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# Rheological test methods — Fundamentals and interlaboratory comparisons —

## Part 1:
## Determination of the yield point

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

*Partie 1: Détermination du seuil d'écoulement*



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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 1:
## Determination of the yield point



## 1 Scope

This document gives information on an interlaboratory comparison for the determination of the yield point, using rheological test methods. The yield point is the shear stress $\tau$ below which a material does not flow.

This document provides examples of fields of applications, in which important material properties are characterized with the aid of the yield point. These fields of application include:

— effectiveness of rheological additives;

— shelf life (e.g. with regard to sedimentation, separation and flocculation);

— stability of the structure at rest;

— behaviour when starting to pump;

— use in scraper systems;

— wet-film thickness;

— 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.

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 Goal of the interlaboratory test

In the interlaboratory test, different possibilities for determining the yield point using the preferred methods were considered.

The samples used in the comparative testing programme consisted of different waterborne basecoats with lower yield points and dispersions with distinctly higher yield points. The samples also included the following limited cases:

— very low yield points (<1 Pa), at which the range of elastic deformation is so low that the material can also be approximately considered as a liquid at the state of rest;

— materials of which the internal structure is disintegrated only stepwise so that a transition range is occurring and a yield zone rather than a punctual yield point is determined.

Furthermore, a non-Newtonian reference sample from the the National Metrology Institute of Germany (PTB) was also included in the comparative testing programme.

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

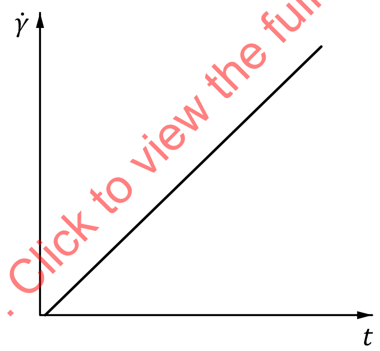
## 5 Metrological determination of the yield point

### 5.1 General

Clause 5 briefly describes all the methods in use at the time of publication. In principle, the yield point 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.

### 5.2 Shear rate-controlled rotational test

The shear rate $\dot{\gamma}$ is specified in the form of a ramp, as shown in Figure 1.




**Key**

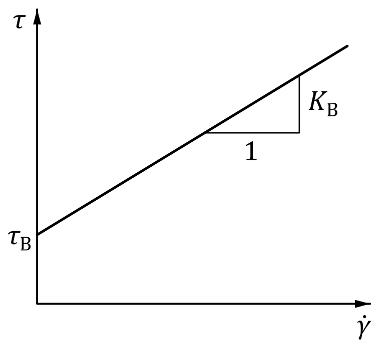
$\dot{\gamma}$ shear rate

$t$ time

**Figure 1 — Shear rate/time function as a ramp**

### 5.3 Yield point evaluation using flow curve regression models

With a linear representation of the flow curve (usually the shear stress $\tau$ as a function of the shear rate $\dot{\gamma}$), the yield point is determined as the axis intercept on the $\tau$ axis (Figure 2).




**Key**

$\tau$ shear stress

$\tau_B$ Bingham yield point

$K_B$ consistency index according to Bingham

$\dot{\gamma}$ shear rate

1 chosen shear rate range

**Figure 2 — Flow curve regression according to Bingham**

This yield point value depends not only on the specified ramp period, but also on the chosen shear rate range and the chosen regression model. In industrial laboratories, the models according to Bingham, Casson or Herschel/Bulkley are widely used.

The model function according to Bingham is given in Formula (1):

$$\tau = \tau_B + K_B \cdot \dot{\gamma} \quad (1)$$

where

$\tau$ is the shear stress;

$\tau_B$ is the calculated Bingham yield point;

$K_B$ is the consistency index according to Bingham;

$\dot{\gamma}$ is the shear rate.

The model function according to Casson is given in Formula (2):

$$\sqrt{\tau} = \sqrt{\tau_C} + \sqrt{(K_C \cdot \dot{\gamma})} \quad (2)$$

where

$\tau$ is the shear stress;

$\tau_C$ is the calculated Casson yield point;

$K_C$ is the consistency index according to Casson;

$\dot{\gamma}$ is the shear rate.

