degreased, or

(5) Solution revived too many times.

#### 5. Class I, Type III<sup>5</sup>

5.1 *Scope*—Class I, Type III treatment is applicable to all types and forms of magnesium-base alloys except M1 alloy<sup>2</sup> and certain rare-earth alloys similar to EK30A.<sup>2</sup> It produces in itself no appreciable dimensional change and is, therefore, applicable to parts machined to fine tolerances. The treatment is applicable to magnesium containing inserts or, attached to, other metals, but in such cases the preliminary treatment (5.2) shall be in the bifluoride bath (Solution No. 2) described in 5.2.2.

NOTE 6—*Causes of Defective Coatings*—The following information is intended to provide guidance on the causes of the more usual defects arising in the application of coatings from the Class I, Type III treatment.

(a) *Nonadherent Powdery Coatings* are caused by:

(1) Over-dilution of the hydrofluoric acid or acid fluoride solution,

(2) Low pH (less than 4.0) of the dichromate solution,

(3) Insufficient precleaning of the metal surface, and

(4) Direct contact between the steel tank containing the dichromate solution and the article being treated.

(b) *Failure to Coat and Nonuniform Coatings* are caused by:

(1) High pH of the dichromate solution,

(2) Low concentration of the dichromate,

(3) Insufficient precleaning of the metal surface,

(4) Omission of fluoride treatment,

(5) Use of an unsuitable alloy for the treatment, for instance, M1 alloy,

(6) Excessive immersion time in the hydrofluoric acid solution or use of an H<sub>2</sub>F<sub>2</sub> concentration in the dichromate solution in excess of 0.2%,

(7) Insufficient rinsing after the hydrofluoric acid dip, and

(8) Insufficient heating of the dichromate solution (minimum temperature should be 200°F (93°C)).

5.2 *Procedure*—Following cleaning as prescribed in Section 2, treat the parts first by immersion at 70 to 90°F (21 to 32°C) in one or other of the following solutions:

##### 5.2.1 *Solution No. 1:*

Hydrofluoric acid (60% H <sub>2</sub> F <sub>2</sub> )	24 fl oz (187 ml)
Water (Note 4)	to 1 gal (1 litre)

<sup>4</sup> Conforming to Class I, Type II treatments are the AMC “L” process, the Dow No. 10 process, and Type II treatment of Military Specification MIL-M-3171A.

<sup>5</sup> Conforming to Class I, Type III treatments are the AMC “G” process, the Dow No. 7 process, and the Type III treatment of Military Specification MIL-M-3171A.

### 5.2.2 Solution No. 2:

Sodium, potassium, or ammonium acid fluoride ( $\text{NaHF}_2$ , $\text{KHF}_2$ , or $\text{NH}_4\text{HF}_2$ )	6½ oz (50 g)
Water (Note 4)	to 1 gal (1 litre)

Solutions No. 1 and No. 2 may be held in tanks consisting of steel lined with lead or rubber. In solution No. 1, immerse AZ31A and AZ31B alloy parts<sup>3</sup> for from 30 s to 1 min; immerse all other alloys for 5 min. In solution No. 2, immerse all the alloys for 5 min. Solution No. 2 is suitable for use with all forms of magnesium alloys except those castings which have *not* been acid-pickled after blasting; these castings shall be treated in the hydrofluoric acid solution (solution No. 1). Following one or other of the above treatments, the parts shall be rinsed thoroughly in cold running water and transferred to a solution conforming to the following composition:

Sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot \text{H}_2\text{O}$ )	1 to 1.5 lb (120 to 180 g)
Calcium or magnesium fluoride ( $\text{CaF}_2$ or $\text{MgF}_2$ )	½ oz (2.5 g)
Water (Note 4)	to 1 gal (1 litre)

Operate the above solution at boiling point and immerse the parts therein for 30 min, following which thoroughly rinse them in cold running water, followed by a hot-water dip to facilitate drying. Preferably, apply the paint coating as soon as possible thereafter. A mild steel tank is suitable for holding the above solution.

