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WORKING GROUP

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SUBJECT \_\_\_\_\_ 0114 Fillers and Pigments \_\_\_\_\_

CATEGORY \_\_\_\_\_ Testing \_\_\_\_\_

RELATED

METHODS \_\_\_\_\_ See "Additional Information" \_\_\_\_\_

**CAUTION:**

This Test Method may include safety precautions which are believed to be appropriate at the time of publication of the method. The intent of these is to alert the user of the method to safety issues related to such use. The user is responsible for determining that the safety precautions are complete and are appropriate to their use of the method, and for ensuring that suitable safety practices have not changed since publication of the method. This method may require the use, disposal, or both, of chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this method, the user must determine whether any of the chemicals to be used or disposed of are potentially hazardous and, if so, must follow strictly the procedures specified by both the manufacturer, as well as local, state, and federal authorities for safe use and disposal of these chemicals.

## **High Shear Capillary Viscosity (ACA Capillary Viscosity) of coating color on paper and paperboard (Proposed new Provisional Method) (Changes from previous drafts incorporated)**

### **1. Introduction**

- 1.1 Coating formulations for paper and paperboard are continuously evolving as new materials, new application processes and new end uses are developed. Even basic formulations (in terms of the simplicity of the formulation or application) can have complex rheological and physical properties that must be understood in order for the coating color to be able to run and perform its intended function.
- 1.2 A key aspect of the rheological properties is understanding that the flow properties (or to use the common term, "viscosity") of the coating color can change as the coating is subjected to different rates of shear as it is mixed, pumped and flowed through pipes, filters and the applicator. For the

relatively low shear regime, the predominant measurement device is a rotational viscometer, meaning that a specially designed rotating shaft is suspended in the coating, and the torque required to maintain a fixed rotation is measured. The most common rotational viscometer was designed by Brookfield Engineering Laboratories, and therefore the low-shear viscosity is being colloquially known as “Brookfield® Viscosity”.

- 1.3 For higher shear regimes – up to about 150,000 s<sup>-1</sup> (reciprocal seconds) – another type of rotational viscometer – colloquially known as “Hercules® Hi-Shear Viscometer” – is used. It measures the drag force between the rotational shaft and the cup containing the coating as the rotation rate (speed) ramps up, then backs down.
- 1.4 For even higher shear regimes, ACA Systems Oy (Finland) has developed a capillary viscometer capable of shear rates up to 1,000,000 s<sup>-1</sup>, which is representative of the shear rates experienced by the coating color in certain phases of different coating processes. Capillary viscosity has proven to be a useful method of predicting runnability of coating color on certain types of coating equipment. It can be used as a quality control tool in production, development tool or prescreening device on coating colors before attempting to apply them on the pilot or production coater, especially using high-speed blade, rod or film transfer coaters. No standard test method to ensure consistent measurement in the high shear rate regime is in place.
- 1.5 Appendix 1 shows shear rate ranges for different rheometers, and a schematic of shear rate ranges for different coating processes.

## **2. Scope**

- 2.1 This method describes a procedure for measuring high shear viscosity of pigment coating colors using an ACA AX-100 Viscometer with a capillary configuration.
- 2.2 In this method, high shear viscosity is determined as mPa·s at the shear rate of 500,000 s<sup>-1</sup>, and simply called ACA Capillary Viscosity.
- 2.3 The method is applicable for water-based pigment coating colors used in various coating processes such as in blade, rod, and film transfer coating. Typically, suitable pigment coating colors have a solids content between 30 % and 80 %, and they contain mineral pigments, synthetic and / or natural binders and coating additives.

## **3. Significance**

- 3.1 Coating color is a non-Newtonian fluid and therefore its rheological properties can be complicated. The key factor is the viscosity of the coating color in the shear regimes that the coating will experience during the process from makedown to application on the substrate. In the majority of paper and paperboard coating processes, the shear rates can vary from almost zero to over a million

$s^{-1}$ . Both wet coating structural factors related to surface chemistry and hydrodynamic factors are present as shown in Appendix 2.

3.2 Low shear viscosity is important in determining the compatibility of various coating materials. It is also relevant in understanding the effects of pumping and mixing. However, hydrodynamic factors are more important in determining the actual coating runnability as high shear rates are present in application and metering. Low shear viscosity of coating colors can be described also as structural viscosity. Appendix 2 shows that a coating color viscosity increases at low shear rates first due to structure formation, but then goes down as shear rate is increased, reaching a level below 100 mPa·s as structures are broken and particles can flow past each other. This happens roughly at shear rates above 200,000  $s^{-1}$ . After that the viscosity is mainly influenced by packing effects of particles i.e. hydrodynamic factors.

