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Rheological test methods — Fundamentals and interlaboratory comparisons —

Part 2: Determination of the time-dependent structural change (thixotropy)

Méthodes d'essai rhéologiques — Principes fondamentaux et comparaisons interlaboratoires —

Partie 2: Détermination de la variation structurelle dans le temps (thixotropie)

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Foreword

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This document was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 9, *General test methods for paints and varnishes*.

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Rheological test methods — Fundamentals and interlaboratory comparisons —

Part 2:
Determination of the time-dependent structural change (thixotropy)

1 Scope

This document gives information on an interlaboratory comparison for the determination of the time-dependent structural change (thixotropy) using rheological test methods. Thixotropy is the reversible, time-dependent decrease of shear viscosity η at a constant shear rate $\dot{\gamma}$ or shear stress τ.

This document provides examples of fields of application, in which important material properties can be characterized by the thixotropy. These fields of application include:

— effectiveness of rheological additives and thixotropic agents, respectively;

— stability of the structure at rest (e.g. behaviour when starting to pump);

— wet film thickness after processing;

— levelling and sagging behaviour (e.g. without brushmarks or sag formation);

— orientation of effect pigments.

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 3219-1, *Rheology — Part 1: Vocabulary and symbols for rotational and oscillatory rheometry*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 3219-1 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/

4 Measuring technique for the determination of thixotropy

4.1 Conditions for the measuring technique

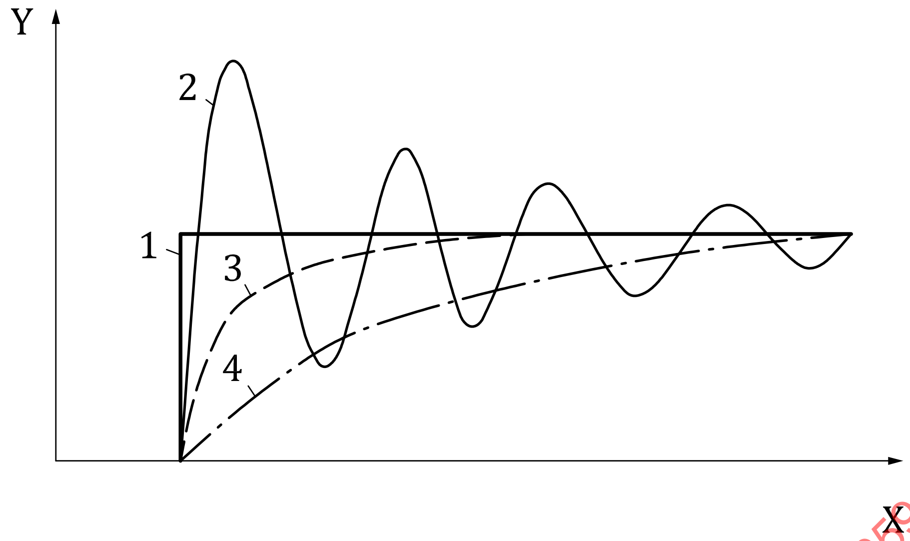
Clause 4 briefly describes methods that are currently in use. In principle, the thixotropy depends on the temperature, the pressure, and the thermal and mechanical history of the material. A detailed specification of the measuring profile is therefore a precondition for reproducible measurements and comparable evaluation; this applies especially for the level of shear load (shear rates, shear stresses, shear strain, oscillation frequencies), the duration of the individual measuring segments and the number of measuring points.

Thixotropy can be determined by rotational as well as by oscillatory tests. Measuring devices equipped with a mechanical bearing or air bearing are suitable for rotational tests. For oscillatory tests, a rheometer with air bearing is used. It is essential to ensure that the measuring device is used in combination with the suitable measuring geometry, i.e. in accordance with the torque range, the torque resolution and the rotational speed range. Typically, rotational viscometers and rheometers that are subject to test equipment monitoring and are regularly calibrated and verified (if necessary), are used. Measuring results that are independent of geometry can only be obtained by using absolute measurement geometries according to ISO 3219-2.

If, independently of the measuring device and the measuring method used, no time-stable measuring results are obtained during the measurement of Newtonian standard samples, then the measuring device, the measuring geometry or the measuring method is unsuitable. If the functional course of these time-stable measured values meets the reference values within the used measuring range, it is guaranteed that the measuring device, the measuring geometry and the measuring method are suitable for the investigation of the sample. Typically, this inspection is carried out under isothermal conditions in the expected viscosity range of the sample by using several Newtonian standard samples. If preliminary tests reveal that the viscosity of the measuring sample varies over three decades, then the verification of the measuring device and measuring geometry are performed with three Newtonian standard samples. This is carried out for all measuring temperatures. The influences due to application, e.g. sample filling, evaporation, shear heating, wrong choice of method and the sample material coming out of the gap, are mostly discernible and detected by this kind of verification.

Upon measurement, the possibility of evaporation is considered. A reduction of this influence can be reached, e.g. by using a sample area coverage. All boundary conditions of the measurement are documented in the record, especially the usage of a coverage, the kind of sample trimming and the adjustment of the gap distance. According to the specifications of the measuring methods described in Clause 4, the methods are changed if influences on the measuring results occur. Another parameter is checking whether the duration of the load is shorter than the medium time scale of the structural changes of the sample. This is determined for each measuring method and its specifications by preliminary tests. However, the duration of the load is selected in consideration of situations where conditions of application of the sample are longer. If this duration is longer than the time scale of structural change of the sample, then a thixotropic behaviour will not be detected; nevertheless, the sample can be still thixotropic. In order to determine the thixotropy in a correct and reproducible manner, when filling the measuring geometry, the influence that the time between filling and the start of the measurement has on the measuring result is taken into consideration. This time is distinctly longer than the time scale of the structural change. This can be determined by preliminary measurements in which the waiting time is varied. The waiting time is sufficiently high if the thixotropy of the sample is comparable for two measurements running after a fresh filling within the limits of the requested precision in accordance with the measuring method chosen.

Measuring points can only be recorded if each single measuring point is controlled by the instrument according to the specification. At every change of the specified value, a transient process of the entire measuring equipment occurs towards the new specified value. This transient process can be different (see Figure 1).



