COATING RHEOLOGY

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Rheology

What is Rheology
How to Measure Rheology
Importance of Rheology on Paint Applications
Limitations of Rheology Measurements

Coating Rheology - Outline

- Rheological Properties of Coatings
- Effect of Rheological Properties on Coating Process
- Effect of Coating Variables on Rheology
- Limitations of Rheology Measurements
- How to modify Rheology

Why is Rheology Important for a Paint

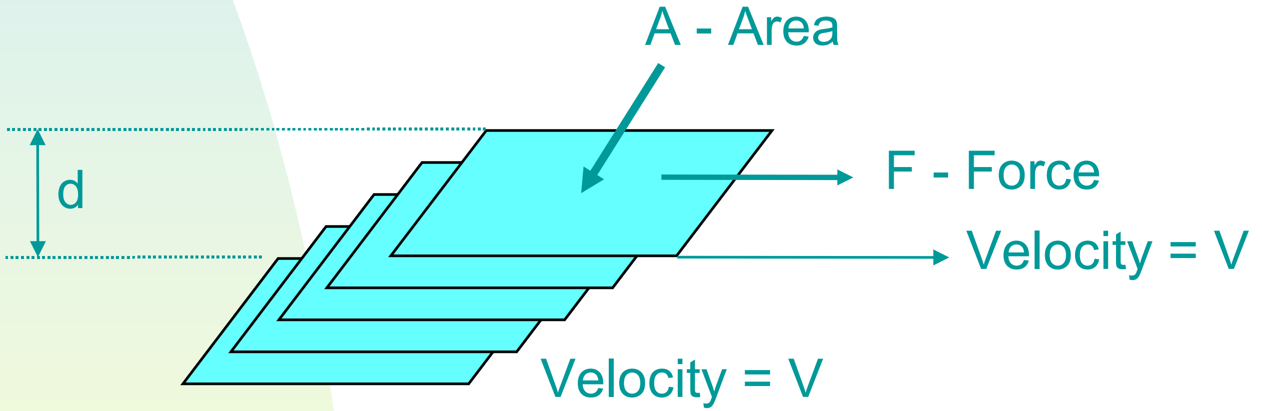
- **Mixing**
  - Pigment Dispersion
  - Pumping
- **Storage**
  - Settling
- **Application**
  - Spray
  - Dip
  - Flow coat
  - Roller coat
  - Brush
- **Film formation**
  - Flow and leveling
  - Coalescence

What is Rheology ?

Science of Deformation and Flow

Flow of Liquids -

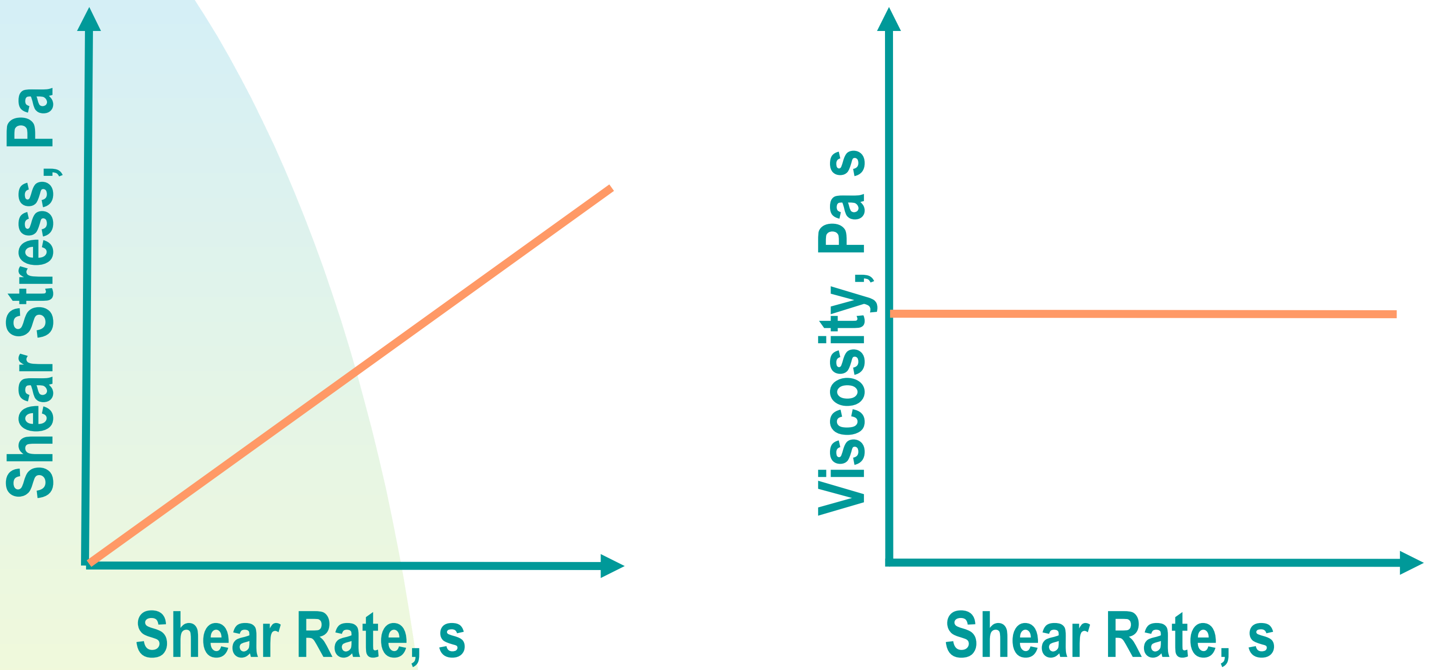
Viscosity - Resistance to flow



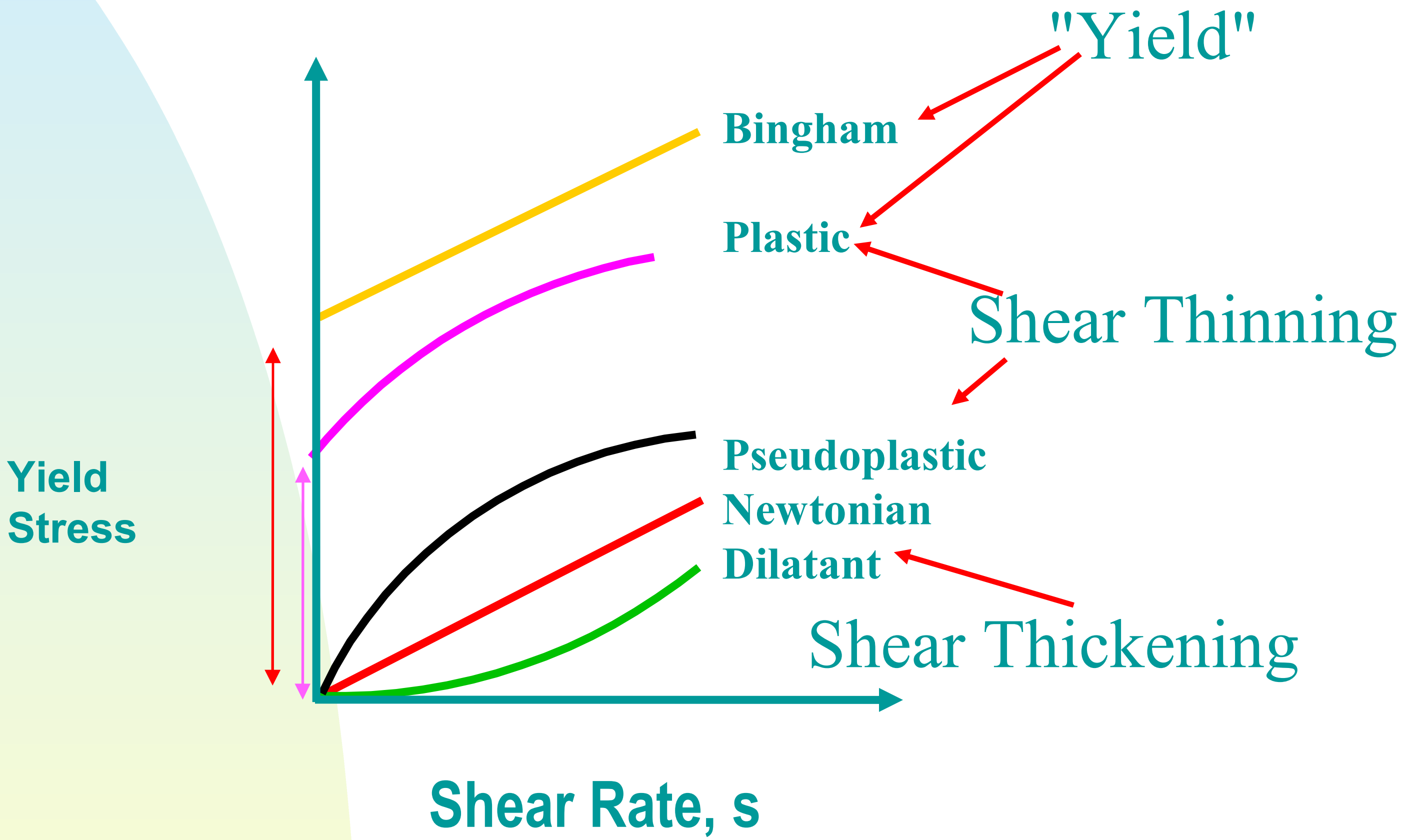
Shear Rate is Velocity Gradient = (V -V)/d [s]

Shear Stress = F/A [N cm]

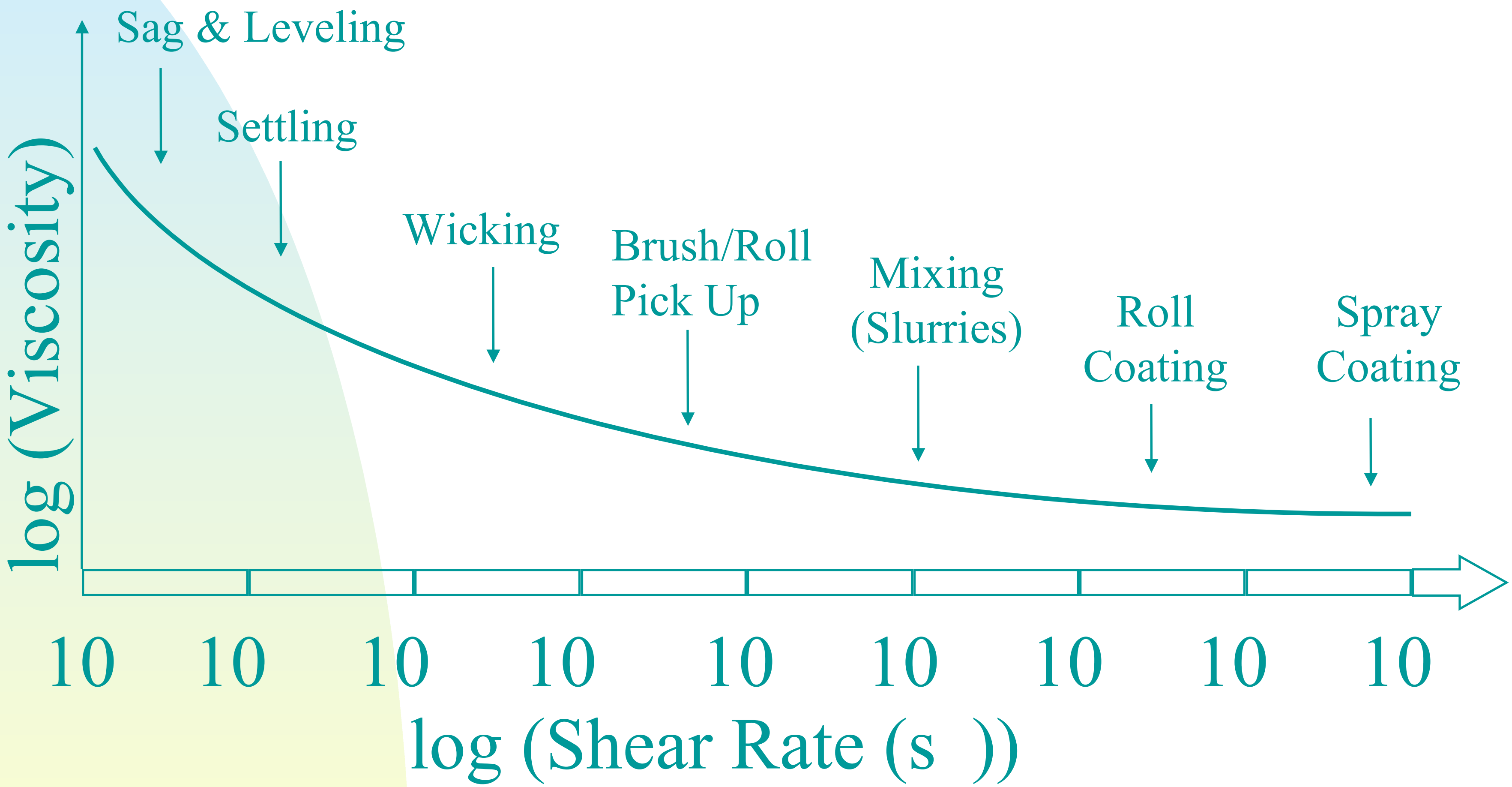
Newtonian Fluids



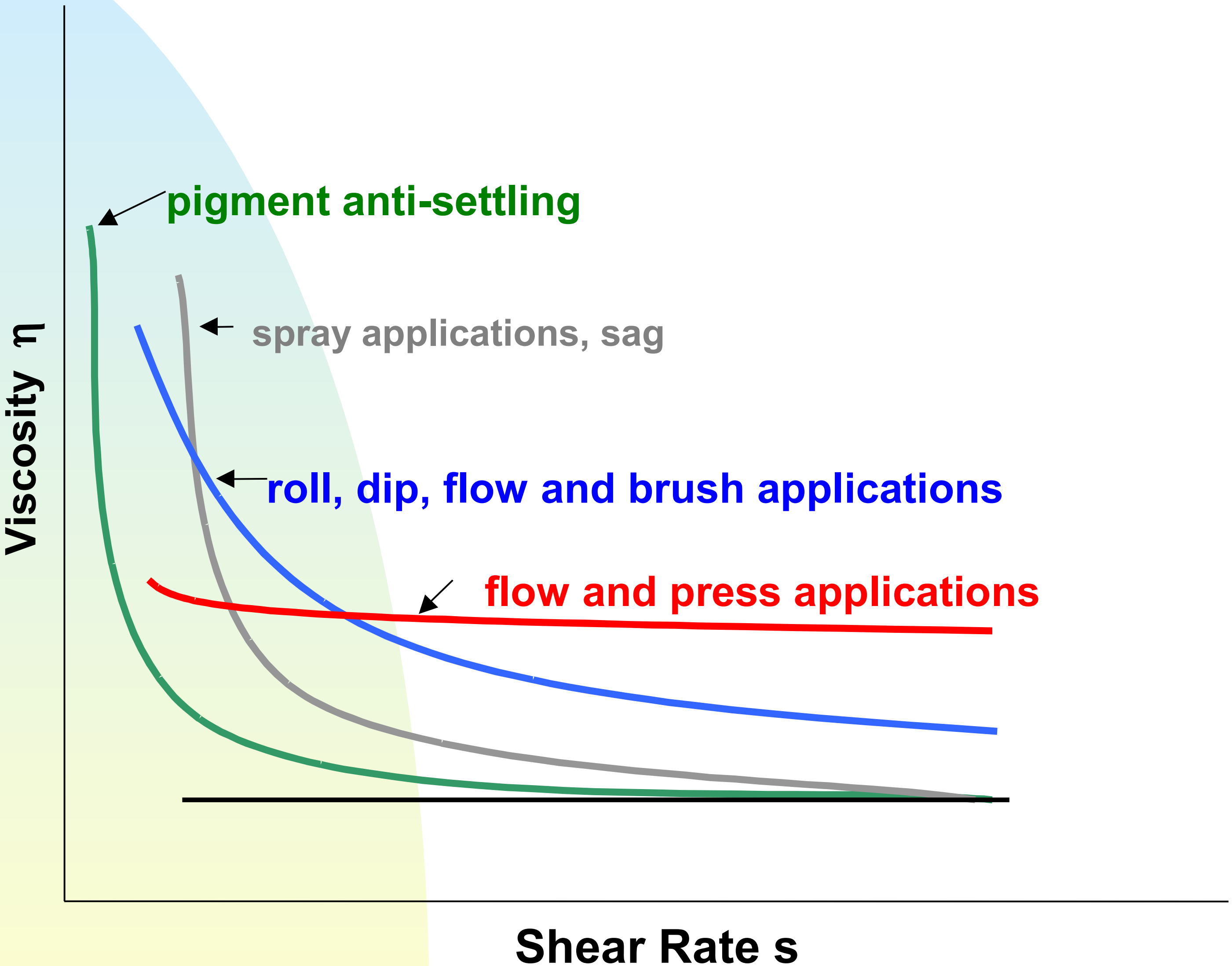
Non-Newtonian Viscosity Behavior



Shear Rates for Various Sub-Processes

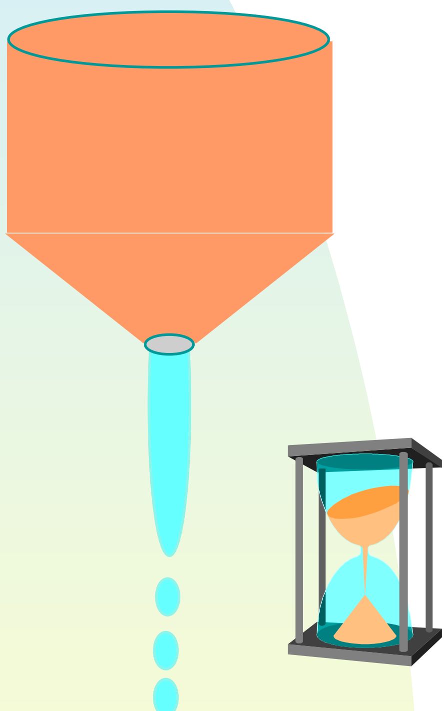


RHEOLOGY PROFILE

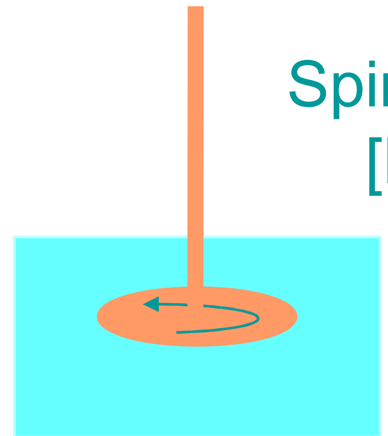


Common Viscosity Measurement Methods

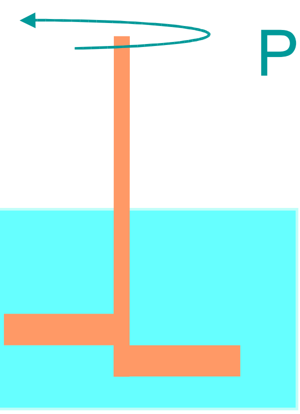
Cup Methods [Zahn]



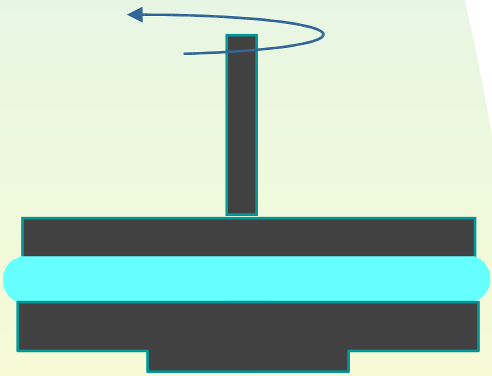
Spindle Methods [Brookfield]



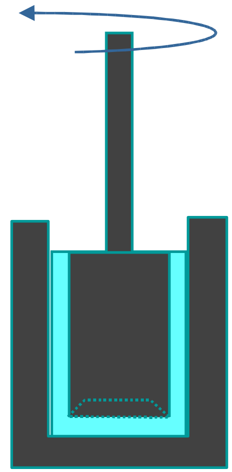
Paddle Methods [Stormer]



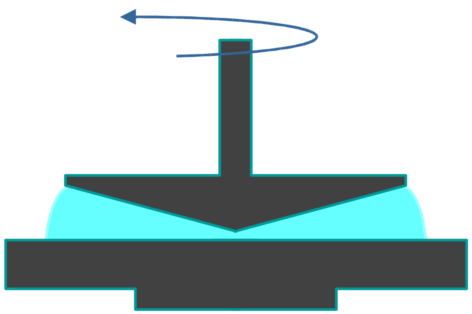
Rotational Rheometers



Parallel Plate



Concentric Cylinder



Cone and Plate

Viscosity Units

Name	Test Methods	Units
Gardner-Holdt	Bubble	Arbitrary
Zahn, Ford	Cup	Seconds
Brookfield	Spindle	Poise
Stormer	Paddle	Krebbs KU
Capillary	Flow	Stokes, Sec.
ICI	Cone-Plate	Poise
Rheometer	Cone-Plate	Poise

Viscosity: Units

The units of Viscosity are:
Pascal.second [Pa s] in SI, Poise in CGS

1 poise = 100 centipoise (cps)
1 poise = 0.1 Pa·sec
1 poise = 0.0671969 lb/(ft·sec)
1 poise = 4.031814 lb/(ft·min)

Pa = Pascal = N·m pressure, stress

$$\text{stoke} = \frac{\eta \text{ (poise)}}{\rho \text{ (g/cm)}}$$

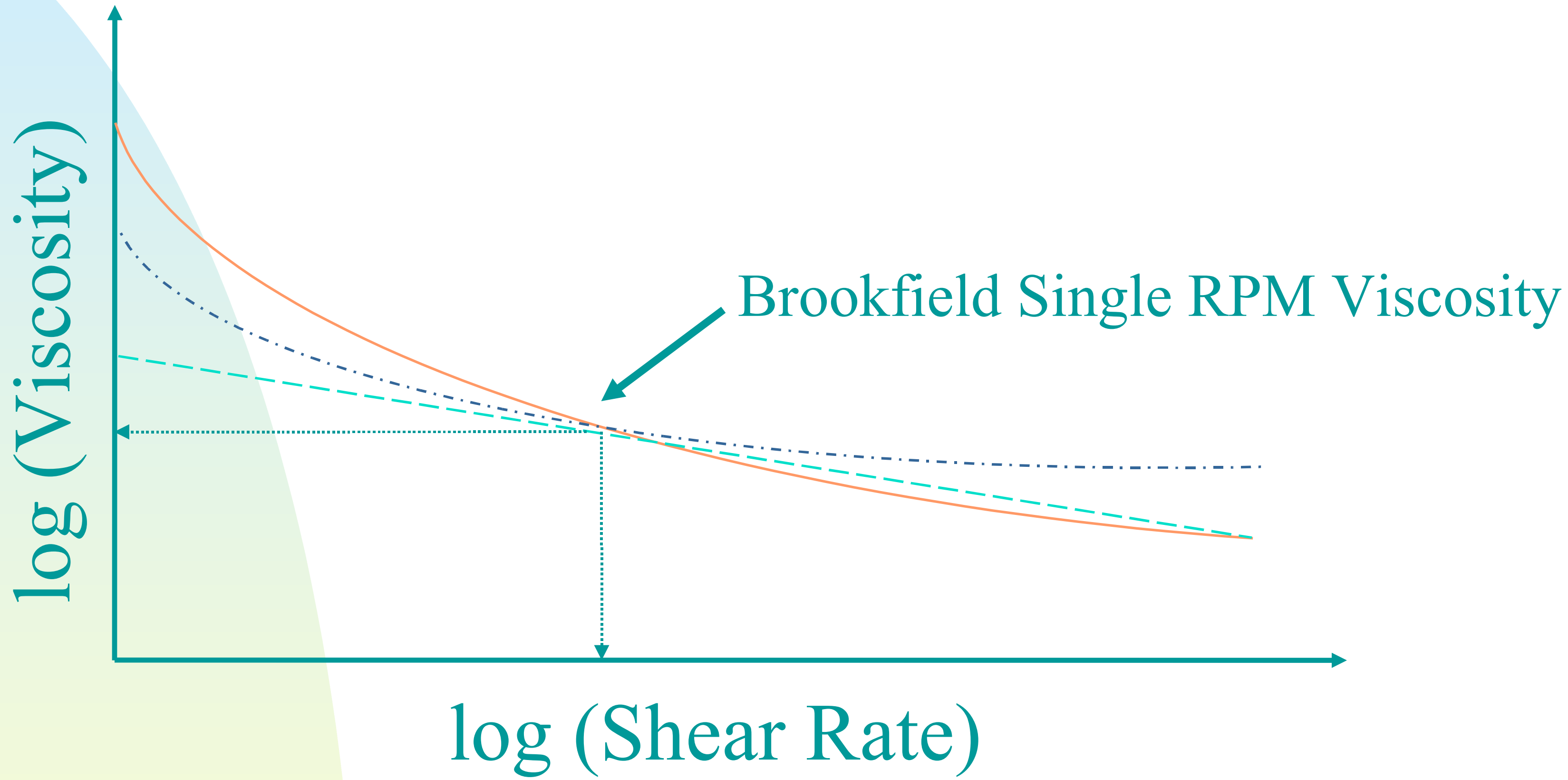
Non-Newtonian Viscosity Behavior

Brookfield Viscosities @ Different RPMs

Waterborne Coating

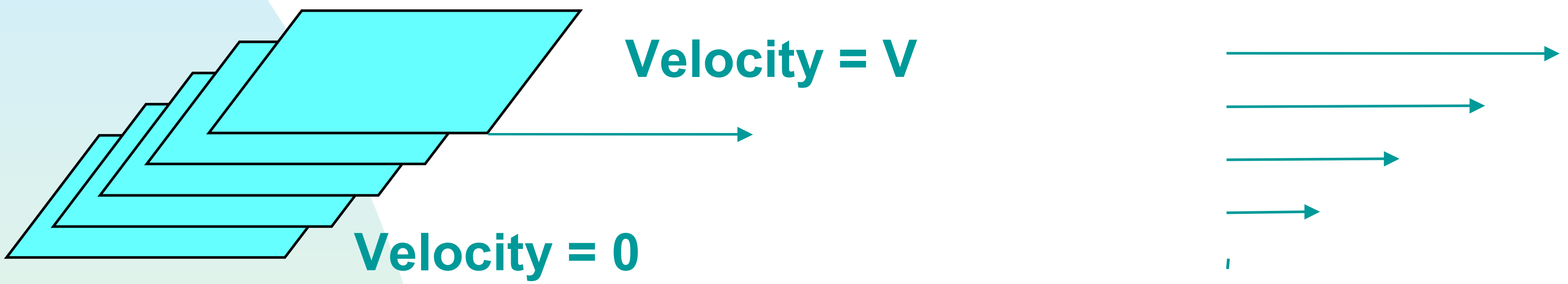
RPM	Viscosity (cps)	Spindle #
0.5	8000	4
1	5000	"
2.5	2560	"
5	1520	"
10	1000	"
20	550	2
50	316	"
100	227	"

