Designation: D 2674 – 72 (Reapproved 2004)$^{\epsilon 1}$

Standard Methods of Analysis of Sulfochromate Etch Solution Used in Surface Preparation of Aluminum[1]

This standard is issued under the fixed designation D 2674; 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.

ϵ^1 Note—Keywords were added editorially in April 2004.

1. Scope

1.1 These methods offer a means for controlling the effectiveness of the etchant which is normally used for preparing the surface of aluminum alloys for subsequent adhesive bonding. As the etchant reacts with the aluminum, hexavalent chromium is converted to trivalent chromium; a measure of the two and the difference can be used to determine the amount of dichromate used.

1.2 The sulfochromate solution can be replenished by restoring the sodium dichromate and the sulfuric acid to the original formulation levels. The lower limit of usefulness will vary depending upon solution storage, adhesives used, critical nature of bond capability, variety of metals processed, etc. and should be determined. Replenishment will be limited to the number of times the chemical ingredients can be restored and maintained to the required levels and should be determined by the user. Sludge collecting in the bottom of a tank should be minimized by periodic removal of sludge. For some applications, the hexavalent chromium should not fall below the trivalent chromium content.

1.3 A typical aqueous sulfochromate acid etch solution formulation is as follows:

Sodium dichromate ($Na_2Cr_2O_7$)	4.5 oz/gal (33.7 g/litre)
Sulfuric acid (sp gr 1.84)	45 oz/gal (337.1 g/litre)

1.4 Maintenance of the aqueous concentrations is suggested as follows by appropriate additions of sodium dichromate or sulfuric acids.

Sodium dichromate	3.0 to 6.0 oz/gal (22.5 to 44.9 g/litre)
Sulfuric acid	40 to 50 oz/gal (299.6 to 374.5 g/litre)

1.5 Method A is intended for measuring the sulfuric acid content of a sulfochromate solution. Method B is intended for measuring the hexavalent and trivalent Chromium content of a sulfochromate solution. Method C is intended as an alternative method for measuring the hexavalent and trivalent Chromium content of a sulfochromate solution.

1.6 *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:* [2]

D 1193 Specification for Reagent Water

E 50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

3. Purity of Reagents and Water

3.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

3.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193.

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[1] These methods are under the jurisdiction of ASTM Committee D14 on Adhesives and are 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] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N. Y., and the "United States Pharmacopeia."

METHOD A

4. Apparatus

4.1 *pH Meter*.

5. Reagents

5.1 *Methyl Orange Indicator Solution*—Prepare in accordance with Practices E 50.

5.2 *Sodium Hydroxide, Standard Solution (1.0 N)*—Dissolve 40 g of sodium hydroxide (NaOH) in 1 liter of water and standardize.

6. Procedure

6.1 Pipet a 5-mL sample of sulfochromate etch solution into a 250-mL beaker. Add 100 mL of water. Titrate the sample with the NaOH solution to a pH of 3.5, using a pH meter.

6.2 An alternative method may be used whereby, instead of the pH meter, 1 drop of methyl orange indicator solution is added and, the titration continued until the color of the solution loses all trace of orange.

7. Calculation

7.1 Calculate the sulfuric acid content of the sulfochromate solution, A in oz/gal, B in g/litre, as follows:

$$A = 1.3\,VN \tag{1}$$

$$B = 9.81\,VN \tag{2}$$

where:
V = milliliters of sodium hydroxide solution, and
N = normality of sodium hydroxide solution.

7.2 Replenish the sulfuric acid content of the solution as follows:

$$W_1 = (A_1 - A)V_1 \tag{3}$$

$$W_2 = (B_1 - B)V_2 \tag{4}$$

where:
W_1 = weight of sulfuric acid (H_2SO_4, sp gr 1.84) to be added to solution, oz,
W_2 = weight of sulfuric acid to be added to solution, g,
A_1 = original concentration of solution, oz/gal,
B_1 = original concentration of solution, g/litre,
V_1 = volume of solution in tank, gal, and
V_2 = volume of solution in tank, litres.

METHOD B

8. Reagents

8.1 *Ammonium Persulfate Solution* ($(NH_4)_2S_SO_8$, *15 weight %*).

8.2 *Ferrous Ammonium Sulfate Solution* (0.05 N)—Dissolve 39.2 g of ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) in 1 litre of cold H_2SO_4(5 + 95) and dilute to 2 litres with H_2SO_4(5 + 95). Standardize this material each time as follows:

8.2.1 Pipet 10 mL into a 400-mL beaker. Add 150 mL of water plus 5 mL of H_2SO_4(sp gr 1.84) and 1 drop of the phenanthroline ferrous complex. Titrate with the $KMnO_4$ solution just to disappearance of the indicator color. If the normality does not fall within 0.051 to 0.049, discard the 0.05 *N* solution.

8.3 *Hydrochloric Acid* (1 + 1)—Mix 1 volume of concentrated hydrochloric acid (HCl) with 1 volume of water.

8.4 *Ortho-Phenanthroline Ferrous Complex Indicator Solution*—Prepare in accordance with Practices E 50.

8.5 *Potassium Permanganate, Standard Solution* (0.05 N)—Dissolve 1.6 g of potassium permanganate ($KMnO_4$) in 1 litre of water and standardize.

8.6 *Silver Nitrate Solution* (1 weight %).

8.7 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4).

