International Standard ISO 6388

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Surface active agents — Determination of flow properties using a rotational viscometer

Agents de surface — Détermination des propriétés d'écoulement au moyen d'un viscosimètre rotatif

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Foreword

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INTERNATIONAL STANDARD **ISO 6388-1983 (E)**

Surface active agents — Determination of flow properties using a rotational viscometer

0 Introduction

The rheological behaviour of surface active agents in general is determined using a rotational viscometer, which is suitable for studying substances having a complex rheological behaviour, e.g. plastics, paints.

In developing this International Standard, reference has been made to ISO 3219, which deals with plastics, for the definitions and the apparatus. The method specified in this International Standard, however, is specific to surface active agents.

1 Scope and field of application

This International Standard specifies a method for the characterization of the flow properties of non-solid surface active agents, either alone or in the form of mixtures, and of products consisting essentially of surface active agents, using a co-axial cylinder, cone and plane, or double cone, etc., rotational viscometer.

NOTE — The rheological behaviour of a system containing surface active agents is frequently marked by anomalies. These are mostly due to the tendency of the molecules of surface active agents to associate. The rheological behaviour varies essentially as a function of the nature and concentration of the surface active agents. Small variations in temperature, in the concentration of mineral salts, and the presence of any other substance, may also cause variations in the rheological behaviour of surface active agents; even the rheological pattern itself may sometimes be changed. The method specified in this International Standard attempts to take account of all these factors. In the case of certain very special surface active agents, other methods of determination may be used. For newtonian systems, for example, reference should be made to ISO 3104 and ISO 1652, which are much more precise.

When the newtonian character of a system is in question, the method specified in this International Standard will make it possible to select measuring equipment which will allow a determination to be carried out.

2 References

ISO 607, *Surface active agents and detergents — Methods of sample division.*

ISO 862, *Surface active agents — Glossary.*[1]

ISO 1652, *Rubber latex — Determination of viscosity.*

ISO 3104, *Petroleum products — Transparent and opaque liquids — Determination of kinematic viscosity and calculation of dynamic viscosity.*

ISO 3219, *Plastics — Polymers in the liquid, emulsified or dispersed state — Determination of viscosity with a rotational viscometer working at defined shear rate.*

3 Definitions, symbols and units

3.1 General

The viscosity of a fluid sheared between two parallel planes, one of which moves in its own plane with linear and uniform motion relative to the other, is defined by Newton's equation :

$$\eta = \frac{\tau}{D}$$

where

η is the (dynamic) viscosity;

τ is the shear stress;

$D = \frac{dv}{dz}$ is the rate of shear

v being the velocity of one plane relative to the other, and

z being the coordinate perpendicular to both planes.

NOTE — Products for which the viscosity is independent of the rate of shear at which the measurement is taken are regarded as having newtonian behaviour and are called "newtonian". Others are regarded as having non-newtonian behaviour and are called "non-newtonian".

The apparent viscosity of a non-newtonian product is the ratio of the produced shear stress to the applied rate of shear.

The value of the apparent viscosity, a function of the rate of shear, can depend on thermal and rheological hysteresis of the sample in the apparatus.

The dimensions of viscosity are $ML^{-1} T^{-1}$, and in the International System of Units (SI), the unit is the newton second per square metre ($N \cdot s/m^2$) or the pascal second ($Pa \cdot s$).[2]

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[1] At present at the stage of draft. (Revision of ISO/R 862.)

[2] $1 \ N \cdot s/m^2 = 1 \ Pa \cdot s = 10^3 \ cP$ (centipoise)

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3.2 Rheological phenomena (see figures 1 and 2).

3.2.1 shear thinning: The reduction under isothermal and reversible conditions and without hysteresis of the apparent viscosity with increasing rate of shear.

3.2.2 dilatancy: The increase under isothermal and reversible conditions and without hysteresis of the apparent viscosity with increasing rate of shear.

