



Standard Test Method for Characteristic Groups in Rubber Extender and Processing Oils and Other Petroleum-Derived Oils by the Clay-Gel Absorption Chromatographic Method¹

This standard is issued under the fixed designation D 2007; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers a procedure for classifying oil samples of initial boiling point of at least 260°C (500°F) into the hydrocarbon types of polar compounds, aromatics and saturates, and recovery of representative fractions of these types. This classification is used for specification purposes in rubber extender and processing oils.

NOTE 1—See Test Method D 2226.

1.2 This test method is not directly applicable to oils of greater than 0.1 mass % pentane insolubles. Such oils can be analyzed after removal of these materials, but precision is degraded (See Appendix X1).

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

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precaution statements are given in 6.1, Section 7, A1.4.1, and A1.5.5.

2. Referenced Documents

2.1 ASTM Standards:

D 86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure²

D 323 Test Method for Vapor Pressure of Petroleum Products (Reid Method)²

D 1159 Test Method for Bromine Number of Petroleum Distillates and Commercial Aliphatic Olefins by Electro-metric Titration²

D 2226 Classification for Various Types of Petroleum Oils for Rubber Compounding Use³

D 5309 Specification for Cyclohexane 999⁴

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method⁵

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 The following terms refer to the hydrocarbon types and structural groups as measured by this test method:

3.1.1.1 *asphaltenes*, or *n-pentane insolubles*—insoluble matter that precipitates from a solution of oil in *n-pentane* under the specified conditions.

3.1.1.2 *polar compounds*—material retained on adsorbent clay after percolation of the sample in *n-pentane* eluent under the conditions specified.

3.1.1.3 *polar aromatics*—synonym for polar compounds.

3.1.1.4 *aromatics*—material that, on percolation, passes through a column of adsorbent clay in a *n-pentane* eluent but adsorbs on silica gel under the conditions specified.

3.1.1.5 *saturates*—material that, on percolation in a *n-pentane* eluent, is not adsorbed on either the clay or silica gel under the conditions specified.

4. Summary of Test Method

4.1 The sample is diluted with solvent and charged to a glass percolation column containing clay in the upper section and silica gel plus clay in the lower section. *n-Pentane* is then charged to the double column until a definite quantity of effluent has been collected. The upper (clay) section is removed from the lower section and washed further with *n-pentane*. A toluene-acetone mixture 50 to 50 by volume is then charged to the clay section for desorption and a specified volume of effluent collected. The lower (gel) column may be desorbed by recirculation of toluene.

4.2 The solvents are completely removed from the recovered *n-pentane* and the toluene-acetone fractions and the residues are weighed and calculated as saturate and polar compounds contents. Aromatics may be calculated by difference, or measured following evaporation of the toluene used for desorption of the gel column.

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.

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² *Annual Book of ASTM Standards*, Vol 05.01.

³ *Annual Book of ASTM Standards*, Vol 09.01.

⁴ *Annual Book of ASTM Standards*, Vol 06.04.

⁵ *Annual Book of ASTM Standards*, Vol 14.02.

4.3 When the sample contains more than 0.1 mass % of *n*-pentane insolubles, this test method cannot be used directly. The insoluble matter must be removed from the sample prior to charging to the column. A method for this removal is given as an appendix.

4.4 Alternative methods are provided (a) for recovery of aromatics from the gel column, and (b) for analysis of oil with high-polar content.

5. Significance and Use

5.1 The composition of the oil included in rubber compounds has a large effect on the characteristics and uses of the compounds. The determination of the saturates, aromatics, and polar compounds is a key analysis of this composition.

5.2 The determination of the saturates, aromatics, and polar compounds and further analysis of the fractions produced is often used as a research method to aid understanding of oil effects in rubber and other uses.

6. Apparatus

6.1 *Beakers, Anticreep*, 150-mL capacity. (**Warning**—Beakers should be examined for sharp edges and fire polished, if necessary.)

6.2 *Clay-Gel Column*, constructed as illustrated in Fig. 1.

