

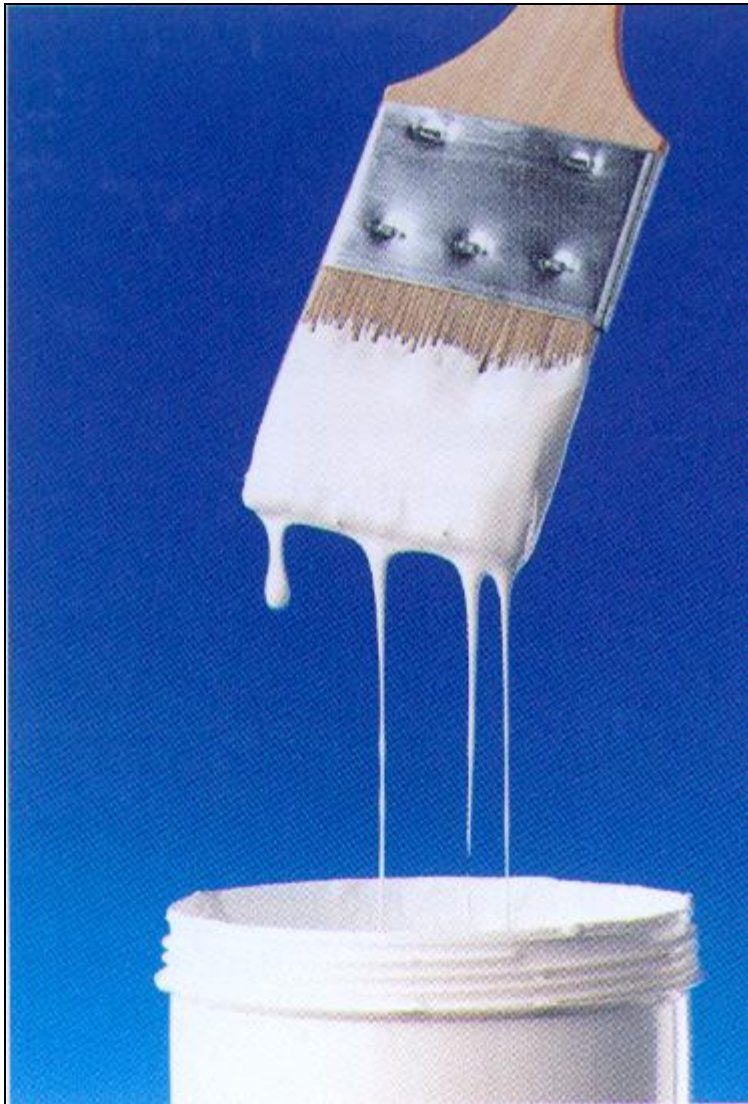
Coatings for Today & Tomorrow! Rheology as a Science!



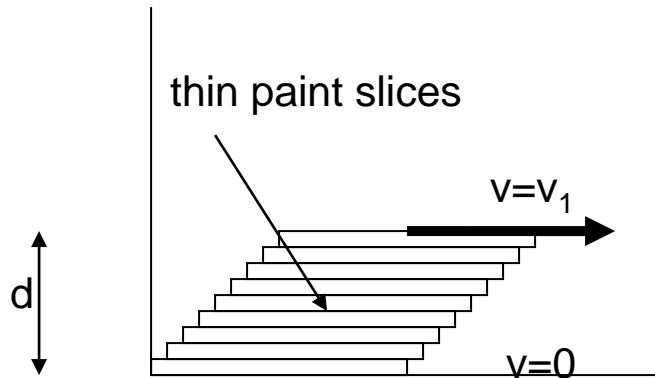
A collection of open paint cans arranged in a cluster. The cans contain various colors of paint, including red, blue, yellow, orange, green, and purple. The paint surfaces are smooth and reflective. The cans are made of metal and have their lids removed, showing the paint inside. The background is a plain, light-colored surface.

Rheology Modifiers And Thickeners

¿ What is Rheology?



Definition of Viscosity



$$\text{shear stress } \tau = \frac{\text{force } F}{\text{surface } A}$$

$$\text{shear rate } D = \frac{\text{velocity } v}{\text{distance } d}$$

Proportionality between τ and D : $D \propto \tau$

constant of proportionality: η

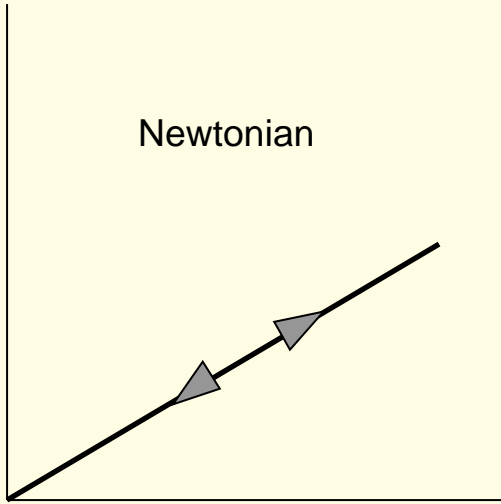
$$D \cdot \eta = \tau$$

$$\text{Viscosity } \eta = \frac{\tau}{D} \quad [1 \text{ mPa} \cdot \text{s} = 1 \text{ cP}]$$