Key

X	time, t
Y	shear stress, τ, or shear rate, $\dot{\gamma}$
1	specified function
2, 3, 4	different adjustment behaviours

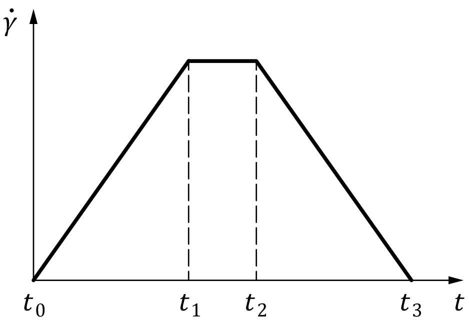
Figure 1 — Different transient behaviour during the controlling of each individual measuring point

The measuring point is not detected until the deviation between the specified value and the desired value is small enough. The integration time (time per measuring point minus adjustment time), which is considered for calculating the average of a data point, influences the measuring result. This condition is valid for constant shear load as well as for a time-dependent change of the load.

4.2 Flow curves, with evaluation of the hysteresis area (rotational test)

4.2.1 Specification of the measuring profile

The specification is provided in the form of three measuring segments comprising a continuous or a step-like discontinuous upward ramp, a holding time and a downward ramp (see Figures 2 and 3). The shear rate $\dot{\gamma}$ is specified as a function of time. Both ramp types can be used with linear and logarithmic distribution. This is valid for the shear rate and for the time duration of the measuring points. At the beginning, this can also be preceded by a segment with defined pre-shear and/or a waiting time without shear (e.g. 5 min).

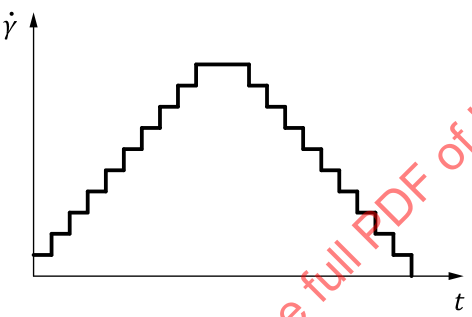


Key

$\dot{\gamma}$ shear rate

t time

Figure 2 — Specified profile: shear rate and time function with the three measuring segments: continuous upward ramp, holding time and continuous downward ramp



Key

$\dot{\gamma}$ shear rate

t time

Figure 3 — Specified profile: shear rate/time function with the three measuring segments: stepped upward ramp, holding time and stepped downward ramp

Proposals for a typical measuring programme include Method A and Method B.

Method A, with a linear ramp for the shear rate, includes:

1) upward ramp with $\dot{\gamma}$ = 0 s^{-1} to 1 000 s^{-1}, duration 3 min, with 45 measuring points;

2) holding time with $\dot{\gamma}$ = 1 000 s^{-1} = constant, duration 1 min, with 15 measuring points;

3) downward ramp with $\dot{\gamma}$ = 1 000 s^{-1} to 0 s^{-1}, duration 3 min, with 45 measuring points.

The period of time for the up- and down-ramps is the same. Moreover, it is defined whether the test is carried out with continuous or step-like ramp.

Method B, with a logarithmic ramp for the shear rate, includes:

4) upward ramp with $\dot{\gamma}$ = 0,1 s^{-1} to 1 000 s^{-1}, duration 3 min, with 61 measuring points. If a viscometer with a mechanical bearing is used, then 10 s^{-1} can be used as the minimum shear rate;

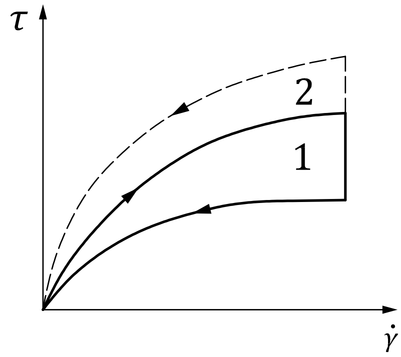
5) holding time with $\dot{\gamma}$ = 1 000 s^{-1} = constant, duration 1 min, with 15 measuring points;

6) downward ramp with $\dot{\gamma}$ = 1 000 s^{-1} to 0,1 s^{-1}, duration 3 min, with 61 measuring points.

The period of time for the up- and down-ramps is the same. Moreover, it is defined whether the test is carried out with continuous or step-like ramp.

4.2.2 Evaluation

If the measuring sample displays behaviour that varies with shear load and time, a so-called hysteresis area is generated between the upward and downward flow curves. Here, hysteresis means curve loop. Flow curves are usually presented as shear stress τ (in Pa) against shear rate $\dot{\gamma}$ (in s^{-1}) (see Figure 4).



Key

τ shear stress

$\dot{\gamma}$ shear rate

1 hysteresis area with reduction of structural strength under shear load

2 hysteresis area with increase in structural strength under shear load

Figure 4 — Measuring result: flow curves with hysteresis area

When the shear rate increases from zero to a maximum value and then decreases to zero following a defined time programme, the hysteresis curve is generated from the two resulting flow curves, which do not overlap.

A larger area is an indication for a stronger change in structure. The structural strength can decrease or increase.

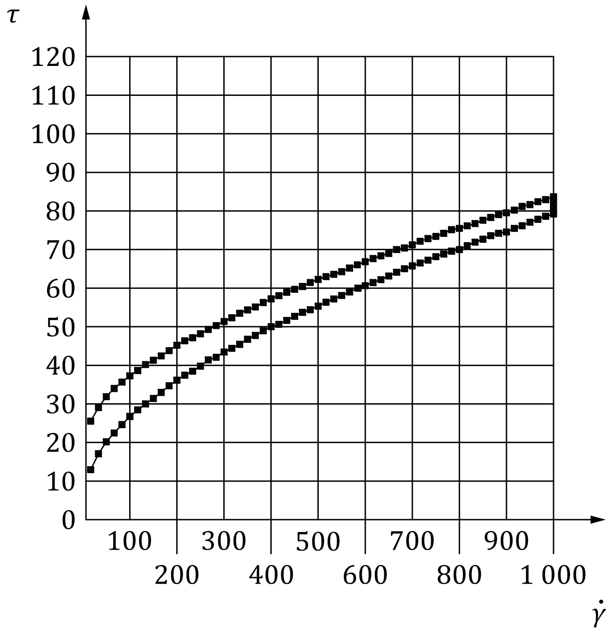
The duration of the upward ramp and downward ramp depends on the material. If it is too long, the superstructure of the measuring sample is reduced too much already during the upward ramp. As a result, the hysteresis area can become too small for a meaningful evaluation.

This evaluation is performed by calculating the hysteresis area in $Pa \cdot s^{-1}$.

Figure 5 and Figure 6 show typical measuring results for a waterborne coating material obtained with the two measuring methods, A and B.

With a linear ramp, the shear load is higher overall across the entire shear rate range compared to the logarithmic ramp. This results in a smaller calculated hysteresis area. The advantage of Method B is that more measuring points are recorded in the lower shear rate range.

