



# Standard Test Method for Rubber, Raw—Determination of Gel, Swelling Index, and Dilute Solution Viscosity<sup>1</sup>

This standard is issued under the fixed designation D 3616; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the determination of the dilute solution viscosity (DSV), the gel characteristics, and the swelling index of raw non-oil-extended and non-pigmented SBR and NBR.

1.2 This test method may be used to determine the dilute solution viscosity and gel characteristics of rubbers other than SBR and NBR, however, solvents other than 2-butanone and toluene may be required.

1.3 This test method is not intended for the measurement of micro-gel.

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.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 446 Specifications and Operating Instructions for Glass Capillary Kinematic Viscometers<sup>2</sup>

D 2857 Practice for Dilute Solution Viscosity of Polymers<sup>3</sup>

D 4483 Practice for Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries<sup>4</sup>

### 2.2 ISO Standard:

ISO/R1628 (Plastics) Directives for the Standardization of Methods for the Determination of the Dilute Solution Viscosity of Polymers<sup>5</sup>

### 2.3 Other Document:

“Reagent Chemicals, American Chemical Society Specifications”<sup>6</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D11 on Rubber and is the direct responsibility of Subcommittee D11.11 on Chemical Analysis.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.01 (formerly D2515 redesignated D446 in 1977).

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 08.02.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 09.01.

<sup>5</sup> Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

<sup>6</sup> Available from the American Chemical Society, Washington, DC.

## 3. Summary of Test Method

3.1 A weighed sample is allowed to stand 16 to 20 h in a suitable solvent. The sol, or soluble portion, is removed from the rubber mixture and the viscosity is determined on this solution.

3.2 A portion of the sol is used for the determination of the dissolved rubber. This is obtained by evaporation of the solvent.

3.3 The swelling index of the gel is determined by comparing the dry gel mass to the swollen gel mass.

## 4. Significance and Use

4.1 These tests are particularly useful for quality control in the production of synthetic rubbers.

4.2 Percent gel is a measure of the amount of insoluble rubber present in the chosen solvent. Gel may be introduced intentionally in some rubbers. Variations from a normal level indicate changes in the polymerization system.

4.3 Swelling index is a measure of the type of gel. Gel with a low-swelling index is referred to as “hard gel” and usually indicates the presence of material that does not break down readily by milling. A high-swelling index normally indicates the presence of a “loose gel” that may be broken down easily by milling.

4.4 In low-gel or gel-free rubbers, the dilute solution viscosity correlates directly with the molecular weight. Since the viscosity is measured only on the soluble portion of the rubber, the use of DSV to predict molecular weight in rubbers having high gel values is meaningless.

## 5. Apparatus

5.1 *Borosilicate Weighing Bottle*, 45/12 standard taper, 40 mm in inside diameter, 100 mm high, with cover.

5.2 *Screen Rack*, consisting of five 300- $\mu$ m (No. 50) circular screens mounted on a stainless steel tube to fit the weighing bottle (5.1). Borosilicate bottle, cover, and rack will be referred to hereafter as “the unit”.<sup>7</sup>(Fig. 1).

<sup>7</sup> Available from the Spencer Machine and Tool Co., P.O. Box 298, 6205 Gheens Mill Rd., Jeffersonville, IN 47131, or manufactured according to the specifications in Fig. 1.

