Designation: D817 – 12

Standard Test Methods of Testing Cellulose Acetate Propionate and Cellulose Acetate Butyrate[1]

This standard is issued under the fixed designation D817; 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 These test methods cover procedures for the testing of cellulose acetate propionates and acetate butyrates. These esters may vary widely in composition and properties, so certain of the procedures can be used only in the ranges of composition where they are suitable.

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

1.3 The test procedures appear in the following sections:

	Sections
Acetyl Propionyl or Butyryl Contents	28 – 37
Acetyl Content, Apparent	18 – 27
Acidity, Free	12 – 17
Ash	7 – 10
Color and Haze	77 – 81
Heat Stability	57 – 65
Hydroxyl Content	38 – 44
Hydroxyl Content, Primary	46 – 50
Intrinsic Viscosity	67 – 71
Moisture Content	5-6
Sulfur or Sulfate Content	51 – 56
Viscosity	74-75
Limiting Viscosity Number	67 – 71

1.4 *This standard does not purport to address 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]

D618 Practice for Conditioning Plastics for Testing

D1343 Test Method for Viscosity of Cellulose Derivatives by Ball-Drop Method

D2929 Test Method for Sulfur Content of Cellulosic Materials by X-Ray Fluorescence

D5897 Test Method for Determination of Percent Hydroxyl on Cellulose Esters by Potentiometric Titration—Alternative Method

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.

4. Conditioning

4.1 *Conditioning*—Condition the test specimens at 23 ± 2°C (73.4 ± 3.6°F) and 50 ± 5 % relative humidity for not less than 40 h prior to test in accordance with Procedure A of Practice D618, for those tests where conditioning is required. In cases of disagreement, the tolerances shall be ±1°C (±1.8°F) and ±2 % relative humidity.

4.2 *Test Conditions*—Conduct tests in the Standard Laboratory Atmosphere of 23 ± 2°C (73.4 ± 3.6°F) and 50 ± 5 % relative humidity, unless otherwise specified in the test methods. In cases of disagreements, the tolerances shall be ±1°C (±1.8°F) and ±2 % relative humidity.

MOISTURE CONTENT

5. Procedure

5.1 Transfer about 5 g of the sample to a tared, low, wide-form weighing bottle and weigh to the nearest 0.001 g. Dry in an oven for 2 h at 105 ± 3°C. Remove the bottle from the oven, cover, cool in a desiccator, and weigh.

[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.

6. Calculation

6.1 Calculate the percentage of moisture as follows:

$$\text{Moisture, } \% = (A/B) \times 100 \quad (1)$$

where:

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

ASH

7. Significance and Use

7.1 Ash content gives an estimate of the inorganic content of cellulose ester samples. The presence of high levels of inorganic content (ash) can be detrimental to the melt stability and optical clarity of a cellulose ester in melt processing or act as a potential source of insolubles when the ester is used in solution.

8. Procedure

8.1 Dry the sample for 2 h at 105 ± 3°C and weigh 10 to 50 g, to the nearest 0.01 to 0.1 g, depending on its ash content and the accuracy desired. Burn directly over a flame in a 100-mL tared platinum crucible that has been heated to constant weight and weighed to the nearest 0.1 mg. Add the sample in portions if more than 10 g is taken. The sample should burn gently and the portions should be added as the flame subsides. Continue heating with a burner only as long as the residue burns with a flame. Transfer the crucible to a muffle furnace and heat at 550 to 600°C for 3 h, or longer if required, to burn all the carbon. Allow the crucible to cool and then transfer it, while still warm, to a desiccator. When the crucible has cooled to room temperature, weigh accurately to the nearest 0.1 mg.

9. Calculation

9.1 Calculate the percentage of ash as follows:

$$\text{Ash, } \% = (A/B) \times 100 \quad (2)$$

where:

A = ash, g, and
B = sample used, g.

10. Precision and Bias

10.1 No statement on bias can be made as no reference material is available as a standard.

FREE ACIDITY

11. Significance and Use

11.1 Free acidity is a measure of unesterified organic acid in the ester. The presence of high levels of free acid is potentially detrimental to melt processing of the ester and can impact the odor of the ester.

12. Reagents

12.1 *Acetone,* neutral.

12.2 *Methyl Red Indicator Solution (0.4 g/L)*—Dissolve 0.1 g of methyl red in 3.72 mL of 0.1000 *N* NaOH solution and dilute to 250 mL with water. Filter if necessary.

12.3 *Phenolphthalein Indicator Solution (1 g/100 mL)*—Dissolve 1 g phenolphthalein in 100 mL of ethyl alcohol (95 %).

12.4 *Sodium Hydroxide, Standard Solution* (0.01 *N*)—Prepare and standardize a 0.01 *N* solution of sodium hydroxide (NaOH).

Test Method A—For Samples Containing Not More than About 30 % Propionyl or Butyryl

13. Procedure

13.1 Shake 5 g of the sample, corrected for moisture content if necessary, in a 250-mL Erlenmeyer flask with 150 mL of freshly boiled, cold water. Stopper the flask and allow it to stand for 3 h. Filter off the cellulose ester and wash it with water. Titrate the combined filtrate and washings with 0.01 *N* NaOH solution, using phenolphthalein indicator solution.

13.2 Run a blank determination on the water, using the same volume as was used in extracting the sample.

14. Calculation

14.1 Calculate the percentage of acidity as free acetic acid as follows:

$$\text{Free acetic acid, } \% = \{[(A - B)C \times 0.06]/W\} \times 100 \quad (3)$$

where:

A = NaOH solution used to titrate the sample, mL,
B = NaOH solution used to titrate the blank, mL,
C = normality of the NaOH solution, and
W = sample used, g.

Test Method B—For Samples Containing More than About 7 %Propionyl or Butyryl and Particularly Suitable for Samples Containing More than 30 % Propionyl or Butyryl

15. Procedure

15.1 Dissolve 10.0 g of the sample, corrected for moisture content if necessary, in 200 mL of neutral acetone plus 20 mL of water. When completely dissolved, add 50 mL of water and shake well to precipitate the ester in a finely divided form. Add 3 drops of methyl red indicator solution and titrate to a lemon-yellow end point and 0.01 *N* NaOH solution.

15.2 Make a blank determination on the reagents.

16. Calculation

16.1 Calculate the free acid content as acetic acid as directed in Section 14.

17. Precision and Bias

17.1 No statement on bias can be made as no reference material is available as a standard.

APPARENT ACETYL CONTENT

18. Scope

18.1 The test methods described in the following Sections 20 to 26 cover the determination of the saponification value of

the sample calculated as percentage of apparent acetyl, equivalent weight 43. This value is required in the calculation of acetyl and propionyl or butyryl contents in 36.1.

18.2 The test method used should be specified or agreed upon. The choice depends on the propionyl or butyryl content and the physical condition of the sample. Ordinarily, Test Method A is recommended for samples having less than about 35 % propionyl or butyryl and Test Method B for samples having more than that amount.

19. Significance and Use

19.1 Apparent acetyl content is a measure of the saponification value of the ester. Apparent acetyl value is required in the calculation of acetyl, propionyl, and butyryl content in 36.1.

Test Method A—For Samples Containing Less than About 35 % Propionyl or Butyryl

20. Apparatus

20.1 *Weighing Bottle,* glass-stoppered, 15-mL capacity, 25-mm diameter by 50 mm high.

20.2 *Tray,* copper or aluminum, approximately 137 mm square, containing 25 compartments 25 mm square. Each compartment shall have the correct dimensions to contain one weighing bottle. The entire tray shall fit inside a desiccator and should have a basket-type handle to facilitate the introduction and removal of the tray (convenient but not essential).

20.3 *Buret,* automatic zero, 35-mL, 25-mL bulb, stem graduated from 25 to 35 mL in 0.05-mL increments; or pipet, automatic zero, 30-mL for NaOH solution (40 g/L).

20.4 *Buret,* automatic zero, 15-mL, 10-mL bulb, stem graduated from 10 to 15 mL in 0.05-mL increments, for 1 *N* H_2SO_4.

20.5 *Buret,* 5-mL, in 0.01 or 0.1-mL divisions, for back titration with 0.1 *N* NaOH solution.

20.6 *Magnetic Stirrer,* for single flask.

20.7 *Magnetic Stirrer,* capacity twelve or more flasks.

20.8 *Stirring Bars,* stainless steel Type 416, length 50 mm, diameter 5 to 6 mm or equivalent, dimensions not critical.

21. Reagents

21.1 *Acetone*—Add one 30-mL portion of 1.0 *N* NaOH solution to a mixture of 150 mL acetone and 100 mL hot water, allow to stand with frequent swirling for 30 min, and titrate with 1.0 *N* H_2SO_4. Add another 30-mL portion of 1.0 *N* NaOH solution to 100 mL of hot water, allow to stand for 30 min, and titrate as above. The difference between the two titrations shall not exceed 0.05 mL.