### 5.3 Maintenance of Solutions:

5.3.1 *Fluoride Solutions*—Keep the concentration of free hydrofluoric acid in the solutions of 5.2.1 and 5.2.2 constant by the addition, as required, of either hydrofluoric acid or acid fluoride, respectively. See Section 9 for the analytical procedure.

5.3.2 *Dichromate Solution*—Keep the pH of the dichromate solution within the limits 4.0 to 5.5, or 4.0 to 4.8 in the case of AZ31A or AZ31B alloy,<sup>2</sup> by addition of chromium trioxide as required. Maintain the level by the addition of water. Maintain the solution saturated with respect to either magnesium or calcium fluoride by continuous immersion of a cloth bag containing excess of one or other of these compounds.

## SURFACE PREPARATION PROCEDURES—ANODIC

### 6. Class II, Type I (Galvanic Dichromate Treatment)<sup>6</sup>

6.1 *Scope*—This treatment produces black coatings of good protective and paint-base qualities, and is applicable to all alloys and forms of magnesium, including M1 alloy,<sup>2</sup> with or without attachments of other metals. No appreciable dimensional change results, and hence the treatment is also applicable to articles machined to fine tolerances.

6.2 *Procedure*—Following cleaning as prescribed in Section 2, treat the articles in fluoride solution No. 1 or No. 2 as prescribed in 5.2. Use the latter solution when other metals are attached to the magnesium. After rinsing, immerse the articles in a solution conforming to the following composition:

Ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ )	4 oz (30 g)
Sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ )	4 oz (30 g)
Ammonia ( $\text{NH}_4\text{OH}$ ) (sp gr 0.880)	½ fl oz (2.6 ml)
Water (Note 4)	1 gal (1 litre)

<sup>6</sup> Conforming to Class II, Type I treatment are the AMC “K” process, the Dow No. 9 process, and Type IV treatment of Military Specification MIL-M-3171A.

Operate the above solution at 120 to 140°F (49 to 60°C). The articles shall be made the anodes in the solution, with the tank, if of mild steel, acting as cathode, or with separate steel cathodes if the tank is lined with nonmetallic materials. No separate generator is necessary, but the magnesium parts must be electrically connected with the tank, or with the separate cathode plates through an external connection, taking care that the parts do not make direct contact with the cathode material.

6.2.1 The time of treatment shall be such that a uniform black coating is obtained on the articles. This takes from 10 to 30 min, and the consumption of from 70 to 150 A·min/ft<sup>2</sup> (929 cm<sup>2</sup>). An anodic current density of not more than 10 A/ft<sup>2</sup> (929 cm<sup>2</sup>) is desirable.

6.2.2 Following the treatment, rinse the parts thoroughly in cold running water, followed by a hot-water dip to facilitate drying.

### 6.3 Maintenance of Solutions:

6.3.1 *Fluoride Solutions*—Maintain the fluoride solutions as under 5.3.1. See Section 9 for the analytical procedure.

6.3.2 *Sulfate-Dichromate Solution*—Maintain the pH of this solution between 5.6 and 6.2 by periodic additions of a solution containing 5 weight % of both chromic anhydride ( $\text{CrO}_3$ ) and concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ , sp gr 1.84).

## 7. Class II, Type II<sup>7</sup>

7.1 *Scope*—This treatment is applicable to all forms and alloys of magnesium. Many aluminum alloys will anodically polarize in the treatment solution, and hence magnesium parts with aluminum attachments or inserts can be anodized. With aluminum alloys containing copper, however, the coating of the magnesium will proceed only if the area of the aluminum alloy is small compared to that of the magnesium. Metals other than aluminum or its base alloys shall not be in contact with the magnesium.

7.2 *Coating Properties*—The anodic coating consists of two phases: the first-formed phase is greenish-tan in color and about 0.0002 in. (5 μm) thick; whereas the second phase, formed only at higher voltages following the production of the tan coating, is fused and vitreous in nature, dark-green in color, and of thickness about 0.0012 in. (30 μm), causing a dimensional increase of about 0.001 in. (25 μm) per surface. The corrosion-resistance and paint-base characteristics are similar, and excellent for both the above phases. The thicker coating possesses high abrasion resistance, but spalls under compression deformation. The dark-green coating can be partially impregnated with low-viscosity, penetrating, organic coating materials, a procedure that considerably reduces its spalling tendency.

