



Designation: **D6019—15 D6019 – 20**

Test Method for Determination of Chromic Oxide in Basic Chromium Tanning Liquors (Ammonium Persulfate Oxidation)¹

This standard is issued under the fixed designation D6019; 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 This test method covers the determination of chromic oxide in chrome tanning liquors, either simple, with added aluminum or zirconium, or with the usual masking complexing agents.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Summary of Test Method

2.1 The solution is oxidized with ammonium persulfate until the chromium is completely converted to the chromate ion. The solution is boiled to complete oxidation of organic materials and to destroy excess ammonium persulfate; it is then cooled and acidified. Potassium iodide is added, and the liberated iodine is titrated with standardized sodium thiosulfate.

3. Terminology

3.1 Definitions:

3.1.1 *recycled chrome (reacidified chrome), n*—the mixture obtained when spent chrome liquor is captured, filtered, precipitated with alkali and the precipitate is reacidified with sulfuric acid.

4. Significance and Use

4.1 The procedure described is for the quality control for manufacturing liquors and specifications for the purchase of such liquors.

4.2 The chromium content of the liquors determines the amount to be used to obtain the desired degree of tannage, and hence may be a matter for specification in the purchase of leather.

5. Reagents and Materials

5.1 *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.² 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.

5.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean distilled water, deionized water or water of equal purity.

5.3 *Ammonium Persulfate*—20 % solution 100 g of persulfate into 500 mL water.

¹ This test method is under the jurisdiction of ASTM Committee D31 on Leather and is the direct responsibility of Subcommittee D31.06 on Chemical Analysis. Current edition approved Dec. 1, 2015 April 1, 2020. Published January 2016 May 2020. Originally approved in 1996. Last previous edition approved in 2015 as D6019 – 10, D6019 – 15. DOI: 10.1520/D6019-15.10.1520/D6019-20.

² *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

5.3.1 Alternatively, ammonium persulfate may be added in [5.56.6](#) as solid form using plastic scoopula.

5.4 *Starch Indicator, 2 %*—Make a paste of 2 g of soluble starch in about 10 mL of water, add 90 mL water, and boil for 1 min with stirring. Cool. Refrigerate after use. The solution is subject to decomposition and should be renewed if a deep blue color is not obtained on addition of one drop of indicator to a solution of 1 drop tincture of iodine in 100 mL of water.

5.5 *Sodium Thiosulfate Solution, 0.1 N*—Dissolve 24.85 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in water, add 1 g Na_2CO_3 , and dilute to 1 L.

5.5.1 *Standardization*—Dry potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in an oven at 130°C for 2 h and cool in a desiccator. Weigh into a glass stoppered Erlenmeyer flask (500 mL) about 0.2 g of potassium dichromate to an accuracy of 0.1 mg. Dissolve in 250 mL water, add 15 mL 1:4 hydrochloric acid, 20 mL of 10 % potassium iodide solution, stopper the flask, and allow to stand 5 min in the dark. Titrate with the sodium thiosulfate to be standardized. When the color of the solution has faded to a brownish-green, add 2 mL of 2 % starch solution, and continue titrating until the deep blue color changes to a clear green. Record the titration.

$$\text{normality of sodium thiosulfate} = \frac{\text{weight potassium dichromate}}{0.04903 \times \text{mL titration}} \quad (1)$$

The thiosulfate solution is quite stable but should be restandardized at least once a month.

5.6 *Potassium Dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$* , primary standard grade.

5.7 *Potassium Iodide, 10 %*—Dissolve 10 g KI in 100 mL water.

5.8 *Hydrochloric Acidacid*, 1:1—Dilute 250 mL concentrated hydrochloric acid (sp gr 1.19) in 250 mL water.

5.9 *Silver Nitrate, 1 %*—Dissolve 1 g of AgNO_3 in 100 mL water.

5.10 *Potassium Permanganate, 1 %*—Dissolve 1 g of KMnO_3 in 100 mL water.

5.11 *Sulfuric acid, concentrated.*

5.12 *Nitric acid, concentrated.*

6. Procedure

6.1 Weigh 11 to 12 g, to the nearest 0.1 mg, of the chrome tanning material to be analyzed. Record weight.

6.2 Quantitatively transfer to a 500 mL volumetric flask. Dilute to the mark and mix thoroughly.

6.3 Pipet 25 mL aliquots into each of 500 mL Erlenmeyer flasks. Add boiling chips or glass beads. Run in triplicate.

NOTE 1—Proceed with step 6.4 (commercially-available chrome tanning liquor) or step 6.5 (recycled chrome) as applicable.

6.4 *Commercially-available chrome tanning liquor*—Dilute to the ~~200~~250 mL mark of the flask with water.

6.4.1 Add 10 mL concentrated sulfuric acid. (Warning—This should be done in a hood. Heat and fumes will be generated).

6.4.2 Proceed to step 6.6.

6.5 *Recycled chrome digestion*—(Warning—This digestion should be done in a hood. Heat and fumes will be generated). Add 20 mL concentrated nitric acid, then 10 mL concentrated sulfuric acid.

6.5.1 Digest the mixture on the hot plate until the flask fills with dense white fumes and the solution is emerald (rich green) in color. (The solution may have whitish residue). Remove the flask from the hot plate and let it cool to room temperature. The solution should retain the emerald (rich green) color upon cooling.

NOTE 2—If the color of the solution is black or brown upon cooling, add additional 20 mL concentrated nitric to the same flask, then re-digest as in 6.5.1.

6.5.2 Dilute to the 250 mL mark of the flask with water. Then proceed to step 6.6.

6.6 Add the following chemicals in this order (chemicals:Warning—This should be done in a hood. Heat and fumes will be generated):

10 mL concentrated sulfuric acid

50 mL of 20 % ammonium persulfate solution or 10 g of ammonium persulfate

8 mL of 1 % silver nitrate solution

1 mL of 1 % potassium permanganate solution

6.7 Add boiling chips or glass beads and bring to a medium-Bring to a boil. At this stage the solution changes to an orange to red-brown color. If the orange to red-brown stage, a permanganate color (dark red; red-brown) should develop. If the permanganate color fails to develop, or fades on boiling, remove the heat and flask from the hot plate. Cool slightly, then carefully add 5-10 mL of additional 20 % ammonium persulfate solution or 1-2 g of additional ammonium persulfate. Swirl to mix. If necessary, continue addition of ammonium persulfate (5-10 mL of 20 % ammonium persulfate solution or 1-2 g of ammonium persulfate, at a time) until the orange to red-brown permanganate color is permanent. This-Then proceed to step 6.7.1. The permanganate color will not be permanent until all of the chromium is oxidized.

6.7.1 Continue the medium boil for 1-1.5 h. Boil the mixture for 20-30 min.

NOTE 3—Additional water may be added to keep final volume at least 200 mL. The permanganate color must hold during this boiling duration. If the