3.2.3 time-dependent viscosity : Under reversible and isothermal conditions, a change of the apparent viscosity during flow with a constant magnitude of the shear rate.

3.2.3.1 thixotropy : The reduction of viscosity or consistency, under isothermal and reversible conditions, by the application of shear from the viscosity or consistency at rest (immediately after beginning to shear) to a final value (dependent on the magnitude of the shear rate).

When the shear is discontinued the viscosity or consistency at rest must be reestablished within a certain time, the "time of thixotropic recovery".

3.2.3.2 rheopexy: The phenomenon in which the time of thixotropic recovery, after discontinuation of a relatively high shear rate, is shortened by applying a small shear rate.

3.2.3.3 anti-thixotropy: The increase of viscosity or consistency under isothermal and reversible conditions, by the application of shear from the viscosity or consistency at rest (immediately after beginning to shear) to a final value (dependent on the magnitude of the shear rate).

When the shear is discontinued, the viscosity at rest must be re-established within a certain time, the "time of thixotropic recovery".

3.2.3.4 rheological hysteresis: If the shear rate under isothermal and reversible conditions is increased linearly with respect to time from zero to a maximum value (up-branch) and then decreased in the same manner (down-branch), the rate of shear-diagram shows a hysteresis loop, which is used to detect and to characterize thixotropy or anti-thixotropy.

3.2.4 plasticity : A plastic body behaves as an elastic body when it is subjected to a stress less than a critical value, τ_o, the "yield stress". Above this limiting value, a flow takes place. When the function $D = f(\tau)$ (D is the rate of shear) for $\tau \geqslant \tau_0$ is represented by a straight line, the substance is said to follow the Bingham model.

4 Principle

Determination of flow properties of a newtonian or non-newtonian test portion by means of a specified rotational viscometer, which will allow, for the newtonian products, the simultaneous measurements of the shear rate at which the determination is carried out, but for the non-newtonian products, possible measurement of various apparent rates of shear used for the determination.

5 Standard substances

Newtonian liquids shall be used as standard substances.

6 Apparatus

6.1 Viscometers, with co-axial cylinders, a cone and plate, a double cone or a combination of two of these types, with the following specifications :

6.1.1 In the case of viscometers with co-axial cylinders, the external and internal diameters of the cylinders (stator and rotor), d_e and d_i respectively, shall be such that the value of the ratio d_e/d_i is as small as possible and, preferably, less than or equal to 1,10, and in no case greater than 1,50. If the ratio has a value greater than 1,10, this shall be indicated in the test report and a correction shall, if possible, be made, which shall also be reported in the test report.[1]

In addition, if the apparatus does not include a geometric device (conical base and guard ring above it) for correcting the end effect, the following additional requirement shall be respected :

$$\frac{h_i}{d_i} \geqslant 1,5$$

where h_i is the height of the inner cylinder.

6.1.2 In the case of viscometers with a cone and plate, or a double cone, the value of the angle α, formed by the generating line of the cone and the plate or by the generating lines of the two cones shall be as small as possible and, preferably, less than or equal to 1°, and in no case greater than 4°. If the angle α has a value greater than 1°, this shall be indicated in the test report and a correction shall, if possible, be made, which shall also be reported in the test report.[1]

6.1.3 In the case of viscometers combining two of the preceding principles, each of the specifications shall be observed, unless one of the devices contributes at a very low percentage and can be regarded as being a correction.

6.1.4 The instrument, shall, in all cases, enable a number of frequencies of rotation to be used.

It shall be accurate to within 2 % of the total scale range for viscosity measurement and for every combination of rotor, stator and frequency of rotation.

The limits of viscosity and the rate of shear which the instrument is able to measure shall be in keeping with the measurements to be taken and the rate of shear required.

NOTE — By means of different stators, rotors and frequencies of rotation, the majority of commercial instruments allow measurements of viscosity in a range which extends at least from 10^{-2} to 10^3 Pa·s (10 to 10^6 cP).

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[1] The correction formulae should usually be supplied by the manufacturer of the apparatus.