Limitation in Single-Point Viscosity Measurements



In Formula Development this behavior must be known before defining production viscosity specs

Flow Patterns

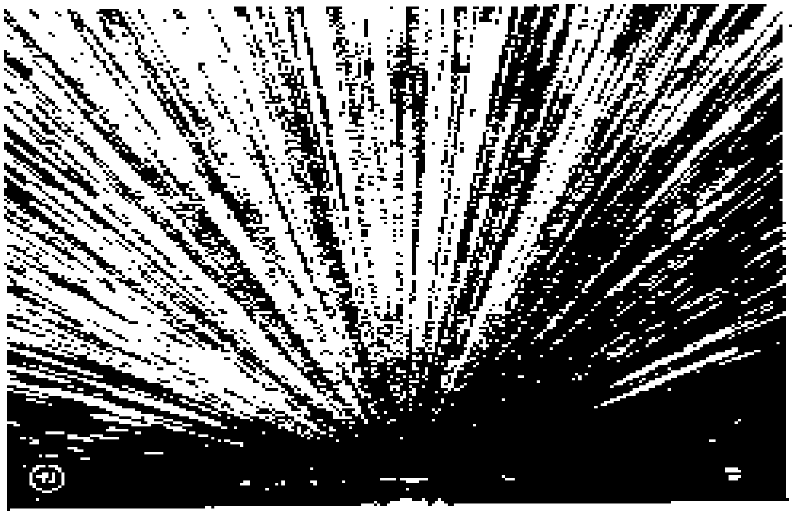


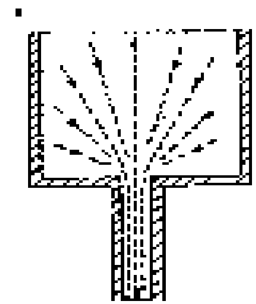
Laminar Flow

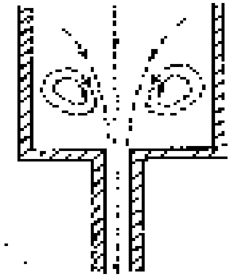
Turbulent Flow

Eddies

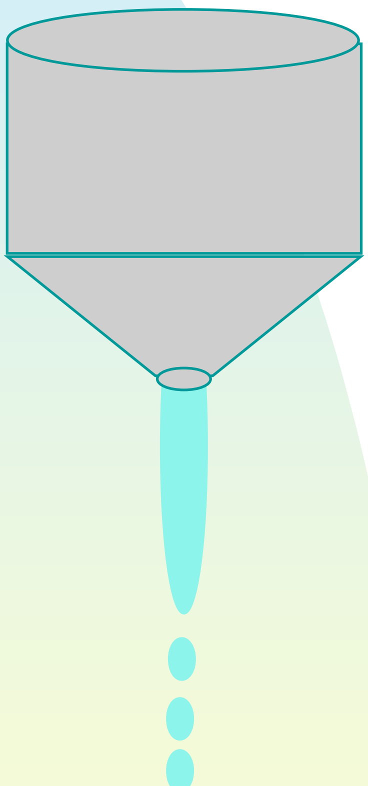
Impact of Rheology on Flow Pattern







Orifice Viscometers (Viscosity Cups)



$$\nu \text{ (stoke)} = \frac{\eta \text{ (poise)}}{\rho \text{ (g/cm)}}$$

For low viscosity (<10cps) Kinetic Energy Correction can be as high as 90%

Not Suitable for non-Newtonian Fluids

Temperature !

Type of Viscosity

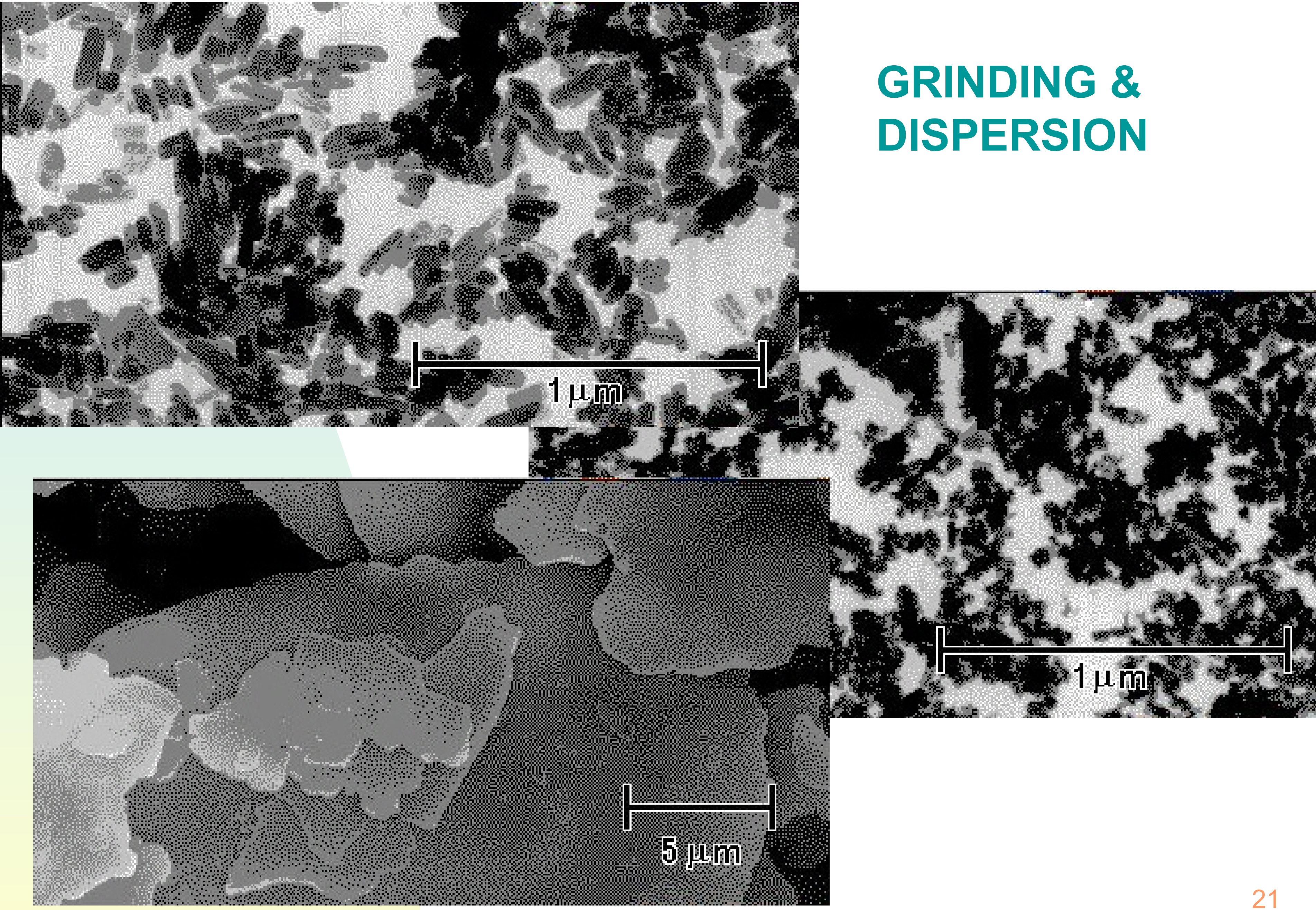
<table>
<tr><th colspan="9">Shear Rate (γ) sec^{-1}</th></tr>
<tr><th></th><th>0.01</th><th>0.1</th><th>1.0</th><th>10</th><th>100</th><th>1000</th><th>10,000</th><th></th></tr>
<tr><td colspan="3">Sag, Leveling</td><td colspan="3">Pumping, Mixing, Pouring</td><td colspan="3">Dispersing</td></tr>
<tr><td colspan="2">Particle Suspension</td><td></td><td colspan="2">Dipping, Flow Coating</td><td></td><td colspan="3">Roller</td></tr>
<tr><td colspan="7"></td><td colspan="2">Spraying and Brushing</td></tr>
<tr><td colspan="9"></td></tr>
<tr><td></td><td colspan="4">Brookfield</td><td colspan="2">Stormer</td><td>ICI</td><td></td></tr>
<tr><td colspan="4"></td><td>Efflux Cup</td><td colspan="4"></td></tr>
<tr><td></td><td colspan="6">Controlled Stress Rheometer</td><td colspan="2"></td></tr>
</table>

Viscosities of Common Materials

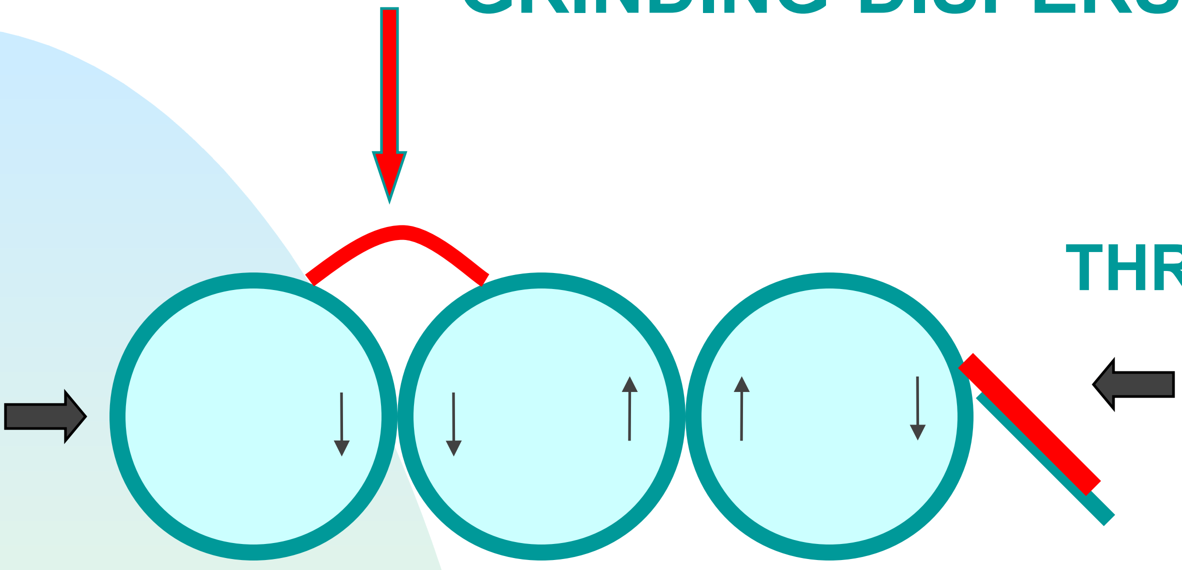
	Viscosity (cps)	Consistency
Air	1.00E-03	Gaseous
Water	1.00E+00	Fluid
Olive Oil	1.00E+02	Liquid
Glycerine	1.00E+03	Liquid
Golden Syrup	1.00E+05	Thick Fluid
Polymer Melts	1.0E+05 - 1.0E09	Toffee-Like
Pitch	1.00E+12	Stiff
Glass	1.00E+24	Rigid

1000 cps = 10 poise = 1 Pa s

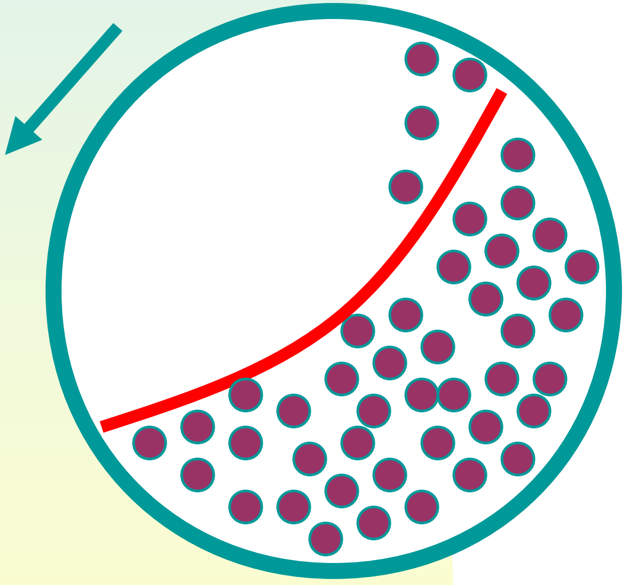
GRINDING & DISPERSION



GRINDING-DISPERSION EQUIPMENT

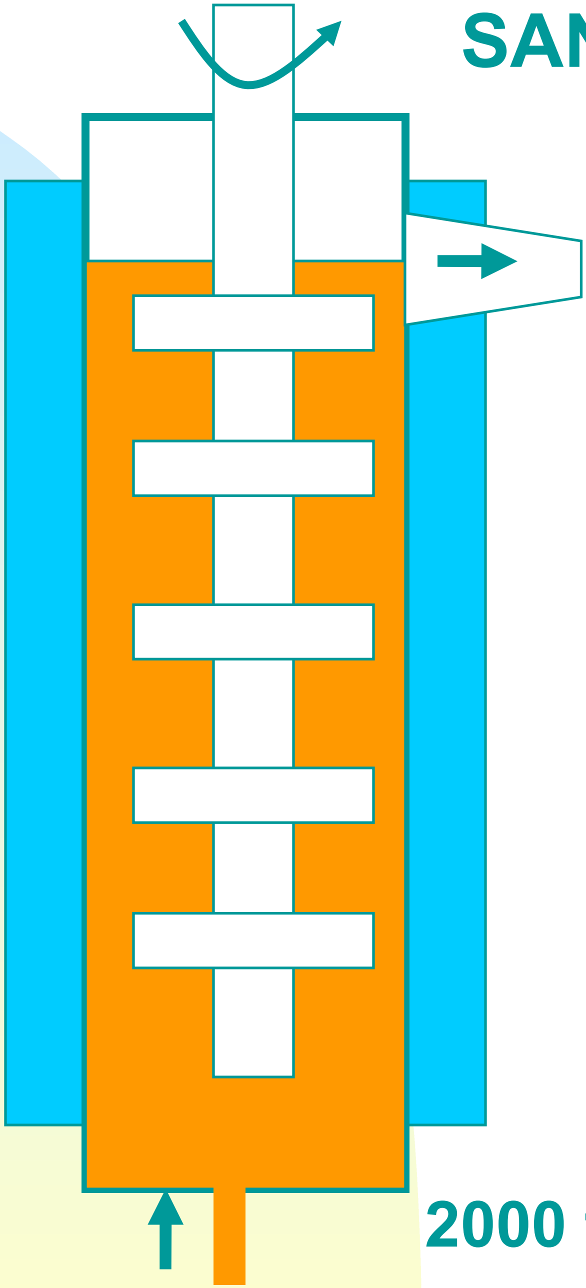


THREE ROLLER MILL



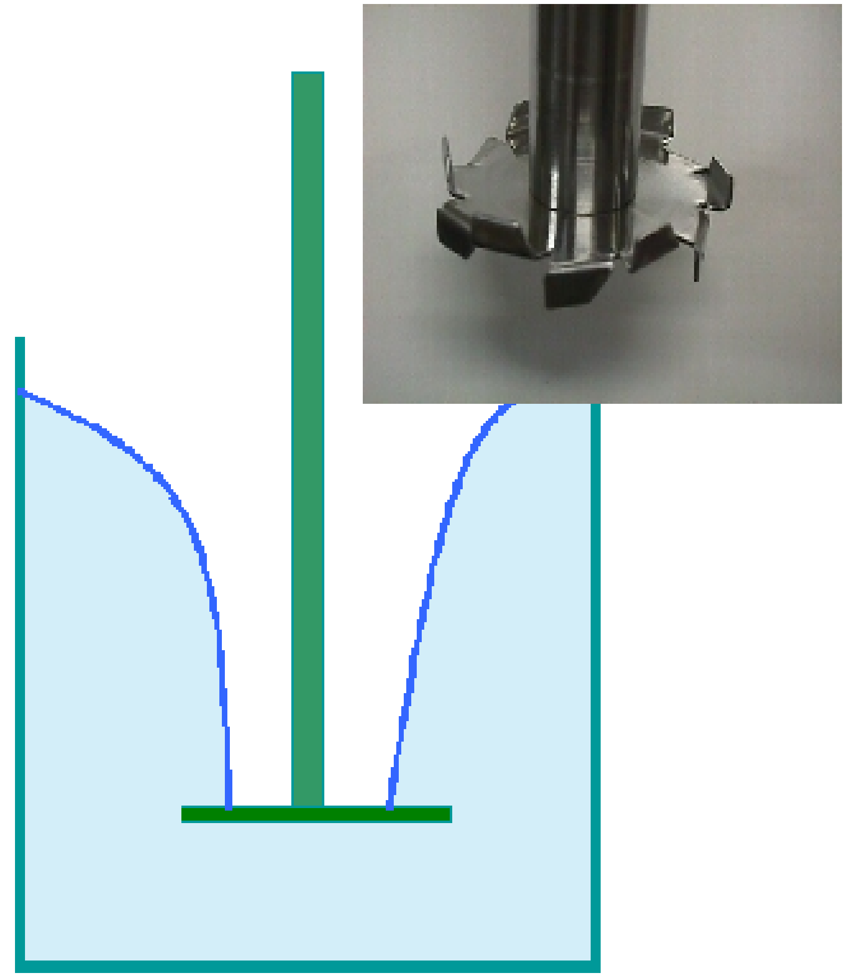
BALL MILL

SAND MILL



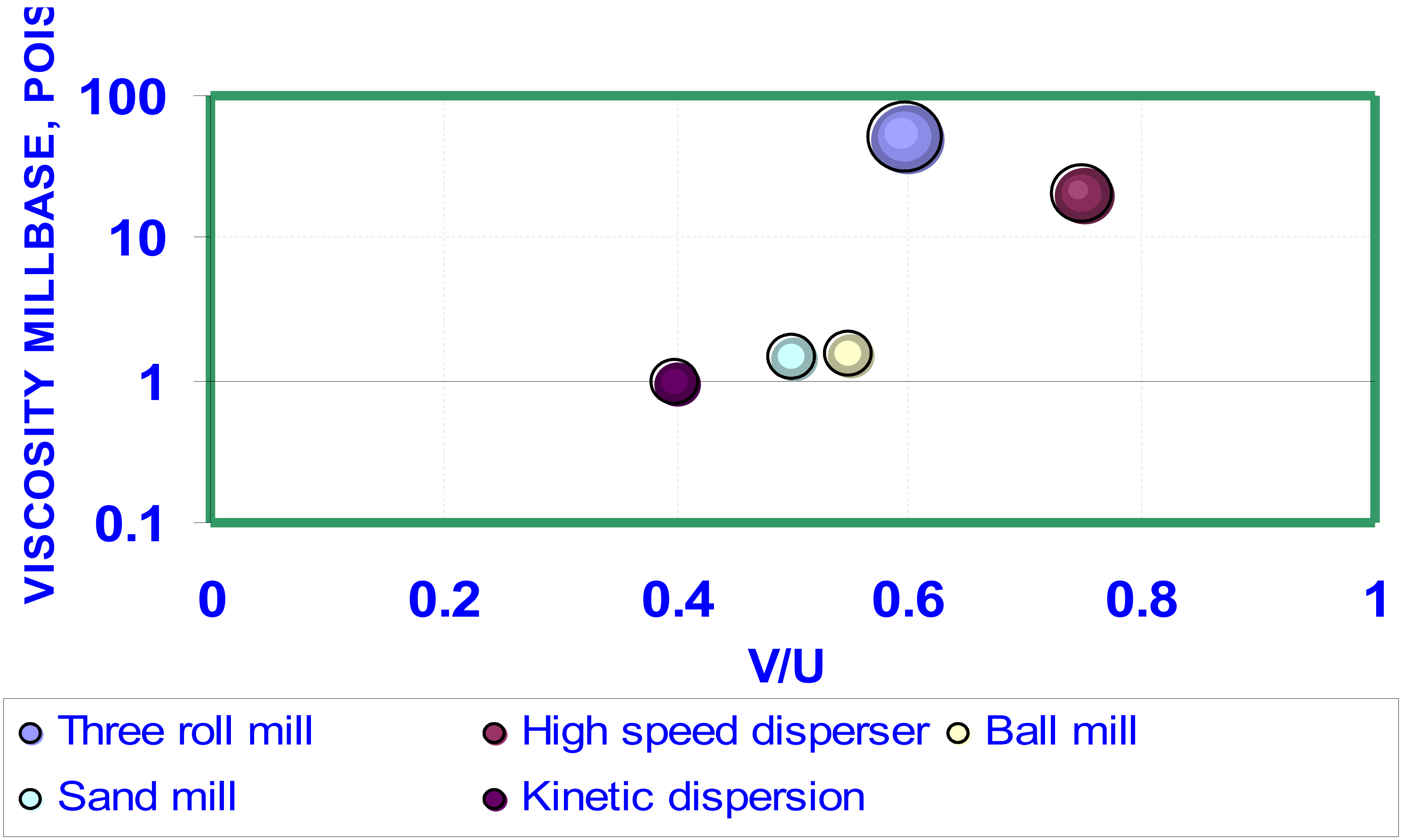
2000 ft/min

DISPERSER



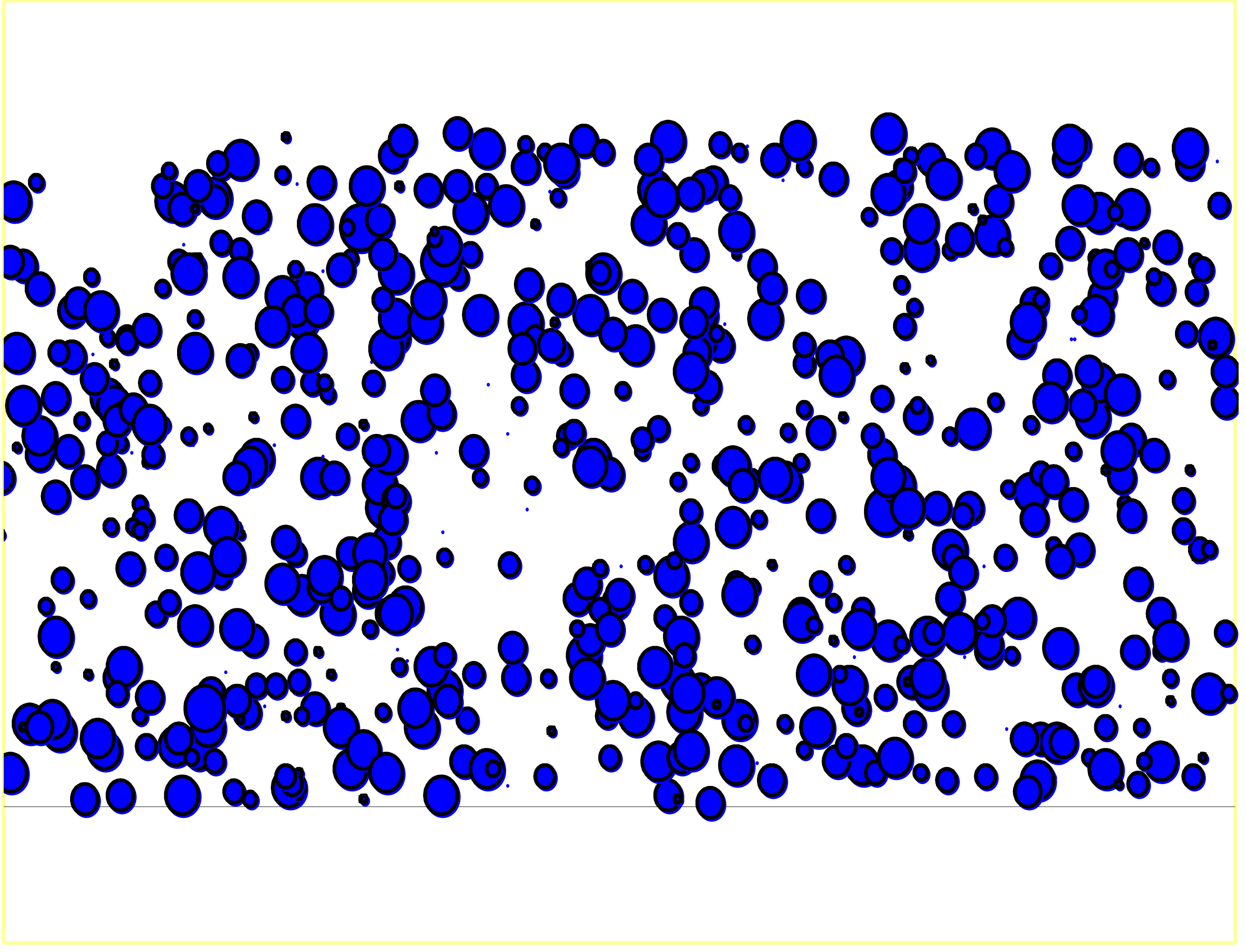
4000 ft/min.

