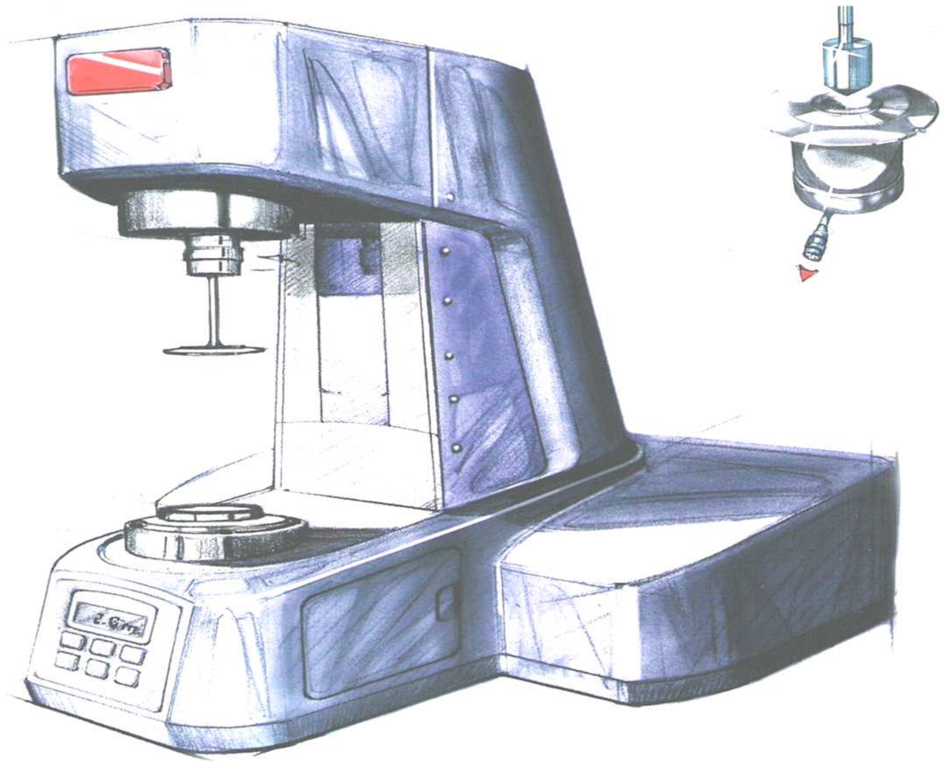
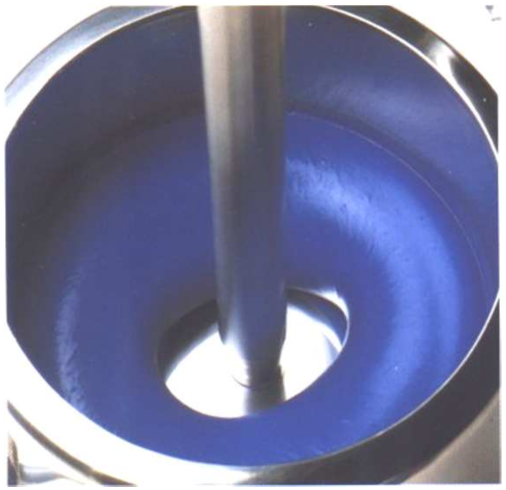


Rheology of thixotropic coatings

Janez Virc

- There are many stress which effects on coating during the **production, storage and application.**

- **It is important that we know, how will our product behave, when it is effected with different deformation and that is what we can find out from rheology tests.**

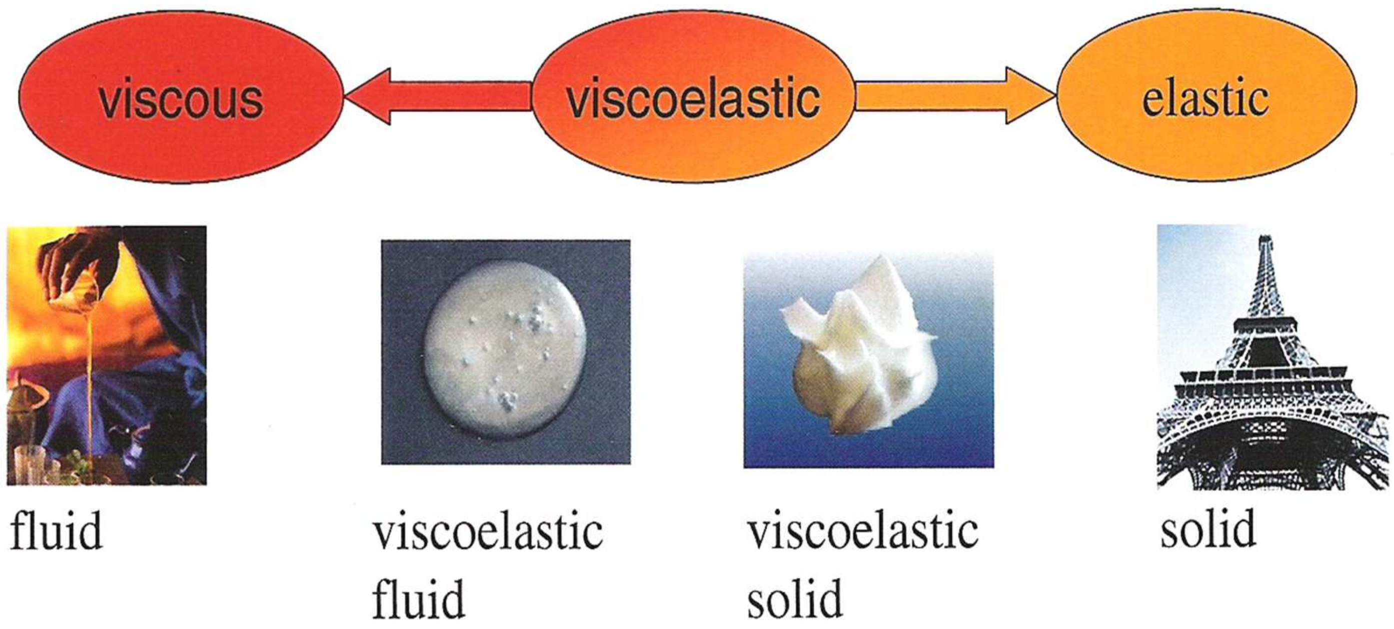


Rheology

- Science of deformation and flow
- Branch of physics and physical chemistry
- Describes the deformation of a body under the influence of stresses
- Flow behavior of liquids and also deformation behavior of solids

Rheology

describes the deformation and flow behavior

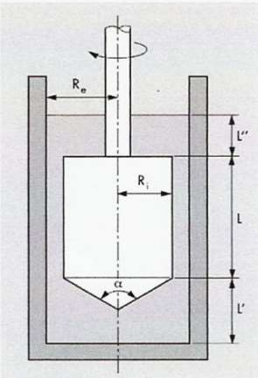


Use of rheology in paint industry

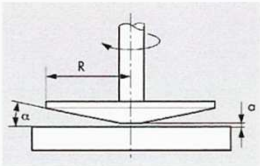
- We can predict how will coating behave during the application. (sagging, levelling)
- Rheology values depends from the use of coating (will it be for decorative use or industrial, application technic brush, roller or spraying)
- Stability and interaction in coatings
- Quality control
- Rheology is also very useful for production plan, it can be calculated what is the need it energy for stirring of different process operation

Rheometer

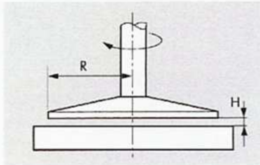
- ***Rheometry is the measuring technology***
- ***Used to determine rheological data***



<u>coaxial cylinders</u>:
for low-viscosity liquids,
not for pastes (air bubbles)



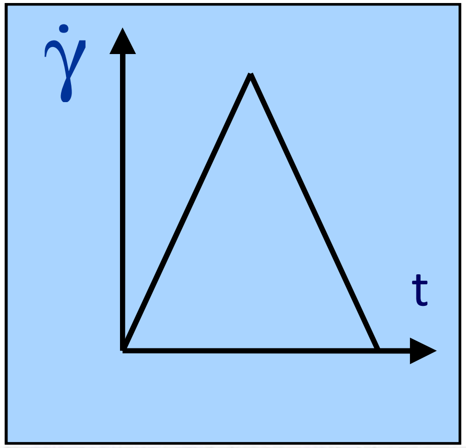
<u>cone-and-plate</u>:
for liquids;
for dispersions
only when
the particle size
< 5µm

