Designation: D5400 – 15

# Standard Test Methods for Hydroxypropylcellulose[1]

## 1. Scope*

1.1 These test methods cover the testing of hydroxypropylcellulose.

1.2 The test procedures appear in the following order:

| | Sections |
|---|---|
| Moisture | 4 – 9 |
| Viscosity | 10 – 16 |
| pH | 17 – 21 |
| Residue on Ignition | 22 – 28 |
| Hydroxypropoxy Content | 29 – 36 |

1.3 The values stated in SI units are to be regarded as the standard. The 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.* For specific hazard statements, see 26.6.

## 2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3876 Test Method for Methoxyl and Hydroxypropyl Substitution in Cellulose Ether Products by Gas Chromatography

E70 Test Method for pH of Aqueous Solutions With the Glass Electrode

## 3. Reagents

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 distilled water.

## MOISTURE

## 4. Scope

4.1 This test method covers the determination of the volatile content of hydroxypropylcellulose.

## 5. Significance and Use

5.1 The results of this test are used for calculating the total solids in the sample; and, by common usage, all materials volatile at this test temperature are designated as moisture.

5.2 Moisture analysis (along with residue on ignition) is a measure of the amount of active polymer in the material and must be considered when determining the amount of hydroxypropylcellulose to use in various formulations.

## 6. Apparatus

6.1 *Oven,* gravity convection, capable of maintaining a temperature of 105 ± 3°C.

6.2 *Weighing Dish,* glass or aluminum, with cover, 50 mm in diameter, 25 mm in height, or equivalent.

6.3 *Analytical Balance.*

## 7. Procedure

7.1 Weigh about 5 g of sample to the nearest 0.001 g in a tared and covered weighing dish.

7.2 Place it in an oven at 105 ± 1°C for 3 h with the cover removed.

7.3 Remove the dish from the oven, immediately replace the cover, cool in a desiccator, and weigh.

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[1] These test methods are under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.36 on Cellulose and Cellulose Derivatives.

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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*, 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.

***A Summary of Changes section appears at the end of this standard**

**TABLE 1 Cylindrical Rotational Elements and Speeds (see Fig. 1)**

| Viscosity Range, (mPa·s) | Diameter (D) (mm) | Length (L) (mm) | Speed (rmin) | Torque Scale Multiplier |
|---|---|---|---|---|
| 10 to 80 | 19 | 65 | 60 | 1 |
| 20 to 160 | 19 | 65 | 30 | 2 |
| 50 to 400 | 10 | 54 | 60 | 5 |
| 100 to 800 | 10 | 54 | 30 | 10 |
| 400 to 1600 | 5.9 | 43 | 60 | 20 |
| 800 to 3200 | 5.9 | 43 | 30 | 40 |
| 2000 to 8000 | 3.2 | 31 | 60 | 100 |
| 4000 to 16 000 | 3.2 | 31 | 30 | 200 |

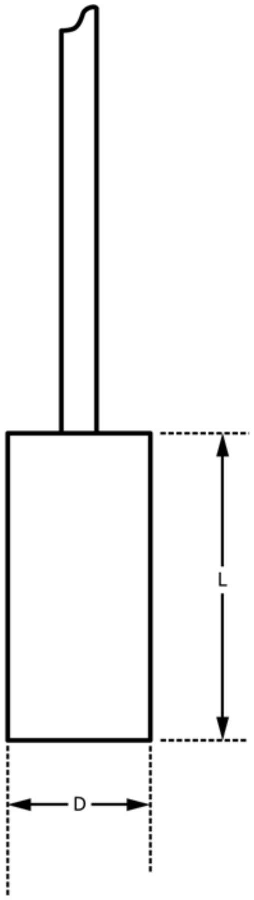

FIG. 1 Cylindrical Rotational Elements and Speeds

## 8. Calculation

8.1 Calculate the percent moisture, $M$, as follows:

$$M = (A/B) \times 100 \tag{1}$$

where:

$A$ = mass loss on heating, g, and
$B$ = sample used, g.