NOTE 7—The dark-green coating of Class II, Type II treatments is recommended in preference to the thin tan coating only when:

- Preliminary removal of surface contamination is not convenient.
- The highest degree of abrasion-resistance is required from the coating.
- A dimensional increase (see above) can be tolerated.
- The article will not be subjected in service to impact, deformation, or flexing likely to cause spalling of the coating.

<sup>7</sup> Conforming to Class II, Type II treatment is the Dow No. 17 process.

7.3 Procedure—The thin tan coating is formed with a current consumption and in a time approximately one quarter of that required to form the dark-green coating. The latter forms only after the voltage across the solution has reached the spark potential. During the ensuing coating formation, surface contamination, including graphite, is concurrently removed. Thus, articles intended to receive the dark-green coating need not first be cleaned. On the other hand, the formation of the thinner tan coating does not concurrently remove surface contamination. Since such contamination can seriously reduce corrosion resistance, it is mandatory that a preliminary cleaning, including acid pickling (2.2) shall be given to articles intended to receive the lower-voltage tan coating.

7.3.1 Rack and clean parts as appropriate (see above), and anodize either by direct or alternating current in an electrolyte conforming to one of the following compositions, respectively:

	Direct Current	Alternating Current
Ammonium acid fluoride (NH <sub>4</sub> HF <sub>2</sub> )	32 oz (240 g)	40 oz (300 g)
Sodium dichromate (Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O)	13.3 oz (99 g)	13.3 oz (99 g)
Phosphoric acid (85% H <sub>3</sub> PO <sub>4</sub> )	11.5 fl oz (90 ml)	11.5 fl oz (90 ml)
Water (Note 4)	to 1 gal (1 litre)	to 1 gal (1 litre)

The temperature of the solution shall preferably be from 160°F to 180°F (71 to 82°C). It will not operate below 140°F (60°C), but temperatures higher than 180°F (82°C) do not deleteriously affect the results. After anodizing rinse the parts in running cold water, followed by a short immersion in hot water, or by treatment with hot air, to facilitate drying. Preferably, apply the paint coating immediately after the parts are dry.

7.4 Power Requirements—A current consumption of from 50 to 500 A·min/ft<sup>2</sup> (929 cm<sup>2</sup>) is necessary, according to both the composition of the alloy being treated and the type of coating desired. Thus, in the case of the dark-green coating on AZ31 alloy, for a 10-min treatment with alternating current, a current density of 30 A/ft<sup>2</sup> (929 cm<sup>2</sup>) is applied; but greater or lesser currents may be utilized by varying the time of treatment as, for example, application of 50 A/ft<sup>2</sup> (929 cm<sup>2</sup>) for 6 min. On the other hand, for the same alloy, the thin tan coating may be applied with alternating current, with a current consumption of 75 A·min/ft<sup>2</sup> (929 cm<sup>2</sup>), equivalent to a treatment time of only 1½ min at 50 A/ft<sup>2</sup> (929 cm<sup>2</sup>). As the coating forms, the resistance of the circuit increases, and consequently the voltage must be increased to maintain a constant current density. Normally the voltage across the bath will reach from 75 to 95 for the dark-green coating (according to alloy composition) and from 60 to 75 for the thin tan coating. In carrying out the treatment, a constant current control is a considerable advantage, inasmuch as the total treatment time can be preset and manual control of the voltage and current then become unnecessary.

7.4.1 As guides to the current consumptions with various alloys, some data are presented in Table 1. It will be appreciated that rigid current consumptions in the formation of the thin tan coating cannot be specified, since this coating can be varied in thickness considerably between say 0.0001 in. (2.5 μm) and

TABLE 1 Current Consumption with Various Alloys

Alloy	Alternating Current				Direct Current			
	Voltage		A·min/ft <sup>2</sup> (929 cm <sup>2</sup> )		Voltage		A·min/ft <sup>2</sup> (929 cm <sup>2</sup> )	
	Dark-Green	Thin Tan	Dark-Green	Thin Tan	Dark-Green	Thin Tan	Dark-Green	Thin Tan
AZ31A or B	90	70	300	75	95	75	190	50
AZ61A	90	68	400	...	95	72	300	...
AZ63A	80	68	600	100	84	72	400	70
AZ91A	75	64	480	...	80	69	280	...
AZ92A	75	64	600	...	80	69	400	...
EK30A	90	70	400	...	95	75	300	...
ZK60A	85	70	300	...	90	75	190	...