3.3 Previously, no standard method existed to describe high shear viscosity in the non-structural regime. ACA Capillary Viscosity, run at 500,000  $s^{-1}$ , describes the purely non-structural (hydrodynamic) viscosity. ACA Capillary Viscosity is influenced mainly by solids content (i.e. volume fraction of particles), particle size, particle size distribution, viscosity of continuous (water) phase, and shape of the particles. Appendix 3 shows practical examples on the influence of particle size distribution in coated fine paper recipes. And Appendix 4 shows that the viscosity data achieved with capillary viscometer is having a higher correlation to actual blade load when compared to low shear regime viscosity measurements.

#### **4. Applicable standards**

4.1 T 648 om-14 Viscosity of coating clay slurry

#### **5. Definitions**

5.1 High shear viscosity in this context is defined as above 100,000  $s^{-1}$  and up to 1,000,000  $s^{-1}$  in shear rate. In this standard, 500,000  $s^{-1}$  is used.

#### **6. Apparatus**

6.1 ACA AX-100 is a capillary viscometer specially designed to measure the viscosity of coating colors in the high shear regime (Appendix 6). Extrusion pressure is measured with a pressure transducer, and the displacement of the sample cylinder is measured with a position sensor. Volumetric flow rate through the capillary is calculated from the displacement of the sample cylinder during the measurement cycle.

It should be noted that the flow velocity of the fluid suddenly increases when sample enters the narrow capillary. Therefore, a certain part of the extrusion (measured) pressure turns into kinetic energy of the fluid. Kinetic energy correction subtracts this pressure from measured pressure. The viscosity is calculated from the flow rate using a kinetic correction as shown in Section 11. Other typical correction factors are introduced in Appendix 5.

6.2 In standard measurements, a 50 mm long (L) 0.5 mm diameter (D) glass capillary is typically used (Appendix 5). However, also other length and diameter capillaries can also be used.

6.3 Pressure and position sensors are initially calibrated by the manufacturer. Calibration must be checked once a month as instructed in the user manual.

6.4 The capillaries are calibrated with water. Since flow of low viscosity fluid like water is always turbulent, actual definition of viscosity is not possible at high shear rate area. However, at constant pressure volumetric flow rate through a capillary of given length is a monotonic function of diameter. Therefore, diameter can be calculated from the volumetric flow rate by using numerical estimation methods and previously measured reference data. Such design of experiment has been conducted and based on data achieved, a calculation formula is stored in easy-to-use software.

It is recommended that after five measurements water is measured through the capillary. If the apparent volumetric flow rate of water is higher than the previous measurement (i.e. capillary worn), the capillary should be calibrated. In any case, the capillary should be calibrated after fifty measurements. Diameter of the standard capillary must be  $0.5 \pm 0.01$  mm. Otherwise, it needs to be replaced by a new capillary. After each calibration the new diameter is entered in the computer program of the viscometer.

6.5 A low-speed laboratory mixer, a 300- $\mu$ m (50-mesh) sieve and a balance with the sensitivity of  $\pm 2\%$  are required for the measuring procedure.

## **7. Reagents and materials**

7.1 The method can be applied to analyze the runnability of different paper and paperboard coating formulations in blade, rod or film transfer coating processes.

## **8. Safety precautions**

8.1 **WARNING!** ACA AX-100 is meant to measure only non-explosive water-based liquids. It is using high pressure at 150 bar maximum.

CAUTION! Be sure that "EMERGENCY STOP" is not activated before measurements, for reset rotate it arrowed direction.

CAUTION! Contact your ACA AX-100 supplier or [service@aca.fi](mailto:service@aca.fi) in case any damages or any abnormal operation of the device occur.

## **9. Sampling and test specimens**

9.1 Max. volume of a coating color sample is 250 ml.

## **10. Procedure**

10.1 Cool down / warm up the sample in a water bath to  $23 \pm 1^\circ\text{C}$  and mix it carefully with a low-speed (< 2000 rpm) laboratory mixer for two minutes.