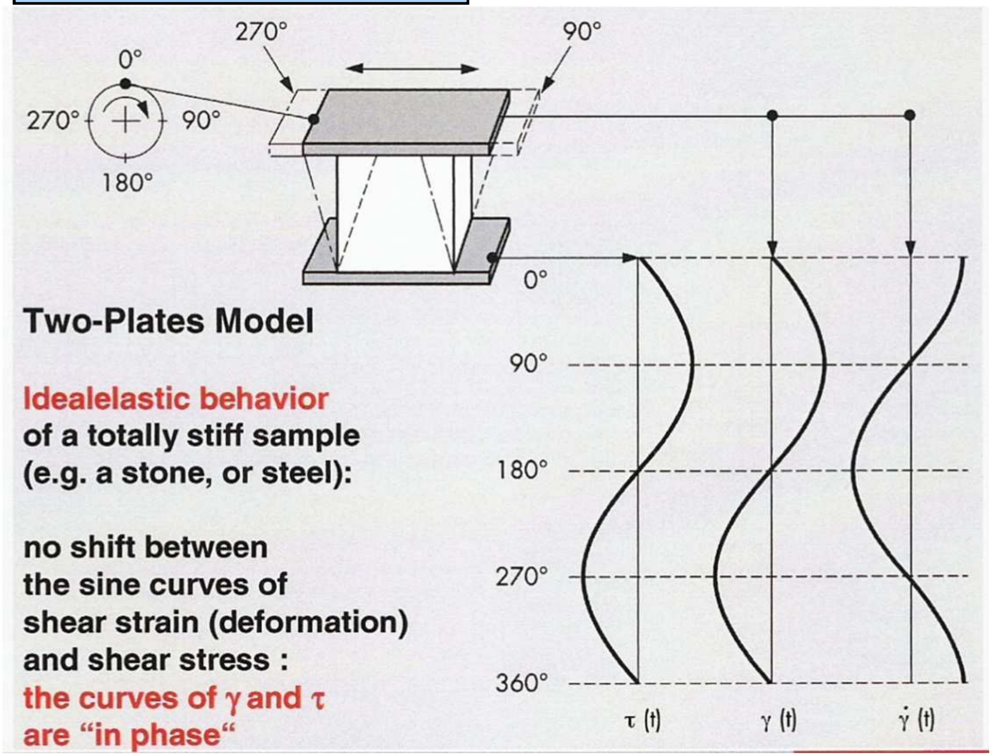


<u>parallel-plates</u>:
useful for
gels, pastes,
soft solids,
polymer melts

- Coaxial cylinder for temperature dependence samples, for fast drying samples
- Cone/Plat, more easy to clean, gap is fix
- Plate/Plate for samples with bigger participles, space between gaps is not fix

- With flow tests structure of the sample is destroyed
- With oscillatory tests structure of the sample is not destroyed



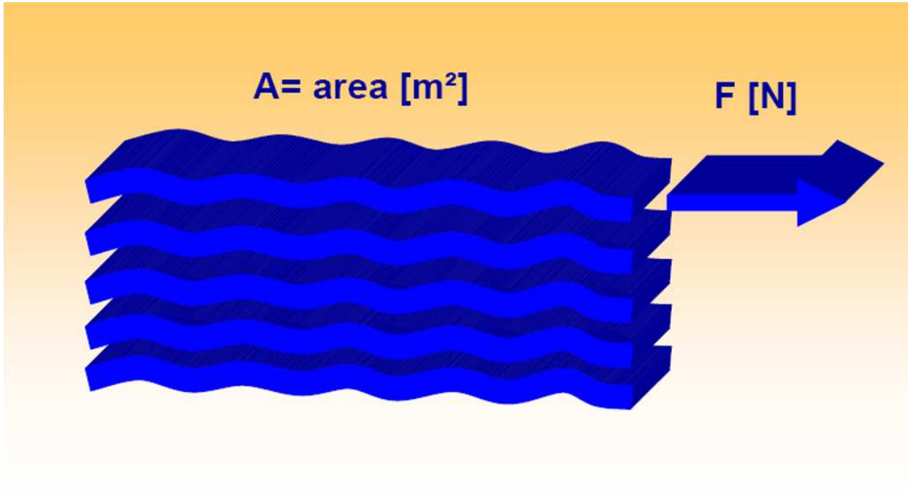


- η – viscosity (flow test)
- G´- storage modulus (oscillatory test)
- G˝- loss modulus (oscillatory test)
- G’, G’’ and η most important Rheology parameters for decorative coatings

- η – viscosity,

- For paints viscosity is important from the point of application
- For user friendly viscosity must be between 0,4 and 0,9 Pas, when shear stress is 1000 s^{-1} (brush)
- If viscosity is more than 0,9 Pas in practice this mean that application with brush will be harder to put on the surface, we will need more force
- By low shear rate (0,1s^{-1}) (storage) is important that viscosity is high (from 7 to 11 Pas depends from the % of pigment in the formulation) to prevent sedimentation

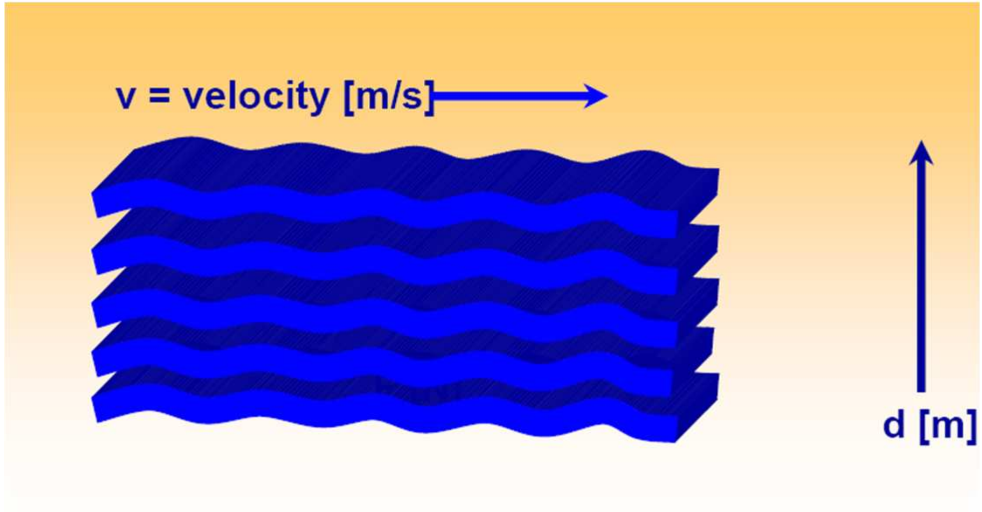
Shear stress



τ = shear stress = F/A [N/m²]

$$\eta = \frac{\tau}{\dot{\gamma}} \quad \left[\frac{Pa}{1/s}\right] = \left[Pas\right]$$

Shear rate



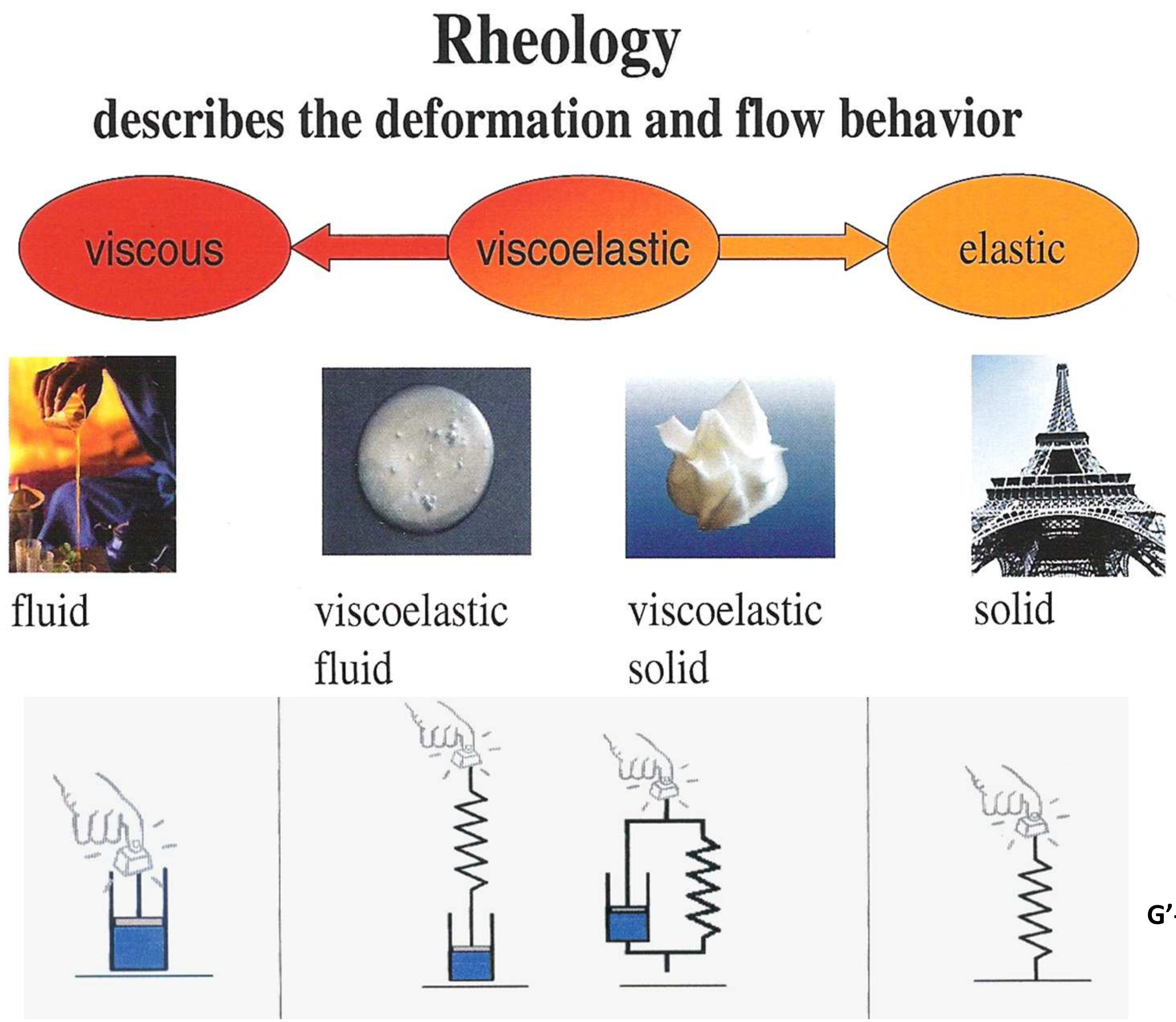
$\dot{\gamma}$ = shear rate = v/d [1/s]

- shear rate is velocity gradient of the sample

- G'- storage modulus
- G''- loss modulus

- Elastic behavior when G'>G'' by low frequency sample has an structure (gel character). For colors this mean that pigment will not sediment
- Viscous behavior when G''>G' by low frequency, sample shows the character of liquid. For colors this means that pigment will sediment

