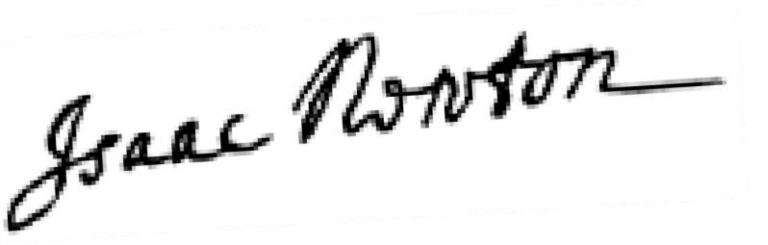


RHEOLOGY
RHEOMETRY

Definition of rheology

- Study of the flow and deformation of materials

- All matter deforms when a **stress** is applied, the resulting deformation being the **strain**

Newton´s law
liquids

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

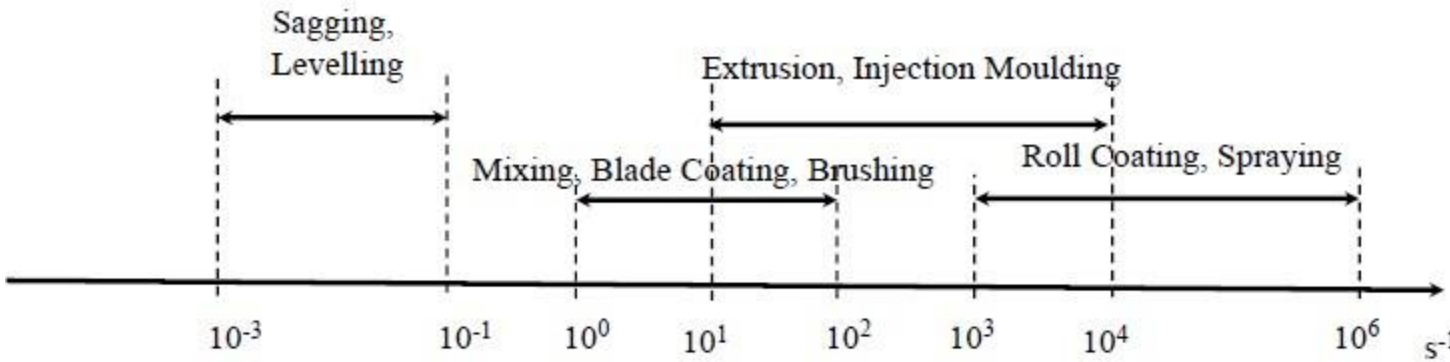
The ratio of stress to strain in liquids is constant

The proportionality constant is viscosity

Viscosity is a measure of liquid´s resistent to flow

- Dynamic viscosity η [Pa.s]
- Kinematic viscosity ν [$m^2.s^{-1}$]

Typical Shear Rate Ranges



Rotational-Rheometer

Sample: Water up to solids
Results: Shear-Viscosity, Yield Stesses, Visco-Elasticity, Relaxation...

High Pressure Capillary-Rheometer

Sample: Water up to high viscous
Results: Shear-Viscosity, Elongational-Viscosity, Wall Slip...

Typical Shear Viscosities

Material	Shear-Viscosity (Pas)
Air	10^{-6}
Aceton	10^{-4}
Water	10^{-3}
Olive Oil	10^{-1}
Glycerol	10^{0}
Molten Polymers	10^{3}
Bitumen	10^{8}
Glass at 500°C	10^{12}
Glass at ambient	10^{40}

Units:		Remember
Pascal second	Pas (SI)	1 Pas = 10 P
Poise	P (CGS)	1 mPas = 1 cP

Match shear rate to processes…

Storage

SAMPLE STORAGE
Very low shear rates: ~ $0.001 s^{-1}$
How stable is it, sample quality…

SAMPLE DELIVERY
Medium shear rates: ~$10 s^{-1}$
Pumpability? Scoopability?

SAMPLE APPLICATION 1
Low shear rates: ~$1 s^{-1}$
Flows away? Flows off hand?

SAMPLE APPLICATION - 2
Higher shear rates: ~$100 s^{-1}$
Too thick to spread? Nice feel?

End use

What Affects the Rheological Property?

Temperature

Many materials are quite sensitive to temperature, and a relatively small variation will result in a significant change in viscosity.

Shear Rate

When a material is to be subjected to a variety of shear rates in processing or use, it is essential to know its viscosity at the projected shear rates.

Measuring Conditions

Viscometer model, spindle/speed combination, sample container size, sample temperature, sample preparation technique, etc.

Others

homogeneity of the sample, time, dissolved gases - bubbles, previous history - storage conditions and sample preparation techniques