10.2 Measure the weight of a known volume of coating color with balance and calculate the density of the sample.

NOTE! Care needs to be taken that during mixing and filtration air is not entrapped as this will impact the density measurements. During the measurement the high pressure will compress the air so that the density used in the calculation of the viscosity could be off.

10.3 Screen 250 ml of coating color through a 300- $\mu\text{m}$  (50-mesh) sieve.

10.4 Make sure the sample cylinder is clean and dry. While washing the sample cylinder, stabilize the cylinder temperature to about  $23^\circ\text{C}$ . Pour the sieved coating color into the sample cylinder and place the cylinder into the device.

10.5 Make sure measurement settings are those described in the manual and start the measurement cycle from the control program.

10.6 Read the ACA Capillary Viscosity value from the touch screen and save it as raw data.

10.7 After the measurement cycle is complete, take the sample cylinder out and wash it under tap water.

10.8 Allow the sample cylinder to come to ambient temperature before the next test.

## **11. Calculations**

Shear rate is calculated as:

$$\dot{\gamma} = \frac{4Q}{\pi R^3}$$

where

Q = volumetric flow rate (m<sup>3</sup>/s)

R = radius of capillary (m)

Kinetic energy correction is defined as:

$$p_{\text{kin}} = m\rho\left(\frac{Q}{\pi R^2}\right)^2$$

where

m = kinetic energy correction coefficient (= 1)

$\rho$  = density of the sample (kg/m<sup>3</sup>)

Shear stress is calculated as:

$$\tau = \frac{(p - p_{\text{kin}})R}{2L}$$

where

p = measured pressure (Pa)

L = length of capillary (m)

Viscosity (Pas) is defined as:

$$\eta = \frac{\tau}{\dot{\gamma}}$$

Viscosity is displayed in millipascal-seconds or centipoises (1 mPa·s = 1 cP)

Reynolds number for the pipe flow is defined as:

$$Re = \frac{2Q\rho}{\pi R\eta}$$

## **12. Reports**

- 12.1 A complete report can be printed from the control program (USB or Ethernet).
- 12.2 Measured points with a Reynolds number above 2,500 are rejected as the flow is turbulent, not laminar.
- 12.3 In the graphics, the viscosity is plotted as a function of shear rate.
- 12.4 ACA Capillary Viscosity is displayed on the main screen and report page.
- 12.5 Description and density of the sample plus measuring time/date are printed on the report in addition to shear rate, shear stress and viscosity values.
- 12.6 Solids content, pH value and Brookfield viscosity may also be included in the report as they are useful values for relating to the ACA Viscosity.

## **13. Precision**

- 13.1 Accuracy of position potentiometer: +/- 0.05 mm
- 13.2 Accuracy of pressure transducer: +/- 0.3 %
- 13.3 Repeatability (within a laboratory): +/- 5.0 %
- 13.4 Reproducibility (between laboratories): +/- 10.0 %

## **14. Keywords**

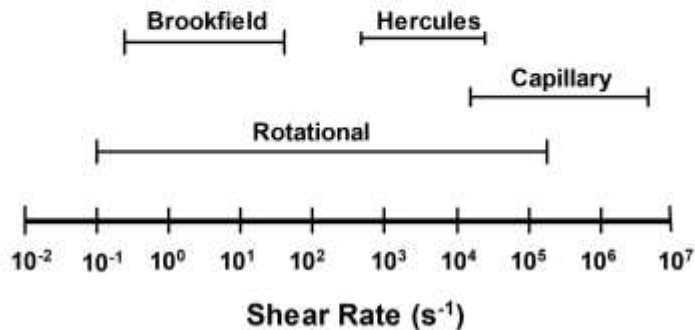
Coating, rheology, viscosity, high shear viscosity, coating color, rheometer, capillary viscometer, ACA

## **15. Additional Information**

- 15.1 Effective date of issue: to be assigned.

