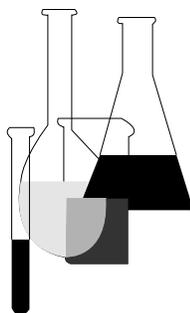




Product Properties Test Guidelines

OPPTS 830.7520 Particle Size, Fiber Length, and Diameter Distribution



INTRODUCTION

This guideline is one of a series of test guidelines that have been developed by the Office of Prevention, Pesticides and Toxic Substances, United States Environmental Protection Agency for use in the testing of pesticides and toxic substances, and the development of test data that must be submitted to the Agency for review under Federal regulations.

The Office of Prevention, Pesticides and Toxic Substances (OPPTS) has developed this guideline through a process of harmonization that blended the testing guidance and requirements that existed in the Office of Pollution Prevention and Toxics (OPPT) and appeared in Title 40, Chapter I, Subchapter R of the Code of Federal Regulations (CFR), the Office of Pesticide Programs (OPP) which appeared in publications of the National Technical Information Service (NTIS) and the guidelines published by the Organization for Economic Cooperation and Development (OECD).

The purpose of harmonizing these guidelines into a single set of OPPTS guidelines is to minimize variations among the testing procedures that must be performed to meet the data requirements of the U. S. Environmental Protection Agency under the Toxic Substances Control Act (15 U.S.C. 2601) and the Federal Insecticide, Fungicide and Rodenticide Act (7 U.S.C. 136, *et seq.*).

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OPPTS 830.7520 Particle size, fiber length, and diameter distribution.

(a) **Scope**—(1) **Applicability.** This guideline is intended to meet testing requirements of both the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (7 U.S.C. 136, *et seq.*) and the Toxic Substances Control Act (TSCA) (15 U.S.C. 2601).

(2) **Background.** The source materials used in developing this harmonized OPPTS test guideline are the OPPT guideline under 40 CFR 796.1520 Particle Size Distribution/Fiber Length and Diameter Distributions and OECD guideline 110 Particle Size Distribution/Fibre Length and Diameter Distributions.

(b) **Introductory information.** Method A: Particle size distribution (effective hydrodynamic radius). Method B: Fiber length and diameter distributions.

(1) **Prerequisites.** Method A: Water insolubility. Method B: Information on fibrous nature of product; Information on stability of fiber shape under electron-microscopic conditions.

(2) **Guidance information.** Method A: Melting point. Method B: Melting point.

(3) **Qualifying statements.** Both test methods can be applied to pure and commercial grade substances.

(i) **Method A:** (A) This method can only be applied to water-insoluble ($<10^{-6}$ g/L), powdered type products.

(B) The equivalence of the six national and international standard methods for particle size distribution was not tested, and is currently not known. There is a particular problem in relation to sedimentation and Coulter counter measurements.

(ii) **Method B:** This method applies only for fibrous products. The effect of impurities on particle shape should be considered.

(4) **Recommendations.** Method A: Equivalence of the methods for determination of particle size distribution should be tested in the laboratory.

(5) **Standard documents.** The “Effective Hydrodynamic Radius Determination” is based on the following standards (refer to paragraph (e) of this guideline for more information):

(i) ASTM—D 3360, D422.

(ii) NF—T 30044.

(iii) DIN—66115.

(iv) DIN—66116, part 1.

(v) ASTM—C 678.

(vi) ANSI—C 690–75.

and on a test principle described in *Chemie Ingenieur Technik* 146: 729 (see paragraph (e) of this guideline).

(c) **Method**—(1) **Introduction, purpose, scope, relevance, application and limits of test.** (i)(A) Many methods are available for particle size measurements, but none of them is applicable to the entire size range. Sieving, microscopic sedimentation and elutriation techniques are most commonly employed. Moreover, in the case of airborne particles (dusts, smokes, fumes), radiation scattering and inertial methods prove particularly useful. Finally, appropriate sampling procedures should be selected in order to prepare specimens really representative of the material under test (method A).

(B) The first method described in this guideline (method A) is designed to provide information on the transportation and sedimentation of insoluble particles in water and air. In the special case of materials which can form fibers, an additional set of measurements (method B) is also recommended to help identify potential health hazards arising from inhalation or ingestion.

(C) Method A is generally applicable, frequent in use and hydrodynamic in character; method B is comparatively specialized, infrequently required and involves microscopic examination. It should be borne in mind, however, that the original particle size distribution is highly dependent on the industrial processing methods used and can also be affected by subsequent environmental or human transformations.