TYPES OF FLOW BEHAVIOR

Newtonian flow

Non-Newtonian flow

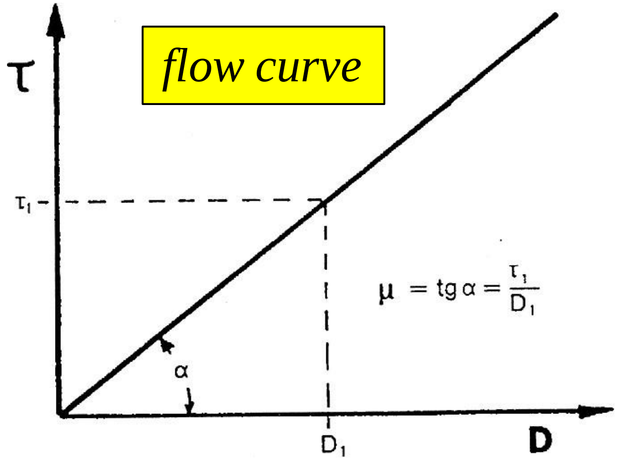
Time independent

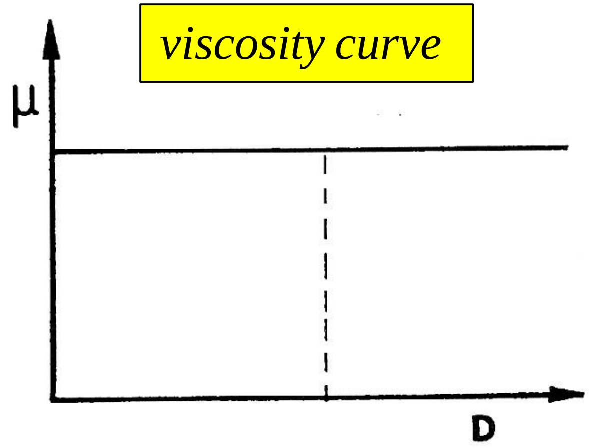
- Pseudoplastic = shear thinning
- Plastic = shear thinning with yield
- Dilatant = shear thickenning

Time dependent

- Tixothropy
- Rheopexy

Newtonian flow





- Direct proportionality between shear stress and shear rate
- Viscosity curve is straight line parallel to *x*-axis (ordinate)
- Viscosity is constant
- Low molecular weight liquids
  water, alcohols, glycerin, and thrue solutions

Non-newtonian flow

Viscosity is not constant changes with shear rate/shear stress
→ ***apparent viscosity***

Power Law (Ostwald-de Waele equation) for liquids

$\tau = K \cdot D^{n}$ $\eta_{app} = K \cdot D^{n-1}$

η_{App}	shear viscosity
D	shear rate
K	Consistency index
n	Power Law Index (Flow index)

Herschel-Bulkely equation for semisolids

$\tau = \tau_y + K \cdot D^{n}$

τ_y	yield stress

Consistency index

Viscosity (or stress) at a shear rate of 1 s^{-1}

The point the viscosity/shear rate curve „hangs from“

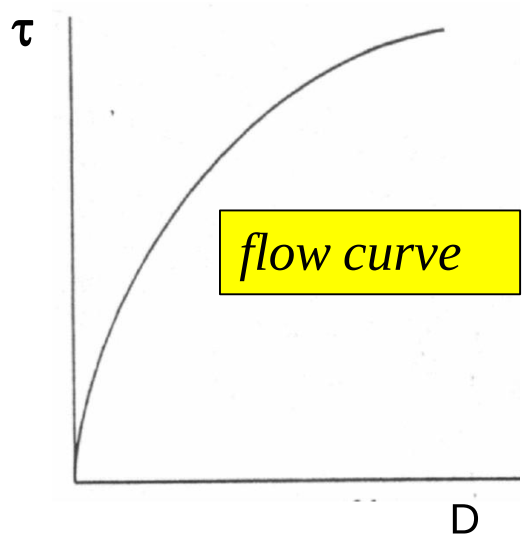
Power Law Index (Flow index)

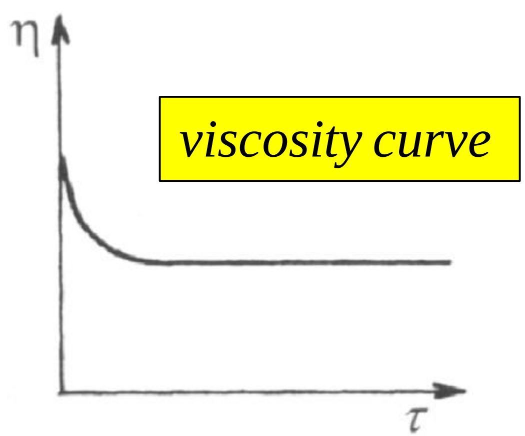
index of the deviation from Newtonian flow

or measure of non-Newtonian-ness

Newtonian flow	$n = 1$
Pseudoplastic flow (shear-thinning)	$0 < n < 1$
Dilatant flow (shear-thickenning)	$n > 1$