21.2 *Dimethyl Sulfoxide.*

21.3 *Pyridine.*

21.4 *Sodium Hydroxide Solution (40 g/L)*—Dissolve 40 g of sodium hydroxide (NaOH) in water and dilute to 1 L.

21.5 *Sodium Hydroxide, Standard Solution* (0.1 *N*)—Prepare and standardize a 0.1 *N* solution of NaOH.

21.6 *Sulfuric Acid Standard* (1.0 *N*)—Prepare and standardize a 1.0 *N* solution of sulfuric acid (H_2SO_4).

21.7 *Phenolphthalein Indicator Solution (1 g/100 mL)*—Dissolve 1 g of phenolphthalein in 100 mL of ethyl alcohol (95 %).

22. Procedure

22.1 Dry the ground well-mixed sample in weighing bottle for 2 h at 105 ± 3°C and weigh 1.9 ± 0.05 g of the dried sample by difference to the nearest 1 mg into a 500-mL Erlenmeyer flask. Prepare a blank by drying approximately 3.8 g of potassium acid phthalate and weighing it by difference into a flask as described above. Carry the blank through the entire procedure.

NOTE 1—Potassium acid phthalate is used so that the concentration of the NaOH in contact with the solvent in the blank will be approximately the same as that in contact with the sample and so that the titration of the blank will be approximately the same as the titration of the sample, thus avoiding errors caused by using a different buret for the titration of the blank and the sample or by refilling the 15-mL buret. If desired, however, the potassium acid phthalate may be omitted.

22.2 For acetone-soluble sample, put the sample into solution as follows: Add 150 mL of acetone and 5 to 10 mL of water and swirl to mix. Stopper the flask and allow it to stand with occasional swirling until solution is complete. Solution may be hastened by magnetic stirring or by any suitable mechanical shaking that will provide a gentle rocking type of agitation to avoid splashing the solution on the stopper. It is essential that complete solution be effected.

22.3 For acetone-insoluble samples of low propionyl or butyryl content, dissolve the sample by either of the following two methods:

22.3.1 Gently rotate the flask by hand to distribute and spread the sample in a thin layer over the bottom of the flask. Add 70 mL of acetone to the flask and swirl gently until the sample particles are completely wetted and evenly dispersed. Stopper the flask and allow it to stand undisturbed for 10 min. Carefully add 30 mL of dimethyl sulfoxide from a graduate to the flask, pouring the solvent down the sides of the flask to wash down any sample particles clinging to the side. Stopper the flask and allow it to stand with occasional swirling until solution is complete. Magnetic stirring or gentle mechanical agitation that will not splash the solution is recommended. When solution appears to be complete, add 50 mL of acetone and swirl or stir for 5 min. Proceed in accordance with 22.4.

22.3.2 Dimethyl sulfoxide is the preferred solvent, but if it is not available, spread the sample in a thin layer over the bottom of the flask, add 15 mL of acetone, swirl to wet the particles with acetone, stopper the flask, and allow the mixture to stand undisturbed for 20 min. Add 75 mL of pyridine without shaking or swirling and allow the mixture to stand for 10 min. Heat the solution just to boiling and swirl or stir for 5 min. Again heat to boiling and swirl or stir for 10 min. Continue to heat and stir until the mixture is homogeneous and all large gel masses are broken down into individual highly swollen particles. When these highly swollen gel particles are well dispersed and are not fused together in large gel masses,

no further heating is necessary. Cool the flask, add 30 mL of acetone, and swirl or stir for 5 min.

22.4 Add 30 mL of NaOH solution (40 g/L) with constant swirling or stirring to the solution of the sample and also to the blank. Use of a magnetic stirrer is recommended (Note 2). It is absolutely necessary that a finely divided precipitate of regenerated cellulose, free of lumps, be obtained. Stopper the flask and let the mixture stand with occasional swirling or stir on the magnetic stirring unit. Allow 30 min for saponification of lower acetyl samples, 2 h for high acetyl samples when dimethyl sulfoxide is the solvent, and 3 h when pyridine is the solvent. At the end of the saponification period, add 100 mL of hot water, washing down the sides of the flask, and stir for 1 or 2 min. Add 4 or 5 drops of phenolphthalein indicator solution and titrate the excess NaOH solution with 1.0 *N* H_2SO_4 (Note 3). Titrate rapidly with constant swirling or stirring until the end point is reached; then add an excess of 0.2 or 0.3 mL of H_2SO_4. Allow the mixture to stand with occasional stirring or preferably stir on the magnetic stirrer for at least 10 min. Then add 3 drops of phenolphthalein indicator solution to each flask and titrate the same excess of acid with 0.1 *N* NaOH solution to a persistent phenolphthalein end point. Take extreme care to locate this end point; after the sample is titrated to a faint pink end point, swirl the mixture vigorously or place it for a moment on the magnetic stirrer. If the end point fades because of acid soaking from the cellulose, continue the addition of 0.1 *N* NaOH solution until a faint persistent end point remains after vigorous swirling or stirring. Titrate the blank in the same manner as the sample.

NOTE 2—While the amount of magnetic stirring is somewhat optional, such stirring during the entire period of the determination is strongly recommended. Solution is more rapid, titrations are more rapid, and the end point can be approached directly and without a back titration.

NOTE 3—It is important to correct all 1.0 *N* H_2SO_4 buret readings for temperature and buret corrections.

23. Calculation

23.1 Calculate the percentage by weight of acetyl as follows (see Note 4):

$$\text{Acetyl, } \% = \{[(D - C)N_a - (B - A)N_b + P] \times 0.04305\}/W \times 100 \quad (4)$$

$$P = (GH \times 1000)/204.2$$

where:

A = NaOH solution required for titration of the sample, mL,
B = NaOH solution required for titration of the blank, mL,
N_b = normality of the NaOH solution,
C = H_2SO_4 required for titration of the sample, mL
D = H_2SO_4 required for titration of the blank, mL,
N_a = normality of the H_2SO_4,
P = milliequivalents of potassium acid phthalate,
G = potassium acid phthalate used, g,
H = purity factor for potassium acid phthalate, and
W = sample used, g.

NOTE 4—When equal volumes of alkali or acid are added to samples and blank, these amounts cancel out. Thus only the amounts of each added in the titration enter into the calculations. Use of potassium acid phthalate in the blank is recommended. When it is not used, the term *P* drops out of the equation.

Test Method B—For Cellulose Esters Containing More than 30 % Propionyl or Butyryl, by Varying the Reagents[4]

24. Reagents

24.1 *Acetone–Alcohol Mixture*—Mix equal volumes of acetone and methyl alcohol.

24.2 *Hydrochloric Acid, Standard* (0.5 *N*)—Prepare and standardize a 0.5 *N* solution of hydrochloric acid (HCl).

24.3 *Phenolphthalein Indicator Solution (1 g/100 mL)*—Dissolve 1 g of phenolphthalein in 100 mL of ethyl alcohol (95 %).

24.4 *Pyridine – Alcohol Mixture*—Mix equal volumes of pyridine and methyl alcohol.

24.5 *Sodium Hydroxide, Aqueous Solution (20 g/L)*—Dissolve 20 g of sodium hydroxide (NaOH) in water and dilute to 1 L with water.

24.6 *Sodium Hydroxide, Methanol Solution (20 g/L)*—Dissolve 20 g of NaOH in 20 mL of water and dilute to 1 L with methyl alcohol.

25. Procedure

25.1 Dry the sample for 2 h at 105 ± 3°C and cool in a desiccator. Weigh 0.5-g portions of the sample to the nearest 0.005 g and transfer to 250-mL glass-stoppered Erlenmeyer flasks. Dissolve each sample in 100 mL of appropriate solvent (see 25.2 and 25.3) and prepare at least two blanks, which shall be carried through all steps of the procedure.

25.2 *Samples Containing 30 to 45 % Propionyl or Butyryl*—Dissolve in 100 mL of the acetone–alcohol mixture. Add water and aqueous NaOH solution from a buret or pipet in the following order and swirl the contents of the flask vigorously during all additions: 10 mL of NaOH solution, 10 mL of water, 10 mL of NaOH solution, 5 mL of water, 20 mL of NaOH solution, and 5 mL of water. Stopper and allow to stand at room temperature for 16 to 24 h.

25.3 *Samples Containing More than 45 % Propionyl or Butyryl*—Dissolve in 100 mL of the pyridine–alcohol mixture. Add 30 mL of the methanol solution of NaOH from a pipet or buret slowly, with swirling. Add 20 mL of water slowly in about 2-mL portions, with swirling, and swirl the flask until the solution becomes turbid. Stopper and allow to stand overnight at room temperature.

25.4 Back-titrate the excess NaOH with 0.5 *N* HCl just to the disappearance of color, using phenolphthalein indicator solution.

