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Pigments and extenders — Dispersion procedure for sedimentation-based particle sizing of suspended pigment or extender with liquid sedimentation methods

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 256, *Pigments, dyestuffs and extenders.*

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Pigments and extenders — Dispersion procedure for sedimentation-based particle sizing of suspended pigment or extender with liquid sedimentation methods

1 Scope

This document specifies sample preparation methods to determine the size distribution of separate particles of a single pigment or extender, which is dispersed in a liquid by application of a standardized dispersion procedure, using an ultrasonic device, shaker device or wet jet mill.

The sample preparation methods described are optimized for measurements carried out with a particle sizing technique based on sedimentation. This technique relies on particle migration due to gravitation or centrifugal forces and requires a density contrast between the particles and the liquid phase.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 9276-1, *Representation of results of particle size analysis — Part 1: Graphical representation*

ISO 13317-1, *Determination of particle size distribution by gravitational liquid sedimentation methods — Part 1: General principles and guidelines*

ISO 13317-2, *Determination of particle size distribution by gravitational liquid sedimentation methods — Part 2: Fixed pipette method*

ISO 13317-3, *Determination of particle size distribution by gravitational liquid sedimentation methods — Part 3: X-ray gravitational technique*

ISO 13317-4, *Determination of particle size distribution by gravitational liquid sedimentation methods — Part 4: Balance method*

ISO 13318-1:2001, *Determination of particle size distribution by centrifugal liquid sedimentation methods — Part 1: General principles and guidelines*

ISO 13318-2, *Determination of particle size distribution by centrifugal liquid sedimentation methods — Part 2: Photocentrifuge method*

ISO 13318-3, *Determination of particle size distribution by centrifugal liquid sedimentation methods — Part 3: Centrifugal X-ray method*

ISO 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling*

ASTM D5965, *Standard Test Methods for Density of Coating Powders*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
nanoscale
length range from approximately 1 nm to 100 nm

Note 1 to entry: Properties that are not extrapolations from a larger size are predominantly exhibited in this size range. For such properties, the size limits are considered approximate.

Note 2 to entry: The lower limit in this definition (approximately 1 nm) is introduced to avoid single and small groups of atoms from being designated as nano-objects or elements of nanostructures, which can be implied by the absence of a lower limit.

[SOURCE: ISO 80004-1:2023, 3.1.1 — modified, notes 1 and 2 to entry have been added.]

3.2
nanoparticle
nano-object with all external dimensions in the *nanoscale* (3.1) where the lengths of the longest and the shortest axes of the nano-object do not differ significantly

Note 1 to entry: If the dimensions differ significantly (typically by more than three times), terms such as nanofibre or nanoplate may are preferred to the term nanoparticle.

[SOURCE: ISO 80004-1:2023, 3.3.4, modified — "where the lengths of the longest and the shortest axes of the nano-object do not differ significantly" has been added to the definition.]

3.3
agglomerate
collection of weakly or medium strongly bound particles where the resulting external surface area is similar to the sum of the surface areas of the individual components

Note 1 to entry: The forces holding an agglomerate together are weak forces, for example van der Waals or simple physical entanglement.

Note 2 to entry: Agglomerates are also termed secondary particles and the original source particles are termed *primary particles* (3.5).

[SOURCE: ISO 80004-1:2023, 3.2.4]

3.4
aggregate
particle comprising strongly bonded or fused particles where the resulting external surface area is significantly smaller than the sum of surface areas of the individual components

Note 1 to entry: The forces holding an aggregate together are strong forces, for example covalent or ionic bonds, or those resulting from sintering or complex physical entanglement, or otherwise combined former *primary particles* (3.5).

Note 2 to entry: Aggregates are also termed secondary particles and the original source particles are termed *primary particles* (3.5).

[SOURCE: ISO 80004-1:2023, 3.2.5, modified — "or otherwise combined former primary particles" has been added to the end of note 1 to entry.]

3.5
primary particle
single nano-object with at least one of three external dimensions at the nanoscale

Note 1 to entry: Sometimes, if the primary particle is present in crystalline form, it also contains twinning boundaries.

3.6
spin fluid
inert liquid which is injected into the disc of a disc centrifuge photosedimentometer prior to the sample to define a certain radius dependent gradient of viscosity for sedimentation

Note 1 to entry: Alkaline conditions minimize agglomeration of dispersed aggregates in most cases.

3.7
wet jet milling
dispersing method of particles in liquid phase using the complex shear force arising from turbulent flow in the channel and cavitation from the abrupt pressure change

Note 1 to entry: This method is also called high pressure homogenizer method.