6.3 *Conical Flasks*, (Erlenmeyer), 250-mL capacity.

6.4 *Solvent Receiver*, capable of collecting solvent, without splashing or loss of material during the analysis. A wide-mouth, graduated, 500-mL capacity Erlenmeyer flask is one such example that has been found suitable to use.

6.5 *Filter Funnel*, long stem, 125-mm diameter; for use with 185 mm ready folded, fine-texture, rapid filter paper.

6.6 *Separatory Funnel*, 500 mL.

6.7 *Hot Plate*, explosion proof, controlled to a surface temperature of 100 to 105°C.⁶

6.8 *Round Bottom Flask*, 3-necked, borosilicate, 500-mL capacity (Fig. 2).

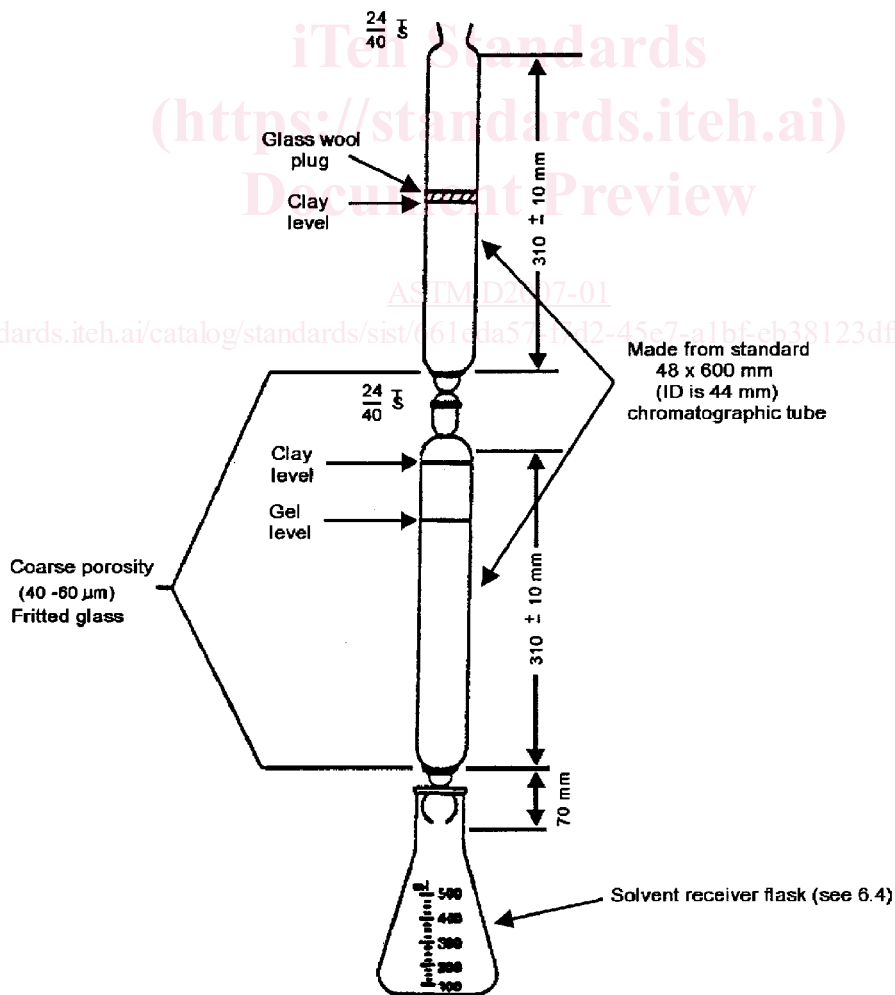
6.9 *Condenser*, borosilicate (Fig. 2).

6.10 *Adapter Tube* with Vigreux column (Fig. 2).⁷

6.11 *Flexible Joint*, TFE-fluorocarbon and borosilicate,

⁶ Temperatures should be uniform on the top of the hot plate. Some laboratory hot plates benefit by the inclusion of an aluminum plate, approximately 6-mm thick, included under or on top of regular plate top.