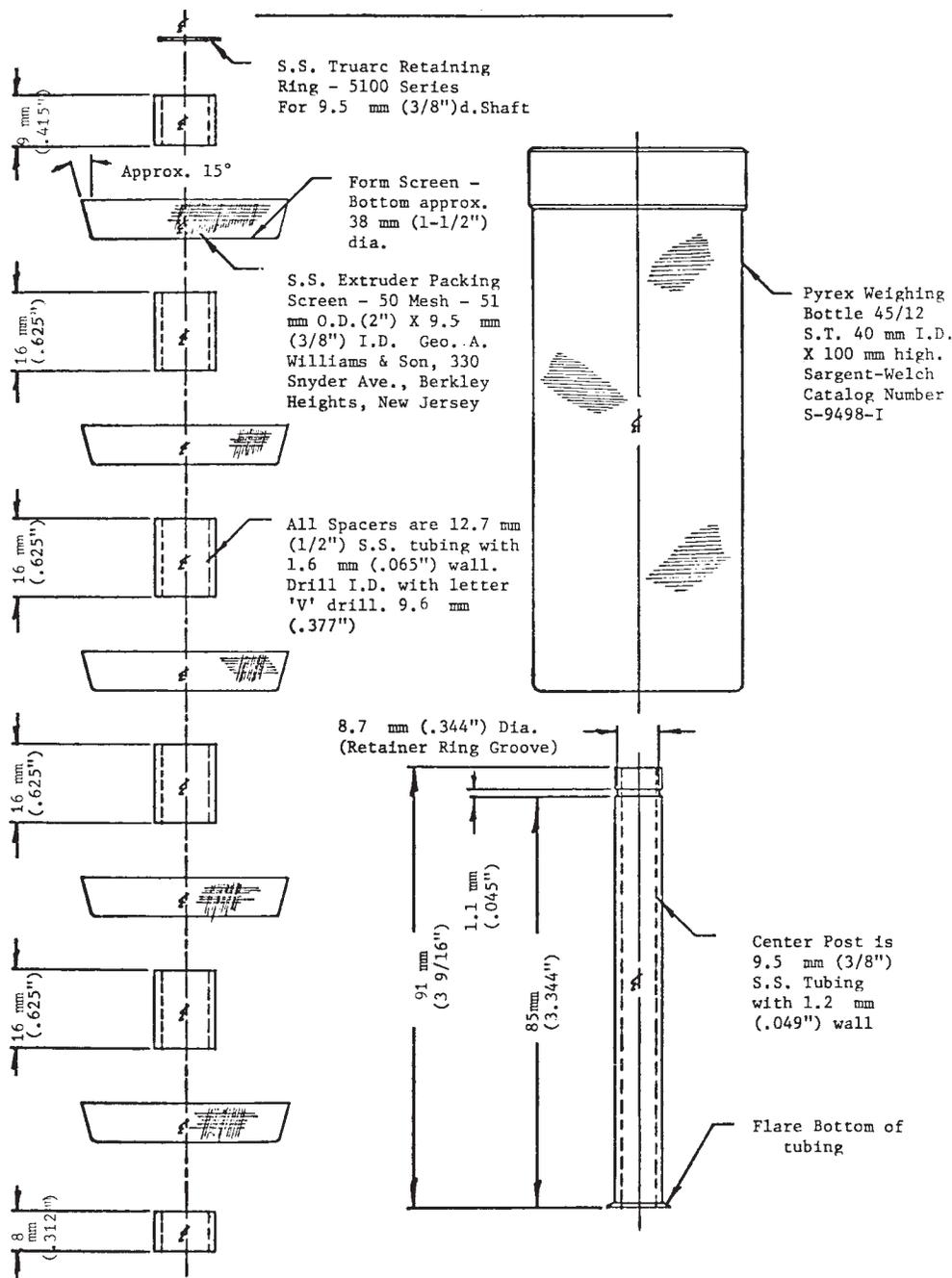


FIG. 1 Gel Test Apparatus

5.3 Pipet, capable of fitting within the tube of the screen rack (5.2).

5.4 Ostwald Cannon-Fenske Viscometer, size 100.

5.5 Constant-Temperature Bath with Stirrer, capable of operating at  $25 \pm 0.1^\circ\text{C}$ .

5.6 Stop Watch or Electric Timer, readable to 0.1 s.

5.7 Additional Glassware, sufficient to carry out the procedure as written. Class "A" pipets of 25 and 100-cm<sup>3</sup> volume are mandatory.

5.8 Disposable Aluminum Dishes.

5.9 Balance, capable of accurately weighing to  $\pm 0.1$  mg.

5.10 Screw-Cap Bottles, 100-cm<sup>3</sup> minimum capacity, or Erlenmeyer flasks, 125-cm<sup>3</sup> capacity.

5.11 Borosilicate Wool or Cotton.

## 6. Reagents

NOTE 1—All recognized health and safety precautions shall be observed in carrying out the procedure as written.