4 Principles of dispersion

4.1 Principles of ultrasonic dispersion

A piezo electrical ceramic material is driven by an applied alternating current electrical field to expand and shrink periodically at an ultrasonic frequency in the range of 15 kHz up to 80 kHz and more. This movement creates acoustic waves moving through the dispersion, which produce cavitation bubbles. The collapse of these cavitation bubbles leads locally to strong thermal effects and shear-stress, which are responsible for the destruction of agglomerates and even aggregates.

Energy density of sonication, temperature and particle volume concentration of the dispersion are critical parameters of sonication and should be held at recipe values strictly.

In addition to probe-type sonicators ultra sonic (US) baths, inverted cup-horn sonicators and so-called vial-tweeters also exist. US baths, cup-horn dispersers and vial-tweeters are known as indirect dispersers, where sound energy is inserted via the wall of the container. Determining the energy input of these dispersers is much more difficult than for probe sonication, but contamination is reduced[9].

4.2 Principle of wet jet mill dispersion

The wet jet milling method is a wet-type milling to disintegrate agglomerates of powder samples in liquid. In this method, particles suspended in a liquid medium are passed through a narrow channel at high pressure. Then, the suspension of the particles is enhanced by the complex shear force arising from turbulent flow in the channel. In addition, the high pressure in the narrow channel induces the cavitation bubbles from the abrupt pressure change. The burst of the cavitation bubbles then work to disperse powder samples in the liquid phase, as in the ultra-sonication method. The advantage of this dispersion technique is that it yields suspensions with low contamination, unlike the ultra-sonic homogenizer method. The pressure range is the important factor to disperse the powder samples in the liquid phase. Typically, the pressure range is from 80 MPa to 245 MPa[10][11].

4.3 Principle of shaker-based dispersion

The shaker device should be built like a plate with holders for the high-density polyethylene (HDPE) bottles (see Annex B). A successful dispersion is achieved when the plate is shaking vertically from back to front with a vibration amplitude of minimum 32 mm and a frequency of 660 Hz.

Important aspects are:

— inclusion of grinding beads, high loading;

— particle dispersion limitations: agglomerates/aggregates <100 µm in a liquid (viscous medium);

— grinding beads are agitated by rotary, tumbling and/or 2D-vibratory motion of the container/vessel;

— shear and elongational stress on agglomerates at squeezing of liquid between colliding grinding beads and impulse exchange from collisions of agglomerates with grinding beads[12][13].

5 Principles of sedimentation-based techniques for particle size analysis

5.1 Stokesian sedimentation analysis

For all sedimentation-based procedures for particle sizing which are cited in this document, Stokesian sedimentation analysis of dispersions is used. ISO 13318-1:2001, 4.1 describes in detail the general procedure and calculations used to approach a particle size distribution of dispersed particles.

5.2 Disk-type centrifuges

The particles settle within an optically clear, rotating disc. When particles approach the outside edge of the rotating disc, they block/scatter a portion of a light beam or X-ray beam that passes through the disc. The change in light intensity shall be continuously recorded, and converted by the operating software into a particle size distribution, in accordance with ISO 13318-1.

Instead of detecting the local particle concentration with optical turbidity, X-ray absorption shall be used in certain instruments with the advantage of direct particle mass dependency, in accordance with ISO 13318-3.

5.3 Cuvette-type centrifuges

The cuvette-type centrifuge is a special analytical centrifuge that instantaneously measures the particle concentration at one or more radial positions within the rotating sedimentation cuvette.

For instance, space- and time-resolved extinction of the transmitted light across the entire length of the sample allows the analysis of particle and droplet velocity distributions for creaming and sedimentation phenomena without the need of any material data. This process additionally performs particle sizing according to ISO 13318-2.

The centrifugal speed of these instruments is typically between 50 min^{-1} and 60 000 min^{-1}. Instruments with a centrifugal speed below 10 000 min^{-1} are typically called cuvette centrifuges. Devices which can rotate above 10 000 min^{-1} rotation are called ultracentrifuge. For centrifugal speeds greater than 6 000 min^{-1}, the detection of particle sizes is limited to 1 µm or below.

5.4 Gravitation-based sedimentation methods

The gravitation-based liquid sedimentation shall be executed using four different techniques: the fixed pipette method in accordance with ISO 13317-2, the X-ray gravitation-based technique in accordance with ISO 13317-3, the balance method in accordance with ISO 13317-4 and gravitation-based photo sedimentation.