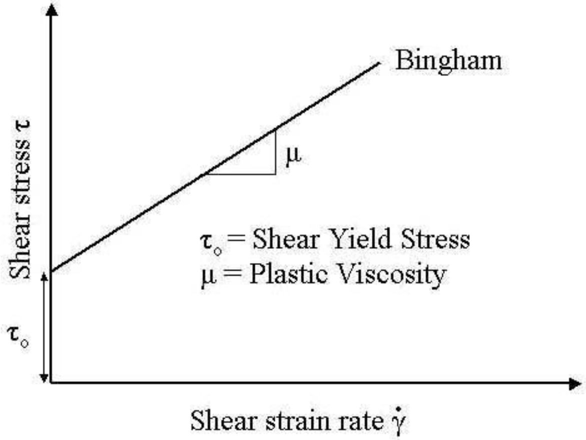
Shear-thinning = Pseudoplastic flow



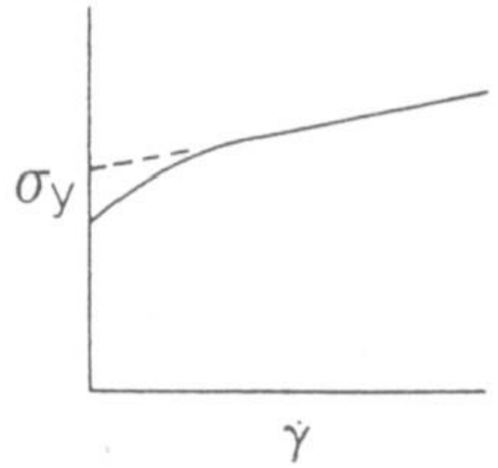


- Rheogram passes throught the origin
- Flow curve is concave towards the shear-rate axis
- Apparent viscosity decreases with increasing shear rate
- Shear rate thinning
- *Low concentration solutions of polymers*

Plastic (Bingham) flow
shear thinning with yield point



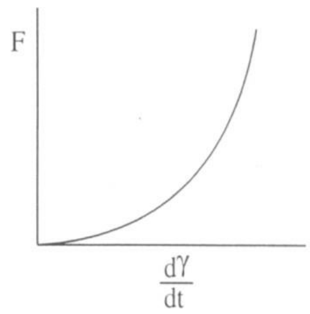
Ideal Bingham flow



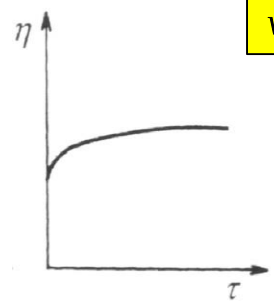
Real Bingham flow

- Rheogram (flow curve) doesn´t lead from the origin
  Yield point - the intercept on the shear stress axis
- Apparent viscosity decreases with increasing shear rate
- hight concentration solutions of polymers, gels, creams, ointments, pastes… semisolid preparations