26. Calculation

26.1 Calculate the apparent acetyl content as follows:

$$\text{Apparent acetyl, } \% = \{[(A - B)N_a \times 0.04305]/W\} \times 100 \quad (5)$$

[4] Malm, C. J., Genung, L. B., Williams, R. F., Jr., and Pile, M. A., "Analysis of Cellulose Derivatives: Total Acyl in Cellulose Organic Esters by Saponification in Solution," *Industrial and Engineering Chemistry*, Analytical Edition, IENAA, Vol 16, 1944, pp. 501–504.

where:

A = HCl required for titration of the blank, mL,
B = HCl required for titration of the sample, mL,
N_a = normality of the HCl, and
W = sample used, g.

27. Precision and Bias

27.1 No statement on bias can be made as no reference material is available as a standard.

ACETYL AND PROPIONYL OR BUTYRYL CONTENTS

28. Scope

28.1 The test methods described in the following Sections 30 to 36 cover the determination of acetyl and propionyl or butyryl contents of cellulose mixed esters by calculation from the apparent acetyl content, determined in accordance with Sections 18 to 26, and the molar ratio of acetyl and propionyl or butyryl, determined in accordance with Sections 30 to 35. The molar ratio of acetyl and propionyl or butyryl is determined by saponifying, acidifying, vacuum distilling off the mixture of acids, and determining the distribution ratio of the acids between *n*-butyl acetate and water. The distribution ratios are also determined for acetic, propionic, and butyric acids, using samples of known high purity, and the molar ratio of the acids in the sample is calculated from these values.[5]

28.2 The saponification conditions are varied depending on the propionyl or butyryl content of the sample. Use Procedure A (Section 32) for samples containing less than about 35 % propionyl or butyryl, and use Procedure B (Section 33) for samples containing more than that amount.

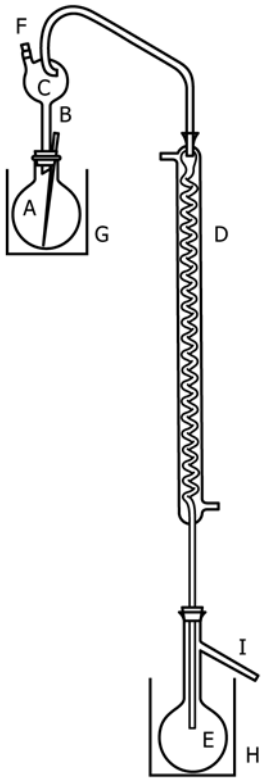
28.3 Analyses for combined acetic, propionic, and butyric acids may be done by gas chromatographic methods. Difficulties encountered include ghosting in the columns, variation of factors with composition, and inconsistencies in the use of pure acids as standards. When such methods are used for this purpose, they shall be cross checked with the following partition method using suitable check batches to establish accuracy.

29. Significance and Use

29.1 Acetyl and propionyl or butyryl content is a measure of the amount of each of these acids esterified onto the cellulose backbone of the polymer. The amount of substitution of these esters has a very strong effect on the polymer's solubility and physical properties.

30. Apparatus

30.1 *Vacuum Distillation Apparatus*—The vacuum distillation apparatus shown in Fig. 1 will be required. The 500-mL round-bottom flask, *A*, shall be fitted with a stopper carrying a very small capillary inlet tube, *B*, and a Kjeldahl distilling head, *C*. The Kjeldahl distilling head shall be connected to a vertical condenser, *D*, having an outlet tube long enough to reach within 76.2 mm of the bottom of the 500-mL distilling flask, *E*, used as a receiver. The Kjeldahl distilling head shall be equipped with a funnel or stoppered opening, *F*, for adding extra water during the distillation. A water bath, *G*, for heating the sample and a cooling bath, *H*, for cooling the receiver shall be provided.



A—Flask containing sample (500-mL, round-bottom).
B—Capillary inlet tube.
C—Kjeldahl distilling head.
D—Condenser.
E—Receiver (500-mL distilling flask).
F—Opening for adding water.
G—Water bath for heating sample.
H—Cooling bath for receiver.
I—Side arm, connected to vacuum line.

FIG. 1 Vacuum Distillation Apparatus for Mixed-Ester Analysis

31. Reagents

31.1 *Acetic, Propionic, and Butyric Acids*—Acetic, propionic, and butyric acids of tested purity.

31.2 *Bromcresol Green Indicator Solution (0.4 g/L)*—Grind 0.1 g of tetrabromo-*m*-cresolsulfonphthalein in a mortar with 14.3 mL of 0.01 *N* NaOH solution and dilute to 250 mL.

31.3 *n-Butyl Acetate*—Prepare *n*-butyl acetate for use as an extraction solvent, free of acidity and water and containing not more than 2 % butyl alcohol. Check for acidity by shaking 60 mL of the *n*-butyl acetate with 30 mL of water in a 125-mL separatory funnel for about 1 min. Allow to settle, draw off the water layer, and titrate with 0.1 *N* NaOH solution, using phenolphthalein as the indicator. If this requires more than 0.02

[5] Malm, C. J., Nadeau, G. F., and Genung, L. B., "Analysis of Cellulose Derivatives: Analysis of Cellulose Mixed Esters by the Partition Method," *Industrial and Engineering Chemistry*, Analytical Edition, IENAA, Vol. 14, 1942, pp. 292–297. This reference may be consulted for application to other mixed esters and to three-component mixtures.

mL of 0.1 *N* NaOH solution, the butyl acetate should be purified or a correction for acidity applied to each titration.

31.4 *Ethyl Alcohol,* Formula 2B, 3A, or 30 (denatured).

31.5 *Phosphoric Acid (1 + 14)*—Dilute 68 mL of phosphoric acid (H_3PO_4, 85 %) to 1 L with water. Titrate the NaOH solution (20 g/L) with this acid to a yellow end point, using bromcresol green indicator solution, and calculate the volume of the acid (approximately 50 mL) required for 100 mL of the NaOH solution.

31.6 *Sodium Hydroxide Solution (20 g/L)*—Dissolve 20 g of sodium hydroxide (NaOH) in water and dilute to 1 L.

31.7 *Sodium Hydroxide, Standard Solution* (0.1 *N*)—Prepare and standardize a 0.1 *N* solution of NaOH.

Isolation of the Mixed Acids

32. Procedure A—For Samples Containing Less than About 35 % Propionyl or Butyryl

32.1 Heat duplicate 3-g portions of the sample, not especially dried nor accurately weighed, with 100 mL of NaOH solution (20 g/L) in 500-mL, round-bottom, chemically resistant glass flasks in a water bath at 40°C for 48 to 72 h. At the end of this time add the required amount (approximately 50 mL) of H_3PO_4 (1 + 14) to each flask to form monosodium phosphate, which liberates the organic acids from their sodium salts.

32.2 Assemble the vacuum distillation apparatus as illustrated in Fig. 1. Heat the 500-mL round-bottom flask containing the sample in a water bath, and vacuum-distill the acid solutions to dryness, allowing a small stream of air bubbles to enter to avoid bumping. Keep the receiver cooled to 0°C. Add 25 mL of water to the residue in each flask and again distill to dryness. Repeat the distillation to dryness with a second 25-mL portion of water.

NOTE 5—In this operation it is not necessary to work with quantitative accuracy at all stages, but it is necessary to obtain water solutions of the acids in the same ratios as they occur in the esters. The volume of the distillate and rinsings is usually 200 to 250 mL, which in the majority of cases automatically adjusts the acidity of the distillate to 0.06 to 0.12 *N*, the range desired for subsequent extractions.

32.3 Continue as directed in Section 34.

33. Procedure B—For Samples Containing More than About 35 % Propionyl or Butyryl

33.1 Weigh duplicate 3-g samples, not especially dried nor accurately weighed, into 500-mL round-bottom flasks and add 100 mL of Formula 2B, 3A, or 30 denatured ethyl alcohol and 100 mL of NaOH solution (20 g/L) to each flask. Allow the samples to stand stoppered at room temperature for 48 to 72 h. At the end of this period, filter off the regenerated cellulose, collecting the filtrates in 500-mL round-bottom flasks.

33.2 Assemble the vacuum-distillation apparatus as illustrated in Fig. 1. Heat the flasks in the water bath and vacuum-distill off all the alcohol. After distilling to dryness, release the vacuum, rinse out the distillation heads, condensers, and receivers, and discard the distillates and rinsings.

33.3 Add the required amount, about 50 mL, of H_3PO_4 (1 + 14) to form monosodium phosphate, which liberates the organic acids from their sodium salts. Also add 100 mL of water to each flask and reassemble the distillation apparatus. Vacuum-distill the volatile acids as described in 32.2.

33.4 Continue as directed in Section 34.

Determination of the Molar Ratios of the Acids

34. Procedure

34.1 Titrate a 25-mL portion of the distillate (32.2) with 0.1 *N* NaOH solution, using phenolphthalein as the indicator. Designate the volume of NaOH solution required as *M*. Shake 30 mL of the distillate in a small separatory funnel with 15 mL of *n*-butyl acetate. Measure these volumes accurately using pipets and burets. Shake the mixture thoroughly for 1 min, allow the layers to separate for 2 min, and draw off the aqueous (lower) layer. Pipet out 25 mL of the solution and titrate with 0.1 *N* NaOH solution (Note 6). Designate the volume of NaOH solution required as M_1. Calculate *K*, the percentage partition ratio of the acids in the distillate, as follows:

$$K = (M_1/M) \times 100 \quad (6)$$

NOTE 6—It should be kept in mind that all these determination are ratios and not quantitative; however, accuracy of duplication is very important. All measurements must be made as exactly as those made by standardizations of the solutions and equipment.