8.2 Report the moisture content to the nearest 0.1 %.

## 9. Precision and Bias

9.1 *Precision*—Statistical analysis of intralaboratory test results on samples containing from 1 to 6 % moisture indicates a precision of ±0.2 % absolute at the 95 % confidence level.

9.2 *Bias*—No justifiable statement on bias can be made as no suitable reference material is available as a standard.

## VISCOSITY

## 10. Scope

10.1 This test method is an arbitrary method of determining the viscosity of aqueous solutions of hydroxypropylcellulose in the viscosity range of 10 to 16 000 mPa · s (cP) at 25°C.

10.2 The concentration to be used for the test shall be agreed upon between the purchaser and the seller. It shall be such that the viscosity of the solution will fall within the range of this test.

10.3 The results for the viscosity of hydroxypropylcellulose by this test method will not necessarily agree with results from other types of instruments used for viscosity measurement.

10.4 The determinations are run on a calculated dry basis; that is, the amount of hydroxypropylcellulose required for the desired concentration on a dry basis is calculated from the known moisture content.

## 11. Significance and Use

11.1 The rotational elements and speeds given in Table 1 are recommended for this purpose. Slight deviations from Table 1 may be found convenient for an individual application.

11.2 This test method determines the relative ability of the polymer to thicken aqueous solutions and is therefore related to the concentration required in various formulations to achieve the desired finished product viscosity.

## 12. Apparatus

12.1 *Viscometer, Rotational*—The essential instrumentation required providing the minimum rotational viscometer analytical capabilities for this method include:

12.1.1 A *drive motor*, to apply a unidirectional displacement to the specimen at a rate from 0.5 to 60 rev/min constant to within ±1 %.

12.1.2 A *force sensor* to measure the torque developed by the specimen.

12.1.3 A *coupling shaft* or other means to transmit the rotational displacement from the motor to the specimen.

NOTE 1—It is helpful to have a mark on the shaft to indicate the appropriate level of the specimen.

12.1.4 A *rotational element, spindle or tool* to fix the specimen between the drive shaft and a stationary position.

NOTE 2—The rotational element shall be of the immersion type. This standard is not intended for cone-and-plate or parallel plate type viscometers.

NOTE 3—Each rotational element typically covers a range of about two decades of viscosity. The rotational element is selected so that the measured viscosity is between 15 and 95 % of the range of the rotational element.

12.1.5 A *guard* to protect the rotational element from mechanical damage.

12.1.6 A *temperature sensor* to provide an indication of the specimen temperature of the range of 20 to 30°C to within 0.1°C.

12.1.7 A *data collection device*, to provide a means of acquiring, storing, and displaying measured or calculated signals, or both. The minimum output signals required for rotational viscometry are torque, rotational speed, temperature, and time.

12.1.8 A *stand*, to support, level, and adjust the height of the drive motor, shaft, and rotational element.

12.1.9 *Container,* glass bottle, 350-cm$^3$ (12-oz) approximately 64 mm (2½ in.) in outside diameter and 152 mm (6 in.) high.

12.2 *Mechanical Stirrer,* agitator as shown in Fig. 2, attached to a variable-speed motor capable of 1500 r/min.

12.3 A constant-temperature *bath*, set at 25°C and capable of maintaining that temperature to within ±0.5°C.

12.4 *Water Bath,* constant-temperature, set at 25°C and capable of maintaining that temperature to within ±0.5°C.