With the balance method as well as with the pipette method in accordance with ISO 13317-2, a resolution below 1 µm is critical because of the limitations of the used detection mechanisms. The X-ray sedimentation on the other hand depends on vibration isolation and detector quality. It can resolve 100 nm, similar to the photo sedimentation.

Therefore, only the liquid X-ray sedimentation in accordance with ISO 13317-1 and ISO 13317-3 is included in this document.

The concentration of a dispersed sample is measured by the attenuation of an X-ray beam. A stable, narrow, monochromatic collimated beam of X-rays passes through a suspension of the sample and is detected at a known distance from the top of the sample cell. The sample cell is filled completely with the sample suspension for the duration of the analysis. The settling height at which the particle concentration is determined may be reduced during the analysis for the purpose of obtaining a more rapid analysis compared to an analysis where all measurements are made at the same height value.

The cumulative mass percentage of the sample present at a given sedimentation height is continuously determined. The X-ray signal attenuation at the known height is compared to the attenuation in the suspending liquid and also to the attenuation in the homogeneously dispersed sample present in the liquid. The attenuation of the emergent X-ray beam is proportional to the mass of the powder in the beam.

5.5 Centrifugal field-flow fractionation method

Field-flow fractionation is a flow-based separation methodology. Centrifugal field-flow fractionation (CF3) is a separation technique that uses a centrifugal field applied perpendicular to a circular channel that spins around its axis to achieve size separation of particles between the limits of 10 nm and 50 µm. In this method, separation is governed by a combination of size and effective particle density, indicating that applicable size range is dependent on and limited by the effective particle density. In CF3, the mobile phase and analyte flow longitudinally through the channel. The channel is designed to separate the sample components along its length, resulting in the elution of constituents at different times. The channel and its large aspect ratio are designed to promote parabolic or near-parabolic laminar flow between two infinite planes under normal operational conditions. Fractionation is achieved during passage through the channel, based on the velocity flow profile, after which the mobile phase containing separated constituents exits to online detectors and/or a fraction collector for off-line analysis. Common detectors used for analysis of pigment and extender include ultraviolet-visible (UV-Vis) absorbance, fluorescence, multi-angle light scattering (MALS), dynamic light scattering (DLS) and element detectors such as the inductively coupled plasma mass spectrometer (ICP-MS). Combinational analysis of the sizing and concentration evaluation detectors, as well as the size distribution analysis have been performed using this method according to ISO/TS 21362.

6 Apparatus

Use standard laboratory apparatus, together with the following.

6.1 Apparatus for ultrasonic dispersion

6.1.1 Probe-type sonicator, with at least 100 W power and a frequency of 10 kHz to 100 kHz.

This type of sonicator has been found to be an effective means of dispersing particulate materials in liquid dispersion from agglomerates into discrete primary particles or/and aggregates. The temperature of the dispersion during sonication should be held as low as possible, around typical room temperature, in order to maintain conditions for good stability of the dispersing agents.

6.1.2 Bath-type sonicator, with at least 50 W power and a frequency of 10 kHz to 100 kHz.

6.2 Apparatus for wet jet milling dispersion

The apparatus for wet jet milling is designed to disperse, crush, emulsify and surface-modify the material pressurized to a maximum of 245 MPa[14][15]. This apparatus consists of various components containing a high-voltage section and ultra-high-pressure section each. In the wet jet milling apparatus, the powder suspension pressurized by the pressure intensifier is branched in the apparatus chamber and accelerated by the nozzle in the chamber so that the dispersions collide with each other to achieve micronization. The maximum jet pressure depends on the nozzle diameter. The typical values of the nozzle diameter are from 0,05 mm to 0,15 mm. Materials with a particle diameter smaller than the nozzle diameter can be applied in order to prevent the nozzle from becoming clogged. It is recommended that the maximum particle diameter is smaller than half of the nozzle diameter. The apparatus should be equipped with a leakage sensor. When a liquid leakage from the high-pressure cylinder is discovered, the instrument stops the milling. The typical handling amount is about 0,1 l/min and the applicable solvents for this system are both organic and aqueous solvents. However, it is recommended to use water as solvent in principle; using organic solvent such as acetone, alcohol, acid or alcohol can influence sealing sections of apparatus for wet jet milling.

WARNING — Ignoring safety precautions and wrong handling or operation can cause serious or minor injuries and damage to this apparatus or other properties.

WARNING — Do not operate the apparatus with the solvent boiling point exceeded. Blow-off of the material or solvent caused by bumping or equipment damage caused by high-pressure steam can injure the body.

