



## 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 D 4616; 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 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 the 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 and health practices and determine the applicability of regulatory limitations prior to use.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 329 Specification for Acetone<sup>2</sup>

D 1160 Test Method for Distillation of Petroleum Products at Reduced Pressures<sup>3</sup>

D 2318 Test Method for Quinoline-Insoluble (QI) Content of Tar and Pitch<sup>4</sup>

D 3104 Test Method for Softening Point of Pitches (Mettler Softening Point Method)<sup>4</sup>

D 4296 Practice for Sampling Pitch<sup>4</sup>

E 11 Specification for Wire-Cloth Sieves for Testing Purposes<sup>5</sup>

E 562 Practice for Determining Volume Fraction by Systematic Manual Point Count<sup>6</sup>

### 3. Terminology

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

3.1.1 *cenospheres*—usually a minor 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 seg-

ments thereof (see Fig. 1), and are typically sized from about 10 to 500  $\mu\text{m}$ . 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).

3.1.2 *coke-oven-coke*—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.

3.1.3 *mineral matter*—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.

3.1.4 *refractory*—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.

3.1.5 *isotropic phase*—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).

3.1.6 *mesophase*—an optically anisotropic liquid crystal carbonaceous phase that forms from the parent liquor when molecular size, shape, and distribution is 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>7</sup>

3.1.6.1 At magnifications of 400 $\times$  and 500 $\times$ , the minimum spheroid size which can be resolved with confidence is 4  $\mu\text{m}$  in

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.05.OF on Industrial Pitches.

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<sup>2</sup> Annual Book of ASTM Standards, Vol 06.04.

<sup>3</sup> Annual Book of ASTM Standards, Vol 05.01.

<sup>4</sup> Annual Book of ASTM Standards, Vol 04.04.

<sup>5</sup> Annual Book of ASTM Standards, Vol 14.02.

<sup>6</sup> Annual Book of ASTM Standards, Vol 03.01.

<sup>7</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.

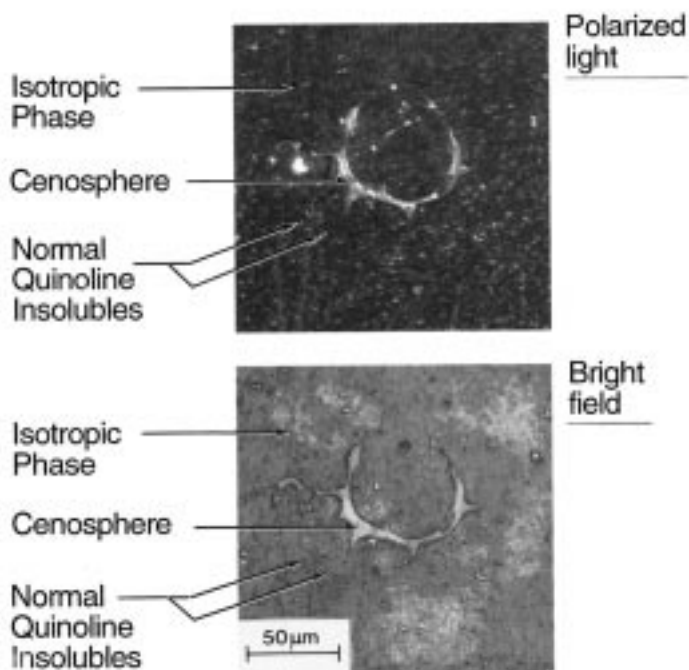


FIG. 1 Photomicrographs of a Coal Tar Pitch at 500× Magnification in Polarized Light (Crossed Polarizers) and Bright Light Showing the Isotropic Phase, Natural Quinoline Insolubles, and a Cenosphere.

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.

3.1.6.2 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).

3.1.7 *natural quinoline insolubles* (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).

NOTE 1—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, etc.).

3.1.7.1 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.

NOTE 2—The quinoline insolubles content is determined by Test Method D 2318 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 by 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>8,9</sup> The quinoline insolubles content determined by Test Method D 2318 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.

3.1.8 *pyrolytic carbon*—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.

3.1.9 *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 3.10 by its relative hardness, which causes it to show up in relief in bright field illumination.