## 13. Preparation of the Test Specimen

13.1 Determine the moisture in accordance with Sections 4 – 9.

13.2 Calculate the sample mass, *S*, in grams necessary to make 250 g of test solution as follows:

$$S = \frac{A \times 100}{100 - B} \tag{2}$$

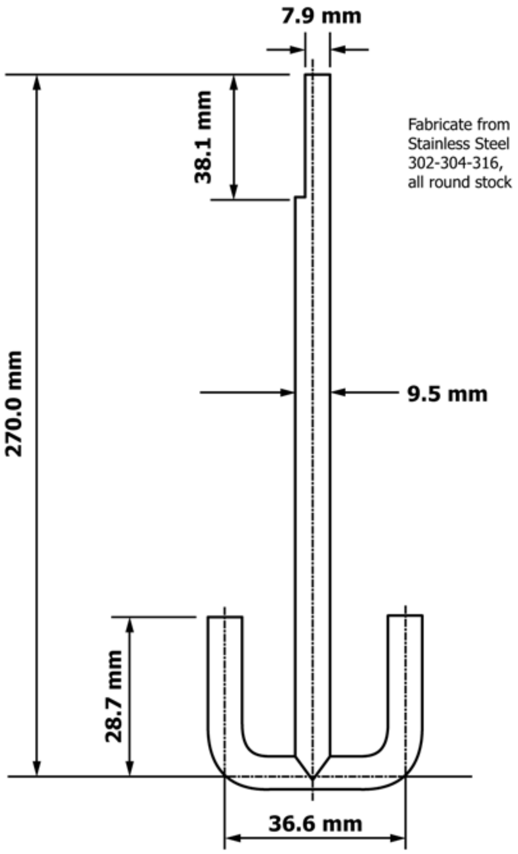

FIG. 2 Stainless Steel Agitator

where:

$A$ = desired dry mass of sample, g, and
$B$ = percent moisture in the weighed sample.

13.3 Calculate the mass of water required, *W*, in grams as follows:

$$W = 250 - S \tag{3}$$

where:

$S$ = sample mass, g.

13.4 Weigh the water into the glass bottle and place it on the stirrer, mixing at a speed sufficient to cause a vortex but not fast enough to splash.

13.5 Sprinkle the hydroxypropylcellulose sample into the water slowly, to prevent lumping. Increase stirring speed to approximately 900 ± 100 r/min and stir until the sample is completely dissolved (1 to 2 h).

13.6 Remove the glass bottle from the stirrer, cap the bottle, and place it in the constant temperature bath for 30 min or as long as necessary to bring the solution to 25 ± 0.5°C.

13.7 Remove the glass bottle from the water bath and invert it slowly 4 to 5 times, taking care to minimize the introduction of air bubbles.

## 14. Procedure

14.1 Select the appropriate rotational element so that the torque reading is near the midpoint of the scale at a rotational speed between 30 and 60 r/min for the viscosity of the test specimen.

14.2 Allow the element to rotate for 3 to 4 min before taking a reading.

14.3 Measure and report the viscosity with the rotational viscometer, following the manufacturer's operating instructions.

NOTE 4—If the room temperature is considerably greater or less than 25°C; the entire operation of stirring, standing, and measurement should be conducted with the glass bottle suspended in the constant temperature bath.

## 15. Report

15.1 Report the following information:

15.1.1 Results, as apparent viscosity in mPa·(cP) at 25°C,

15.1.2 Solution concentration,

15.1.3 A complete description of the viscometer including manufacturer, model number, rotational element, and rotational speed and temperature used.

## 16. Precision and Bias

16.1 *Precision*—Statistical analysis of interlaboratory test results indicates a precision of ±10 % at the 95 % confidence level.

16.2 *Bias*—No justifiable statement on bias can be made as no suitable reference material is available as a standard.

## pH

## 17. Scope

17.1 This test method covers the determination of the pH of aqueous solutions of hydroxypropylcellulose.

## 18. Significance and Use

18.1 This test method determines the relative acidity or alkalinity of aqueous solutions of hydroxypropylcellulose. This must be taken into consideration when determining materials of construction for equipment and packaging for handling and storing these solutions. Also, pH may affect suitability for certain end-use applications.

## 19. Apparatus

19.1 *pH Meter,* with glass electrodes.

## 20. Procedure

20.1 Determine the pH of the viscosity solution from 13.5, using a suitable pH meter that has been standardized according to Test Method E70.

