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## Standard Test Method for Microscopical Analysis by Reflected Light and Determination of Mesophase in a Pitch<sup>1</sup>

This standard is issued under the fixed designation D4616; 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~~ Scope\*

1.1 This test method covers laboratory procedures for the preparation of granular and melted samples for microscopic analysis using reflected light to identify and estimate the amount and size of the mesophase.

1.2 The values stated in inch-pound units are to be regarded as standard. The values given in parentheses are mathematical conversions to SI units that are provided for information only and are not considered standard.

1.3 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:<sup>2</sup>

- [D329 Specification for Acetone](#)
- [D1160 Test Method for Distillation of Petroleum Products at Reduced Pressure](#)
- [D2318 Test Method for Quinoline-Insoluble \(QI\) Content of Tar and Pitch](#)
- [D3104 Test Method for Softening Point of Pitches \(Mettler Softening Point Method\)](#)
- [D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants](#)
- [D4296 Practice for Sampling Pitch](#)
- [E11 Specification for Woven Wire Test Sieve Cloth and Test Sieves](#)
- [E562 Test Method for Determining Volume Fraction by Systematic Manual Point Count](#)

### 3. Terminology

#### 3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminology [D4175](#).

#### 3.2 Definitions of Terms Specific to This Standard:

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.05 on Properties of Fuels, Petroleum Coke and Carbon Material.

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<sup>2</sup> 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.

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

3.2.1 *cenospheres*—*cenospheres, n*—usually a minor in crude oil, component of coal tar pitch. They are formed by the rapid pyrolysis of unconfined coal particles that are carried over from the coke oven to the tar. Microscopically, they appear like hollow spheres or segments thereof (see an inert, hollow sphere, with diameter Fig. 1), and are typically sized from about typically ranging from 10 μm to 500 μm. In polarized light (crossed polarizers), a cenosphere may be optically active. The size of the anisotropic pattern or mosaic depends upon the rank of the coal carbonized. Cenospheres are harder than the continuous phase and polish in relief (see Fig. 1):

3.2.1.1 *Discussion*—

Cenospheres are typically usually a minor component of coal tar pitch.

3.2.1.2 *Discussion*—

Cenospheres are formed by the rapid pyrolysis of unconfined coal particles that are carried over from the coke oven to the tar. Microscopically, they appear like hollow spheres or segments thereof (see Fig. 1).

3.2.1.3 *Discussion*—

In polarized light (crossed polarizers), a cenosphere may be optically active. The size of the anisotropic pattern or mosaic depends upon the rank of the coal carbonized. Cenospheres are harder than the continuous phase and polish in relief (see Fig. 1).

3.2.2 *coke-oven-coke*—*coke-oven-coke, n*—usually a minor component of coal tar pitch. It originates in carry-over from the coke oven to the tar side. It differs from cenospheres only in terms of its shape and porosity. Coke-oven-coke is angular and less porous.

3.2.3 *isotropic phase*—*phase, n*—usually the predominant, and continuous, phase. It is a complex mixture of organic aromatic compounds composed mainly of carbon and hydrogen. At room temperature, the isotropic phase is a glass-like solid. It is optically inactive in polarized light (see Fig. 1 and Fig. 2).

3.2.4 *mesophase*—*mesophase, n*—an optically anisotropic liquid crystal carbonaceous phase that forms from the parent liquor when molecular size, shape, and distribution are favorable. In the early stages of its development, mesophase usually appears as spheroids. The planar molecules are lined up equatorially as shown schematically in Fig. 3. This equatorial arrangement may be distinguished in crossed polarized light. Under crossed polarizers, the distinctive mesophase spheroids, with their complex extinction patterns shown in Fig. 2, can be readily seen.<sup>3</sup>

3.2.4.1 *spheroids*—*spheroids, n*—At magnifications of 400× and 500×, the minimum spheroid size which can be resolved with confidence is 4 μm in diameter. At magnifications of 1000× to 1800×, the minimum spheroid size that can be resolved with confidence is about 2 μm in diameter. Typically, the upper size may be 100 μm. Mesophase spheroids are relatively soft and do not form relief structures (see Fig. 4). Quinoline insoluble particles often aggregate at the interface between the continuous isotropic phase and mesophase.

