An American National Standard

Standard Test Method for Microscopical Analysis by Reflected Light and Determination of Mesophase in a Pitch[1]

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 (ε) 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:*[2]

D 329 Specification for Acetone

D 1160 Test Method for Distillation of Petroleum Products at Reduced Pressure

D 2318 Test Method for Quinoline-Insoluble (QI) Content of Tar and Pitch

D 3104 Test Method for Softening Point of Pitches (Mettler Softening Point Method)

D 4296 Practice for Sampling Pitch

E 11 Specification for Wire Cloth and Sieves for Testing Purposes

E 562 Test Method for Determining Volume Fraction by Systematic Manual Point Count

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 segments thereof (see Fig. 1), and are typically sized from about 10 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).

3.1.2 *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.[3]

3.1.4.1 *spheroids*—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

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

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[2] 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] 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.

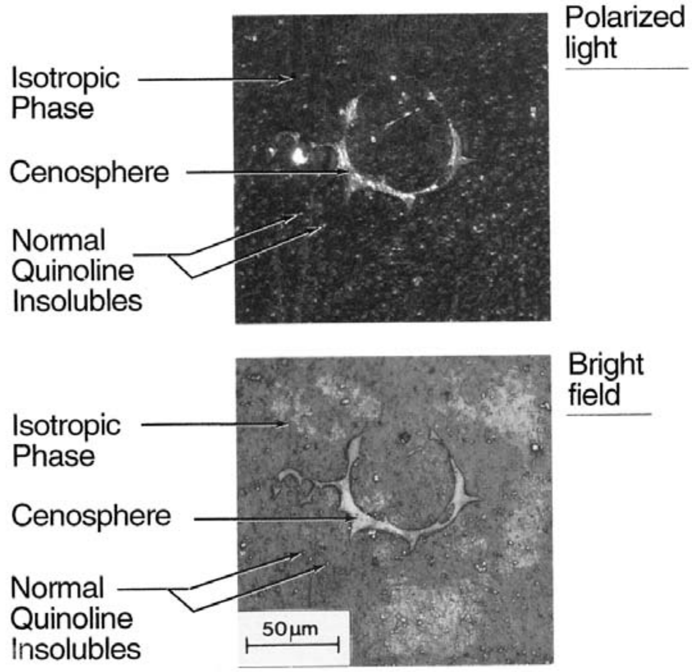

FIG. 1 Photomicrographs of a Coal Tar Pitch at 500× Magnification in Polarized Light (Crossed Polarizers) and Bright Light Showing the Isotropic Phase, Natural Quinoline Insolubles, and a Cenosphere.

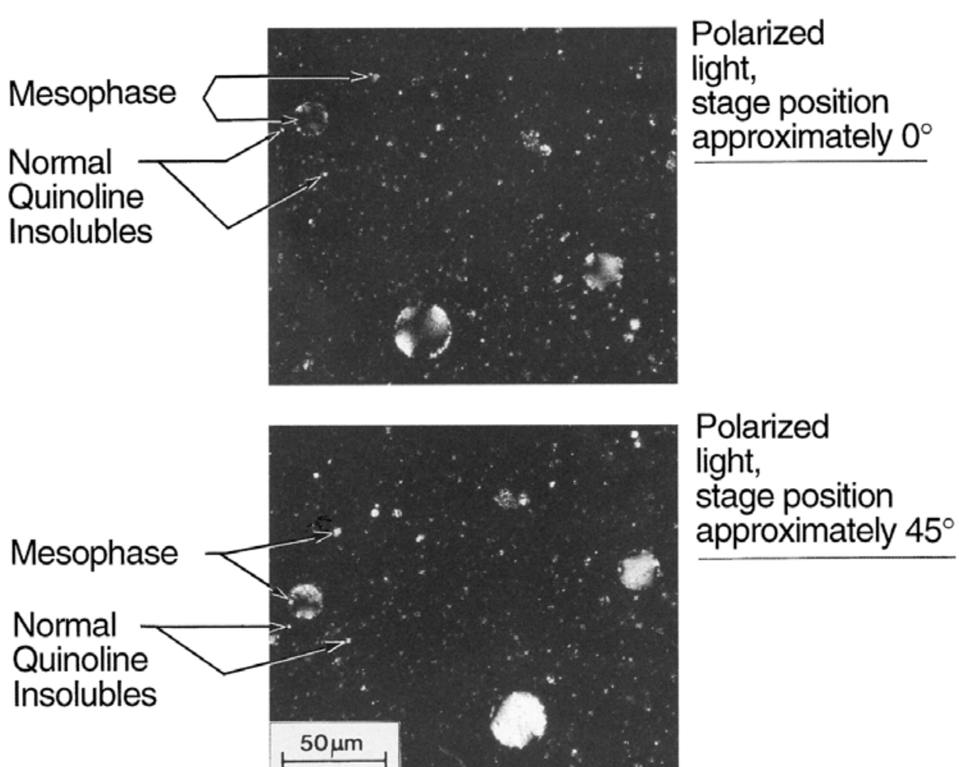

FIG. 2 Photomicrographs of a Heat-Treated Coal Tar Pitch at 500× Magnification in Polarized Light (Crossed Polarizers) Showing Natural Quinoline Insolubles and Mesophase Spheroids

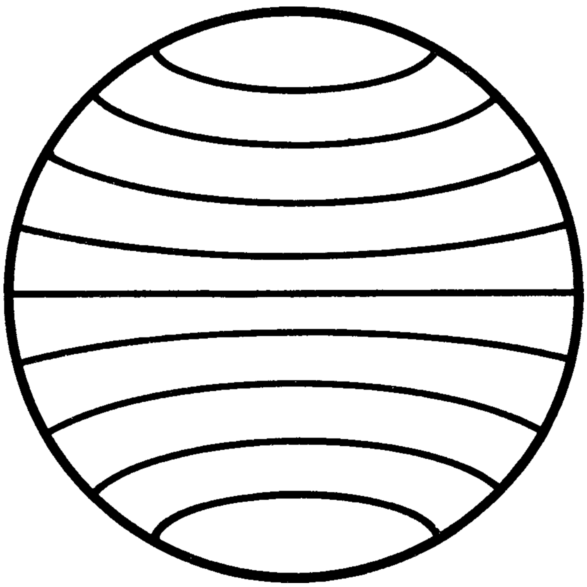

FIG. 3 Structure of Mesophase Spheroid

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.

3.1.4.2 *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, 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 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).

3.1.6.1 *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 μm at high magnification (1000 to 2000×) under cross polarizers.

3.1.6.3 *Discussion*—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 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.[4,5] 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.

3.1.7 *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 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.

3.1.8 *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 3.1.9

[4] 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.

[5] 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.