Designation: D 3933 – 98 (Reapproved 2004)

Standard Guide for
Preparation of Aluminum Surfaces for Structural Adhesives Bonding (Phosphoric Acid Anodizing)[1]

1. Scope

1.1 This guide describes the requirements for phosphoric acid anodizing of aluminum and its alloys for structural adhesive bonding.

1.2 The procedure included herein is based on the commercial practice of numerous agencies and organizations. The method may be revised or supplemented, as necessary, to include methods based on proven performance.

1.3 The surface preparation of metal systems used for qualification and quality-control testing of the adhesive should be agreed upon between the manufacturer and the user.

1.4 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.5 *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.* A specific precaution is given in 5.5.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 907 Terminology of Adhesives

D 2651 Guide for Preparation of Metal Surfaces for Adhesive Bonding

2.2 *Federal Specifications:*

0-0-670 Orthophosphoric Acid, Technical[3]

3. Terminology

3.1 *Definitions*—Many terms in this guide are defined in Terminology D 907.

4. Significance and Use

4.1 Durable adhesive bonds between metal to metal, metal to composites can be obtained reliably only through proper selection and careful control of the materials used and the steps in the bonding process. The preparation of the metallic substrates to obtain surfaces with appropriate characteristics is a critical step. Improper surface preparation can produce seemingly acceptable bonds that can degrade rapidly with time. This guide describes one method on how to properly prepare aluminum surfaces can be obtained.

4.2 The formation of reproducible, durable, adhesive bonds in structural assemblies requires great care in the selection of materials, the preparation of the surfaces of the components to be bonded, the fit of the components, and the performance of the steps in the bonding process. Experience has shown that when adhesively bonded aluminum surfaces which have been prepared in accordance with this guide produce relatively reproducible, durable bonds.

5. Apparatus

5.1 Locate surface preparation and drying facilities separate from other activities or equipment, or both, to preclude contamination by substances detrimental to adhesion.

5.2 Facilities should be arranged such that parts can flow from the beginning of surface preparation to the priming operation without being touched.

5.3 Filters or traps, or both, should be installed for removing airborne dust, moisture, and oil from all air lines or ducts used for solution agitation and parts drying. Periodically check, clean, or replace filters to ensure proper operation.

5.4 Surface preparation facilities should not be used for purposes other than the preparation of parts for adhesive bonding and subsequent finishing.

5.5 Equipment requirements for this process include equipment normally used in the chemical processing of aluminum alloys, with the following special provisions:

5.5.1 Racks and frames that are electrically anodic shall be constructed of materials that will not cause corrosive reactions with the suspension wires or clips, or the parts, during the entire process. "Picture-frame"-type racks have performed satisfactorily.

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[1] This guide is under the jurisdiction of ASTM Committee D14 on Adhesives and is the direct responsibility of Subcommittee D14.80 on Metal Bonding Adhesives.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

5.5.2 Parts shall be attached to racks or frames with conductive material that anodizes, that is, aluminum or titanium in the form of wire, hooks, springs, clips, etc.

5.5.3 The phosphoric acid anodizing tank lining shall be of such material that interaction between the solutions, parts, frames, racks, or clips and hangers does not interfere with the anodic process and is suitable for use as a cathode. Tanks should be equipped with a surface skimming device to remove surface contamination, a filtering system, and an agitation system for mixing the tank contents.

5.5.4 Terminals for electrical current shall be designed and positioned such that parts cannot be "burned."

5.5.5 The electrical system used during a *single*-rack anodic process shall be adequate for producing 10-V dc and maintaining any set voltage within ±1-V dc.

5.5.6 The electrical system used during a *multiple*-rack process shall be adequate for producing 15-V dc and maintaining any set voltage within ±1-V dc.

5.5.7 Rinse tanks should be placed adjacent to processing tanks in such a manner that parts can be easily and quickly moved from one solution to another so that the parts will not become dry during successive steps of the process.

5.5.8 Incoming solution makeup water and rinse water shall contain not more than the "recommended upper limit" for fluoride and not more than the "highest desirable level" of dissolved chemicals based on American Chemical Society standards for deionized or distilled water, or both (1.7 ppm fluoride, 500 ppm total dissolved solids, etc.) except that:

5.5.8.1 Chloride shall not exceed 25 ppm.

5.5.8.2 pH shall be between 5.5 and 8.0.

NOTE 1—Most regionally distributed potable water will meet these requirements.

5.5.8.3 If the above requirements cannot be met, the incoming water shall be deionized and maintained within the following limits:

(*a*) Total dissolved solids shall not exceed 150 ppm.

(*b*) pH shall be between 5.5 and 8.0.