3.2.4.2 *isotropic phase*—*phase, n*—The isotropic phase is more soluble than the mesophase in solvents such as toluene. Solvent etching is achieved by soaking the polished surface in toluene for a few seconds, rinsing the surface with cold flowing water, and drying in a current of hot air. Etching produces sharply defined mesophase spheroids (see Fig. 4).

3.2.5 *mineral matter*—*matter, n*—formed when minute particles of the coke oven charge are carried over into the coke oven collecting main during the charging operation. The tiny coal particles are digested in the collecting main tar, resulting in a residue that is rich in mineral matter. This mineral matter is identified under bright field illumination by its high reflectivity, in the case of pyrite, and its low reflectance in the case of clay, quartz, and carbonates. The association of mineral matter with insoluble organic matter from coal aids in its identification.

3.2.6 *normal quinoline insolubles*—*insolubles, n*—(sometimes termed “true,” natural or “primary” quinoline insolubles)—a carbon black-like solid phase in coal tar pitch that is produced by thermal cracking of organic compounds in the tunnel head above the coal charge in a by-product coke oven. The individual spherically-shaped particles are usually less than 2 μm in diameter. A typical coal tar pitch may contain from about 1 % to about 20 % (by weight) of normal quinoline insolubles. The normal quinoline insolubles are relatively hard. They are outlined in bright incident light because they stand out in relief from the softer isotropic phase (see Fig. 1).

3.2.6.1 *Discussion*—

Sometimes the term primary QI is used to describe all quinoline insoluble materials that are carried over during the coking operation (cenospheres, mineral matter, normal, QI, and so forth).

<sup>3</sup> A more complete discussion will be found in a paper by Honda, H., Kimura, H., and Sanada, Y., “Changes of Pleochroism and Extinction Contours in Carbonaceous Mesophase,” *Carbon*, 9, 1971, pp. 695–697.

3.2.6.2 *normal quinoline insoluble material*—~~material, n—~~Observed under crossed polarizers, the normal quinoline insoluble material displays a Brewster cross pattern (see Fig. 1 and Fig. 2). This interference figure remains stationary when the specimen is rotated through 360°. The onionskin arrangement can be observed in particles with a minimum diameter of 2 µm at high magnification (1000× to 2000×) under cross polarizers.

### 3.2.6.3 *Discussion*—

~~The quinoline insolubles content is determined by Test Method D2318 and represents the total amount of natural quinoline insolubles, cenospheres, coke-oven-coke, pyrolytic carbon, refractory, reactor coke, and free ash in a pitch. Additionally, the quinoline insolubles will contain any insoluble species from the isotropic phase and the insoluble portion of the mesophase. Hence, the quinoline soluble fraction is composed of the bulk of the isotropic phase and the soluble fraction of the mesophase. However, the quinoline insoluble test is not necessarily a true measure of the solid constituents of pitch.~~

~~Normal~~The quinoline insolubles content is determined by Test Method D2318 and represents the total amount of natural quinoline insolubles, cenospheres, coke-oven-coke, pyrolytic carbon, refractory, reactor coke, and free ash in a pitch. Additionally, the quinoline insolubles will contain any insoluble species from the isotropic phase and the insoluble portion of the mesophase. Hence, the quinoline soluble fraction is composed of the bulk of the isotropic phase and the soluble fraction of the mesophase. However, the quinoline insoluble test is not necessarily a true measure of the solid constituents of pitch.