MILLBASE FORMULATION



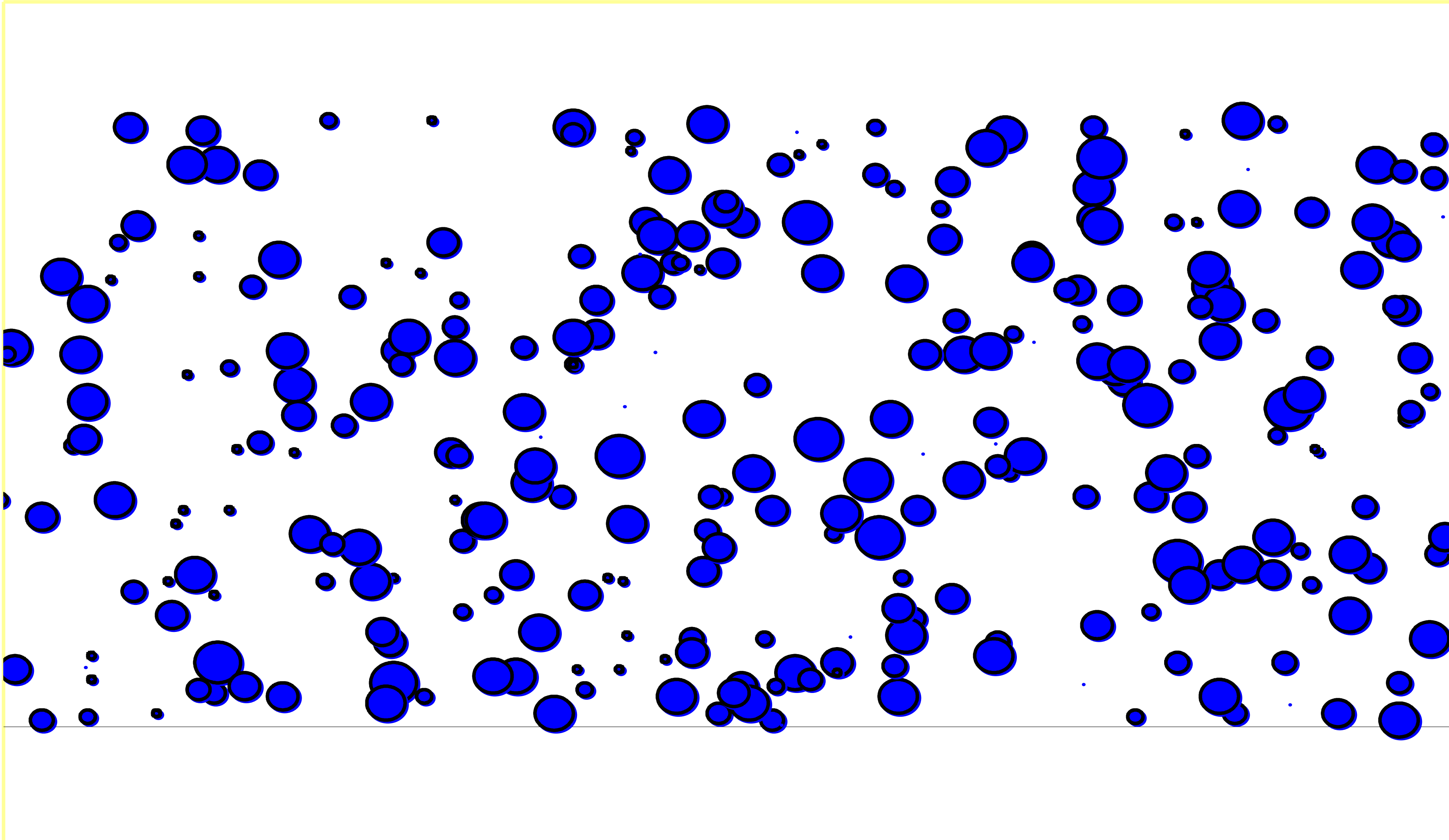
V/U ratio Fractional pigment vol./ultimate pigment vol.

PIGMENT PARTICLES

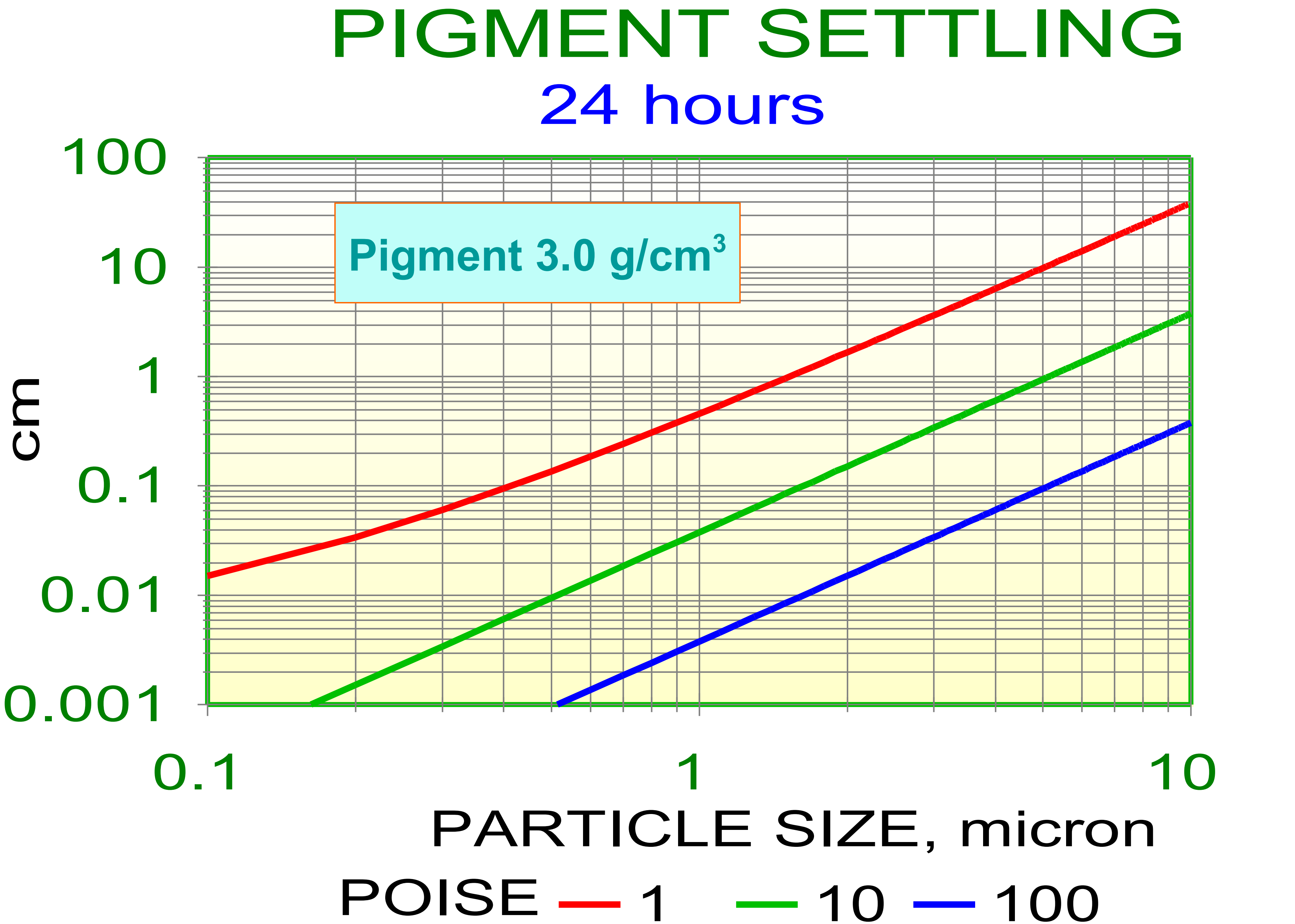


Flocculation

PIGMENT PARTICLES



Dispersed


PIGMENT SETTLING
24 hours
Pigment 3.0 g/cm3
100
10
1
0.1
0.01
0.001
cm
0.1
1
10
PARTICLE SIZE, micron
POISE
1
10
100

APPLICATION PROCESS

BRUSH
SPRAY
- AIRLESS
- ELECTROSTATIC, BELL, DISK
- HVLP Guns
- POWDER

DIP - FLOW COATING
- FLUIDICED BED

CURTAIN COATING
ROLLER COATING
- DIRECT - REVERSE

KNIFE COATING
ELECTROCOATING

Brush Application

Shear thinning-easy brushing
low resistance

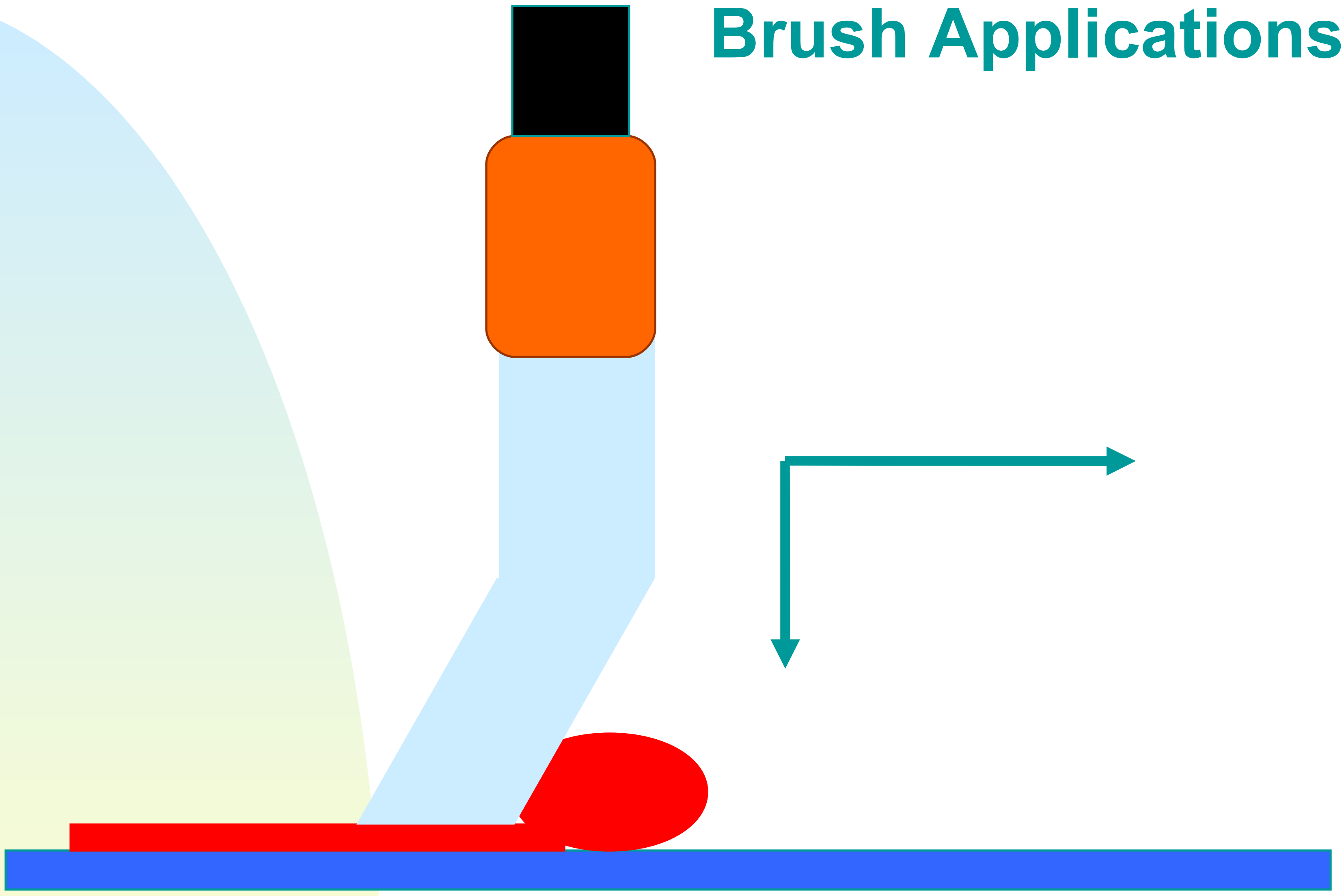
Flow and Leveling - recovery

Sagging - high low shear viscosity

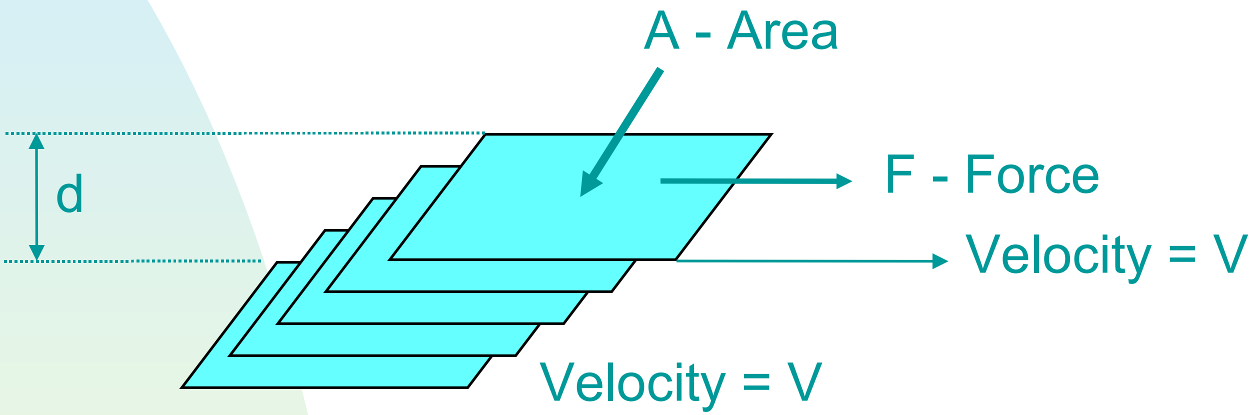
Open time - lapping

Settling - thixotropic

Brush Applications



Viscosity - Definition



Shear Rate is Velocity Gradient = (V -V)/d [s]

Shear Stress = F/A [N cm]

Viscosity = Shear Stress / Shear Rate [Pa s]

What Effects Spray Performance

Paint Viscosity (Elongational)
- **Surface tension**

Shear thinning
- **Thixotropy**
- **Pseudo plastic flow**

Solvent evaporation

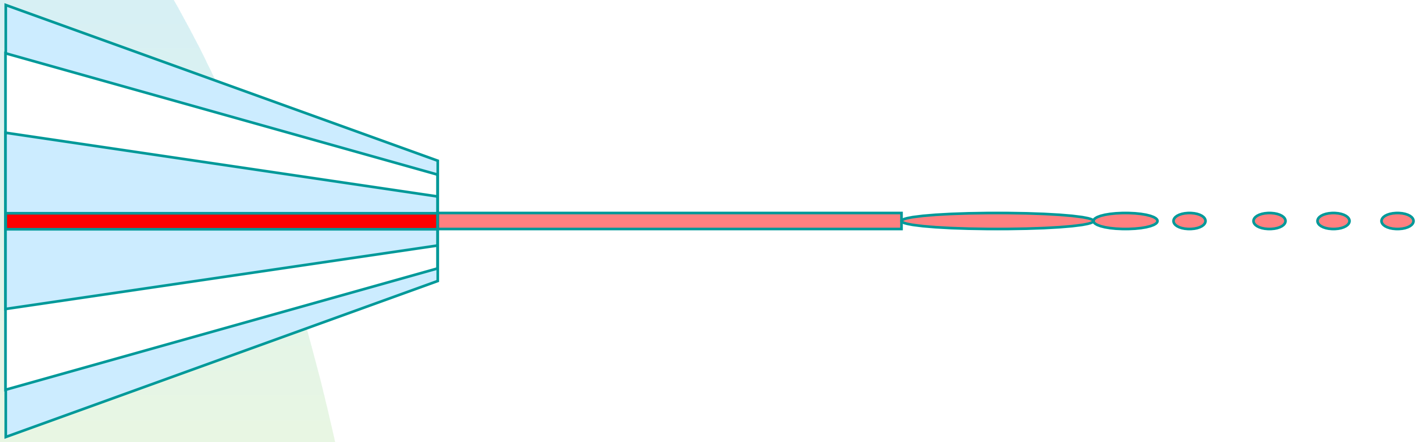
Thixotropy

Sagging

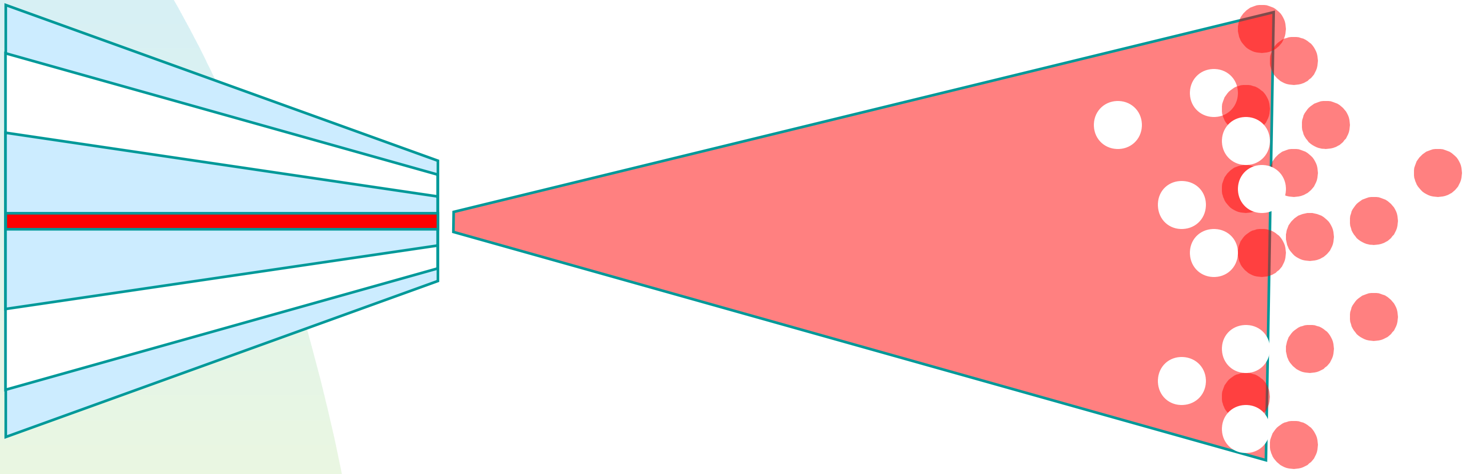
Flow and Leveling

Application Spray

Formation of droplets by surface tension



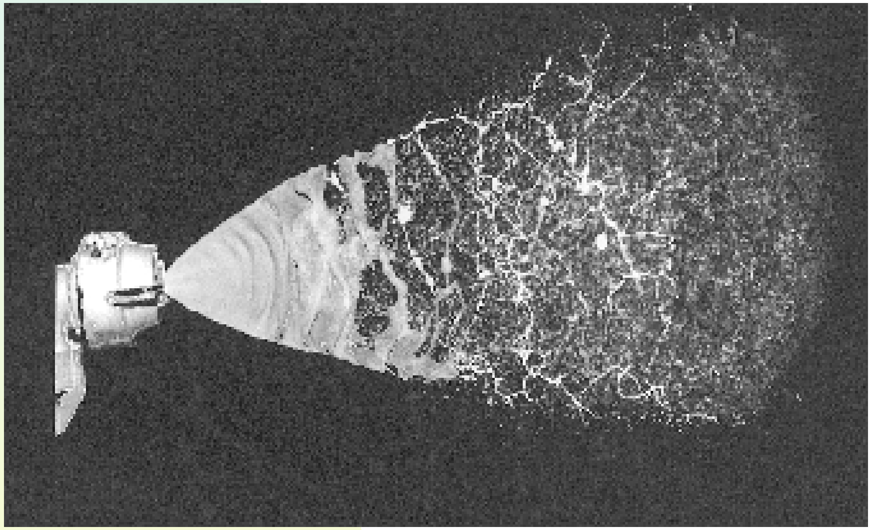
Application Spray



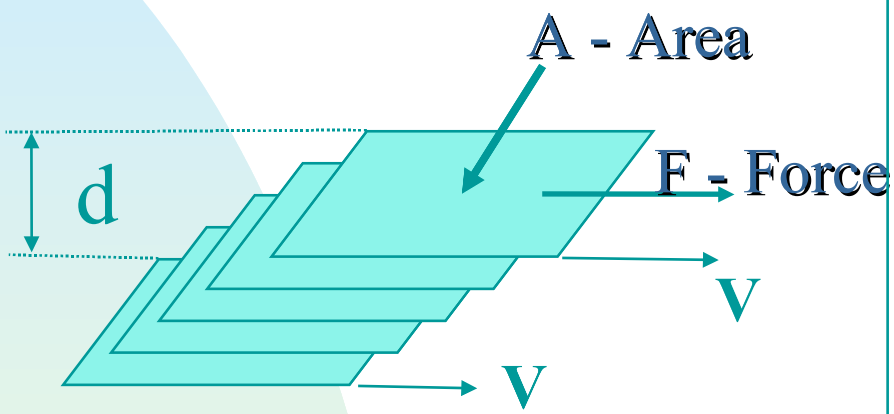
Extension of the coating film

Spray Rheology

- Primary Mode of Deformation in Spray is **Extensional, not Shear**
- Coating Ligaments are stretched and disintegrated in to droplets in the spray process

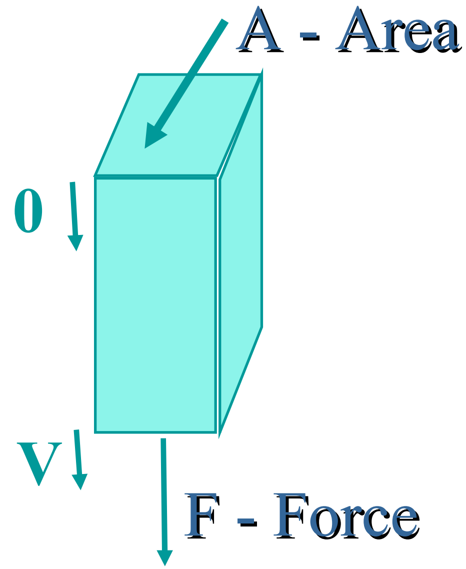


Shear & Extensional Viscosities



Shear Viscosity[Pa s]