0.0005 in. (12.7 μm), and still be formed below the critical spark potential at which the dark-green vitreous coating begins to develop.

7.5 Solution Control—With depletion of the bath upon use, the final voltage required to impress the above currents on the article will slowly rise, but even for the full green coating at least 20 ft<sup>2</sup> (50 dm<sup>2</sup>) of surface can be treated per gallon (1.0 litre) of solution before any change in the final voltage is experienced; and up to 40 ft<sup>2</sup> (98 dm<sup>2</sup>)/gal (1 litre) can be treated before revivification of the solution becomes necessary.

7.5.1 Prior to revivification, analyze for dichromate and phosphoric acid (see Sections 10 and 12), and make up differences from the original composition by additions of sodium dichromate and phosphoric acid.

7.5.2 A simple method for the determination of fluoride in the solution is not yet available. The fluoride concentration, however, is not critical, provided it always exceeds minimum concentration, below which pitting of the articles may ensue during their treatment. When revivifications are made by additions of sodium dichromate and phosphoric acid, make a concurrent addition of ammonium acid fluoride, equal to three times the weight of sodium dichromate added. Secondly, if pitting of the articles should occur under treatment, it is an indication that the fluoride content of the solution is too low, and about 5 oz (38 g)/gal (1 L) of ammonium acid fluoride shall then be added in order to relieve the trouble.

7.6 Tank and Rack Materials—Mild steel is suitable for tanks and heating coils. Other metals, such as copper, aluminum, lead, zinc, Monel, and stainless steels are attacked by the electrolyte. When direct current is used the tank itself can be the cathode, but, when alternating current is used, at least two magnesium parts are necessary, of area ratios not more than 3 to 1, each one serving as electrode. The articles shall not contact the tank, otherwise pitting will ensue.

7.6.1 Racks shall be normally made of magnesium alloy, but aluminum alloys containing magnesium, such as ASTM alloy No. GR20A, or its Aluminum Association equivalent, alloy No. 5052, can be used if desired, provided they are not allowed to be in the solution on open circuit. Use a spring clip with magnesium ends for providing contact with thin sheet material, the liquid level not being allowed to extend beyond the limit of the magnesium ends of the clip. No solution-line attack is experienced on magnesium. Magnesium racks may be stripped by immersion for 2 min in hot 20% chromium trioxide solution

or by immersion at room temperature for about 8 min in the chromium trioxide-nitrate solution bath described in Section 2.3.3.2.

## 8. Class II, Type III<sup>8</sup>

8.1 *Scope*—This treatment is applicable to all forms and alloys of magnesium, free from attachments or inserts of other metals.

8.2 *Coating Properties*—The anodic coating consists of two phases: The first-formed subcoating phase is a light tan in color, and causes a dimensional increase of about 0.0002 in. (5 μm) per side; the second and thicker phase, formed at higher voltages, is dark brown and causes a dimensional increase of from 0.001 in. to 0.0012 in. (25 μm to 30 μm) per surface. The paint-base characteristics are similar, and excellent for both the above phases.

8.2.1 The dark-brown coating is hard and highly abrasion-resistant, but it spalls under compression deformation and its formation can cause a loss of fatigue strength of the metal. Such loss is negligible with metal of thickness 0.1 in. (2.5 mm) or over, rising to 3% and 9% for thicknesses of 0.094 in. (2.4 mm) and 0.040 in. (1 mm), respectively, all under reversed bending and corrected for coating thickness. No loss of fatigue strength arises from application of the thin tan coating, and neither is this coating subject to spalling.