(D) These tests are applicable only to water insoluble (solubility $<10^{-6}$ g/L) substances. Method B for fibers will be applied only if light microscopic examination, similarities to known fibrous or fiber-releasing substances or other data indicate a likelihood that fibers are present. In this context, a fiber is a water insoluble particle, of aspect ratio (length/diameter) ≥ 3 and diameter $\leq 100 \mu\text{m}$. Fibers of length $< 5 \mu\text{m}$ need not be considered. Method A, which determines the effective hydrodynamic radius, R_s , will be used for both fibrous and nonfibrous particulates without prior inspection. It is useful only in the range $2 \mu\text{m} < R_s < 100 \mu\text{m}$.

(ii) Definitions and units. (A) For method A the parameter of interest is the effective hydrodynamic radius, or effective Stokes radius R_s . The terminal velocity of a small sphere falling under the influence of gravity in a viscous fluid is given by:

$$v = 2gR_s^2(d_1 - d_2)/9\eta$$

where

v = velocity (m/sec),

g = gravitation constant (m/sec²),

R_s = Stokes radius (m)

d_1 = density of sphere (kg/m³),

d_2 = density of fluid (kg/m³),

η = dynamic viscosity (Nsec/m² = Pa s) of the the fluid

(B) In other situations, similar relationships apply. Particle size is usually measured in micrometers (a micrometer = 10^{-6} m = μm).

(C) Method B provides histograms of the length (l) and diameter (d) distributions of fibers. The ordinate is the absolute number of particles in each interval of l or d. Typical plots are provided in figures 1 and 2 under paragraph (c)(1)(iv) of this guideline.

(iii) Reference substances. (A) Five reference substances of defined particle size covering the overall range 0.35 to 650 μm (excepting the 50 to 200 μm region) have been certified with respect to the cumulative mass distribution of particles versus equivalent settling rate diameter or equivalent volume diameter. The materials will be made available from the Community Bureau of Reference of the European Economic Community and they will be issued with certificates of measurement. The certification report under paragraph (e)(4) of this guideline will also be available from the Community Bureau of Reference.

(1) The certification report of five reference materials will be available from: Commission of the European Community, Directorate—General for Research, Science and Education, Community Bureau of Reference BCR, rue de la Loi 200, B-1049 Brussels.

(2) Filter equipment for sample preparations according to method B is available commercially through the following manufacturers:

(i) Nuclepore Corporation, 7035 Commerce Circle, Pleasanton, California 94566.

(ii) Millipore Corporation, Order Service Department, Bedford, Massachusetts 01730.

(iii) Whatman Filters, W&R Balston Limited, England.

(B) Calibration materials—(1) Method A. A binary or ternary mixture of latex spheres ($2 \mu\text{m} \leq d \leq 100 \mu\text{m}$) is suggested.

(2) Method B. No standard reference materials are readily available.

(C) Evaluation materials—(1) Method A. A ternary mixture of latex spheres, 2, 50, and 100 μm (which provides a discrete calibrated distribution) plus a sample of crushed quartz (continuous distribution).

(2) Method B. Fibrous chrysotile asbestos is recommended (specific properties not essential as long as enough of a thoroughly mixed sample is available for identical distribution in a ring test).

(iv) Principle of the test methods—(A) Method A. (1) There are several standard methods available which meet the sensitivity requirements (refer to paragraph (e) for more information):

Principle	Methods
Sedimentation	ASTM—D 3360, D 422, NF—T 30044 DIN—66—115
Centrifugation	ASTM—C 678, <i>Chemie Ingenieur Technik</i> 146: 729 (1974)
Coulter counter	ANSI—C 690—75.

(2) The comparability of these methods (especially the sedimentation) and the other methods must be determined.

(3) The sample should also be subjected to a simple light microscopic examination to determine the approximate nature of the particles (e.g., plates, needles, etc.).