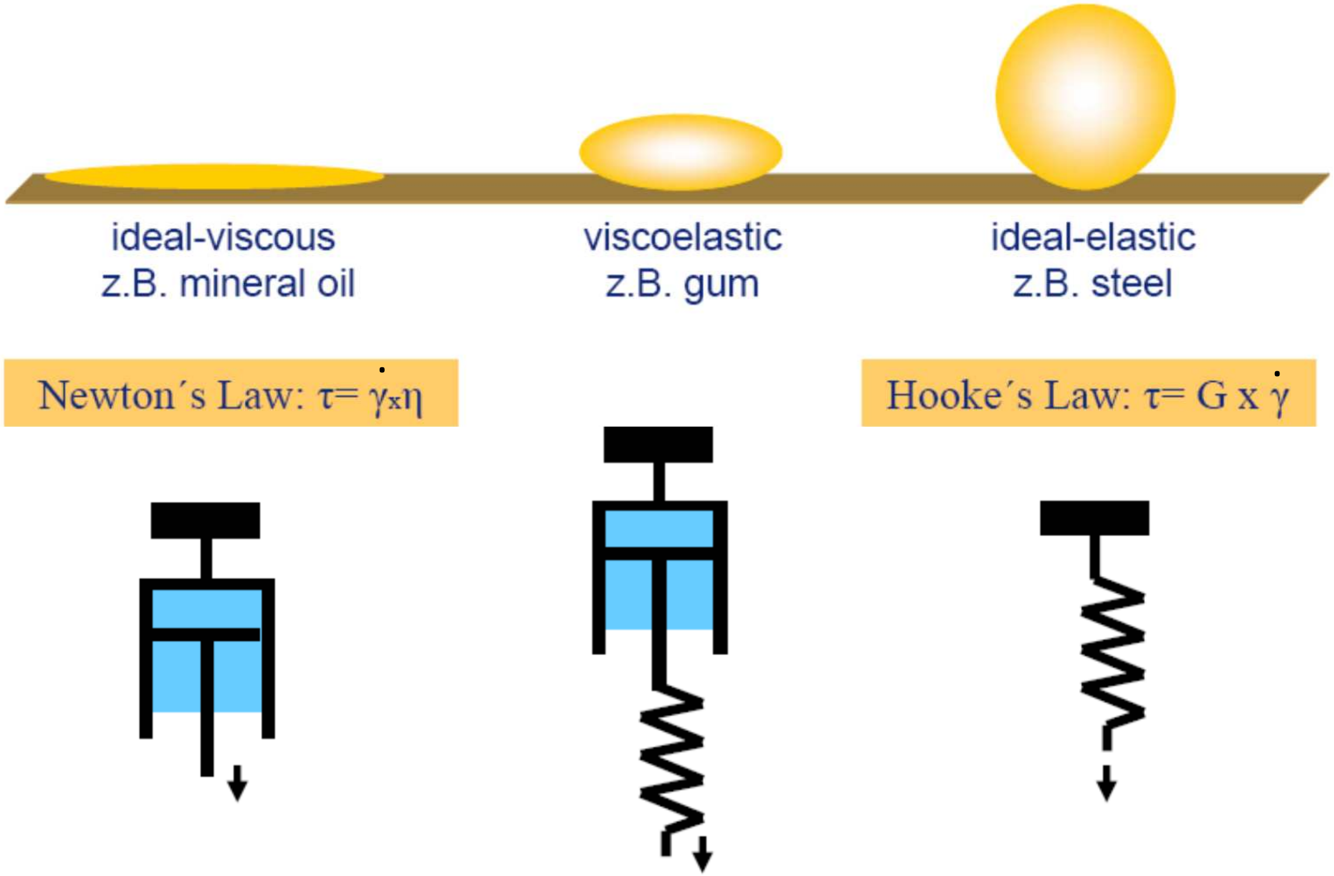
Coating viscoelastic fluid



G''- loss modulus

G'- storage modulus

Coating viscoelastic fluid



Maxwell model: $$\dot{\gamma} = \frac{\tau}{\eta} + \frac{\frac{d\tau}{dt}}{G}$$

Liquids can be put in two groups

- Newtonian liquids

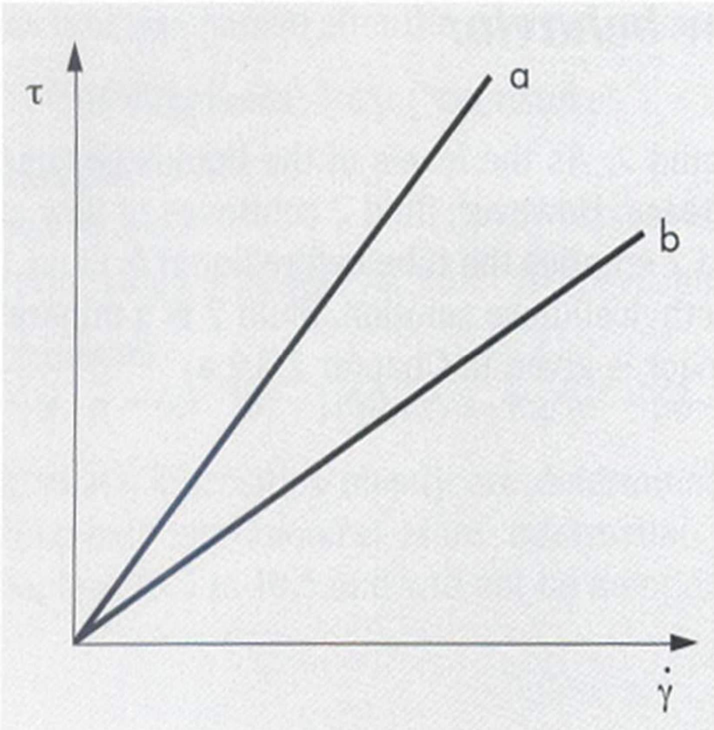
 - idealviscous materials (water, solvents, mineral oils)

- Non-Newtonian liquids

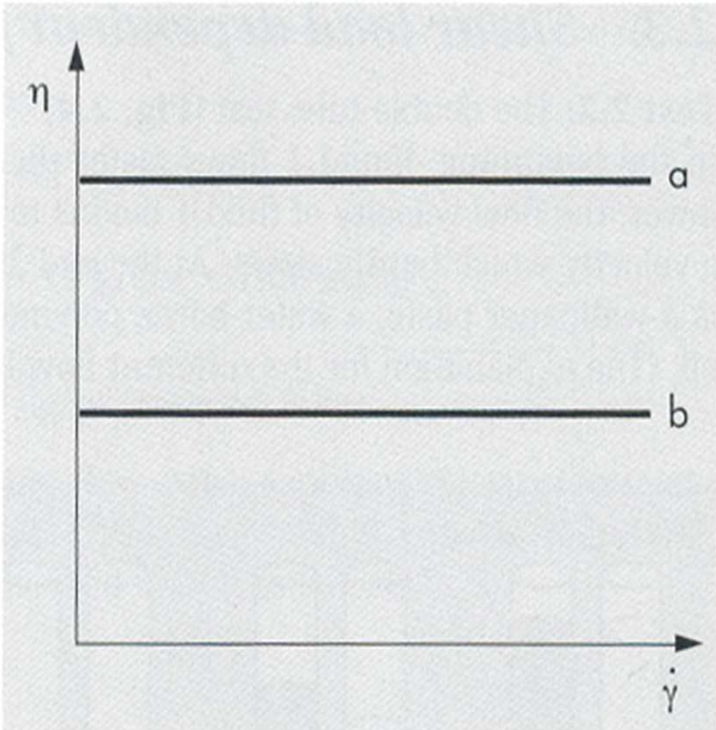
- Pseudoplastic flow behavior
- Dilatant flow behavior
- Thixotropic flow behavior
- Rheopectic-anti-thixotropic flow behavior

