



Designation: D4616 – 95(Reapproved 2008)

# 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

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

## 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)

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 of Terms Specific to This Standard:*

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

Current edition approved Dec. 1, 2008. Published February 2009. Originally approved in 1986. Last previous edition approved in 2005 as D4616–95(2005). DOI: 10.1520/D4616-95R08.

<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.

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 segments 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 *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).

3.1.4 *mesophase*—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>

3.1.4.1 *spheroids*—At magnifications of 400 $\times$  and 500 $\times$ , the minimum spheroid size which can be resolved with confidence is 4  $\mu\text{m}$  in diameter. At magnifications of 1000 to 1800 $\times$ , the minimum spheroid size that can be resolved with confidence is about 2  $\mu\text{m}$  in diameter. Typically, the upper size may be 100  $\mu\text{m}$ . 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.

<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.

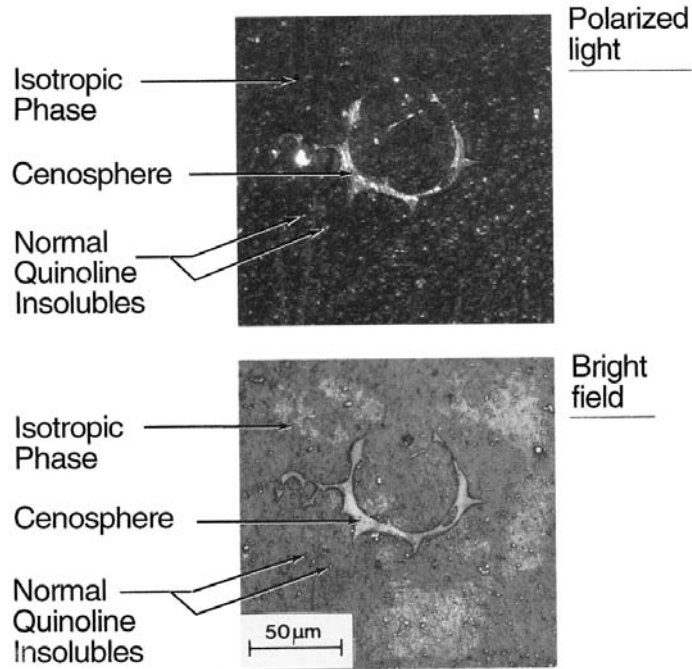


FIG. 1 Photomicrographs of a Coal Tar Pitch at 500x Magnification in Polarized Light (Crossed Polarizers) and Bright Light Showing the Isotropic Phase, Natural Quinoline Insolubles, and a Cenosphere.

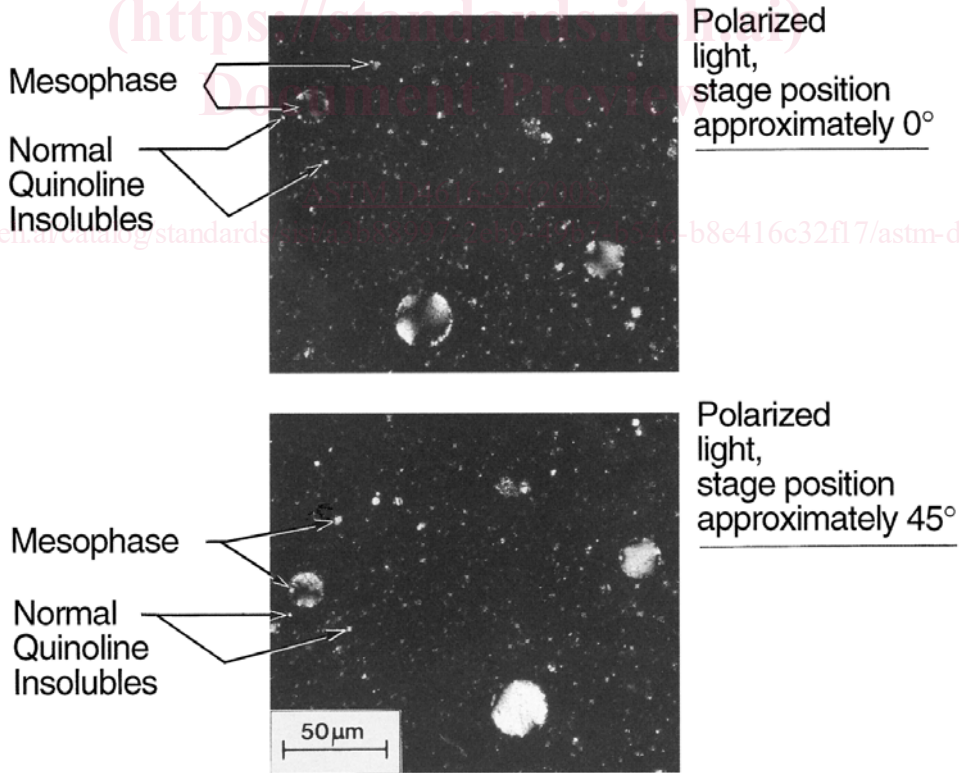


FIG. 2 Photomicrographs of a Heat-Treated Coal Tar Pitch at 500x Magnification in Polarized Light (Crossed Polarizers) Showing Natural Quinoline Insolubles and Mesophase Spheroids