See Annex D for an example of a detailed procedure of wet jet milling dispersion, as well as a detailed description for energy estimation.

6.3 Apparatus for shaker-based dispersion, such as Disperser DAS[1)].

6.4 Analytical balance, accurate to the nearest 0,1 mg.

6.5 Beaker, based on the sonicator size, 50 cm^3 to 300 cm^3 tall-form.

6.6 Magnetic stirring device with stirrer bar

6.7 Syringes, 1 cm^3, 2 cm^3, 10 cm^3 and 20 cm^3 or better corresponding pipettes.

6.8 Cooled bath

6.9 Liquid sedimentation-based detection systems for particle size measurement

Table 1 and Table 2 show liquid sedimentation-based device examples for measuring instruments which are available at the time of publication of this document.

Table 1 — Examples for currently available measuring instruments

Type	**Photo-centrifuge**		**X-ray-centrifuge**		**Analytical ultra-centrifuge**
	Disc centrifuge	**Cuvette centrifuge**	**Disc centrifuge**		**Cuvette centrifuge**
Wavelength	405 nm or 470 nm or 650 nm	Multiple wavelengths 405 nm to 870 nm	Data to be delivered from apparatus manufacturer		Optical multiple wavelengths or xenon light
Acceleration range at the bottom Not preferred: Rotation speed	600 min^{-1} to 24 000 min^{-1}	500 min^{-1} to 4 000 min^{-1} 5 times to 2 300 times earth gravity (at cell bottom)	600 min^{-1} to 18 000 min^{-1}		(middle of cell) 1 000 min^{-1} to 60 000 min^{-1}
Type of detection	Light extinction versus time	Light extinction versus time and position	X-ray extinction versus time		Light extinction or refractive index versus time
Sample volume	100 µl to 400 µl	100 µl to 2 000 µl	100 µl to 400 µl		350 µl to 400 µl
Typical sample concentration in volume	0,01 % to 10 % (volume fraction)	0,01 % to 20 % (volume fraction)	0,1 % to 30 %		0,01 % to 1 % (mass fraction)
Spin fluid volume	10 ml to 20 ml	-	10 ml to 40 ml		-
Number of samples	1	Up to 12	1		Up to 14

1) Disperser DAS is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

Table 1 *(continued)*

Type	Photo-centrifuge		X-ray-centrifuge		Analytical ultra-centrifuge
	Disc centrifuge	**Cuvette centrifuge**	**Disc centrifuge**		**Cuvette centrifuge**
Sample containment	Disc rotor	Disposable or reusable cells	Disc rotor		Re-usable cells
Temperature control	No	4 °C to 60 °C (±0,5 °C)	No		0 °C to 40 °C (±0,5 °C)
Range of particle size	5 µm to 50 nm	500 µm to 50 nm	5 µm to 50 nm		800 nm to 2 nm

Table 2 — Examples for currently available measuring instruments

Type	X Ray Cuvette sedimentation – movable cuvette	Sedi-balance	X-ray Cuvette sedimentation	CF3
Test methods in accordance with	ISO 13317-3	ISO 13317-4	ISO 13317-3	ISO/TS 21362
Wavelength / excitation energy	0,138 nm / $1{,}442 \cdot 10^{-15}$ J (9 keV)		0,071 nm / $2{,}801 \cdot 10^{-15}$ J (17,48 keV)	Optical multiple wavelengths are available
Acceleration range at the bottom Not preferred: Rotation speed	-	-	-	0 min^{-1} to 12 000 min^{-1}
Type of detection	X-ray extinction versus time	computational detection using a commercial balance	X-ray extinction versus time and space STEP (space- and time-resolved extinction profiles) Technology	Light scattering UV-Vis absorption Refractive index Fluorescence ICP-MS
Sample volume	80 ml	1 l	0,2 ml to 1,6 ml	20 µl to 100 µl
Min. Sample concentration in mass or volume	2,5 % mass density dependent	2,5 % density dependent	2 % mass density dependent	Dependent on the samples
Number of samples	1	1	1	1
Sample containment	glass beaker	class cylinder beaker	cuvette, different materials	Flow channel
Temperature control	Yes	No	No	No
Range of particle size	1 mm to 100 nm	1 mm to 5 µm	1 mm to 200 nm	40 µm to 10 nm

7 Settings for dispersion

7.1 Procedure of ultrasonic dispersion using a probe-type sonicator

Ultrasonic sources other than probe-type ones are not recommended and can lead to wrong results because of the principle difficulties to calibrate the energy input.