The model function according to Herschel/Bulkley is given in Formula (3):

$$\tau = \tau_{HB} + K_{HB} \cdot \dot{\gamma}^p \quad (3)$$

where

$\tau$ is the shear stress;

$\tau_{HB}$ is the calculated yield point according to Herschel/Bulkley;

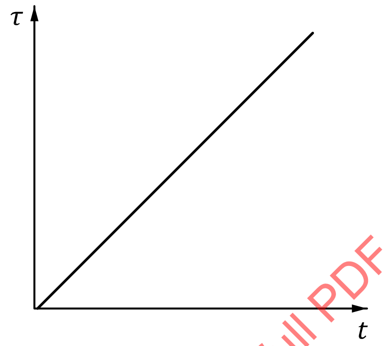
$K_{HB}$ is the consistency index according to Herschel/Bulkley;

$\dot{\gamma}$ is the shear rate;

$p$ is an exponent; if $p < 1$, the flow behaviour is shear thinning (structural viscosity, pseudoplastic), and if $p > 1$, the flow behaviour is shear thickening (dilatant).

## 5.4 Shear stress-controlled rotational test

The shear stress, $\tau$, is specified in the form of a ramp, as shown in Figure 3.




**Key**

$\tau$ shear stress

$t$ time

**Figure 3 — Specified profile: shear stress/time function as a ramp**

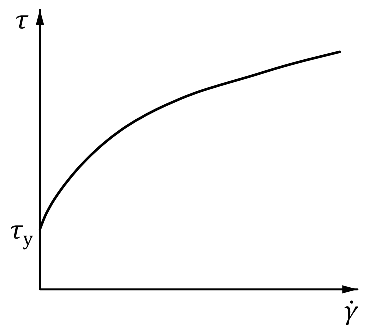
## 5.5 Evaluation methods for yield points

### 5.5.1 General

Besides the specified ramp period, the yield point value above all depends on the resolution of the rheometer for the lowest rotational speed. At shear rates of $\dot{\gamma} < 1\ s^{-1}$, time-dependent (transient) effects are expected if the measuring point duration is too short.

### 5.5.2 Axis intercept for presentation of the flow curve using a linear scale

This is the "classic method" of the yield point determination. In the case of the upward ramp, the yield point $\tau_y$ is determined as the last $\tau$ value at which the rheometer does not yet detect movement of the measuring system, i.e. at which $\dot{\gamma} = 0\,s^{-1}$ is still measured. By contrast, in the case of the downward ramp, the yield point is determined as the first $\tau$ value at which the rheometer no longer detects movement, i.e. at which $\dot{\gamma} = 0\,s^{-1}$ is measured (see Figure 4).




**Key**

$\tau$ shear stress

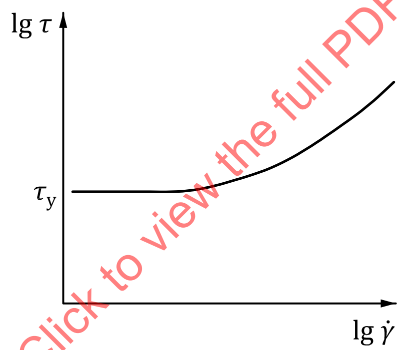
$\tau_y$ yield point

$\dot{\gamma}$ shear rate

**Figure 4 — Flow curve in a linear scale with the yield point as an axis intercept on the $\tau$ axis**

### 5.5.3 Plateau value for presentation of the flow curve using a logarithmic scale

If the flow curve approaches a plateau value in the range of low shear rates, this $\tau$ value is taken as the yield point $\tau_y$, as shown in Figure 5.