Different Graphical Representations

Newtonian

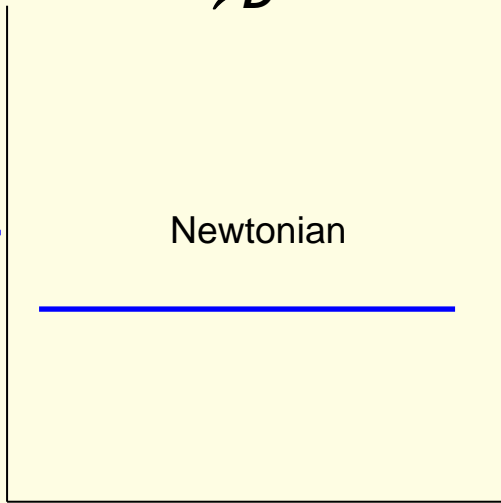
τ
↑



→ D

Newtonian

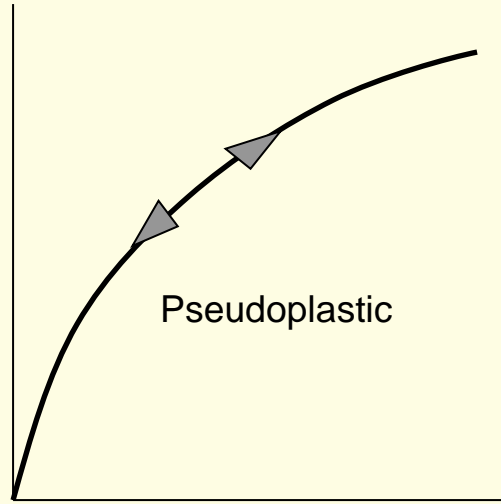
η
↑



→ D

Pseudoplastic

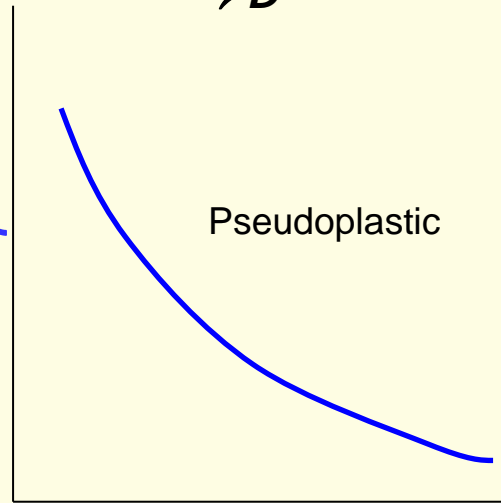
τ
↑



→ D

Pseudoplastic

