Designation: D 301 – 95 (Reapproved 2004)

Federation of Societies for
Paint Technology Standard No. Cs-2-58

Standard Test Methods for Soluble Cellulose Nitrate[1]

This standard is issued under the fixed designation D 301; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 These test methods cover the material known as soluble cellulose nitrate (also known as soluble nitrocellulose), which is shipped wet in conformance with regulations of the Interstate Commerce Commission.

1.2 The test methods appear in the following sections:

	Sections
Ash	5-7
Drying Samples	4
Nitrogen	8-10
Stability	11-13
Toluene Dilution	22-24
Viscosity	14-18

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

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see 12.2, 13.3, 16.1, and 16.2.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 302 Specification for Ethyl Acetate (85 to 88 Percent Grade)[3]

D 303 Specification for *n*-Butyl Acetate (90 to 92 % Grade)[3]

D 362 Specification for Industrial Grade Toluene[3]

D 1343 Test Method for Viscosity of Cellulose Derivatives by Ball-Drop Method

D 4795 Test Method for Nitrogen Content of Soluble Nitrocellulose—Alternative Method

E 1 Specification for ASTM Liquid-in-Glass Thermometers

3. Sampling

3.1 Samples shall be taken from not less than 10 % (at least two barrels) of each lot or batch in the shipment. In sampling the barrels, two samples of approximately 0.5 dm^3(1 pt) each shall be taken from two well-separated points at least 0.3 m (1 ft) beneath the surface of the material in the barrel. These samples shall then be composited to represent each lot or batch in the shipment.

3.2 The samples shall meet the following requirements:

3.2.1 *Appearance*—The cellulose nitrate shall not be discolored and shall be free of lumps and foreign matter, such as charred particles.

3.2.2 *Ash*—Ash content shall not exceed 0.30 %, calculated on the basis of dry-weight soluble cellulose nitrate.

3.2.3 *Nitrogen*—The percent nitrogen, calculated on the basis of dry-weight soluble cellulose nitrate, shall be within the limits agreed upon by the purchaser and the manufacturer for the particular type of soluble cellulose nitrate.

3.2.4 *Stability*—The stability as determined by the 134.5 C test shall be not less than 25 min.

3.2.5 *Viscosity*—The viscosity shall be within the limits agreed upon by the purchaser and the manufacturer for the particular type of soluble cellulose nitrate.

3.2.6 *Solubility and Appearance of the Solution*—The solubility and appearance of the sample shall be equal to the reference standard for the particular type of soluble cellulose nitrate.

3.2.7 *Film Test*—The film test of the sample shall be equal to that of the reference standard for the particular type of soluble cellulose nitrate.

3.2.8 *Toluene Dilution Test*—The toluene dilution value of the sample shall be equivalent to that of the reference standard for the particular type of soluble cellulose nitrate.

DRYING SAMPLES

4. Procedure

4.1 Soluble cellulose nitrate is a flammable material, the degree of flammability varying with the extent and nature of the wetting medium. Cellulose nitrate is always wet with water or alcohol in commercial handling, shipping, and storage, in

[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] Withdrawn.

which condition it presents no unusual hazard. Dry cellulose nitrate, if ignited by fire, spark, or static electricity, burns very rapidly. Samples of dry cellulose nitrate *must not* be stored at any time. Dry only that portion required for immediate test. Wet the excess material and the samples left after testing with water and dispose of by burning on a safe burning ground.

4.2 Dry small quantities required for ash and nitrogen tests by spreading in a thin layer on a tray at room temperature for 12 to 16 h, followed by oven-drying in crucibles or weighing bottles 1 h at 100 to 105°C. The oven used for drying cellulose nitrate should have the latch removed. Wear a face mask (see 12.2) when the oven is opened after samples have been heated.

4.3 Dry larger quantities of *water-wet* material required for viscosity and toluene dilution tests, or a small quantity for stability tests, by blowing warm compressed air (at a temperature of 60 to 65°C, and a pressure of 275 to 415 kPa (40 to 60 psi)) through the sample placed in a cylindrical holder with a screen over one end for ½ to 1 h. Provide the compressed air line with a safety plug (Note 1) of Wood's metal, which melts at 70 to 75°C, so the air will be diverted from the sample if a temperature of 70°C is exceeded.