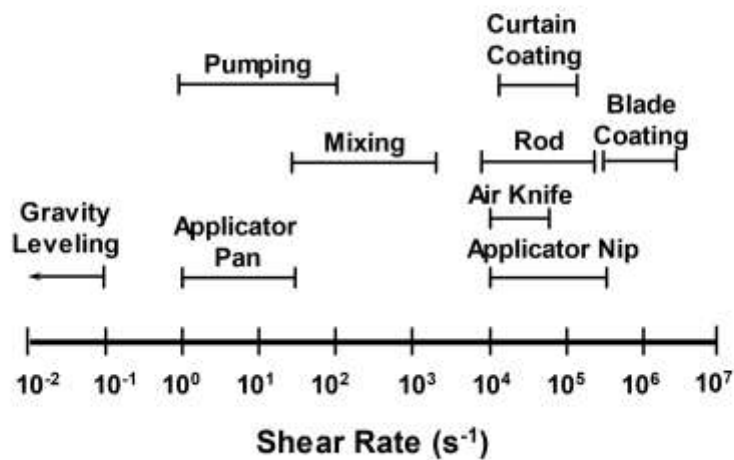
**Appendix 1:** Shear rate ranges for different rheometers, and a schematic of shear rate ranges for different coating processes.

## Shear-Rate Ranges for Different Types of Rheometers



Source: John A. Roper, PaperCote LLC

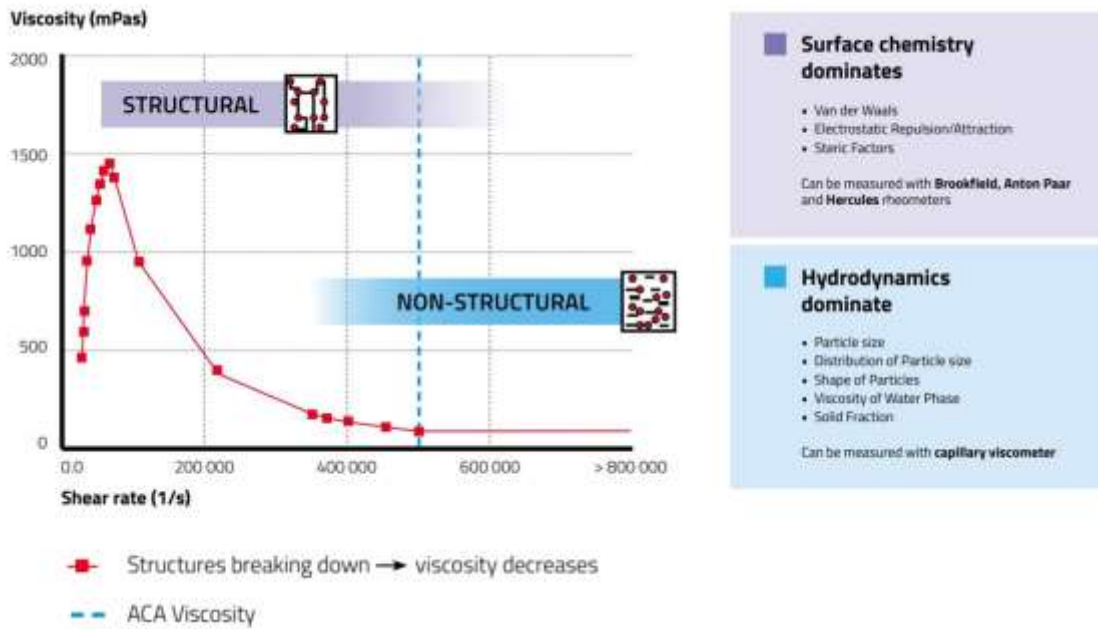
## Shear-Rate Ranges for Paper Coating Processes