Viscoelastic flow behavior

Idealviscous materials

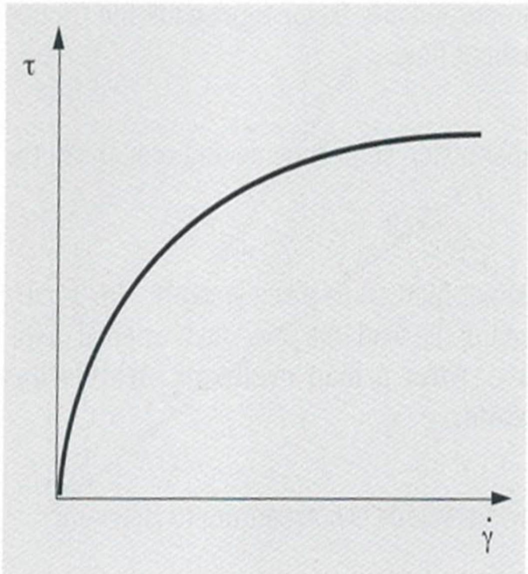


Flow curves of two idealviscous fluids

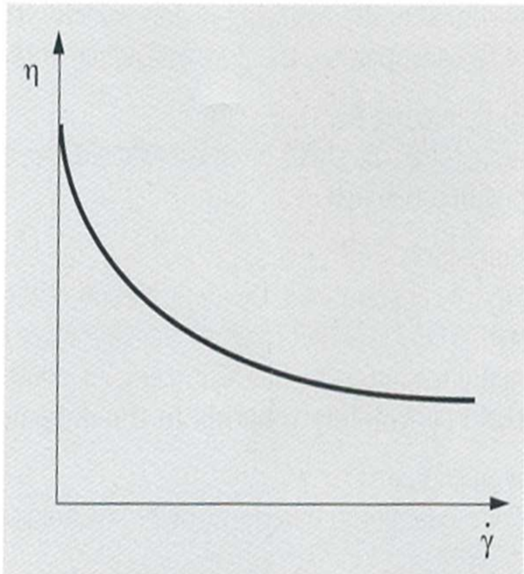


Viscosity curves of two idealviscous fluids

Pseudoplastic flow behavior

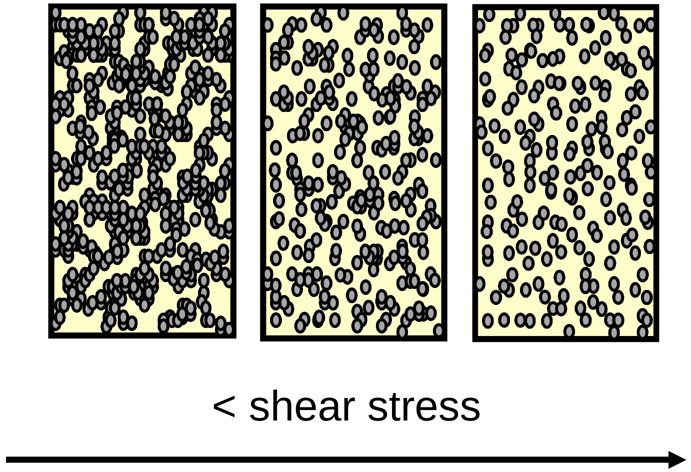


Flow curve of a shear-thinning material

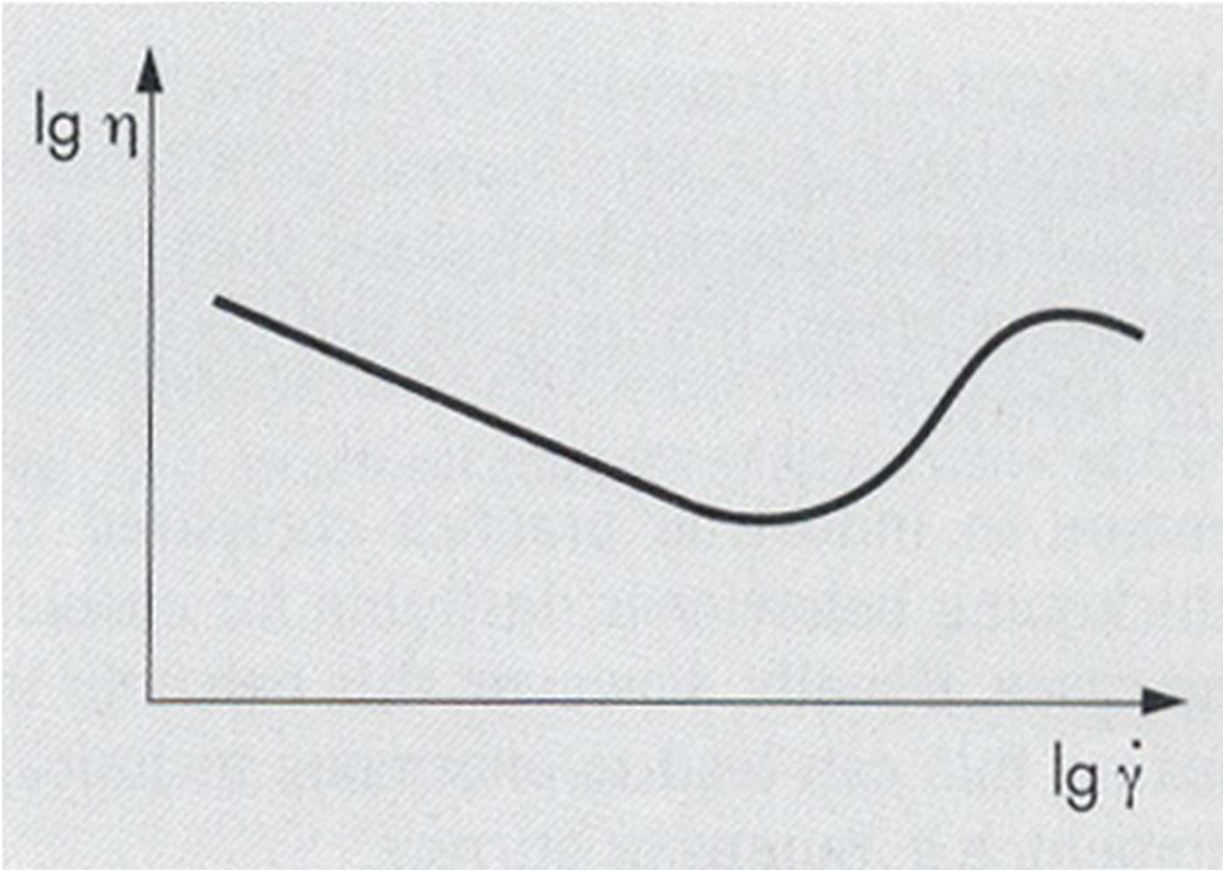


Viscosity curv eof a shear-thinning material

Pseudoplastic behavior when shear stress is raising

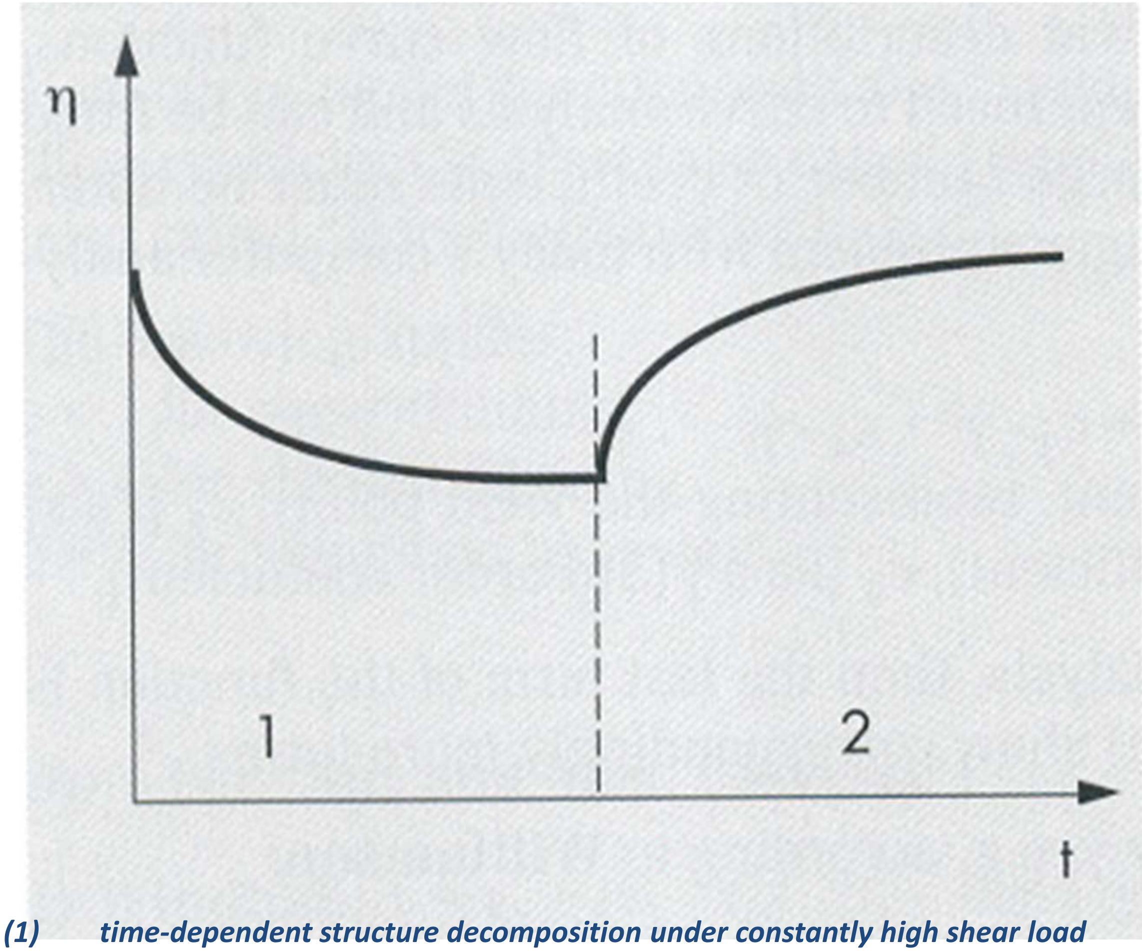


Dilatant flow behavior



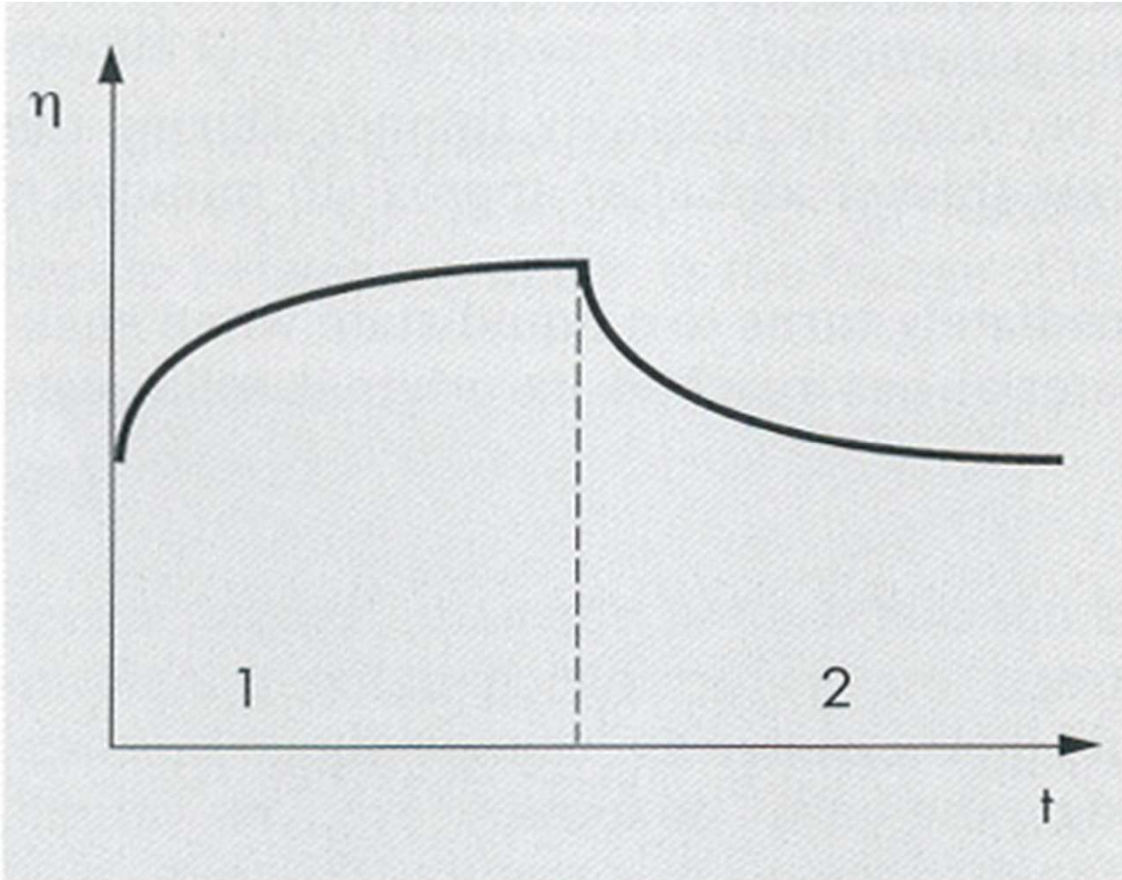
Viscosity curve of a shear-thickening material, showing a dilatant peak

Thixotropic flow behavior



(1) time-dependent structure decomposition under constantly high shear load
(2) Time-dependent structural regeneration when at rest
Haigh solid

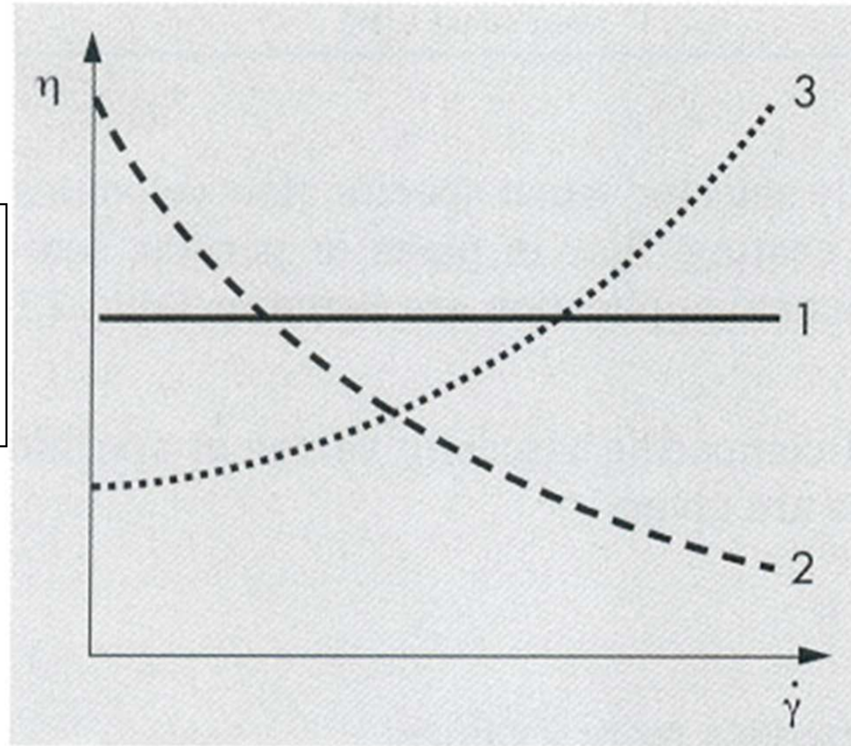
Rheopectic – anti – thixotropic flow behavior



(1) time-dependent increase in structural strength under constantly high shear load
(2) Time-dependent decrease in structural strength when at rest