34.2 In the same manner determine the distribution ratios for acetic, propionic, and butyric acids. Dilute a sample of each acid of tested purity with water to give an approximately 0.1 *N* solution. Titrate 25-mL portions and extract 30-mL portions, following exactly the same procedure as used for the mixtures (34.1). Calculate the partition ratios for the pure acids, as decimal fractions, as follows (Note 7):

$$k = M_1/M \quad (7)$$

where:

k_a = distribution ratio for acetic acid under the conditions described,
k_p = distribution ratio for propionic acid under the conditions described, and
k_b = distribution ratio for butyric acid under the conditions described.

NOTE 7—The constants must be checked occasionally and must be determined by each operator for each supply of butyl acetate. Blanks should be run on the butyl acetate, since it may develop acidity on standing, particularly if it contains a little water. All measurements should be made with good pipets or burets and extreme care and cleanliness observed during the whole operation. The accuracy of the procedure can be checked by testing an acid mixture of known composition.

35. Calculation

35.1 Calculate the molar ratios of acetic and propionic or butyric acids in the mixed acids as follows (Note 8):

$$P = (100k_a - K)/(k_a - k_p) \quad (8)$$

$$A = 100 - P \quad (9)$$

$$B = (100k_a - K)/(k_a - k_b) \quad (10)$$

$$A = 100 - B \quad (11)$$

where:

P = percentage of propionic acid, mol,
B = percentage of butyric acid, mol,
A = percentage of acetic acid, mol,
K = percentage distribution ratio of the acids in the distillate (34.1),
k_a = distribution ratio of acetic acid (34.2),
k_p = distribution ratio of propionic acid (34.2), and
k_b = distribution ratio of butyric acid (34.2).

NOTE 8—In order to evaluate two unknowns, two simultaneous algebraic equations involving the two unknown quantities are necessary. In the case of a binary acid mixture, the sum of the mol percentages of the acids present represents the total acidity, or 100 %. If A and B represent the mole percentages of acetic and butyric acids, respectively:

$$A + B = 100 \quad (12)$$

$$Ak_a + Bk_b = K \quad (13)$$

The distribution ratios k_a and k_b are known and refer to the pure individual acids, whereas the distribution ratio K refers to the binary mixture. By solving these equations for B, the equations given in this section may be derived.

Calculation of Acetyl, Propionyl, and Butyryl Contents

36. Calculation

36.1 Calculate the percentages by weight of acetyl, propionyl, and butyryl as follows:

$$\text{Acetyl, \%} = AC/100 \quad (14)$$

$$\text{Propionyl, \%} = (PC/100) \times (57/43) \quad (15)$$

$$\text{Butyryl, \%} = (BC/100) \times (71/43) \quad (16)$$

where:

A = percentage of acetic acid (Section 35), mol,
P = percentage of propionic acid (Section 35), mol,
B = percentage of butyric acid (Section 35), mol, and
C = percentages by weight of apparent acetyl (Sections 23 and 26).

36.2 Hydroxyl can be measured precisely, particularly at high degrees of esterification (Sections 38 to 44). It is therefore sometimes advantageous to base the calculation of weight percentages of acetyl, propionyl, and butyryl on hydroxyl content rather than on apparent acetyl as in 36.1. The equations for this calculation are as follows:

For cellulose acetate propionates:

$$\text{Acetyl, \%} = 9.15A\,(31.5 - h)/(786 - A) \quad (17)$$

$$\text{Propionyl, \%} = 2.93P\,(31.5 - h)/(786 - A) \quad (18)$$

For cellulose acetate butyrates:

$$\text{Acetyl, \%} = 4.88A\,(31.5 - h)/(443 - A) \quad (19)$$

$$\text{Butyryl, \%} = 8.05B\,(31.5 - h)/(443 - A) \quad (20)$$

where, in addition to the definitions of terms in 36.1:
h = weight percentage of hydroxyl (Section 44).

NOTE 9—This calculation involves the assumption that there are exactly three hydroxyls, free plus esterified, for each anhydroglucose unit of cellulose.

37. Precision and Bias

37.1 No statement on bias can be made as no reference material is available as a standard.

HYDROXYL CONTENT

38. Scope

38.1 This test method is applicable to pyridine-soluble cellulose esters and is especially useful when the hydroxyl content is low. (Samples containing plasticizer may be analyzed directly by this test method because the plasticizer is removed during washing of the carbanilate).

38.2 A preferred method is available in Test Method D5897.

39. Summary of Test Method

39.1 Hydroxyl in cellulose esters is determined by reaction with phenyl isocyanate in pyridine solution under anhydrous conditions to form the carbanilate derivative. The derivative is then analyzed for its carbanilate content by ultraviolet absorption.

40. Significance and Use

40.1 Hydroxyl content is a measure of the free hydroxyl on the cellulose backbone of the polymer. Hydroxyl content has a strong effect on the polymer's solubility and physical properties. Hydroxyl content also impacts the propensity for this polymer to crosslink with various crosslinking agents.

41. Apparatus

41.1 *Spectrophotometer,* complete with hydrogen light source and a set of four 1.00-cm quartz cells or an equally suitable apparatus. The wavelength calibration, as checked against a mercury lamp, shall be within the manufacturer's tolerances. As a further check, measure the density of a potassium chromate (K_2CrO_4) solution prepared as follows: Dissolve 0.0400 g of K_2CrO_4 or 0.0303 g of potassium dichromate ($K_2Cr_2O_7$) in 0.05 *N* potassium hydroxide (KOH) solution and dilute to 1 L in a volumetric flask with 0.05 *N* KOH solution. Using the hydrogen lamp measure the absorbance at 280 nm of a silica cell filled with the K_2CrO_4 solution and also of the same cell filled with water. The absorbance of the solution minus that of the blank shall be 0.723 ± 0.023.

41.2 *Bottles,* 112-g (4-oz), with screw caps, for washing the samples.

41.3 *Special Reflux Tubes* for the carbanilation, constructed as follows (see Fig. 2): Make a test tube approximately 20 by 150 mm from the outer part of a standard-taper 24/40 ground-glass joint by closing the open end in a blast lamp. Draw the tubing on the inner joint to a constriction just above the joint. Cut the glass at the point and seal on a short length of 8-mm tubing to provide a bearing for a glass stirrer. Make a stirrer of 4-mm glass rod with a semicircle at right angles to the shaft at the bottom and small enough to fit into the test tube. When properly constructed this unit acts as an air condenser, thus preventing the loss of solvent by evaporation.

41.4 *Pipet,* serological type, 5-mL capacity, graduated in 0.1-mL divisions.

41.5 *Büchner Funnel,* of a size accommodating 90-mm filter paper.

41.6 *Automatic Shaker,* with speed regulator mechanism.

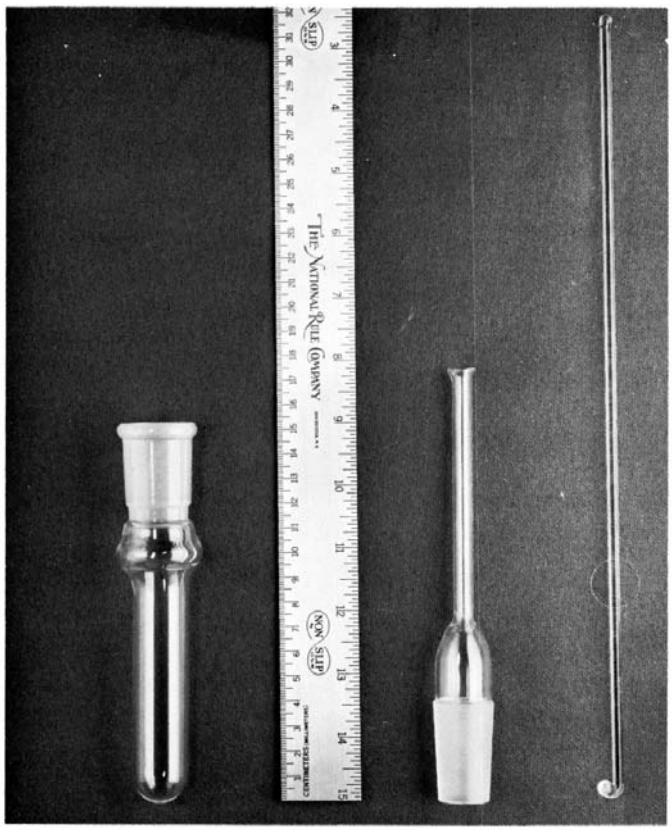


FIG. 2 Special Reflux Tube for Carbanilation

41.7 *Electric Oven,* maintained at 105 ± 3°C.