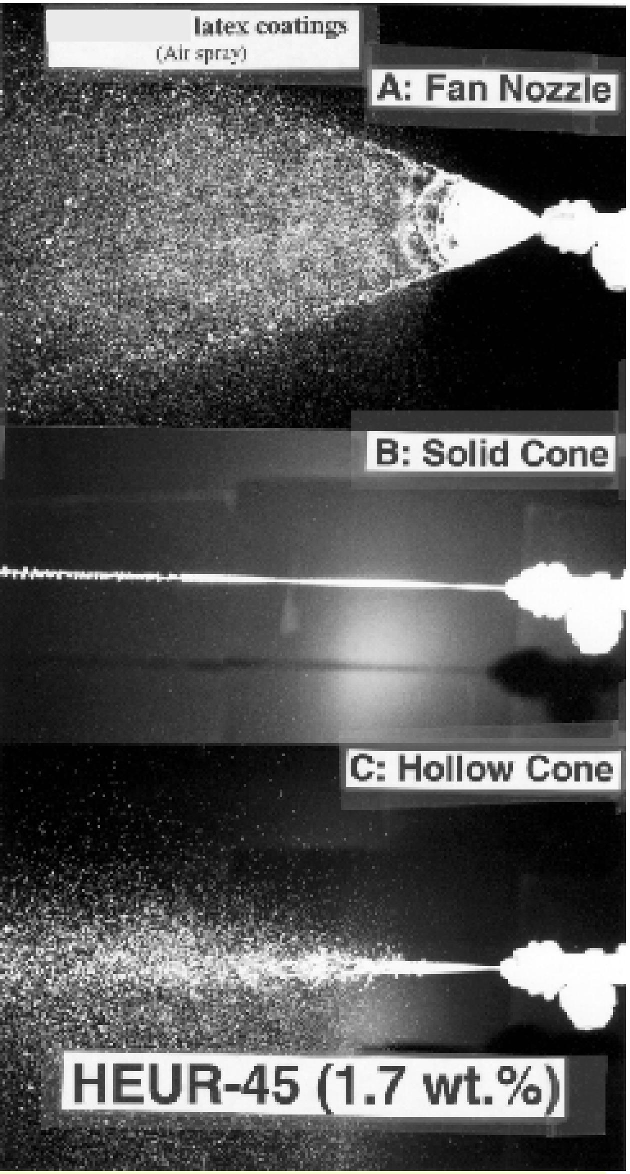
= Shear Stress / Shear Rate



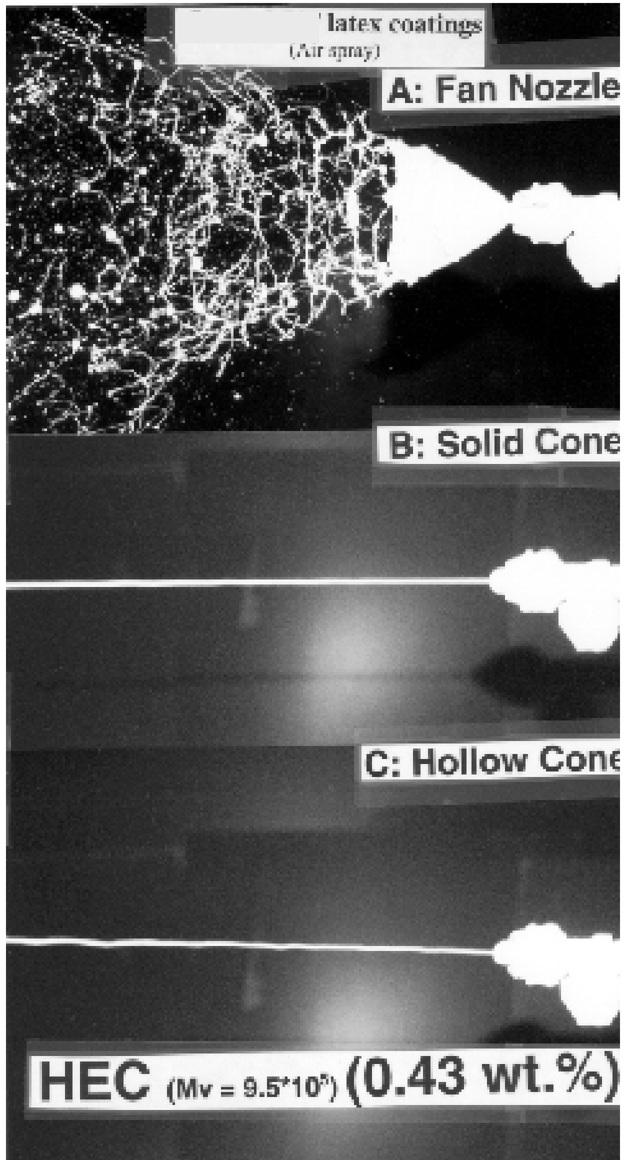
Extensional Viscosity

= Extensional Stress / Extension Rate

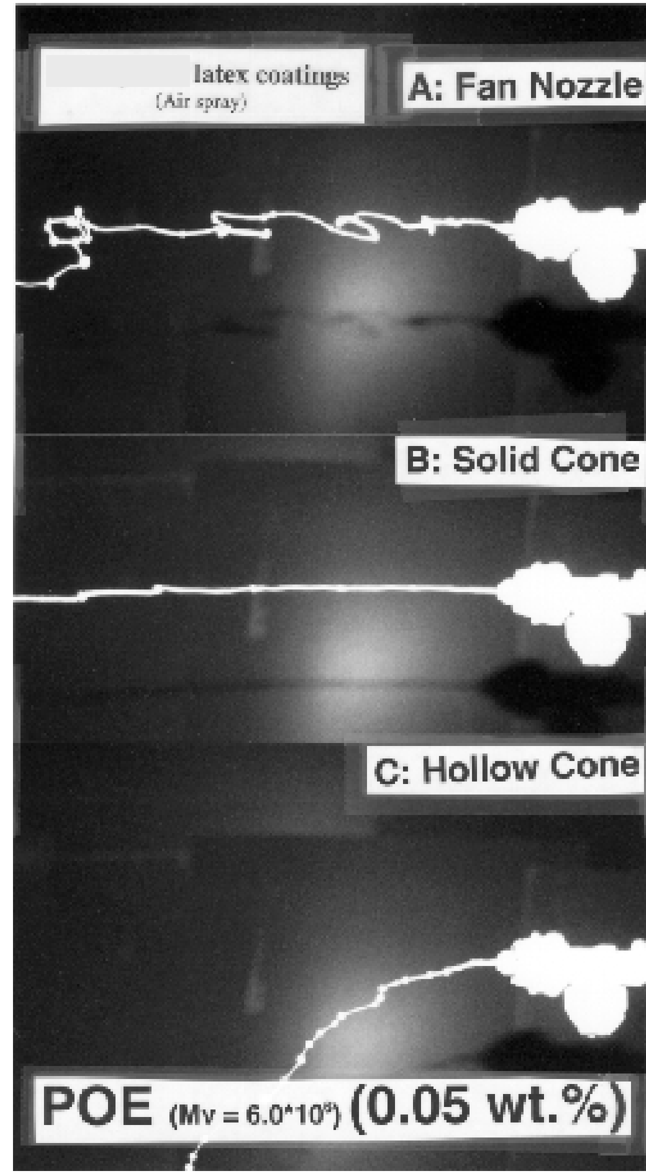
For Simple (Newtonian) Fluids,
Extensional Viscosity (EV) = 3 x Shear Viscosity(SV)
For Complex Fluids, EV can be as high as 10000 x SV



latex coatings
(Air spray)
A: Fan Nozzle
B: Solid Cone
C: Hollow Cone
HEUR-45 (1.7 wt.%)

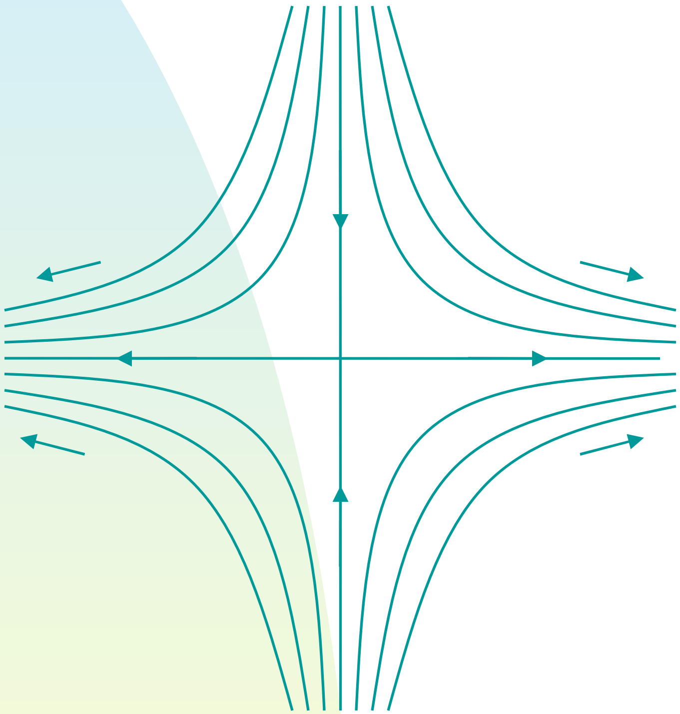


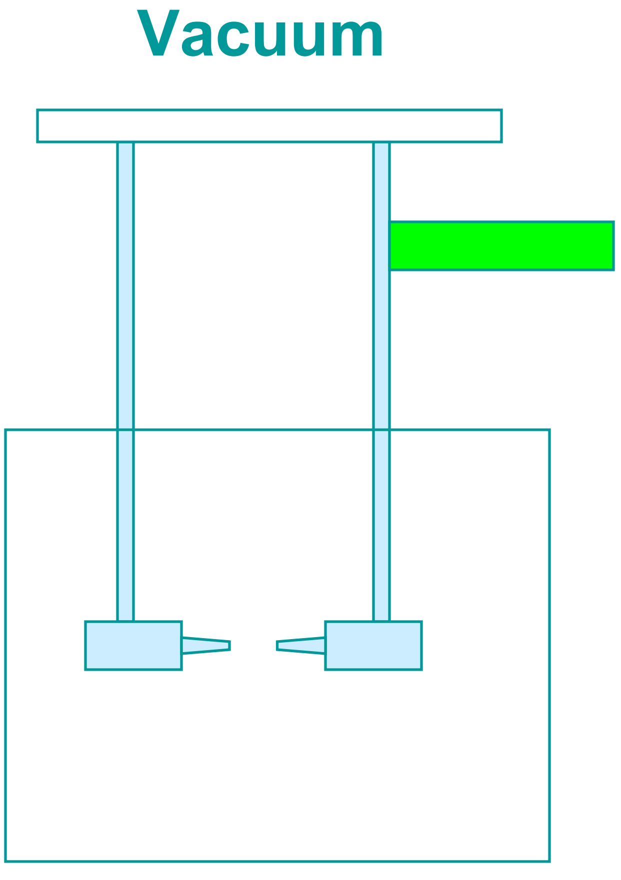
latex coatings
(Air spray)
A: Fan Nozzle
B: Solid Cone
C: Hollow Cone
HEC (Mv = 9.5*10) (0.43 wt.%)



latex coatings
(Air spray)
A: Fan Nozzle
B: Solid Cone
C: Hollow Cone
POE (Mv = 6.0*10) (0.05 wt.%)

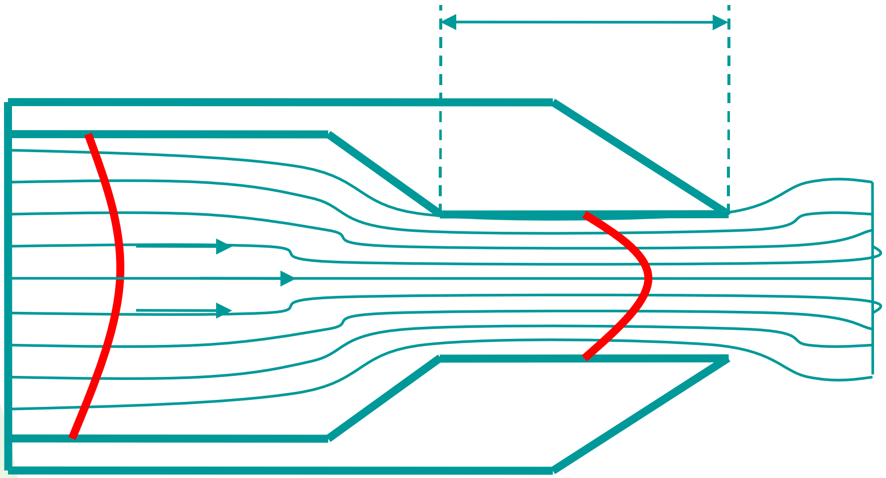
ELONGATIONAL VISCOSITY





ELONGATIONAL VISCOSITY

Contraction Flow

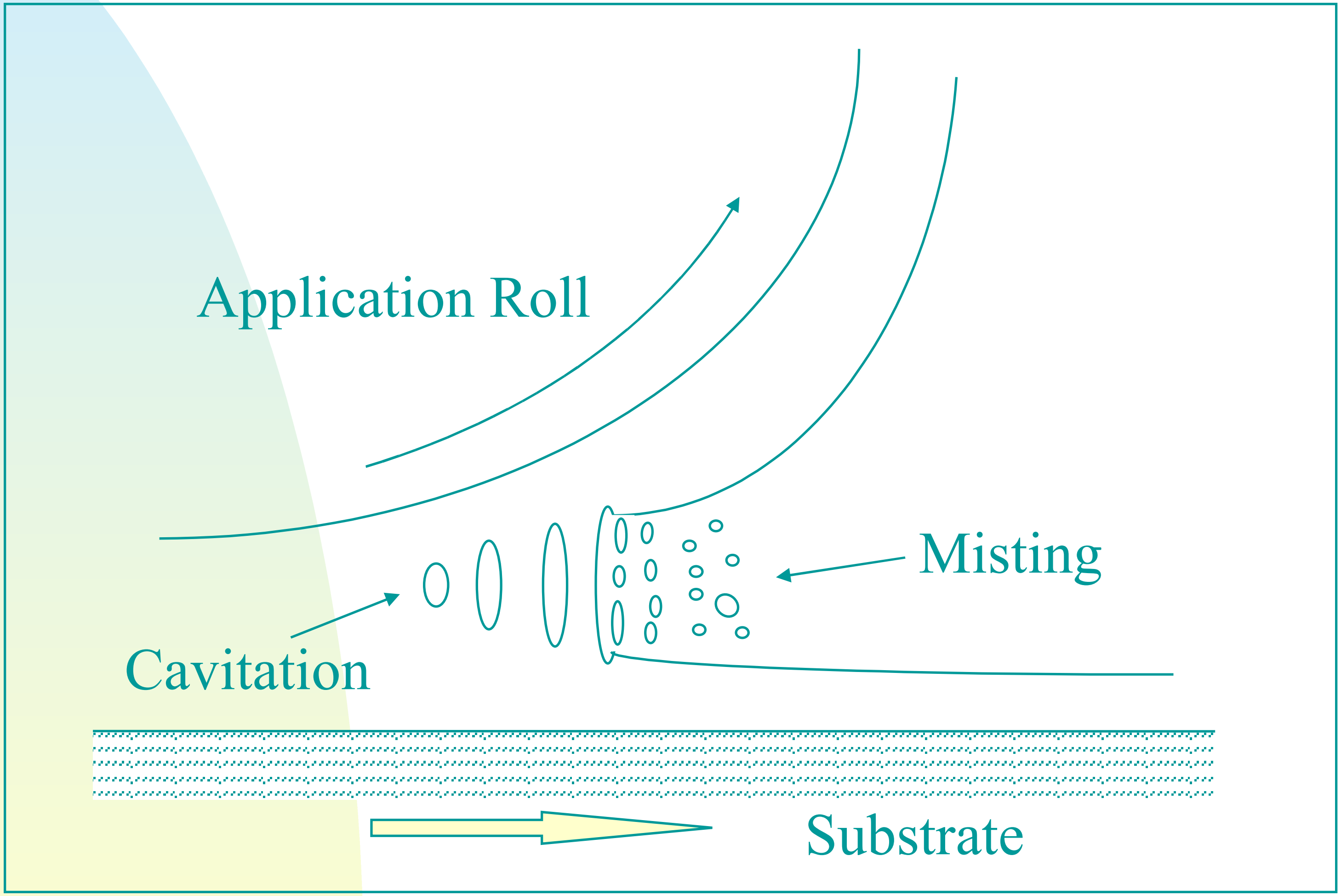


ROLLER COATING

Direct Roller Coating
Reverse Roller Coating

Roller pick up
Ribbon Formation
Misting and Spattering
Flow-Out and Leveling

Coating Application



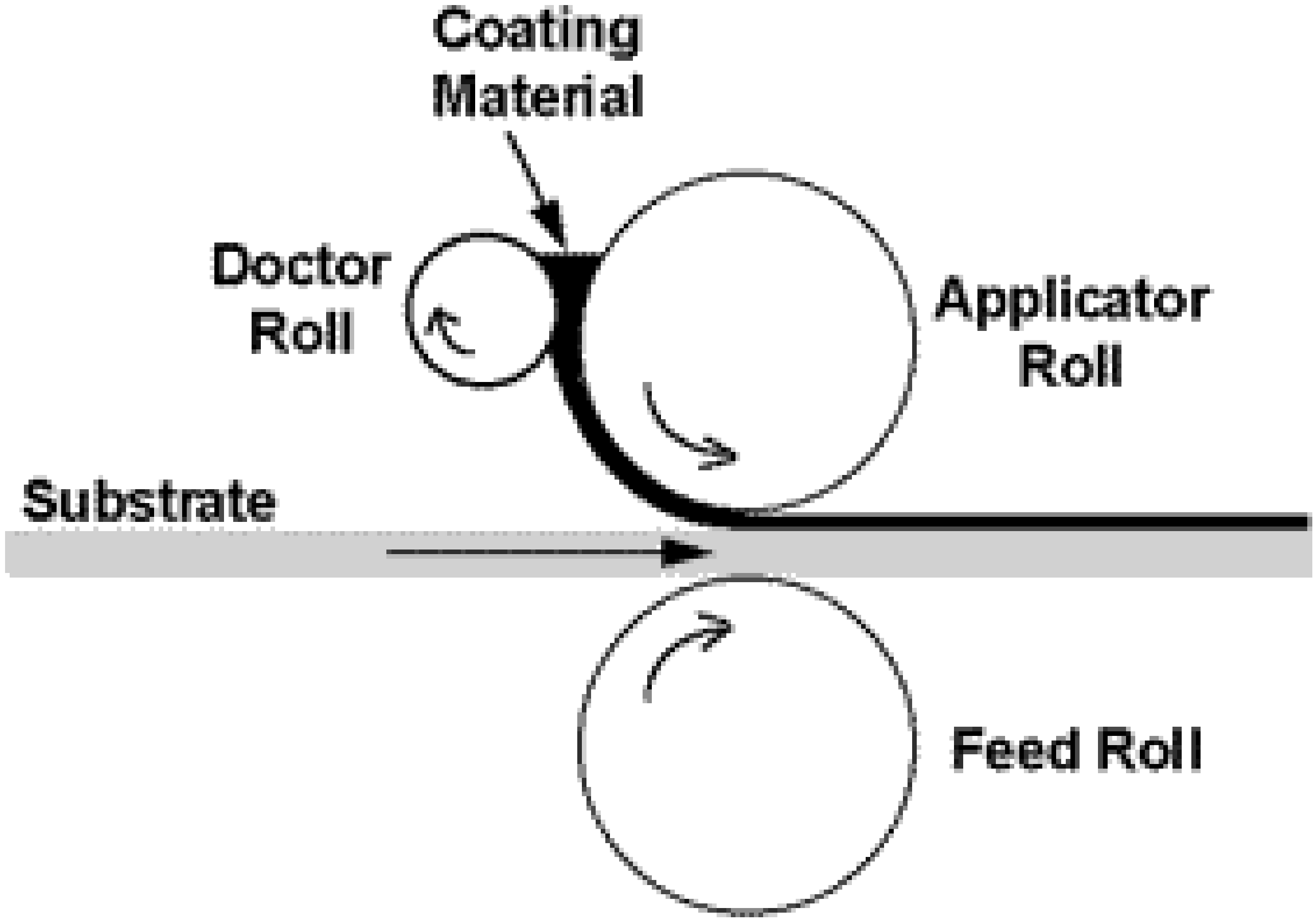


Figure 1: Direct Roll Coater

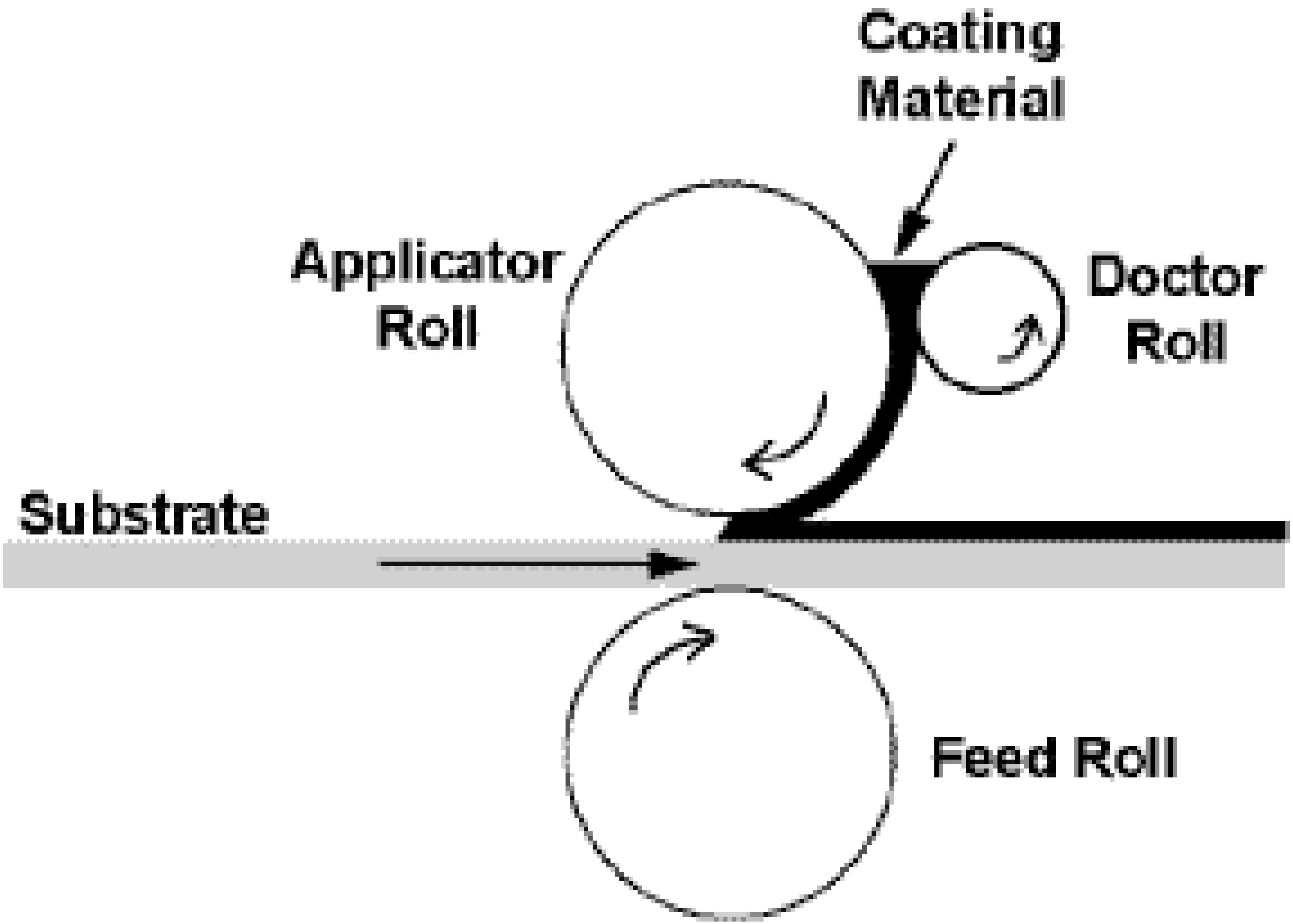
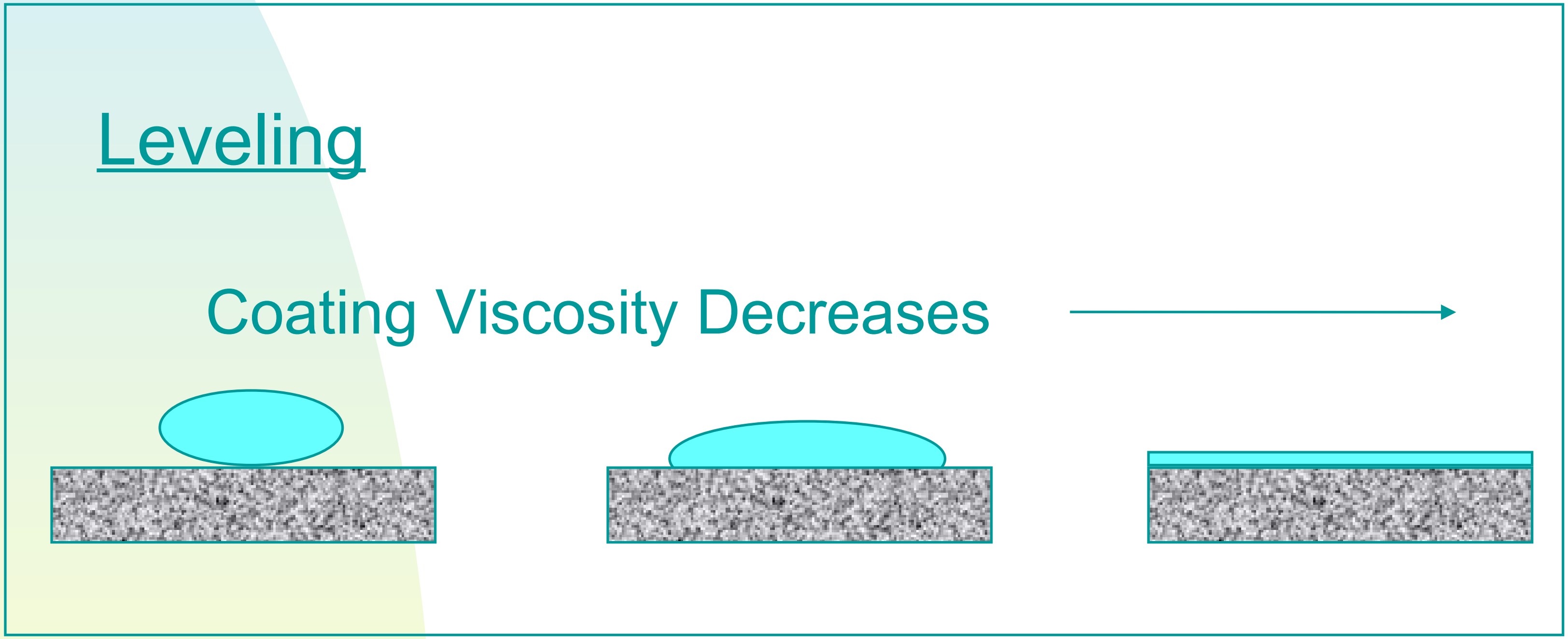
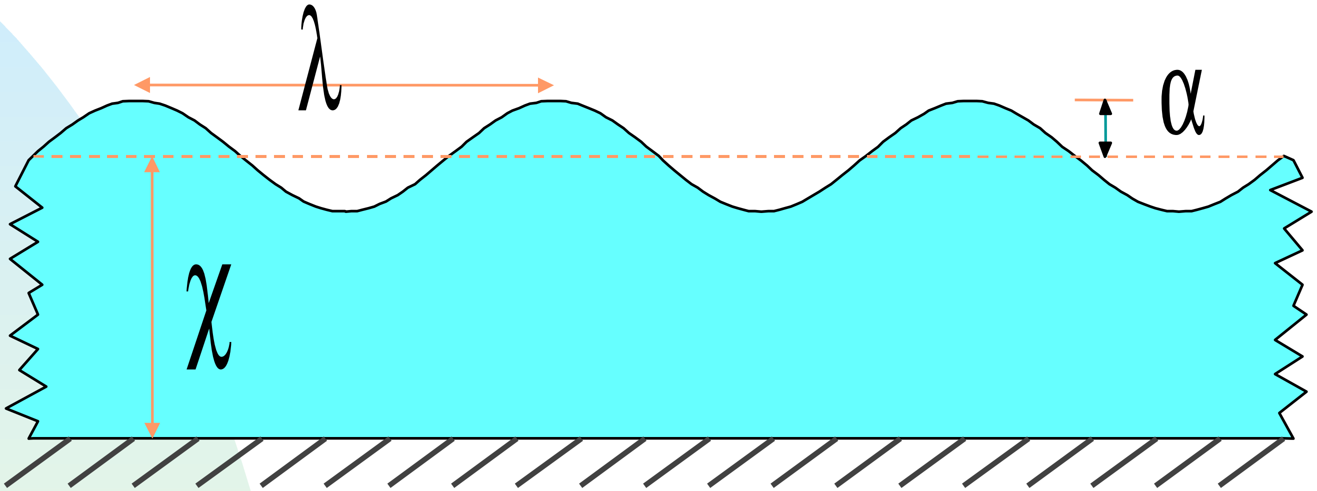