Shear rate thickenning = Dilatant flow



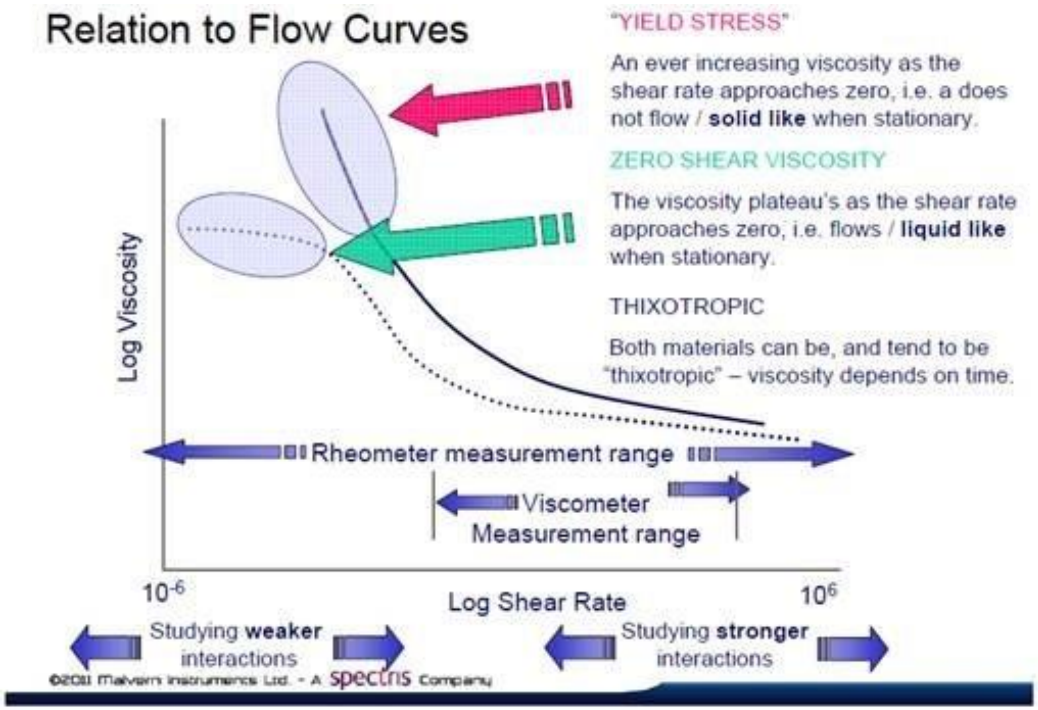
flow curve

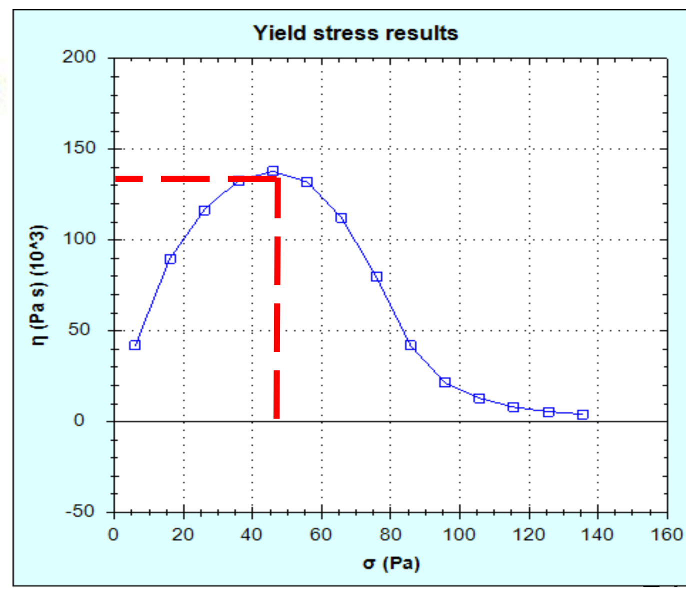


viscosity curve

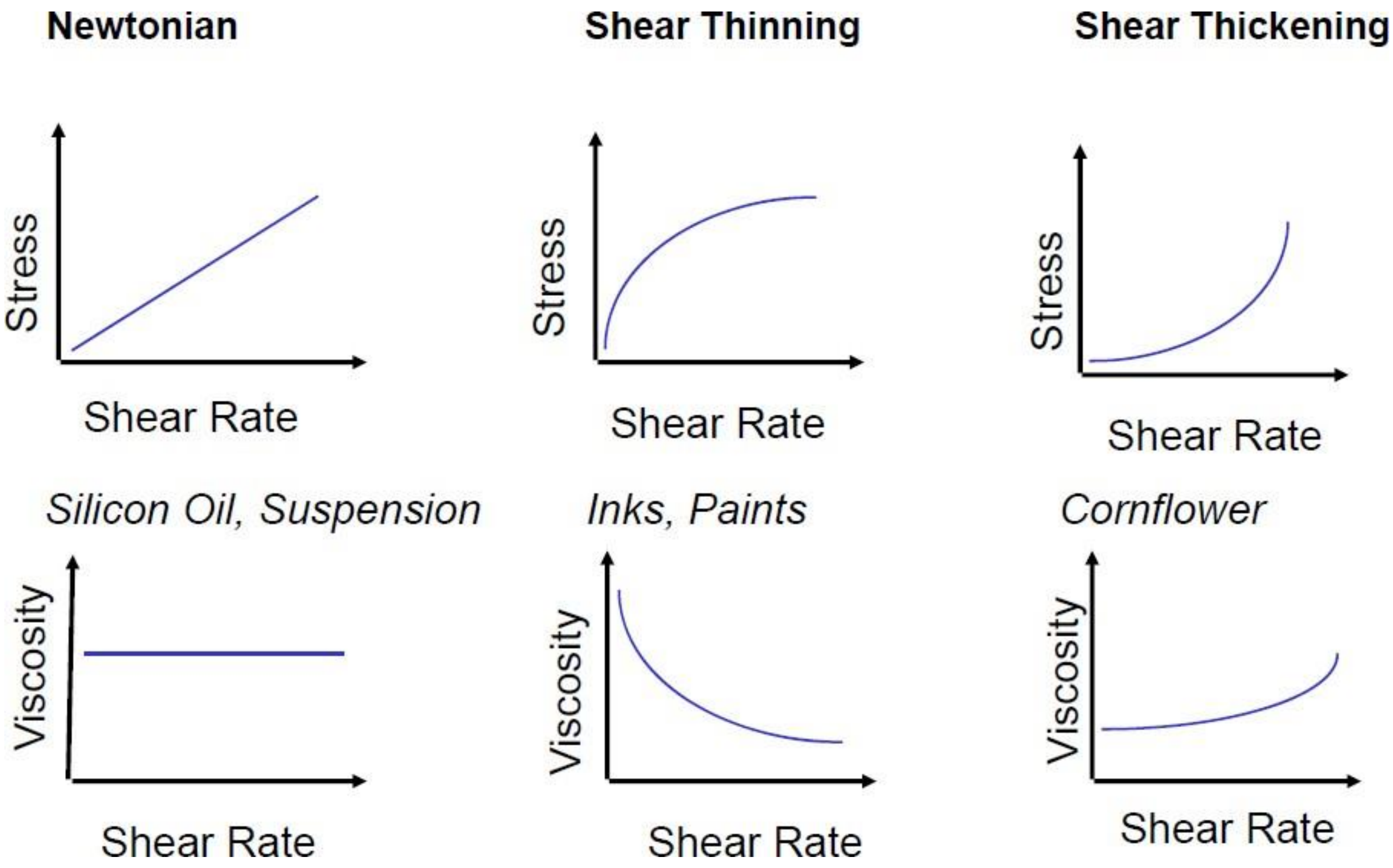
- Rheogram passes throught the origin
- Apparent viscosity increases with increasing shear rate
- Technologically undesirable phenomenon
- *Highly concentrated, deflocculated suspensions*
  insufficient liquid to fill completely all the voids between the particles results in a three-phase mixture - solids, liquids, and usually air; due to the presence of air, the mixture is compressible, and therefore, the more you compress it, the greater the resistance to flow
  Sand that is completely soaked with water also behaves as a dilatant material. This is the reason why when walking on wet sand, a dry area appears underneath your foot.

http://en.wikipedia.org/wiki/Dilatant
http://www.che.udel.edu/research_groups/wagner/stf.html


Relation to Flow Curves
"YIELD STRESS"
An ever increasing viscosity as the shear rate approaches zero, i.e. a does not flow / solid like when stationary.
ZERO SHEAR VISCOSITY
The viscosity plateau's as the shear rate approaches zero, i.e. flows / liquid like when stationary.
THIXOTROPIC
Both materials can be, and tend to be "thixotropic" – viscosity depends on time.
Log Viscosity
Rheometer measurement range
Viscometer Measurement range
10-6
Log Shear Rate
106
Studying weaker interactions
Studying stronger interactions
©2011 Malvern Instruments Ltd. - A spectris Company