41.8 *Oil Bath,* equipped with a rack to hold several of the special reflux tubes. This bath shall be kept between 115 and 120°C.

42. Reagents

42.1 *Acetone.*

42.2 *Ethyl Alcohol,* Formula 2B, 3A, or 30 (denatured).

42.3 *Methylene Chloride–Methyl Alcohol Mixture*—Mix 9 parts by weight of methylene chloride with 1 part of methyl alcohol. This mixture should have an absorbance of less than 0.2 at 280 nm in a 1.00-cm silica cell measured against air. Pure methylene chloride has an absorbance of about 0.05, but the commercial product may have an absorbance as high as 1.00. The methylene chloride and methyl alcohol should be selected to have low absorbance; otherwise, they should be redistilled.

42.4 *Phenyl Isocyanate.*

42.5 *Pyridine,* redistilled, of low water content, preferably less than 0.05 %.

43. Procedure

43.1 In the following procedure the phenyl isocyanate reagent shall be used under anhydrous conditions. Therefore, the sample, containers, pipet, and all other equipment shall be thoroughly dried.

43.2 Place a 0.5-g sample in a special reflux tube and dry in an electric oven at 105 ± 3°C for 2 h. Remove the tube from the oven, add 5 mL of pyridine, assemble the reflux apparatus complete with glass stirring rod, and place in the 115 to 120°C oil bath. Stir occasionally until the sample is completely dissolved. Add 0.5 mL of phenyl isocyanate, stir thoroughly, and reflux in the oil bath for ½ h to complete the reaction. Use 0.1 mL of phenyl isocyanate for each 1 % of estimated hydroxyl content, but never less than 0.5 mL.

43.3 At the end of the reaction time, remove the sample and dilute it with acetone to the proper viscosity for precipitation. The amount of acetone used to thin the solution is a critical factor in acquiring a good precipitate. Samples having low viscosity require little, if any, dilution. The average sample requires the addition of about an equal volume of acetone. Precipitate the carbanilate by pouring the solution into about 200 mL of ethyl alcohol, or if the ester contains more than 20 % propionyl or butyryl, into the same volume of cold 80 % alcohol. Stir the alcohol vigorously during the precipitation. The precipitate should be fluffy and white. Sticky precipitates indicate too little dilution. Filter off the precipitate using paper on a Büchner funnel, with suction applied only as long as is necessary to remove the bulk of the solvent; prolonged suction may cause undesirable clumping together of the precipitate.

43.4 Wash the precipitate with alcohol, unless the sample was precipitated in cold 80 % alcohol. In this case, wash the precipitate in cold 90 % alcohol. Washing is best accomplished by transferring the precipitate to a 4-oz screw cap bottle containing about 75 mL of alcohol and shaking for ½ h on an automatic shaker. Filter, pressing out as much liquid as possible with a glass stopper. Repeat the washing and filtering operations twice more.

NOTE 10—Samples of high hydroxyl content and large amounts of propionyl or butyryl may give gummy precipitates when poured into cold 80 % alcohol. Samples of this type give improved precipitates when precipitated in the reverse manner. Pour the diluted reaction solution into a 600-mL beaker, taking care to distribute the solution evenly on the bottom. Chill the beaker in a brine bath for 30 to 60 s. Pour about 200 mL of cold 80 % alcohol onto the chilled liquid. Wash the resulting precipitate and filter in the usual manner using cold 90 % alcohol.

43.5 Allow the precipitate to air-dry 1 to 2 h at room temperature with good ventilation or preferably overnight to ensure complete removal of the alcohol. (Samples wet with alcohol may sinter and stick to paper or glass when dried at 105°C.) Dry the sample at 105°C in the oven for 1 h and cool in a desiccator. Small manila envelopes are convenient for drying and cooling the samples.

43.6 Weigh 0.1231 g of the dry precipitate into a 100-mL volumetric flask fitted with a ground-glass stopper. Add 60 to 80 mL of methylene chloride-methyl alcohol mixture, and shake occasionally until complete solution occurs. Dilute to 100 mL and mix thoroughly. Using the spectrophotometer with a 1-cm silica cell, measure the absorbance of the solution at 280 nm against the solvent mixture as a reference.

44. Calculations

44.1 Calculate the percentage of carbanilate, *c*, for a sample weight of 0.1231 g as follows:[6]

$$\text{Carbanilate, } \% = A \times 17.1 \quad (21)$$

where:

A = absorbance.

44.2 Calculate the percentage of hydroxyl as follows:

$$\text{Hydroxyl, } \% = 14.3c/(100 - c) \quad (22)$$

45. Precision and Bias

45.1 No statement on bias can be made as no reference material is available as a standard.

PRIMARY HYDROXYL CONTENT

46. Summary of Test Method

46.1 The primary hydroxyl content of cellulose ester is determined by formation of the triphenylmethyl (trityl) ether and measurement of the trityl group by ultraviolet absorbance.[6] Trityl chloride reacts preferentially with primary hydroxyls. Since there is also a slight reaction with secondary hydroxyls, standardized reaction conditions are important.[7]

47. Apparatus

47.1 See Section 41.

48. Reagents

48.1 *Acetone.*

48.2 *Ethyl Alcohol,* Formula 2B, 3A, or 30 (denatured).

48.3 *Methylene Chloride-Methyl Alcohol Mixture*—Mix 9 parts by weight of methylene chloride with 1 part of methyl alcohol. This mixture should have an absorbance of less than 0.2 at 259 mm in a 1-cm silica cell measured against air; otherwise, the solvents should be redistilled.

48.4 *Pyridine,* redistilled to a water content less than 0.05 %. The water content may be reduced further by storing over a suitable drying agent, such as a molecular sieve, Type 4A.

48.5 *Trityl Chloride* (Chlorotriphenylmethane or Triphenylmethyl Chloride).

49. Procedure

49.1 The reagents must be used under anhydrous conditions. It is imperative that the sample and all equipment be thoroughly dry.

49.2 Place a 0.5-g sample in the test tube of the special reflux apparatus and dry for 2 h at 105 ± 3°C. Add 5 mL of pyridine, insert the top of the reflux apparatus and the stirring, and heat with stirring in a 115 to 120°C oil bath. After the sample has dissolved, add 0.5 g of trityl chloride. If the total hydroxyl content exceeds 3 %, use an additional 0.075 g of trityl chloride for each additional 1 % hydroxyl. Stir the mixture thoroughly and reflux in the oil bath for exactly 2 h at 115 to 120°C. Remove the tube and cool.

49.3 Dilute the sample with acetone to the proper viscosity for precipitation. The amount of acetone used to thin the solution is a critical factor in obtaining a good precipitate. Samples having low viscosity require little, if any, dilution. The average sample requires the addition of about an equal volume of acetone. Precipitate the trityl derivative by pouring the solution into about 200 mL of ethyl alcohol with vigorous stirring. The precipitate should be fluffy and white. Sticky precipitates indicate too little dilution. Separate the precipitate by filtering through paper on a Büchner funnel, with suction applied only as long as necessary to remove the bulk of the solvent; prolonged suction may evaporate the alcohol and cause the precipitate to partially redissolve in the remaining pyridine.

49.4 Wash the precipitate by transferring it to a 4-oz screw cap bottle containing 75 mL of ethyl alcohol, capping securely, and shaking for ½ h on a shaker at medium speed. Again collect the precipitate on a Büchner funnel, pressing out as much liquid as possible with a glass stopper. Repeat this washing and filtering operation twice more, or until the absorbance of the filtrate at 259 nm is about the same as that of an alcohol blank. Allow the precipitate to air-dry on the filter paper for ½ h at room temperature with good ventilation, or preferably overnight, to remove most of the alcohol. (Samples wet with alcohol may sinter or stick to paper or glass when dried at 105°C). Transfer the sample to a manila envelope, dry it for 1 h at 105°C, and cool in a desiccator.

49.5 Weigh a 0.1231-g sample of the dry trityl ether derivative into a 100-mL volumetric flask fitted with a ground-glass stopper, and dissolve in the methylene chloride-methyl alcohol mixture. Dilute to 100 mL and mix thoroughly. Measure the absorbance of this solution in a 1-cm silica cell using a spectrophotometer at 259 nm against the solvent as a reference.

50. Calculation

50.1 Calculate the trityl content, *t*, for this concentration of 0.1 g/100 g and with a correction of 0.015 for the absorbance of the cellulose acetate as follows:[7]

$$\text{Trityl, } \% = 25.25(A - 0.015) \quad (23)$$

where:

A = absorbance.

[6] Malm, C. J., Tanghe, L. J., Laird, B. C., and Smith, G. D., "Determination of Total and Primary Hydroxyl in Cellulose Esters by Ultraviolet Absorption Methods," *Analytical Chemistry*, ANCHA, Vol 26, 1954, p. 189.

[7] Malm, C. J., Tanghe, L. J., and Laird, B. C., "Primary Hydroxyl Groups in Hydrolyzed Cellulose Acetate," *Journal of the American Chemical Society*, JACSA, Vol 72, 1950, p. 2674.