Figure 2: Reverse Roll Coater

Higher Viscosity Hinders Flow and Leveling

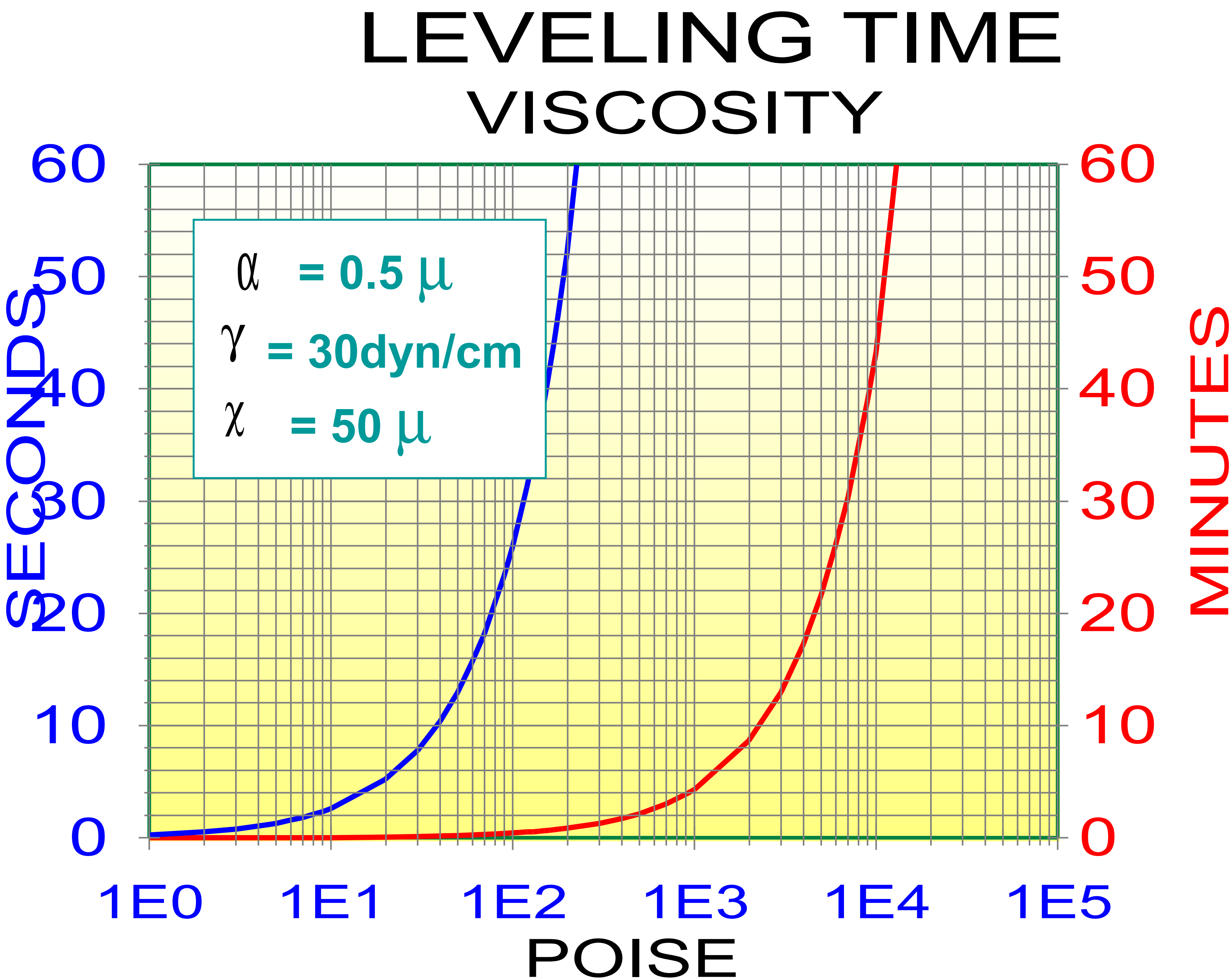


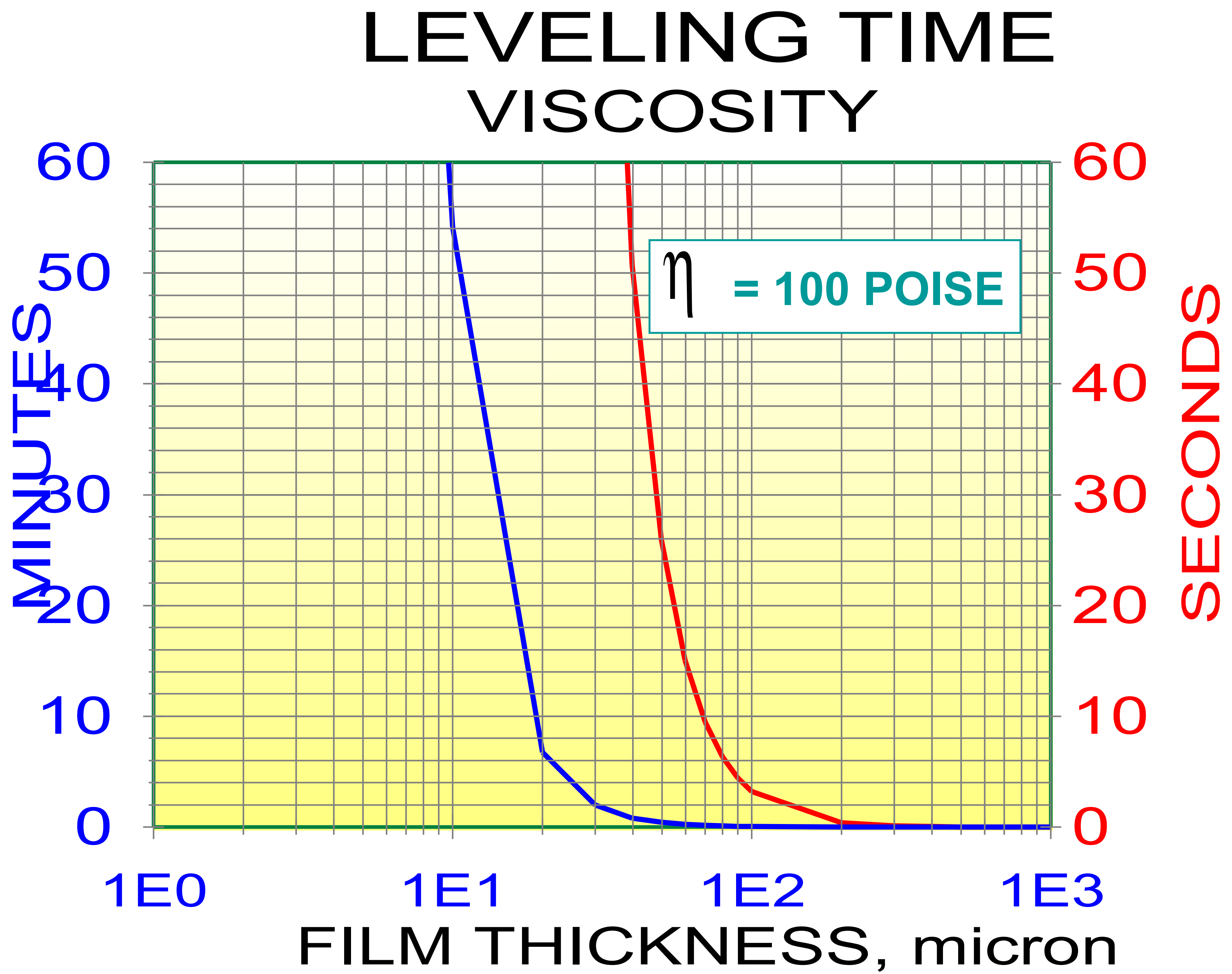
Coating Leveling



$$\Delta t = \frac{\log(\alpha_0/\alpha_t)\lambda^4\eta}{226\gamma\chi^3}$$

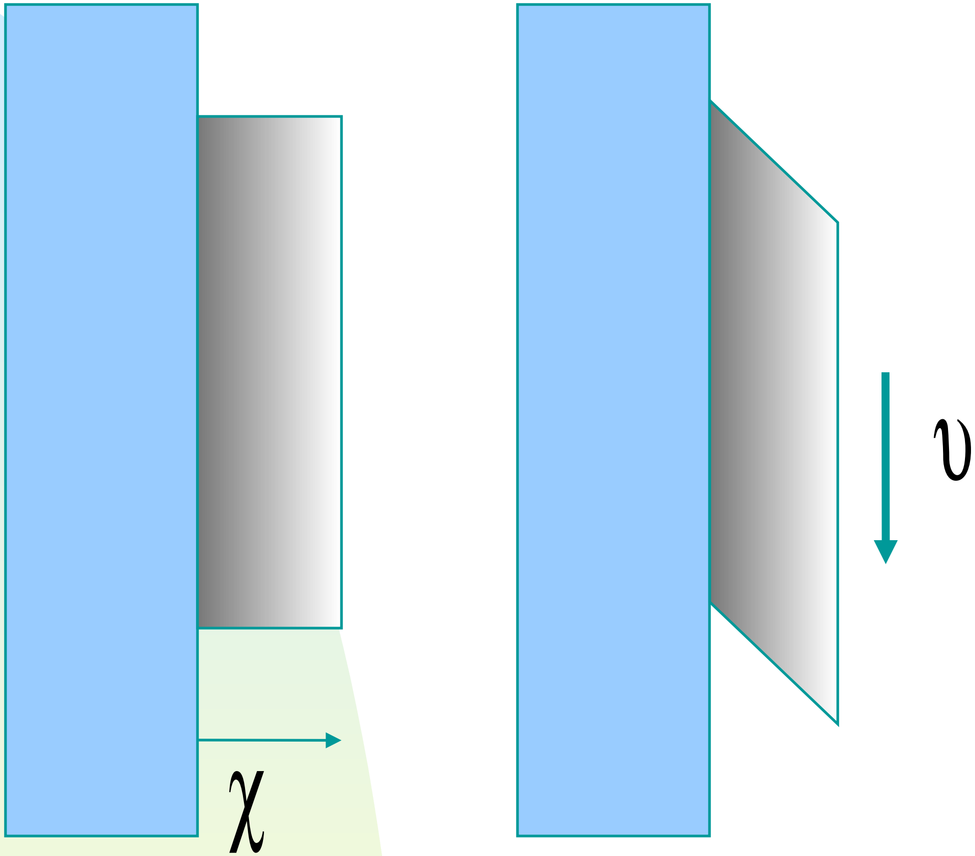
γ **= dynes/cm**


LEVELING TIME
VISCOSITY
α = 0.5 μ
γ = 30dyn/cm
χ = 50 μ
SECONDS
MINUTES
0
10
20
30
40
50
60
1E0
1E1
1E2
1E3
1E4
1E5
POISE



LEVELING TIME
VISCOSITY
η = 100 POISE
MINUTES
SECONDS
60
50
40
30
20
10
0
1E0
1E1
1E2
1E3
FILM THICKNESS, micron

SAGGING

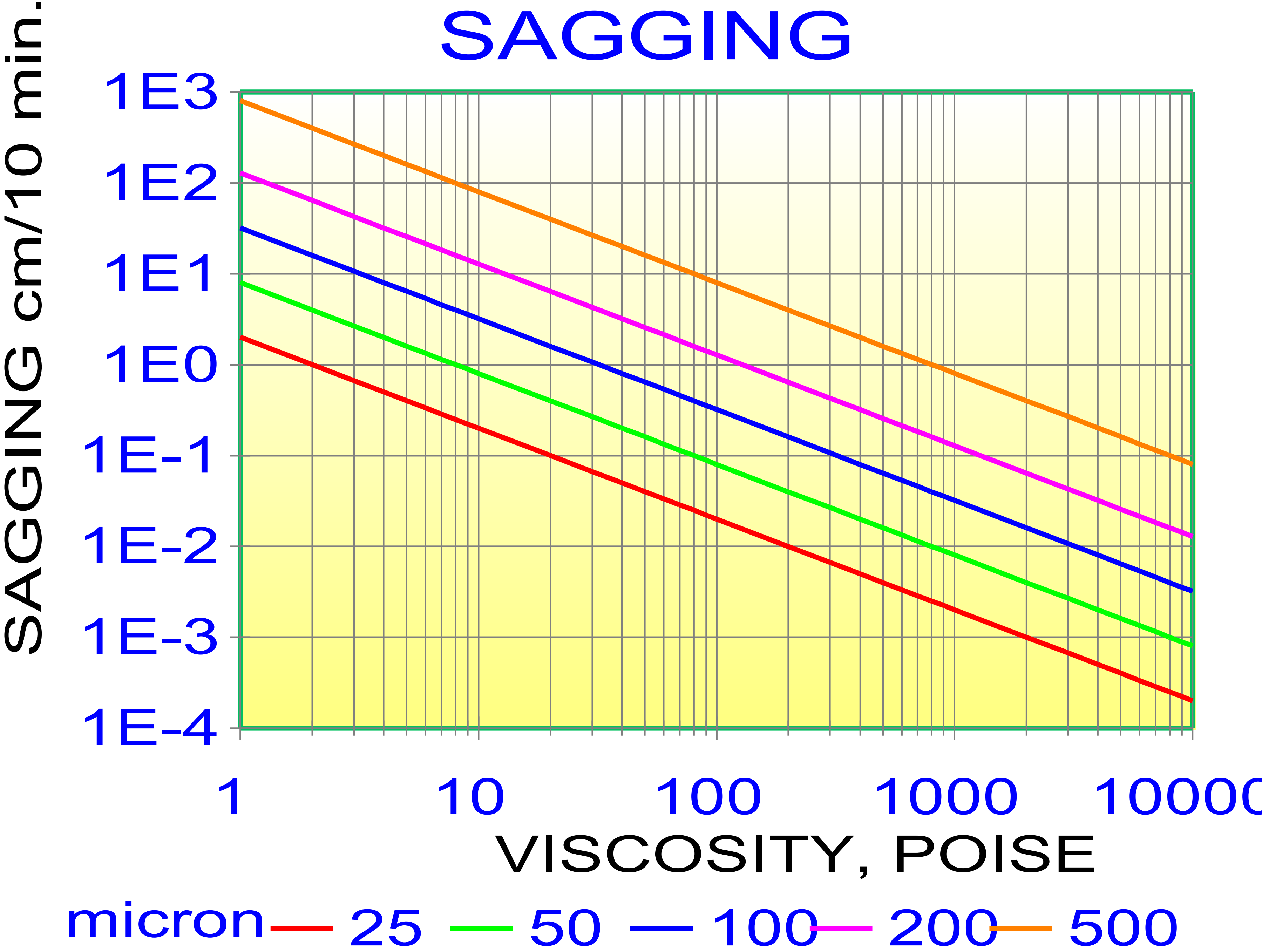


η = Poise

$\rho = g/cm^3$

$g = 980\ cm/sec^2$

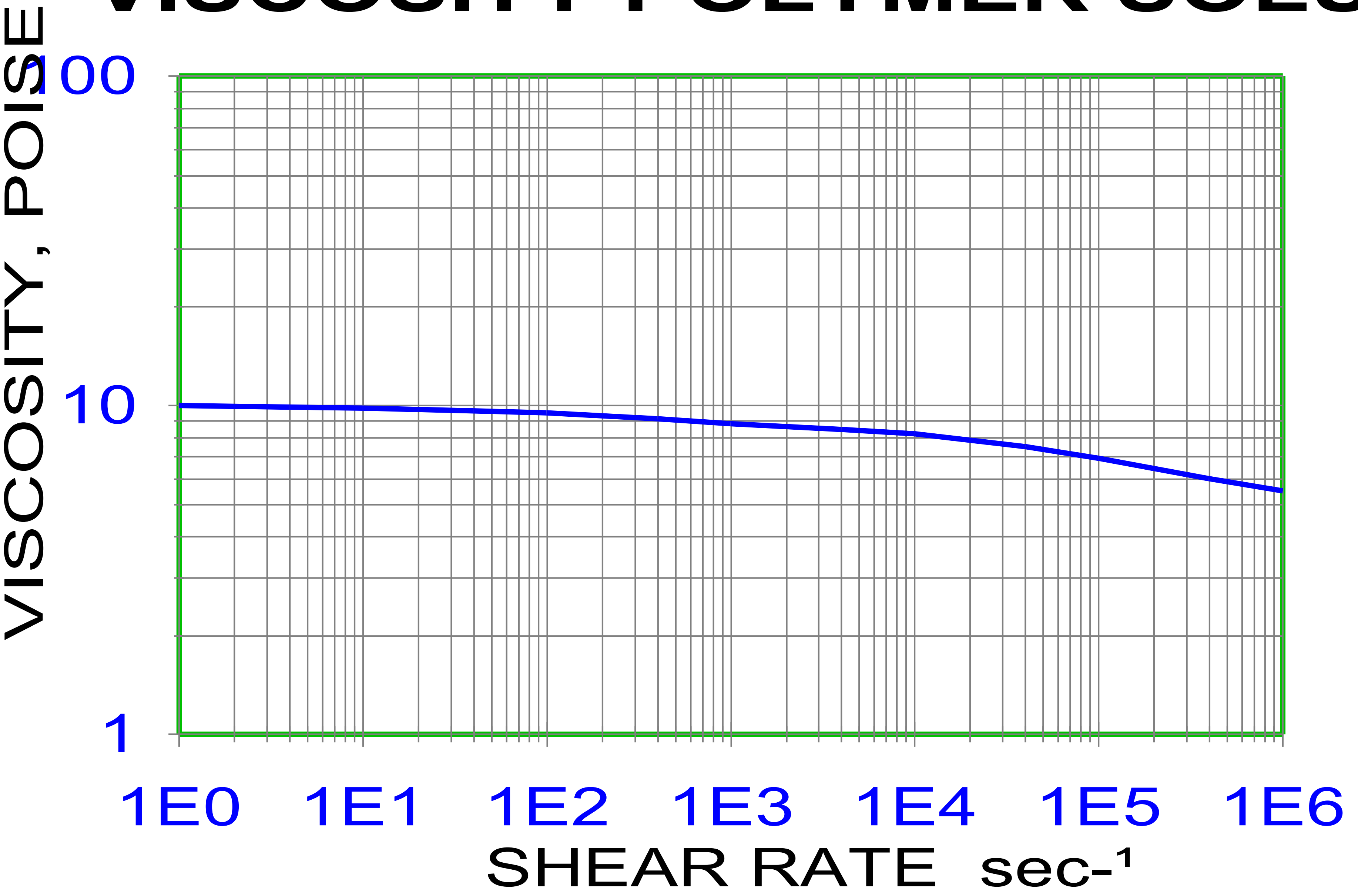
$$\upsilon = \frac{\rho g \chi^2}{2\eta}$$


SAGGING
SAGGING cm/10 min.
1E3
1E2
1E1
1E0
1E-1
1E-2
1E-3
1E-4
1
10
100
1000
10000
VISCOSITY, POISE
micron
25
50
100
200
500

Effect of Coating Variables on Rheology (Structure / Property Relationships)

- Effect of Coating Ingredients
  - Binders (Solutions Vs Dispersions)
  - Pigments & Fillers
  - Dispersants & Surfactants
  - Rheology Modifiers
- Coating Rheology Customization
  - Criteria for Rheology Modifier Selection
  - Criteria for Other Additives Selection