8.3 *Procedure*—Rack and clean with hot alkaline cleaner (2.2) or chromium trioxide (2.3.2), or both, as appropriate, and anodize with alternating current in an electrolyte conforming to the following composition:

Potassium hydroxide (KOH)	18 to 20 oz (135 to 150 g)
Aluminum hydroxide (Al(OH) <sub>3</sub> ) soluble in hot KOH solution (Note 8)	4 oz (30 g)
Potassium fluoride (K <sub>2</sub> F <sub>2</sub> )	4.5 oz (34 g)
Trisodium phosphate (Na <sub>3</sub> PO <sub>4</sub> )	4.5 oz (34 g)
Potassium manganate (K <sub>2</sub> MnO <sub>4</sub> ) (Note 9)	2.5 oz (19 g)
Water (Note 4)	to 1 gal (1 litre)

Dissolve the constituents of the electrolyte in the above order. Maintain the temperature of the electrolyte between 77 and 100°F (25 to 38°C).

NOTE 8—If an exceptionally hard, abrasion-resistant dark-brown coating is desired, the aluminum hydroxide in the above electrolyte shall be increased to 6 to 7 oz (45 to 52 g)/gal (1 L).

NOTE 9—Potassium manganate (K<sub>2</sub>MnO<sub>4</sub>) in the above electrolyte may be replaced with an equal weight of potassium permanganate (KMnO<sub>4</sub>), but in such case the permanganate shall be completely dissolved in water before it is added to the solution and an additional 1½ oz (11 g) of potassium hydroxide shall also be added. During operation of the bath, the permanganate is slowly reduced to manganate, complete conversion taking place after a metal area of approximately 2 ft<sup>2</sup> (18.6 dm<sup>2</sup>)/gal (1 L) of electrolyte has been treated.

8.4 *Post-Treatment*—After the electrolytic treatment, rinse the parts well in water and immerse for 1 min at room temperature in a solution consisting of 2.7 oz (20 g) of sodium dichromate (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O) and 13.3 oz (99 g) of ammonium bifluoride (NH<sub>4</sub>HF<sub>2</sub>)/gal (1 L) of solution. Following the immersion, remove the parts and dry without rinsing. Paint at any convenient time after the parts have dried.

8.5 *Power Requirements*—The practical range from current density is from 15 to 20 A/ft<sup>2</sup> (9.3 dm<sup>2</sup>) with voltages rising to from 70 to 86 (depending on alloy) for the hard brown coating and to 58 V for the thin tan coating. In this current density range, the terminating voltage is reached in from 45 to 60 min for the hard brown coating and in 10 min or less for the thin tan coating. Raise the voltage quickly from zero to 40 or more, and adjust the current and retain at the density desired. Normally the voltage will rise to 55 or more within 1 min, but as the coating forms, the resistance of the circuit increases and the voltage must be raised continuously to maintain the desired current density.

NOTE 10—If, at low initial voltages, the current remains high and coating formation does not proceed, a “surge” current shall be imposed by rapidly raising the voltage to 40, followed by immediately lowering it to zero. The voltage shall then be adjusted in the normal manner to maintain the desired current density.

8.6 *Solution Control*—The operating life of the electrolyte is extremely long, and under normal conditions of use it need never be discarded. Manganate and aluminate deplete slowly with use, whereas the depletion of fluoride and phosphate is extremely slow.

8.6.1 In the case of the dark-brown coating, a lightening of the normal color indicates a depletion of manganate in the solution, and additions shall then be made of 1 oz (7.5 g) of potassium manganate plus 1½ oz (11 g) of aluminum hydroxide for each gal (1 litre) of solution. Add the aluminum hydroxide after first dissolving it in a solution containing a weight of potassium hydroxide equal to that of the aluminum hydroxide to be added.

8.6.2 A rough coating indicates either a low, or an excessively-high, alkalinity in the electrolyte. The alkalinity shall be maintained between 10 and 12% free KOH, as determined by the method described in Section 13.

8.7 *Tank and Rack Materials*—Plain black iron is suitable for tanks and cooling coils. Suspend the parts by magnesium-base alloy clips or the like and protect them at the solution level by electroplaters’ vinyl tape. Magnesium racks may be stripped of coating when necessary by immersion in hot 20% chromium trioxide solution (Note 11).