(B) Method B. Since data must be collected on small diameter fibers ($\geq 0.1 \mu\text{m}$), scanning electron microscope (SEM) or transmission electron microscopy (TEM) is required. There is no standard procedure at present, and those currently under development for asbestos contamination (in which the fibrous material is already identified and in high concentration) are often more complex and expensive than necessary for the needs of this program. Extreme care must still be taken during sample preparation to avoid fiber breaking, clumping and contamination. A simple initial procedure is suggested below (Description of the test procedures). The length and diameter of the fiber images can be measured manually, semiautomatically or automatically and the results tabulated in histogram form (see the following figures 1 and 2):

FIGURE 1—SAMPLE FIBER LENGTH DISTRIBUTION (METHOD B)

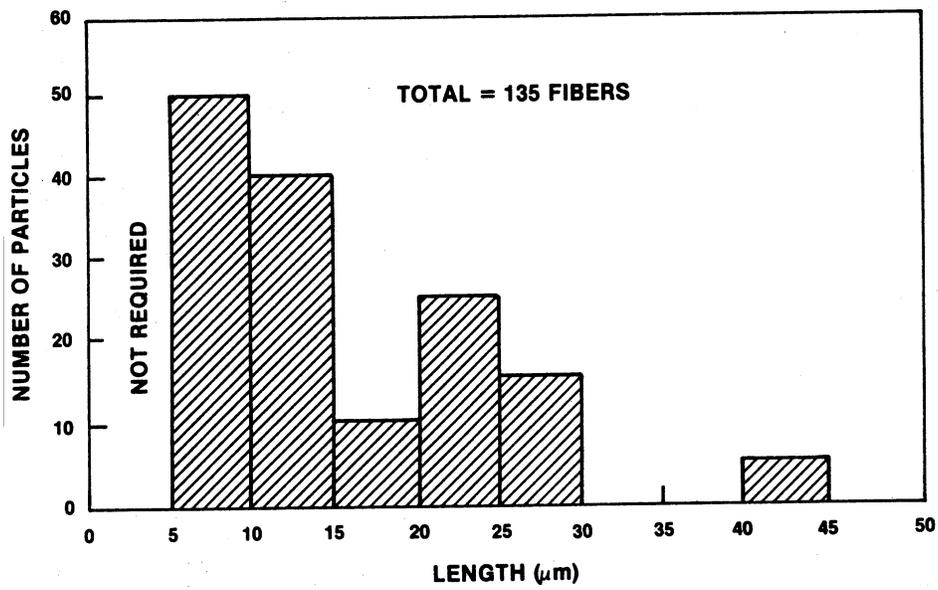
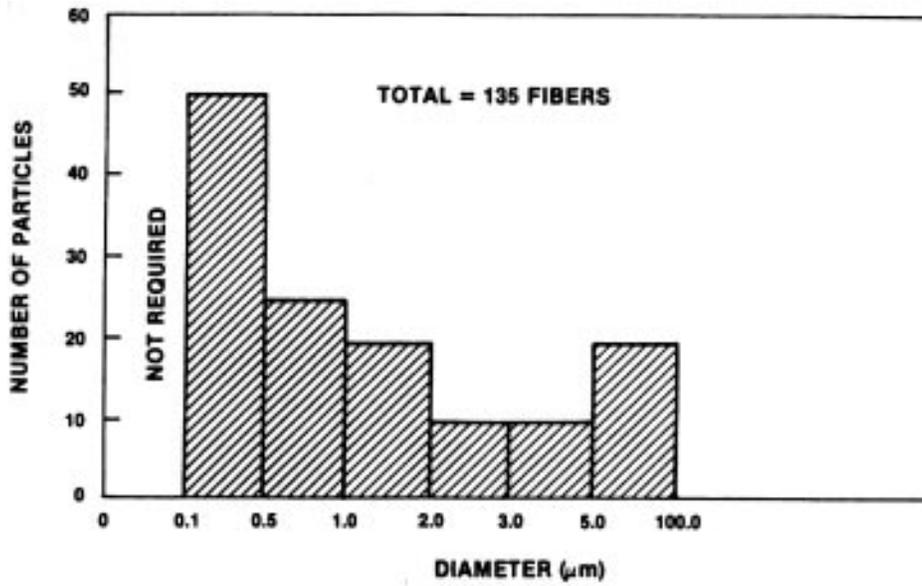


FIGURE 2—SAMPLE FIBER DIAMETER DISTRIBUTION (METHOD B)



(v) Quality criteria—(A) Repeatability. (1) The effective hydrodynamic radius distribution (method A) should be measured three times, with no two values differing by more than 20 percent.