**Key**

$\tau$ shear stress

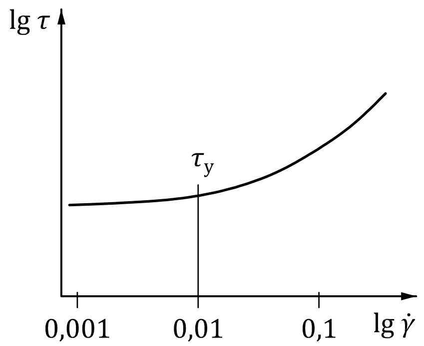
$\tau_y$ yield point

$\dot{\gamma}$ shear rate

**Figure 5 — Flow curve in a double-logarithmic scale with the yield point as a plateau value of the shear stress in the range of low shear rates**

### 5.5.4 Yield point evaluation at a reference value

The flow curve specification can take the form of a $\dot{\gamma}$ ramp or a $\tau$ ramp. The yield value is determined as shown in Figure 6 as the $\tau$ value at a shear rate previously defined by the user, e.g. $\dot{\gamma} = 0{,}01\ \text{s}^{-1}$.




**Key**

$\tau$ shear stress

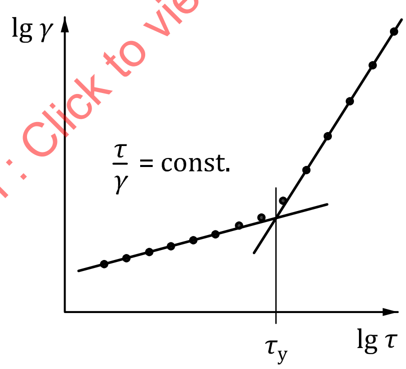
$\tau_y$ yield point

$\dot{\gamma}$ shear rate

**Figure 6 — Flow curve, determination of the yield point $\tau_y$ as the $\tau$ value with $\dot{\gamma} = 0{,}01\ s^{-1}$**

### 5.5.5 Methods with regression lines for presentation in the lg $\gamma$/lg $\tau$ diagram

If a yield point is present, then a straight line becomes visible in the range of low shear load because then the shear stress $\tau$ and the shear strain γ are proportional at low values. The measured sample then demonstrates reversible linear-elastic deformation behaviour in accordance with Hooke‘s law on elasticity. At higher loads the structure-at-rest disintegrates and the deformation then becomes disproportionately high, i.e. the material now demonstrates irreversible viscoelastic or viscous flow behaviour. The yield point is exceeded if the measuring points no longer lie on a straight line. If it is also possible to apply a second line through the measuring points in the flow range, i.e. when the deformation is high, the intersection point between the lines is evaluated as the yield point (see Figure 7).




**Key**

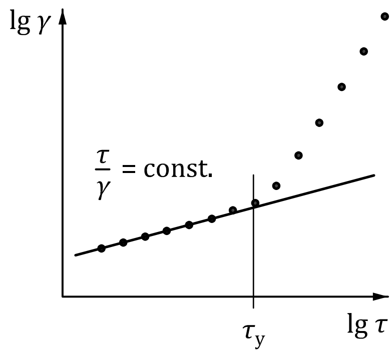
$\gamma$ shear strain

$\tau$ shear stress

$\tau_y$ yield point

**Figure 7 — Determination of the yield point using the method of the intersection point between two regression lines**

If it is not easily possible to apply a second line, the regression line is only fitted in the lower range, i.e. in the linear-elastic range. The yield point is then the $\tau$ value at which the measuring curve deviates upwards from this line into the flow range (see Figure 8). If the internal structure of a material is disintegrated stepwise only so that no sharp edge but a transition range becomes visible, it is preferred to talk of a “yield transition zone” instead of a “yield point”. In this case, the evaluation method shown in Figure 8 is preferred.




**Key**

$\gamma$ shear strain

$\tau$ shear stress

$\tau_y$ yield point

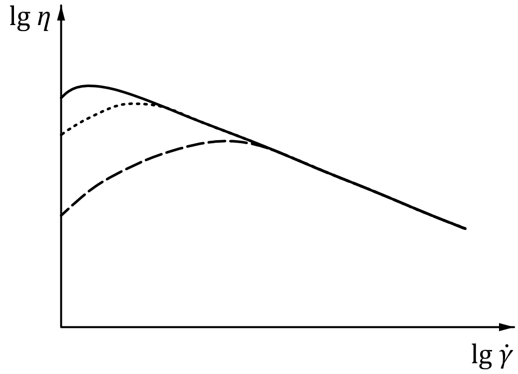
**Figure 8 — Determination of the yield point $\tau_y$ using a regression line in the linear-elastic deformation range**

### 5.5.6 Rotational test: viscosity maximum method

For rotational tests, the specification can take the form of a $\dot{\gamma}$ ramp or $\tau$ ramp. The yield point is determined at the maximum value $\eta_{max}$ of the shear viscosity function $\eta(\tau)$ or $\eta(\dot{\gamma})$.