High solid

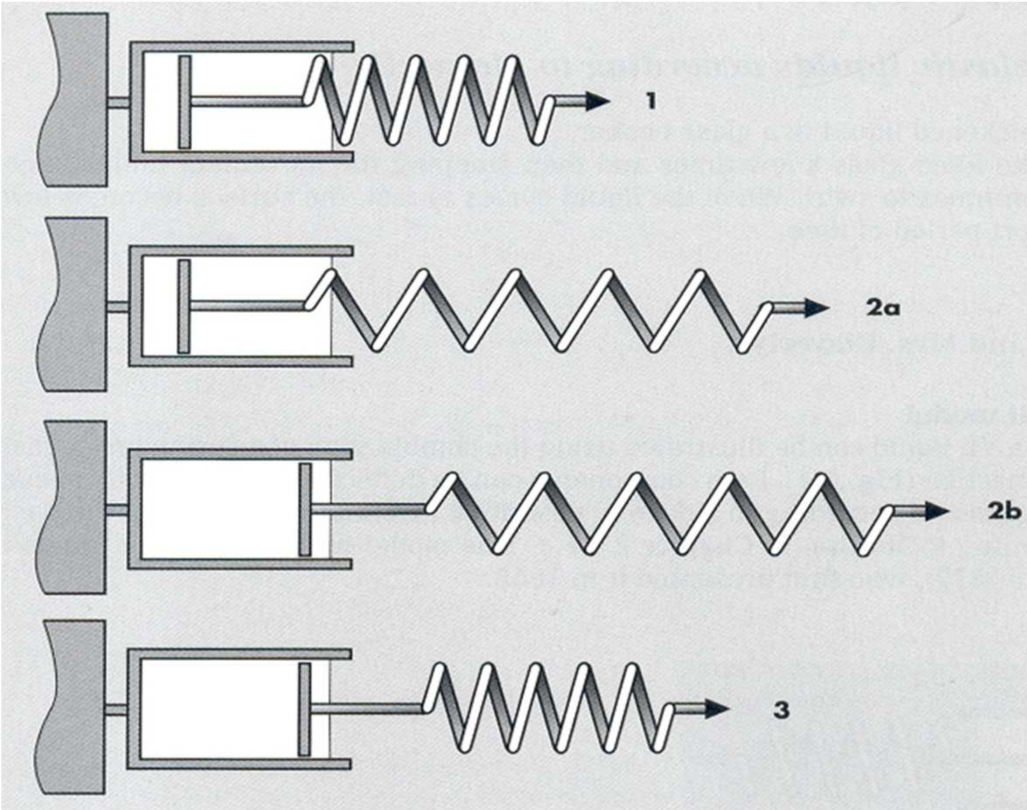
Main three options of rheological behavior

- Idealviscous - Newtonian liquids - 1
- Pseudopalstic fluid - 2
- Dilatant fluid - 3



Viscosity curves

Maxwell model



Deformation behavior of a viscoelastic liquid

- Viscoelastic flow behavior
- Shows elastic and viscous behavior
- Hooke‘s law and Newton‘s law
- They can behave pseudoplastic, dilatant, **thixotropic** or rheopectic

Viscoelastic thixotropic behavior:

- Sedimentation
- leveling

- Decorative coatings
- VOC (volatile organic compounds)
- 2007 limit 400 g/l VOC; 2010 300 g/l VOC; work on solventborne products (enamels)

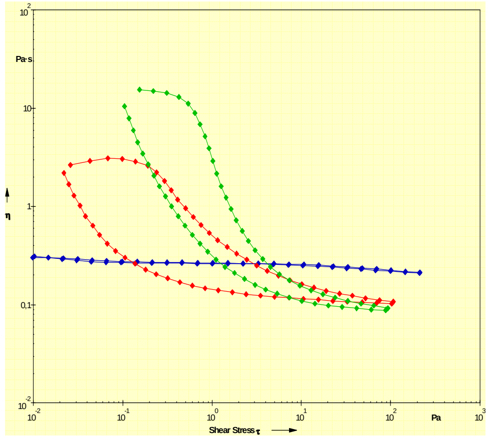
Reason for solventborne:

- Waterborne coatings are not the same quality
- Price
- Future normally without solventborne paints in decorative

Which is the best way to predict rheology behavior

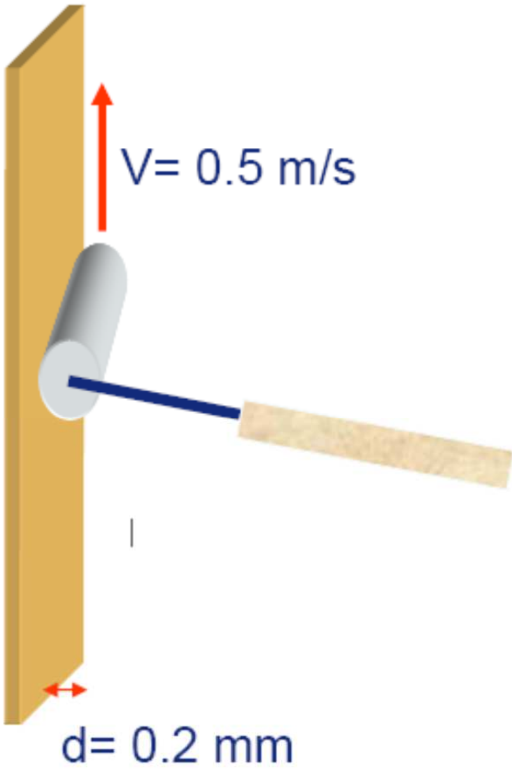
Measurements of rheology many samples

Analize and changing recipis



Checking with application

Shear Rate-Roller Application



Assumption:

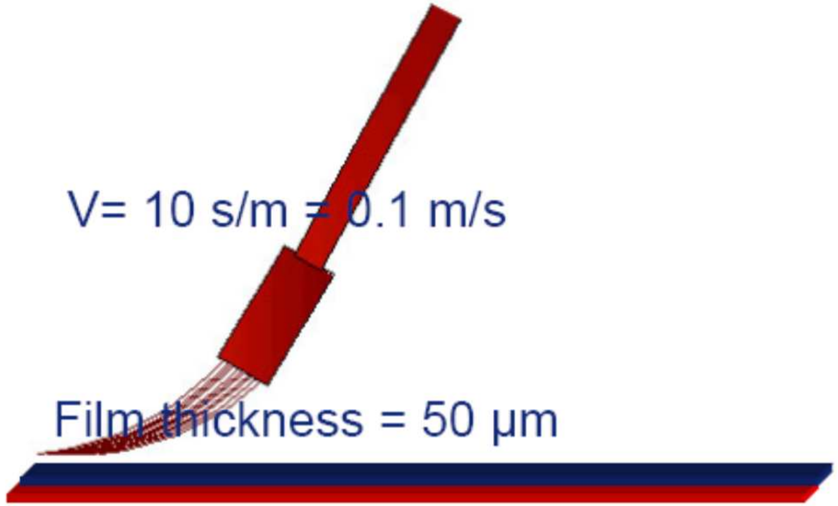
linear velocity (V) = 0.5 m/s

d = 0.2 mm

$$\text{shear rate} = \frac{V}{d} = \frac{0.5\ \text{m/s}}{0.0002\ \text{m}}$$

shear rate = 2500 1/s

Shear Rate-Brush Application

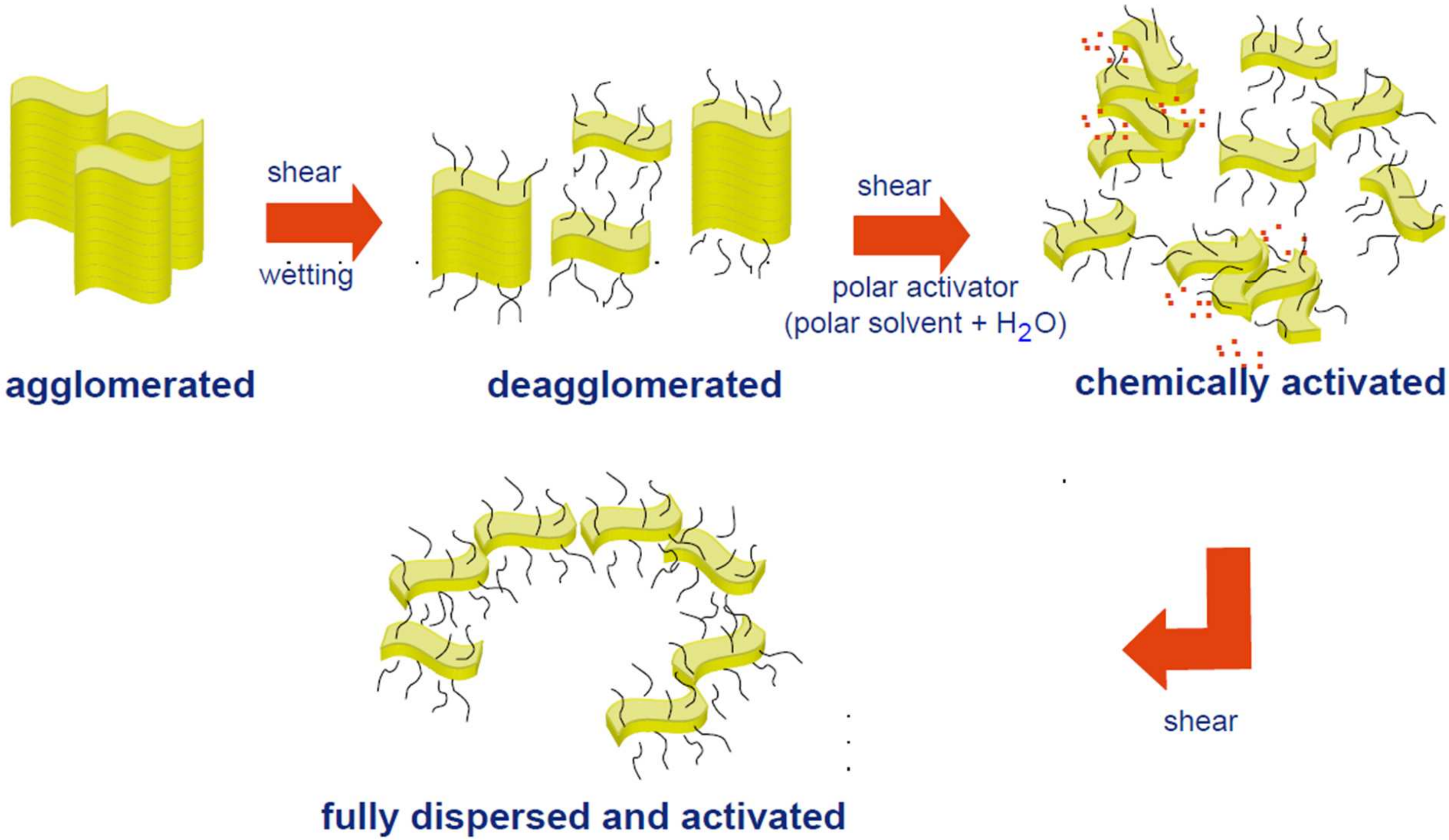


$$\text{shear rate [1/s]} = \frac{0.1 \quad \text{m}}{5^{*}\, 10^{-5} \quad \text{m s}} = 2000\ \text{s}^{-1}$$

Coatings main raw materials

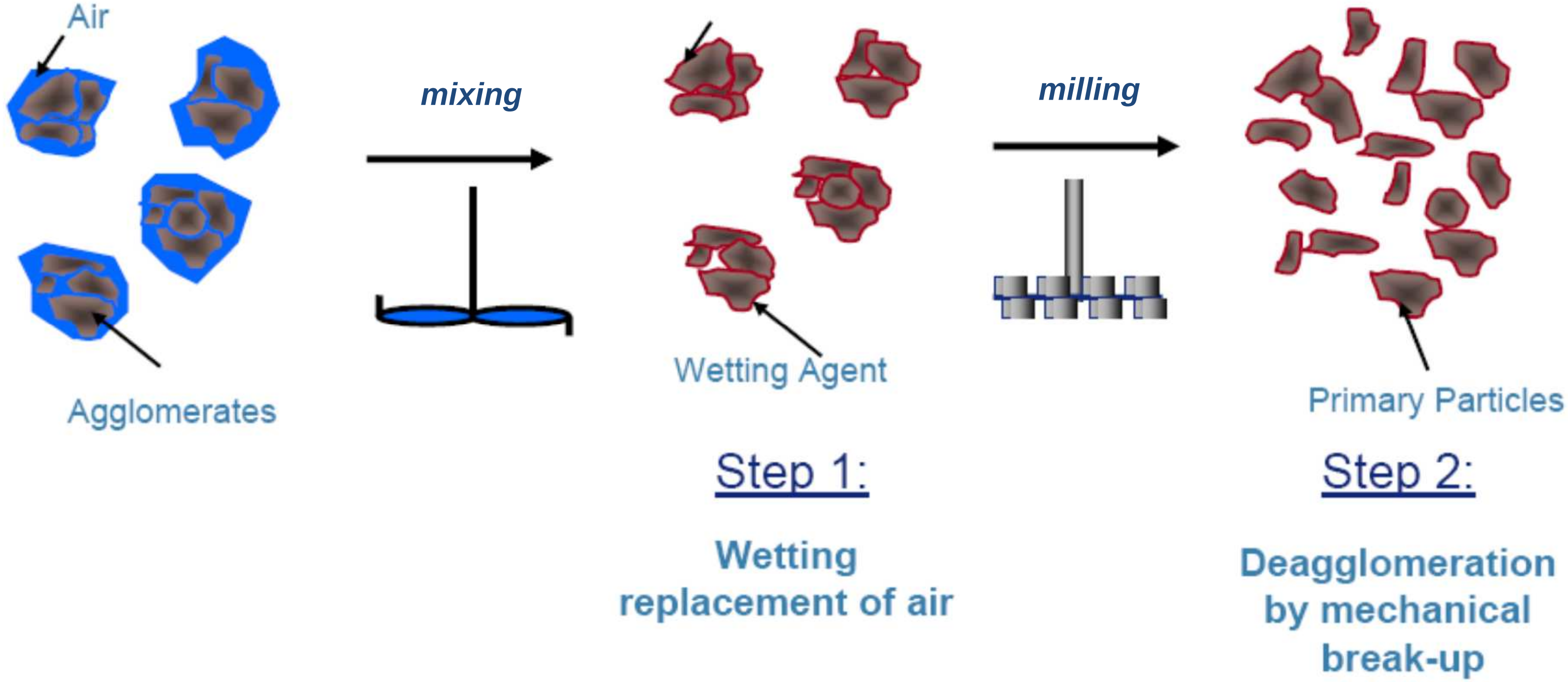
- Resin
- Additives
- Pigment
- Dryers
- Solvent