VISCOSITY POLYMER SOLU



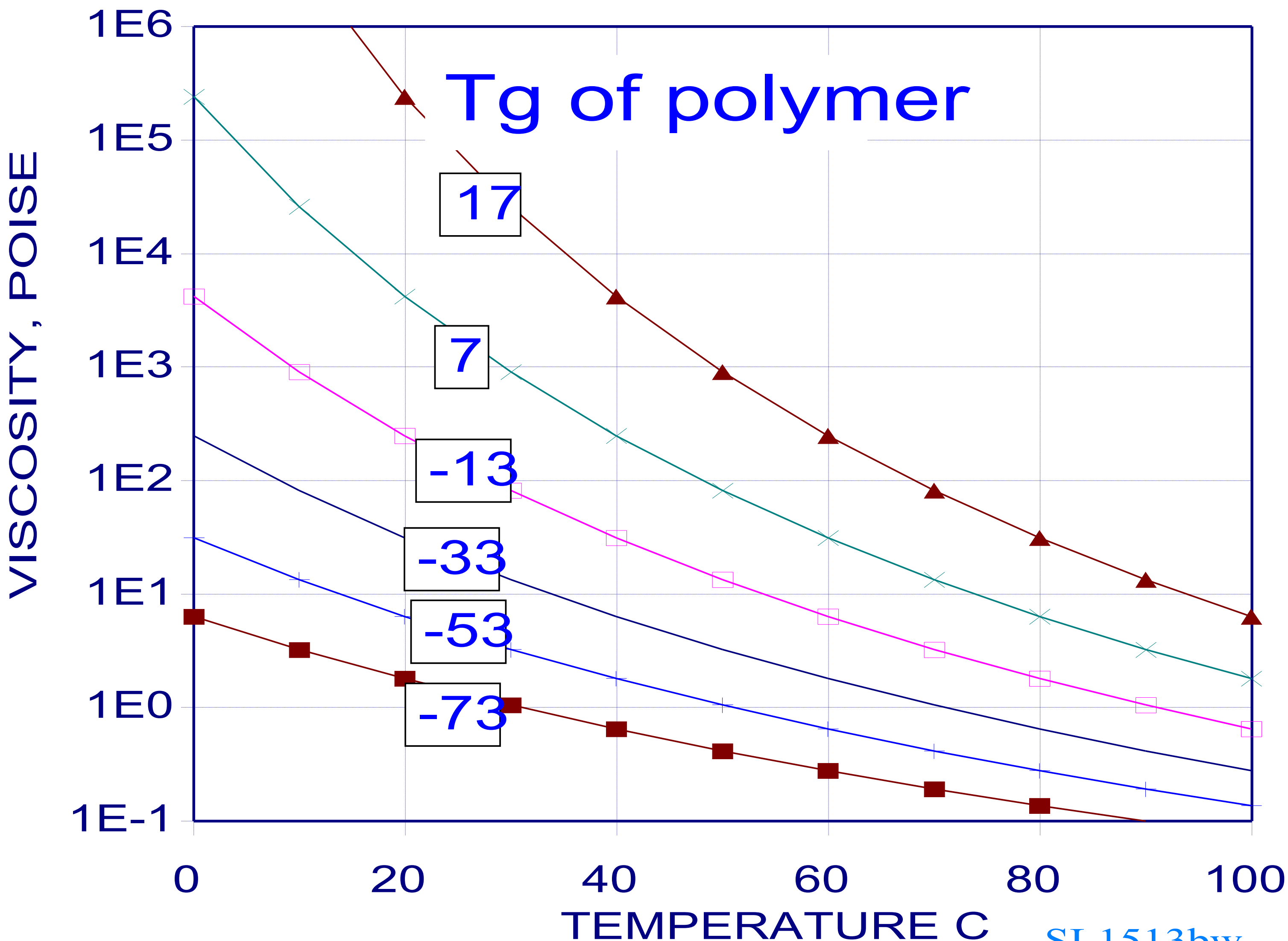
WLF Equation

$$\log \eta_T = 13 - \frac{17.44(T-Tg)}{51.6+(T-Tg)}$$

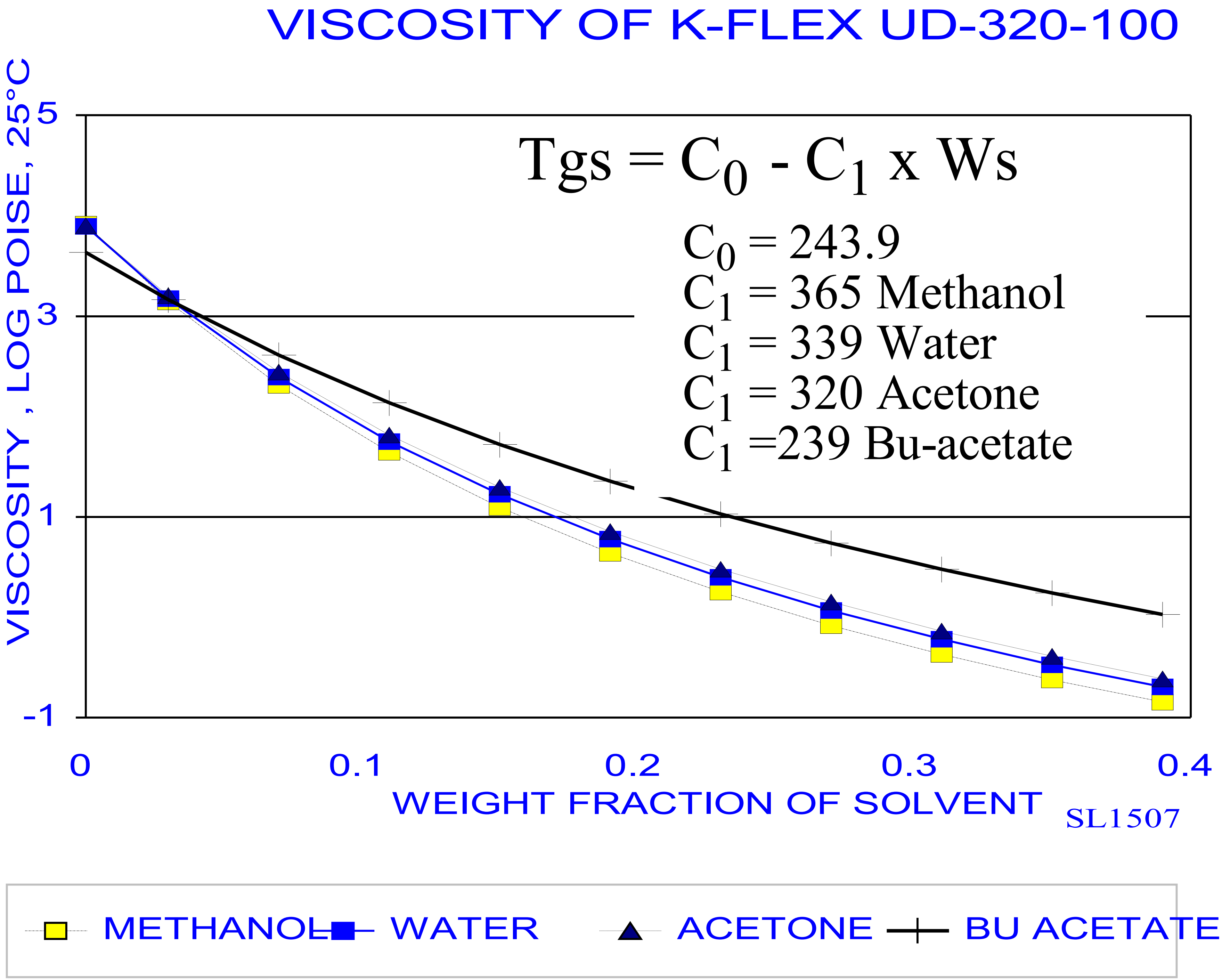
$$Tg_s = C_o - C_1 \times W_s$$

VISCOSITY as a FUNCTION OF Tg

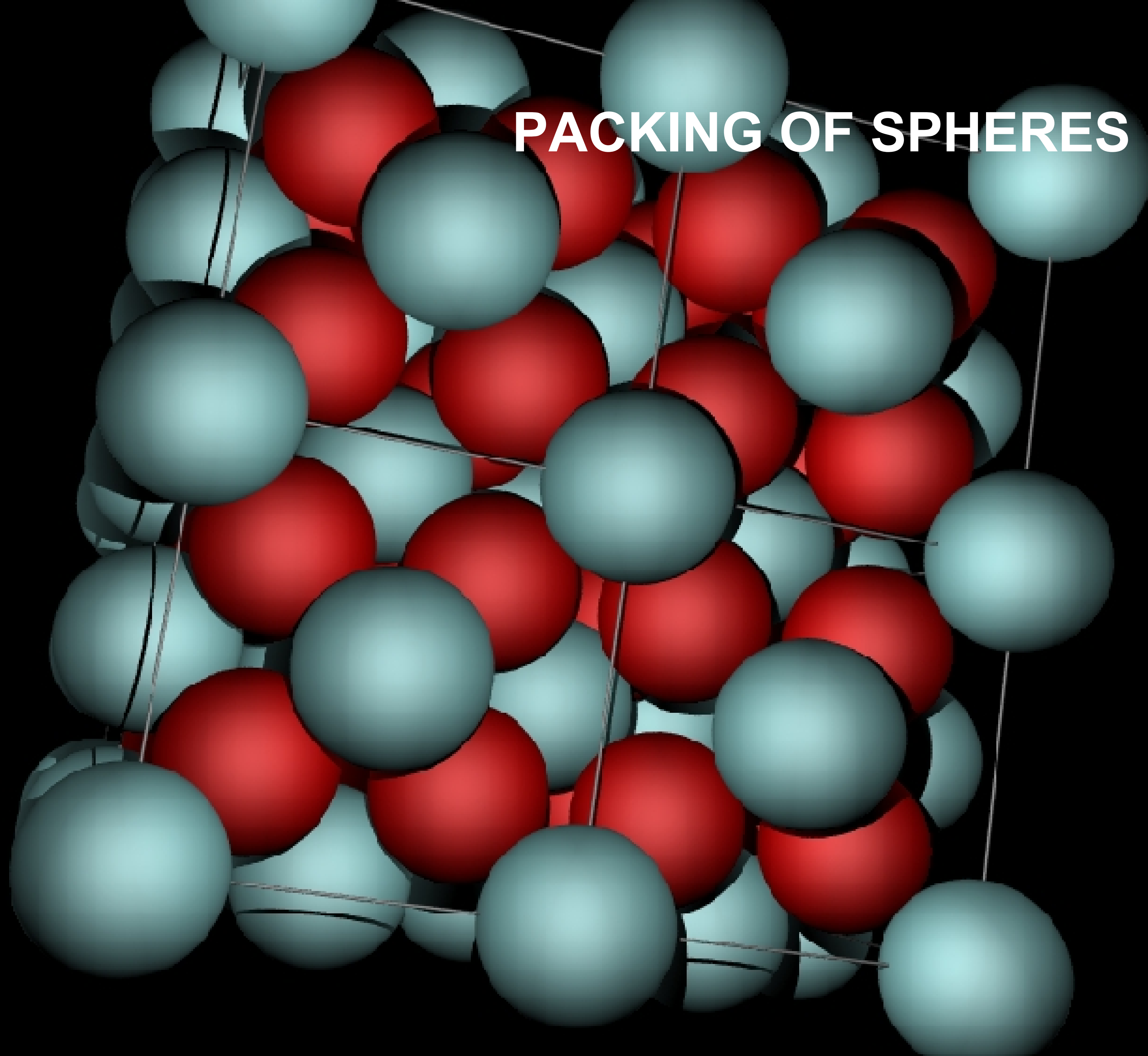
WILLIAMS,LANDEL,FERRY EQUATION



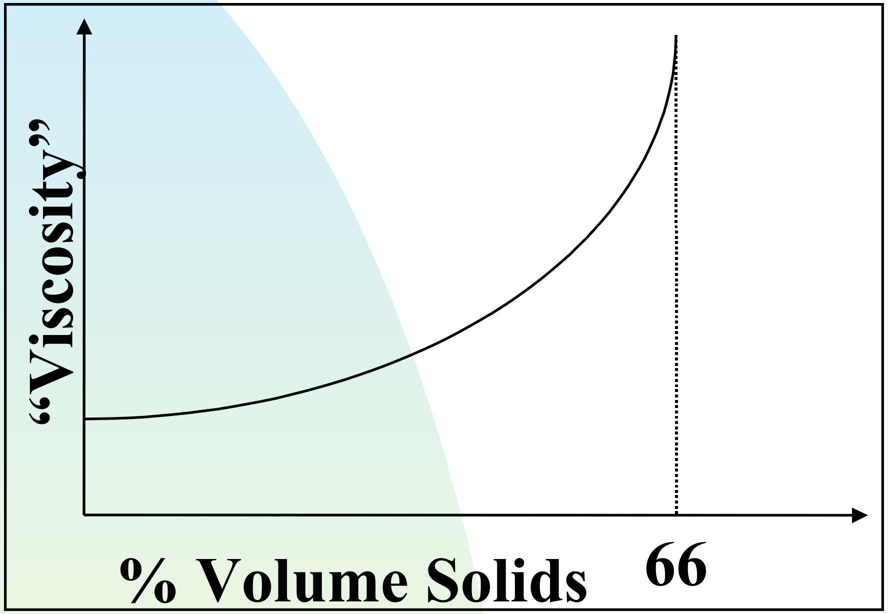
SL1513bw

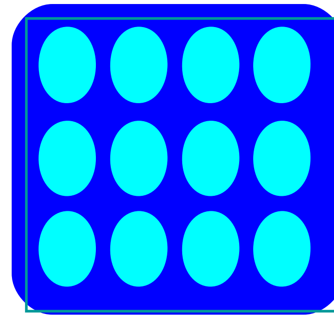

VISCOSITY OF K-FLEX UD-320-100
VISCOSITY , LOG POISE, 25°C
5
3
1
-1
Tgs = C0 - C1 x Ws
C0 = 243.9
C1 = 365 Methanol
C1 = 339 Water
C1 = 320 Acetone
C1 =239 Bu-acetate
0
0.1
0.2
0.3
0.4
WEIGHT FRACTION OF SOLVENT
SL1507
METHANOL
WATER
ACETONE
BU ACETATE

PACKING OF SPHERES

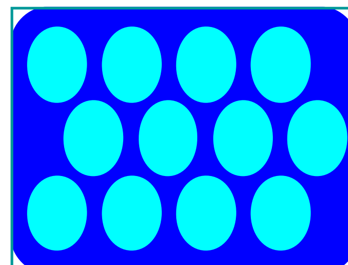


Effect of Dispersed Coating Ingredients





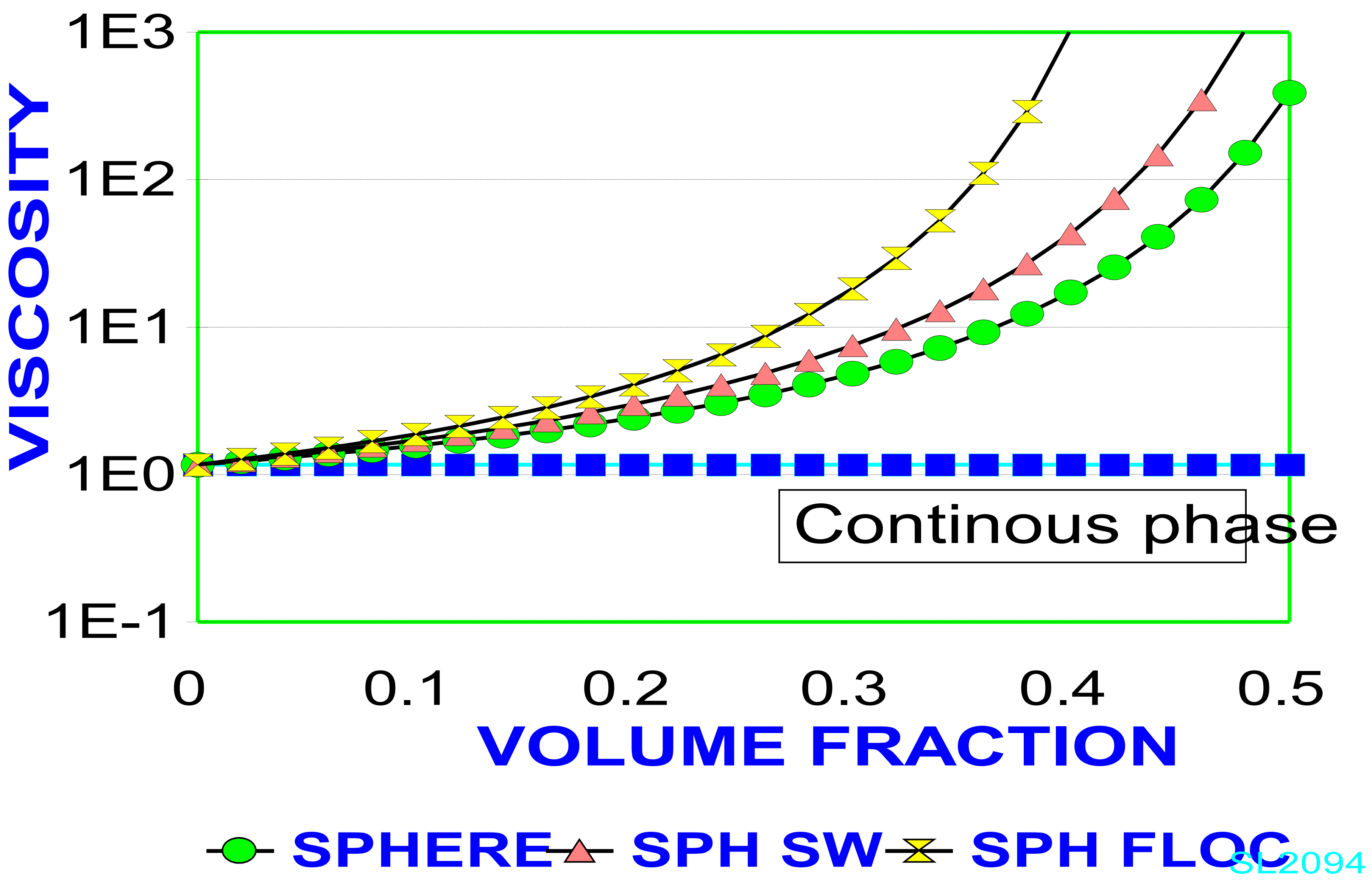
Cubic Packing
Critical Volume Fraction - 0.5236

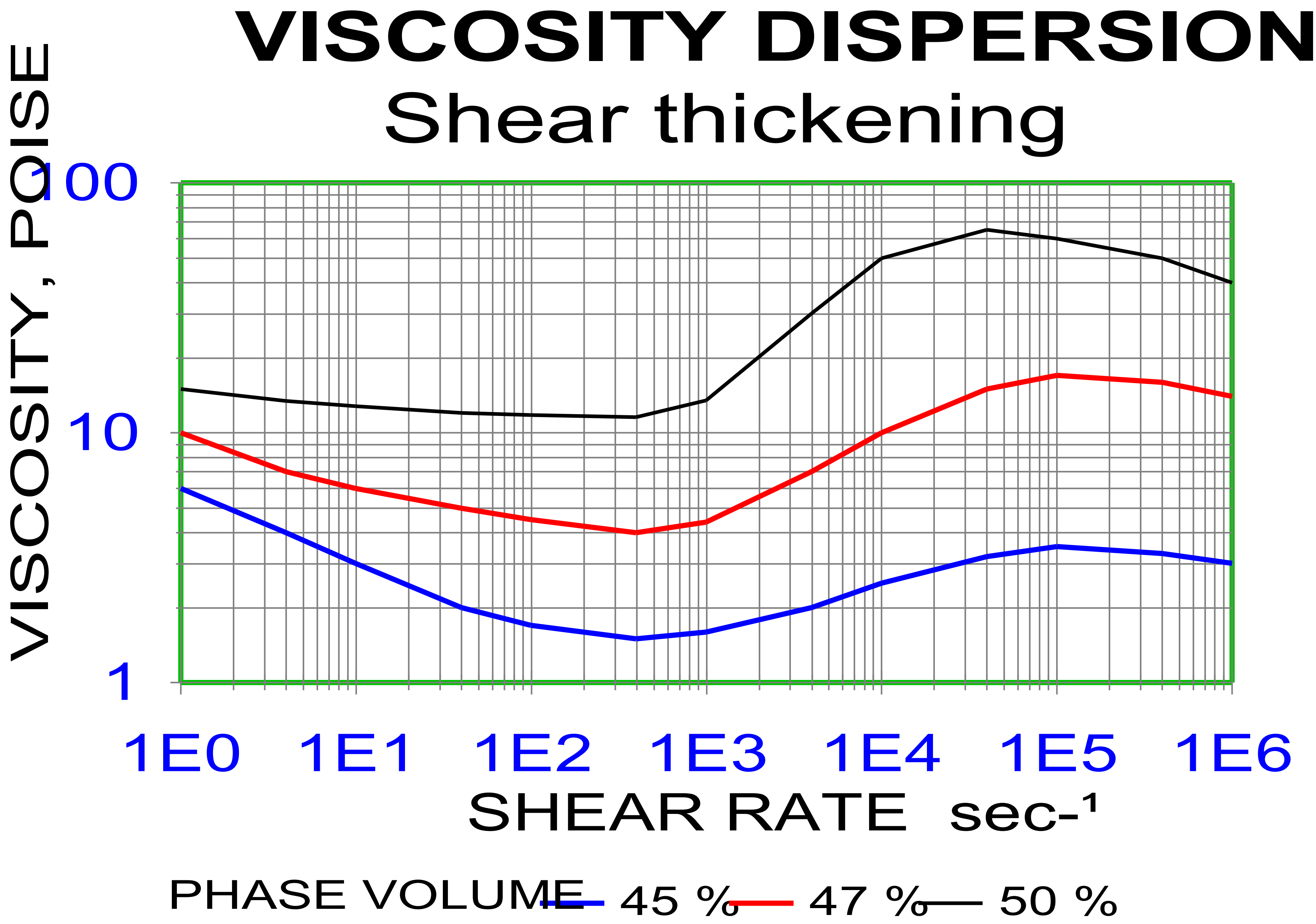


Tetrahedral Packing
Critical Volume Fraction - 0.7405

For Random Packing, Critical Volume Fraction - 0.66

VISCOSITY OF DISPERSIO




VISCOSITY DISPERSION
Shear thickening
VISCOSITY, POISE
100
10
1
1E0
1E1
1E2
1E3
1E4
1E5
1E6
SHEAR RATE sec-¹
PHASE VOLUME
45 %
47 %
50 %

