4

Quality Control of Fillers

This chapter contains discussion of analytical methods which are used to determine properties of fillers discussed in Chapter 2. Only a general principle of each method is given. The details of the method can be found in the referenced standards. The goals of the chapter are to:

- Provide background on the data included in the Chapter 2
- Clarify situations where differences exist between standards which may create discrepancies in data presented by different suppliers

The methods are generally very simple. The information gleaned from these tests gives a good indication of the filler's properties but is usually not sufficient to use as a set of data for screening fillers for potential applications. Substantially more information is required to assess quality of particular product.

4.1 ABSORPTION COEFFICIENT[1]

The spectrophotometric method measures the amount of light transmitted through a film of ethylene polymer containing carbon black. The absorption of the sample is compared with a standard to evaluate carbon black dispersion and the amount of carbon black.

4.2 ACIDITY OR ALKALINITY OF WATER EXTRACT[2-3]

Part 4 of ISO 787 specifies the method of determination and Part 3 specifies how the extract should be prepared. The material for testing is extracted in boiling water for 5 minutes and filtered to obtain a clear filtrate. An aliquot of filtered extract is titrated either with hydrochloric acid or sodium or potassium hydroxide solution in the presence of an indicator or evaluated by potentiometric determination.

The ASTM method differs from ISO in extract preparation which is obtained by a 5 minute extraction at room temperature. The method of determination is based on titration in the presence of an indicator. The acid used for titration is sulfuric acid.

4.3 ASH CONTENT[3-4]

The sample of filler or pigment is dried at 105^{o}C to remove water and then ashed at 900-1000^{o}C for a total 30 minutes.[3] This method is mostly used for mineral fillers.

The ash in carbon black is determined after drying at 125^{o}C in a 550^{o}C muffle furnace.[4] The duration in the furnace is up to 16 hours depending on crucible type.

The furnace treatment is continued until a constant weight is obtained unlike in the previous standard where constant (short) ashing time is used. The method permits the use of a microwave furnace which typically shortens the time to 2 to 6 hours.

When the instruments are available, the above methods can be replaced by thermogravimetric analysis which is more informative and simpler to conduct.

4.4 BRIGHTNESS[5]

Brightness is the term for a numerical value of reflectance of blue light (400-500 nm) from a sample under 45^{o} illumination. The method is used to compare materials in paper and other industries. The specimen of material is compared in a brightness tester with standard specimens made from paper or opal glass which should be replaced monthly. The method gives results which measure the effectiveness of the bleaching process and accounts for the amount and the type of optical brighteners used. The result is a measure of paper quality and gives an indication of its price.

4.5 COARSE PARTICLES[6]

The method is used for determination of the amount of coarse particles in a particulate material or their dispersion. The particles are considered coarse if they do not pass through a 45 μm sieve. The process of sieving is conducted with wet material and it is aided by water flushing and brushing. The material retained on the sieve is determined gravimetrically after drying.

4.6 COLOR[2,7]

The Part 1 of ISO 787 gives a color comparison method for pigments and extenders. The specimen and the standard pigment are dispersed in a specific binder under controlled conditions. The resultant pastes of pigments are spread on a substrate and visually compared.

The Part 25 of ISO 787 specifies a colorimetric method of comparison. The similar method of dispersion is used but a more precise definition of binder is given. In addition, fumed silica is used as an ingredient in the dispersion. The results of testing give relative hue and lightness differences for a broad range of materials from white to black.

The ASTM standard specifies details of method which is in principle a method of using color computer to determine CIE tristimulus values and other parameters of color which can be calculated.

Each method discussed in this section has different precision of determination and results are not comparable. In evaluation of this data it is essential to take note of the method used.

4.7 CTAB SURFACE AREA[8]

This method gives a specific surface area contained in micropores of carbon black. The micropores cannot be penetrated by hexadecyltrimethylammonium bromide

(CTAB). The method is used to characterize rubber grades of carbon black. A sample of carbon black, previously dried at 125°C is treated with a standard solution of hexadecyltrimethylammonium bromide and mixed to aid its adsorption. The excess of hexadecyltrimethylammonium bromide is determined by titration of the filtrate.