## 21. Precision and Bias

21.1 *Precision*—Statistical analysis of intralaboratory test results on samples with pH values of 4.5 to 8.5 indicates a precision of ±5 % at the 95 % confidence level.

21.2 *Bias*—No justifiable statement on bias can be made as no suitable reference material is available as a standard.

## RESIDUE ON IGNITION

## 22. Scope

22.1 This test method covers the determination of the amount of residue left from igniting a sample of hydroxypropylcellulose after being moistened first with sulfuric acid and then with hydrofluoric acid.

## 23. Significance and Use

23.1 Excessive residue on ignition can affect solution clarity and film properties. The residue on ignition (along with moisture) is a measure of the amount of active polymer in the material and must be considered when determining the amount of hydroxypropylcellulose to use in various formulations.

23.2 Commercially available hydroxypropylcellulose most often has up to 0.60 % silica added as an anti-caking agent. Therefore, a hydrofluoric acid ashing step is required to remove the silica.

## 24. Apparatus

24.1 *Dishes,* platinum, 75-mL capacity.

24.2 *Hot Plate.*

24.3 *Muffle Furnace,* capable of reaching 1000 ± 25°C.

## 25. Reagents

25.1 *Sulfuric Acid (sp gr 1.84)*—concentrated sulfuric acid ($H_2SO_4$).

25.2 *Hydrofluoric Acid* (48 %).

## 26. Procedure

26.1 Weigh, to the nearest 0.0001 g, about 1 g of hydroxypropylcellulose into a tared platinum dish. Using a hot plate, heat the dish containing the sample (gently at first) until the sample is thoroughly charred. Cool the dish for several minutes.

26.2 Moisten the residue with about 1 mL of sulfuric acid and heat gently on the hot plate until white fumes are no longer evolved.

26.3 Place the dish in a muffle furnace at 800 ± 25°C for 30 min. Allow the dish to cool.

26.4 Repeat 26.2 and 26.3. Cool in a desiccator. Weigh the residue ($R_1$).

26.5 Moisten the residue with up to 1 mL of water and carefully add about 5 mL of hydrofluoric acid, in small portions. Evaporate to dryness on a hot plate in a fume hood. Allow the dish to cool.

26.6 Carefully add about 5 mL of hydrofluoric acid and 0.5 mL of sulfuric acid and evaporate to dryness on a hot plate in a fume hood. (**Warning**—Hydrofluoric acid is a poisonous and extremely hazardous acid because of its ability to cause severe burns that are not immediately painful or visible. Use extreme care in handling.)

26.7 Place the dish in a muffle furnace at 1000 ± 25°C for 20 min. Allow the dish to cool in a desiccator. Weigh the residue ($R_2$).

## 27. Calculations

27.1 Calculate the percent residue on ignition, *RI*, as follows:

$$RI = \left(R_2/S\right) \times 100 \tag{4}$$

where:

$R_2$ = ash after ignition with hydrofluoric acid, g, and
$S$ = sample used, g.

27.2 The percent silica content, Si, may be calculated as follows:

$$\mathrm{Si} = \left(R_1 - R_2\right) / S \times 100 \tag{5}$$

where:

$R_1$ = ash after ignition with sulfuric acid, g,
$R_2$ = ash after ignition with hydrofluoric acid, g, and
$S$ = sample used, g.

## 28. Precision and Bias

28.1 *Precision*—Statistical analysis of intralaboratory test results on samples containing 0.00 to 0.30 % residue on ignition indicates a precision of ±10 % at the 95 % confidence level.

28.2 *Bias*—No justifiable statement on bias can be made as no suitable reference material is available as a standard.