6.1 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. Other grades may be used, provided it is ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 The following solvents are used:

6.2.1 *2-Butanone (-Methyl Ethyl Ketone)*, for NBR rubbers, and

6.2.2 *Toluene*, for SBR rubbers.

## 7. Sampling

7.1 Select a representative sample of the rubber to be tested.

7.2 Do not mill the sample prior to testing except for rubbers in the powdered form (see 8.2).

NOTE 2—The presence of dusting agents may result in erroneous values for total solids or viscosity of the solution.

## 8. Procedure

8.1 Using a clean scissors, cut the sample into strips less than 1 mm in thickness and about 5 mm long.

8.2 In the case of rubbers in powdered form, the sample may be massed or compacted by the use of a hand press with platens at 50°C. It may then be cut into appropriate strips. Rubbers that will not fall through the screen may be placed on the screen without prior treatment.

8.3 Weigh 0.39 to 0.41 g of the prepared sample to the nearest 0.1 mg and distribute evenly over the four lowest screens of the unit (5.2). Place the pieces near the center of each screen.

8.4 Gently place the screen rack into the borosilicate weighing bottle (5.1) and deliver 100 cm<sup>3</sup> of the chosen solvent into the bottle. Tip the container to assure complete wetting of each screen.

8.5 Cap the bottle and allow to stand for 16 to 20 h at 25 ± 2°C, in the dark.

## 9. Gel

9.1 After 16 to 20 h, remove the cap from the unit, lift the screen, and examine for visible gel.

NOTE 3—Some rubbers will not go into solution as readily as others. It is necessary for the analyst to distinguish between undissolved polymer and true gel. A thinner or more porous sample will aid the solution and an extending standing period—up to 48 h may be helpful in distinguishing gel from true polymer solution. It should be noted, however, that the precision statements in Section 13 were obtained using the time interval stated in 8.5.

9.2 Pipet the liquid from the unit into a screw-cap bottle or Erlenmeyer flask by inserting the pipet (5.3) through the center of the screen rack. Filter the liquid through cotton or borosilicate glass wool.

9.3 Pipet exactly 25 cm<sup>3</sup> of this liquid into a dried and weighed aluminum dish (5.8) and place the dish on a steam or electric hot plate at 100 ± 10°C. Alternately heat and weigh the dish to the nearest 0.1 mg, until a constant mass is achieved. Record this value for use in Section 9.

9.4 Determine the gel content as follows:

$$A \times 4 = B \quad (1)$$

$$\text{Gel, \%} = \left( \frac{C - B}{C} \right) \times 100 \quad (2)$$

where:

*A* = mass of the dried sol, 25 cm<sup>3</sup> volume,

*B* = mass of the total dried sol, and

*C* = mass of the original sample.

9.5 A test result is the average of two determinations.

## 10. Swelling Index

10.1 Remove the final traces of solvent from the unit, using suction. Do not disturb the gel on the screens.

10.2 Cap the unit and weigh quickly to ±1 g. Record this as the wet mass of the unit plus swollen gel.

10.3 Determine the wet mass of the unit alone, without sample, at frequent intervals, by filling and emptying the unit exactly as described in 8.4 and 9.2. Standing for 16 h is unnecessary.

10.4 Determine the swelling index as follows:

$$\text{Swelling index} = (E/D) \quad (3)$$

where:

*E* = (*F* − *G*)

*D* = (*C* − *B*)

*B* = mass of the dried sol (4 × *A*), 9.4,

*C* = mass of the original sample,

*D* = mass of the dried gel,

*E* = mass of the swollen gel,

*F* = mass of the wet unit containing gel, 10.2, and

*G* = mass of the wet unit without gel, 10.3.