4.8 DBP ABSORPTION NUMBER[9]

The method is based on the measurement of the torque required to mix carbon black with n-dibutyl phthalate (DBP). n-dibutyl phthalate is added from a constant rate burette to a powdery sample of carbon black. The end of the titration is detected by reaching a predetermined torque level. The test helps in determining and controlling the quality of carbon black and relating values to its structure. It also helps to predict formulation that will give good processing characteristics. A simplified procedure uses manual mixing of fillers (see oil absorption below) but the results are not comparable.

4.9 DENSITY[2,10,11]

Part 10 of ISO 787 gives a pycnometer method of density determination.[2] Two methods are suggested. One method uses simple wet pycnometer in which the sample displaces water or some other liquid and the result is determined by a gravimetric method. The other method uses vacuum to remove air from the sample followed by the introduction of a portion of the liquid under vacuum. There is an inevitable difference in the results and the precision of each method. The differences in the determined values may also come from the choice of liquid used for displacement.

Part 23 of ISO 787 contains a description of an alternative method which allows to remove air entrained in the sample of a powdered material. The powder is placed in a special tube, mixed with an excess of the displacement liquid more than sufficient to cover its surface, and placed in centrifuge to remove air.

The change in a material's density caused by a filler addition can be measured by a method which relies on the change of weight of the material when immersed in a liquid (either water or other liquid). The method discussed here[10] is fast and precise and it is suitable for the determination of density of filled materials.

A Scott volumeter is suggested as being suitable for measuring the density of metal powders.[11] The method gives a bulk density of the metal powder and results can be related to the measurement of tamped volume (see below). The Scott volumeter is more complex and precise than the ISO method. The result is given as apparent density.

4.10 ELECTRICAL PROPERTIES[12,13]

Methods of testing conductive materials are used to evaluate specimens containing conductive fillers. Two ASTM standards contain details of specimen testing for

resistance[12] and EMI shielding effectiveness.[13] The details of specimen preparation are given.

4.11 EXTRACTABLES[14]

The method employs the fact that toluene discolors as it dissolves extractable substances in carbon black.[14] A previously dried sample of carbon black at 125°C is extracted in toluene for 60 seconds, filtered, and its color intensity is measured in a spectrophotometer at 425 nm. The change in transmission of solution of extractables is recorded.

4.12 FINES CONTENT[15]

This method determines fines present in pelleted carbon black. Material passing through a 125 μm sieve is considered fines. The material remaining on the sieve is weighed to determine the percent fines.

4.13 HEATING LOSS[16]

Heating loss is used to determine moisture content in carbon black. The drying is performed at 125°C for 30 min. Under these conditions moisture is removed but some other volatile materials may also be lost. The automatic equipment such as drying balances is also used (note that carbon black does not absorb infrared rapidly therefore, other sources of heat are normally used). This method gives precise readings because it avoids errors due to reabsorption of moisture.

4.14 HEAT STABILITY[2]

Heat stability is determined according to the Part 21 of ISO 787. The specimen is dispersed in a binder and tested in the form of a film having a wet thickness of 75 to 120 μm. The temperature of exposure in a ventilated oven is selected based on the anticipated exposure of the material in its intended application.

4.15 HEGMAN FINENESS[17]

This method is used to determine the fineness of grind of a pigment in a vehicle. It uses a gage with a wedge shaped depression which has depth starting at zero and going to 100 μm. The paste material is spread with the use of metal spreader and result read from a scale of 0 to 8 (0 means depth of 100 μm, 3 - 65 μm, 6 - 25 μm, and 8 - 0 μm). The point of termination of the speckled pattern on the surface of the sample is the measure of the fineness of grind.

4.16 HIDING POWER[18]

Hiding power of pigment in paint can be measured by reflectometry without the use of standard. It is calculated from the determined values of reflectivity and the scattering coefficient.

4.17 IODINE ABSORPTION NUMBER[19]

A carbon black sample is treated with excess of iodine. The excess iodine is then titrated with a sodium thiosulfate solution. The result is expressed as adsorbed iodine per unit of mass of the sample. The iodine number depends on amount of volatiles, surface porosity, and extractables. The iodine number correlates with the nitrogen specific surface area. It is a simple method used to evaluate the quality of carbon black.