NOTE 1—Information on the availability of a suitable fusible plug assembly may be obtained from ASTM International Headquarters.

4.4 If the material is *alcohol-wet*, it is necessary to modify the drying procedure. After placing the required amount of cellulose nitrate in the cylindrical holder, pour in sufficient distilled or iron-free water to fill it. Allow the bulk of the liquid to drain off. Then dry by blowing warm air through the holder as described in 4.3.

ASH

5. Significance and Use

5.1 Ash accounts for the nonsoluble, nonfilm forming portion of the polymer. It may affect solution clarity and film properties.

6. Apparatus

6.1 *Porcelain Crucibles*, Coors No. 3 or equivalent.

6.2 *Muffle Furnace*, maintained at 550 ± 25°C.

7. Reagents

7.1 *Ethyl Alcohol*.

7.2 *Acetone*.

7.3 Castor Oil.

8. Procedure

8.1 Dry the cellulose nitrate as described in 4.2 and place a specimen of approximately 4.0 g in a tared and ignited crucible. Moisten the sample in the crucible with ethyl alcohol, then gelatinize by adding a sufficient amount of 5 % solution of castor oil into the acetone. Place the crucible in a draft-free hood and ignite the contents with a Bunsen flame. Allow the material to burn without further addition of heat until a charred residue remains. Place the crucible in a muffle furnace at 550 ± 25°C for 90 min. Remove carefully the crucible from the muffle furnace to avoid loss of ash, cool in a desiccator, and weigh accurately.

9. Calculation

9.1 Calculate the percent ash as follows:

$$\text{Ash, \%} = (\text{wt of ash/wt of dry sample}) \times 100$$

10. Precision and Bias

10.1 *Precision*—Statistical analysis of intralaboratory (repeatability) test results on a sample containing approximately 0.015 % ash indicates a precision of ±0.015 % absolute at the 95 % confidence level.

10.2 *Bias*—No statement of bias can be made as no suitable reference material is available as a standard.

NITROGEN

11. Significance and Use

11.1 The nature and strength of solvent systems required for cellulose nitrate are dependent upon the nitrogen content. Mismatches of solvent with nitrogen level can result in poor solution quality and colloid and gel formation.

11.2 An alternative preferred method can be found in Test Method D 4795.

12. Apparatus

12.1 *Nitrometer*—Use the duPont Nitrometer, which is illustrated in Figs. 1-4.

12.2 *Face Mask*—A face mask, so constructed that a heavy piece of cellulose acetate sheeting protects the face. (**Warning**—The cellulose acetate mask must be worn during the generation and measurement of the gas as a precaution in case of an explosion.)