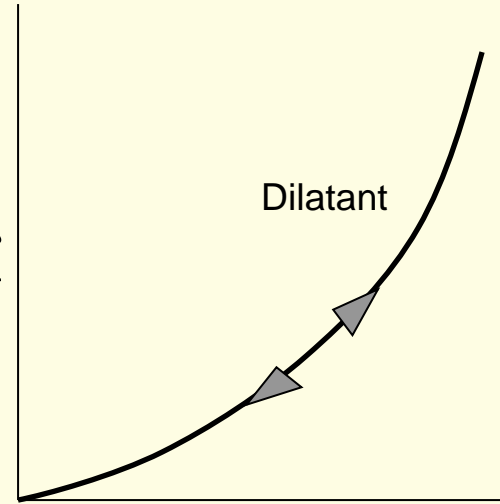
η
↑



→ D

Dilatant

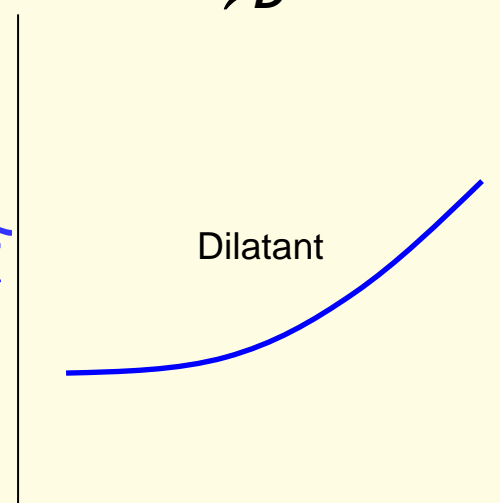
τ
↑



→ D

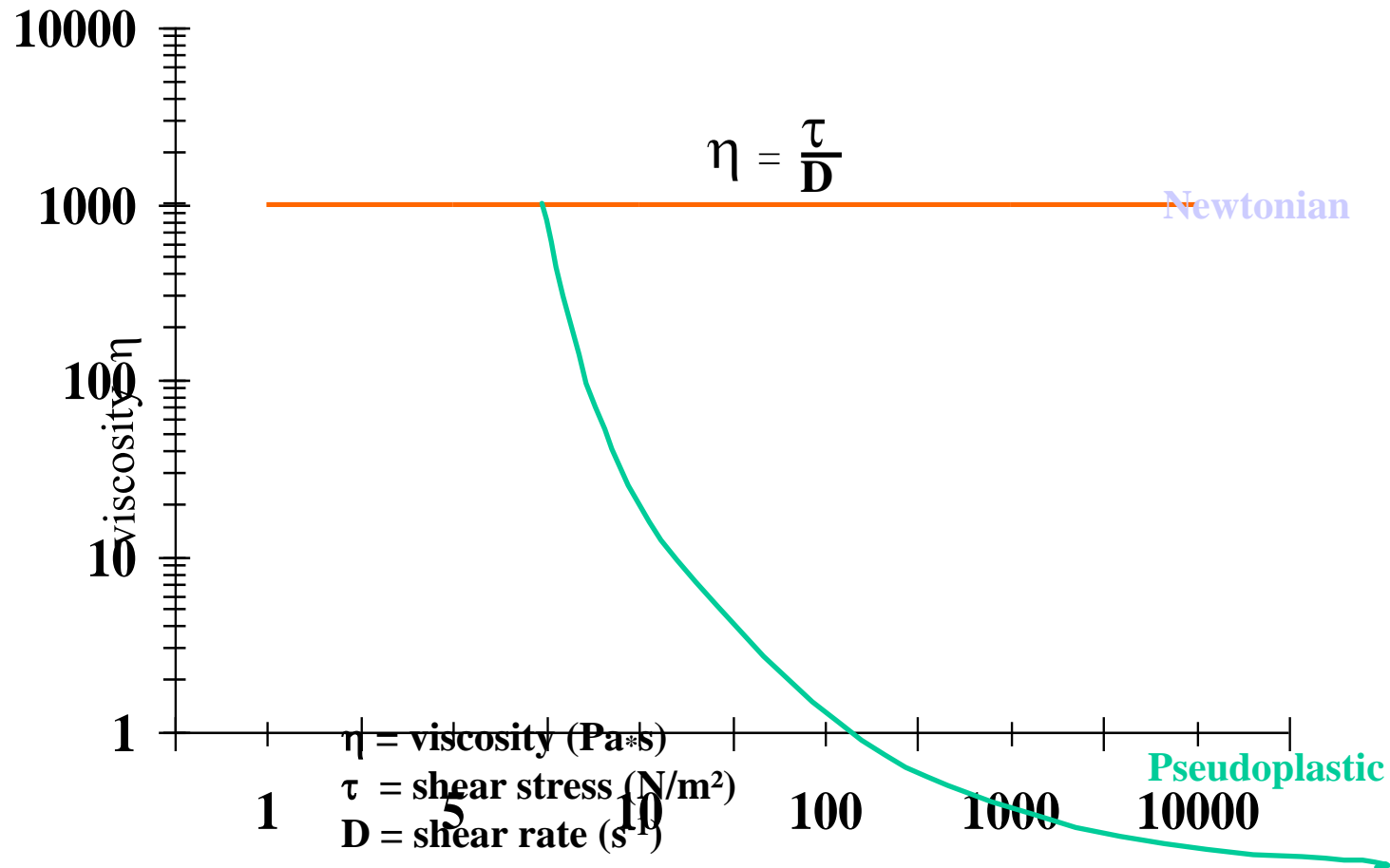
Dilatant

η
↑



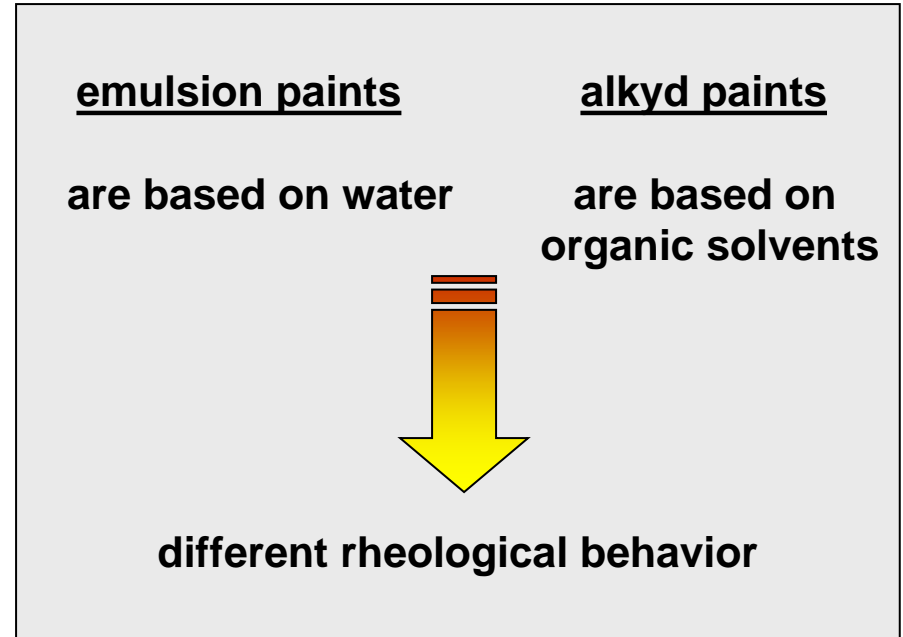
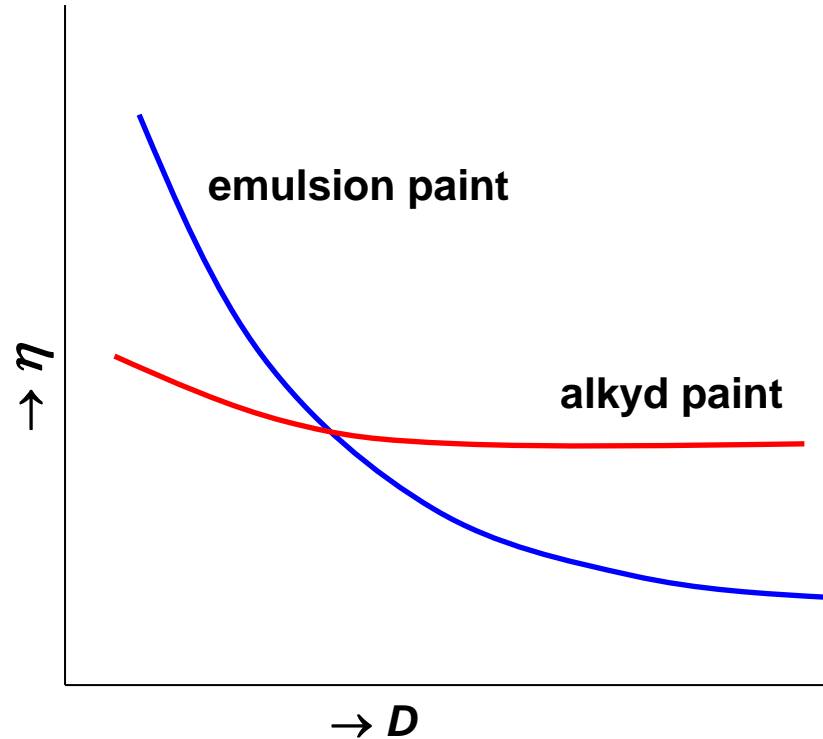
→ D