Normal QI with radial symmetry is produced by oxycracking during the early portion of the coking cycle when partially oxidizing conditions can exist, and is referred to as combustion black (see Fig. 5a). Normal QI with concentric symmetry is produced by thermal cracking later in the coking cycle under reducing conditions, and is referred to as thermal black (see Fig. 5b). These two symmetries can only be differentiated using electron microscopy.<sup>4,5</sup> The quinoline insolubles content determined by Test Method D2318 is sometimes greater than that anticipated on the basis of the concentration of the quinoline insolubles during distillation or heat treatment to produce the final pitch. The difference is known as the “secondary” quinoline insolubles content, and is traditionally regarded as the mesophase content. This equivalence of secondary quinoline insolubles and mesophase is erroneous because the mesophase may be partially soluble in quinoline.

3.2.7 *pyrolytic carbon*—~~carbon, n—~~a carbon that originates as a deposit on the upper walls, tunnel head, and standpipes of a coke oven due to thermal cracking. It is usually a minor phase in coal tar pitch, highly variable in shape and porosity, and may be sized up to 500 µm. It is usually optically active under crossed polarizers. The fine sized domains are commonly referred to as spherulitic, while the coarser anisotropic domains are called pyrolytic. Spherulitic and pyrolytic carbons are highly reflecting, relatively hard materials and stand out in relief from the softer isotropic phase.

3.2.8 *reactor coke*—a material that originates on the walls of the pipestill reactor used in the distillation or heat treatment to produce pitch from either coal tars or petroleum oils. It is thermally more advanced than reactor mesophase. It is usually a minor component of pitch and may be sized up to 200 µm. It may be angular or rounded, and it may be relatively porous with a coarse appearance under crossed polarizers. It is distinguished from the reactor mesophase mentioned in 3-1.93.2.9 by its relative hardness, which causes it to show up in relief in bright field illumination.

3.2.9 *reactor mesophase*—~~mesophase, n—~~a material that originates on the walls of the pipestill or reactor used in the distillation or heat treatment to produce pitch from either coal tars or petroleum oils. It is usually a minor component of pitch and may be sized up to 200 µm. It may be angular or rounded, and it may be relatively porous. Under crossed polarizers reactor mesophase has a coarse mosaic appearance. In contradistinction to the reactor coke mentioned in 3-1.83.2.8, reactor mesophase is comparatively soft and shows no relief in bright field illumination.

3.2.10 *refractory*—~~refractory, n—~~usually a minor component that originates from the coke oven walls, doors, and patches due to wear and degeneration; another component is charge hole sealant. It can be recognized under the microscope through optical properties, hardness, shape, and associated minerals.

## 4. Summary of Test Method

4.1 A representative sample with a softening point of at least 212 °F (100 °C), as measured by Test Method D3104 (Mettler method), is crushed to a specific particle size and encapsulated in resin. Alternatively, a representative molten pitch sample is poured into a mold, or a representative crushed sample is melted and poured into a mold. If the Mettler softening point is less than 212 °F (100 °C), it is raised to 212 °F to 248 °F (100 °C to 120°C) by vacuum distillation. The encapsulated, or molded, sample is ground and polished to a flat surface for examination in reflected light.

<sup>4</sup> Bertau, B.L., and Souffrey, B., “Composition of Tar and Pitches as a Result of the Specific Aspects of the Coking Plant,” *Coke Making International*, Vol 2 , 1990, pp. 61–63.

<sup>5</sup> Lafdi, K., Bonnamy, S., and Oberlin, A., “TEM Studies of Coal Tars—Crude Tar and its Insoluble Fractions,” *Carbon*, Vol 28, No. 1, 1990, pp. 57–63.

4.2 The mesophase spheroid content of a representative sample is identified and the proportion determined on a volume basis by observing a statistically adequate number of points. Only the area proportion is determined on a surface section of a sample; however, the area and volume proportion are the same when the components are randomly distributed throughout the sample.