This measuring method provides information about the behaviour of the measuring sample in a continuous shear process, but not about what happens when the shear load occurs at rest, for example whether and to what extent recovery of the structure takes place. The method yields a first overview of the behaviour of the investigated material.



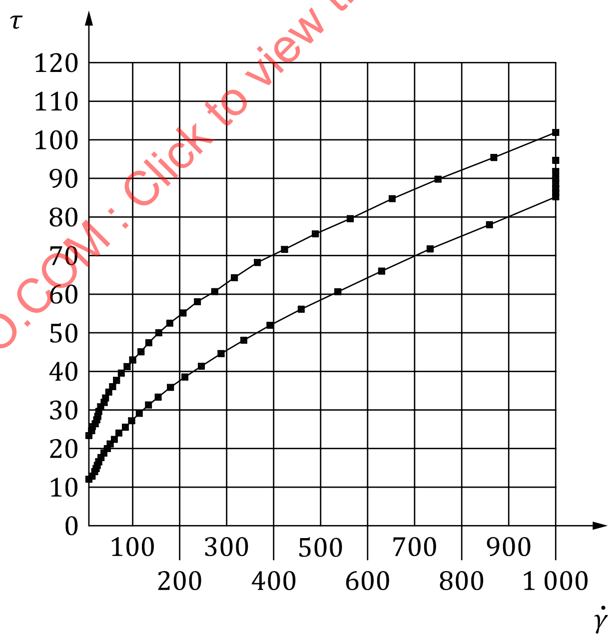
Key

τ shear stress

γ̇ shear rate

NOTE The calculated hysteresis area for this method is 7 167 Pa·s^{-1}.

Figure 5 — Flow curves measured using a linear ramp, with evaluation according to Method A



Key

τ shear stress

γ̇ shear rate

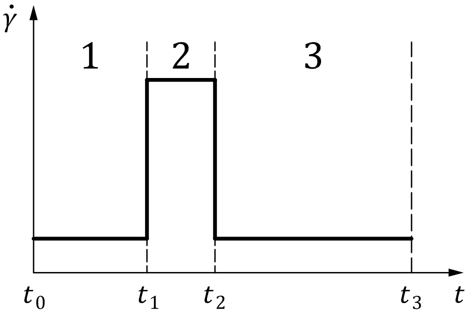
NOTE The calculated hysteresis area for this method is 16 810 Pa·s^{-1}.

Figure 6 — Flow curves measured using a logarithmic ramp, with evaluation according to Method B

4.3 Step test with recovery, as a rotational test with controlled shear rate

4.3.1 Specification of the measuring programme

The shear load is specified in the form of three measuring segments, first with a constant low shear rate, then with a constant high shear rate, and finally again with a constant low shear rate $\dot{\gamma}$ (see Figure 7). At the beginning, this can also be preceded by a segment with defined pre-shear and/or a waiting time without shear (e.g. 5 min).



Key

$\dot{\gamma}$ shear rate

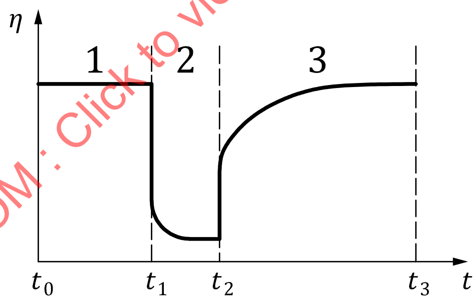
t time

1 low shear rate

2 high shear rate

3 low shear rate

Figure 7 — Specified profile: three measuring segments with a low shear rate, high shear rate and then low shear rate again



Key

η shear viscosity

t time

1 low shear load

2 high shear load with reduction of structural strength

3 low shear load with structural recovery

Figure 8 — Measuring result of time-dependent viscosity function of a thixotropic material

Proposals for a typical measuring programme are as follows:

1) low shear rate with $\dot{\gamma}$ = 0,1 s^{-1} = constant, duration 2 min, with 30 measuring points. If a viscometer with a mechanical bearing is used, then 10 s^{-1} can be used as the minimum shear rate;

2) high shear rate with $\dot{\gamma}$ = 1 000 s^{-1} = constant, duration 2 min, with 30 measuring points;

3) low shear rate with $\dot{\gamma}$ = 0,1 s^{-1} = constant, duration 5 min, with 100 measuring points.

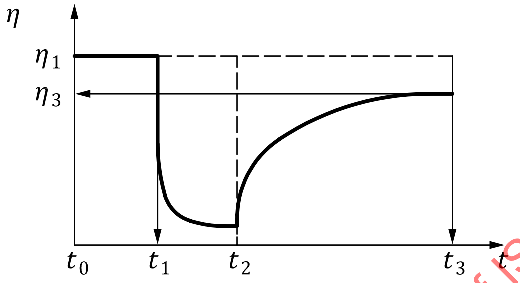
The shear rate for the measuring segments 1 and 3 is the same.

4.3.2 Evaluation

As a preparatory step, the average of the last 5 measuring points is formed for each of the three measuring segments. Proposals for evaluation programmes are as follows (see also Figure 8):

1) Percentage structural recovery, expressed as a viscosity value at the end of measuring segment 3 in comparison to the reference value of the end of measuring segment 1, with the result stated in per cent;

EXAMPLE 1 Reference value η_1 = 10 Pa·s; and at the end of measuring segment 3 η_3 = 8 Pa·s. Calculation: (8 Pa·s/10 Pa·s) × 100 % = 80 %. See Figure 9.



Key

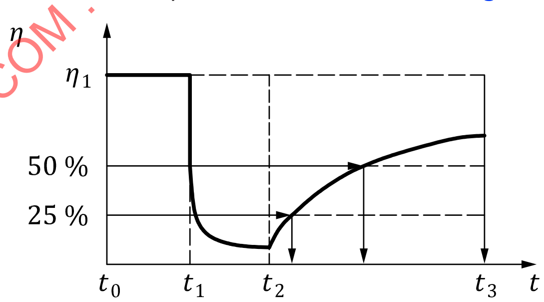
η shear viscosity

t time

Figure 9 — Evaluation of the percentage structural recovery

2) Time points for 25 % and 50 % structural recovery in measuring segment 3 in comparison with the reference value from the end of measuring segment 1, data in s;

EXAMPLE 2 Reference value η_1 = 10 Pa·s; from the diagram or from the table of measuring data, the two time points are determined at 25 % of the reference value on the one hand, therefore η = 2,5 Pa·s, and at 50 % of the reference value on the other hand, therefore η = 5 Pa·s, is reached. See Figure 10.