13. Procedure

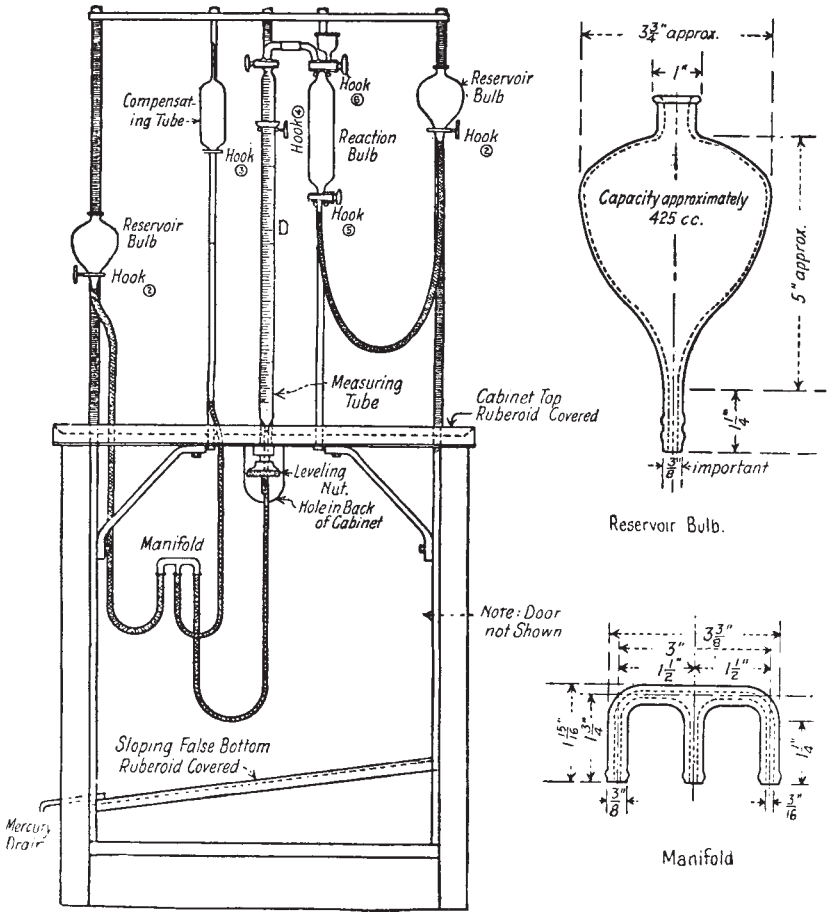
13.1 Calibrate the measuring tube accurately in the usual manner, using mercury as the calibrating liquid.

13.2 Standardize the apparatus as follows:

13.2.1 Fill the compensating, measuring, and reaction tubes and their rubber connections with mercury. Run 20 to 30 mL of H_2SO_4 (ACS grade, 94.5 ± 0.5 %) into the reaction bulb through the cup at the top and admit about 210 mL of air. Close the stopcocks, shake the bulb well, and allow to stand overnight. This desiccates the air which is then run into the compensating tube until the mercury is about on a level with the 12.50 % mark on the measuring tube, the two tubes being held at the same height. Then seal the compensating tube using a small blowpipe flame.

13.2.2 As a preferred alternative, nitrogen may be used in place of air.

13.2.3 Place in weighing bottles 0.95 ± 0.05-g portions of ACS grade KNO_3 that has been recrystallized twice from distilled water and ground to pass a No. 100 (150-µm) sieve. Dry the specimens 2 to 3 h at 135 to 150°C. Stopper the bottles, cool in a desiccator, and weigh accurately. Transfer the KNO_3 to the cup of the reaction bulb and weigh the weighing bottle to obtain the weight of sample used. Add 1.0 mL of water and stir the mixture in the cup with a small glass stirring rod to liberate the entrained bubbles of air; work the undissolved crystals into the lower part of the cup, keeping them below the surface of the solution. It is not necessary that the KNO_3



NOTE 1—1 in. = 25.4 mm.

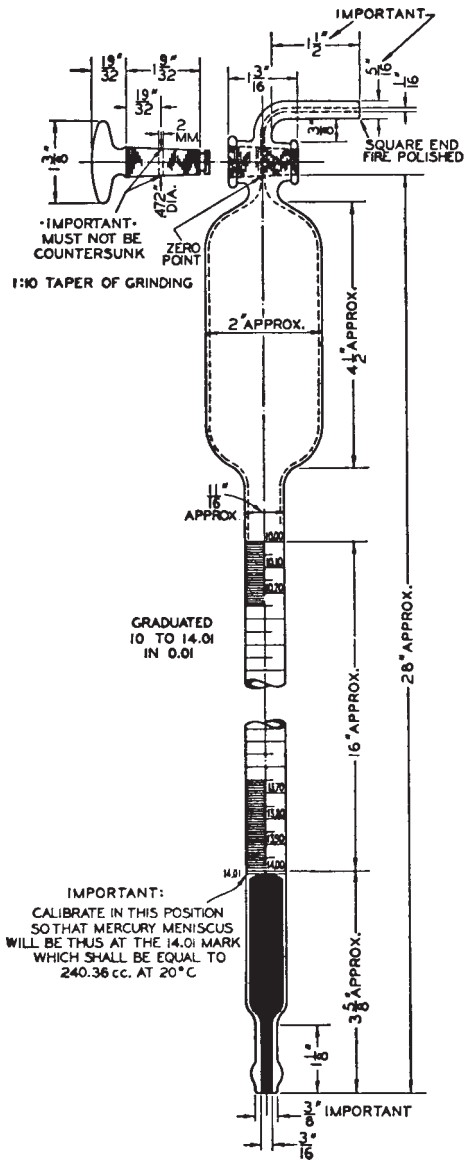
FIG. 1 General Assembly of Apparatus for Nitrogen Determination