50.2 Calculate the weight percentage of primary hydroxyl as follows:

$$\text{Primary hydroxyl, \%} = 7.02\,t/(100.4 - t) \quad (24)$$

50.3 Calculate the percentage primary hydroxyl of the total hydroxyl as follows:

$$\text{Primary hydroxyl of total hydroxyl, \%} = (B/C) \times 100 \quad (25)$$

where:

B = value of primary hydroxyl as determined in 50.2, and
C = value of total hydroxyl as determined in 44.2.

SULFUR OR SULFATE CONTENT

51. Summary of Test Method

51.1 The sulfur or sulfate content of cellulose acetate is measured by oxidizing the sample in a nitric acid-perchloric acid mixture and determined gravimetrically as barium sulfate. To determine combined sulfur the sample must first be reprecipitated into dilute acid to remove noncombined sulfur compounds.

51.2 The sulfur or sulfate content may also be determined by Test Method D2929, The X-ray method shall be calibrated against the chemical method following in Sections 53 to 54, and the sample shall be treated in accordance with 53.1, if combined sulfur is to be determined.

52. Significance and Use

52.1 Sulfur and sulfate content indicates the amount of sulfur in the cellulose ester either as inorganic salts (usually sulfates) or as organic sulfate (usually as sulfate ester combined to the cellulose backbone). The presence of high levels of sulfur and sulfate can be detrimental to the melt stability of the ester.

53. Apparatus

53.1 *Funnel,* modified by cutting the stem off at the apex of the funnel and fire polishing.

53.2 *Crucibles,* 30-mL, extra-fine porosity.

53.3 *Oven,* controlled at 120 to 125°C.

53.4 *Muffle Furnace,* controlled at 800 ± 50°C.

54. Reagents

54.1 *Acetone.*

54.2 *Acetic Acid (1 + 49)*—Mix 1 volume of glacial acetic acid with 49 volumes of water.

54.3 *Barium Chloride Solution (100 g/L)*—Dissolve 100 g of barium chloride ($BaCl_2 \cdot 2H_2O$) in water and dilute to 1 L.

54.4 *Hydrochloric Acid (1 + 1)*—Mix 1 volume of concentrated hydrochloric acid (sp gr 1.19) with 1 volume of water.

54.5 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO_3).

54.6 *Nitric Acid (2 + 3)*—Mix 2 volumes of concentrated nitric acid (sp gr 1.42) with 3 volumes of water.

54.7 *Nitric Acid-Perchloric Acid Mixture*—Mix 5 volumes of concentrated HNO_3 with 1 volume of concentrated perchloric acid ($HClO_4$, 70 %).

54.8 *Phenolphthalein Indicator Solution (1 g/100 ml)*—Dissolve 1 g of phenolphthalein in 100 mL of ethyl alcohol (95 %).

54.9 *Silver Nitrate Solution (50 g/L)*—Dissolve 50 g of silver nitrate ($AgNO_3$) in water and dilute to 1 L.

54.10 *Sodium Carbonate*—(Na_2CO_3).

54.11 *Sodium Hydroxide Solution* (400 g/L)—Dissolve 400 g of sodium hydroxide (NaOH) in water and dilute to 1 L.

55. Procedure

Treatment Prior to Analysis

55.1 Remove uncombined sulfur as follows (Note 11): Dissolve 25 g of sample in approximately 300 mL of acetone, depending on the viscosity. If the sample is of too high acetyl content to be directly soluble in acetone, cool in a dry ice cabinet overnight; then allow to come to room temperature while tumbling or stirring. Filter the solution, if necessary, through felt or a coarse sintered-glass crucible. Precipitate with rapid stirring into a beaker or pail containing 2 to 3 L of acetic acid (1 + 49). Filter through a cloth bag or a Büchner funnel and give two 15-min washes with water using mechanical agitation. A little Na_2CO_3 may be added to the last wash to stabilize samples of high sulfur content. Filter and dry overnight at 60°C.

NOTE 11—To analyze for total sulfur content omit this treatment.

Decomposition

55.2 Weigh 10 ± 0.1 g of cellulose acetate and transfer to a clean wide-mouth, 500-mL Erlenmeyer flask. Add 50 mL of the HNO_3–$HClO_4$ mixture to the flask, and swirl the flask gently to wet the sample thoroughly. Place the modified funnel in the mouth of the flask and heat the flask carefully on a hot plate in a fume hood. (**Warning**—Use the utmost care in handling the HNO_3–$HClO_4$ mixture. If a spill occurs, wash down with plenty of water. Wear safety glasses or a face shield.)

55.3 After the mixture becomes hot and less viscous, increase the heat of the hot plate. Continue the digestion until all the sample has been oxidized and the thick reddish-brown fumes of nitric oxide have been expelled. At this point, white fumes will appear and a rather vigorous reaction will occur that is caused by the last traces of organic material being oxidized and the nitric acid fuming off.

55.4 When this reaction starts, remove the flask from the hot plate, swirl gently for a few seconds, and set it on the shelf in front of the hood until the reaction is complete. Place the flask back on the hot plate and continue the digestion until the $HClO_4$ refluxes about half way up the side of the Erlenmeyer flask and about 5 mL is left in the flask. The HNO_3–$HClO_4$ mixture should be clear and colorless. If it is not, set the flask off the hot plate to cool and then add 3 to 5 mL of HNO_3 (sp gr 1.42). Replace the flask on the hot plate and continue heating

until the $HClO_4$ refluxes half way up the flask. Remove the flask from the hot plate and allow the flask and its contents to cool.

Determination of Barium Sulfate

55.5 Wash the modified funnel top thoroughly with water, collecting the rinsings in the flask. Add 50 mL of water. Swirl the flask to mix the solution thoroughly. Add 2 drops of phenolphthalein indicator solution and neutralize the acid with the NaOH solution to a faint pink. Acidify immediately with HCl (1 + 1), dropwise, until the solution is just acid to phenolphthalein; then add 2 mL of HCl (1 + 1).

55.6 Filter through a 12.5-cm fine-porosity paper into a clean 400-mL beaker. Wash the flask thoroughly with water, filtering the washings through the paper. Finally wash the paper thoroughly with ten portions of hot water. Dilute the filtrate to approximately 200 mL. Place the beaker on the hot plate and heat almost to boiling. Slowly add 10 mL of $BaCl_2$ solution from a pipet, stirring the solution during the addition. Do not add the $BaCl_2$ solution rapidly, as from a graduate, since the rapid addition will produce an impure precipitate. Remove the stirring rod from the beaker and wash it with a stream of water from the wash bottle, collecting the washings in the beaker. Cover the beaker with a watch glass and keep the mixture near the boiling temperature for 6 h or overnight. Do not allow the liquid to evaporate to dryness.

55.7 Using suction, decant the supernatant liquid through an extra-fine porosity porcelain filter crucible that has been previously rinsed with acetone, ignited, and weighed to the nearest 0.1 mg. Transfer the precipitate with the aid of a stream of hot water. Always use a stirring rod in this transfer. Scrub the sides and bottom of the beaker with a rubber policeman to remove any adhering precipitate. The crucibles may be used to collect several precipitates one on top of the other. Close control of temperature and time of heating and cooling are necessary. Cleaning with hot water is generally sufficient; drastic attack with cleaning solution should be avoided.

55.8 Wash the precipitate on the filter until free of chlorides by the following test: To 5 mL of wash water, collected in a separate test tube or on a watch glass, add 1 mL of HNO_3 (2 + 3) and 1 mL of $AgNO_3$ solution. The appearance of a milky white precipitate indicates the presence of chlorides, and the washing should therefore continue until the test is negative. Do not attempt to get a completely negative test for chloride. Discontinue washing when no more than a faint opalescence is produced in the test.

55.9 Finally pour a few millilitres of pure acetone through the filter and suck it dry. Place the crucible in a larger crucible or in a metal tray with perforated sides and bottom for protection and place it in an oven at 120 to 125°C for 1 h. Do not handle the crucibles with the fingers between ignition and the completion of weighing; use forceps.

55.10 Remove the crucible from the oven and ignite it for 10 min in a muffle furnace at 800 ± 50°C. Cool in a desiccator for 75 ± 15 min and weigh to the nearest 0.0001 g. It is permissible to return the crucible to the oven for at least 15 min before transferring to the desiccator.

55.11 From time to time, and especially when using new reagents, run a blank in duplicate in the reagents. If the weight of the precipitate exceeds 0.0005 g, investigate and eliminate the cause. This is equivalent to an error of 0.002 % on a 10-g sample.

56. Calculation

56.1 Calculate the percentage of sulfur and sulfate as follows:

$$\text{Sulfur, } \% = \{[(C - B) - (E - D)] \times 0.1374/A\} \times 100 \quad (26)$$

$$\text{Sulfate, } \% = \{[(C - B) - (E - D)] \times 0.4115/A\} \times 100 \quad (27)$$

where:

A = weight of sample, g,
B = weight of crucible for sample, g,
C = weight of crucible and $BaSO_4$ for sample, g,
$C - B$ = weight of $BaSO_4$ for sample, g,
D = weight of crucible for blank, g,
E = weight of crucible and $BaSO_4$ for blank, g, and
$E - D$ = weight of $BaSO_4$ for blank, g.