Key

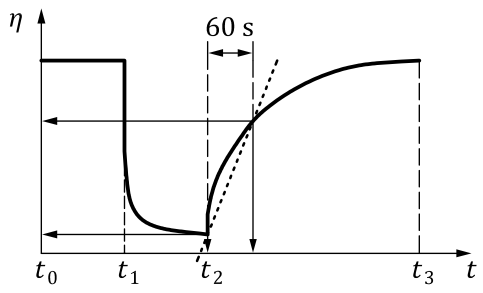
η shear viscosity

t time

Figure 10 — Time points for 25 % and 50 % structural recovery

3) Slope of the curve during structural recovery in the first 60 s of measuring segment 3, data in Pa·s/s;

EXAMPLE 3 Between the two viscosity values at the end of measuring segment 2 and after 60 s in measuring segment 3, the slope of the connecting line is determined; this can be done by means of the diagram or with the table of measuring data (see Figure 11).



Key

η shear viscosity

t time

Figure 11 — Slope of the curve during structural recovery

4) Structure-recovery index (SRI) calculated as logarithm of the viscosity value after the beginning of measuring segment 3 (e.g. after 30 s), minus the logarithm of the viscosity value at the end of measuring segment 2;

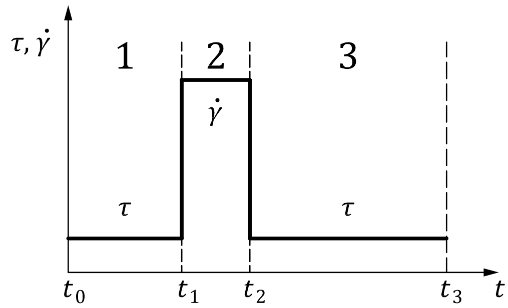
5) Thixotropy index (TI) calculated as logarithm of the viscosity value at the end of measuring segment 3 (e.g. after 300 s) minus the logarithm of the viscosity value at the end of measuring segment 2.

4.4 Step test with recovery, as a rotational test with alternating controlled shear stress and shear rate

4.4.1 Specification of the measuring programme

The shear load is specified in the form of three measuring segments, first with a constant low shear stress τ, then with a constant high shear rate, and finally again with a constant low shear stress τ (see Figure 12). At the beginning, this can also be preceded by a segment with defined pre-shear and/or a waiting time without shear (e.g. 5 min).

In order to determine a meaningful specification value for the shear stress in measuring segments 1 and 3, preliminary tests for determination of the yield point are performed (see ISO/TR 20659-1). The specified value lies above the yield point value.



Key

τ shear stress

$\dot{\gamma}$ shear rate

t time

1 low shear stress

2 high shear rate

3 low shear stress

Figure 12 — Specified profile: three measuring segments with low shear stress, high shear rate, and again with low shear stress

Proposals for a typical measuring programme are as follows:

1) low shear stress with τ = constant (the specified value for τ is dependent upon the preliminary test), duration 2 min, with 30 measuring points;

2) high shear rate with $\dot{\gamma}$ = 1 000 s^{-1} = constant, duration 2 min, with 30 measuring points;

3) low shear stress with τ = constant, duration 5 min, with 100 measuring points.

The shear stress for the measuring segments 1 and 3 is the same.

4.4.2 Evaluation

With this measuring method, the evaluation is performed in the same way as described in 4.3 and shown in Figure 8 to Figure 11.

NOTE A disadvantage of this method is that preliminary tests are crucial in order to find meaningful specification values for the shear stress in measuring segments 1 and 3.

4.5 Step test with recovery, as a combined oscillatory and rotational test with controlled shear strain and shear rate, respectively

4.5.1 Specification of the measuring programme

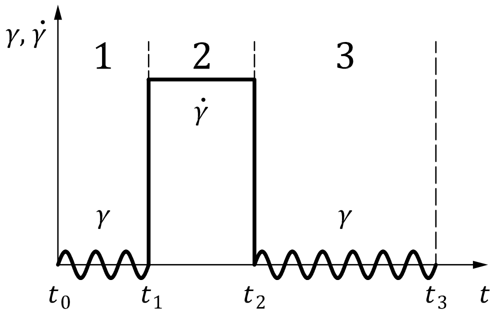
For carrying out the step tests, a rheometer with air bearing can be used.

The shear load is specified in the form of three measuring segments, the first with a constant low shear strain γ and constant frequency in the form of an oscillatory test, then with a constant high shear rate $\dot{\gamma}$ as a rotational test, and finally again with a constant low shear strain γ and constant frequency as an oscillatory test (see Figure 13).

The speed of oscillation can be stated both as a frequency f (in Hz) and as an angular frequency ω (in s^{-1}) (the following applies: $\omega = 2\,\pi \cdot f$).

A shear strain value is deemed to be low enough, and therefore suitable, if it lies in the linear viscoelastic region. This specification is examined in advance with an amplitude sweep.

At the beginning, this can also be preceded by a segment with defined pre-shear and/or a waiting time without shear (e.g. 5 min).



Key

γ shear strain
$\dot{\gamma}$ shear rate
t time
1 low shear strain (as an oscillation)
2 high shear rate (as a rotation)
3 low shear stress (as an oscillation)

Figure 13 — Specified profile: step function with the three measuring segments

Proposals for a typical measuring programme are as follows:

1) low shear strain as an oscillation with f = 1 Hz and γ = constant (the specified value for γ is dependent upon the preliminary test, e.g. γ = 1 %), duration 2 min, with 30 measuring points;

2) high shear rate with $\dot{\gamma}$ = 1 000 s^{-1} = constant, duration 2 min, with 30 measuring points;

3) low shear strain as an oscillation with f = 1 Hz and γ = constant [as in 1) above, the specified value for γ is dependent upon the preliminary test], duration 5 min, with 100 measuring points. The frequency and the shear strain for the measuring segments 1 and 3 are the same.

4.5.2 Evaluation

When using oscillatory tests, the following measured parameters can be evaluated:

— the shear storage modulus G' (in Pa) describes the elastic part of the viscoelastic behaviour of the measuring sample;

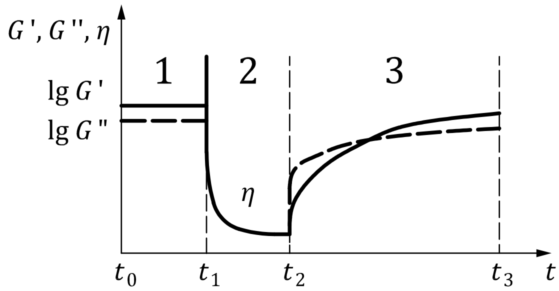
— the shear loss modulus G'' (in Pa) describes the viscous part;

— the absolute value of the complex shear viscosity $|\eta^*|$ (in Pa·s);

— the loss angle δ (in °, i.e. degrees) represents the time delay (phase shift) between the specified measured value and the resulting measured value;

— the loss factor $\tan\delta = G''/G'$ is the ratio of G'' to G'.