dissolve before drawing it into the reaction bulb. *Make sure the lower stopcock is open*; then admit the mixture to the bulb by a series of quick openings of the upper stopcock, in the meantime keeping the crystals below the surface of the liquid. In this way, all but a small amount of the KNO_3 may be run into the bulb. Rinse the cup with a second 1.0-mL portion of water; then repeat with a third 1.0-mL portion (3 mL in all). This should be sufficient to dissolve all remaining particles of KNO_3 in the cup. Transfer 25 mL of the H_2SO_4 (94.5 ± 0.5 %), divided in several portions, to the cup, and subsequently to the bulb by lowering the reservoir slightly and opening and closing the upper stopcock, care being taken that no air enters even the bore hole in the stopcock. There must always be a slight suction when introducing the specimen, the wash water, and the acid, but never enough to cause air to be sucked into the reaction bulb. The quantities of water and H_2SO_4 used should be constant. Then with the bottom stopcock still open, lower the reservoir bulb to give reduced pressure in the reaction bulb and gently shake the reaction bulb to start the decomposition.

13.3 After the evolution of NO has become slow (**Warning**—It is extremely important that the bottom stopcock be left open until the major part of the decomposition has occurred; otherwise, sudden evolution of gas will burst the bulb, scattering acid and glass), lower the reservoir bulb until all but 25 mL of the mercury in the reaction bulb is withdrawn, close the bottom stopcock, and shake the reaction bulb vigorously for 5 min.

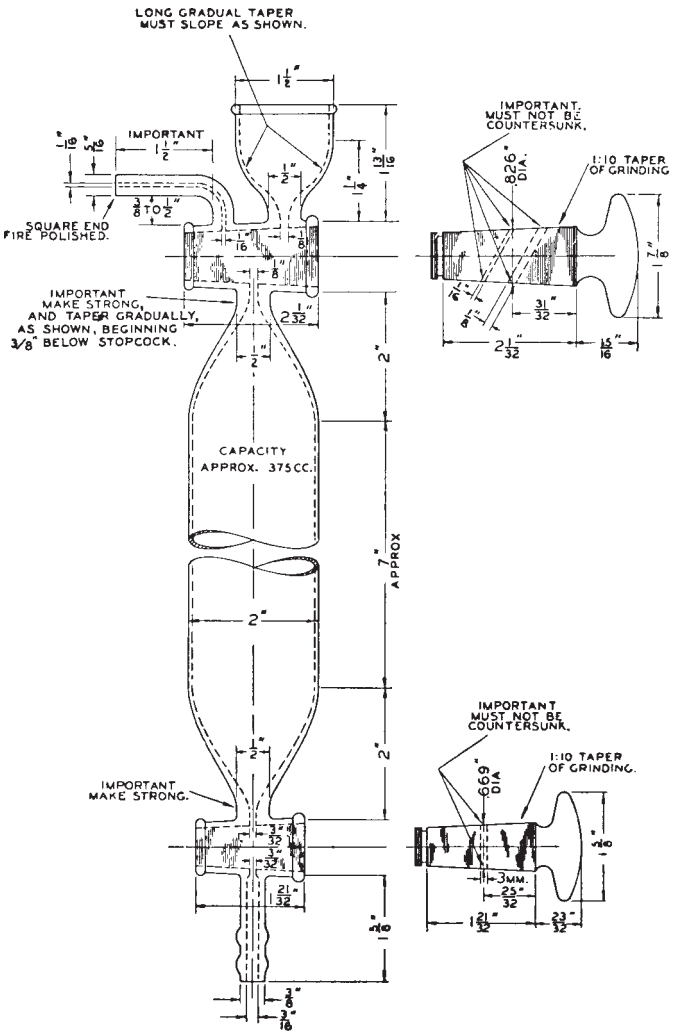
13.4 When the reaction is completed, allow the gas to cool for 20 min; then transfer the gas to a measuring tube. By means of the leveling device make careful adjustment of the mercury levels so that the mercury in the measuring tube is at the 13.85 % mark (the theoretical percent nitrogen in KNO_3) if an exactly 1.000-g specimen was used, or a proportional reading if less was used. Paste a strip of paper on the compensating tube at the level of the mercury, and the standardization is completed. It is advisable to make several check determinations, preferably on different days, to ensure accurate standardization. Determinations should check within ±0.01 %.