8.7.1 Divide parts to be treated into two batches each of approximately the same surface area. Rack each of the batches and connect electrically to one or other of the inlet terminals of the power supply so that the magnesium parts constitute both electrodes of the electrolysis bath (Note 12).

NOTE 11—*Safety Precautions*—Consideration should be given to the health hazards associated with the procedures covered by this specification. Precautions must be taken to avoid skin contact with any of the solutions involved, and to avoid inhalation of vapors, fumes, or spray arising therefrom. Baths containing dichromate or fluoride shall be fitted with exhausts to remove all spray arising therefrom.

NOTE 12—*Repair Treatments*—Pretreatment films that have been damaged shall be repaired before painting. Repair shall be effected by one of the treatments below. The phosphate touch-up solution of 8.2 below necessitates special preparation, whereas a chrome pickle solution is often already available. Nevertheless, for brush-on treatment, the phosphate solution possesses the advantages of being nontoxic and nonirritant.

(a) *Chrome Pickle Repair Treatment*—The chrome pickle solution for Class I, Type I treatments (for wrought parts) shall be copiously and continuously applied to the damaged area by brush for at least 1 min. The

<sup>8</sup> Conforming to Class II, Type III treatment is the HAE process.

treated surface shall then be thoroughly flushed with water and, when dry, rubbed vigorously with a clean dry rag to remove loose powdery matter which, if allowed to remain, would deleteriously affect the adhesion of superimposed paint.

(b) *Phosphate Repair Treatment*—A solution shall be used conforming to the following composition:

Monoammonium phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ )	16 oz (84 g)
Ammonium sulfite ( $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ )	4 oz (30 g)
Ethylene glycol monobutyl ether	13 to 20 fl oz (101 to 156 ml)
Water (see <a href="#">Note 4</a> )	1 gal (1 litre)

The above solution shall be applied copiously to the damaged area by brush in sufficient quantity to keep the surface wet for at least 1 min, or until a medium to dark-gray continuous coating is formed. The treated metal surface shall then be well flushed with water and allowed to dry before the paint is applied.

## ANALYTICAL PROCEDURES

### 9. Fluoride Solutions

9.1 This method is applicable to the relevant baths of Class I, Type III (Section [5](#)) and Class II, Type I (Section [6](#)) treatments. The concentrations of both hydrofluoric acid (HF) and bifluoride shall be determined by titration with 1 *N* sodium hydroxide (NaOH) with 1 *N* sodium hydroxide (NaOH) solution, using phenolphthalein as indicator.

9.2 Maintain the hydrofluoric acid solution described in [5.2](#) by additions of fresh acid to give a titration of between 10 and 20 ml of 1 *N* NaOH solution per 2 ml of sample. Maintain the bifluoride solution described in [5.2](#) so that 10 ml thereof gives a titration of 4.5 to 5.5 ml of 1 *N* NaOH solution.

9.3 For the hydrofluoric acid the sample shall be drawn into a wax-lined pipet, discharged therefrom into at least 100 ml of distilled water, and titrated immediately. A rubber bulb, or a length of rubber tubing fitted to the suction end of the pipet, shall be used in drawing the sample into the pipet.

### 10. Dichromate Solutions

10.1 This method is applicable to solutions of the following treatments: Class I, Types I, II, and III; and Class II, Types I and II (Sections [3 – 7](#), respectively).

10.2 Add 1 ml of the dichromate solution concerned to 150 ml of distilled water, and mix therewith 5 ml of concentrated hydrochloric acid (HCl, sp gr 1.19) and 5 g of potassium iodide (KI). After at least 2 min, titrate the liberated iodine in the solution with 0.1 *N* sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) solution using starch as an internal indicator.

#### 10.3 Calculation:

$$A \times 0.0415 = B \quad (1)$$

$$A \times 4.96 = C \quad (2)$$

where:

*A* = millilitres of 0.1 *N*  $\text{Na}_2\text{S}_2\text{O}_3$  solution,  
*B* = pounds per gallon of sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ), and  
*C* = grams per litre of sodium dichromate.