Due to time-dependent (transient) rheological effects, this yield point value depends strongly on the measuring point duration. The reason for this is inhomogeneous deformation behaviour and flow behaviour of the measured sample in the shear gap at very low shear rates during the transition from the state at rest to the flow state. This can be seen in Figure 9, in which the results from three shear rate-controlled tests are presented. For the curve at the bottom, the shortest time for the ramp was specified. For the curve on top, the longest time for the ramp was specified. With increasing ramp duration, increasingly higher values for the relevant viscosity maximum $\eta_{max}$ are obtained (until, at the end, it would even transition to an infinitely high initial value of the shear viscosity function at the shear rate of zero). The corresponding shear rate then shifts to increasingly lower values, as does the corresponding limiting shear stress (yield point). The yield point value, $\tau_{y,}$ is calculated by multiplying the viscosity maximum $\eta_{max}$ with the shear rate $\dot{\gamma}$ according to Formula (4).

$$\tau_y = \eta_{max} \cdot \dot{\gamma} \quad (4)$$




**Key**

$\dot{\gamma}$ shear rate

$\eta$ shear viscosity

NOTE The longer the measuring point duration, the higher the resulting viscosity maxima, and the lower the corresponding shear rate value and therefore the lower the yield point value.

**Figure 9 — Dependency of the yield point from the measuring point duration**

### 5.5.7 Tests with constant shear rate

This test is mainly done with a vane rotor (see Figure 10) which is a relative measuring method for rapid routine tests, i.e. the results are relative viscosity values. The particular advantage of this test method is that when the measuring spindle (with its thin blade sheets) is immersed into the measuring sample, the structure of the measuring sample is disturbed very little during the in situ measurement.

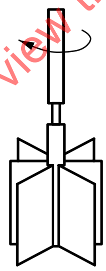
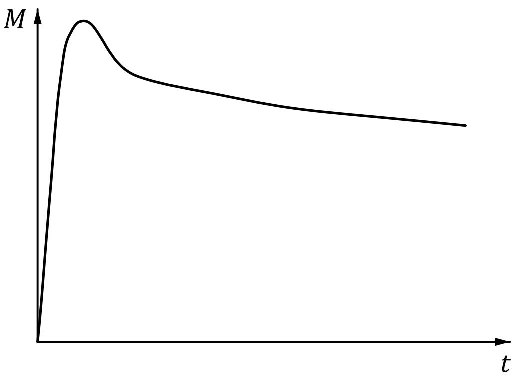


**Figure 10 — Vane rotor**

Two methods can be used:

a) Specification: constant, low rotational speed $n$ (or shear rate $\dot{\gamma}$ )

Increasing strain is applied to the measuring sample. Here, the maximum torque $M_{max}$ (or the maximum shear stress $\tau_{max}$) of the time-dependent curve is evaluated as the relative yield point. After this, the shear stress maximum is exceeded and the structure-at-rest of the sample breaks (see Figure 11).




**Key**

*M* torque

*t* time

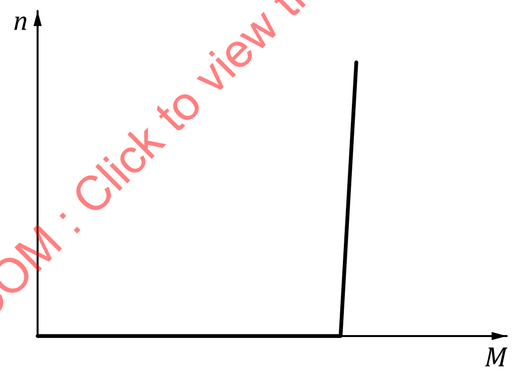
NOTE The maximum of the torque corresponds to the relative yield point.