Gel Development

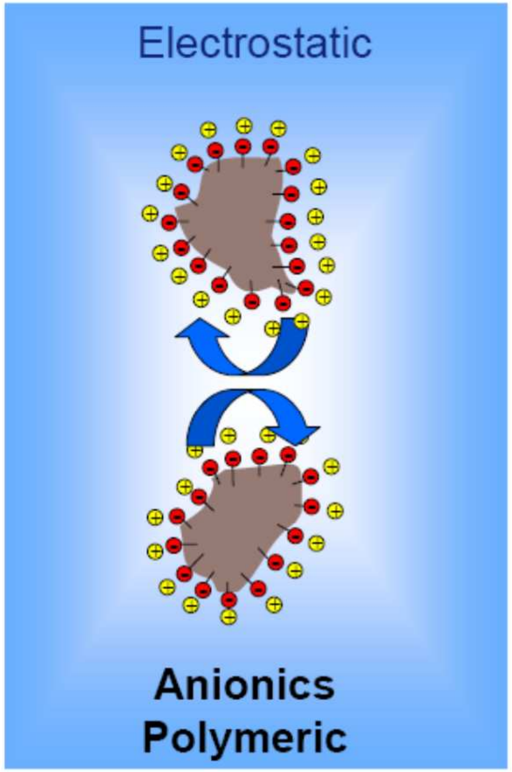


- *Reological additive which improves thixotropic behavior to the fluid (colour)*