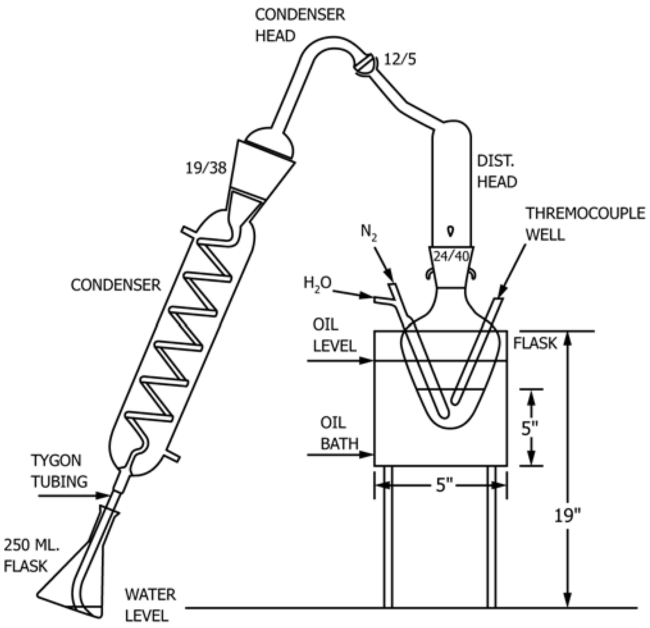

**FIG. 3 Oxidation and Distillation Apparatus**

## HYDROXYPROPOXY CONTENT[4,5]

### 29. Scope

29.1 This test method covers the determination of the hydroxypropoxy content of hydroxypropylcellulose.

### 30. Summary of Test Method

30.1 A sample of hydroxypropylcellulose is refluxed with aqueous chromic acid solution. The resulting acetic acid is distilled and titrated with standard sodium hydroxide solution.

### 31. Significance and Use

31.1 This test method determines the amount of substituent groups added to the cellulose backbone. The level can affect solution properties, rheology, solubility parameters, and film properties.

31.2 Gas chromatographic procedures involving cleavage of side groups with hydriodic acid (see Test Method D3876) are not applicable for highly substituted hydroxypropylcellulose because the amount of hydriodic acid and the temperature required to achieve complete reaction lead to side reactions that render the method non-quantitative.

### 32. Apparatus

32.1 *Chromic Acid Oxidation Apparatus,* as illustrated in Fig. 3. The inlet for nitrogen and water in the reaction flask is a 1-mm capillary tip.

32.2 *Oil Bath,* equipped with an electrical heating device so the bath can be maintained at 155°C.

32.3 *Analytical Balance,* capable of weighing to 0.0001 g.

### 33. Reagents

33.1 *Chromium Trioxide Solution (30 %)*—Dissolve 30 g of chromic trioxide ($CrO_3$) in 70 ml of water.

33.2 *Nitrogen*—Use a nitrogen cylinder with suitable reducing valve.

33.3 *Potassium Iodide (KI).*

33.4 *Sodium Bicarbonate* ($NaHCO_3$)—powder.

33.5 *Sodium Hydroxide Standard Solution (0.02 N),* carbon dioxide free.

33.6 *Sodium Thiosulfate Standard Solution (0.02 N).*

33.7 *Sulfuric Acid Solution (10 %)*—Carefully add 60 mL of concentrated sulfuric acid to 940 mL of water, slowly while stirring.

33.8 *Phenolphthalein Indicator Solution,* 1 %.

33.9 *Starch Indicator Solution.*

### 34. Procedure

34.1 Weigh to the nearest 0.0001 g, 70 to 80 mg of hydroxypropylcellulose, previously dried at 105°C for 1 h, into the reaction flask. Add 10 mL of water and swirl gently for 5 min. Then add 10 mL of chromium trioxide solution and assemble the apparatus as shown in Fig. 2.

34.2 Immerse the reaction flask in the oil bath slightly above the level of the chromium trioxide solution. Start the condenser cooling water, and pass nitrogen gas through the flask at a rate of 70 to 75 mL/minute. Raise the temperature of the oil bath to 155°C over a 30-min time period, and maintain it at that temperature throughout the determination. Too rapid an initial rise in temperature results in high blanks.

34.3 Monitor the temperature of the reaction mixture using a thermocouple or thermometer in a well as shown in Fig. 2. When the temperature of the reaction mixture reaches 101 to 103°C, add water through the water inlet until the temperature drops to 96 to 98°C. Continue this cycle until 100 mL of distillate has been collected. Detach the condenser from the distillation head and wash with water, collecting the washings in the flask containing the distillate.

