ASTM INTERNATIONAL

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Standard Test Method for
Repassivation Potential of Aluminum and Its Alloys by Galvanostatic Measurement[1]

This standard is issued under the fixed designation D 6208; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 A procedure to determine the repassivation potential of aluminum alloy 3003-H14 (UNS A93003) **(1)**[2] as a measure of relative susceptibility to pitting corrosion by conducting a galvanostatic polarization is described. A procedure that can be used to check experimental technique and instrumentation is described, as well.

1.2 The test method serves as a guide for similar measurement on other aluminum alloys and metals **(2-5)**.

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

1.4 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*
D 1193 Specification for Reagent Waters[3]
D 3585 Specification ASTM Reference Fluid for Coolants Tests[4]
G 3 Practice for Conventions Applicable to Electrochemical measurements in Corrosion Testing[5]
G 15 Terminology Relating to Corrosion and Corrosion Testing[5]
G 16 Guide for Applying Statistics to Analysis of Corrosion Data[5]
G 46 Guide for Examination and Evaluation of Pitting Corrosion[5]
G 107 Guide for Formats for Collection and Compilation of Corrosion Data for Metals for Computerized Database Input[5]

3. Terminology

3.1 *Definitions:* An attempt to avoid terminology is made, with an explanation provided where applicable. Terms used in this test method can be found in Practice G 3 and Terminology G 15.

3.2 *Symbols:*

3.2.1 E_B—break potential, potential at which the passive aluminum oxide layer breaks down.

3.2.2 E_G—protection potential as measured in this galvanostatic method, potential at which oxide layer repassivates.

3.2.3 J—current density, in A/m^2

4. Summary of Test Method

4.1 The test method described is an adaptation of the method described in FORD Motor Company standards **(6)**.

4.2 An aluminum alloy specimen is polarized at fixed current density for 20 min. in a solution of coolant and corrosive water containing chloride. The potential as a function of time is recorded.

4.3 The maximum potential, E_B reached upon polarization is determined, as is the minimum potential following the maximum potential, E_G.

4.4 Visual examination of the specimen may be made using Guide G 46 as a guide after disassembly and rinsing.

5. Significance and Use

5.1 This test method is designed to measure the relative effectiveness of inhibitors to mitigate pitting corrosion of aluminum and its alloys, in particular AA3003-H14, rapidly and reproducibly. The measurements are not intended to correlate quantitatively with other test method values or with susceptibility to localized corrosion of aluminum observed in service. Qualitative correlation of the measurements and susceptibility in service has been established **(1)**.

5.2 The maximum potential reached upon initial polarization, E_B, is a measure of the resistance to breakdown of the aluminum oxide film. Lower susceptibility to initiation of pitting corrosion is indicated by a more noble potential (See

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[2] The boldface numbers in parentheses refer to the list of references at the end of this standard.

[3] *Annual Book of ASTM Standards,* Vol 11.01.

[4] *Annual Book of ASTM Standards,* Vol 15.05.

[5] *Annual Book of ASTM Standards,* Vol 03.02.

Practice G 3 and Terminology G 15.) This potential, as measured in this test method, is not very sensitive to the inhibitors present.

5.3 The minimum potential, E_G, following the maximum potential is a measure of the protection against continued pitting corrosion by the inhibitors. Again, a more noble potential indicates better protection. This potential is sensitive to the inhibitors present.

5.4 Visual examination of the specimens can provide information about subleties of the pitting and inhibition mechanisms. Number of pits, pit depth, amount of deposit, and surface discoloration are some examples of recordable observations, which can assist evaluation of inhibitor effectiveness.

5.5 The presence of chloride in the test solution is critical to observation of pitting corrosion. Also, a coolant/corrosive water solution in which gas bubbles evolve spontaneously on the aluminum (indicating general corrosion) is unlikely to have a significant amount of observable pitting corrosion.

6. Apparatus

6.1 *General Description*—The apparatus for the electrochemical test consists of a cell, current supply, recorder, and three electrodes. Fig. 1 is a generalized schematic of the arrangement. More specific requirements for each component are given below.

6.2 *Cell*—The cell consists of a No.25 O-ring borosilicate glass joint held vertically using standard laboratory clamps and ring stand. The working electrode will be clamped to the bottom using the matching O-ring clamp and viton or silicone rubber gasket.