Rheological Behavior



Shear rate D

η -D-Curves

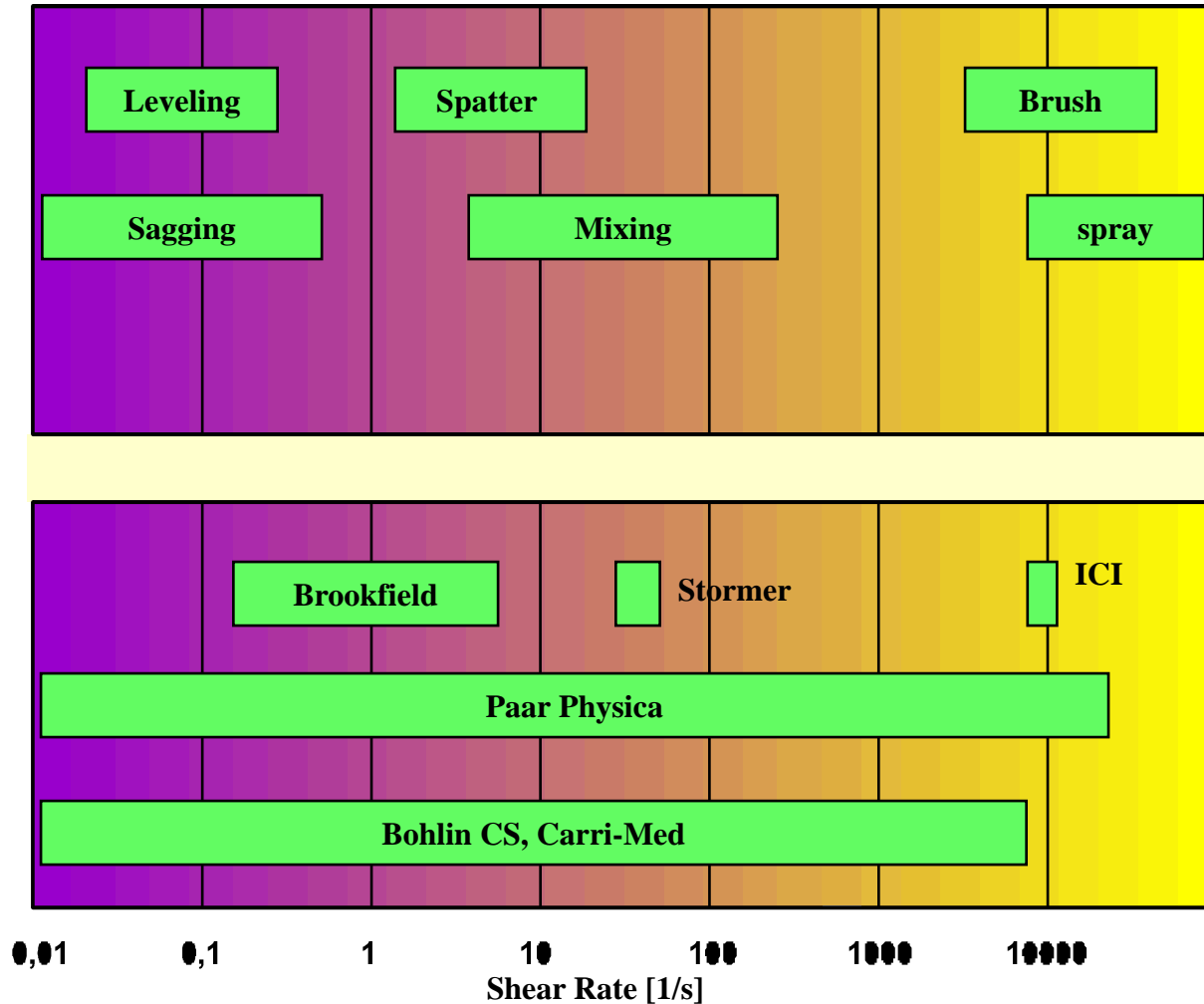


Water molecules have a strong tendency to associate both with themselves and other polar molecules / particles.

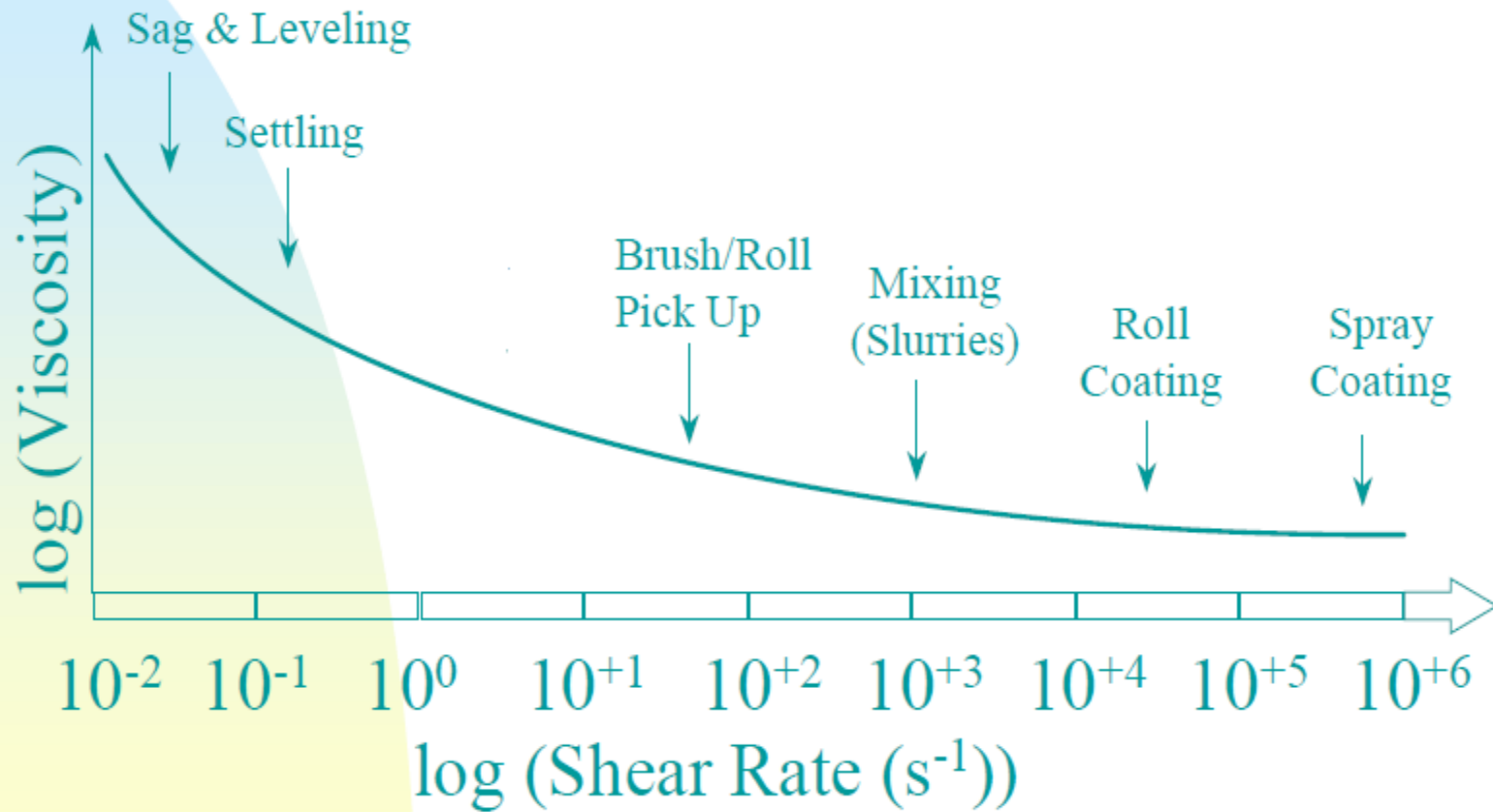
⇒ Associates will be destroyed during stirring / applying the paint.

⇒ Shear-thinning

Paint Properties Vs Shear Rate



Shear Rates for Various Sub-Processes



In-Can Appearance and “Feel”



- How does paint look and feel as it is stirred
- Difficult to quantify, but important to paint user
- Occurs in shear rate range of 10 - 100 sec^{-1}
- Krebs - Stormer measures viscosities in this range
- Brookfield also important

Paint Application

- Film Build and Brush Drag



- Brush drag refers to resistance encountered when applying coating by brush
- factors which determine the film build
 - amount of paint loaded onto brush
 - resistance to spreading by brush
- brushing generates 5000 sec^{-1} or greater
- ICI viscosity correlates

Paint Application

- Film Build and Brush Drag (cont.)



- In general, higher viscosity at high shear rates will contribute to greater film build via more resistance to spreading of the paint
- Low ICI viscosity can lead to “overspreading”
 - thin film build which contributes to low hiding, reduced durability, poorer flow

Paint Application

- Brush Loading and Dripping



- occurs in $1 - 10 \text{ sec}^{-1}$ shear rate range
- viscosity in this range should be:
 - high enough to allow good loading
 - give desired in-can appearance.