13.5 Dry the cellulose nitrate as described in 4.2 and place a specimen of 1.0 to 1.2 g in a weighing bottle. After drying at 100 to 105°C for 1 h, stopper, cool in a desiccator, and weigh accurately. Transfer the specimen to the cup of the decomposition bulb; then reweigh the empty bottle to get the weight of the specimen by difference. Add 5 to 10 mL of H_2SO_4 (94.5 ± 0.5 %) to the cup and stir the mixture with a small stirring rod. Lower the mercury reservoir and then, with the lower stopcock open, draw the mixture in by opening the upper stopcock. Take care that no air is drawn in. Rinse the cup of the decomposing bulb several times with H_2SO_4, using a total of 25 mL for



NOTE 1—1 in. = 25.4 mm.

FIG. 2 Measuring Tube for Nitrogen Determination



NOTE 1—1 in. = 25.4 mm.

FIG. 3 Reaction Bulb

dissolving and rinsing. Complete the determination in accordance with the procedure described in 10.2 for standardization of the apparatus, and take a reading after adjusting the level of the mercury in the reading tube to the mark on the compensating tube. The reading divided by the weight of the specimen gives the percent nitrogen.

STABILITY

14. Significance and Use

14.1 Nitrocellulose stability is measured by detecting the evolution of nitrogen oxides under elevated temperature. The results are not necessarily a predictor of shelf life.

15. Apparatus

15.1 *Copper Bath*—Copper bath with copper or brass condenser, as shown in Fig. 5 and Fig. 6. These baths are usually made to hold 13 to 15 test tubes. To aid in heat transfer, add 15 to 25 mL of mineral oil to each copper well, in order to fill the space between the glass tube and the well. To maintain the bath at a temperature of 134.5 ± 0.5°C, fill to within 3 in. (76 mm) of the top with a mixture consisting of ten parts of a commercial ethylene glycol solution (automobile radiator antifreeze containing a corrosion inhibitor) and one part of water. Adjust the temperature of the boiling liquid in the bath to 134.5 ± 0.5°C by adding more glycol or water, as necessary.

15.2 *Test Tubes*—Heat-resistant glass[4] tubes, with an outside diameter of 18 mm, a wall thickness of 1.5 mm, and a length of 290 mm.

15.3 *Heater*—An electric hot plate for heating the bath.

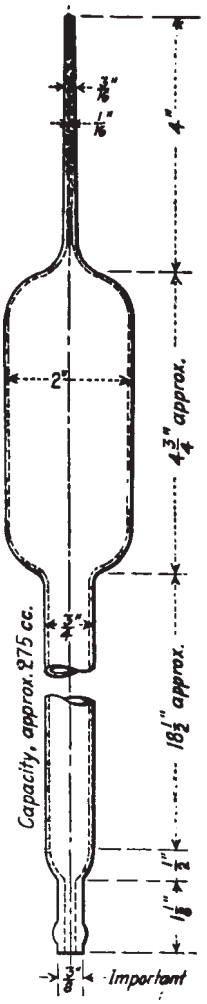
15.4 *Face Mask*—See 12.2.

15.5 *Gloves*—A pair of heavy gloves.

15.6 *Pincers*—Long pincers for handling the test tubes.