6.3 *Current Supply and Recorder*—A constant current supply capable of generating 872 µA continuously is required. The recorder must have a high input impedance ($> 10^{12}$ Ohms), be capable of recording potentials of ± 2 V with mV accuracy, and have a low gain. These capabilities are typical of commercial potentiostat/galvanostat instruments connected to either a strip chart recorder or computer, for experimental control and data acquisition. The schematic in Fig. 1 shows connections using a current supply and mV strip chart recorder, and Fig. X2.1 shows a schematic for using a computer and potentiostat/galvanostat.
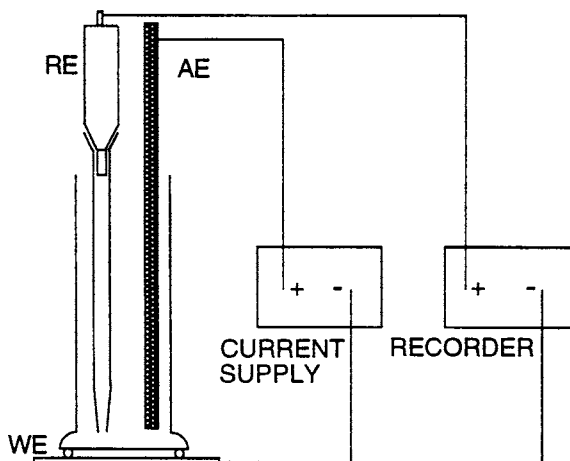
6.4 *Electrodes*:

6.4.1 *Working Electrode (WE)*—The working electrode, aluminum test coupon, is cut as 51×51 mm (2 in. $\times$ 2 in.) squares from aluminum sheet 2 to 6 mm (1/16 in. to 1/4 in.) thick. The standard material is AA3003-H14 (UNS A93003), used to develop the precision and bias statements. The coupon is rinsed thoroughly (both sides) with methanol and placed in a low temperature drying oven. No additional surface preparation is desirable. Prior to testing, a coupon is allowed to cool to room temperature. Then it is clamped to the bottom of the O-ring joint using the matching O-ring (viton or silicone rubber) and clamp. The clamping screw may be tightened to finger tightness, if desired. Excessive tightening must be avoided. This gives an area of 8.72 cm^2 aluminum exposed to the solution.

6.4.2 *Auxiliary Electrode (AE)*—Ultrafine grade graphite rod, 6-8 mm (1/4 in.) in diameter and at least 20 cm (8 in.) long. Avoid coarse grades as they can adsorb inhibitors.

6.4.3 *Reference Electrode (RE)*—The reference electrode can be of any convenient type, for example saturated calomel (Hg/HgCl) or silver chloride (Ag/AgCl). The electrode must be in good working order and stable in the solution to be measured. The reference electrode is placed in Luggin probe to avoid solution impedance bias. Appendix X2 contains two suggestions for easily constructed Luggin probes.

6.5 *Timer*—Timer with 1 s resolution out to 30 min.

7. Preparation of Apparatus

7.1 *Assembly*—Prior to running tests, assemble the cell and electrodes, using an unprepared Al specimen as the "working" electrode using appropriate clamping. The auxiliary electrode is positioned so that the tip is from 5 to 10 mm from the working electrode surface. The Luggin probe is positioned so that the tip is from 1 to 3 mm from the working electrode surface. It is most convenient if the clamping arrangement is such that this electrode configuration is maintained easily. The cell is then removed and Al specimen unclamped.

8. Procedure

8.1 A corrosive water containing chloride, sulfate, and bicarbonate is prepared by dissolving the following amounts of anhydrous salts in distilled or deionized water, ASTM Type II (see Specification D 1193):

Sodium sulfate	592 mg
Sodium chloride	660 mg
Sodium bicarbonate	552 mg

The solution is made up to a total weight of 1 kg with distilled or deionized water at 20°C. A 4-kg batch size is convenient if many tests are to be run, multiply amounts above by four. This will give a solution, which is 400 ppm in chloride, sulfate, and bicarbonate.

8.2 Rinse cell, O-ring, Luggin probe (inside and out), auxilliary electrode, and reference electrode thoroughly with Type II water.

8.3 Prepare the aluminum specimen as the working electrode (see 5.4.2). Clamp to cell, using O-ring, and set to one side.

8.4 Prepare the test solution as 25 vol % of the coolant to be tested, 25 vol % of the corrosive water from 6.1, and the

FIG. 1 Generalized Experimental Set-up

remainder deionized or distilled water. The amount to be made depends on one's exact cell configuration. Sufficient test solution is required to fill the cell (about 50 mLs) and the Luggin probe assembly. For the configurations of Luggin probe given in Appendix X2, 160 mLs is more than sufficient.

8.5 Fill the Luggin probe with test solution sufficient to cover the tip of reference electrode when inserted. Insert reference electrode. Gently tap Luggin to remove any bubbles between the tip and reference electrode. If a vertical Luggin is used, as in Fig. X2.2, then bubbles can be removed by allowing solution to drain slowly into a waste container.