Paint Application

- Roller Spatter

- spots of paint which distribute over a wide area surrounding the paint area when roller applying a paint
- the amount of spatter is a function of the nature of the:
 - roller fabric
 - substrate
 - speed of application
 - rheological properties of the paint *



Paint Application

- Roller Spatter

- Moderate to high shear rates involved during formation
- Paints that impart “elastic” tendencies more susceptible
 - conventional cellulosic thickeners are bad
 - Associatives usually not a problem



Paint Application

- Lapping
 - extent to which region where a coat of paint extends over an adjacent, fresh coat
 - usually the result of first coat drying too quickly
 - rheology plays a minor role
 - film build can attribute
 - ICI can affect

Paint Application

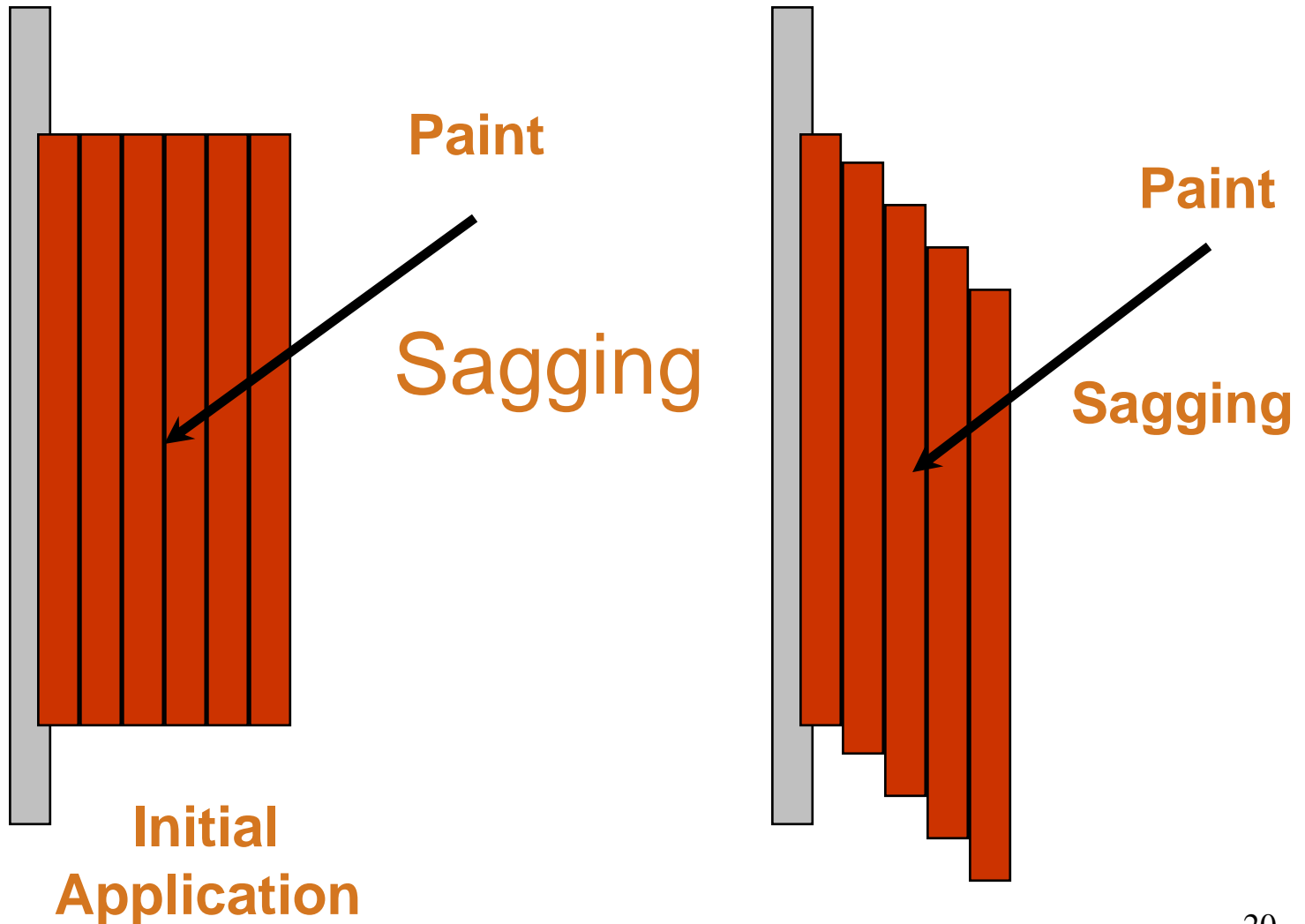
- Penetration

- necessary for good adhesion
- factors which help penetration:
 - smaller latex particle size
 - longer open time
 - lower volume solids
 - surface tension; good wetting
 - lower viscosity in low shear rate range (less than 1 sec^{-1})

Film Formation and Appearance

- Sagging
 - occurs in low shear rate range; less than 10^{-2} sec^{-1}
 - key factors
 - **film thickness**
 - thicker the film = poorer sag resistance
 - **viscosity at low shear rates**
 - high viscosities = better sag resistance

Film Formation and Appearance



Film Formation and Appearance

- Sagging (cont.)
 - can be improved by:
 - minimizing levels and types of solvent*
 - minimizing use of surfactants
 - increasing low shear viscosity by adding more efficient thickener in this region (e.g. Adding cellulosic (0.5 - 2.0 lb./100 gallons))
 - adding attapulgite clay (e.g. Attagel 50); 2-10 lb./100 gallons

Film Formation and Appearance

- Leveling

- key factor is viscosity at low shear rate
 - occurs at 10^{-1} sec^{-1} or lower
 - higher viscosity at low shear rate = poorer flow
- Brookfield viscosity not a reliable indicator
- Method of application can matter
 - Brush vs. Leneta bar

Film Formation and Appearance

- Leveling (cont.)
 - occurs during drying of paint film
 - as water is lost, viscosity is increasing
 - slowing dry time may aid leveling process
 - use of wet edge extenders like propylene glycol
 - thixotropic paints

Film Formation and Appearance

Acrylic sheen @ 100 Ku Viscosity

Leveling

(0-10,best)

ACRYSOL ASE 60	2
cellulosic	3
hydrophobically-modified cellulosic	4
ACRYSOL RM-825	8
ACRYSOL RM-5	8
ACRYSOL RM-5000	9+

High Shear Viscosity ICI-builders

- RM-5000
- RM-6000
- RM-2020NPR
- RM-5
- RM-6
- RM-7
- DR-73

Mid-Shear Viscosity KU-builders

- RM-6000
- RM-825/RM-8W
- SCT-275
- TT-935
- DR-300
- DR-1
- DR-72

Thickeners – WB Coatings

Organic Thickeners

Waterborne Coatings do not possess the same rheological properties as Solventborne Coatings. Without the proper use of water soluble polymers, WB Coatings usually have inferior flow/leveling, poor film build and spattering during application.

In order to achieve “similar” application rheology to SB Coatings WB Coatings require the addition of water soluble polymeric Thickeners and Rheology Modifiers.