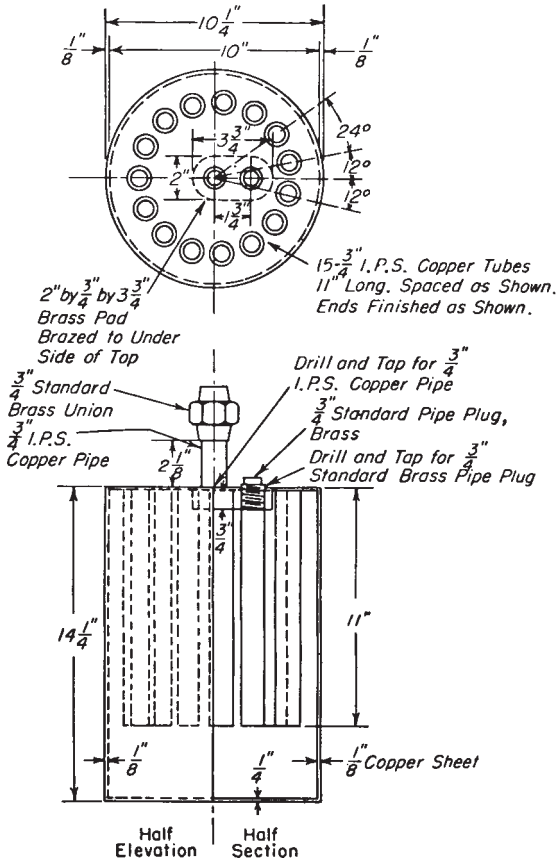
15.7 *Thermometer*—An ASTM Stability Test Thermometer having a range from 130 to 140°C and conforming to the

[4] Borosilicate glass has been found satisfactory for this purpose.



NOTE 1—1 in. = 25.4 mm.

FIG. 4 Compensating Tube



NOTE 1—1 in. = 25.4 mm.

FIG. 5 Copper Bath for Stability Test

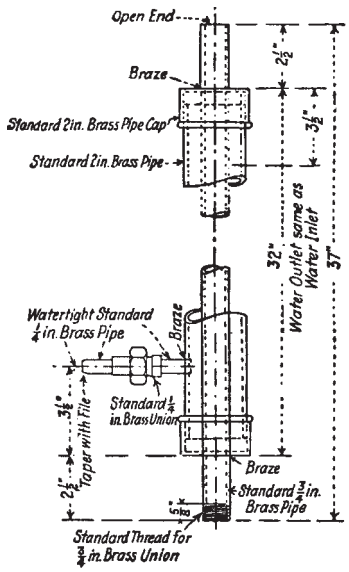


FIG. 6 Brass Condenser for Stability Test Apparatus

requirements for Thermometer 26C as prescribed in Specification E 1. The thermometer should be fitted with a cork stopper and placed in an empty glass tube in the bath.

15.8 *Methyl Violet Test Paper*.

16. Procedure

16.1 Conduct the test in a room that is free of acid fumes. (**Warning**—It is important that the operator wear the cellulose acetate mask and heavy gloves and the tubes be handled with long pincers.)

16.2 Dry the sample as described in 4.2. Weigh duplicate specimens of 2.5 ± 0.1 g into test tubes and press the specimens down so that they occupy the lower 51 mm (2 in.) of the tubes; then swab out all cellulose nitrate particles adhering to the inside wall of the tubes. Crease a piece (20 by 70 mm) of normal methyl violet test paper for one half its length; then insert it in the tube with the uncreased portion downward, until the lower edge is 1 in. above the top of the specimen. The paper must remain in this portion throughout the test. Stopper the tube with a cork provided with hole or notch 4 mm in diameter. Place the tube, without jarring, in the heating bath maintained at 134.5 ± 0.5°C. Beginning at the end of the first 20 min, inspect the tube at 5-min intervals by lifting the tube until the methyl violet paper, but not the cellulose nitrate, is visible above the surface of the bath. The end point is reached when the entire test paper changes in color to salmon pink. For example, if the color is not completely changed at 20 min but is completely changed at 25 min, record

the stability of the specimen as 25 min. (**Warning**—As a safety measure, immerse the specimen in cold water immediately upon completion of the test.)