⁷ This item can be fabricated at any scientific glassblowing shop. It is also available from Owens Glass Apparatus, Inc., 128 River Road, Channelview, TX 77530.



NOTE 1—Check to ascertain ID is 44 mm.

FIG. 1 Clay-Gel Percolating Column

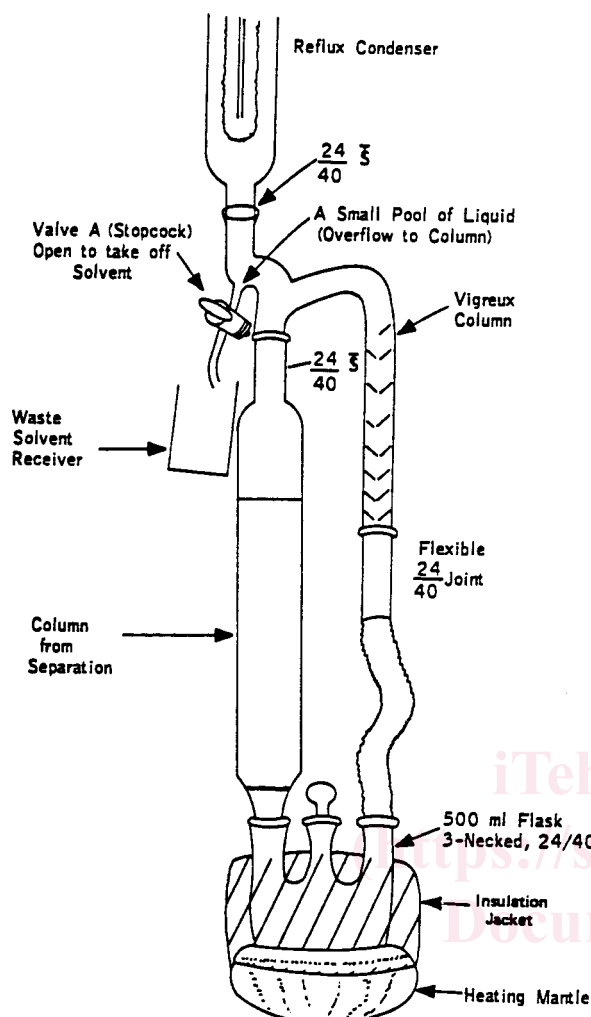


FIG. 2 Extraction Apparatus

24/40 T_S ground glass joints on each end.⁸

7. Reagents and Materials

7.1 *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.⁹ 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.

7.2 *Acetone*, reagent grade, minimum purity. (**Warning**—Acetone is extremely flammable.)

7.3 *Calcium Chloride*, anhydrous granules.

7.4 *Clay Adsorbent*, 500 to 250 μm (30 to 60 mesh)

Attapulugus.¹⁰ Clay quality may be determined using the azobenzene equivalence test shown in Annex A1. The azobenzene activity test measures the adsorptive characteristics of the clay. Azobenzene equivalence value should be 30 to 35. Clay outside of these limits should be discarded.

7.5 *Cyclohexane*, conforming to Specification D 3055. (Optional, see 8.1.9.) (**Warning**—Cyclohexane is extremely flammable. Harmful if inhaled.)

7.6 *Pentane*,¹¹ reagent grade minimum purity: (**Warning**—*n*-Pentane is extremely flammable. Harmful if inhaled.)

Distillation (Test Method D 86).

Initial boiling point, min	33.4°C (92°F)
Dry point, max	40.5°C (105°F)

Reid vapor pressure (Test Method D 323), max 110 kPa (17 psi); Bromine number (Test Method D 1159), 0.5 maximum; Isopentane, maximum, 10 %; *n*-pentane, minimum, 80 %.

7.7 *Silica Gel*, activated, conforming to the following inspections:¹²

Sieve analysis	> 30 sieve size, 5 % (mass) maximum;
	> 50 sieve size, 45 % (mass) min
	> 100 sieve size, 80 % (mass) min
	> 200 sieve size, 94 % (mass) min

7.7.1 Gel should be activated for 4 h in an air oven at 190°C in a shallow pan.

7.8 *Toluene*, reagent grade minimum purity. (**Warning**—Toluene is flammable. Vapor harmful.)