## 5. Significance and Use

5.1 Sometimes coal tar and petroleum pitches are heat treated thereby forming mesophase spheroids. The mesophase may be partially soluble in quinoline and cannot be estimated by the quinoline insoluble test (Test Method **D2318**). This test method provides for the identification, quantitative estimation, and size determination of mesophase spheroids.

5.2 The mesophase initially forms as spheroids that may coalesce to form a variety of asymmetrical shapes. The smallest mesophase particle that can be detected with certainty at 400× or 500× magnification is 4 μm in diameter; mesophase particles sizes less than 4 μm should be ignored. If mesophase material less than 4 μm in size is of interest, then magnifications of 1000× to 1800× shall be used and the results should be appropriately identified. This method is limited to determining minor levels of mesophase, that is, ≤20 % mesophase.

## 6. Apparatus

6.1 *Grinder, Pulverizer, or Mill*, for crushing the representative sample and mortar and pestle or other equipment suitable for reducing the particle size of a 100 g sample to less than 8 mesh (2.4 mm).

6.2 *Sieves*—U. S. sieve No. 8. See Specification **E11**.

6.3 *Vacuum Distillation Apparatus*, such as that specified in Test Method **D1160**.

6.4 *Vacuum Chamber*, equipped with an observation window.

6.5 *Hotplate or Laboratory Oven*, possibly fitted to receive inert gas.

6.6 *Bakelite Rings*,<sup>6-8</sup> 1 in. (25 mm) or 1¼ in. (32 mm) in diameter.

6.7 *Grinding and Polishing Equipment*—One or several laps on which the pitch specimens can be ground and polished to a flat, scratch-free surface. Laps may be made of aluminum, iron, brass, bronze, lead, glass, wax, or wood. Equipment that has 8 in. (203 mm) diameter disk laps that can rotate at 150 to 400 r/min, and that has an automatic sample holder attachment is recommended.<sup>9,8</sup>

6.8 *Sample Cleaner*—Some equipment is essential for cleaning the specimens between the different grinding or polishing stages. This may be an ultrasonic device or a simple stream of water and an air jet for drying.

6.9 *Microscope*—Any polarizing microscope with the capability for observations by reflected light (for example, metallurgical or opaque-ore microscopes) may be employed. The polarizer may be of the Nicol prism or sheet type. All optical components (objective, eyepiece, polarizer, and analyzer) shall be of a quality to permit examination of the dry specimen at magnifications up to 400× to 500× under crossed polarizers. For magnifications greater than 500×, 0.1 immersion objectives shall be used. The analyzer should be oriented 90° with respect to the polarizer for cross polarizer examination. Any light source that can be regulated for stable output with sufficient intensity for photography with cross polarizers may be used. The microscope shall have a circular stage that is capable of rotating a specimen through 360°. The stage shall also be of such type that the specimen can be quickly advanced by definite fixed increments in two perpendicular directions, such as a stage with click stops. If an electrically operated stage is used, incremental steps in one direction across the specimen may be actuated by the counter switches. One eyepiece of

<sup>6</sup> Bakelite is a trademark of the Union Carbide Corporation, Old Ridgebury Road, Danbury, CT, 06817.

<sup>7</sup> Rings supplied by Buehler Ltd., 41 Waukegan Road, Lake Bluff, IL, and Leco Corporation, 3000 Lakeview Ave., St. Joseph, MI, 49085.

<sup>8</sup> If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend.

<sup>9</sup> Grinding and polishing machines with automatic attachments supplied by Buehler Ltd., 41 Waukegan Road, Lake Bluff, IL, Struers, Inc., 20102 Progress Drive, Cleveland, OH, 44136 and Leco Corporation, 3000 Lakeview Ave, St. Joseph, MI, 49085.

the microscope should be fitted with a graticule or cross-hair. If other than cross-hairs are used, the eyepiece disk shall contain a Whipple graticule or one of such design that four or twenty-five points are visible, lying at the corners of a square covering most of the field of view.