8.6 Set up current generator to output 872 µA (J = 100 µA/cm^2) continuously, set recorder to a range of ±2 V (other settings may be used if found to be necessary to achieve accurate and representative potentials, chart speed as desired (5 mm/min is reasonable). If acquiring data by computer, set data acquisition rate to 1 point/s. Do not turn either generator or recorder on at this time.

8.7 Fill cell with approximately 50 mL of test solution, about 25 mm from the top of the cell. Start timer. Do not start generator at this time. Recorder may be turned on at this time. Assemble cell over Luggin probe and auxiliary electrode. Attach wires to reference electrode, auxiliary electrode, and working electrode. Check for bubbles in Luggin, tap gently to remove.

8.8 At 5 min on the timer, turn on current generator, and recorder, if not already on. Record potential versus time response for 20 min. Turn off current generator and recorder (see Note 1).

NOTE 1—A computer controlled system can be used in place of a current generator and recorder. In this case the current generator consists of a potentiostat/galvanostate operated in galvanostatic mode. The recorder is the computer. Software is used to control all aspects of the test protocol, including controlling the galvanostate, acquiring the data, plotting, and analysis.

8.9 Run the test in duplicate, steps 8.2-8.8

9. Interpretation of Results

9.1 *Break Potential, E_B*—The graph in Fig. 2 illustrates two
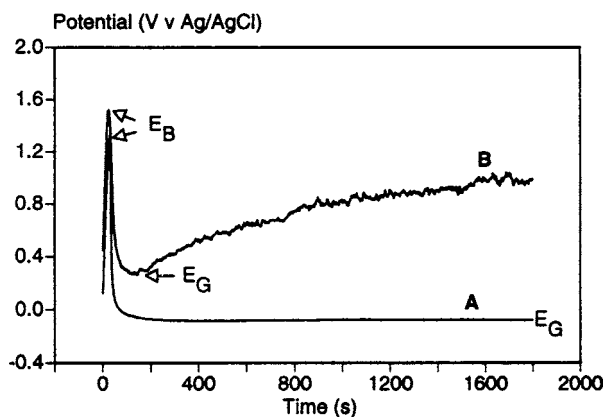
of the three possible forms of curve obtained in the experiment. In Fig. 2 there is an initial rapid rise in potential followed by a decrease. Record the maximum potential reached in this period as E_B. The third possibility is that the potential rises continuously, though perhaps oscillating. Record the maximum potential reached throughout the run. Express potential as *V v SHE* correcting for type of reference electrode used (see Appendix X1).

9.2 *Protection Potential E_G*—For curves similar to curve A in Fig. 2, asymptotic decrease in potential after break, record the minimum potential reached, typically at the end of the run. For curves similar to curve B in Fig. 2, there is a decrease after the "break" followed by a series of rises and falls, record the lowest potential reached on the first fall. Typically, subsequent rises and falls are small and appear as oscillations. For curves where the potential rises continuously, E_G will be equal to E_B. Express potential as *V v SHE*, correcting for type of reference electrode used (see Appendix X1).

9.3 *Curve Type*—Record whether curve is asymptotic (Type A), rising and falling (Type B), or rising only (Type C).

9.4 *Observations (optional)*—The following are optional observations that can be recorded as: evolution of gas bubbles during the test, description of surface after test, location of pits (for example, along scratch lines, etc. number of pits, depth of pits, area of pits, color of deposits, location of deposits in relation to pits, and other pitting evaluations as described in Guide G 46).

10. Report

10.1 Report the following information:

10.1.1 Report aluminum alloy tested.

10.1.2 Report the average E_B and E_G of all experimental runs, at least two, for the formula.

10.1.3 Report type of curves obtained, A, B, or C. Report multiple types if obtained.

10.1.4 Report any visual observation made.

10.1.5 Many other relevant test parameters are given in Guide G 107. These parameters should be recorded properly in laboratory notebooks for future reference.

11. Precision and Bias

11.1 *Precision*—The precision of this test method has not been determined. Round-robin testing will commence once final details of the method are determined. It is expected that the precision associated with the "break" potential will be less than the precision associated with the "protection" potential. It is also expected that precision will be constant over the range of measurement as opposite to being relative to the value of the measurement and insignificantly affected by the choice of aluminum alloy tested.

11.2 *Bias*:

11.2.1 *Statement on Bias*—This procedure has no bias because the values for the "break" and "protection" potentials are defined only in terms of this test method. An apparent bias will exist if the user does not correct the potentials for the specific reference electrode used. Potential always must be expressed as relative to a standard hydrogen electrode (SHE) at the pH of use (see Appendix X1).

NOTE 1—Break potential, E_B, and protection potential, E_G, is indicated for each type of transient.

FIG. 2 Two Common Potential/Time Transient Profiles After Polarization