HEAT STABILITY

57. Summary of Test Method

57.1 The heat stability of a cellulose ester is one indication of its quality. It is measured by heating the sample for a specified time and temperature, observing it for amount and uniformity of color developed, and possibly also measuring the loss of viscosity as a result of heating. Suggested times of heating are 8 h at 160°C, 8 h at 180°C, or 2 h at 190°C. The time and temperature of heating, method of grading, and limits are matters for agreement between the purchaser and the seller.

58. Significance and Use

58.1 The heat stability of a cellulose ester is one indication of its quality.

59. Apparatus

59.1 *Heater Block*—A metal block of suitable size heated electrically and maintained at the specified temperature within ±1°C. This is best accomplished by providing continuous heat to hold the temperature a few degrees below the specified temperature, and providing intermittent additional heat thermostatically controlled. Holes shall be drilled in the top of the block to hold test tubes, a thermoregulator, and a thermometer. The block should be insulated.

59.2 *Test Tubes,* either 18 by 150-mm or 20 by 150-mm, fitted with corks. The corks shall be fitted with glass tubes the length of the cork and 4 mm in inside diameter or shall have a small V-shaped notch of equivalent cross-section cut in a vertical position.

60. Solvent

60.1 *Methylene Chloride-Methyl Alcohol Mixture*—Mix 9 parts by weight of methylene chloride with 1 part of methyl alcohol.

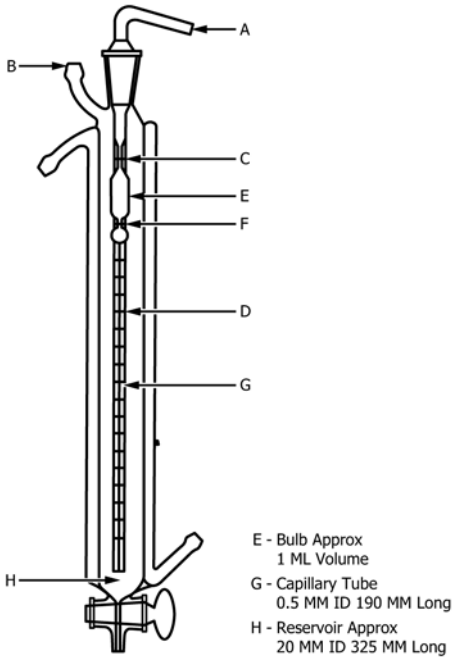


FIG. 3 Wagner Capillary Tube Viscometer[9]

61. Heat Treatment

61.1 Place the sample, ground to pass a No. 20 (841-µm) sieve, in a clean, dry test tube and pack it firmly and uniformly. Stopper with a cork having a notch or tube as described in 59.2. Heat the tube and contents for 8 h at 180°C or as otherwise specified.

62. Dry Color Evaluation

62.1 Examine the heated sample for uniformity of color and for the presence of charred or decomposed spots. Compare the color of the material at the bottom of the tube with standards prepared as follows: Heat portions of a check batch of similar particle size, representative quality and stability, and accepted by mutual agreement between the purchaser and the seller. Pack portions of this check batch firmly in each of twelve clean, dry test tubes and stopper with corks as described in 59.2. Heat the tubes at 180°C, or as otherwise specified, remove one tube each 2 h, and mark the time of heating in hours on each tube. This set of numbered tubes serves as the color standards. They should be checked and renewed if necessary every 6 months.

63. Solution Color Using Platinum–Cobalt Standards

63.1 Heat a 1-g sample for the specified time and temperature and, after cooling, examine for charred or decomposed spots. Dissolve the heated sample in 15 mL of the methylene chloride–methyl alcohol mixture. Compare the color of the solution (viewing transversely) with test tubes of platinum-cobalt color standards, prepared as described in Section 80. (It may be necessary to prepare standards having as much as 2000 ppm of platinum for this purpose or to dilute the sample solution before grading.)

64. Solution Color by Spectrophotometer

64.1 The color of the solution prepared as described in Section 63 may also be measured spectrophotometrically. Measure the absorbance at 400 nm against the solvent, using a suitable spectrophotometer with a 1-cm silica cell.

65. Viscosity Change

65.1 Measure the limiting viscosity number of the heated sample and of an unheated sample as described in Sections 67 to 71 of this test method. The percentage loss of viscosity as the result of heating is a measure of heat stability.

66. Precision and Bias

66.1 No statement on bias can be made as no reference material is available as a standard.

LIMITING VISCOSITY NUMBER

67. Summary of Test Method

67.1 Limiting viscosity number, expressed in millilitres of solution per gram of solute, is determined by measuring the flow times of a solution of known concentration and also of the solvent used and making a calculation by means of the modified Baker-Philippoff equation.

67.2 Intrinsic viscosity, expressed in decilitres per gram of solute, is determined in the same way by expressing *c* in grams per 100 mL in 71.2. Limiting viscosity number is thus 100 × intrinsic viscosity.

68. Significance and Use

68.1 Limiting viscosity number can be used to estimate the molecular weight of a cellulose ester by using the Mark-Houwink equation and constants measured for the solvent, temperature, and ester of concern.

69. Apparatus

69.1 *Capillary Viscometer,* such as the Wagner apparatus (see Fig. 3)[8] or an Ostwald-Fenske-Cannon pipet, that will give a flow time for the solvent of not less than 70 s.

69.2 *Water Bath*—A constant-temperature water bath controlled at 25.0 ± 0.1°C and with a pump for circulating the water through the viscometer jacket or tank.

69.3 *Stop Clock or Watch,* calibrated in ⅒ s.

70. Procedure

70.1 *Sample Preparation*—Dry about 0.26 g of sample in a weighing bottle at 105 ± 3°C for 2 h, stopper, and cool in a desiccator. Weigh the bottle containing the sample to the nearest 0.001 g, transfer the sample to a 250-mL flask, and reweigh the bottle. Pipet into the flask 100 mL of solvent at 25 ± 0.1°C. The solvent used should be mutually agreed upon by the purchaser and the seller. Suitable solvents are listed in Table 1. After the sample is completely dissolved, place it in

[8] Wagner, R. H., and Russell, John, "Capillary Tube Viscometer for Routine Measurement of Dilute High Polymer Solutions," *Analytical Chemistry*, Vol 20, 1948, pp. 151–7.

TABLE 1 Solvents for Limiting Viscosity Number Determination

Solvent[A]	Ingredients, % by weight	Value of *k* for Calculation (71.2)
A	90 % acetone[B] 10 % ethyl alcohol[C]	10
B	acetone[B]	10
C or D	90 % methylene chloride[D] 10 % ethyl alcohol[C]	3
E	96 % acetone[B] 4 % water	10
F	90 % methylene chloride[D] 10 % methanol[E]	3

[A] Solvent designations conform to those used in Table 2 for viscosity determinations.
[B] Acetone (99.4 ± 0.1 %) containing 0.3 to 0.5 % water and under 0.3 % ethyl alcohol.
[C] Ethyl alcohol (95 % by volume). Formula 2B or 3A denatured ethyl alcohol may be used.
[D] Methylene chloride having a boiling range of 39.2 to 40.0°C and less than 0.001 % acidity calculated as HCl.
[E] Methyl alcohol (sp gr 20/20°C = 0.785 to 0.795).

the constant-temperature bath at 25°C along with a portion of the solvent used, and allow sufficient time for both to come to temperature before making the viscosity measurements. During this conditioning period, water at 25°C should be circulating through the water jacket of the viscometer to allow ample time for the pipet to reach temperature equilibrium.

70.2 *Viscosity Measurements*—Rinse the reservoir and the outside of the capillary tube thoroughly with solvent. Rinse the inside of the capillary tube twice by alternately applying pressure at points *B*and *A*(see Fig. 3). Discard the wash portion of the solvent. Pour more solvent into the reservoir and allow several minutes for complete drainage and thermal equilibrium to be obtained. Adjust the outer meniscus to a reference point, *D*, that will give a flow time between 70 and 100 s. Apply air pressure at *B* to force the solvent up through the capillary past the upper timing mark, *C*, on the measuring bulb, *E*. Record the time in seconds required for the meniscus to fall between the timing marks, *C* and *F*. Take a minimum of two readings. Repeat these operations, substituting the solution for the solvent.

71. Calculation

71.1 Calculate the viscosity ratio, η/η_0 as follows:

$$\text{Viscosity ratio} = t_1/t_2 \tag{28}$$

where:

t_1 = efflux time of solution, and
t_2 = efflux time of solvent.