Source: John A. Roper, PaperCote LLC

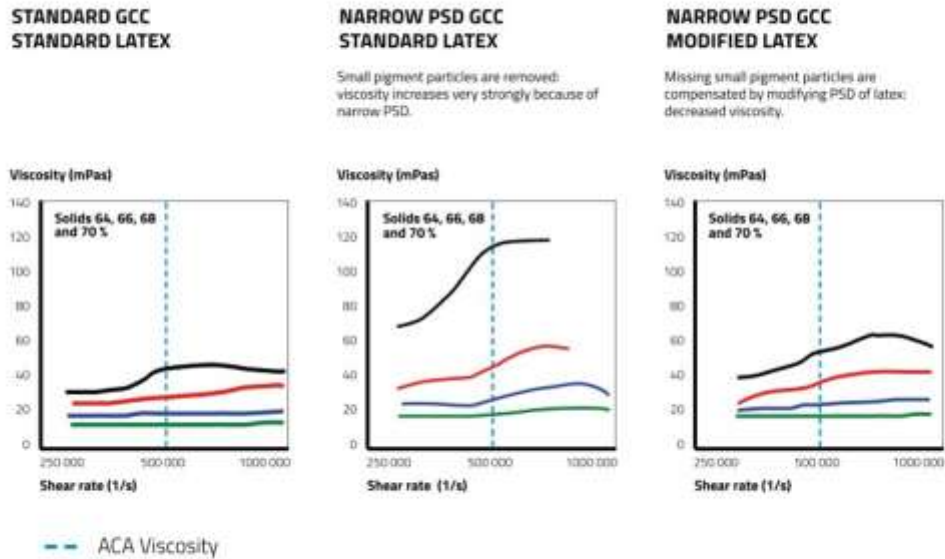


Appendix 2: Structural (low shear) and non-structural (high shear) viscosities



Source: ACA Systems Oy / Prof. Martti Mäkinen “Fundamentals of Rheology – training”

**ACoating Fundamentals.** Practical example of ACA Capillary Viscosity (Effect of total particle size distribution on coated fine paper recipes)

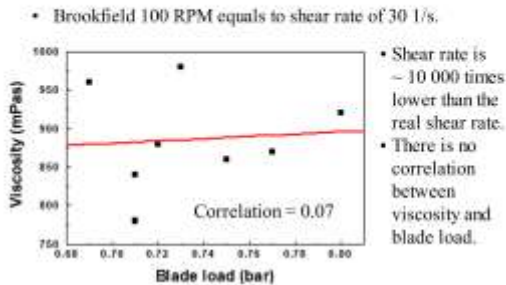


These graphs are shown for general information only. Details for specific coating formulations will vary.

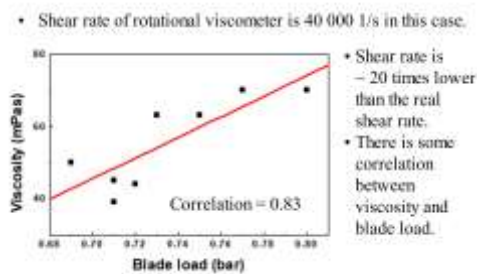
Source: ACA Systems Oy / Prof. Martti Mäkinen “Fundamentals of Rheology – training”

**Appendix 4.** Correlation of viscosity measured with various methods and the blade load of an industrial blade coating machine.

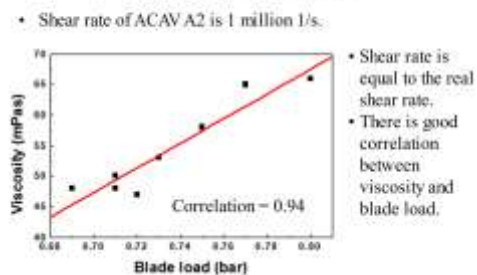
Correlation of viscosity and blade load:  
Brookfield viscometer



Correlation of viscosity and blade load:  
Rotational viscometer



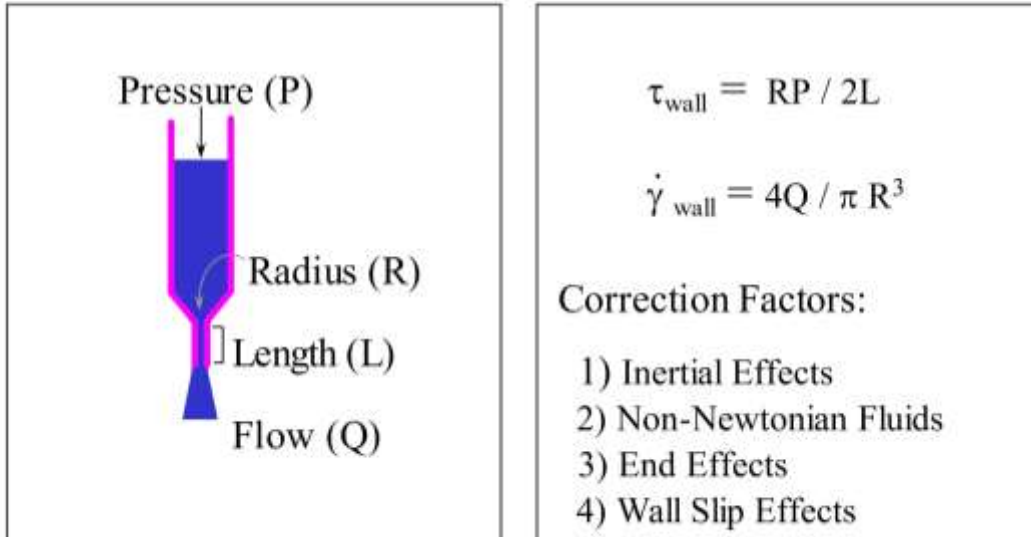
Correlation of viscosity and blade load:  
Capillary viscometer