TABLE 1 Solutions for Viscosity and Film Tests

	Formula A	Formula B	Formula C
Ingredients:			
Soluble cellulose nitrate (dried), weight percent	12.2	20.0	25.0
Completely denatured ethyl alcohol (188 to 190 proof), weight percent	22.0	20.0	18.75
Toluene,[A] weight percent	48.3	44.0	41.25
Ethyl acetate,[B] weight percent	17.5	16.0	15.0
Density of solution at 25°C (g/mL)	0.90	0.93	0.97

[A] Toluene conforming to Specification D 362.
[B] Ethyl acetate conforming to Specification D 302.

17. Precision and Bias

17.1 *Precision*—Statistical analysis of intralaboratory (repeatability) test results indicates a precision of ±5 min at the 95 % confidence level.

17.2 *Bias*—No statement of bias can be made as no suitable reference material is available as a standard.

VISCOSITY

18. Significance and Use

18.1 Coating and lacquer formulations are based on percent solids in a solvent system. Viscosity is a determining factor in limiting the percent solids in a given solvent system.

19. Solutions Required

19.1 Determine viscosity by dissolving the cellulose nitrate, dried as described in 4.3, according to a standard formula (Table 1) and noting the time for a steel ball to fall through a measured depth of the solution at 25°C. Use formula A for types designated as 5 s or over. Use formula B for types designated as ½ and ¾ . Use formula C for types designated as ¼ s and 30 to 35 cp. Cellulose nitrate will dissolve more quickly if it is first wet with alcohol and toluene and the mixture then allowed to stand a few minutes before the ethyl acetate is added. Completely dissolve the sample in the solvent mixture by agitating in a tightly closed bottle.

20. Viscosity Determination

20.1 Measure the viscosity, using the apparatus and following the procedure described in Test Method D 1343.

21. Report

21.1 Report the results in seconds (Note 2) for a 2.4-mm (3⁄32-in.) steel ball (density 7.7 ± 0.1) and a 50.8 ± 0.5-mm (2.00 ± 0.02-in.) drop. The viscosity value shall be prefixed with the letter A, B, or C, corresponding to the formula of the solution employed.

NOTE 2—Results in seconds for a 3⁄32-in. steel ball may be converted to poises as follows:

$$n = 0.560\,(a - b)\,t$$

where:
n = viscosity at the specified temperature, P,
a = ball density, g/mL,
b = solution density, g/mL, and
t = time of fall, s.

22. Precision and Bias

22.1 *Precision*—Statistical analysis of intralaboratory (repeatability) test results indicates a precision of ±5.2 % at the 95 % confidence level. The results of an interlaboratory (reproducibility) test study are shown in Test Method D 1343.

22.2 *Bias*—No statement on bias can be made at this time as no material is available to serve as a standard.

TOLUENE DILUTION

23. Significance and Use

23.1 This test method can ascertain whether cellulose nitrate of a given percent nitrogen is contaminated with material of a significantly different nitrogen content. Such cross contamination may adversely affect solution and film quality.

24. Procedure

24.1 Prepare a solution containing 12.2 weight percent of cellulose nitrate dried as described in 4.3, and 87.8 weight percent of butyl acetate conforming to Specification D 303. To 50 mL of this solution in a stoppered bottle add toluene, conforming to Specification D 362 in small quantities from a buret, shaking well after each addition.

25. Calculation and Report

25.1 Report as the dilution value the volume of toluene required to effect the first permanent separation of cellulose nitrate, calculated as a percent by volume of the original solution, as follows:

$$\text{Dilution value} = (\text{mL toluene} \times 100)/50$$
$$= \text{mL toluene} \times 2$$

NOTE 3—Large quantities of butyl acetate and toluene should be reserved for this test to avoid possible variation between different lots. The test should be run at 25°C.

26. Precision and Bias

26.1 *Precision*—Statistical analysis of intralaboratory (repeatability) test results indicates a precision of ±2 mL at the 95 % confidence level.

26.2 *Bias*—No statement of bias can be made as no suitable reference material is available as a standard.

27. Keywords

27.1 ash; cellulose nitrate; drying; nitrogen content; stability; toluene dilution; viscosity