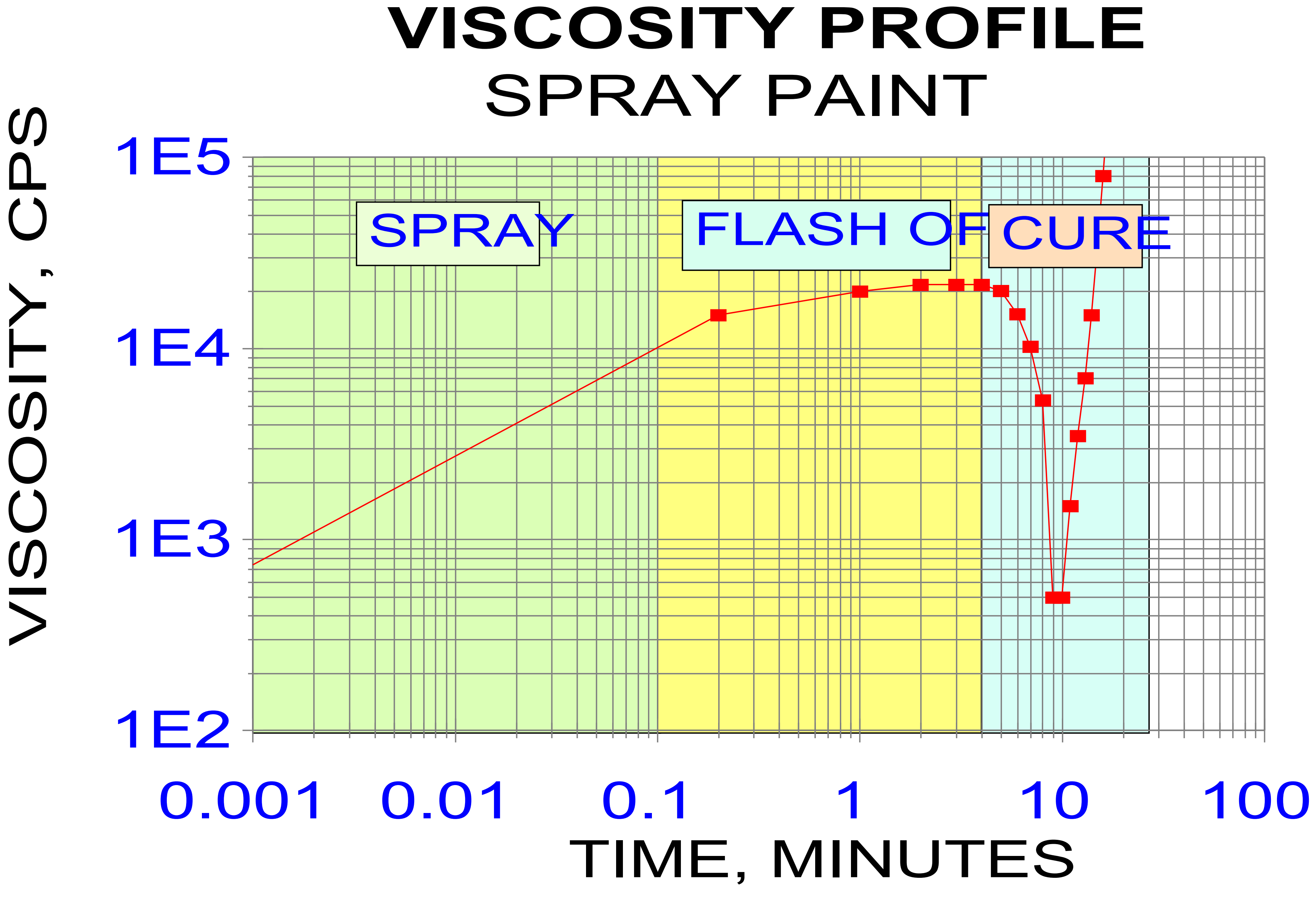
RHEOLOGY CONTROL SOLVENT BORNE COATINGS

EFFECT OF RHEOLOGY CONTROL

SAGGING
PIGMENT SETTLING
FLOW LEVELING
INTERCOAT ADHESION
FLOATING AND FLOODING
GLOSS
SEEDING

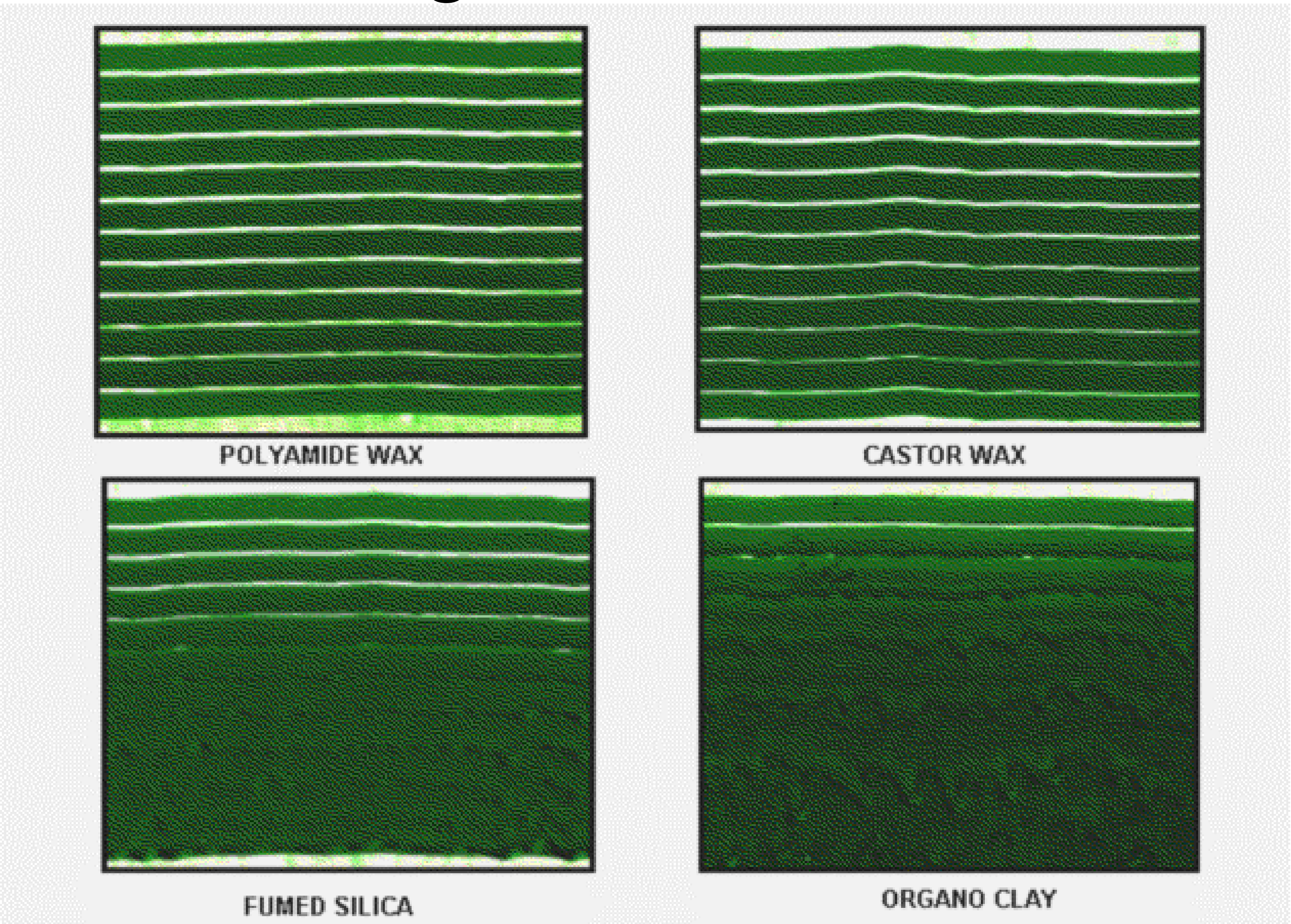
EFFECTIVENESS

POLARITY SOLVENT
DISPERSION PROCESS
TEMPERATURE
RESIN COMPOSITION



VISCOSITY PROFILE
SPRAY PAINT
VISCOSITY, CPS
1E5
1E4
1E3
1E2
SPRAY
FLASH OF
CURE
0.001
0.01
0.1
1
10
100
TIME, MINUTES

Sag Resistance



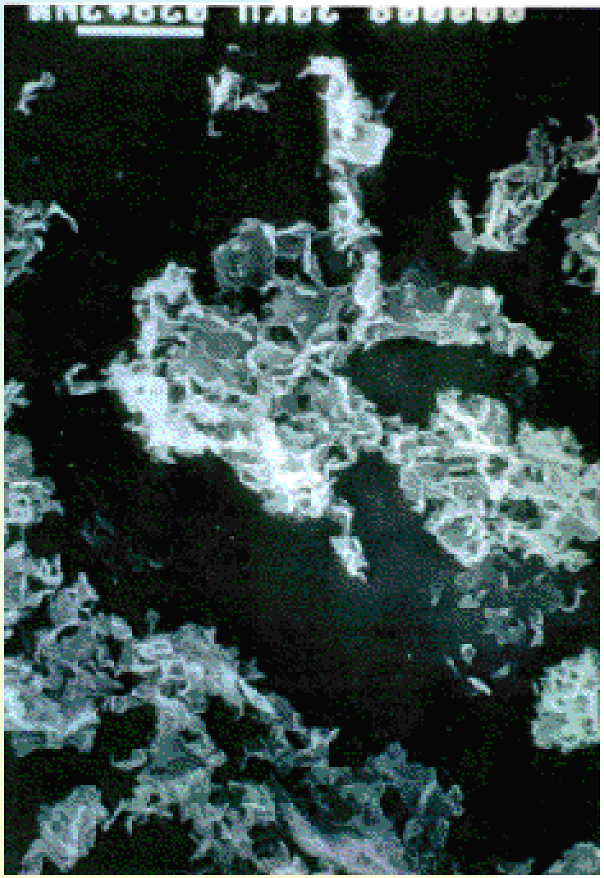
RHEOLOGY MODIFIER

- ATTAPULGITE
- SMECTITE
- ORGANO CLAY
- ORGANO SULFONATE
- SILICA
- TITANATE

- POLYOLEFIN
- ASSOCIATIVE
- POLYESTER
- POLYACRYLATE
- POLYAMIDE
- CASTOR DERIVATIVE
- POLYUREA

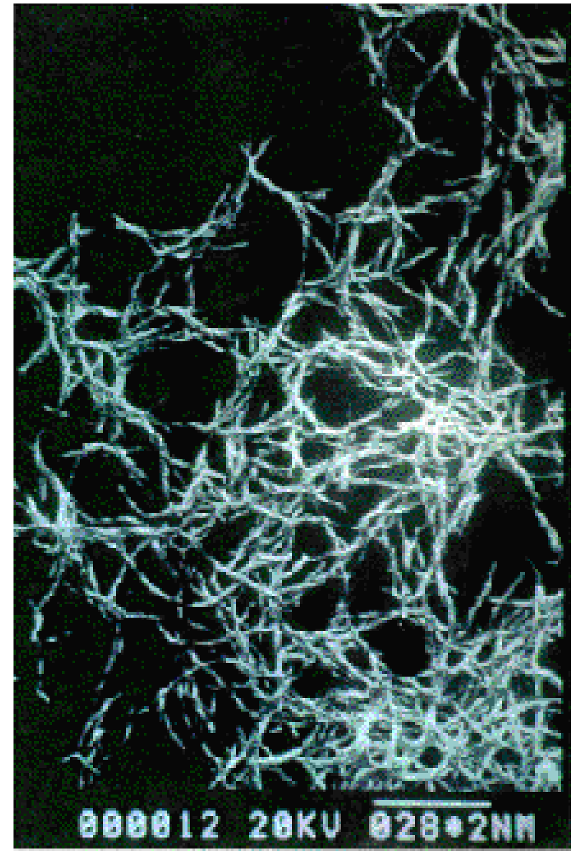
SEPARATE PHASE - ASSOCIATION

Micrographics



Organo Clay -
Platelet Structure
Hydrogen Bonding

Polyamide -
3D Branching

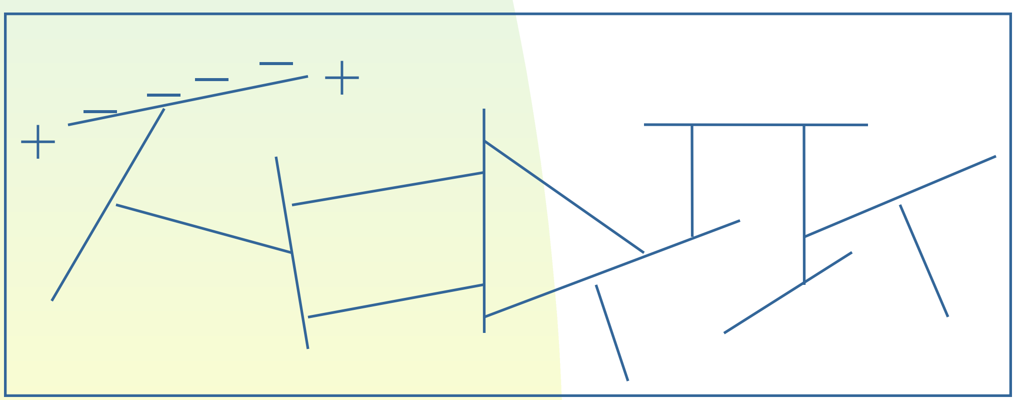


Inorganic Rheology Modifiers (Thickeners)

Inorganic

→ Ultra-Fine Clays (Laponites)

→ Other Inorganics (Bentonite, Attapulgite)



Positive Edges & Negative Faces

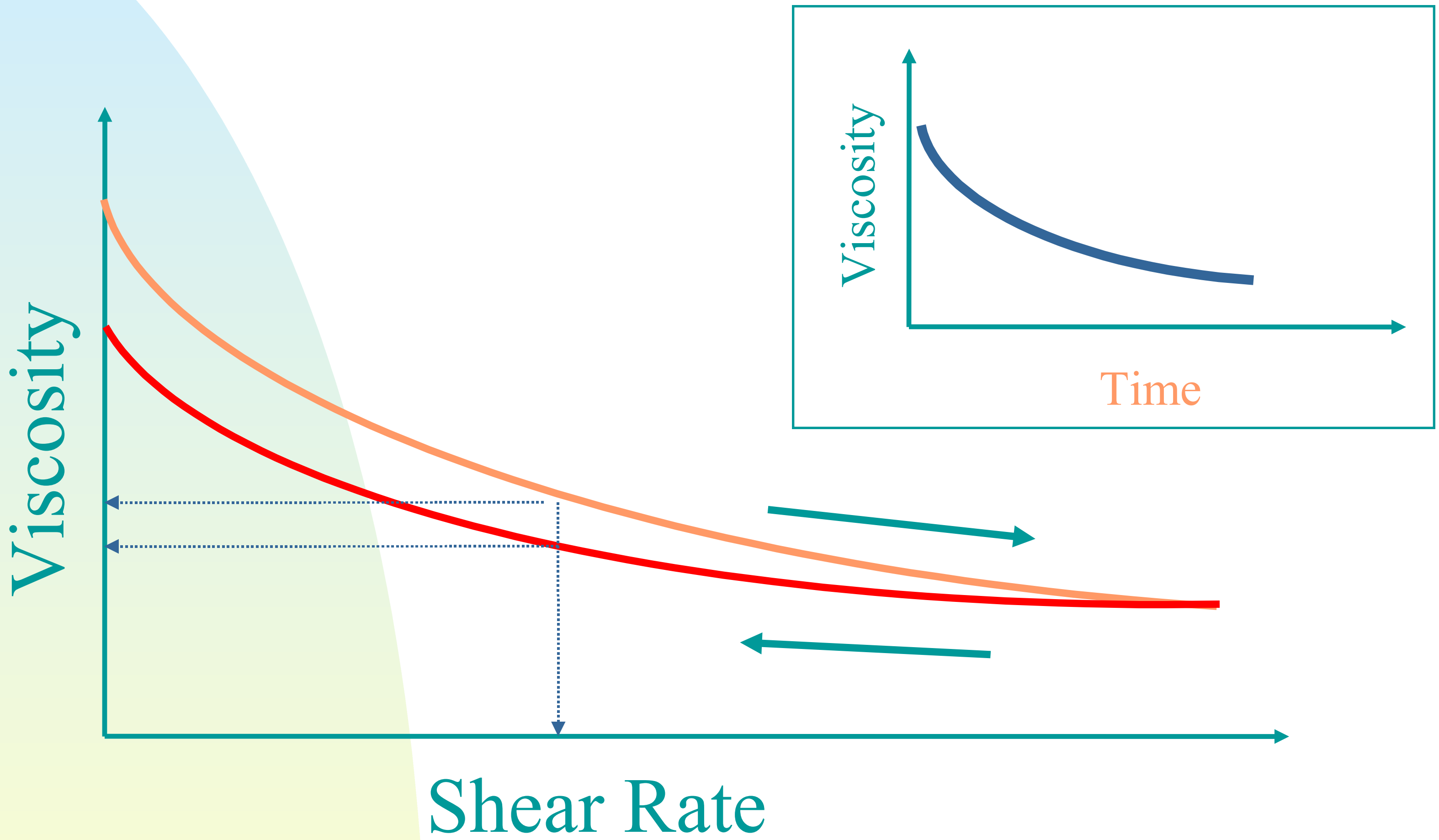
Weak Structure, Highly Shear Thinning

SHEAR THINNING

THIXOTROPE

PSEUDOPLASTIC

Thixotropy



Thixotropy can increase viscosity measurement error

Settling at 140°F

Polyamide | Hydrogenated Castor

Thixotropes - Incorporation

- Organo-Clay
  - Milled with pigments -- Moisture in platelets
- Fumed Silica
  - Added during letdown
- Hydrogenated Castor Wax
  - Heat activated in mill stage--mix while cooling
- Polyamide
  - Heat activated in mill stage--mix while cooling
  - Or -- Preactivated added during letdown

High Solids Epoxy/Polyamide Marine Primer

Polyamide Component	
Thixotrope	10
Polyamide adduct	300
Polyamide	35
Titanium dioxide	100
Talc	414
Yellow iron oxide	20
Phthalocyanine blue	1
Butyl alcohol	252

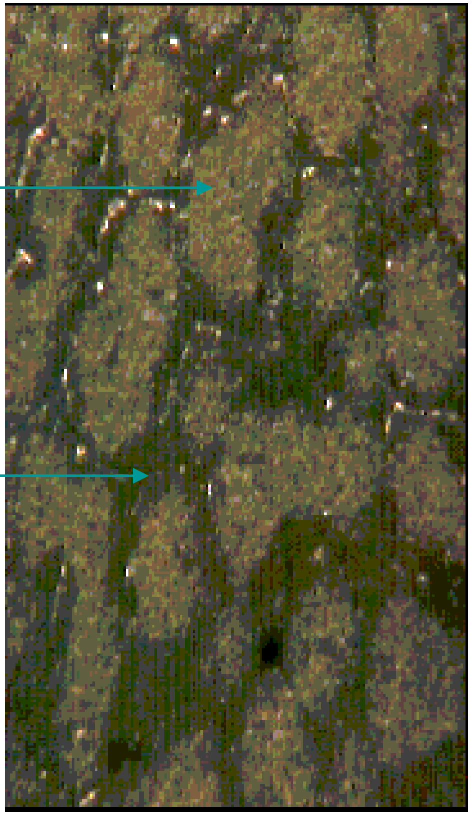
Epoxy Component	
Thixotrope	15
Bis A epoxy	500
Talc	286
Hydrous kaolin clay	150
Naphtha	200

Orientation of Particles

<u>Oil Modified Urethane</u>
<u>Silica Flatting Agent</u>

Silica
Agglomerates

Areas
of higher gloss!



Organoclay

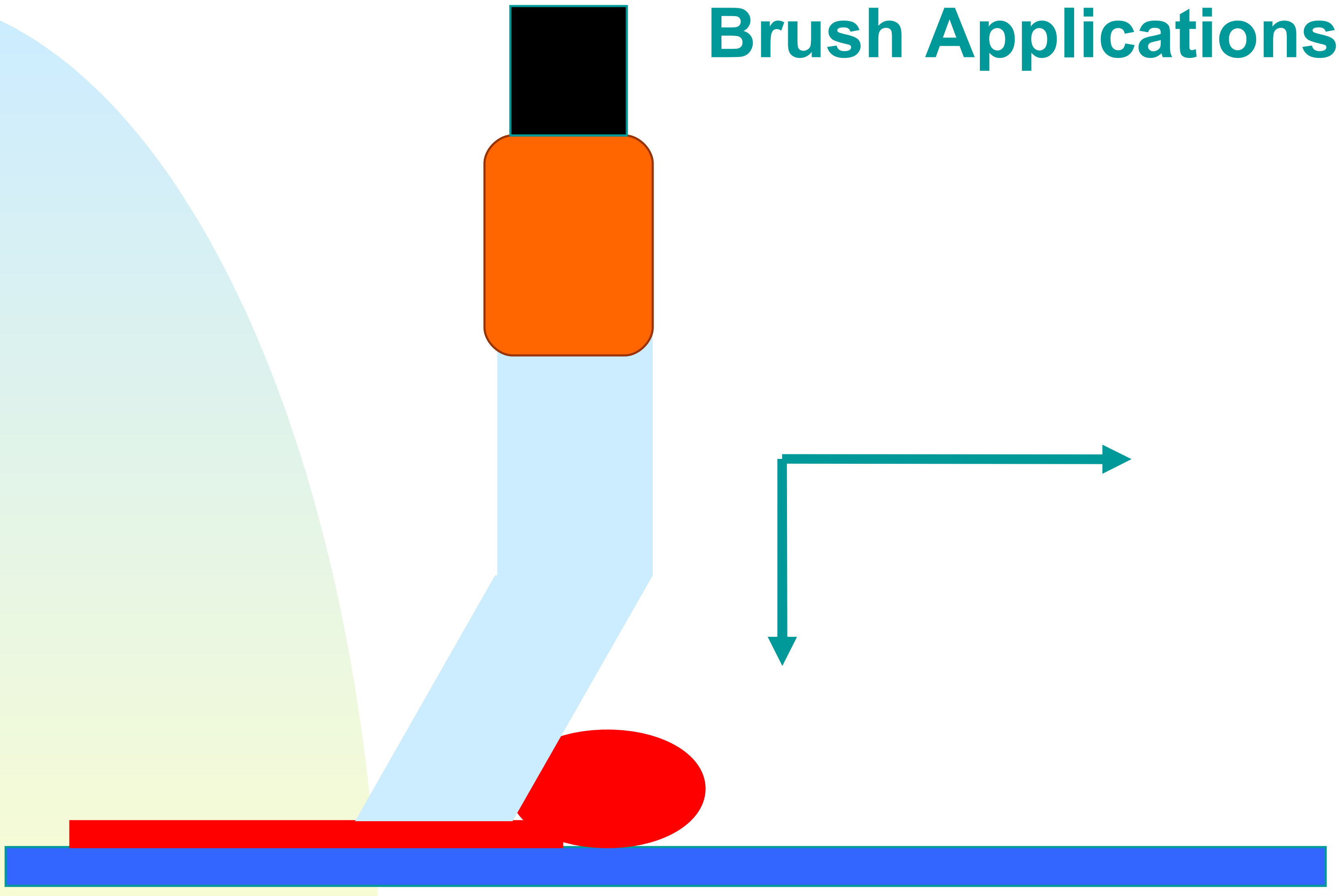
Polyamide

RHEOLOGY FOR WATERBORNE COATINGS

- CELLULOSE DERIVATIVES
  - Hydroxyethyl cellulose
  - Carboxymethyl cellulose
  - Methyl cellulose
- CARBOXYL FUNCTIONAL ACRYLIC
- ASSOCIATIVE THICKENER
  - HEUR (PEO-hydrophob)
  - HASE (Acrylic- Hydrophob)
  - HMHEC
- POLYAMIDES

- INORGANIC
  - Synthetic Clays
  - Colloidal Silica

Brush Applications

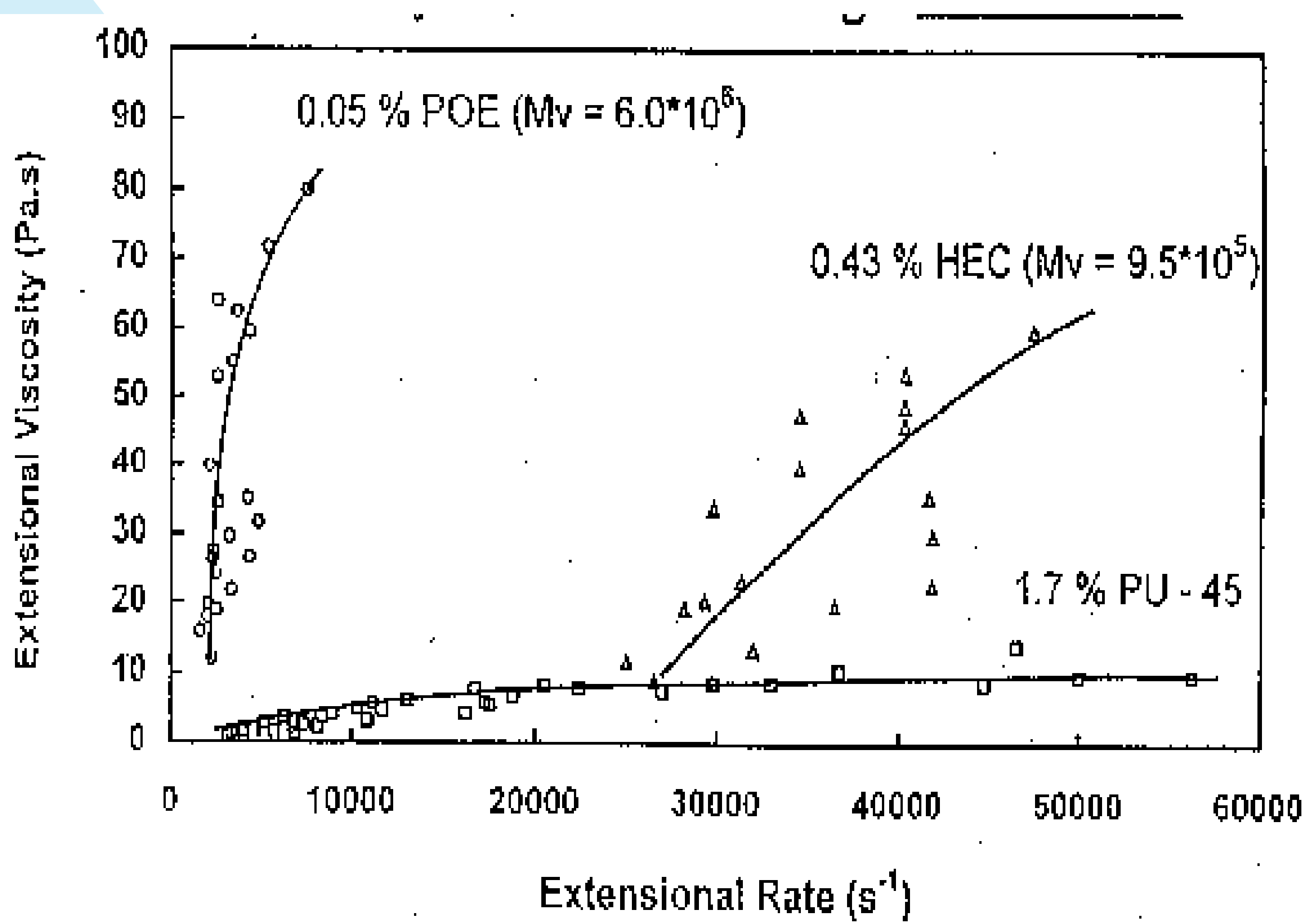


BRUSH APPLICATION

SETTLING **THIXOTROPY**
LOW RESISTANCE TO BRUSHING **HSV**
GOOD FILM THICKNESS AND HIDING POWER **HSV/HSV**
NOT SAGGING **LSV**
FLOW AND LEVELING **LSV**