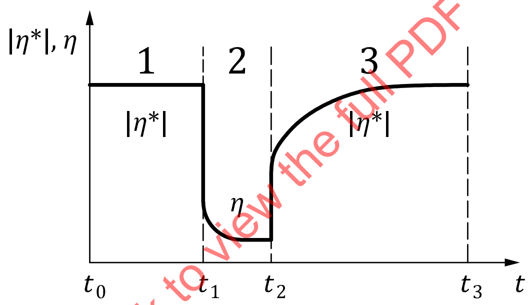
In the following, proposals for evaluation programmes are shown (see also Figure 14). Instead of the G' values, the values for the absolute value of the complex shear viscosity $|\eta^*|$ can be chosen as an alternative (see Figure 15).



Key

G' shear storage modulus
G'' shear loss modulus
η shear viscosity
t time
1 low shear load
2 high shear load with reduction of structural strength
3 low shear load with structural recovery

Figure 14 — Measuring result: time-dependent functions of a thixotropic material as shear storage modulus G' and shear loss modulus G''



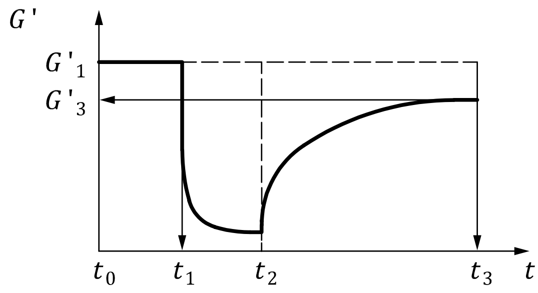
Key

$|\eta^*|$ complex shear viscosity
η shear viscosity
t time
1 low shear load
2 high shear load with reduction of structural strength
3 low shear load with structural recovery

Figure 15 — Measuring result: time-dependent functions of a thixotropic material as the absolute value of complex shear viscosity $|\eta^*|$

1) Percentage structural recovery expressed as the value of the shear storage modulus G' at the end of measuring segment 3 in comparison with the reference value from the end of measuring segment 1, data in %;

EXAMPLE 1 Reference value G'_1 = 20 Pa, and at the end of measuring segment 3 G'_3 = 16 Pa. Calculation: (16 Pa/20 Pa) · 100 % = 80 %. See Figure 16.



Key

G' shear storage modulus

t time

Figure 16 — Evaluation of the percentage structural recovery

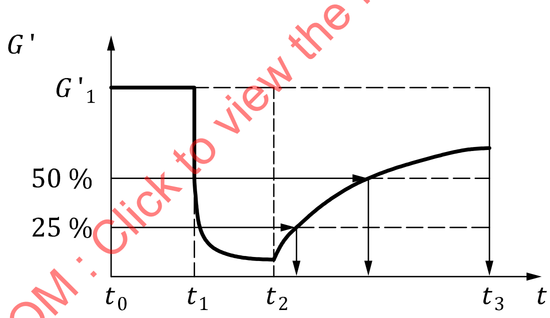
2) Time points for 25 % and 50 % structural recovery in measuring segment 3 in comparison with the reference value from the end of measuring segment 1, data in s;

EXAMPLE 2 Reference value G'_1 = 20 Pa. From the diagram or from the table of measuring data, the two time points are determined at which:

a) on the one hand 25 % of the reference value, here therefore G' = 5 Pa is reached;

b) on the other hand 50 % of the reference value, here therefore G' = 10 Pa, is reached.

See Figure 17.



Key

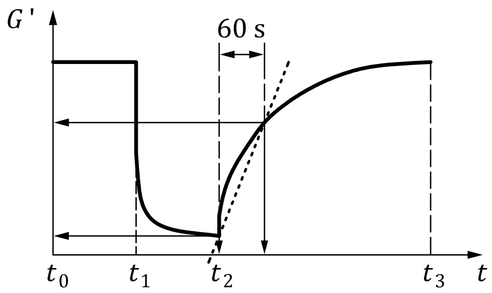
G' shear storage modulus

t time

Figure 17 — Time points for 25 % and 50 % structural recovery

3) Slope of the curve during structural recovery in the first 60 s of measuring segment 3, data in Pa·s^{-1};

EXAMPLE 3 The slope of the connecting line between the two shear storage modulus values at the end of measuring segment 2 and after 60 s in measuring segment 3 is determined; this can be done with the aid of the diagram or the table of measuring data. See Figure 18.



Key

G' shear storage modulus

t time

Figure 18 — Slope of the curve during structural recovery

4) Time point of the sol/gel transition in measuring segment 3 (when $\delta = 45°$ or $\tan\delta = G''/G' = 1$ is attained), data in s.

EXAMPLE 4 The point of intersection of the curves of *G*' and *G*" is determined; this can be done by means of the diagram or with the table of measuring data. See Figure 14.

5 Comparative testing programme

5.1 Aim of the comparative testing programme

Two comparative testing programmes were carried out in the laboratories of the working group members. The first comparative testing programme was carried out to prove the fundamental suitability of the four methods for determination of the thixotropic properties of coating materials. Moreover, it has been investigated which preconditions concerning the measuring run and the measuring procedure are made to guarantee an acceptable reproducibility of the results. In the second comparative testing programme, special emphasis was given to the determination of precision data (repeatability, reproducibility).

Some background information on the original interlaboratory test is given in Annex B.

5.2 Performance of the tests

5.2.1 Preliminary test

In first comparative testing programmes, a Newtonian reference sample of the National Metrology Institute of Germany (PTB) was measured together with five samples (three waterborne basecoats, a pasty sealing compound and a dispersion). The samples were provided by members of the working group. Eight laboratories contributed to the comparative testing programme. First, the measuring instruments used were checked by measuring a flow curve of the Newtonian reference sample. Afterwards, each sample was measured following the four methods described in 4.2 to 4.5. The respective measuring parameters (shear time and shear stress, shear rate and amplitude, respectively) were given by the sample supplier and were forwarded with the samples. Due to the fact that the measuring parameters of a method varied with the samples, a broad spectrum of measuring procedures resulted.