Source: ACA Systems Oy / Prof. Martti Mäkinen “Fundamentals of Rheology – training”

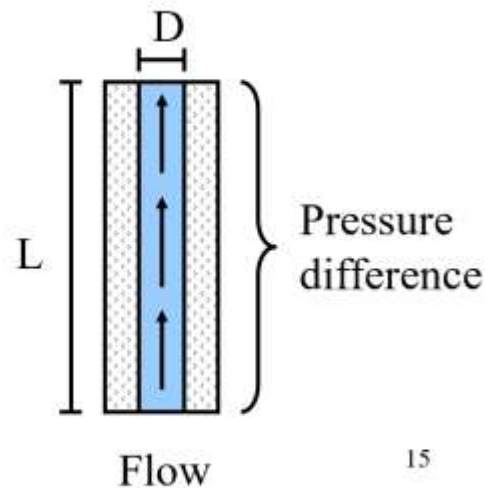
Appendix 5: Principle of capillary rheometer, and correction factors

# Capillary Rheometer



Source: John A. Roper, PaperCote LLC

- Principle is to measure flow rate through the capillary, and pressure difference required for maintaining the flow.
- Dimensions of capillary (L,D) are known: shear rate, shear stress and viscosity may be calculated.



Source: ACA Systems Oy / Prof. Martti Mäkinen “Fundamentals of Rheology – training”

- **Basic calculations**

The formulas used in AX-100 software are the basic ones usually used in capillary measurements.

Shear rate:	$\dot{\gamma} = \frac{4Q}{\pi R^3}$
Shear stress	$\tau = \frac{pR}{2L}$
Viscosity	$\eta = \frac{\tau}{\dot{\gamma}}$

- **Symbols**

p	Measured (uncorrected) pressure
Q	Volumetric flow rate
$\dot{\gamma}$	Shear rate
$\tau$	Shear stress
$\eta$	Viscosity
$\rho$	Density
R	Radius of capillary
L	Length of capillary
h	Gap of the Slit
w	Width of the Slit
L	Length of the Slit
m	Kinetic energy correction coeff.
$\zeta$	Couette correction coeff.
k,n	Variables in power law, $\tau = k\dot{\gamma}^n$

## Correction factors

### 1. Inertial effects (Kinetic Correction)

Flow velocity of the fluid suddenly increases when a sample enters the narrow capillary. Therefore, a certain part of the extrusion (measured) pressure turns into kinetic energy of the fluid. Kinetic energy correction subtracts this pressure from the measured pressure. Kinetic energy correction is recommended in the high shear rate area and is used by AX-100 viscosity calculation.

Kinetic correction	$p_{kin} = m\rho \left( \frac{Q}{\pi R^2} \right)^2$
Corrected pressure	$p_{cor} = p - p_{kin} = p - m\rho \left( \frac{Q}{\pi R^2} \right)^2$
Corrected shear stress	$\tau_{cor} = \frac{p_{cor} R}{2L}$
Corrected viscosity	$\eta_{cor} = \frac{\tau_{cor}}{\dot{\gamma}}$

Default value of coefficient m is 1, but user may define it.

## 2. Non-Newtonian fluids (Rabinowitsch-Mooney Correction)

Shear rate equation is valid only for Newtonian fluids. Rabinowitsch correction calculates real shear rate for non-Newtonian fluids. Use of Rabinowitsch correction is not recommended, because a small error in measured values may result in a large error in Rabinowitsch corrected results. Furthermore, most coating colors are rather Newtonian in high shear rate area.

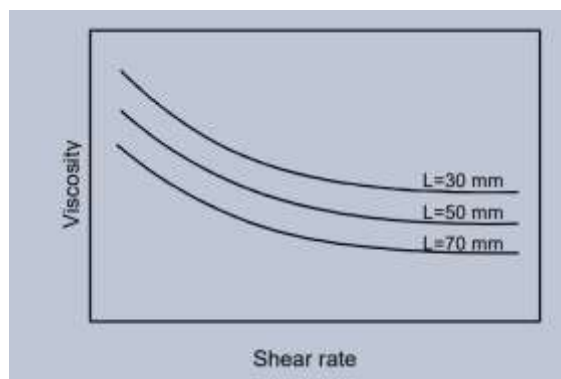
Shear rate	$\dot{\gamma}_{cor} = \frac{3n+1}{4n} \dot{\gamma} = \left( \frac{3n+1}{4n} \right) \frac{4Q}{\pi R^2}$
Corrected viscosity	$\eta_{cor} = \frac{\tau}{\dot{\gamma}_{cor}}$

Coefficient n (power law) is calculated from local shape of the viscosity curve for each measured data point.