(2) The length and diameter distributions of fibers (method B), if required, should be measured at least twice—using separate samplings and preparations—with at least 70 fibers per histogram. No two values in a given histogram interval should differ by more than 50 percent or 3 fibers, whichever is larger. Such repeatability should be sufficient for the modeling and decision-making procedures currently envisaged; however, the presence of long, thin fibers—due to their potential adverse health effects—would indicate a need for further, more precise measurements.

(B) Sensitivity. In the general case (method A) particles as small as 2 μm and as large as 200 μm must be measurable. The method requires that sufficient numbers of radius intervals be used to resolve the radius distribution curve. In the case of fibers (method B), diameters as small as 0.2 μm and as large as 100 μm and lengths as small as 5 μm and as large as 300 μm , must be measurable.

(C) Specificity. See paragraph (c)(1) of this guideline.

(D) Possibility of standardization. The method procedures can be readily standardized, if desired, but nonuniformity of sampling, preparation and prior handling may still cause considerable variation in results in method B.

(E) Possibility of automation. Automation or semiautomation of these procedures if possible. Full automation of fiber l and d measurements and analysis is also possible.

(2) **Description of the test procedures—(i) Preparations—(A) Method A.** The small quantities used as samples must be representative of product batches comprising many kilograms; therefore, sampling and sample handling require great care. For example, small particles often form agglomerates; therefore, sample pre-treatment (e.g., the addition of dispersing agents, agitation, or low-level ultrasonic treatment) may be required before the primary particle size can be determined. However, great care must be taken to avoid changing the particle size distribution. In the case of highly stable aggregates, a strict distinction between primary particles and agglomerates is not always useful. Some representative sample preparation methods will be found in the standard procedures listed in Principle of the test methods (method A) under paragraph (c)(1)(iv) of this guideline.

(B) **Method B.** Two simple sample preparation procedures (B-1, B-2) for scanning electron microscopy can be suggested.

(1) **Sample preparation B-1.** Suspend a given amount of sample in 10–100 mL of filtered distilled or deionized water (the suspension should be relatively light, not a slurry). Distribution of the particles in suspension may be aided by use of a surfactant, such as small amounts (~1 part/100) of absolute ethyl alcohol or a nonionic detergent. Suspension of the powder is achieved by gentle hand agitation, vortex mixing or magnetic stirring. Filter the suspension directly onto a 47 mm diameter Nuclepore® filter overlaying a 47 mm diameter Millipore® membrane filter housed in a 47 mm diameter Millipore® filter holder (Hydrosol, stainless) using gentle vacuum. Ensure that the powder has not precipitated out of suspension. Depending on the size of particles of interest various pore-sized filters may be used. The concentration of suspended particles determines the amount filtered. A less concentrated suspension will give a more even distribution of particles on the filter surface under paragraph (e)(2) of this guideline. Remove the Nuclepore® filter from the filter housing, being careful not to disturb the particles on the surface. Place the filter—particle-coated face upward—into a glass or plastic Petri dish containing Whatmann No. 1 filter paper; cover Petri dish and store in a dry box or under vacuum. When completely dried, the filter is cut into pieces of appropriate size and mounted, filter face up, onto copper tape which has been previously mounted onto an SEM specimen holder (using double face tape). To ensure stickiness of the tape, preheat using infrared or similar heat source for 5 to 15 min. Trim the edge of the filter to fit the SEM specimen holder.

(2) **Sample preparation B-2.** An alternate sample preparation method is the direct transfer of the dry powder onto copper tape (adhesive electrical tape) which has been mounted onto a scanning electron microscope (SEM) specimen holder. The powder may also be sprayed onto the copper tape surface by using an atomizer or pipet equipped with a large rubber bulb.

(ii) **Test conditions and apparatus—(A) Method A.** Ambient conditions. Measuring apparatus for all methods are readily available. Pipets and sedimentation balances are used for the sedimentation methods.

(B) **Method B.** (1) Contamination by air-borne fibers can be a problem. A hood or “clean room” should be used if available.

(2) A small electron microscope and support equipment are required.

(iii) **Performance of the tests.** (A) methods:

(1) **Method A.** To be selected from standard procedures listed above (Principle of the test methods).