Yield stress results
200
150
100
50
0
-50
η (Pa s) (10^3)
0
20
40
60
80
100
120
140
160
σ (Pa)

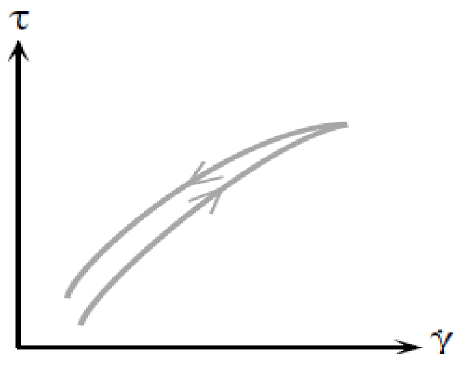
Overview of the flow types



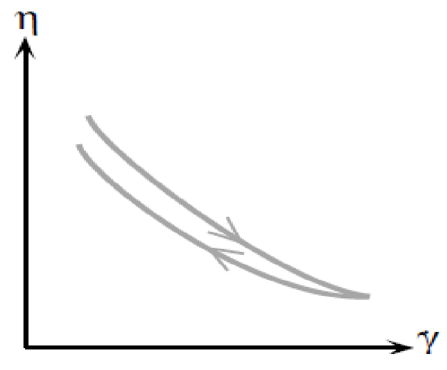
Thixotropy

- Time dependent flow
- Reversible loss of viscosity, as a function of time, at a constant shear rate
- Isothermal gel-sol-gel transformation
- The mechanism: breakdown and re-forming of the structure
- Rheogram: thixotropic hysteresis loop
- Very often, and technologically convenient

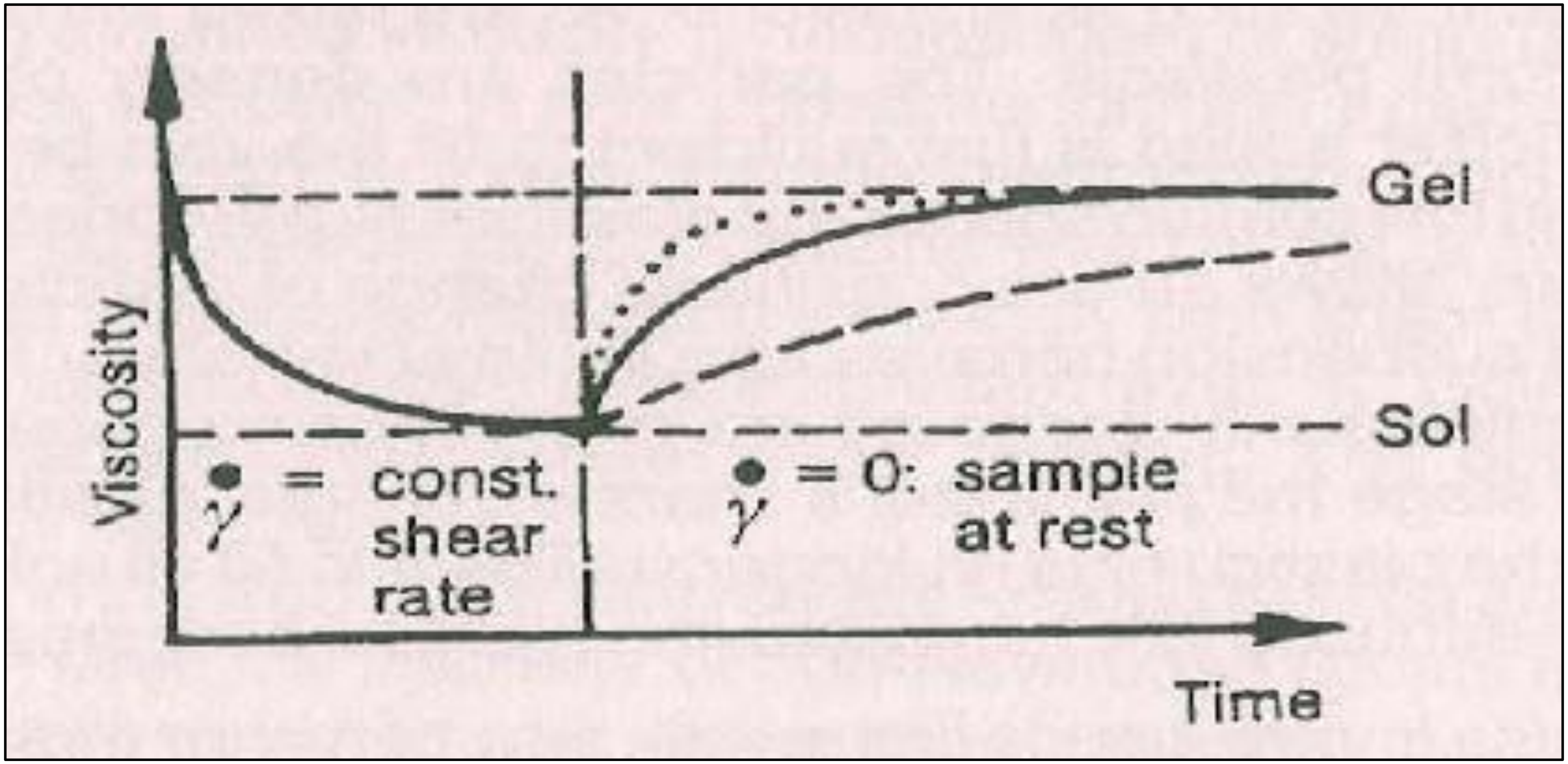
Flow curve(s)