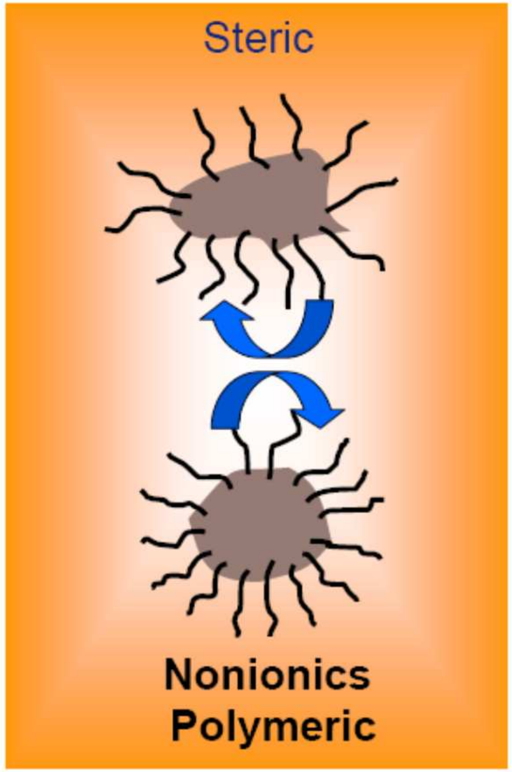
Mechanisem – Wetting&Deagglomeration



Stabilisation



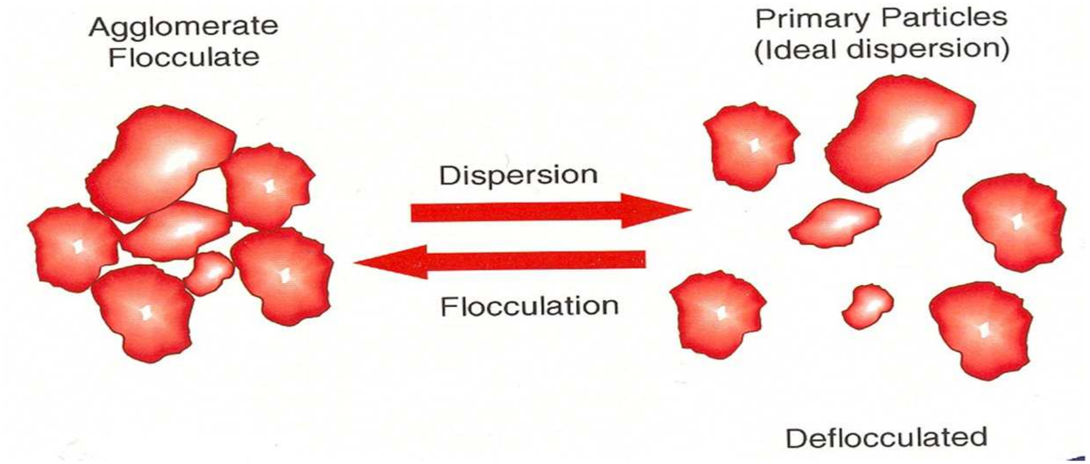
Only in polar medium – e.g. water



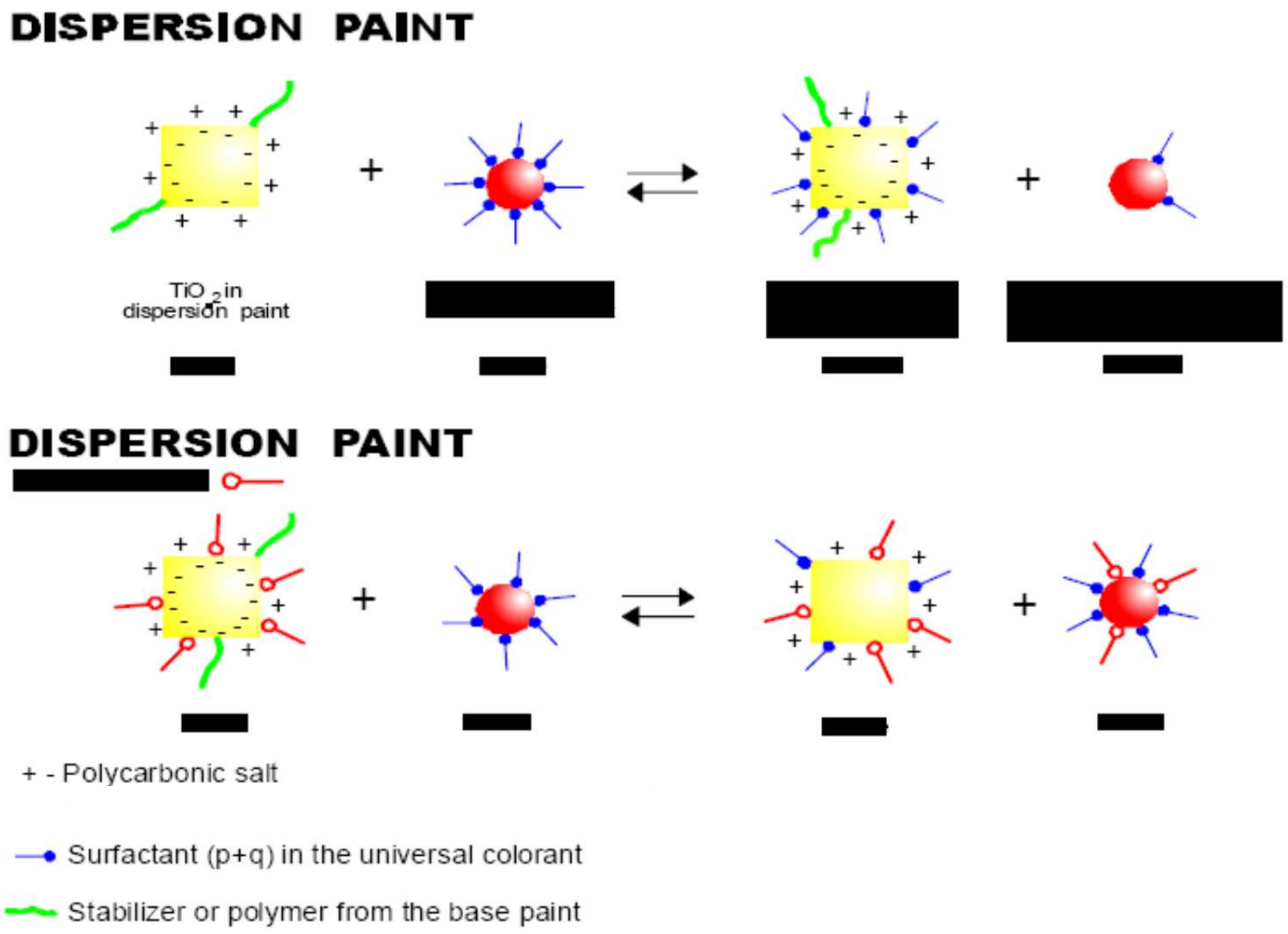
- *Steric more stable*
- *Expensive*

Colour Development Problem

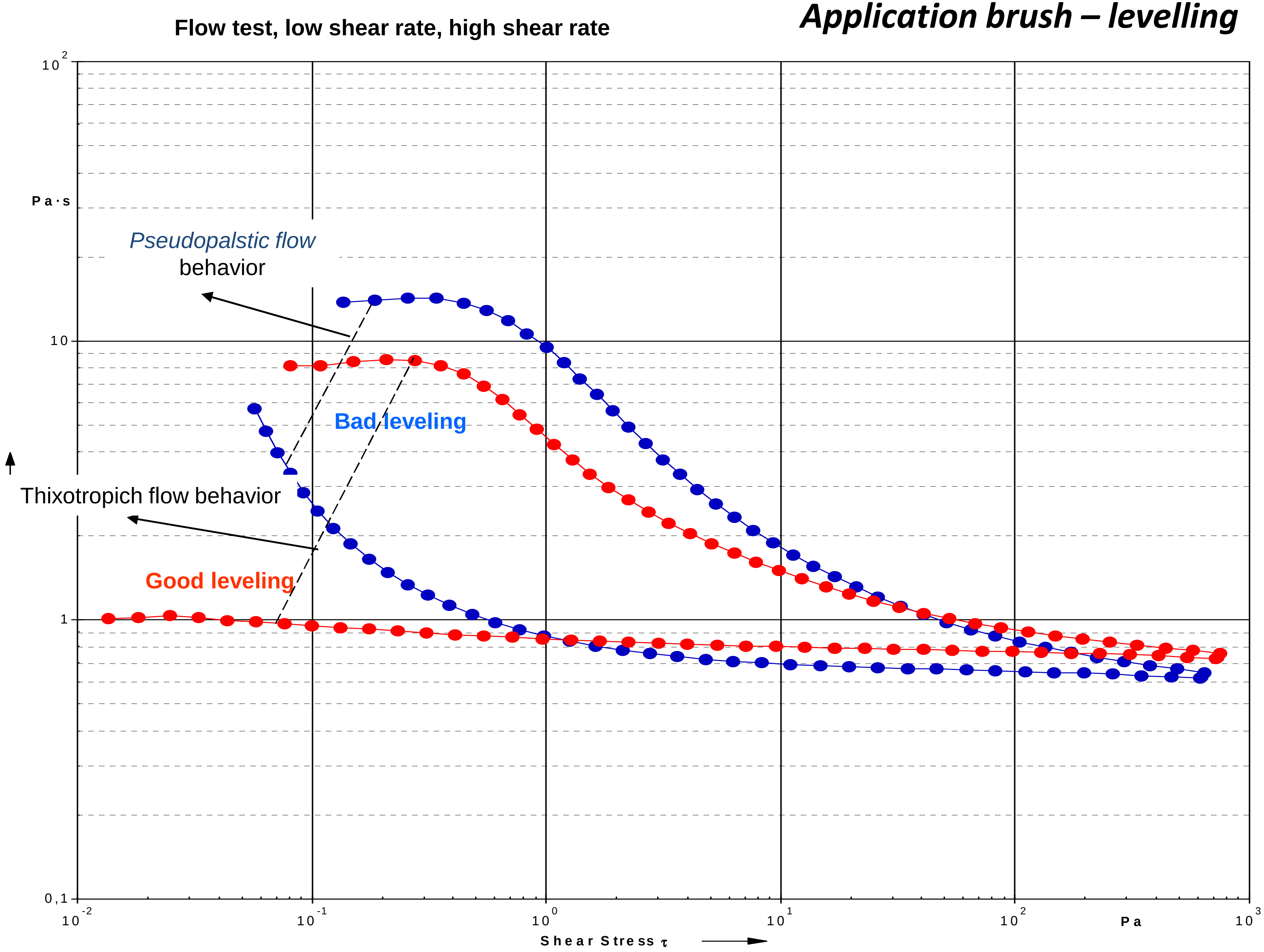
- Compatibilty problems
- Dispersing agent
- Additives



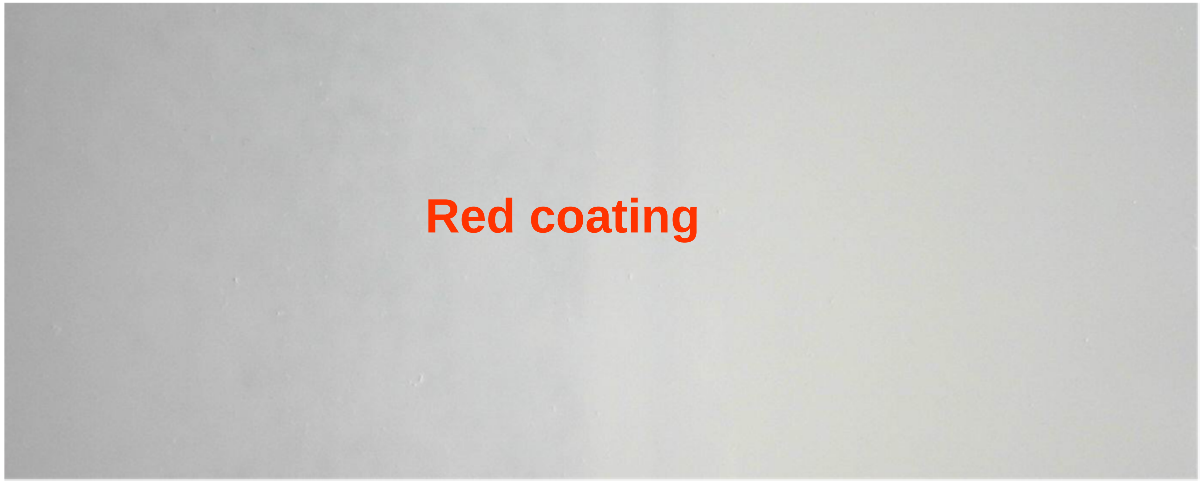
Compatibility problem/Surfactant 'drift'

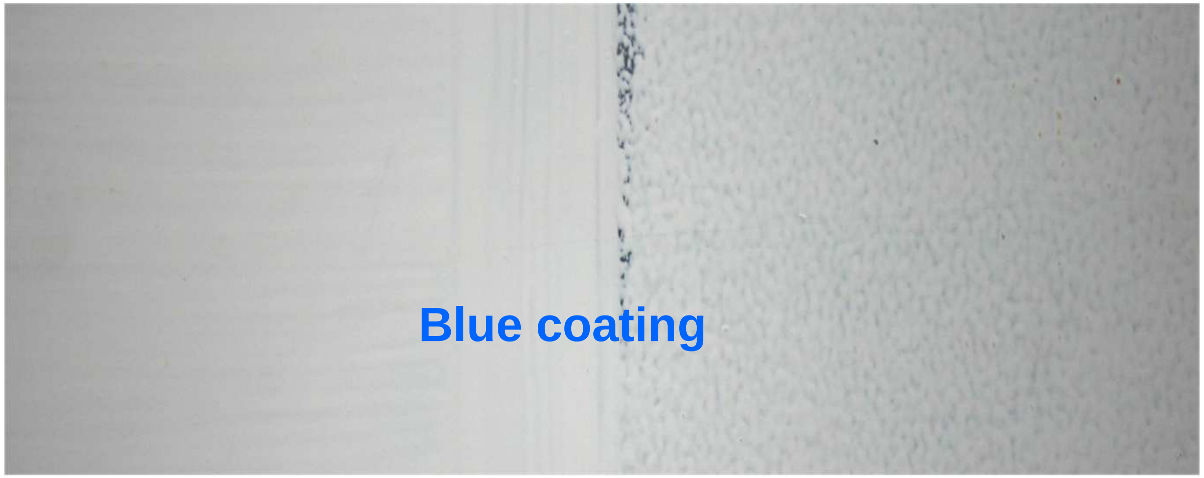


Application brush – levelling



Application brush – levelling



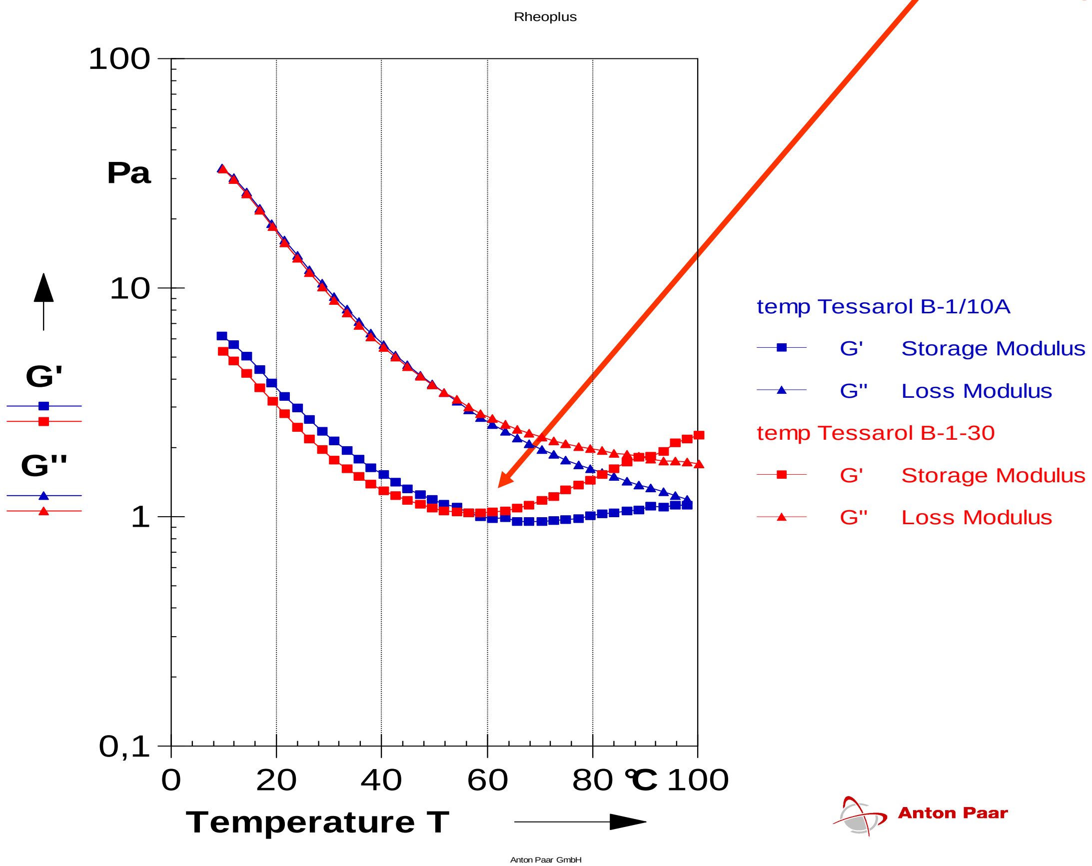


Temperature test – start of flocculation

Oscillatory test, low frequency

No flocculation with higher temp. – more stable system

On 55℃ start of flocculation less stable system



Interpretation of results

- Results are useful for relative comparison
- Storage stability and sedimentation control. For elasticity, viscosity must be higher when low shear stress is input.
- For good levelling and flow. Viscosity should dominate after stresses are removed
- In research department rheology tests are very important they help us understand which raw materials are suitable in order to have stable system
- Rheology tests are also very useful in production, where we can confirm or correct the rheology parameters from the measurements which we did in laboratory

Summary

- History, products on the market
- Compatibility of different raw materials
- Fast and reliable results.

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[7] H. A. Barnes, *A Handbook of elementary rheology*, University of Wales, Institute of Non-Newtonian Fluid Mechanics, 2000.

Thank you for your attention!