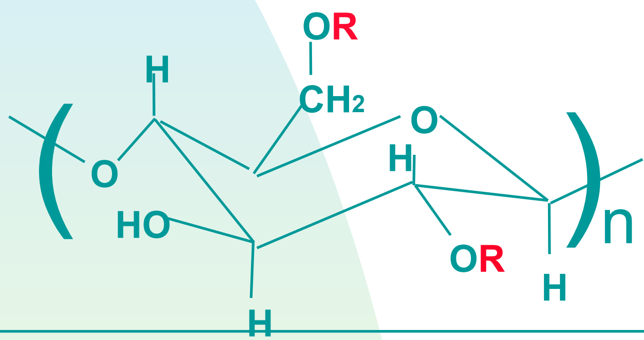
LSV = LOW SHEAR VISCOSITY
HSV = HIGH SHEAR VISCOSITY

Extensional Viscosities of Waterborne Latex Paints



Organic Rheology Modifiers (Cellulosics)

Hydroxyethyl Cellulose



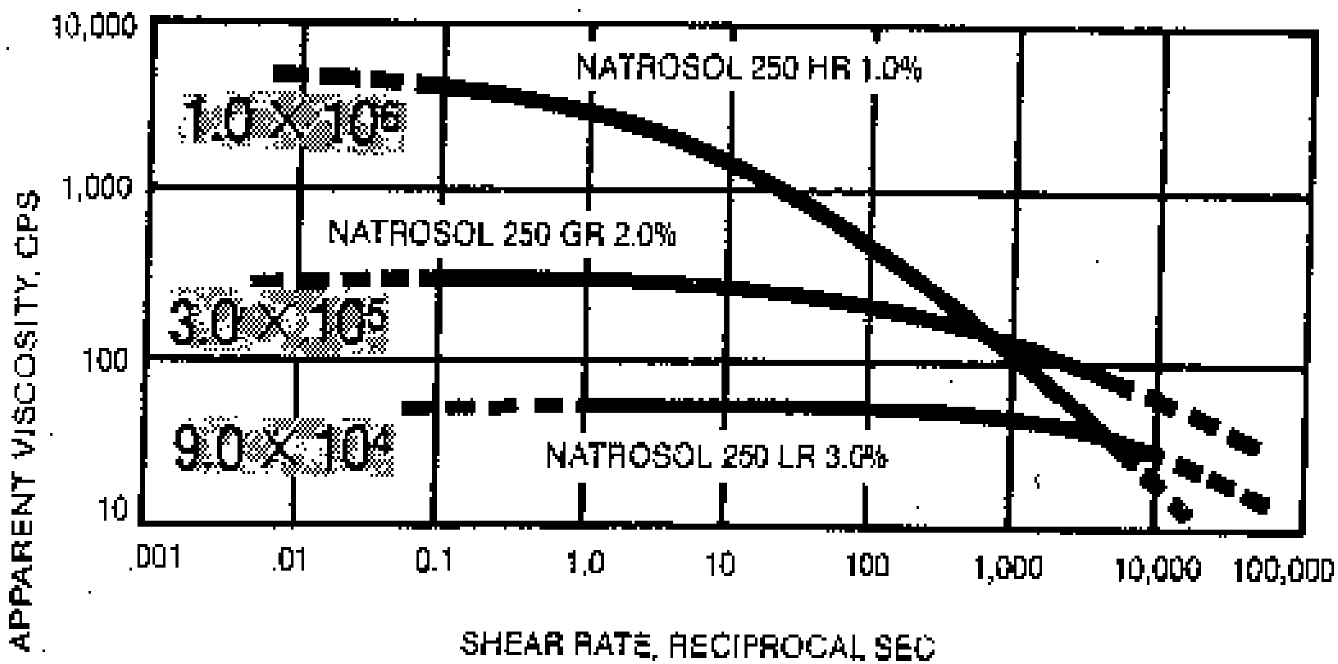
R = $-CH_2CH_2OH$ = Hydroxyethyl
R = $-CH_2COONa$ = Carboxymethyl
R = - C_2H_5, $-CH_2CH_2OH$,= Ethyl, Hydroxyethyl
R = - CH_3, $-CH_2CH_2OH$,= Methyl, Hydroxyethyl

<u>Natrosol 250 HR</u>

MS - 2.5; M -715,000;

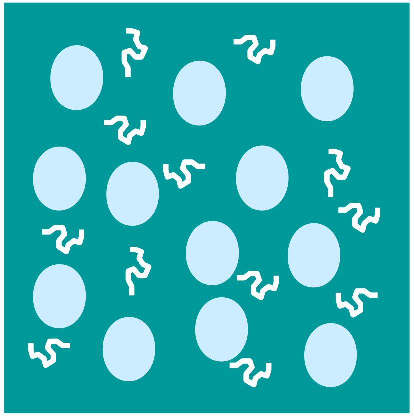
Effect of Molecular Weight on Thickening

MW effect

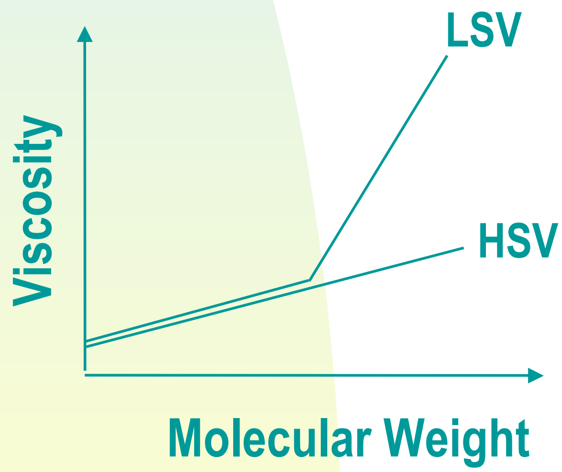


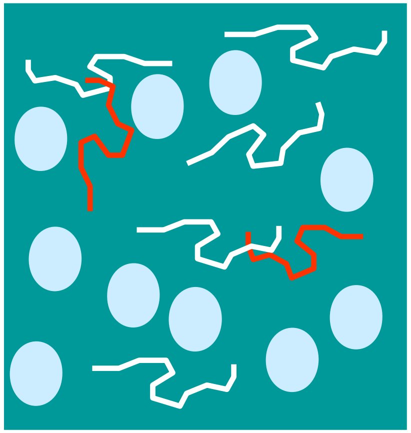
Cellulosics -Thickening Mechanisms

A. Contribution to Hydrodynamic Volume



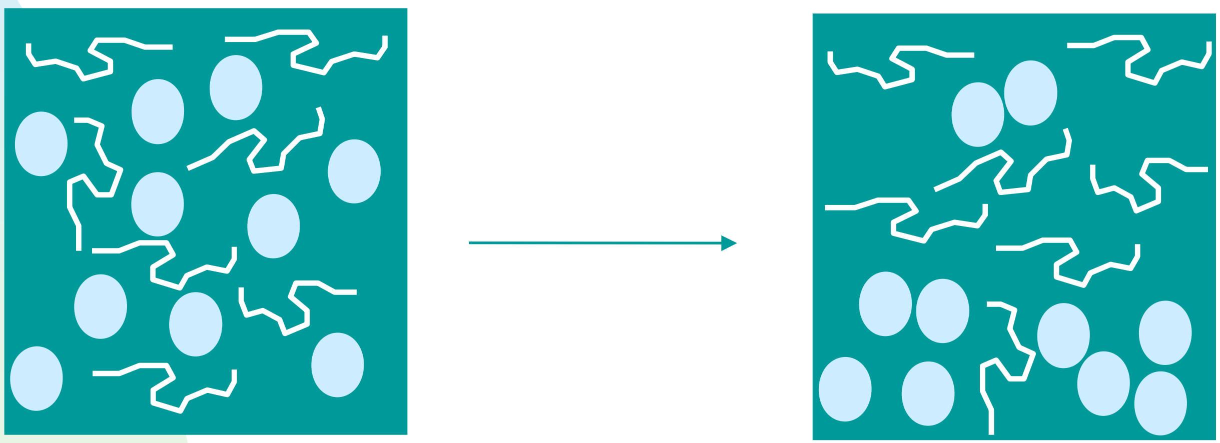
B. Chain Entanglements (Croll & Kleinlein, 1986)





Cellulosics - Thickening Mechanisms

C. Depletion Flocculation (Asakura & Oosawa, 1958; Sperry et al., 1981)



Lower Entropy

Higher Entropy

When Interparticle Distance Approaches WSP Molecular Dimensions
There is a Loss of Conformational Degrees of Freedom

$$\Delta G = \Delta H - T\Delta S$$

Cellulosics - Advantages & Disadvantages

Cellulosics Low Cost Thickeners

- Poor Leveling (High LSV; Yield Stress)
- Reduction of Gloss (Depletion Flocculation; Poor Leveling)
- Roller Spatter (Extensional Viscosity)
- Water Sensitivity (WSP Hydrophilicity)
- Bio-degradation (Enzyme Attack on beta 1-4 Linkage)
- Syneresis (Depletion Flocculation)

Associative Thickeners

Several Different Types Currently in the Market

- HEUR (Hydrophobically-Modified Ethoxylated Urethanes)
- HASE (Hydrophobically-Modified Alkali-Swellable Emulsions)
- HEURASE
- HMHEC (Hydrophobically-Modified HEC)

Associative Thickeners - HEUR Type

R-NH-C(=O)-(O-CH -CH) -[O-C(=O)-NH-R”-NH-C(=O)-(O-CH -CH)] -O-C(=O)-NH-R’

R, R’ = C -C ; R” = C -C ; x = 90 - 455; n = 1-4

Acrysol QR-708 ⇨ Acrysol RM-8 ⇨ Acrysol RM-825 K-STAY 700

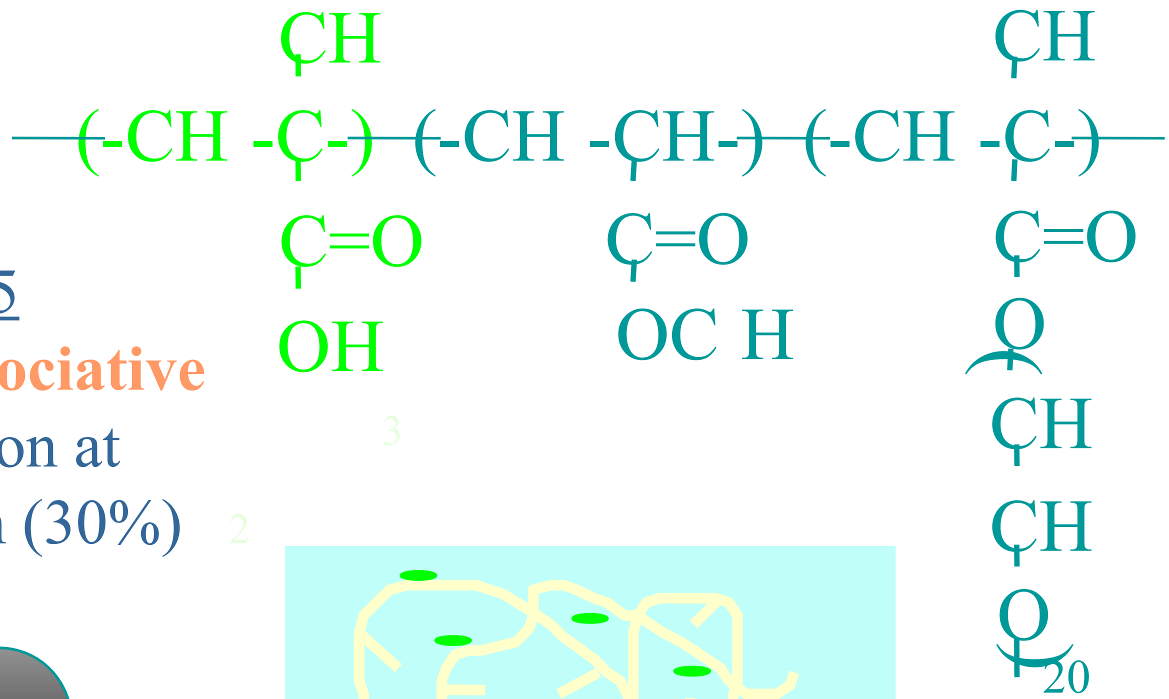
(C H Terminal Hydrophobes; 40,000 Approx.. M.W.)

Acrysol RM-2020

UCAR SCT-275 ⇨ Acrysol SCT-275

(Comb-type; 120,000 Approx.. M.W.)

Associative Thickeners - HASE Type

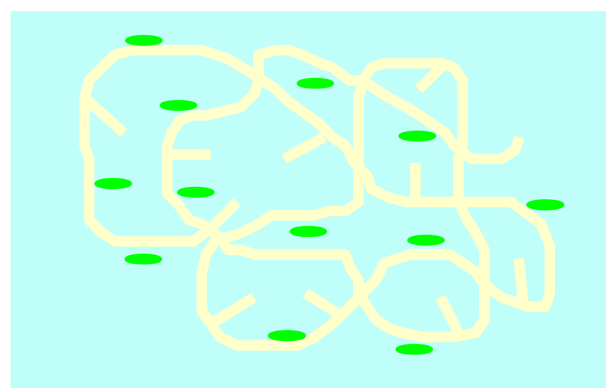


K-STAY 800

Acrysol TT-615

Alkali-Swellable, Associative

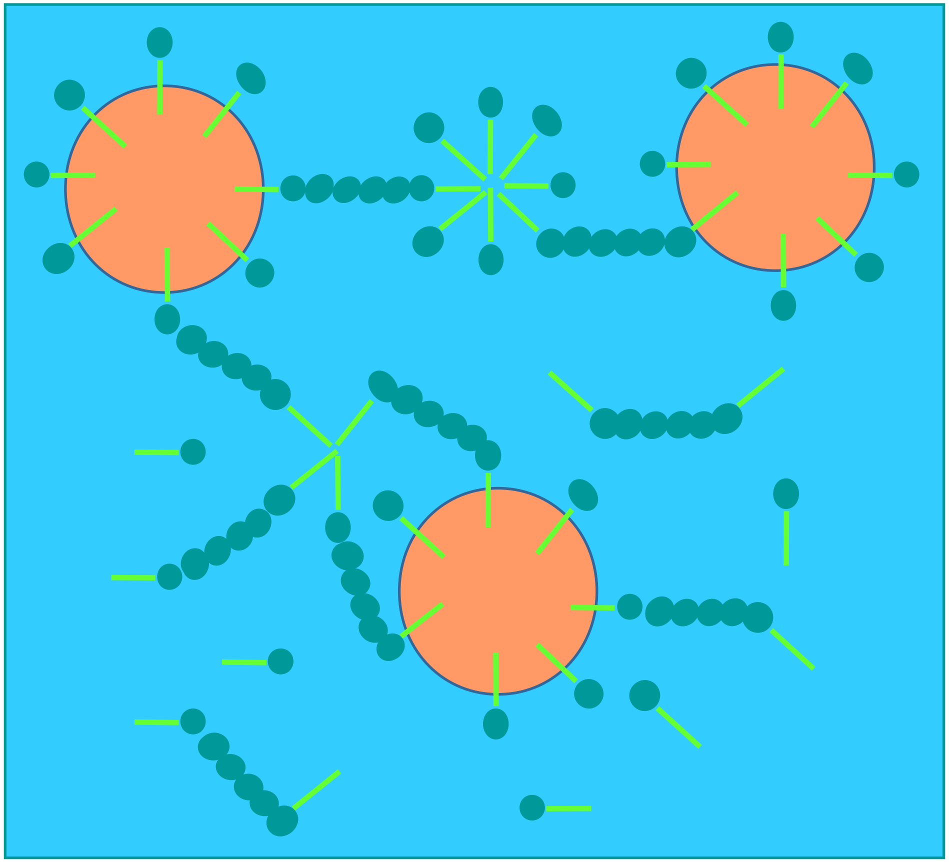
Thickener Dispersion at "High" Concentration (30%)



Associative Thickeners - HEUR Association Modes

Many Association Modes Possible Depending on Molecular Architecture

- Adsorption
  - Hydrophobic
  - Ion-Dipole
- Self Association
  - Intra-Molecular
  - Inter-Molecular
- Mix Micelle Formation

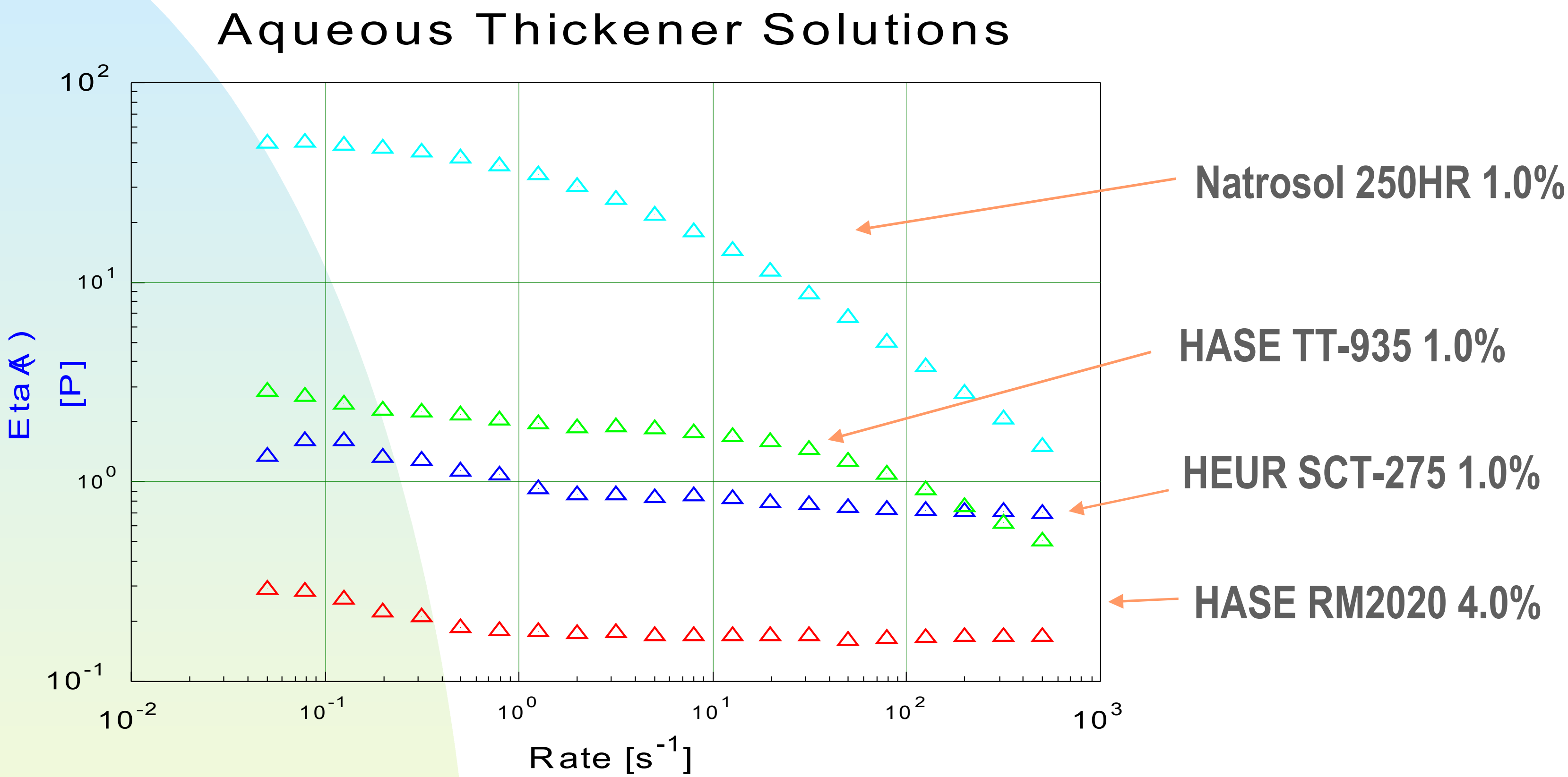


Sensitivity of Associative Thickeners

Performance Sensitivity

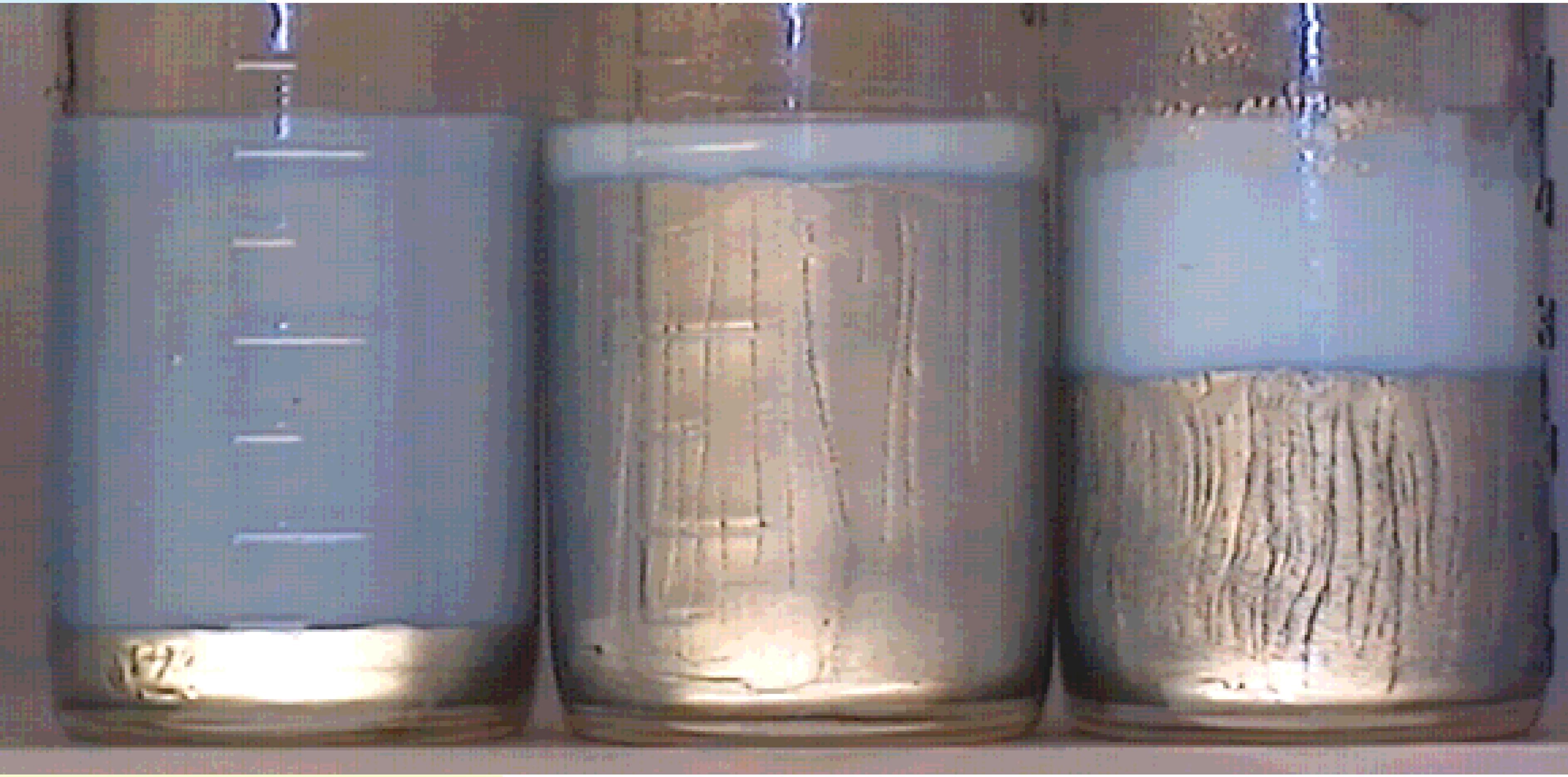
- Latex Particle Surface Characteristics
- Surfactants
- Dispersants
- Cosolvents

Viscosities of Aqueous Thickener Solutions



ACRYLIC EMULSION
Leafing Aluminum Flake Pigment
8 microns

49 DAYS



No additive | Polyamide 607 | Polyamide 610

SUMMARY

RHEOLOGY IS IMPORTANT

- PREPARATION
- APPLICATION
- FILM FORMATION
- STORAGE

ADDITIVES CAN CONTROL RHEOLOGY

RHEOLOGY CAN BE MEASURED

NOT ALL MEASUREMENTS ARE MEANINGFUL

WE STILL HAVE TO RELY ON APPLICATION TESTS

REFERENCES:

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T. C. Patton, Wiley Interscience
Dynamics of Polymeric Liquids, Fluid Mechanics
R. B. Bird, Wiley Interscience
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A Handbook of Elementary Rheology
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