Viscosity curve(s)

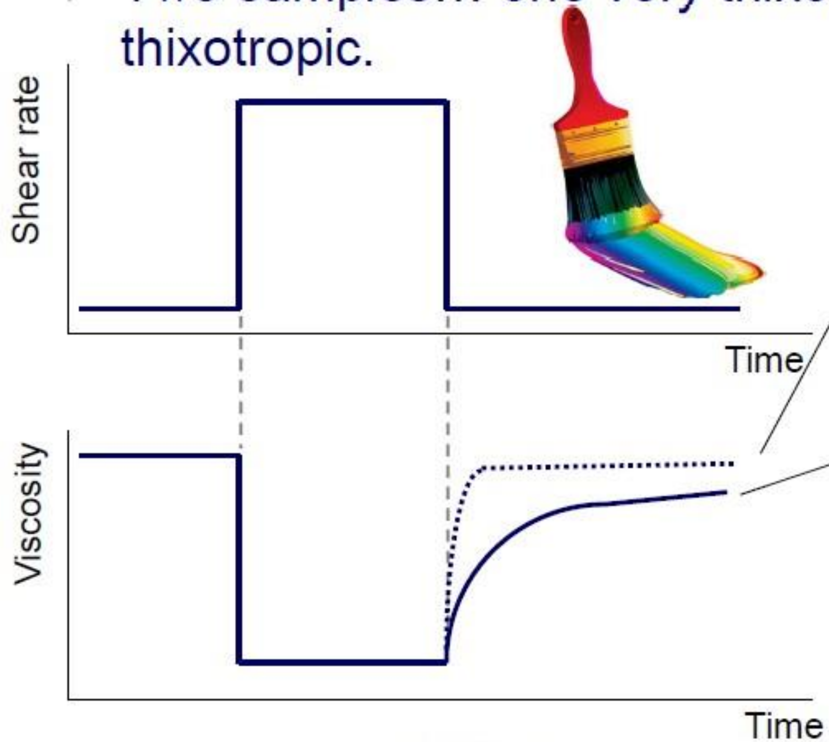


Viscosity – time - curve



Thixotropic Example

- Two samples… one very thixotropic, one not so thixotropic.

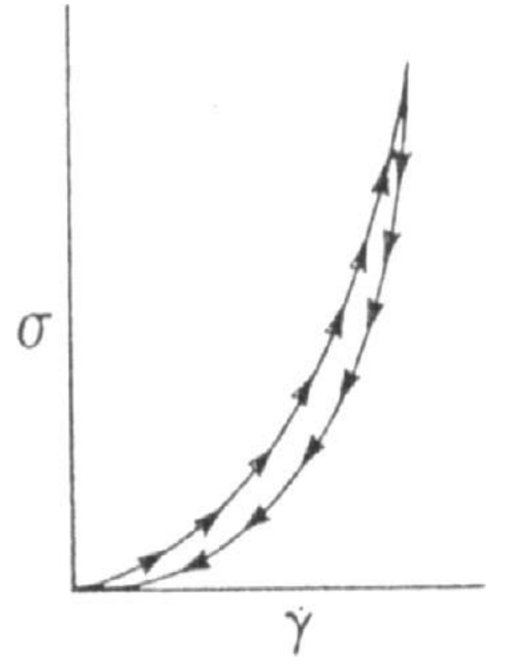


Bad paint – leaves brush marks.
Rebuilds too thick too quickly.

Good paint – leaves smooth finish.
Rebuilds quite slowly. Enough time to allow ridges to smooth out.

Rheopexy

- Inverse to thixotropy
- reversible increase of viscosity,
  as a function of time,
  at a constant shear rate
- Isothermal transformation sol-gel-sol
- Rare, undesirable phenomenon



Reasons for making rheological measurements

- To quantitate the effects of time, temperature, ingredients, and processing parameters on a formulation
- To describe quantitatively the flow behavior of material for the purpose of quality control
- To measure the ease of product dispensation from a tube, bottle, or jar
- To measure spreadability
- To understand the fundamental nature of the system

Capillary viscometers

- The time taken for a known volume of liquid to flow through a capillary tube is measured
- Precision instruments - good temperature control is essential (20±0.01°C)