**Figure 11 — Test using a vane rotor with controlled rotational speed**

By using an absolute measuring geometry, the curve is evaluated as the yield point.

b) Specification: linear increase over time of the torque *M* (or shear stress $\tau$)

The structure at rest of the sample is deformed increasingly (it is “creeping”). Here, the *M* value (or $\tau$ value) at the start of the abrupt increase in the rotational speed curve (or shear rate curve) is evaluated as the relative yield point. The “breakaway point” is then exceeded and the sample now flows (see Figure 12).




**Key**

*n* rotational speed

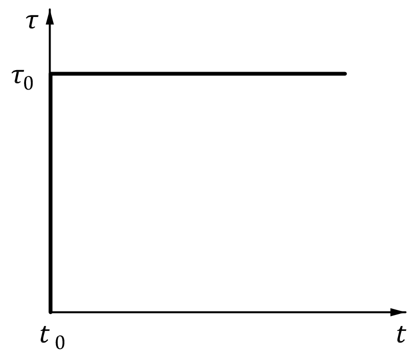
*M* torque

NOTE The relative yield point corresponds to the last torque value before the first rotational speed is detected (“breakaway point”).

**Figure 12 — Test using a vane rotor with controlled torque**

### 5.5.8 Creep test

In the creep phase, a step to the shear stress $\tau_0$ is specified; then the measuring sample remains exposed to this constant load (see Figure 13).




**Key**

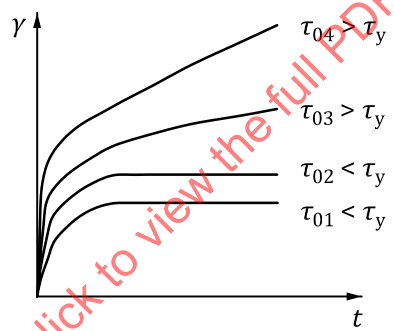
$\tau$ shear stress

$t$ time

$t_0$ time at $\tau = 0$

**Figure 13 — Constant shear stress $\tau_0$ as a specification for the creep test**

The determination of the yield point using the creep function is as follows: the yield point value is exceeded if the specified $\tau$ value leads to shear strain values that constantly increase over time, i.e. to stationary flow. Then the creep curve, i.e. the time-dependent shear strain curve $\gamma(t)$, will continue to rise steadily at the end (see Figure 14).




**Key**

$\tau$ shear stress

$\tau_y$ yield point

$t$ time

$\gamma$ shear strain

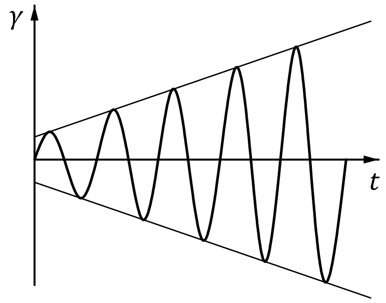
NOTE If the specified shear stress $\tau_0$ exceeds the yield point $\tau_y$ then the $\gamma(t)$ curve will continue to rise steadily at the end.

**Figure 14 — Creep curves for four different loads**



### 5.5.9 Oscillatory test: amplitude sweep

In the amplitude sweep, the magnitude of the oscillation amplitude varies while the oscillation frequency remains constant (see Figure 15).




**Key**

$\gamma$ shear strain

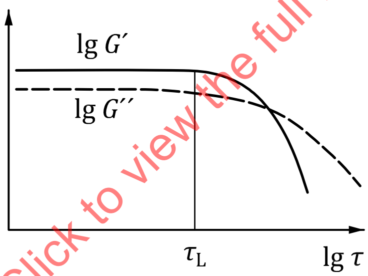
$t$ time

**Figure 15 — Specification for an amplitude sweep (with controlled shear strain)**

For gel-like structures, determination of the linearity limit $\tau_L$ of the shear stress as the limit of the linear-viscoelastic range is the prerequisite for the existence of a frequency depending relative yield point.