7.9 *Toluene-Acetone Mixture* (50 to 50 by volume), mix equal volumes of toluene and acetone.

7.10 In order to obtain results that are consistent with those obtained elsewhere, it is very important that only the reagents and materials described in this section be used.

8. Procedure

8.1 Fractionation:

8.1.1 Prepare the adsorption column (Fig. 1) by placing 100 g of clay adsorbent in the upper section of the column and 200 g of silica gel plus 50 g of clay on top of the gel in the lower section (Note 4). Place a piece of glass wool (of about 25-mm loose thickness) over the top surface of the clay in the upper column to prevent agitation of the clay while charging the eluent solvents. Join the columns (clay over gel) after lubricating the joint with hydrocarbon-insoluble grease. It is important that the adsorbents in each column be packed to a constant level. A minimum of ten taps with a soft rubber hammer at different points up and down and 25 taps on top of each column should be employed to achieve constant level. A suitable rubber hammer may be assembled by fastening two No. 7 or 8 rubber stoppers on one end of a small rod about 200-mm long. Use fresh adsorbents for each determination.

8.1.2 If *n*-pentane insolubles were not determined, select the appropriate sample size in accordance with the following polar

¹⁰ Available from Forcoven Products, P.O. Box 1556, Humble, TX 77347-1556. Packaged in moisture resistant twinned packets of 50 and 100 g (sufficient for one determination). These packets are packed 50 sets per case. It is important that extremes of temperature be avoided on stored clay samples.

¹¹ Available from Special Products Div., Phillips Petroleum Co., Bartlesville, OK.

¹² Gel meeting these specifications is available from Forcoven Products, P.O. Box 1556, Humble, TX 77347-1556, packaged in 200 g moisture resistant packets. Sieve analysis should be checked on other sources of gel.

⁸ Cole Parmer No. 6675-40 has been found suitable for this purpose.

⁹ *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.

content ranges, if the proper range can be anticipated; otherwise, use a 10 ± 0.5 g sample.

Polar Content Range, mass percent	Sample Size, g
0–20	10 ± 0.5
Above 20	5 ± 0.2

8.1.3 Dilute with 25 mL of *n*-pentane solvent and mix well to ensure a uniform solution of the sample. The sample should not display precipitate or flocculate at this point. If a precipitate is present *asphaltenes* may be removed by the procedure of Appendix X1, however, the precision statement no longer applies. It is important that the polar content result obtained be not greater than that for the sample size as specified above, since the capacity of the clay for retaining polar constituents becomes limited at these concentrations. If results exceed this specification, repeat the test using a smaller sample. Partitioning between aromatics and polar compounds is affected by sample size. Results using different sample size may not be equivalent.

NOTE 2—For viscous oils, dilutions of the sample with 25 mL of cyclohexane is more convenient and does not affect the results. Cyclohexane used in this manner will not detect small quantities of *asphaltenes*, however.

8.1.4 Add 25 mL of *n*-pentane to the top of the clay portion of the assembled column and allow to percolate into the clay. As soon as nearly all of the *n*-pentane has entered the clay, charge to the column the diluted sample of 8.1.1. Wash the sample beaker (or flask) with *n*-pentane and add the washings to the column. After nearly all of this material has entered the clay, wash the walls of the column above the clay free of sample with *n*-pentane. The sample and eluent solvent can be added to the column through a 65-mm diameter, wide-stem funnel (the funnel can be left on top of the column). At no time during the run should air be allowed to enter the clay bed.

8.1.5 When nearly all of the washings have entered the clay, charge *n*-pentane to the column and maintain a head level well above the clay beds (Note 3) to wash the saturate portion of the sample from the adsorbents. Recover 280 ± 10 mL of the first *n*-pentane effluent from the column in a graduated, 500-mL wide-mouth conical flask.