3.1.10 *reactor mesophase*—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

<sup>8</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>9</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.

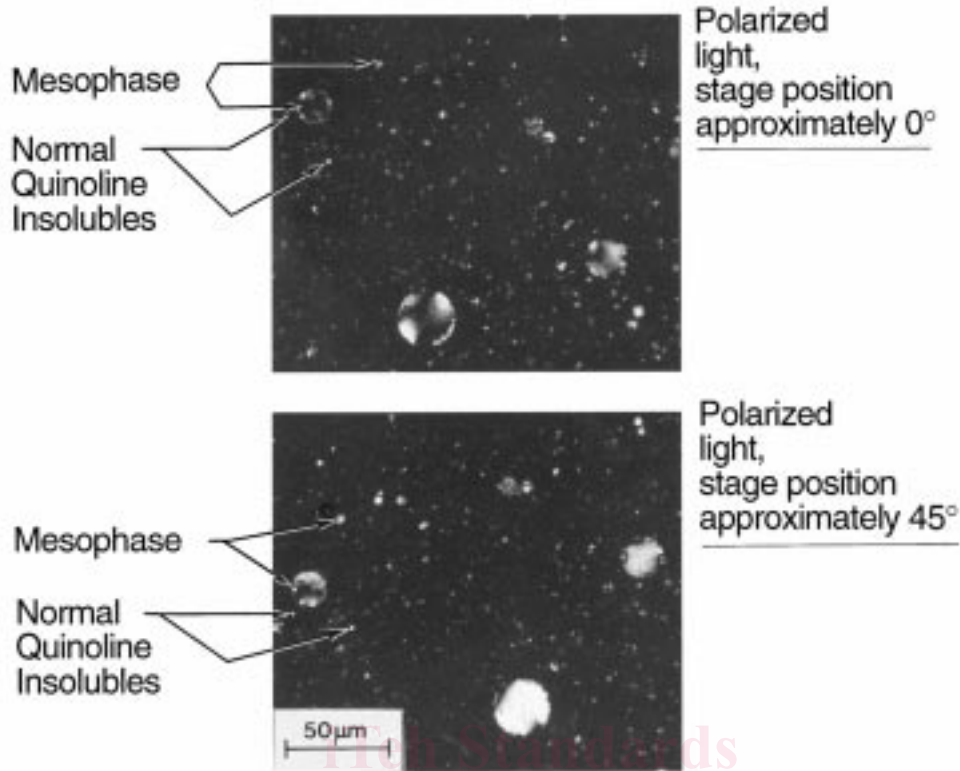


FIG. 2 Photomicrographs of a Heat-Treated Coal Tar Pitch at 500× Magnification in Polarized Light (Crossed Polarizers) Showing Natural Quinoline Insolubles and Mesophase Spheroids

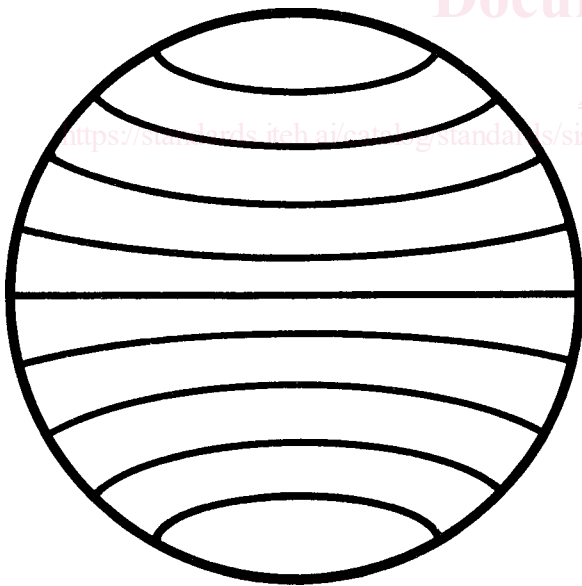


FIG. 3 Structure of Mesophase Spheroid

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 3.8, reactor mesophase is comparatively soft and shows no relief in bright field illumination.