6. Manufacturing

6.1 Parts shall be racked or suspended from frames such that they all have firm, reliable electrical contact with the anode connections, so that the parts do not contact each other and that rinse water contacts all surfaces and drains freely.

6.2 Take the utmost care that the parts are not touched at any time during the entire process, such as touching of adjacent parts, the rack or supporting frame, or any other item, since the surfaces and the phosphoric acid anodic coating are susceptible to contamination or physical damage prior to the application and cure of the primer.

6.3 If it becomes necessary to handle or touch parts, clean white gloves should be used and contact should be limited to surfaces not to be adhesively bonded.

6.4 If parts become contaminated, either prior to or subsequent to anodizing, corrective action shall be accomplished by reprocessing, beginning with alkaline cleaning.

6.5 To ensure solution homogeneity, agitate immediately prior to process use and after every addition of water or chemicals. (**Warning—**Solutions used in this process are corrosive and toxic. Avoid breathing solution mists or vapors. Do not allow solutions to get on the eyes, on the skin, or on clothing.)

6.5.1 Consult Industrial Hygiene for safety precautions.

6.6 Control the time interval between withdrawal from processing solutions and rinsing so that there is no drying of the solution on the details.

6.7 Parts must be water-break-free following rinsing after alkaline cleaning, after deoxidizing, and after anodizing.

7. Procedure

7.1 Perform the surface preparation process in a continuous operation as detailed in the flow chart, Fig. 1.

7.2 Complete all fabrication processes, inspections, prefit, etc. before the start of the preparation cycle.

7.3 Complete all "hand work" before solvent cleaning.

7.4 Once racked for alkaline cleaning, parts shall not be touched by anything except the applicable processing solution and rinse waters, until the parts are dried after primer application (5.2).

7.5 The "wet" processing steps, from alkaline cleaning through drying after phosphoric acid anodizing, should be performed in one continuous uninterrupted sequence of processes, with the parts not drying at any time until the oven drying after the rinse following phosphoric acid anodizing.

7.5.1 Should the parts become delayed prior to anodizing during this wet processing, hold the parts in the applicable rinse tank.

7.5.2 There shall be no holding of parts in the processing sequencing after anodizing.

7.6 Should the electric current fail or otherwise be interrupted during the phosphoric acid anodizing, anodizing may be continued for an additional 20 to 25 min, if the potential can be reestablished within 2 min. If the potential cannot be reestablished within 2 min, then rinse and reprocess starting with the deoxidizer.

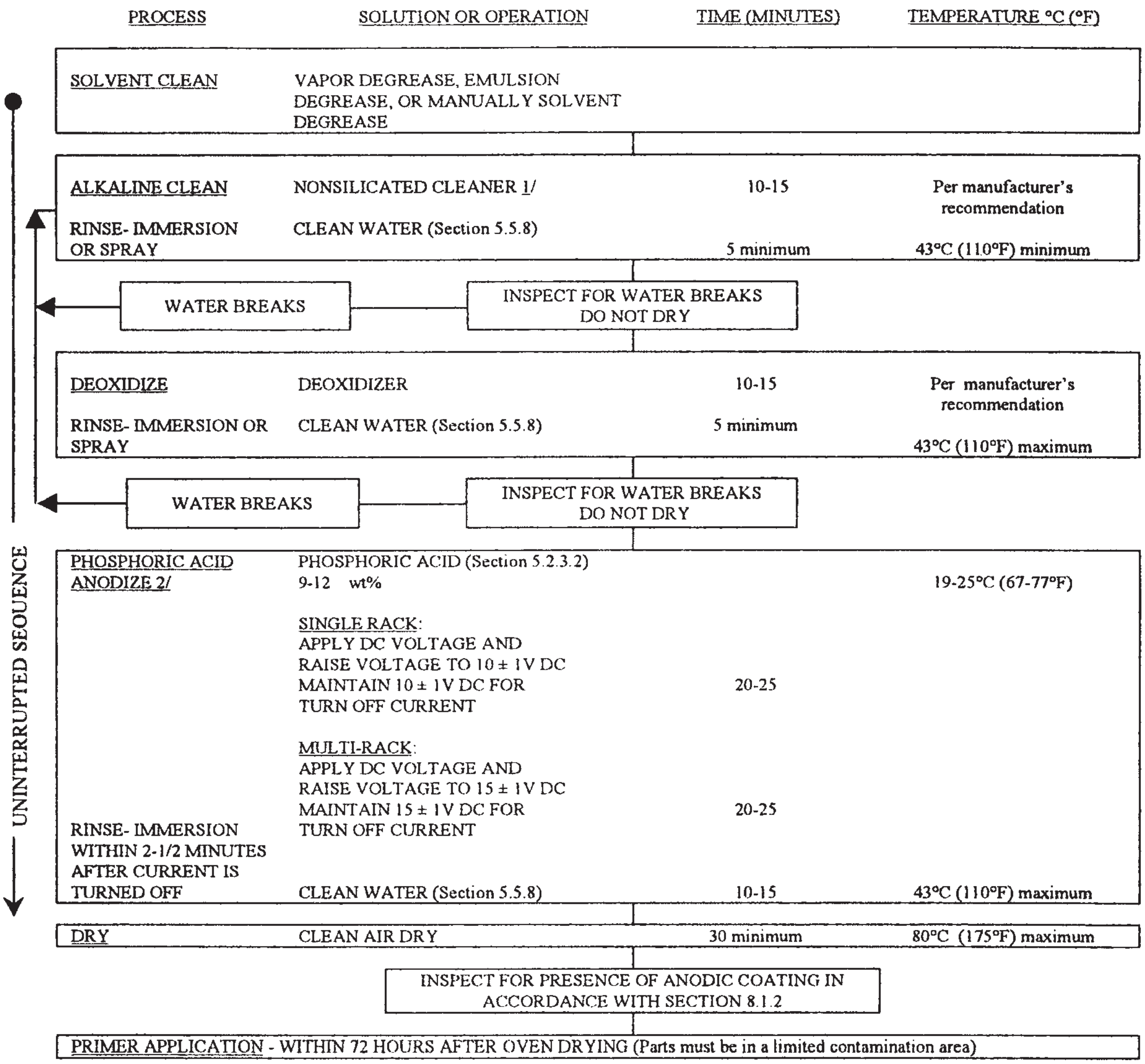
7.7 Apply adhesive primer within 72 h after oven drying following the phosphoric acid anodizing. Parts should be held in a limited contamination area prior to priming and should not be handled (5.2). However, it is most desirable to prime parts as soon as possible to minimize the possibility of inadvertent contamination.