The typical procedure is the following:

— fill beaker with a corresponding mass of water, depending on the size of the beaker;

- place beaker in the insulating foam;
- put the ultrasonic probe and thermometer with short response-time in the water;
- the probe should be immersed in the same depth as later for dispersion;
- wait for thermal equilibration;
- the start temperature should be in defined, narrow range (e.g. between 20 °C and 25 °C);
- start ultrasonication.

It is important to keep the temperature constant. Cooling is recommended.

It is important to use the correct energy density to disintegrate the particulate sample. Setting the energy density too low can lead to remaining agglomerates. If the energy density is too high, the piezo ceramic sonicator can be destroyed and can contaminate the dispersion with nanoparticles. In addition, a destruction of the particulate material can occur when using energies which are too high. In some cases, the treated material can lose its pigmentary or extender properties when energy density treatments are too high.

The energy estimation shall be calculated in accordance with Annex A.

7.2 Procedure of ultrasonic dispersion using a bath-type sonicator

It is important to use the correct energy density to disintegrate the particulate sample. Setting the energy too low can lead to remaining agglomerates. In addition, a destruction of the particulate material can occur when using energies which are too high. In some cases, the treated material can lose its pigmentary or extender properties at energy treatments which are too high.

Carry out an energy density estimation similar to the procedure for a probe-type sonicator specified in Annex A. Consider the warming of the whole bath together with the beaker. For weak sonicators, enhance the time of sonication until temperature changes are measurable.

The procedure is similar to the procedure of ultrasonic dispersion using a probe-type sonicator (7.1), except that the beaker is put into an ultrasonic bath:

- weigh out 0,1 % to 1,0 % (mass fraction), depending on the type of pigment or extender, in a 50 cm^3 to 300 cm^3 tall-form beaker, depending on the size of the ultrasonic bath;
- fill the beaker with a corresponding mass of water, depending on the size of the beaker;
- place the beaker in a cooled bath to prevent heating above 40 °C. the upper limit of the temperature shall be defined depending on the types of pigments or extenders;
- wait for thermal equilibration;
- the start temperature should be in defined, narrow range (e.g. between 20 °C and 25 °C);
- start ultrasonication.

It is important to always put the dispersion at the same geometric position with the same amount of bath water to ensure it remains reproducible and to maintain homogenous mixing inside the beaker.

7.3 Procedure of shaker-based dispersion

The typically used device (6.3) shakes small bottles filled with dispersion in a vertical direction. Typically, between 1 and 30 bottles can be put into a bottle holder. They are fixed between a platform and a stamp coming from above. During dispersion, the whole platform is shaken oscillatory in a vertical direction.

To enhance the dispersion properties, milling beads should be inserted into the bottles. Typically, the effectivity of dispersion is correlated to the shaking speed, the volume percent of milling beads and the particle sizes as well as to the material of the milling beads.

The procedure is as follows:

— Take one 15 ml HDPE screw cap bottle and fill in the following dispersion: 12,475 ml dispersion having 5 % to 20 % of particle volume concentration in aqueous solution together with the particle amount adopted dispersant e.g. 5 g TiO_2 in 7,475 g H_2O and 0,025 g hexametaphosphate (HMP) or other polyphosphate;

— add 28 g ZrO_2 milling particles (0,5 mm);

— put the bottle into a shaker (6.3)

— select energy input to 60 W/(ml × min);

— shake the bottle for 5 min.

If the energy cannot be adjusted, measure energy input per minute and adopt the shaking time to 300 W/ml. A detailed description for the energy estimation is given in Annex A.

8 Dispersion procedure

8.1 General

The dispersion process is dependent on the operation time, power and dimension of dispersion devices. To optimize the operation, it is recommended to find the operation level which achieves stable size distribution. For appropriate dispersing of pigment and extender, the choice of the liquid phase and dispersant are also critical.

8.2 Sampling for dispersion

Select pigment or extender samples from larger-sized lots at random, in either pelletized or non-pelletized form, in accordance with ISO 15528. Label and retain samples for storage or further analysis.

8.3 Reagents

Unless stated otherwise, use only reagents of recognized reagent grade.

8.3.1 Water, distilled or deionized, quality 3 in accordance with ISO 3696.

The water shall be free of particles. To ensure this, filtration shall be used (e.g. membrane filter - cut-size 50 nm or smaller). Similar filtration shall also be used for any added additional solvents.

The liquids used shall not solve the particles to be measured.