WB Coatings
Organic Thickeners

1. **HEC** – Hydroxy Ethyl Cellulose
2. **HMHEC** – Hydrophobically Modified HEC
3. **ASE** – Alkali Swellable Emulsions
4. **HASE** – Hydrophobic Alkali Swellable Emulsions
5. **HEUR** – Hydrophobic Ethoxylated Urethanes
6. **HEAT** – Hydrophobic Ethoxylated Aminoplasts

Organic Thickeners Thickening Mechanisms

ASE – Anionic alkali swellable emulsion thickeners are supplied as turbid emulsions in the pH range of 3-5. Upon neutralization above pH 7, the carboxylic acid groups ionize and expand due to charge repulsion of the anionic carboxylate and provide thickening and suspending properties. This thickening is known as **Hydrodynamic** thickening.

Disadvantages

- Film water sensitivity
- Other formulation ingredients that are “electrolytes” reduce thickening efficiency
- Addition of more ASE can be done, but more water sensitivity will result

Organic Thickeners Thickening Mechanisms

HEC – High molecular weight cellulosic thickeners (and clays) replaced casein and starch thickeners. Hydroxy ethyl cellulose thickens water based coatings by polymer chain entanglement and hydrogen bonding to water molecules.

Disadvantages

- Poor film build, particularly with brush and roll application
- Poor flow and leveling
- Poor spatter resistance, particularly with roll application

Advantages

- Low cost
- Superior spray atomization

Organic Thickeners Thickening Mechanisms

HMHEC – Hydrophobic modified HEC have a balanced compromise between the application performance of HEC thickened paints and other Associative (next set of slides) thickened paints.

Advantages

- Lower cost than associative thickeners
- Improved application performance vs HEC systems

Organic Thickeners Thickening Mechanisms

HASE – Hydrophobic alkali swellable emulsions contain water soluble-hydrophilic portions and incorporated hydrophobic portions. These hydrophobic modified emulsions are termed **Associative Thickeners** and they thicken by association of the hydrophobic portions by intra- and intermolecular clustering with other hydrophobic surfaces such as latex and pigment particles.

Disadvantages

- Maximum thickening is only in pH range of 8-9
- Evaporation loss of amine neutralizers, lowers pH, and thickening
- Water sensitivity

Advantages

- No hydrolysis above pH of 9

Organic Thickeners Thickening Mechanisms

HEUR – Hydrophobic ethoxylated urethane
Associative thickeners function in the same manner as HASE thickeners.

Advantages

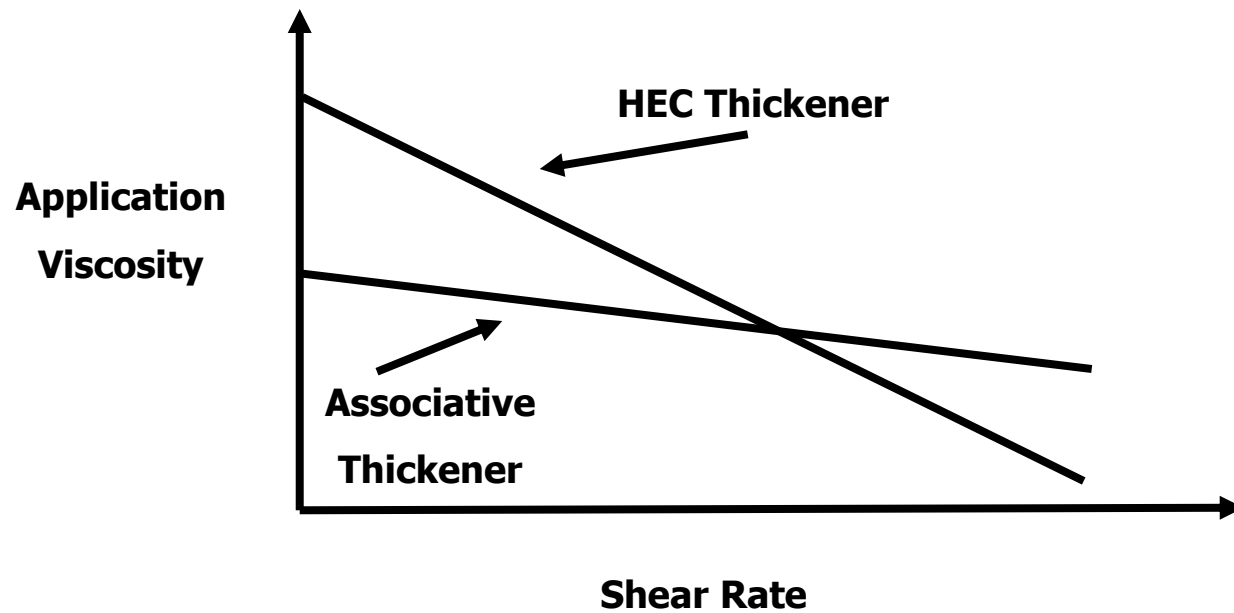
- Film Build improved
- Flow and Leveling improved
- Spatter Resistance improved

Disadvantages

- Hydrolytic instability above pH of 9
- Formulation sensitivity
- Syneresis in Medium/Deep Tint Bases

Rheology Comparison

Associative vs HEC Thickeners



General Market Comments – US

HEC vs Associative Thickeners

- *Higher end/higher price* point paints use the more expensive *associative thickeners sometimes combined with Cellulosics*.
- *Mid range/mid price* point paints tend to use **Associative /Cellulosic thickeners**. Balance compromise between application performance of associative thickened vs HEC paints.
- *Low end/low price point* paints usually based on **HEC**. Paint contractors normally use these paints and in many cases use spray application. HEC based paints possess superior spray atomization.