Several methods for the evaluation of amplitude sweeps can be used:

a) Linearity limit as $\tau_L$ value at the limit of the linear-viscoelastic range: the reversible elastic deformation behaviour ends when this limit is exceeded. At higher loads, the curves of $G'$ and $G''$ will drop (see Figure 16). Alternatively, the value of the loss angle $\delta$ or of the loss factor tan $\delta = G''/G'$ is considered. Above the limit of the linear viscoelastic range, the curves of these two parameters are rising.




**Key**

$G'$ shear storage modulus

$G''$ shear loss modulus

$\tau$ shear stress

$\tau_L$ linearity limit

**Figure 16 — Result of the amplitude sweep: linearity limit $\tau_L$ as the shear stress limit at the boundary of the linear-viscoelastic range**

b) Regression lines can be fitted to all curves mentioned – one in the linear-viscoelastic range and one outside of it. Here, the yield point is the $\tau_y$ value at the intersection point between the lines.

c) An alternative representation is the lg $\gamma_A$/lg $\tau_A$ diagram for yield point analysis with the aid of the regression lines. See Figure 7 and Figure 8 (however, the oscillatory test is shown with the shear strain amplitude $\gamma_A$ and the shear stress amplitude $\tau_A$).

d) Shear stress value at the intersection point $G' = G''$, or with tan $\delta = 1$. Then, in the viscoelastic behaviour of the sample, the liquid character will be predominant.

NOTE The linear-viscoelastic range with reversible elastic deformation behaviour has already been exceeded at this point.

# 6 Results of the comparative testing programme

## 6.1 Performance of the tests

### 6.1.1 Preliminary tests

The first comparative preliminary tests carried out by the working group showed the following results.

The differing measuring results of the preliminary tests can be due to the following reasons:

— Different preparation of samples or measurement with or without pre-application of shear.

— Samples stressed by shearing appeared not yet recovered after a period of rest. For this reason, the samples were taken and measured after periods of rest of 2 min to 10 min without pre-application of shear.

— The evaluation of the tests was carried out following the reference value method (see 5.5.4), via flow curve regression models and, additionally, via the intersection point between two regression lines (in the diagram shear strain lg $\gamma$ over shear stress lg $\tau$). When using automatic evaluation methods, the limits of commercially available software were sometimes reached when the operator could not influence given evaluation routines (yield point calculation by the intersection point method). Therefore, the members of the working group elaborated a further evaluation method. Also, the determination of the yield point from the value of the maximum viscosity was rejected and considered as unsuitable.

### 6.1.2 Comparative testing programme

Based on the experiences from the results of the preliminary tests, the following procedure for performance of the tests was agreed in January 2002.

These tests were only carried out with the test type shear stress ramp. The samples were prepared in such a way that one decade each was available for the evaluation below and above the assumed yield point, i.e. the shear stress ramp started at least one decade below the assumed yield point and ended at least one decade above the yield point value.

When using this method, a range from $\tau_{min}$ = 0,1 Pa to $\tau_{max}$ = 100 Pa can be covered. Specific details of the procedure are described as follows.

— The measurements were all carried out within a period of 2 weeks.

— Measurement geometry: cone-plate with a diameter of 50 mm to 60 mm and cone angles from 1° to 2° (see ISO 3219-2). The exact geometry was recorded in each case.

— Preparation of samples: fill the sample and then allow 5 min for temperature adjustment at 23 °C without application of shear. Afterwards, the measurement was started straight away.

— Measurement: shear stress ramp from 0,1 Pa (or less) to 100 Pa within 5 min with a logarithmic increase. Here, 100 measuring points (equidistant in the lg scale) were recorded. The test was stopped when a shear rate of 50 $s^{-1}$ was exceeded (criterion for stopping $\dot{\gamma}$ = 50 $s^{-1}$).

## 6.2 Measuring samples

Five samples were examined:

— Sample A and sample B: waterborne basecoats;

— Sample C and sample D: dispersions;

— Sample E: non-Newtonian reference sample.