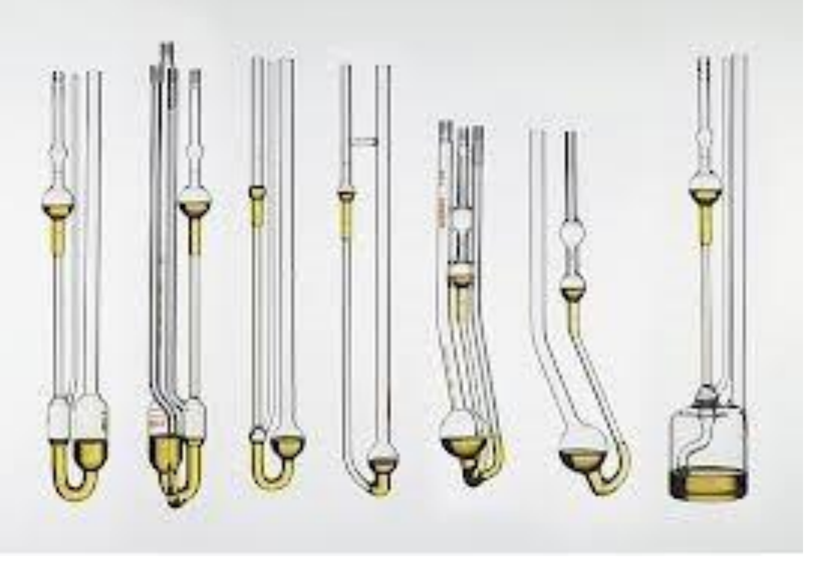
Kinematic viscosity ν [$mm^2 s^{-1}$]

$$\nu = k\,t$$

Dynamic viscosity η [mPa.s]

$$\eta = k\rho\,t$$

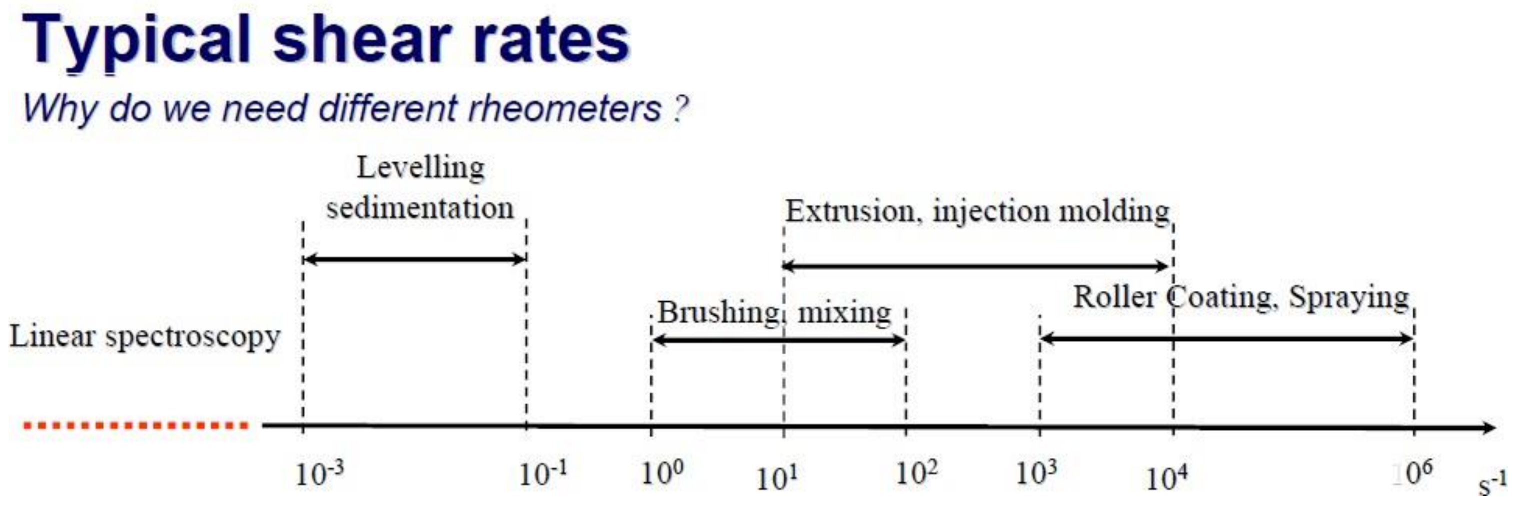
k	constant of the viscometer
ρ	density of the liquid
t	flow time



Rotational rheometers/viscometers

Viscometry: shear rate range from 10^{-1} to 10^{1} s^{-1}
Rheometry: shear rate range from 10^{-3} to 10^{3} s^{-1}

Viscosity of Newtonian (shear-independent viscosity) or non-Newtonian liquids (shear dependent viscosity or appatent viscosity)



Absolute rotational rheometers

- The flow in the measuring geometry is well defined
- The measurements result in absolute viscosity values, which can be compared with any other abolute values

Relative spindle viscometers

- The flow in the measuring geometry is not defined
- The measurements result in relative viscosity values, which cannot be compared with abolute values or other relative values if not determined by the same relative viscometer method

- *CS-rheometers (controlled stress)*
  stress is set
  and resulting strain is measured
- *CR-rheometers (controlled rate)*
  share strain si set and resulting stress is measured

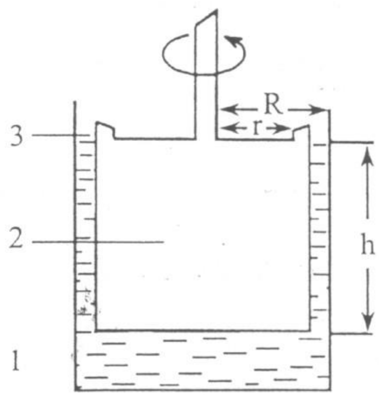
- *Searl´s type*
  inner (upper) spinning part
- *Couett´s type*
  outer cone or lower plate is spinning

Spindle viscometers
(relative viscometers)