#### 4. Summary of Test Method

4.1 A representative sample with a softening point of at least

100°C (212°F), as measured by Test Method D 3104 (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 100°C (212°F), it is raised to 100 to 120°C (212 to 248°F) by vacuum distillation. The encapsulated, or molded, sample is ground and polished to a flat surface for examination in reflected light.

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 D 2318). 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

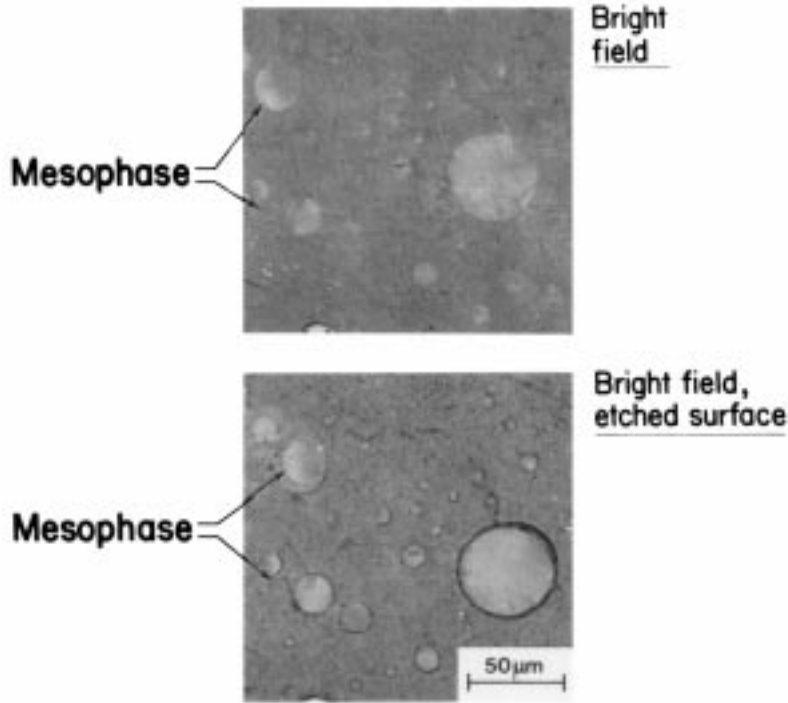


FIG. 4 Photomicrographs of a Heat Treated Coal Tar Pitch at 500× Magnification in Bright Field Showing the Effectiveness of Etching With Toluene to Accentuate the Interface Between Mesophase Spheroids and the Isotropic Phase

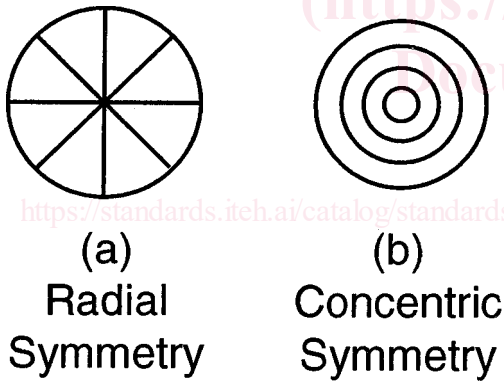


FIG. 5 The Structure of a Normal Quinoline Insoluble Particles

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 E 11.

6.3 *Vacuum Distillation Apparatus*, such as that specified in Test Method D 1160.

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>10</sup> 1 in. (25 mm) or 1¼ in. (32 mm) in diameter.<sup>11</sup>

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 rpm, and that has an automatic sample holder attachment is recommended.<sup>12</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*<sup>13</sup>—Any polarizing microscope with the capability for observations by reflected light (for example, metallurgical or opaque-ore microscopes) may be employed.

<sup>10</sup> Bakelite®, a trademark of the Union Carbide Corporation, Old Ridgebury Road, Danbury, CT, 06817, has been found satisfactory for this purpose.

<sup>11</sup> Rings supplied by Buehler Ltd., 41 Waukegan Road, Lake Bluff, IL, and Leco Corporation, 3000 Lakeview Ave., St. Joseph, MI, 49085, have been found satisfactory for this purpose.

<sup>12</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, have been found satisfactory for this purpose.

<sup>13</sup> Leitz, Olympus, and Zeiss microscopes have been found satisfactory for this purpose.