4.18 LIGHTENING POWER OF WHITE PIGMENTS[2]

Two alternate methods are proposed in the Part 27 of ISO 787. In both cases a standard blue paste is dispersed with the white pigment to be tested in an automatic muller or by hand using a hand muller or a palette knife. In the first method, two sample pastes containing the same amounts of the test and the standard pigment are dispersed. The amount of pigment added is normalized for the frequently used pigments such as zinc oxide, lithopone, and titanium dioxide. The mulled samples are compared for intensity of color. In the second method, the sample is compared with a set (usually five) of standard pigments at different concentrations. From a visual comparison, the match closest to the standard sample is selected and that value is used to calculate the hiding power of pigment which is expressed as a ratio of the weight of pigment in the test to that of the standard sample.

4.19 LOSS ON IGNITION[3]

This method of determination is identical to that described above for the method of ash determination.

4.20 MECHANICAL AND RELATED PROPERTIES[20-27]

The mechanical properties of filled materials are evaluated using standard methods developed for specific matrix materials. Carbon black is usually evaluated in natural rubber. There is a standard method of sample preparation and tensile strength, modulus, and elongation of the prepared samples are determined.[20] A similar standard was developed for styrene-butadiene rubber.[21] Other materials are tested according to a general standard for plastic materials which gives procedures of testing shrinkage,[22] flexural properties,[23] deflection temperature under load,[24] tensile properties,[25] impact resistance,[26] and compressive strength.[27]

4.21 OIL ABSORPTION[2,28]

The Part 5 of ISO 787 gives a method for determining the oil absorption of pigments and extenders.[2] A refined linseed oil is dispersed in small portions from a burette and mixed with powder using palette knife until smooth consistency is obtained. Different amounts of powder are taken depending on the expected oil absorption. Oil absorption is expressed as a percent of the mass of powder.[2]

A simple spatula method is also given by the ASTM standard which is essentially similar to that described above. The only difference is in the method of

endpoint detection which in the ASTM standard is a very stiff, putty-like paste. The result is expressed as the amount of oil absorbed by 100 g of powder.

4.22 PARTICLE SIZE[29,30]

The average particle size of metal powders is determined by the Fisher sub-sieve sizer. The method uses air permeability to determine particle size. The method is designed for coarser metal powders having particle sizes in the range of 0.2 to 50 μm. The method should not be used for flakes or fibers.

The most frequently used method for particle size distribution is based on an optical particle counter.[30] Determination of monosize particles, flakes, and fibers is not accurate. In these cases either electron or optical microscopy are the most suitable techniques.

4.23 PELLET STRENGTH[31]

The automated pellet hardness tester is computer controlled and transports pellets to a measuring gage. The result is given as the force required to crush a pellet of a measured diameter.[31]

4.24 pH[2,3,32]

According to the Part 9 of ISO 787, a 10% suspension of filler is made up in freshly distilled water at room temperature and pH measurement of suspension is made.[2]

In an ASTM standard method,[3] a suspension is made with warm water and cooled to room temperature for measurement. An alternative method allows one to use colorimetric indicators in the measurement.

The method developed for carbon black uses either a boiling slurry or a sonically dispersed slurry of carbon black in water.[32]

4.25 RESISTANCE TO LIGHT[2]

Resistance to light is determined for pigments dispersed in the material in which they to be used. Two methods of exposure are used: under glass outdoors or in an artificial weathering unit equipped with a xenon arc as a source of radiation. The result of exposure is compared with a standard exposed to the same conditions. The evaluation is based on the color differences between the exposed and shadowed parts of the specimens.

4.26 RESISTIVITY OF AQUEOUS EXTRACT[2]

The Part 14 of ISO 787 gives details of the method.[2] A sample is prepared in boiling water. If the filler is hydrophobic some methanol is added to increase its wettability. The extract is filtered, cooled to room temperature, and measured in a conductivity cell. The result is expressed as resistivity.