NOTE 12—Strictly, the viscosity ratio is defined as η/η_0 where η and η_0 are the viscosities of the solution and solvent, respectively, and are related to the corresponding efflux times by:

$$\eta = Ct - E\rho/t^2 \tag{29}$$

$$\eta_0 = Ct_0 - E\rho_0/t_0 2 \tag{30}$$

where:
C and *E* are constants for the particular viscometer used.
The equation in 71.1 follows if the second term in these relations, a kinetic energy correction, is negligible and the respective solvent and solution densities, ρ_0 and ρ, are substantially equal.

71.2 Calculate the limiting viscosity number, [η], as follows:

$$[\eta] = (k/c)[\text{antilog}\,((\log\eta/\eta_0)/k) - 1] \tag{31}$$

where:

k = values from Table 1 (Note 13), and
c = concentration in g/mL.

NOTE 13—Different values may be used by agreement between the purchaser and the seller.

71.3 Calculate intrinsic viscosity, η, in accordance with 71.2, but express *c* in grams per 100 mL.

72. Precision and Bias

72.1 No statement on bias can be made as no reference material is available as a standard.

VISCOSITY

73. Significance and Use

73.1 A measurement of viscosity is of great practical utility in determining the proper processing equipment and process concentrations for cellulose esters.

74. Procedure

74.1 *Solution*—Dry the sample for 1 to 2 h at 105 ± 3°C and cool in a desiccator. Prepare a solution of the dried sample in a solvent and at a concentration mutually agreed upon by the purchaser and the seller. Suitable solutions are listed in Table 2.

74.2 *Viscosity Determination*—Prepare the solution and measure the viscosity in accordance with Test Method D1343, (see Note 16 in Section 81).

75. Report

75.1 Report the results in poises, unless otherwise specified. The viscosity value shall be prefixed with the letter A, B, C, etc., corresponding to the formula of the solution employed.

TABLE 2 Solutions for Viscosity Determination

	Formula					
	A	B	C	D	E	F
	Ingredients, Weight %					
Cellulose ester	20[A]	20[A]	20[B]	15[C]	20[A]	10[C]
Acetone[D]	72	80	...	...	...	...
Acetone, 96 percent Water, 4 percent	...	...	...	...	80	...
Ethyl alcohol[E]	8	...	8	8.5	...	...
Methyl alcohol[F]	...	...	...	...	...	9
Methylene chloride[G]	...	...	72	76.5	...	81
	Typical Solution Densities, g/mL at 25°C					
	0.85	0.86	1.25	1.23	0.86	1.24

[A] Suitable for most mixed esters having less than about 40 % acetyl and more than about 8 % propionyl or butyryl.
[B] Suitable for most of the commercial cellulose acetate propionates and acetate butyrates.
[C] Suitable for most of the commercial cellulose acetate propionates and acetate butyrates. Particularly good for esters containing more than 40 % acetyl.
[D] Acetone (99.4 ± 0.1 %) containing 0.3 to 0.5 % water and under 0.3 % ethyl alcohol.
[E] Ethyl alcohol (95 % by Vol). Formula 2B, 3A, or 30 denatured ethyl alcohol may be used.
[F] Methyl alcohol (sp gr 20/20C = 0.785 to 0.795).
[G] Methylene chloride having a boiling range of 39.2 to 40.0°C and less than 0.001 % acidity calculated as HCl.

76. Precision and Bias

76.1 No statement on bias can be made as no reference material is available as a standard.

COLOR AND HAZE

77. Summary of Test Method

77.1 Color and haze determinations on cellulose ester solutions are made by comparison with standards. Simultaneous measurement of these properties is desirable because haze reduces the amount of color observed.

78. Significance and Use

78.1 Solution color and haze of a cellulose ester is a measurement of the optical properties of cellulose esters when dissolved in a specific solvent.

79. Apparatus

79.1 *Light Box*—A suitable light box (Fig. 4) is described as follows: The light source consists of a mercury vapor bulb which requires an autotransformer for the current source. The bulb is mounted horizontally across the lower front part of a plywood box 356 mm (14 in.) wide, 430 mm (17 in.) high, and 330 mm (13 in.) deep. This box is lined with a heat resistant board and is painted black inside, except that the inside back surface toward the viewer is white. A bottle holder large enough to hold four bottles is built onto the front of the light box, and a 64 by 150-mm (2½ by 6-in) horizontal viewing hole is cut through the front of the box. This opening is covered with clear glass, and a 6-mm (¼-in.) strip of black tape is fastened to the glass horizontally to aid in judging haze in the solution. Holes are cut in the bottom and top of the box for cooling by air convection. For continuous use, forced circulation of air would be desirable. A black metal baffle over the bulb prevents direct light on the viewing glass.

79.2 *Sample Bottles*—The bottles used for the sample solutions are French square bottles, 470-mL (16-oz), with screw caps. These same bottles may be used for the color and haze standards.

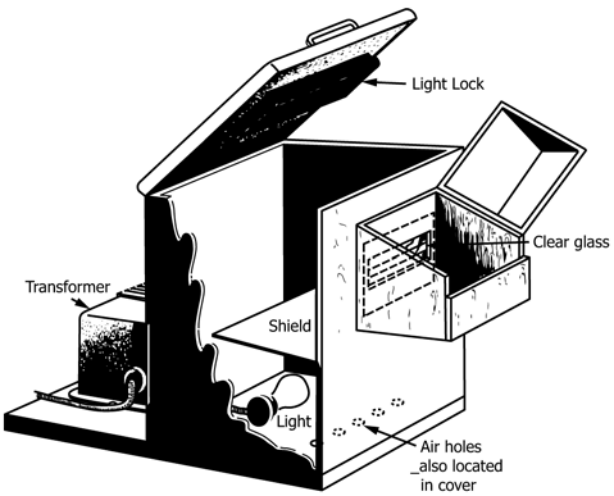


FIG. 4 Color and Haze Apparatus

NOTE 14—These bottles may also be used for determination of viscosity, as described in 74.2.

79.3 *Cap Liners*—Cap liners shall be of a composition not affected by the solvents used. Liners of fiber board covered with cellophane or aluminum foil are usually satisfactory, but vinyl resin or waxed liners may cause interference with viscosity, color, or haze measurements.

80. Reference Standards

80.1 *Color Standards*—A color standard containing 500 ppm of platinum may be purchased or the solution may also be prepared as follows: Dissolve 1.245 g of potassium platinum chloride (K_2PtCl_6), containing 0.500 g of platinum, and 1.000 g of crystallized cobalt chloride ($CoCl_2 \cdot 6H_2O$), containing 0.248 g of cobalt, in water, add 100 mL of HCl (sp gr 1.19), and dilute to 1 L with water. Prepare standards containing 50, 60, 70, 80, 90, 100, 125, 150, 175, 200, 250, 300, 350, 400 and 500 ppm of platinum by diluting suitable aliquots of the standard solution to 500 mL with water. Place these standards in the special bottles (see 79.2), taking care to select bottles with good clarity and free of flaws. Label and cap tightly.

80.2 *Haze Standards*—Prepare haze standards by diluting a stock solution having a turbidity of 1000 ppm. Prepare bottles containing 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 175, 200, and 400 ppm of turbidity, label, and cap tightly.

NOTE 15—The previously recommended stock solution for preparing these standards was made from fuller's earth, water, and hydrochloric acid. This solution is no longer available. A comparable stock solution can be made using diatomaceous earth. To obtain haze levels equivalent to the fuller's earth standard, 1.1 parts of diatomaceous should be used in place of 1.0 parts of fuller's earth in preparing the aqueous suspension. No hydrochloric acid is needed.

81. Procedure

81.1 Prepare the solution to be graded by dissolving the cellulose ester in the specified amount and kind of solvent, in one of the square bottles. See Table 2 for suitable solutions. At least 350 mL are required. Tumble until a uniform solution is obtained. Allow the solution to stand until it is free of bubbles before grading it for color and haze.

81.2 Place the bottle containing the solution to be graded at the front of the shelf on the apparatus and place a similar bottle containing water behind it. Place the freshly shaken haze standard at the front of the shelf beside the bottle containing the solution to be tested and place the color standard behind it. Determine the amount of color and haze in the solution by changing the color and haze standards until as good a match as possible has been obtained. The haze standards settle out quickly so they must be reshaken at short intervals. Report results in parts per million for both color and haze.

NOTE 16—When viscosity, color, and haze determinations, and an observation of general appearance are to be made on a cellulose ester sample, a considerable saving in time can be made by using one solution in a square bottle for all three determinations. Dry the cellulose ester as required for the viscosity determination, prepare the solution carefully, and allow the bottle to stand long enough to form a thick solution before tumbling, to avoid solvent loss around the cap. Use a large enough sample to provide at least 350 mL of solution in the bottle. Measure the viscosity as described in Test Method D1343.

82. Precision and Bias

82.1 No statement on bias can be made as no reference material is available as a standard.

83. Keywords

83.1 apparent acetyl; ash; cellulose acetate butyrate; cellulose acetate propionate; cellulose esters; color; free acidity; haze; hydroxyl; limiting; partition; sulfate content; viscosity