From the results, the following conclusions can be drawn:

— the measured values in measuring segment 1 of the three step methods (4.3 to 4.5) varied significantly. For this reason, standardized pre-treatment of the samples (pre-shear and waiting time) can therefore be used;

— the viscosity of some samples in the recovery phase clearly exceeded the viscosity in measuring segment 1. This is an indication that, after application of a shear rate of 1 000 s^{-1}, the structure does not recover into the same original form that was present at the start of the measurement. In this case, the viscosity of measuring segment 1 cannot be included in the evaluation. In the same way, the evaluation of a hysteresis area for these samples is questionable;

— in order to minimize the evaporation of solvents, particularly when performing a measurement with a cone-plate or plate-plate measuring geometry, the sample area is covered, as otherwise the viscosity can change;

— the evaluation of the flow curves (viscosity at a defined shear rate) is usually made by a linear interpolation procedure incorporated in the software. A large distance between measuring points, between which the interpolation is carried out, distorts the result. For this reason, during the measurement of flow curves, not only the number of measuring points but also their distribution is defined;

— the optimum shear stress during the performance of the shear stress-controlled step test is above the yield point but, by contrast, during oscillatory recovery it is below the yield point, i.e. in the linear viscoelastic region;

— the measurements were performed by all participants within a narrow time frame to rule out any influence of the sample age.

5.2.2 Comparative testing programme

In order to check the rheometers, the flow curve of a certified Newtonian reference sample from PTB (EF 166) was measured. The measurements were recorded three times.

Afterwards, a waterborne basecoat (WBC) and a conventional clear coat were measured following all four methods described in Clause 4. The measurements were recorded three times.

The measurements of the flow curves were performed exclusively in accordance with 4.2, Method B, with a logarithmic ramp.

The optimum shear stress for performance of the step test with specification of the shear stress in the recovery phase as well as the optimum shear strain during the step test with recovery as an oscillatory test were determined beforehand in test measurements. In a preliminary test with specification of the shear stress below the yield point, severely varying measured values were obtained. As an outcome, the shear stress in the first case is selected as a value above the yield point. By contrast, in the second case the shear strain is expected to be within the linear viscoelastic region.

Based on the experiences of the first comparative testing programme, the following agreements were reached:

— the measurements can be carried out by all participants within a defined week;

— the choice of the measuring geometry (cone-plate and/or coaxial cylinder) was left to the participants, but was required to be noted in the table of results;

— in measurements with a cone-plate geometry, the use of a cover was mandatory in order to restrict evaporation of solvents. No solvents were filled into the sample area coverage;

— defined sampling and filling the measuring geometry;

— after filling the measuring geometry, a shear rate was initially applied to the samples for 1 min at 100 s^{-1}, then tempered for 5 min without shearing at 23 °C;

— the number of measuring points was defined for all tests.

5.3 Evaluation

The measuring results were evaluated following the methods described in Clause 4. Moreover, further evaluations were carried out to get as complete a picture as possible for repeatability and reproducibility. The following evaluations were carried out:

Flow curve:

— shear viscosity during the upward ramp for the shear rates 1 s^{-1}, 10 s^{-1} and 100 s^{-1} obtained by linear interpolation;

— shear viscosity at the shear rate of 1 000 s^{-1} (last data point of the corresponding measuring segment);

— shear viscosity during the downward ramp for the shear rates 1 s^{-1}, 10 s^{-1} and 100 s^{-1} obtained by linear interpolation;

— hysteresis area between the shear rates 1 s^{-1} and 1 000 s^{-1}.

Step test with controlled shear rate in the recovery phase/step test with controlled shear stress in the recovery phase:

— shear viscosity at the end of measuring segments 1 and 2;

— shear viscosity in measuring segment 3 after 30 s, 60 s and at the end;

— time needed for structural recovery of 50 %. The reference value for 100 % recovery is calculated from the difference between the viscosities at the end of measuring segment 3 and at the end of measuring segment 2;

— slope of the viscosity curve during the first 60 s of measuring segment 3 according to

$\Delta\eta/\Delta t = [\eta \text{ (at 1 s}^{-1}\text{ after 60 s)} - \eta \text{ (at 1 000 s}^{-1})]/60 \text{ s}$;

— SRI, calculated as

$\lg \eta$ (at 30 s, measuring segment 3) − $\lg \eta$ (at 1 000 s^{-1}, at the end of measuring segment 2);

— TI, calculated as

$\lg \eta$ (at 300 s, measuring segment 3) − $\lg \eta$ (at 1 000 s^{-1}, at the end of measuring segment 2);

— percentage recovery at the end of measuring segment 3 in relation to the viscosity at the end of measuring segment 1 (= 100 %).

Step test with recovery, as an oscillatory test:

— absolute value of the complex shear viscosity at the end of measuring segment 1;

— absolute value of the complex shear viscosity in measuring segment 3 after 30 s, 60 s and at the end;

— percentage recovery at the end of measuring segment 3 in relation to the absolute value of the complex shear viscosity at the end of measuring segment 1 (= 100 %).

Repeatability and reproducibility were calculated according to ISO 5725-2.

The results are included in Annex A.

6 Result

6.1 General

In some cases, different measured values were observed in measurements with a cone-plate measuring geometry and with a coaxial cylinder measuring geometry.

6.2 Measurement of the Newtonian reference sample

The measured values for the coaxial cylinder measuring geometry from one laboratory deviated by more than 5 % from the specified standard value. For this reason, the remaining results of the laboratory obtained with this measuring geometry were not included in the evaluation.

Due to the Newtonian properties, the evaluation of the hysteresis area were not carried out.

The result was a repeatability standard deviation of 0,7 %, and a reproducibility standard deviation of 3,1 %. This was independent of the shear rate.

6.2.1 Flow curve

NOTE This test was performed according to 4.2.

— The repeatability standard deviation s_r for the shear viscosity is between 1 % and 3 % for all shear rates and both coatings. The exceptions are the WBC and the clear coat at 1 s^{-1} with the upward ramp. A distinct variation within the laboratories was observed, which is probably caused by transient effects. The results show that it is not preferable to perform the evaluation with the first measuring point of the ramp. If necessary, the ramp can be started with a lower shear rate.

— The reproducibility standard deviation s_R is significantly higher and in the same order of magnitude for both the WBC and the clear coat. The higher the shear rate, the smaller the reproducibility standard deviation.

— The evaluation of the hysteresis area shows a significantly higher repeatability standard deviation and reproducibility standard deviation as the evaluation started from 1 s^{-1}. Values with good reproducibility are obtained with an evaluation starting from 10 s^{-1}.

6.3 Step test with specification of the shear rate in measuring segments 1 and 3

NOTE This test was performed according to 4.3.