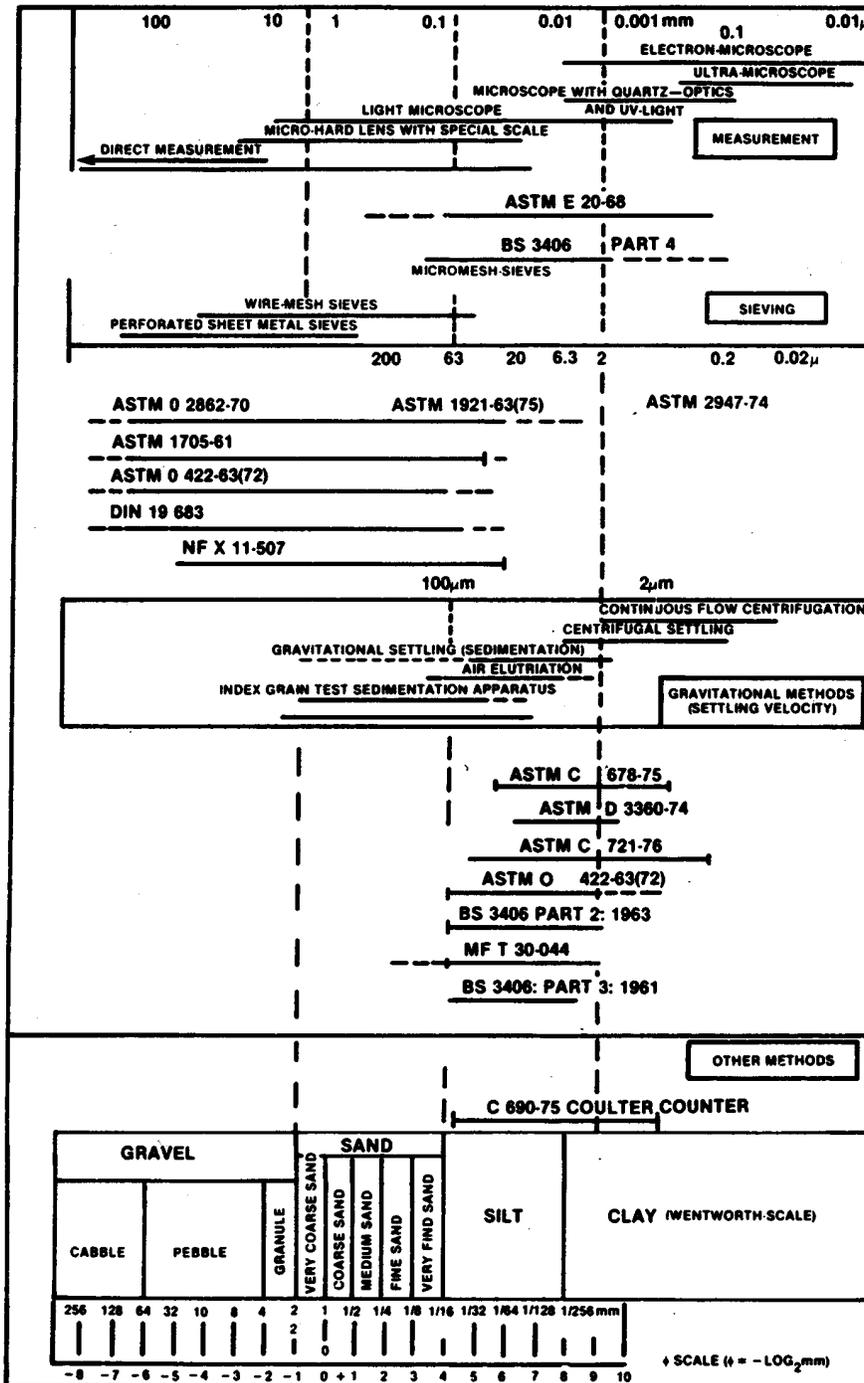
(2) **Method B.** Both preparation methods (B-1 and B-2) provide a particulate sample on filter paper or copper tape mounted on an SEM specimen holder. This can then be examined in the SEM, or first coated with

metal film using a sputtering device or vacuum evaporator. Representative fields within the sample surface are photographed at various magnifications to yield a representative sample of the population of interest. (If desired, energy dispersive X-ray analysis (EDXA) of representative particles—to check sample contamination—could be performed at this time.)

(B) Particle size distribution can be determined by measuring the screen directly or from measurements on photographs. If the SEM is equipped with an image analysis system, population statistics can be determined directly. Such measurements can be automated or semi-automated when desired (see paragraph (e)(3) of this guideline). If the image indicates the sample is too concentrated, repeat again with a more dilute solution.