7.8 *Rinse Requirements*:

7.8.1 Rinsing may be by spray or immersion. Single spray or double counter-current immersion rinsing are commonly used.

7.8.2 Feed water to rinse operations may be direct from source water in accordance with 5.5.8 or from any subsequent rinse operation, except that acid rinse waters shall not be fed into alkaline rinse waters.

7.8.3 Final immersion rinse water after alkaline cleaning, deoxidizing, and anodizing shall not exceed 1000 ppm total dissolved solids above that of the incoming rinse water (5.5.8). When double independent feed or double-counter current immersion rinse is used, the first rinse after anodizing shall not exceed 5000 ppm, and the time in first rinse shall not exceed 2 min from time of starting immersion to complete withdrawal. Immersion rinse tank(s) used for anodize rinse shall be used for anodize rinse only.



NOTE 1—Experience has proved nonsilicated cleaners to be preferable when reprocessing might be involved.

NOTE 2—A single-rack facility is one with a single anode rack between each set of cathodes. A multi-rack has two or three anode racks between each set of cathodes.

FIG. 1 Process Flow Chart

7.8.4 Agitate immersion rinse tanks during rinsing to aid rinsing and prevent stratification.

7.8.5 Allowable concentration limits may exceed normal control limits for the first 30 s of rinsing.

8. Quality Assurance Provisions

8.1 *Part Inspection During Processing*—Parts should be inspected during the continuous processing, as noted in Fig. 1.

8.1.1 *Water-Break Inspection*:

8.1.1.1 On removal from rinses, cleaned parts shall pass water-break inspection as indicated by maintenance of a continuous film of water on the surface for not less than 30 s.

8.1.1.2 Parts failing water-break inspection shall be reprocessed through the applicable cleaning operation until the surface can maintain the continuous film of water.

8.1.2 *Phosphoric Acid Anodic Coating Inspection*:

8.1.2.1 After anodizing and during rinsing and draining, there shall be no evidence of a water break. There shall be no stains, streaks, discoloration, or residue on surfaces of anodized parts after rinsing (5.5.8).

8.1.2.2 The anodic coating should be continuous, smooth, uniform in appearance, and when examined visually, should be free from discontinuities, such as scratches, breaks, burned areas, and areas that are not anodized. Small irregularities at points of electrical contact are acceptable. If practical, put electrical contacts in areas that will not be bended or in a trim tab that will be removed from the finished part.

8.1.2.3 The anodized surfaces shall pass the following polarized color change examination:

(*a*) Illuminate the surface at a low angle using any white or near-white lamp.

(*b*) Observe the reflected light at a low angle (0–10°) by placing a light-polarizing filter either between the light and the surface or between the surface and the observer.