The rates of shear permitted by different instruments vary greatly from one instrument to another.

The adjustment and calibration of the instruments is normally carried out by the manufacturer.

It is recommended that checking of the adjustment and calibration carried out from time to time, using liquids of known viscosity, either in the user laboratories, or in official laboratories.

6.2 Viscometers, having measuring systems which do not have a defined geometry (plate, T-shape, etc.).

6.3 Thermostatically controlled baths, which enable the product under examination to be brought to, and maintained at, the testing temperature (usually 23 °C), to the nearest 0,2 °C.

This tolerance of ± 0,2 °C is applicable to temperatures between 0 and 50 °C. However, a stricter tolerance (± 0,1 °C, for example), may be required for precision measurements and in the ordinary range of temperatures.

It should be noted that, in cases where the rate of shear is high, the measuring process itself causes heating of the sample, and it is necessary to take precautions to prevent this, or to take it into account by applying a correction (often provided by the manufacturer of the viscometer).

NOTE — In general, commercially available viscometers include a built-in thermostatic device.

7 Sampling

Prepare and store the laboratory sample of surface active agent in accordance with ISO 607.

8 Procedure

8.1 Test portion

Carefully take a test portion from the homogenized laboratory sample (clause 7), ensuring that it is completely free of air bubbles.

NOTES

1 When dealing with products likely to separate into two phases over a particular temperature range, care should be taken to ensure that the determination is carried out outside this range.

2 In the case of products with time-dependent behaviour, care should be taken to ensure that the handling operations (including heating) to which the products are subjected are always identical and are reported in the test report.

8.2 Determination

8.2.1 Place the test portion (8.1) in the thermostatically controlled measuring vessel, and adjust to the temperature selected for the determination. Then insert the co-axial measuring cylinder, or any other chosen measuring device, into the measuring vessel. Operate the apparatus at a constant frequency of rotation and measure the moment of the applied couple (torque).

Carry out several measurements on the same sample, and repeat the measurements at different rates of shear of the viscometer.

8.2.2 In the case of instruments with co-axial cylinders, the radial distribution of shear stress τ_r within the gap between the co-axial cylinders is given by the formula

$$\tau_r = \frac{M}{2\,\pi\,h} \times \frac{1}{r^2}$$

where

M is the moment of the applied couple;

h is the length of the gap between the coaxial cylinders;

r is the radius considered.

Taking into account the special cases for the shear stresses at the walls of the inner and outer cylinders, τ_i and τ_e, respectively, are given by the formulae

$$\tau_i = \frac{2\,M}{\pi\,h} \times \frac{1}{d_i^2}$$

and

$$\tau_e = \frac{2\,M}{\pi\,h} \times \frac{1}{d_e^2}$$

where

M and h have the same meanings as before;

d_i is the diameter of the internal cylinder;

d_e is the diameter of the external cylinder.

8.2.2.1 Case of newtonian products

In the case of measurements on newtonian products, the rate of shear may be calculated by multiplying the frequency of rotation of the cylinder by a coefficient, the value of which is given by the manufacturer. In principle, one calculates the shear rate at the wall of the cylinder on which also the torque is measured. The rate of shear, is, theoretically, given by the formulae

$$D_i = \frac{4\,\pi\,N}{60} \times \frac{d_e^2}{d_e^2 - d_i^2}$$

and

$$D_e = \frac{4\,\pi\,N}{60} \times \frac{d_i^2}{d_e^2 - d_i^2}$$

where

D_i and D_e are the shear rates, in reciprocal seconds, at the internal cylinder and external cylinder, respectively;

N is the frequency of rotation of the rotor, per minute;

d_e and d_i have the same meanings as before.

NOTE — When applying the above formulae, it does not matter which of the two cylinders is actually rotating.

8.2.2.2 Case of non-newtonian products

In the case of measurements on non-newtonian products, the rate of shear at the wall of the moving part of the instrument cannot be calculated by multiplying the frequency of rotation of the cylinder by the coefficient for newtonian bodies. In this case the value obtained corresponds to the "apparent rate of shear", symbol D_a.