NOTE 3—Columns may be briefly separated, if necessary, to give a solvent head 5- to 10-mm deep in the second (lower) column. Loss of the head will give channeling in the lower column, with inaccurate results.

NOTE 4—With long use, the frits in the absorption columns become progressively less porous. If the time for percolation doubles over that for a new column, the slow columns are to be discarded.

8.1.6 Disconnect the two sections. Allow the lower section to drain into a receiver. Continue washing the upper clay section with *n*-pentane. Maintain a moderate liquid head level above the clay during this wash and adjust *n*-pentane additions so that the level is about 25 mm when 150 mL have been collected in the receiver. Discontinue additions at this point and allow the liquid to essentially drain from the column. The quantity in the receiver should then be about 200 mL. The *n*-pentane from this step and from the draining of the lower column should be discarded if aromatics are to be determined by difference. This *n*-pentane should be added to the aromatics solution from the gel column during solvent evaporation (8.3) if aromatics are to be recovered.

NOTE 5—This extra *n*-pentane washing of the clay section is necessary in order to ensure complete removal of aromatics from the clay.

8.1.7 After *n*-pentane effluent has essentially drained from the column, charge a 50 to 50 volume mixture of toluene–acetone. Collect the effluent in a 500-mL separatory funnel. Collect 250 mL of the toluene-acetone (plus *n*-pentane) effluent or until the effluent is practically colorless (only in exceptional cases will more than 300 mL of effluent be required).

8.1.8 Stopper the separatory funnel containing the toluene-acetone fraction and swirl it a few times to aid in settling the water. Then let it stand for about 5 min. Drain off and discard the lower (aqueous) layer. Add approximately 10 g of anhydrous calcium chloride granules to the fraction remaining in the separatory funnel and shake for about 30 s; vent frequently during the shaking period. Allow the mixture to settle for at least 10 min.

8.1.9 Filter the fraction through a rapid folded filter paper catching the filtrate in a 500-mL conical flask. Rinse the separatory funnel with approximately 25 mL of *n*-pentane, filter and collect with the mixed solvent fraction. Wash the filter paper with an additional 10 to 15 mL of *n*-pentane and collect with the mixed solvent fraction. **IMPORTANT**—Make all transfers of organic solvents from the separatory funnels through the top and avoid transferring any water that may have accumulated around the calcium chloride.

8.2 Desorption of Aromatics:

8.2.1 If it is desired to determine the aromatics by isolation rather than by difference, the gel column (lower column of the clay gel adsorption column of 8.1, Fig. 1), after the 280 ± 10 mL of *n*-pentane have been collected, is placed in the extraction assembly of Fig. 2.

8.2.2 Toluene (200 ± 10 mL) is placed in the 500-mL flask and refluxed at such a rate of 10 ± 2 mL/min for 2 h.

NOTE 6—Toluene reflux can be measured by collection for a 1 min period using a graduated cylinder through valve A, Fig. 2.

8.2.3 At the end of this time, the valve (A) is opened and the toluene removed into a waste solvent receiver to a volume of approximately 50-mL in the flask. The solution remaining is then combined with the *n*-pentane from 8.1.6 for recovery of aromatics. Do not go further by distillation, as oil will be lost, giving inaccurate results.

8.3 Solvent Removal:

8.3.1 Label and weigh for tare the anti-creep beakers that are to be used for the evaporation of solvent (one each for polar compounds, saturates, and aromatics desorbed). Place them on the controlled hot plate at surface temperature of 100°C to 105°C , fill approximately half full with the respective solutions (saturates from 8.1.4, aromatics from 8.1.6 and 8.2.3, polars from 8.1.8), refilling as this volume is reduced to one-quarter full. A gentle nitrogen sweep may be used over the surface of the liquid. It should not ruffle the surface nor should this nitrogen jet be placed below the surface. The flasks which contained the fractions should be rinsed with *n*-pentane, and this *n*-pentane added to the respective anti-creep beakers.

8.3.2 When essentially all the solvent is evaporated, weigh the beakers at 10 min intervals. Solvents are considered removed when the weight loss between weighings is less than 10 mg.