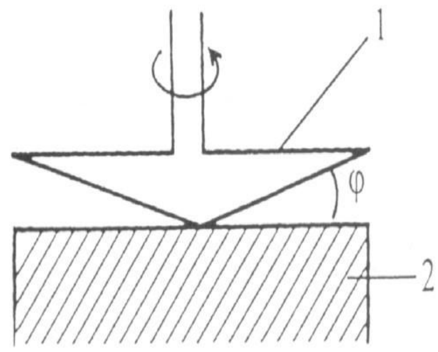
- Speed of the spindle from 0.3 to 100 RPM
- 3 types (L, R, H) for various extent of viscosity
- Set of the standard spindles (disc, cylinder, rod) (4 or 6)

Rotational rheometers

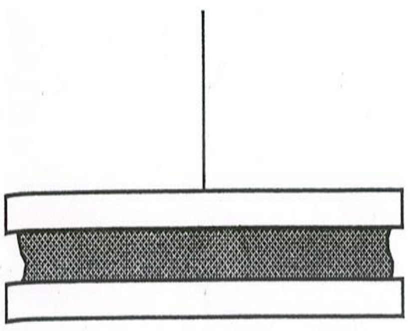
(absolute viscometers arrangement)



2 concentric cylinders (cup&bob)



cone-plate

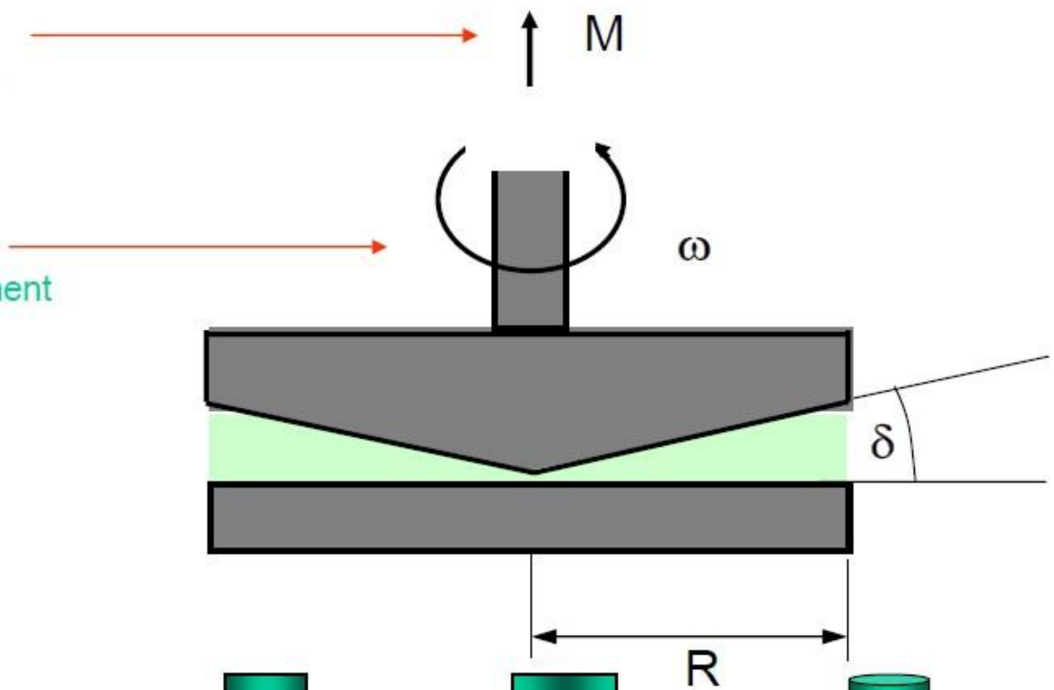


2 parallel plates

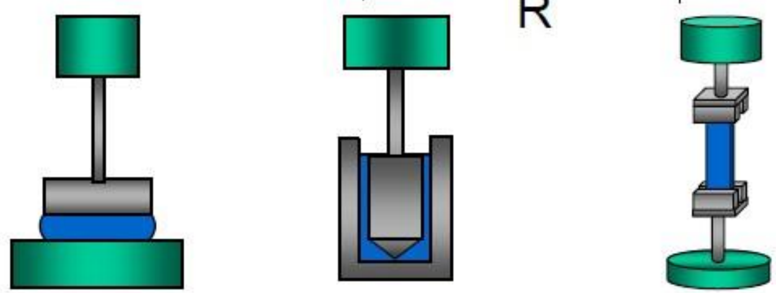
Choice of Geometry: From Fluids to Solids

Apply Torque / Measure Torque

Measure Displ. Apply Displacement



*Rule of Thumb for dispersions: Gap Size > 10 * D90*



Parallel Plates **Cup&Bob** **Solids Fixture**

- the higher the viscosity, the smaller the geometry
- the higher the shear rate, the smaller the gap.

Rotational rheometers

Penetrometers

- Measuring of the consistency of semisolids
- A cone or needle of known weight is allowed to fall through the test material
- The depth of penetration in a fixed time is inversely related to the consistency (0.1 mm)
- Consistency (technical quantity, no units)
- (25 ±0,5) °C

Ph. Eur. Paraffin, White Soft

Consistency (*2.9.9*) *60 to 300*

(depth of penetration 6 to 30 mm)

Thank you for your atention

http://en.wikipedia.org/wiki/Viscosity
http://en.academic.ru/dic.nsf/enwiki/415268
http://www.medicinescomplete.com/mc/rem/current/c37.htm