4.27 SIEVE RESIDUE[2,33,34]

Two methods of determining of sieve residue are given in ISO 787. The Part 7 describes manual procedure.[2] A suspension of powder in water is prepared with the aid of a dispersion agent. The suspension is poured onto the sieve and washed with water containing the dispersing agent. The amount of residue is determined by a gravimetric method. The result is given as a percentage of the total mass of the tested powder. The Part 18 describes a mechanical flashing procedure. A system of rotating jets is used for flushing. Other details of the methods are similar.

When determining carbon black residue on a sieve, the method uses water to transfer carbon black to sieve through funnel. The sieve is then flushed with water from rubber hose. The residue is dried at 125°C and the results presented in ppm.[33] A similar method of determination is described for lime and limestone.[34]

4.28 SOLUBLE MATTER[2,3]

ISO 787 specifies two methods of determination of matter soluble in water. The Part 3 gives the hot extraction method. The material is boiled in water for 5 min, cooled to room temperature, filtered, extract is evaporated, and soluble matter determined gravimetrically. In Part 8, the cold extraction method is specified. Extraction is done at room temperature for 1 h. The next steps are the same as in hot extraction method.

The ASTM method is the same as hot extraction method in ISO procedure.[3]

4.29 SPECIFIC SURFACE AREA[35,36]

Details of several different methods for determining the specific surface area of carbon black are described in ASTM D 3037. The different types of equipment used and procedures are included in separate sections. Another standard[36] gives full details of procedure of conventional Brunauer, Emmett, and Teller (BET) method based on multilayer gas adsorption. The results of determination are in both cases given in the surface area in square meters per gram of substance.

4.30 SULFUR CONTENT[37]

Several methods of sulfur determination are used for carbon black. They include oxygen bomb calorimetry, high-temperature combustion with an iodometric detection procedure and an infrared detection procedure.[37] The results are given as percentage of sulfur.

4.31 TAMPED VOLUME[2]

The tamped volume or apparent density is determined according to Part 11 of ISO 787. The material is passed through a sieve to disperse agglomerates and placed in tarred graduated measuring cylinder. The cylinder is then placed in a tamping volumeter and tamped for 250 revolutions. The volume read from the cylinder is divided by the mass of powder and given as a percent.

4.32 TINTING STRENGTH[2,38-40]

ISO 787 gives a choice of two methods of determination of tinting strength. The visual comparison method is given in Part 16. A standard white paste is prepared either with a mechanical muller or spatula mixing. In a similar method, tinting pastes of a standard pigment and the test pigment are prepared. The pastes are mixed in the right proportions with white pigment paste and their tinting strength and undertones compared visually. Part 24 describes a photometric method. In essence, the method is the same but in place of a visual comparison, tristimulus values are measured or samples are measured at 550 nm.

For printing ink dispersions, either a visual comparison is made or the tinting strength is calculated according to the equation from spectrophotometric data.[38] The specimen is prepared by mixing tinting paste with base and comparing the result with a standard tinting paste mixed in the same proportions.

A carbon black test sample is obtained by mixing carbon black and zinc oxide with epoxidized soybean oil. The mixture is milled in a mechanical muller with frequent scraping. The specimen is prepared by film drawdown, roller spreader or by the glass slide method. Reflectometer readings are obtained. The result is a comparison of the tint strength of standard with the test sample expressed in tint units.[39]

White pigments are measured in compositions containing a black letdown vehicle using a reflectance measurement. The test pigment is compared with a standard sample.[40]

There is much compositional freedom in these methods which makes a comparison of results from different sources very difficult and unreliable.

4.33 VOLATILE MATTER[2]

The volatile matter according to the Part 2 of ISO 787 is determined gravimetrically by weighing the sample to a constant mass after a series of drying intervals at 105°C.[2]

4.34 WATER CONTENT[3]

The water content is determined by azeotropic distillation in the Dean-Stark apparatus.[3]

4.35 WATER-SOLUBLE SULFATES, CHLORIDES AND NITRATES[2]

Part 13 of ISO 787 determines water-soluble sulfates, chlorides and nitrates. The sample extract can be prepared by either cold or hot extraction method described in Section 4.28. The sulfates in the extract are determined by precipitation with barium chloride, the chlorides are determined by titration with silver nitrate, and the nitrates are determined by a colorimetric method using Nessler reagent.[2] Part 19 gives an alternative method of determination of nitrates by a salicylic acid method.

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