(iv) **Analysis.** Measuring the physical parameters by different methods can result in somewhat different particle size distributions; therefore, the measuring techniques used should always be reported. Representative analysis methods are discussed in reference under paragraphs (e)(1) through (e)(6) of this guideline, and the following “Summary of the Usual Methods for the Determination of Particle Size and the Important Granular Size Classes,” (adapted from G. Müller, *Methoden der Sedimentuntersuchungen*, 1964, p. 303, Stuttgart, revised with appropriate supplements):

FIGURE 3.—SUMMARY OF METHODS



(d) **Data and reporting**—(1) **Data**—(i) **Method A:** Data should be obtained for 3 size ranges: $>200\ \mu\text{m}$, $<2\ \mu\text{m}$ and the region 2 to $200\ \mu\text{m}$. Only in the latter range should the distribution curve be prepared. It should have sufficient μm increments to resolve the curve (subpopulations). A histogram presentation is required plus a statement on the weight percent of material $>200\ \mu\text{m}$ and $<2\ \mu\text{m}$.

(ii) **Method B:** Full length (l) and diameter (d) data are needed on fibers of dimensions $d \geq 0.1\ \mu\text{m}$ and $l \geq 5\ \mu\text{m}$. Two histogram distributions, based on examination of at least 50 fibers each, should be prepared. For diameters, the ranges should be 0.1–0.5, 0.5–1.0, 1–2, 2–3, 3–5 μm and $>5\ \mu\text{m}$. For lengths they should be 0–5, 5–10, 10–15, 15–20, μm (etc.). This is illustrated in figures 1 and 2 in paragraph (c)(1)(iv)(B) of this guideline.

(2) **Test report**—(i) **Method A:** The following information should be presented:

(A) Expected percent change of reported values in the future (e.g., variations between production batches).

(B) Sample preparation methods used.

(C) Analysis methods used.

(D) Approximate information on particle shape (e.g., spherical, plate-like, needle shaped).

(E) Lot number, sample number.

(F) Suspending medium, temperature, pH.

(G) Concentration.

(H) Stoke's (effective hydrodynamic) radius R_s distribution for $2 \leq R_s \leq 200\ \mu\text{m}$.

(I) Mean value and approximate "area" (percent) of any resolvable peaks in R_s distribution.

(J) Percent of particles with $R_s \leq 2\ \mu\text{m}$.

(K) Percent of particles with $R_s \geq 200\ \mu\text{m}$.

(ii) **Method B:** The following information should be presented:

(A) Sample description, method description.

(B) Number of particles per field.

(C) Total number of fibers measured.

(D) l, d distributions (histograms).

(E) Mean value and approximate “area” (percent) of any resolvable peaks in the R_s distribution.

(e) **References.** The following references should be consulted for additional background material on this test guideline.

(1) Allen, T., *Particle Size Measurement*. (Chapman and Hall: London, 1975).

(2) Irani, R.R., and Callis, C.F., *Particle Size Measurement*. Interpretation and Application.

(3) Orr, S., and Dallavalle, J.M., *Fine Particle Measurement*.

(4) *Certification Report on Particles of Defined Particle Size*. (Community Bureau of Reference: Brussels, 1979).

(5) McGrath, P.P., and Ewell, J.B., “Application of Electron Microscopy to Problem of Particulate Contaminants in Food, Drugs and Biologicals,” *Scanning Electron Microscopy*, part III (1976).

(6) *Symposium on Electron Microscopy of Microfibers*, ed. Asher I.M., and McGrath, P.P., Proceedings of the First FDA Office of Science Summer Symposium, (August 23–25, 1976).

(7) *Chemie Ingenieur Technik* 146: 729 (1974).

(8) American Society for Testing and Materials, ASTM, 1916 Race St., Philadelphia PA 19103. Annual Book of ASTM Standards (latest edition).

(9) British Standards Institution, BSI. American National Standards Institute, Sales Department, 1430 Broadway, New York, NY 10018. Book of British Standards (latest edition).

(10) Das 1st Norm., DIN. American National Standard Institute, Sales Department, 1430 Broadway, New York, NY 10018. Book of British Standards (latest edition).

(11) American National Standards Institute, ANSI, Sales Department, 1430 Broadway, New York, NY 10018. Book of British Standards (latest edition).

(12) *Organization for Economic Cooperation and Development, Guidelines for The Testing of Chemicals*, OECD 110, Particle Size Distribution/Fibre Length and Diameter Distributions, OECD, Paris, France.