— In measuring segment 1 at 1 s^{-1}, s_r and s_R are better than for the flow curve (upward ramp) as only the first measuring point was evaluated for the flow curve. In the step test with controlled shear rate however, the shear rate was already specified across the entire measuring segment 1 before the measured value was recorded at the end of the measuring segment 1.

— The SRI and TI display very good values concerning repeatability and reproducibility. This is also valid for the percentage recovery at the end of measuring segment 3.

— The following applies to the absolute values during structural recovery and to the slope within the first 60 s: good repeatability but moderate reproducibility.

A disadvantage of this test is that some samples pass through a maximum in measuring segment 3 which makes the evaluation difficult.

6.4 Step test with controlled shear stress in measuring segments 1 and 3

NOTE 1 This test was performed according to 4.4.

— Here, a clear influence of the measuring geometry used (coaxial cylinder or cone-plate) on the characteristics of the structural recovery of the WBC was observed. Based on this, no precision data are provided for these values.

— During measurement of the clear coat both the reproducibility standard deviation and the repeatability standard deviation are approximately two to three times higher than the corresponding values of the step test with controlled shear rate in measuring segments 1 and 3.

An advantage of this test is that there was no formation of maxima in measuring segment 3 (see 4.4).

NOTE 2 The suitable shear stress is evaluated in preliminary tests at first (above the yield point).

6.5 Step test as oscillatory test in measuring segments 1 and 3

NOTE 1 This test was performed according to 4.5.

— Repeatability and reproducibility were comparable in all measuring segments with the other step tests.

NOTE 2 The suitable oscillation amplitudes is determined in preliminary tests (within the linear viscoelastic region).

7 Analysis

The results of the preliminary tests and of the comparative testing programme show that the method for the determination of thixotropy via the quantitative calculation of the hysteresis area based on flow curves is only partly suitable. This method often does not allow clear findings to structural recovery. However, the method can be used to get a first overview about the flow behaviour of a material.

It is important that the parameters for the measuring procedure are defined exactly. For example, it is important that the time to reach the maximum shear rate (ramp times), holding times and the number of measuring points is fixed. In addition, exact temperature control of the sample and, if necessary, a time at rest or pre-shear before performing the actual measurement are always significant for every measuring procedure.

Methods combining various loads (low, high shear rate, oscillation, etc.) in different time segments allow better findings concerning the thixotropy. These methods are usually separated into three measuring segments. In measuring segment 1, the sample is first subjected to a low shear rate, shear stress or shear strain in the form of rotation or oscillation. In measuring segment 2, a high load is applied under rotation with a high shear rate, followed by the structure-recovery phase with a low load under the same parameters as in measuring segment 1.

A detailed analysis of the tests carried out for this document yielded the following key findings:

— in the step test with recovery as a rotational test with specification of the shear rate, the SRI and TI in particular display good values for repeatability and reproducibility;

— in the step test with recovery as a rotational test with alternating specification of the shear stress and shear rate: the observed structural recovery depends significantly on the measuring geometry used (coaxial cylinder or cone-plate). It is important that the suitable shear stresses are determined in preliminary tests at first, before starting the actual measurement (consider the yield point);

— in the step test with recovery as a combined oscillatory and rotational test with controlled shear strain and shear rate, respectively: the suitable oscillation amplitudes for the investigations are first determined in preliminary tests (consider the linear viscoelastic region);

— the comparison of the measuring results involves adherence to previously exactly specified measuring conditions.

In the tests carried out, the step test with controlled shear rate proved to be the simplest to implement in practice. The step test as a combined oscillatory and rotational test with controlled shear strain and shear rate, respectively, is more complex to implement but this test provides additional information about the viscoelastic behaviour of the sample.

Annex A
(informative)

Details of the comparative testing programme

A.1 General

Up to nine laboratories took part in the comparative testing programme. Each measurement was recorded three times. The measured data was checked for outliers according to Grubbs and Cochran. Conspicuous data was eliminated from the comparative testing programme. Repeatability and reproducibility were calculated in accordance with ISO 5725-2. In the evaluation, no distinction was made between cone-plate and coaxial cylinder measurement geometries. Of the nine participants of the comparative testing programme, five carried out the measurements with the cone-plate geometry and four carried them out with the cylinder geometry.

A.2 Measurement of the Newtonian reference sample

The measurement data are shown in Table A.1.

Table A.1 — Measurement of the Newtonian reference sample

Number of participating laboratories (*P*)		9
Number of participating laboratories after outlier test (*p*)		8
Number of results in all laboratories (*n*)		18
Total average value	mPa·s	52,5
Repeatability standard deviation (s_r)	%	0,7
Repeatability limit (*r*)	%	2,0
Reproducibility standard deviation (s_R)	%	3,1
Reproducibility limit (*R*)	%	8,6

A.3 Flow curve

A.3.1 Waterborne basecoat

Measurement data of the waterborne basecoat are shown in Table A.2.

Table A.2 — Measurement of the waterborne basecoat

		Shear viscosity at specified shear rate $\dot{\gamma}$ and ramp							Hysteresis area
		$\dot{\gamma}$ = 1 s^{-1} upward ramp	$\dot{\gamma}$ = 10 s^{-1} upward ramp	$\dot{\gamma}$ = 100 s^{-1} upward ramp	$\dot{\gamma}$ = 1 000 s^{-1}	$\dot{\gamma}$ = 100 s^{-1} down-ward ramp	$\dot{\gamma}$ = 10 s^{-1} downward ramp	$\dot{\gamma}$ = 1 s^{-1} downward ramp	
Number of participating laboratories (P)		9	9	9	9	9	9	9	9
Number of participating laboratories after outlier test (p)		8	8	8	7	7	7	7	7
Number of results in all laboratories (n)		24	24	24	21	21	21	21	21
Total average value		5 983 mPa·s	828 mPa·s	211 mPa·s	78 mPa·s	185 mPa·s	747 mPa·s	4 856 mPa·s	2 966 Pa·s^{-1}
Repeatability standard deviation (s_r)	%	5,7	1,7	1,2	0,8	1,5	1,6	1,8	6,4
Repeatability limit (r)	%	15,8	4,8	3,5	2,2	4,1	4,5	5,1	17,8
Reproducibility standard deviation (s_R)	%	22,0	10,6	5,8	4,8	6,9	10,9	11,1	11,5
Reproducibility limit (R)	%	61,5	29,6	16,3	13,5	19,3	30,6	31,1	32,3

A.3.2 Clear coat

Measurement data of the clear coat are shown in Table A.3.