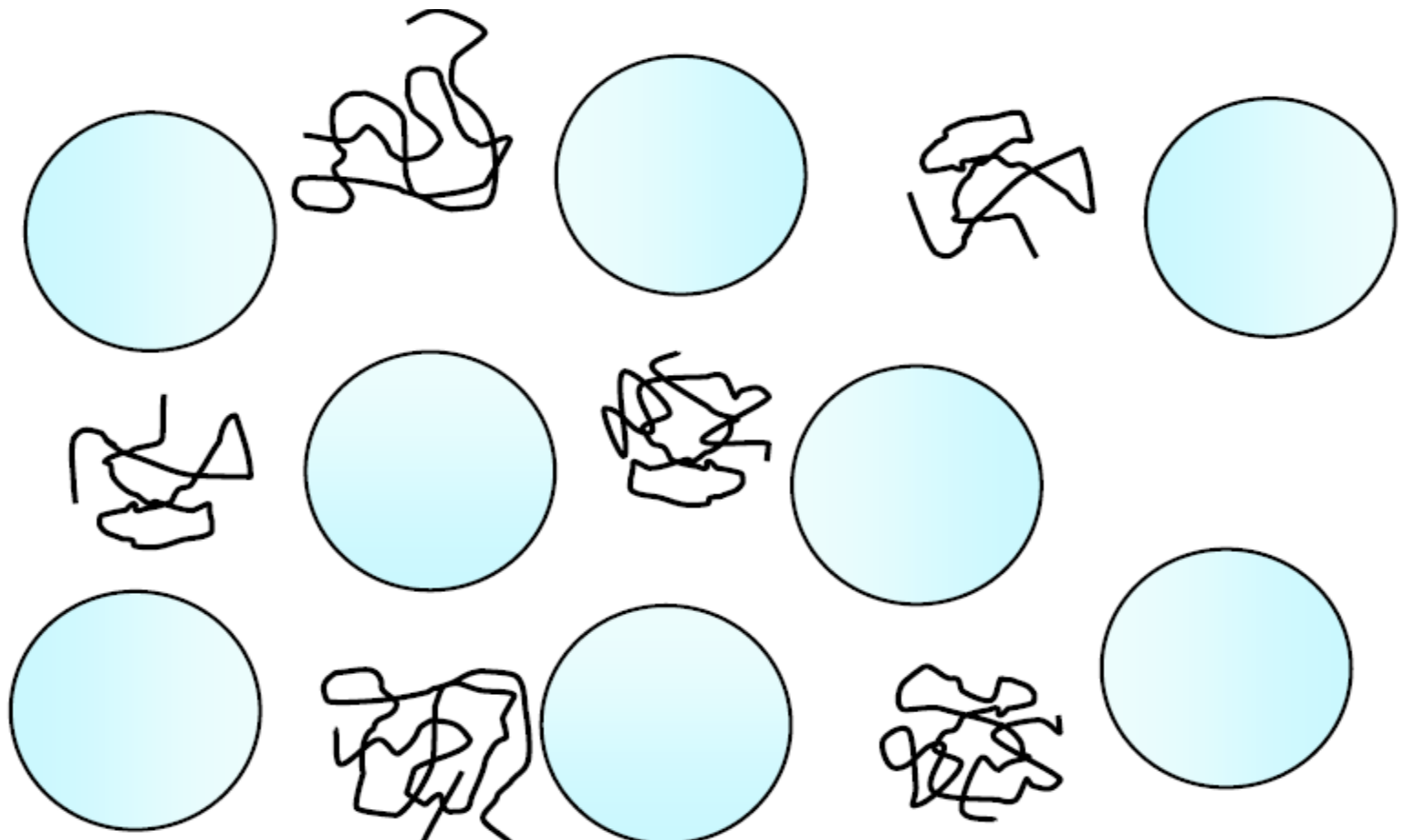
Things That You Can Adjust to Change Rheology

- Concentration (solids)
- Resin flexibility (T_g) and molecular weight
- Pigments and their dispersion quality
- Solvent viscosity
- Additives
 - sag and pattern control agents
 - wetting agents, pigment dispersants
 - catalysts

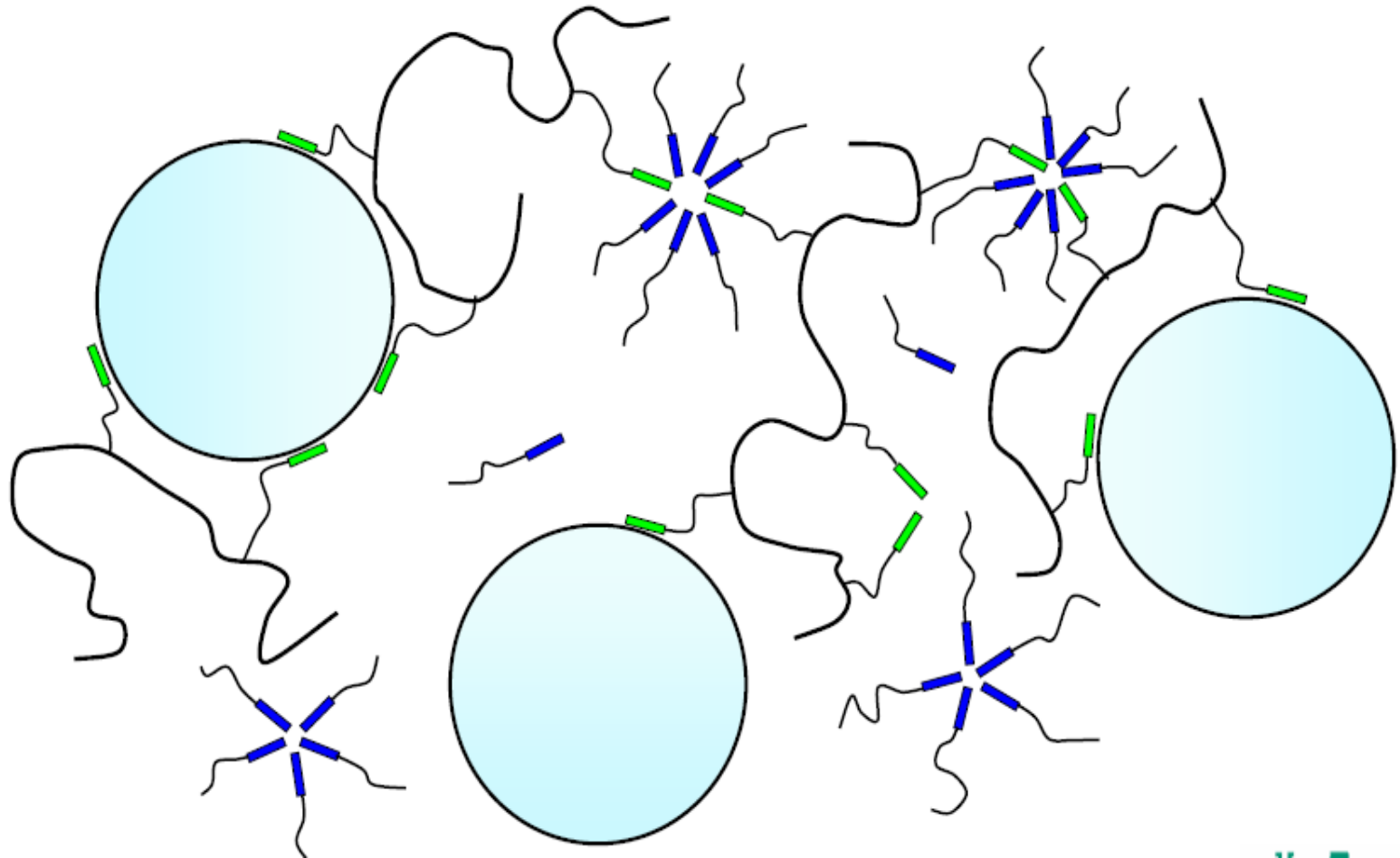
Thickeners (Waterborne Paints)

- Non-Associative – thickener raises viscosity of continuous phase, may interact with latex or pigments.
- Associative – thickener can form a network by itself, but main effect is to interact with latex and/or pigment to build structure.