## 3. End effects (Bagley-correction)

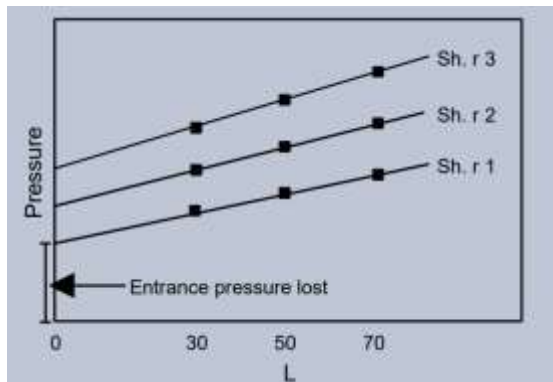
- Background

For calculating viscosity accurately, it is necessary to know what is pressure lost inside the capillary. As capillaries are very narrow, in practice pressure has to be measured from a wider pipe close to the entrance of the capillary. Flow velocity of the fluid increases strongly at the entrance of the capillary. Therefore, a certain amount of pressure is converted to kinetic energy of the fluid. Kinetic energy correction takes into account this pressure lost. Especially elongational viscosity (resistance to accelerating flow) may cause additional pressure lost at the entrance, as there is a converging flow field. It is impossible to study the effect of elongational viscosity, if the sample is measured with one capillary only. If the sample is measured with two capillaries of the same diameter but different length, the effect of the entrance effects may be calculated by using Bagley-correction. When kinetic energy is the only source of pressure lost at the entrance, calculated viscosity (at the same shear rate) is the same regardless of the length of the capillary. However, if there are additional entrance effects, such as pressure lost due to extensional viscosity, a shorter capillary apparently gives higher viscosity, as shown below. Studies have shown that extensional viscosity effects are an important factor for blade and rod runnability, so by including these effects in the measurement by using only a single capillary often gives a better correlation with runnability.



- **Calculation**

It is reasonable to believe that entrance pressure lost is depending only on the shear rate and diameter of the capillary, i.e. it is not depending on the length of the capillary. On the other hand, viscous pressure lost inside the capillary is directly proportional to the length of the capillary. As a consequence, a line could be drawn through the data points, when total pressure lost is plotted as a function of the length of the capillary for a constant shear rate (or flow rate) value. Entrance pressure lost could be detected by extrapolating the lines to the zero length of the capillary, and it is equal to the intercept of the extrapolated line and pressure axis. Entrance pressure lost is always a function of shear rate, and almost invariably it increases with increasing shear rate.



From the mathematical point of view, it is not necessary to actually draw the plot. Entrance pressure lost could be calculated by finding parameters of the line (least squares fit). Real (corrected) viscosity is calculated by subtracting entrance pressure lost from the measured pressure. After the correction is applied, viscosity (at constant shear rate) is the same regardless of the length of the capillary. In addition to corrected viscosity, also the extent of entrance pressure lost may be important. As an example, there is a number of converging flow fields in coating process, and therefore elongation viscosity may have a significant effect on the rheological behavior of the coating color. Higher entrance pressure lost means higher elongation viscosity.

**Note!**

- It is possible to calculate Bagley-correction only when the diameters of the capillaries are the same and the lengths of the capillaries are different.
- There is an overlapping shear rate / flow rate area in selected measurements.
- If the measured viscosity is not depending on the length of the capillary after a kinetic energy correction, there is no need to calculate Bagley-correction: it would be equal to kinetic correction.