The relation between D_a and τ_i or τ_e is represented by a curve of "apparent fluidity" (or mobility). The ratio τ_i/D_a or τ_e/D_a corresponds to the apparent viscosity.

NOTES

1 If the value of the ratio d_e/d_i is less than or equal to 1,10, and for the liquids of almost newtonian behaviour, the difference between D_i, D_e and D_a is small. The viscosity η can then be considered as the apparent viscosity η_a, i.e. there is no appreciable difference between the rheological behaviour and the apparent rheological curve.

2 In case of non-newtonian behaviour of the liquid, or if the value of the ratio d_e/d_i is greater than 1,10 for the coaxial system, or even much larger in the case of an instrument of undefined geometry, the frequency of rotation (N) of the rotor has to be taken instead of D_a. A comparison of these curves with the curves of D_a as a function of τ_i or τ_e is not possible.

8.3 Calibration

Use the method described in 8.2 with the standard substances (clause 5). Measure the viscosity of each of these substances. Use the appropriate standard substance for each instrument.

The curve showing D as a function of τ will necessarily pass through the origin. For instruments of undefined geometry, the calibration curve shall be a straight line passing through the origin, irrespective of the units on the coordinate axes.

9 Expression of results

9.1 The results shall preferably be given in the form of a flow curve D_a as a function of τ_i or τ_e or as a diagram or a table representing the apparent viscosity η_a as a function of D or τ.

9.2 The results obtained using instruments of undefined geometry are usually presented as a curve with values of N as abscissae and the values of apparent viscosity corresponding to the frequency of rotation N as ordinates :

$$\frac{CM}{N} = \eta_a(N)$$

where

M is the moment of the applied couple (or any other value proportional to this);

N is the frequency of rotation of the rotor.

The calibration constant C is determined beforehand by measuring $\eta_a(N)$ for a newtonian reference substance of known viscosity η.

9.3 When measurements are made on a plastic body, it is essential to state the yield stress τ_o if an accurate value is known.[1]

NOTES

1 When conducting hysteresis tests on thixotropic or anti-thixotropic products, it is essential to report the shear programme and the way in which the product has been handled.

2 The flow curve and the apparent viscosity depend, among other factors, upon the geometry of the body used, whether the instrument has a defined geometry or not. Curves can only be compared with one another when they have been obtained using the same type of instrument.

By virtue of their composition, a large number of concentrated solutions or pastes give uncertain results from one determination to another. In practice, it is difficult to specify methods for the preparation of reproducible samples.

Thus, the only information available relates to the aspects of the curves which can be plotted, and it is not possible to draw conclusions on the rheology of the system.

Particular emphasis is laid up on the fact that the rheological behaviour of a large number of surface active agents is altered by the presence of small quantities of impurities, electrolytes, solvents, hydrophobic agents, as well as by temperature variations.

9.4 The accuracy of the measurements obtained is particularly dependent on the characteristics of the flow. Added to this, there are also the effects of the sample, the shear programme and the measuring system used. It is for these reasons that the accuracy required, in each particular case, shall be stated.

10 Test report

The test report shall include the following information :

a) all the information necessary for the complete identification of the sample;

b) the reference of the method used (reference to this International Standard);

c) the results obtained, together with the form in which they are expressed;

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[1] Many rotational viscometers are fitted with devices which permit accurate measurement of the yield stress.

d) the testing conditions :

- data on the homogeneity of the sample,
- description of test sample and of the preparation of the sample (especially when this is affected by the length of time for which the shear is applied),
- test temperature,
- measuring system, with details of the measuring unit used, the ratio of the diameters of the cylinders and the length of the gap between them,
- the shear programme, number of settings of frequency of rotation, time taken for the measurement at each setting, total shear time;

e) details of any operations not specified in this International Standard, or regarded as optional, together with details of any incidents likely to have affected the results.