If no data are available, the water shall be qualified by a blind test particle measurement in accordance with this document.

8.3.2 Organic solvent, free of nanoparticles when measured in accordance with this document.

If no data are available, the solvent shall be qualified by a blind test particle measurement in accordance with this document. If used, a blind measurement shall be performed in accordance with this document using water, solvent and surfactant together in the planned concentrations.

The liquids used shall not solve the particles to be measured.

8.3.3 Surfactant, free of nanoparticles when measured in accordance with this document, in relation to the surface properties of the pigment of extender particles.

If no data are available, the surfactant shall be qualified by a blind test particle measurement in accordance with this document. If used, it is important to make some blind measurement in accordance with this document using water, solvent and surfactant together in the planned concentrations.

8.4 Recommendations for sample preparation

Examples of procedures for different materials are given in Annexes C, D, E and F. For other materials, an example of a procedure is specified in Annex G.

9 Sampling

Select pigment or extender samples from larger-sized lots at random, in either pelletized or non-pelletized form, in accordance with ISO 15528. Label and retain samples for storage or further analysis.

10 Measurement and expression of results

Perform the particle sizing using sedimentation methods in accordance with ISO 13317-1, ISO 13317-2, ISO 13317-3, ISO 13317-4, ISO 13318-1, ISO 13318-2 or ISO 13318-3. One of these methods shall be performed at least three times for each dispersion. Express the volume based on the average of the volume-weighted particle size distributions as the cumulative function and as the transformed density function in accordance with ISO 9276-1. In addition, the results of the particle size distribution (PSD) measurement shall be presented as numbers in a table containing the single measurement results and the resulting average values for d50V, d10V, d90V, as well as the precision of the average values.

For measurement, use material density measured by He-Pygnometry in accordance with ASTM D5965 or the literature values for bulk material, at least.

11 Test report

The test report shall include the following information:

a) all information necessary to identify the tested product;

b) a reference to this document, i.e. ISO 20427:2023;

c) the type of instrument and software used; including the instrument identification number and the date of the last successful calibration (performance qualification) as well as the version of the software;

d) the material data (including the reference to the international or national standard, product specification or other document supplying the information or how it was determined):

   1) composition of pure liquid phase, mass concentration (in case of solutions), density, viscosity and refractive index;

   2) composition of dispersed phase, density and refractive index (pigment or extender);

e) the sample preparation; this includes dispersion instruments, dispersion procedures (sonication time, energy power and suspension volume), but also possible adjustments of pH, addition of surfactants, filtration of pure dispersion media and possible dilution of dispersed sample;

f) the test parameters

   1) for the disc centrifuge: rotational speed of disc, kind and volume of spin fluid, density gradient, viscosity, calibration system, material, wavelength;

   2) for the cuvette centrifuge: rotational speed of the rotor, type of cuvettes, wavelength;

g) temperature at the beginning and at the end of the sedimentation measurement;

h) results of the test;

i) any deviations from the procedure specified;

j) any unusual features (anomalies) observed during the test;

k) investigator, the date of receiving the sample and the date of the test;

l) precision found;

m) reproducibility 3 times measurement with average and standard deviation.

Annex A
(normative)

Protocol for the determination of energy input

A.1 Protocol for the determination of energy input at ultrasonication

A.1.1 Procedure

— Fill the beaker with a corresponding mass of water, depending on the size of the beaker.

— Place the beaker in the temperature reservoir.

— For probe-based sonication put the ultrasonic probe and thermometer with short response-time into the water. The probe should be immersed in the same depth as for dispersion procedure. For bath-based sonication put the beaker into the bath and thermometer into the beaker.

— Wait for thermal equilibration. The start temperature should be in a defined, narrow range (e.g. 20 °C to 25 °C).

— Start ultrasonication and record temperature against time.

A.1.2 Data analysis

Evaluate the initial slope of the temperature increase ($\Delta T \leq 4$K) using Formula (A.1) (as shown in NIST Special Publication 1200-2)[6]:

$$P_{\text{cal}} = \left(c_{p,\,\text{beaker}} \times m_{\text{beaker}} + c_{p,\,\text{water}} \times m_{\text{water}}\right) \times \frac{\mathrm{d}T}{\mathrm{d}t} \tag{A.1}$$

where:

P_{cal} delivered acoustic power, in watts;

$c_{p,\,\text{beaker}}$ specific heat capacity of the beaker, in joules per gram and kelvin;

m_{beaker} mass of the beaker, in grams;

$c_{p,\,\text{water}}$ specific heat capacity of water, in joules per gram and kelvin;

m_{water} mass of the water, in grams;

T temperature, in kelvins;

t time, in seconds;

$\mathrm{d}T$ differential of temperature;

$\mathrm{d}t$ differential of time.