6.10 *Sample Leveling Process*—A conventional manual leveling device may be employed to level the polished specimens when they are mounted on microscope slides with clay for observations with an upright microscope.

6.11 *Counter*—The counter shall be capable of recording counts for two or more components.

## 7. Reagents and Materials

7.1 *Epoxy*<sup>10,8</sup>—Any epoxy binding system fulfilling the following requirements may be used:

7.1.1 The epoxy-hardener system shall cure at room temperature. The epoxy should be easily poured at room temperature (typically with a viscosity of less than 1000 cP at 77 °F (25 °C)).

7.1.2 There will be minimal mutual solubility between the resin and the pitch. In other words, there will be minimal discoloration of the epoxy; therefore, the original epoxy should be clear (not colored).

7.1.3 The epoxy shall hold all pitch particles securely during grinding, polishing, and observation.

7.1.4 The epoxy curing exotherm will not melt the pitch.

7.1.5 The epoxy shall be such that a substantially flat surface with minimal scratches can be obtained as a result of the grinding and polishing procedure.

7.1.6 Under the microscope in bright field illumination the epoxy shall contrast with the pitch.

7.2 *Cement*, or double-sided masking tape.<sup>11,8</sup>

7.3 *Acetone*, meeting the requirements of Specification **D329**.

7.4 *Grinding Abrasives*—Water-resistant silicon carbide papers of grit numbers 240, 400, and 600.

7.5 *Polishing Abrasives*—Diamond compound of 3 μm particle size and aluminum oxide powder of 0.05 μm particle size.

7.6 *Lap Coverings*—Nap-free cloths of cotton and silk and chemotextile material backed with water-resistant adhesive<sup>12</sup> are used primarily with the diamond abrasive. Microcloth,<sup>13,8</sup> Texmet,<sup>12,8</sup> and Kempad<sup>14,8</sup> are recommended for use with the alumina abrasive.<sup>15,8</sup>

7.7 *Extender*—Any extender compatible with the diamond compound and the pitch-epoxy specimen.<sup>16,8</sup>

7.8 *Detergent*—Any nonoxidizing detergent may be used for cleaning the specimen after each grinding or polishing stage.

7.9 *Wetting Agent*—Ultramet ultrasonic cleaning solution.<sup>17,8</sup>

<sup>10</sup> Suitable systems for this purpose have been found to be: (1) Eight parts by weight Shell resin Epon 815 and one part by weight Ceilcote hardener 4D which fully hardens at 23°C within 12 h, and (2) Four parts by weight Armstrong resin C-4 and one part by weight Armstrong hardener D.

<sup>11</sup> Duco is a trademark of the Dupont Co., 1007 Market St., Wilmington, DE, 19898.

<sup>12</sup> Texmet, or Metcloth supplied by Buehler Ltd., 41 Waukegan Road, Lake Bluff, IL, 60044.

<sup>13</sup> Metcloth is a referenced trademark of Buehler Ltd., 41 Waukegan Road, Lake Bluff, IL, 60044.

<sup>14</sup> The sole source of supply of the apparatus known to the committee at this time is available from Dunnington Co., Rt. 100, Chester Springs, PA 19425.

<sup>15</sup> Microcloth is a registered trademark of Buehler, Ltd., 41 Waukegan Road, Lake Bluff, IL.

<sup>16</sup> Extenders supplied by Buehler, Ltd., 41 Waukegan Road, Lake Bluff, IL, 60044, and Leco Corporation, 3000 Lakeview Ave., St. Joseph, MI, 49085.

<sup>17</sup> The sole source of supply of the apparatus known to the committee at this time is supplied by Buehler, Ltd., 41 Waukegan Rd., Lake Bluff, IL 60044.