Determination of Hexavalent Chromium as Sodium Dichromate

9. Procedure

9.1 Pipet 1 mL of the sample into a 400-mL beaker. Add 150 mL of water, followed by 5 mL of H_2SO_4 (sp gr 1.84). Titrate with the standard ferrous ammonium sulfate solution (using 1 drop of the ferrous complex indicator) (Note 1) until the indicator turns pink and then add about 5 ml of the standard ferrous ammonium sulfate solution in excess. Record the total volume of the standard ferrous solution added. Back-titrate with the potassium permanganate solution until the color of the solution becomes very slightly green.

NOTE 1—Barium diphenylamine sulfonate indicator may be used if preferred. This indicator gives a purple to green end point. If performed with care, back titration is not necessary.

NOTE 2—Upon reaching the end point, the solution will be colorless, then it will carry over by itself to a slightly green color. Any violet color will indicate the back titration has gone over the end point.

9.2 Record the amount of potassium permanganate used to reach this end point. Use an average of three determinations in the calculation.

10. Calculation

10.1 Calculate the hexavalent chromium as sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$), C in oz/gal, and D in g/L, as follows:

$$C = (V_1N_1 - V_2N_2)6.63 \tag{5}$$

$$D = (V_1N_1 - V_2N_2)49.7 \tag{6}$$

where:
V_1 = millilitres of ferrous ammonium sulfate solution,
N_1 = normality of ferrous ammonium sulfate solution,
V_2 = millilitres of potassium permanganate solution, and
N_2 = normality of potassium permanganate solution.

Determination of Trivalent Chromium as Sodium Dichromate

11. Procedure

11.1 Pipet 1 mL of the sample into a 400-mL beaker. Add 150 mL of water followed by 10 mL of H_2SO_4 (sp gr 1.84).

Heat to boiling. While hot, add 5 mL of the 1.0 % $AgNO_3$ solution and 20 mL of the ammonium persulfate solution. Boil for 20 min and then cool to room temperature. Add 1 drop of HCl and 1 drop of the phenanthroline ferrous complex indicator (Note 1). Titrate with the standard ferrous ammonium sulfate solution until the color of the solution turns pink. Add an excess of 5 mL of titrating solution and record the total volume added. Backtitrate with the potassium permanganate solution until the color of the solution becomes apple green. Record the amount of the potassium permanganate used to reach this end point. Use an average of three determinations in the calculations.

12. Calculations

12.1 Calculate the total chromium as sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$), *X* in oz/gal, *Y* in g/L, as follows:

$$X = 3.4\,(V_1N_1 - V_2N_2) \tag{7}$$

$$Y = 25.1\,(V_1N_2 - V_1N_2) \tag{8}$$

where:

V_1 = millilitres of ferrous ammonium sulfate solution,
V_2 = millilitres of potassium permanganate solution,
N_1 = normality of ferrous ammonium sulfate solution, and
N_2 = normality of potassium permanganate solution.

12.2 Calculate the trivalent chromium, *E* in oz/gal, *F* in g/L, as follows:

$$E = X - C \tag{9}$$

$$F = Y - D \tag{10}$$

12.3 *Replenishment of the Sodium Dichromate Content*—Calculate the weight, W_1 in oz, W_2 in g, of $Na_2Cr_2O_7 \cdot 2H_2O$ to be added to the solution as follows:

$$W_1 = (C_1 - C)\,V_1 \tag{11}$$

$$W_2 = (D_1 - D)\,V_2 \tag{12}$$

where:

W_1 = weight of sodium dichromate to be added to solution, oz,
W_2 = weight of sodium dichromate to be added to solution, g,
C_1 = original concentration of solution, oz/gal,
D_1 = original concentration of solution, g/L,
V_1 = volume of solution in tank, gal,
V_2 = volume of solution in tank, L.

METHOD C

13. Reagents

13.1 *Ammonium Bifluoride* (NH_4HF_2)

13.2 *Hydrochloride Acid* (1 + 1)—Mix 1 volume of concentrated hydrochloric acid (HCl) with 1 volume of water.

13.3 *Potassium Iodide* (KI), or 10 % potassium iodide solution.

13.4 *Sodium Thiosulfate, Standard Solution* (0.1 N)—Dissolve 24.8 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in 1 L of water and standardize.

13.5 *Starch Indicator Solution* (1 weight %).

Determination of Hexavalent Chromium as Sodium Dichromate

14. Procedure

14.1 Pipet a 25-mL sample into a 250-mL volumetric flask, dilute to the mark, and mix thoroughly. Pipet a 20-mL aliquot from the flask into a 300-mL Erlenmeyer flask. Add 120 mL of water. Add 2.0 g of ammonium bifluoride. Add 15 mL of HCl. Add 2 g of KI crystals or 10 mL of a 10 % KI solution. Titrate with the standard sodium thiosulfate solution until the color of the solution just changes to a light straw color. Add 3 mL of starch solution. Continue the titration until the blue color just disappears. Use an average of three determinations in the calculations.

15. Calculation

15.1 Calculate the hexavalent chromium as sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$), *G* in oz/gal, *H* in g/L, as follows:

$$G = 6.63\,VN \tag{13}$$

$$H = 49.7\,VN \tag{14}$$

where:

V = millilitres of sodium thiosulfate solution, and
N = normality of sodium thiosulfate solution.

16. Report

16.1 The report shall include the following:

16.1.1 Date solution was prepared,

16.1.2 Date tested,

16.1.3 Amount of sulfuric acid present,

16.1.4 Amount of sulfuric acid added,

16.1.5 Amount of hexavalent and trivalent chromium present,

16.1.6 Amount of sodium dichromate added,

16.1.7 Test method used, and

16.1.8 Number of tests made.

17. Keywords

17.1 acid etch; aluminum; chromate; sodium dichromate

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