10.5 A test result is the average of two determinations.

## 11. Dilute Solution Viscosity

11.1 Place the viscometer (5.4) into the constant temperature bath (5.5) and allow the temperature to equilibrate.

11.2 Obtain the flow time of 10 cm<sup>3</sup> of the chosen solvent, used for the determination of gel and swelling index for a particular rubber. Duplicate flow times should agree to ±0.3 s. Repeat this determination at least once daily so that a reliable figure is obtained. Record this as solvent flow time, *T*<sub>0</sub>.

NOTE 4—Viscometers must be scrupulously clean; otherwise discrepancies will be evident in the solvent flow times. Cleaning can be accomplished with dichromate cleaning solutions, detergents, and ultrasonic cleaners, or in stubborn cases, heating the dry viscometer at approximately 400°C. (This is below the melting point of borosilicate glass.)

11.3 Remove the solvent and dry the viscometer by rinsing with acetone. Use compressed air or vacuum to remove the residual acetone.

11.4 Pipet exactly 10 cm<sup>3</sup> of solution in accordance with 9.2 into the dry viscometer. Place the viscometer into the constant temperature bath (5.5) and allow the viscometer and contents to equilibrate to 25°C.

11.5 Determine the flow time as for the solvent in accordance with 11.2. Record this as sample flow time, *T*.

11.6 Determine the DSV as follows:

$$\text{DSV} = (2.303 \times \log T/T_0)/(4 \times A) \quad (4)$$

**TABLE 1 Type 1 Precision—Gel Content**

NOTE 1— $S_r$  = repeatability standard deviation, in measurement units.  
 $r$  = repeatability, in measurement units.  
 $(r)$  = repeatability, (relative) percent.  
 $SR$  = reproducibility standard deviation, in measurement units.  
 $R$  = reproducibility, in measurement units.  
 $(R)$  = reproducibility, (relative) percent.

Material	Average Level, %	Within Laboratories			Between Laboratories		
		$S_r$	$r$	$(r)$	$SR$	$R$	$(R)$
C (NBR)	0.82	0.254	0.719	87.7	0.398	1.126	137.
E (SBR)	3.11	0.527	1.491	48.0	3.691	10.44	335.
B (NBR)	58.5	0.408	1.155	1.97	0.667	1.888	3.23
D (SBR)	77.4	0.577	1.633	2.11	1.456	4.121	5.32
A (NBR)	85.8	0.373	1.056	1.23	2.11	5.97	6.96

where:

- 2.303 = factor for converting  $\log_{10}$  to natural log of the viscosity ratio (relative viscosity),
- $T$  = flow time for the sample,
- $T_0$  = flow time for the solvent, and
- $A$  = mass of 25 cm<sup>3</sup> of dried sol.

## 12. Report

12.1 Report the following information:

- 12.1.1 Complete identification of the sample, and
- 12.1.2 The average of two individual determinations for gel, swelling index, and dilute-solution viscosity.

## 13. Precision and Bias <sup>8</sup>

13.1 These precision statements have been prepared in accordance with Practice D 4483. Please refer to this practice for terminology and other testing and statistical concepts.

### 13.2 Gel:

13.2.1 The Type 1 precision of this test method was determined from an interlaboratory program based on three samples of NBR (A, B and C) and two samples of SBR (D and E). The NBR had gel contents of about 0, 60, and 85 % with the 85 % sample in powdered form. The SBR samples had about 0 to 75 % gel. The samples were tested by five laboratories in duplicate on three separate days. All gel values of 1 % or less were treated as 0.5 %.

13.2.2 The Type 1 precision data are given in Table 1 on the basis of the average of duplicate determinations constituting a test result as specified in 9.5.

### 13.3 Swelling Index:

13.3.1 Measurable results were obtainable only on materials A, B and D in five laboratories on each of three days.

13.3.2 The Type 1 precision is given in Table 2 in terms of test results that are the average of two determinations as specified in 10.5.

13.3.3 There appears to be no pronounced dependence of test standard deviation (within or among laboratories) on the mean value of swelling index in the 15 to 30 range.

### 13.4 Dilute-Solution Viscosity (DSV):

<sup>8</sup> Supporting data have been filed at ASTM Headquarters. Request RR: D-11-1012.