A.1.3 Assumptions

The following assumptions apply:

— the temperature of the water, beaker and ultrasonic probe at the beginning are uniform;

— the ultrasonic probe has zero-heat capacity;

— there is no heat transfer out of the system beaker-water.

A.2 Protocol for the determination of energy input at shaker-based dispersion

A.2.1 General

The shaker-based dispersion is very close to the wet ball milling process. Typically, the impulse-based processes are the driving force of disintegration. Therefore, any estimates of the disintegration impact with the energy dissipated are approximations. For each material to be treated, the limit for the set-on of milling shall be investigated before using the method for particle sizing.

A.2.2 Procedure

— Prepare five solutions of 12,475 g H_2O together with 0,025 g of polyphosphate.

— Fill each solution as well as 33 g milling particles e.g. $YZrO_2$ or ZrO_2 (0,5 mm) into one 15 ml HDPE screw cap bottle.

— Equilibrate the temperature of filled bottles to the lab temperature.

— Put the bottles into a shaker (6.3).

— Shake the five sample bottles for the duration in accordance with the shaking times in Table A.1.

Table A.1 — Shaking times for the five sample bottles

Bottle No.	1	2	3	4	5
Shaking time	2 min	4 min	7 min	10 min	15 min

— Measure the temperature change in the bottle. The most efficient way would be by connecting a PT 100 diving thermo element with corresponding measurement electronics and performing a live measurement while shaking the bottle.

A.2.3 Data analysis

— Take the average curve from all five measurements and calculate the energy input from temperature increase, using Formula (A.2):

$$P_{cal} = \left(c_{p,\text{bottle}} \times m_{\text{bottle}} + c_{p,\text{ZrO}_2} \times m_{\text{ZrO}_2} + c_{p,\text{water}} \times m_{\text{water}} \right) \times \frac{\text{d}T}{\text{d}t} \quad \text{(A.2)}$$

where

P_{cal} delivered acoustic power, in watts;

$c_{p,\text{bottle}}$ specific heat capacity of the bottle, in joules per gram and kelvin;

m_{bottle} mass of the bottle, in grams;

c_{p,ZrO_2} specific heat capacity of the milling particles, in joules per gram and kelvin;

m_{ZrO_2} mass of the milling particles, in grams;

$c_{p,\text{water}}$ specific heat capacity of water, in joules per gram and kelvin;

m_{water} mass of the water, in grams;

T temperature, in kelvins;

t time, in seconds.

— Formula (A.2) is similar to NIST Special Publication 1200-2, Formula (1)[6].

A.3 Protocol for the determination of energy input at wet jet milling

A.3.1 Procedure

— Put a corresponding mass of water, depending on the size of the material tank, into the material tank of the wet jet milling system[14][15].

— Wait for thermal equilibration. The start temperature should be in a defined, narrow range (e.g. 20 °C to 25 °C).

— Start the jet milling and record temperature against time in the material tank of wet jet milling system for the determination of direct calorimetric curves[14][15].

A.3.2 Data analysis

— Evaluate the initial slope of temperature increase ($\Delta T \leq 4\text{K}$) after obtaining the best linear fit for the curve using the least squares regression, using Formula (A.3):

$$P_{\text{cal}} = \left(c_{p,\,\text{tank}} \times m_{\text{tank}} + c_{p,\,\text{water}} \times m_{\text{water}} \right) \times \frac{\mathrm{d}T}{\mathrm{d}t} \tag{A.3}$$

where

P_{cal} delivered jet milling power, in watts;

$c_{p,\,\text{tank}}$ specific heat capacity of the material tank, in joules per gram and kelvin;

m_{tank} mass of the material tank, in grams;

$c_{p,\,\text{water}}$ specific heat capacity of water, in joules per gram and kelvin;

m_{water} mass of the water, in grams;

T temperature, in kelvins;

t time, in seconds.

A.3.3 Assumptions

The following assumptions apply:

— the temperature of water and tank is uniform at the beginning;

— the wet jet milling system has zero-heat capacity;

— there is no heat transfer out of the material tank of wet jet milling system.