34.4 Add 2 or 3 drops of phenolphthalein indicator solution to the distillate and titrate with 0.02 *N* sodium hydroxide solution until a pink color persists momentarily. Place the flask on a hot plate, boil for one minute, cool, and continue the titration to a pink color which persists for 10 s. Record the total volume of sodium hydroxide solution used, $A$.

34.5 Add 0.5 g of sodium bicarbonate to the flask and swirl to mix. Then add 10 mL of sulfuric acid solution (10 %), swirl, and allow to stand until carbon dioxide evolution ceases. Add 1 g of potassium iodide, stopper, and mix well to dissolve. Allow the solution to stand in the dark for 5 min. Titrate the liberated iodine with 0.02 *N* sodium thiosulfate solution,

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[4] References for the hydroxypropoxy determination are as follows: *United States Pharmacopeia XXII*, General Chapter 421, "Hydroxypropoxy Determination," 1990, p. 1537, *National Formulary XVII*, "Monograph for Hydroxypropyl Cellulose," 1990, p. 1938, United States Pharmacopeial Convention, Inc., 12601 Twinbrook Parkway, Rockville, MD 20852.

[5] Hercules Test Method No. K45-3, "Klucel Molecular Substitution," Hercules Test Method No. M100-53, "Terminal Methyl Groups (Chromic Acid Oxidation)," available from Hercules, Inc. c/o Aqualon Co., P.O. Box 271, Hopewell, VA 23860-5245. Klucel is a registered trademark of Aqualon Co.

adding starch indicator near the end point. Record the total volume of sodium thiosulfate solution used, *B*.

34.6 *Empirical Factor, K*—The empirical factor, *K*, for each apparatus is obtained by running a blank determination in which the hydroxypropylcellulose is omitted.

## 35. Calculations

35.1 The empirical factor, *K*, is calculated as follows:

$$K = \frac{\text{mL NaOH for the blank} \times N}{\text{mL Na}_2S_2O_3 \text{ for the blank} \times N'} \tag{6}$$

where:

$N$ = normality of the 0.02 $N$ NaOH solution, mL, and
$N'$ = normality of the 0.02 $N$ $Na_2S_2O_3$ solution, mL.

35.2 The percent hydroxypropoxy, *HP*, is calculated as follows:

$$HP = \left( \frac{[(A \times N) - K(B \times N')] \times F}{W} \right) \times 100 \tag{7}$$

where:

$A$ = volume of NaOH solution used, mL,
$N$ = normality of the 0.02 $N$ NaOH solution,
$K$ = empirical factor,
$B$ = volume of $Na_2S_2O_3$ solution used, mL,
$N'$ = normality of the 0.02 $N$ $Na_2S_2O_3$ solution,
$W$ = sample used, g, and
$F$ = molecular weight of group determined/1000 × recovery.

Recovery for propylene glycol was found to be 0.95 and the molecular weight of the hydroxypropoxy group is 75. Therefore, $F = 0.079$ in this case.

## 36. Precision and Bias

36.1 *Precision*—Statistical analysis of intralaboratory test results on samples containing 65 to 80 % hydroxypropoxy content indicates a precision of ±15 % at the 95 % confidence level.

36.2 *Bias*—No justifiable statement on bias can be made as no suitable reference material is available as a standard.

## 37. Keywords

37.1 hydroxypropoxy content; hydroxypropylcellulose; moisture; pH; residue on ignition; viscosity

## SUMMARY OF CHANGES

Committee D01 has identified the location of selected changes to this standard since the last issue (D5400-03(2013)) that may impact the use of this standard. (Approved December 1, 2015.)

*(1)* Sections 10 to 16 are revised to include a generic apparatus description for a rotational viscometer.
*(2)* Figure 1 is added.
*(3)* Figure 2 is revised to include metric dimensions.