3.1.4.2 *isotropic phase*—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,

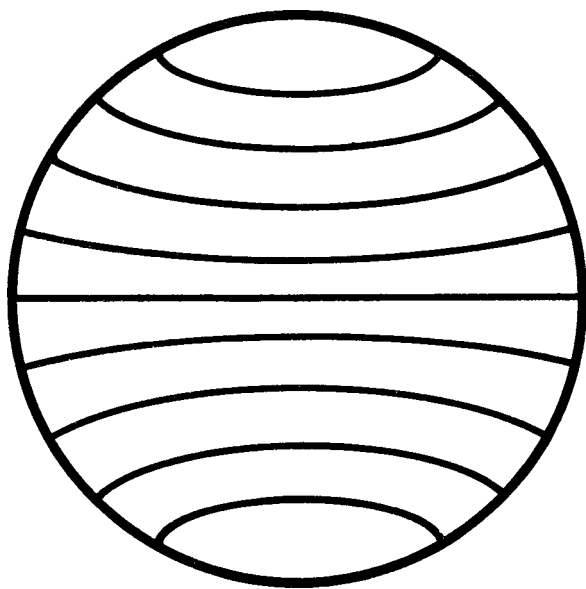


FIG. 3 Structure of Mesophase Spheroid

and drying in a current of hot air. Etching produces sharply defined mesophase spheroids (see Fig. 4).

3.1.5 *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.

3.1.6 *normal 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  $\mu\text{m}$  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).

3.1.6.1 *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).

3.1.6.2 *normal quinoline insoluble material*—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  $\mu\text{m}$  at high magnification (1000 to 2000 $\times$ ) under cross polarizers.

3.1.6.3 *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 QI with radial symmetry is produced by oxy-cracking 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.

3.1.7 *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  $\mu\text{m}$ . 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.

3.1.8 *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  $\mu\text{m}$ . 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 3.1.9 by its relative hardness, which causes it to show up in relief in bright field illumination.

3.1.9 *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 up to 200  $\mu\text{m}$ . It may be angular or rounded, and it may be relatively porous. Under crossed polarizers reactor mesophase

<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.

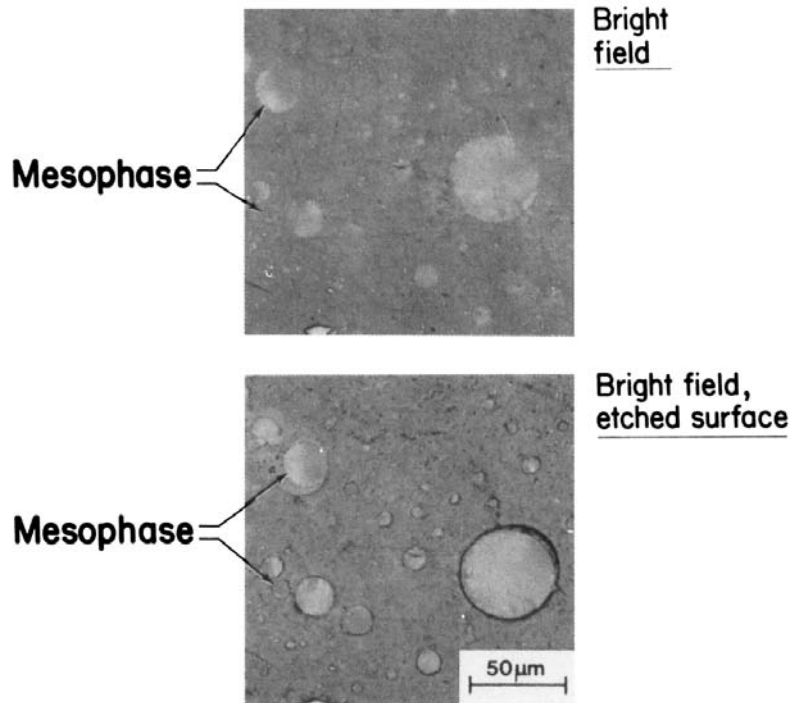


FIG. 4 Photomicrographs of a Heat Treated Coal Tar Pitch at 500x Magnification in Bright Field Showing the Effectiveness of Etching With Toluene to Accentuate the Interface Between Mesophase Spheroids and the Isotropic Phase

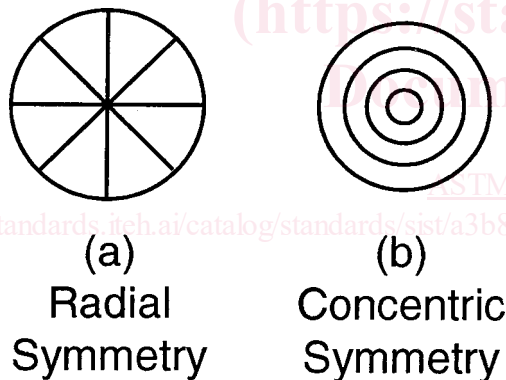


FIG. 5 The Structure of a Normal Quinoline Insoluble Particles

poored 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 to 248°F (100 to 120°C) 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 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 400x or 500x 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 1800x shall be used and the results should be

has a coarse mosaic appearance. In contradistinction to the reactor coke mentioned in 3.1.8, reactor mesophase is comparatively soft and shows no relief in bright field illumination.

3.1.10 *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.

### 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