#### **4. Wall slip effects**

- **Background**

In capillary viscometer equations, it is assumed, that the flow profile (velocity profile) inside the capillary is parabolic, the sample is homogenous and the flow velocity at the wall is zero. In case of suspensions / dispersions a certain part of the fluid phase may be separated from the bulk of the sample. The separated fluid may form a thin low viscosity layer at the wall of the capillary. This layer may lubricate the flow of the bulk of the sample, and therefore the volumetric flow rate through the capillary is higher than it would be in the case of a homogenous sample. This phenomenon is called wall slipping. The proportional effect of the low viscosity fluid layer is more significant when the diameter of the capillary is narrow. Therefore, a narrower capillary apparently gives lower viscosity (at the same shear rate) than wider capillary, if there is slipping at the wall. Usually there is no slipping, and measured viscosity does not depend on the diameter of the capillary. The experience has shown that for most paper coating colors wall slip effects are minor and can be ignored.

- **Calculation**

The fundamental equation of viscometry:

$$\eta = \frac{\tau}{\dot{\gamma}}$$

In the case of capillary viscometer, shear stress is proportional to applied pressure and shear rate is proportional to flow rate through the capillary. Viscosity depends on the shear rate, but it does not depend on the diameter of the capillary. Therefore, the same applied shear stress should always result in the same shear rate regardless of the diameter. However, if there is slipping at the wall, flow rate through the capillary is increased by

$$\Delta Q = v_s \pi R^2,$$

where  $v_s$  is slip velocity (m/s) and R is radius of the capillary. The proportional effect of slipping depends on the diameter of the capillary, and therefore the same applied shear stress gives a higher apparent shear rate, when the capillary is narrower. As a consequence, the narrower capillary apparently gives lower viscosity. It is believed that slip velocity is a function of shear stress only. Therefore, it is possible to calculate the effect of slipping, if two capillaries with different diameters are used. By using the equations of shear rate and shear stress slip, velocity could be calculated for each shear stress value. When slip velocity is found, the effect of slipping

$$(\Delta Q = v_s \pi R^2)$$

is subtracted from the measured flow rate. A corrected shear rate and viscosity values are calculated from the corrected flow rate value.

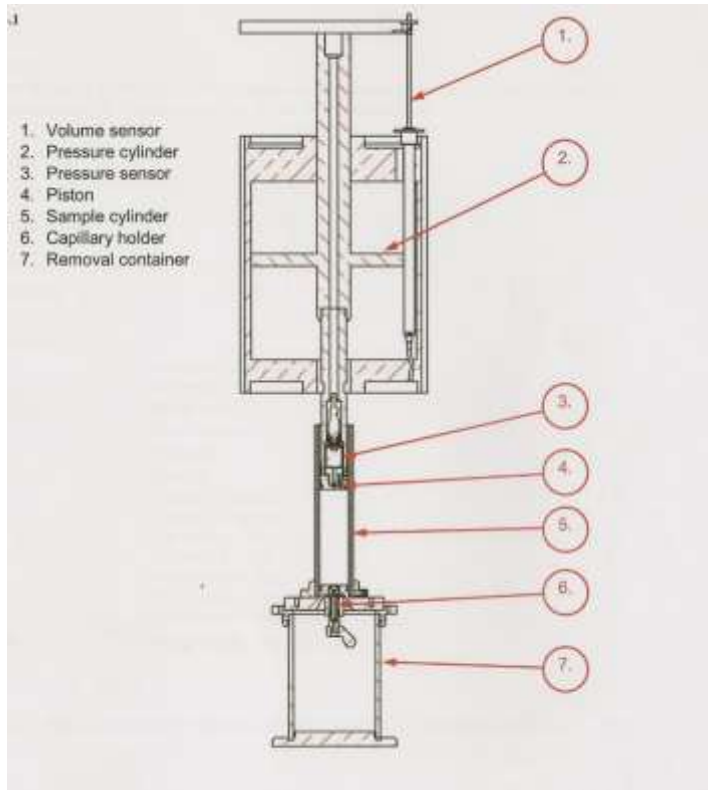
It is believed that slip velocity correlates with dynamic water retention of coating color, as in both cases some amount of water phase is separated from the bulk of the coating color. According to this theory, a higher slip velocity means poorer water retention.

Notes:

- It is possible to calculate a wall slip correction only when capillary diameters are different. There is an overlapping shear stress area in selected measurements.
- If measured viscosity is not depending on the diameter of the capillary, there is no need to calculate a wall slip correction as slip velocity would be zero. The theoretical background of the wall slip phenomenon is questionable. Wall slip correction may sometimes result in invalid results.



**Appendix 6: Schematic of ACA AX-100 Capillary Viscometer**



*Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Standards Department. ■*