### 11. Nitric Acid Solution

11.1 This method is applicable to Class I, Types I and II treatment solutions.

11.2 Mix 50 ml of distilled water with 1 ml of the solution in question, and titrate the mixture with 0.1 *N* sodium hydroxide (NaOH) solution to a pH of 4.0 to 4.05, using a pH meter with a glass electrode.

#### 11.3 Calculation:

$$A \times 0.0505 = B \quad (3)$$

$$A \times 6.34 = C \quad (4)$$

where:

*A* = millilitres of 0.1 *N* NaOH solution, and  
*B* = pints per gallon of nitric acid ( $\text{HNO}_3$ ),  
*C* = millilitres of 70% nitric acid per litre.

### 12. Phosphoric Acid Solution

12.1 This method is applicable to the Class II, Type II treatment solution. The phosphoric acid is precipitated as ammonium phosphomolybdate, which is dissolved in an excess of sodium hydroxide, such excess being titrated with standard acid. Interference from fluoride is prevented by converting it to fluoborate, by addition of boric acid.

12.2 *Molybdate Reagent*—Prepare as follows: mix 118 g of 85% molybdic acid ( $\text{H}_2\text{MoO}_4$ ) with 400 ml of distilled water, add 80 ml of ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) solution (sp gr 0.880) with stirring, and filter when solution is complete. Slowly pour the filtrate, with stirring, into a cold mixture of 400 ml of concentrated nitric acid ( $\text{HNO}_3$ , sp gr 1.42) and 600 ml of water. Allow the solution to stand over night, and filter.

12.3 *Procedure*—Dilute a 14-ml weighed sample of the solution under examination to 500 ml, and then further dilute 50 ml of this diluted solution to 500 ml. Then again dilute 25 ml of the latter solution to 100 ml, and add 10 g of ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), 1 g of boric acid ( $\text{H}_3\text{BO}_3$ ), and 15 ml of concentrated nitric acid ( $\text{HNO}_3$ , sp gr 1.42). Heat the mixture to 104°F (40°C) and slowly add 40 ml of molybdate reagent. Allow the resulting precipitate of ammonium phosphomolybdate to stand for 30 min, and then filter through a fine-texture, low-ash paper. Wash the precipitate free from acid by means of a 1% solution of potassium nitrate ( $\text{KNO}_3$ ), and mix, together with the filter paper, with an excess of 0.1 *N* sodium hydroxide (NaOH) solution, using phenolphthalein as indicator. Titrate the excess of NaOH with 0.1 *N* hydrochloric acid (HCl).

#### 12.4 Calculation:

$$\text{Phosphoric acid } (\text{H}_3\text{PO}_4), \% = [(A - B)/C] \times 0.426 \quad (5)$$

where:

*A* = millilitres of 0.1 *N* NaOH solution,  
*B* = millilitres of 0.1 *N* HCl, and  
*C* = grams of sample in aliquot.

### 13. Free Alkali

13.1 This method is applicable to the Class II, Type III solution. Manganate, fluoride, and phosphate are precipitated by barium nitrate addition, and the filtrate therefrom is titrated with standard acid.

13.2 Pipet a 2-ml sample of the solution under examination into a 25-ml glass-stoppered graduated cylinder, followed by addition of 10 ml of 0.25 *N* sodium hydroxide (NaOH) solution

and 0.5 g of barium nitrate ( $\text{Ba}(\text{NO}_3)_2$ ) crystals. Shake this mixture vigorously for 1 min, filter through a medium-texture, low-ash paper, and wash the precipitate free from alkali, preserving all filtrate. Using a pH meter with a glass electrode, titrate the free alkali in this filtrate to pH 10.5, with 0.25 *N* hydrochloric acid (HCl).

### 13.3 Calculation:

$$\text{Potassium hydroxide, \%} = 2.805 \times [(A/4) - 2.5] \quad (6)$$

where:

A = millilitres of acid used.

## 14. Keywords

14.1 anodic treatments; magnesium; painting; surface preparation

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