Sample A was found to be unsuitable for the specified measuring method and for the requirements for performance of the tests. This sample showed very low viscosity with the yield point in a measuring range which could not be covered reasonably when using the agreed measuring method.

The measuring results returned for sample B and sample C were in relatively good agreement.

Sample D had a high solid matter content, which led to long standing times. As a result, this sample appears to be not well suited to the applied measuring methods and procedures.

The rheology of samples C and D is complicated. With sample D in particular, there can be different interpretations as to which measured values within the measuring result (shear stress ramp) are considered the definite yield point. In addition, this sample was at the upper end of the range covered by the specified procedure so that only insufficient quantification was possible.

## 6.3 Method used for determination of the yield point

The evaluation of the measuring curves was performed following the method with regression lines introduced in 5.5, with representation in the lg $\gamma$/lg $\tau$ diagram (see Figure 17).

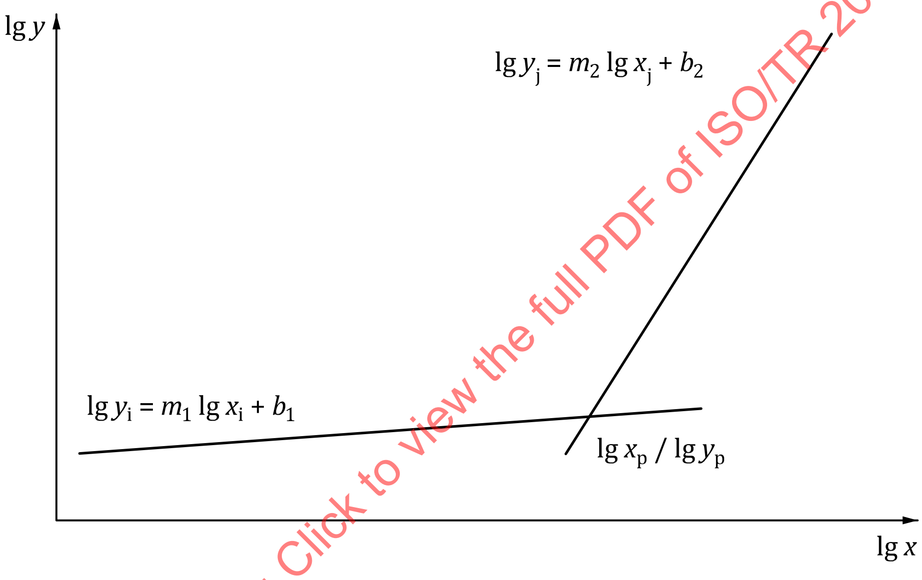



**Figure 17 — Diagram for calculation of the intersection point**



The intersection point can be calculated using the algorithm $\lg x_p/\lg y_p$ .

Starting from the number of all measuring points $h$, Formulae (5) to (8) apply to the first regression line (with the measuring points 1 to $k$ and the number of points $k$):

$$m_1 = \frac{\sum_{i=1}^{k} \lg x_i \sum_{i=1}^{k} \lg y_i - \frac{1}{k} \sum_{i=1}^{k} \lg x_i \sum_{i=1}^{k} \lg y_i}{\sum_{i=1}^{k} (\lg x_i)^2 - \frac{1}{k} \sum_{i=1}^{k} \lg x_i \sum_{i=1}^{k} \lg x_i} \tag{5}$$

$$b_1 = \frac{1}{k} \sum_{i=1}^{k} \lg y_i - \frac{m_1}{k} \sum_{i=1}^{k} \lg x_i \tag{6}$$

and for the second regression line (with the measuring points $g$ to $h$ and the number of points $f$):

$$m_2 = \frac{\sum_{g=1}^{h} \lg y_g \sum_{g=1}^{h} \lg y_g - \frac{1}{f} \sum_{g=1}^{h} \lg x_g \sum_{g=1}^{h} \lg y_g}{\sum_{g=1}^{h} (\lg x_g)^2 - \frac{1}{f} \sum_{g=1}^{h} \lg x_g \sum_{g=1}^{h} \lg x_g} \tag{7}$$