Table A.3 — Measurement of the clear coat

		Shear viscosity at specified shear rate $\dot{\gamma}$ and ramp							Hysteresis area
		$\dot{\gamma}$ = 1 s^{-1} upward ramp	$\dot{\gamma}$ = 10 s^{-1} upward ramp	$\dot{\gamma}$ = 100 s^{-1} upward ramp	$\dot{\gamma}$ = 1 000 s^{-1}	$\dot{\gamma}$ = 100 s^{-1} downward ramp	$\dot{\gamma}$ = 10 s^{-1} downward ramp	$\dot{\gamma}$ = 1 s^{-1} downward ramp	
Number of participating laboratories (P)		9	9	9	9	9	9	9	8
Number of participating laboratories after outlier test (p)		9	6	8	7	7	7	6	6
Number of results in all laboratories (n)		27	18	24	21	21	21	18	18
Total average value		472 mPa·s	283 mPa·s	146 mPa·s	111 mPa·s	133 mPa·s	239 mPa·s	971 mPa·s	2 323 Pa·s^{-1}
Repeatability standard deviation (s_r)	%	6,0	1,8	1,1	1,2	1,3	2,0	3,4	2,9
Repeatability limit (r)	%	16,7	4,9	3,0	3,3	3,6	5,5	9,5	8,0
Reproducibility standard deviation (s_R)	%	8,0	3,5	4,6	7,0	7,1	5,4	15,7	36,6
Reproducibility limit (R)	%	22,3	9,9	12,9	19,6	20,0	15,1	43,9	102,6

A.4 Step test with specification of the shear rate in measuring segments 1 and 3

A.4.1 Waterborne basecoat

The measurement data of the waterborne basecoat are shown in Table A.4.

Table A.4 — Measurement of the waterborne basecoat

		Shear viscosity for the corresponding measuring segment					Seg. 3 50 % time	Seg. 3 slope 60 s $\Delta\eta/\Delta t$	Structural recovery from 3rd to 1st seg.	SRI	TI
		End of seg. 1	End of seg. 2	Seg. 3 after 30 s	Seg. 3 after 60 s	Seg. 3 after 300 s					
Number of participating laboratories (P)		9	9	9	9	9	8	9	9	9	9
Number of participating laboratories after outlier test (p)		8	7	7	8	8	7	8	7	8	8
Number of results in all laboratories (n)		24	21	21	24	24	21	24	21	24	24
Total average value		4 622 mPa·s	76 mPa·s	3 446 mPa·s	4 296 mPa·s	5 690 mPa·s	16 s	70,3 mPa	123,2 %	1,66	1,86
Repeatability standard deviation (s_r)	%	1,5	0,8	2,0	2,7	1,9	3,5	2,8	0,8	0,6	0,4
Repeatability limit (r)	%	4,3	2,3	5,6	7,6	5,2	9,8	7,7	2,2	1,7	1,0
Reproducibility standard deviation (s_R)	%	5,9	2,4	12,2	12,2	10,8	19,1	12,4	4,6	3,0	2,1
Reproducibility limit (R)	%	16,4	6,7	34,0	34,2	30,2	53,6	34,7	12,9	8,5	5,8

Key

SRI structure-recovery index

TI thixotropy index

seg. segment

A.4.2 Clear coat

The measurement data of the clear coat are shown in Table A.5.

Table A.5 — Measurement of the clear coat

		Shear viscosity for the corresponding measuring segment					Seg. 350 % time	Seg. 3 slope 60 s $\Delta\eta/\Delta t$	Structural recovery from 3rd to 1st seg.	SRI	TI
		End of seg. 1	End of seg. 2	Seg. 3 after 30 s	Seg. 3 after 60 s	Seg. 3 after 300 s					
Number of participating laboratories (P)		9	9	9	9	9	8	9	9	9	9
Number of participating laboratories after outlier test (p)		8	8	8	8	8	8	8	8	8	8
Number of results in all laboratories (n)		24	24	24	24	24	24	24	24	24	24
Total average value		1 101 mPa·s	112 mPa·s	485 mPa·s	671 mPa·s	962 mPa·s	32 s	9,3 mPa	87 %	0,63	0,93
Repeatability standard deviation (s_r)	%	2,1	1,6	2,7	2,2	2,2	1,8	2,3	0,7	0,7	0,3
Repeatability limit (r)	%	5,8	4,4	7,5	6,2	6,2	5,1	6,3	1,9	1,9	0,9
Reproducibility standard deviation (s_R)	%	9,0	8,4	12,8	10,1	9,8	14,5	10,7	4,2	4,6	3,8
Reproducibility limit (R)	%	25,2	23,5	36,0	28,2	27,5	40,7	29,9	11,8	12,9	10,6

Key

SRI structure-recovery index

TI thixotropy index

seg. segment

A.5 Step test with controlled stress in measuring segments 1 and 3

A.5.1 Waterborne basecoat

The measuring geometry used (coaxial cylinder or cone-plate) had a clear influence on the characteristics of the structural recovery of the waterborne basecoat. For a separate statistical evaluation, the amount of data is too low. Based on this, no precision data are provided for these values.

A.5.2 Clear coat

The measurement data of clear coat are shown in Table A.6.

Table A.6 — Measurement of the clear coat

		Shear viscosity for the corresponding measuring segment					Seg. 3 50 % time	Seg. 3 slope 60 s $\Delta\eta/\Delta t$	Structural recovery from 3rd to 1st seg.	SRI	TI
		End of seg. 1	End of seg. 2	Seg. 3 after 30 s	Seg. 3 after 60 s	Seg. 3 after 300 s					
Number of participating laboratories (P)		9	9	9	9	9	8	9	9	9	9
Number of participating laboratories after outlier test (p)		8	8	8	8	8	7	8	8	8	8
Number of results in all laboratories (n)		24	24	24	24	24	21	24	24	24	24
Total average value		1 365 mPa·s	110 mPa·s	423 mPa·s	588 mPa·s	982 mPa·s	37 s	8,0 mPa	73 %	0,58	0,94
Repeatability standard deviation (s_r)	%	5,2	1,4	3,3	3,7	4,5	3,8	4,3	1,7	1,9	1,6
Repeatability limit (r)	%	14,5	3,8	9,3	10,3	12,5	10,6	12,1	4,8	5,2	4,5
Reproducibility standard deviation (s_R)	%	22,0	7,3	15,4	17,4	19,9	10,3	20,5	12,0	8,1	7,4
Reproducibility limit (R)	%	61,5	20,6	43,1	48,8	55,7	28,8	57,3	33,5	22,6	20,8

Key

SRI structure-recovery index

TI thixotropy index

seg. segment