7.10 *Toluene*—Reagent grade shall be used conforming to the specification of the Committee on Analytical Reagents of the American Chemical Society.<sup>18</sup>

7.11 *Immersion Oil*—An oil used with oil immersion objective to enhance the contrast between materials being analyzed. An acceptable oil is Cargille B.<sup>19,8</sup>

## 8. Bulk Sampling

8.1 Samples from shipments shall be taken in accordance with Practice **D4296** and shall be free of foreign substances. Thoroughly mix the sample immediately before removing a representative portion for dehydration or for preparation for microscopical examination.

## 9. Preparation of Working Sample

9.1 If the solid bulk sample contains free water, air-dry a representative portion at 140 °F (60 °C) or less, either in a vacuum oven or in a forced-circulation air oven.

9.2 If the pitch (with a Mettler softening point of at least 212 °F (100 °C)) is a solid sample, prepare a 100 g working sample by suitable crushing, mixing, and quartering of a representative portion of the dry sample. Crush so that all of the sample passes through a No. 8 sieve (2.4 mm). The crushing can be done with a small jaw crusher or Holmes mill and a mullite mortar and pestle.

9.3 If the Mettler softening point is less than 212 °F (100 °C), then the reduced sample of 20 g to 200 g should be vacuum distilled to a final softening point of 212 °F to 248 °F (100 °C to 120 °C). The distillation can be carried out in an apparatus such as that specified in Test Method **D1160**, or some alternative apparatus, provided the temperature of the sample does not exceed 482 °F (250 °C), in order to avoid heat treatment.

## 10. Preparation of Specimen

### 10.1 *Resin-Encapsulated Granular Specimen:*

10.1.1 Spread a thin coating of cement over an area of about 1.75 in.<sup>2</sup> (1130 mm<sup>2</sup>) on a thin card, such as an index card. Double-sided masking tape may be used as an alternative to the cement. In this case, it is not necessary to use acetone. Place a 1 in. (25 mm) or 1¼ in. (32 mm) diameter Bakelite ring on the cemented area, such that a seal is created between the card and the ring. The cemented rings are usually made up in a batch several days in advance. Lightly moisten the cemented area enclosed by the ring with acetone to soften the cement. Cover the inside area with pitch particles until most is occupied by the cemented pitch.

10.1.2 Cover the cemented particles in the Bakelite ring with an epoxy resin-hardener mixture.<sup>20</sup> After the resin hardens, fill the ring with epoxy resin-hardener and allow to cure.

10.1.3 If digestion of the pitch or resin system is necessary, place the encapsulated specimen in a vacuum chamber of the type in which the specimen can be observed. The purpose of the present step is to de-gas the resin system and the pitch specimen and achieve complete penetration of any porosity in the pitch. Take care, otherwise the resin will foam out of the ring and the preparation will have to be restarted. Typically, an absolute pressure of 0.4 in. (10 mm) Hg is drawn for a few seconds and the chamber repressurized to 24 in. (600 mm) Hg before the resin rises out of the ring. An absolute pressure of 0.4 in. (10 mm) is pulled carefully for a second time for a few seconds, followed by repressurization to 24 in. (600 mm) Hg. Finally, an absolute pressure of 0.4 in. (10 mm) Hg is pulled for a few seconds before the resin encapsulated specimen is brought up to ambient pressure.

10.1.4 Take the degassed encapsulated specimen from the vacuum chamber, fill to the brim with the balance of the resin-hardener mixture mentioned under **10.1.2**, and allow to cure by standing overnight at ambient temperature and pressure.

<sup>18</sup> *Reagent Chemicals, American Chemical Society Specifications, ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

<sup>19</sup> The sole source of supply of the apparatus known to the committee at this time is available from R.P. Cargille Laboratories, Cedar Grove, NJ 07009.

<sup>20</sup> Epoxy resin-hardener mixtures, such as Shell Epon 815-Ceilocote 4D, eight parts and one part by weight, respectively, or Armstrong C-4-Armstrong activator D, four parts and one part by weight, respectively, or APCO R313 with Applied Plastics hardener B, approximately four parts and one part by weight, respectively.