**TABLE 2 Type 1 Precision—Swelling Index**

NOTE 1— $S_r$  = repeatability standard deviation, in measurement units.  
 $r$  = repeatability, in measurement units.  
 $(r)$  = repeatability, (relative) percent.  
 $SR$  = reproducibility standard deviation, in measurement units.  
 $R$  = reproducibility, in measurement units.  
 $(R)$  = reproducibility, (relative) percent.

Material	Average Level, %	Within Laboratories			Between Laboratories		
		$S_r$	$r$	$(r)$	$SR$	$R$	$(R)$
A (NBR)	15.1	1.155	3.27	21.7	4.28	12.1	80.2
B (NBR)	17.97	0.866	2.451	13.6	0.85	2.41	13.4
D (SBR)	28.07	1.478	4.183	14.9	2.85	8.07	28.7

13.4.1 The DSV results were obtained on all five materials (A to E) in four laboratories with tests being conducted on each of three days.

13.4.2 The Type 1 precision is given in Table 3 in terms of test results that are the average of two determinations as specified in 11.7.

13.4.3 The repeatability standard deviation decreases with increasing DSV level, while the reproducibility standard deviation fails to show this response.

13.4.4 Materials B and C (high DSV NBR) show poorer reproducibility than A, D, and E.

### 13.5 General Discussion of Precision:

13.5.1 The results of the precision calculations for repeatability and reproducibility are given in Tables 1-3, in ascending order of material average or level, for each of the materials evaluated.

13.5.2 The precision of these test methods may be expressed in the format of the following statements that use an appropriate value of  $r$ ,  $R$ ,  $(r)$ , or  $(R)$ , that is, that value to be used in decisions about test results (obtained with the test method). The *appropriate value* is that value of  $r$  or  $R$  associated with a mean level in the precision tables closest to the mean level under consideration (at any given time, for any given material) in routine testing operations.

13.5.3 *Repeatability*— The repeatability  $r$ , of these test methods have been established as the *appropriate value* tabulated in the precision tables. Two single test results, obtained under normal test method procedures, that differ by

**TABLE 3 Type 1 Precision—Dilute Solution Viscosity**

NOTE 1— $S_r$  = repeatability standard deviation, in measurement units.  
 $r$  = repeatability, in measurement units.  
 $(r)$  = repeatability, (relative) percent.  
 $SR$  = reproducibility standard deviation, in measurement units.  
 $R$  = reproducibility, in measurement units.  
 $(R)$  = reproducibility, (relative) percent.

Material	Average Level, %	Within Laboratories			Between Laboratories		
		$S_r$	$r$	$(r)$	$SR$	$R$	$(R)$
A (NBR)	0.220	0.0700	0.198	90.	0.0817	0.231	105.
D (SBR)	0.495	0.0864	0.245	49.5	0.0870	0.246	49.7
B (NBR)	0.818	0.0354	0.100	12.3	0.119	0.336	41.2
C (NBR)	1.062	0.0293	0.083	7.8	0.166	0.470	44.3
E (SBR)	1.990	0.0295	0.0835	4.2	0.045	0.127	6.4

more than this tabulated  $r$  (for any given level) must be considered as derived from different or non-identical sample populations.

13.5.4 *Reproducibility*—The reproducibility  $R$ , of these test methods have been established as the *appropriate value* tabulated in the precision tables. Two single test results obtained in two different laboratories, under normal test method procedures, that differ by more than the tabulated  $R$  (for any given level) must be considered to have come from different or non-identical sample populations.

13.5.5 Repeatability and reproducibility expressed as a percentage of the mean level, ( $r$ ) and ( $R$ ), have equivalent

application statements as above for  $r$  and  $R$ . For the ( $r$ ) and ( $R$ ) statements, the difference in the two single test results is expressed as a percentage of the arithmetic mean of the two test results.

13.5.6 *Bias*—In test method terminology, bias is the difference between an average test value and the reference (or true) test property value. Reference values have not been determined for these test methods. Bias, therefore, cannot be determined.

#### **14. Keywords**

14.1 dilute solution viscosity; DSV; gel; raw rubber; swelling index

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