(*c*) An anodized surface shall display an“ interference color,” which should change to another color when the filter is rotated 90° (for example, from purple to yellow green).

(*d*) Rotation of the filter is necessary since some colors may be pale and not discernible until another color is observed by rotation of the filter.

(*e*) Different pieces of aluminum alloy anodized under the same loads may show different colors through the polarizing filter due to differences in alloy composition, metallurgical condition, and specific anodizing conditions at different positions in the tank during anodizing. The colors most frequently seen are purple, yellow, blue, and green hues.

(*f*) All surfaces to be adhesively bonded shall exhibit the color changes noted above. Abrupt differences in color of local areas, except at electrical contact points, from the background color are not acceptable. Causes of such differences may be fingerprints, abrasion, or other contamination.

NOTE 2—The color change may be difficult or impossible to detect on surfaces that have been etched by marking ink, roughened by machining, sanding, deburring, etc., or uninspectable because of shape. In these cases, the presence of color on tool tabs or on the opposite surface, or on undisturbed surfaces, may be evidence that the surface is acceptably anodized.

(*g*) Parts not passing the polarized color change test shall be rejected or reprocessed starting with the alkaline cleaning step.

8.2 *Makeup and Process Control of Processing Solutions*:

8.2.1 *Alkaline Cleaner*—Makeup, replenishment, and replacement of alkaline cleaning solutions should be developed to produce effective processing.

8.2.2 *Deoxidizer*—Makeup, replenishment, and replacement of deoxidizer should be defined to produce effective processing. The sulfuric acid-sodium dichromate etch (Method G for Aluminum Alloy in Guide D 2651) has been an effective etch.

8.2.3 *Phosphoric Acid Anodizing Solution*:

8.2.3.1 *Initial Tank Makeup*

(*a*) Fill the tank approximately three-quarters full of clean water (5.5.8).

(*b*) Agitate the water and slowly add 7 parts of phosphoric acid (A–A–55820, Class I, 85 % phosphoric acid) for each 100 parts of final solution.

(*c*) Bring mixture to operating level of the tank with clean water (5.5.8) and mix thoroughly.

8.2.3.2 *Maintenance*—Maintain the phosphoric acid concentration and operating conditions as specified in Table 1. The level of solution in the tank should be within the effective operating level for the surface skimming equipment.

TABLE 1 Phosphoric Acid Anodizing Solution

Material/Operation	Range
Phosphoric acid, 85%	9–12 weight %
Temperature	19–25°C (67–77°F)
Voltage, d-c	9–11 (single rack) 14–16 (multi-rack)
Anodizing time	20–25 min

8.2.3.3 *Qualification of Phosphoric Acid Anodizing Solution*—Each freshly mixed tank of phosphoric acid anodizing solution shall be qualified before being used for processing production parts. Qualification should be accomplished by processing and adhesive bonding not less than five control specimens required by the applicable adhesive bonding specification. These control specimens should exceed the minimum strength and durability requirements.

8.2.3.4 *Determination of Phosphoric Acid Concentration*—Titrate a 10-mL sample of anodizing solution to a pH of 4.2 with 1.0 *N* NaOH with a correction for aluminum concentration. Use the following formula:

$$\text{oz/gal } H_3PO_4 = 1.3 \times NaOH \text{ normality m}L \; NaOH - 0.7 \; (\text{g/}L \; of \; A1) \qquad (1)$$

$$\text{g/}L \; H_3PO_4 = 9.8 \times NaOH \text{ normality m}L \; NaOH - 0.7 \; (\text{g/}L \text{ of } A1) \qquad (1)$$

(*a*) The aluminum content is not controlled; however, the aluminum content must be known to calculate the H_3PO_4 concentration.

(*b*) The aluminum concentration should be determined using a method confirmed by analysis of solutions of known aluminum concentration (atomic absorption utilized to an accuracy of 5 % has proven adequate).

8.2.4 *Replenishment and Replacement of Solutions*—Tank solutions shall be replenished to maintain the required concentrations, and replaced when the solutions cannot be adequately controlled or when the solutions become contaminated to the point of no longer processing parts satisfactorily.

9. Precision and Bias

9.1 Precision and bias information does not exist for this guide because resources necessary for round-robin testing have not been forthcoming.

9.2 The precision and bias of this guide are a function of the adhesive system, surface preparation, substrate, test temperature, and other factors related to test apparatus, laboratory and operator variabilities. Precision shall be reported in terms of the standard deviation of the data and the standard error of the mean.

10. Keywords

10.1 aluminum adhesive bonding; anodize; phosphoric acid; surface preparation