Annex B
(informative)

Limits for ultrasonic dispersion procedure

Weigh out 0,1 % to 1,0 % (mass fraction), depending on the type of pigment or extender, in a 50 cm^3 to 300 cm^3 tall-form beaker, depending on the size of the ultrasonic probe (5 mm to 20 mm probe diameter corresponding to 30 cm^3 to 250 cm^3 of dispersion).

The beaker shall be placed in a cooled bath to prevent heating above 40 °C. Ultrasonic dispersion and ultrasonic disintegration, for example 10 min at 60 % of the amplitude scale, is efficient. A suspension volume specific (electrical) energy input of about 100 J/ml to 1 000 J/ml is recommended, depending on the type of pigment or extender.

In most cases the maximum energy input per millilitre shall be set much lower than 1 000 J/ml. For example, for SiO_2, Fe_2O_3 and TiO_2 and other materials with Mohs hardness below 7, the maximum energy should be not more than 250 J/ml, otherwise particles can be damaged. An energy level above 1 000 J/ml sonication tip can release TiO_2 nanoparticles from the sonication tip.

NOTE Commercially available electrical power meters have been shown to be partly suitable for measuring the energy input. For measuring the power input into the disintegration dispersion, the procedure described in NIST Special Publication 1200–2[6] has been shown to be suitable (see A.1).

Annex C
(informative)

Procedures for dispersion of TiO_2 pigments

C.1 Procedure for dispersion of TiO_2 pigments with ultrasonic probe

— Use a 100 ml laboratory glass beaker (preferably a 100 ml rosette beaker such as Sonopuls RZ[2)]). Fill it with the following dispersion: 2 g of pigment together with 80 g of 0,5 % aqueous NaHMP or polyphosphate solution using milipore water.

— Insert ultrasonic probe into the beaker leaving a 5 mm gap to the bottom of the beaker.

— Start ultrasonic treatment for 250 J/ml.

— Put beaker on magnetic stirring device (6.6) after ultrasonic treatment and add stirrer bar.

— Take out a 2 ml sample with a Pasteur pipette or similar tool.

— Prepare the sample for the selected particle size measurement method.

C.2 Procedure for dispersion of TiO_2 pigments with a shaker

— Take one 15 ml HDPE screw cap bottle and fill in the following dispersion: use 40 % of particle mass concentration in aqueous solution together with 0,5 % of polyphosphate (e.g. 5 g of TiO_2 in 7,475 g of H_2O and 0,025 g HMP or polyphosphate).

— Add 28 g of ZrO_2 milling particles (0,5 mm).

— Put bottle into shaker (6.3).

— Select energy input to 250 J/ml.

— Shake the bottle for a well-defined shaking time, in minutes, which can be calculated using Formula (C.1):

$$t = \frac{E_{input} \times V}{P_{cal}} \times \frac{1}{60} \tag{C.1}$$

where

t shaking time, in minutes;

E_{input} energy input, in joules per millilitre;

V volume of the bottle content, in millilitres;

P_{cal} delivered acoustic power, in watts [see Formula (A.2)].

2) Sonopuls RZ is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

Annex D
(informative)

Procedure for dispersion of $CaCO_3$ with wet jet milling

— Prepare the following dispersion: 50 mg of pigment together with 20 mg of 0,02 % aqueous polyoxyethylene alkylether solution (e.g. Softanol® 70[3)]) using ultrapure water of 100 ml.

— Pressurize the suspension by the pressure intensifier, accelerated by the nozzle in the chamber (2 kW/ml: typical pressure for jet milling is 180 MPa in this case)[14][15].

— Take out a 2 ml sample with a Pasteur pipette or similar tool.

— Prepare the sample for the selected particle size measurement method.

In order to validate the dispersing ability of $CaCO_3$ by individual wet jet milling, it is recommended to perform the same process using $CaCO_3$ particles (e.g. Hakuenka-CC-R®[4)]); then, the mean size will be approximately 170 nm.

3) Softanol® 70 is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

4) Hakuenka-CC-R® is the trade name of a product supplied by Shiraishi Kogyo Kaisha, Ltd. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

Annex E
(informative)

Procedure for the dispersion of Fe_2O_3 with an ultrasonic probe

— Use a 100 ml laboratory glass beaker or alternatively, a 100 ml disposable plastic beaker, and fill it with: 2 g of pigment together with 80 g of 0,5 % aqueous sodium polyphosphate solution using distilled water or water of comparable quality.

— Place the ultrasonic probe 5 mm above the bottom of the beaker.

— Start ultrasonic treatment for 240 W/ml.

— Take out a 2 ml sample with pipette or similar tool.

— Prepare the sample for the selected particle size measurement method.