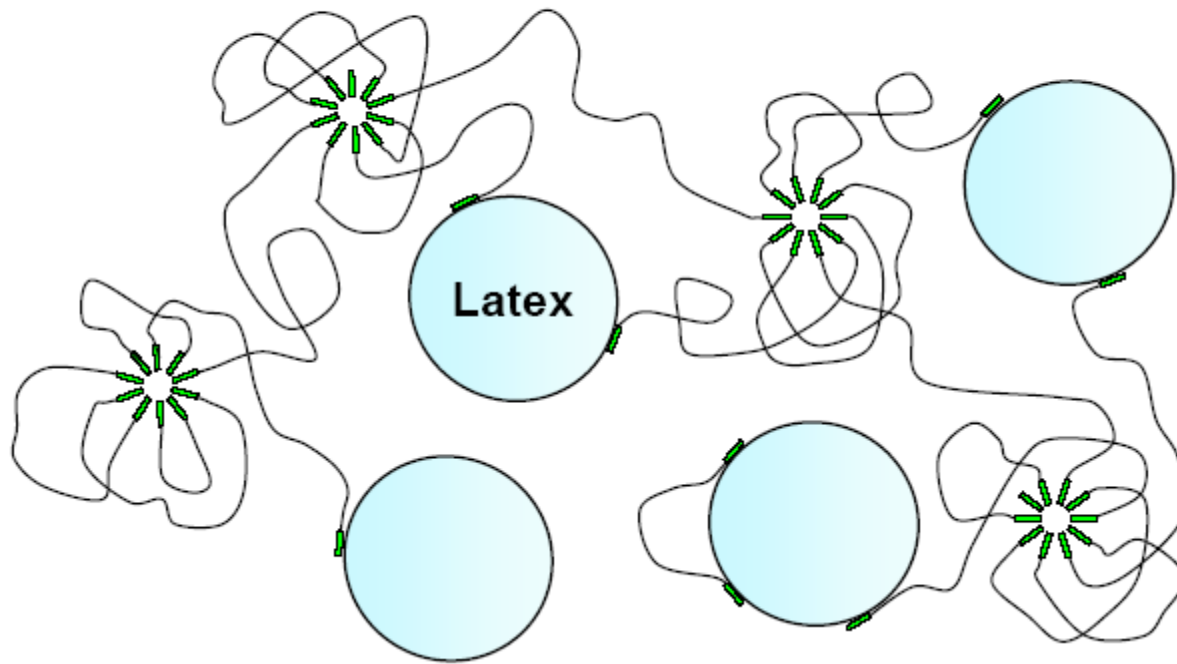
Conventional Thickening Mechanism



Associative Thickening Mechanism (HASE)



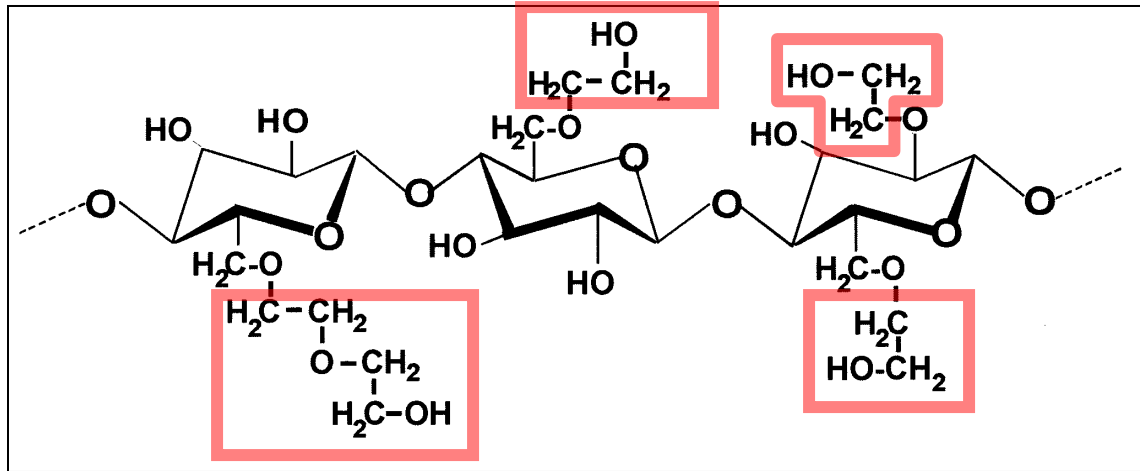
Associative Thickening Mechanism (HEUR)



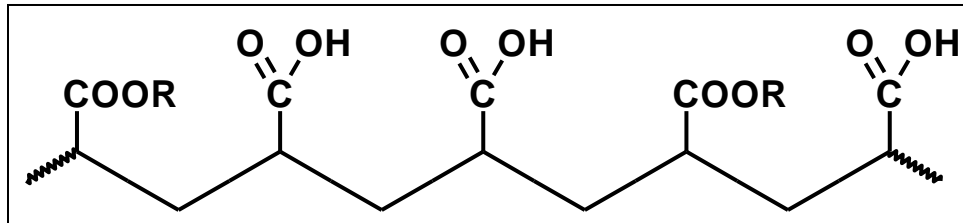
Non-Associative Thickeners

- Cellulosics
- Other polysaccharides
- Water soluble/swellable polymers
- Clays
- Solvents

Types of Thickeners (1)

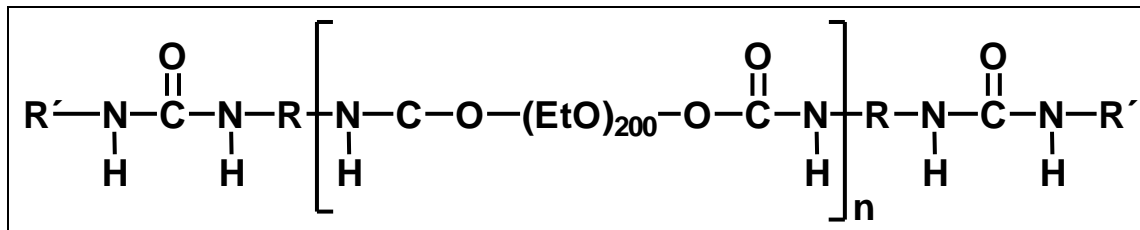


cellulosic ether **HEC**
(**H**ydroxy **E**thyl **C**ellulose)



ASE
(**A**lkali **S**wellable **E**mulsion)
→ conventional acrylic thickener

Mowilith LDM 7010



HEUR
(**H**ydrophobically Modified
Ethylene Oxide - **U**rethane
Rheology Modifier)

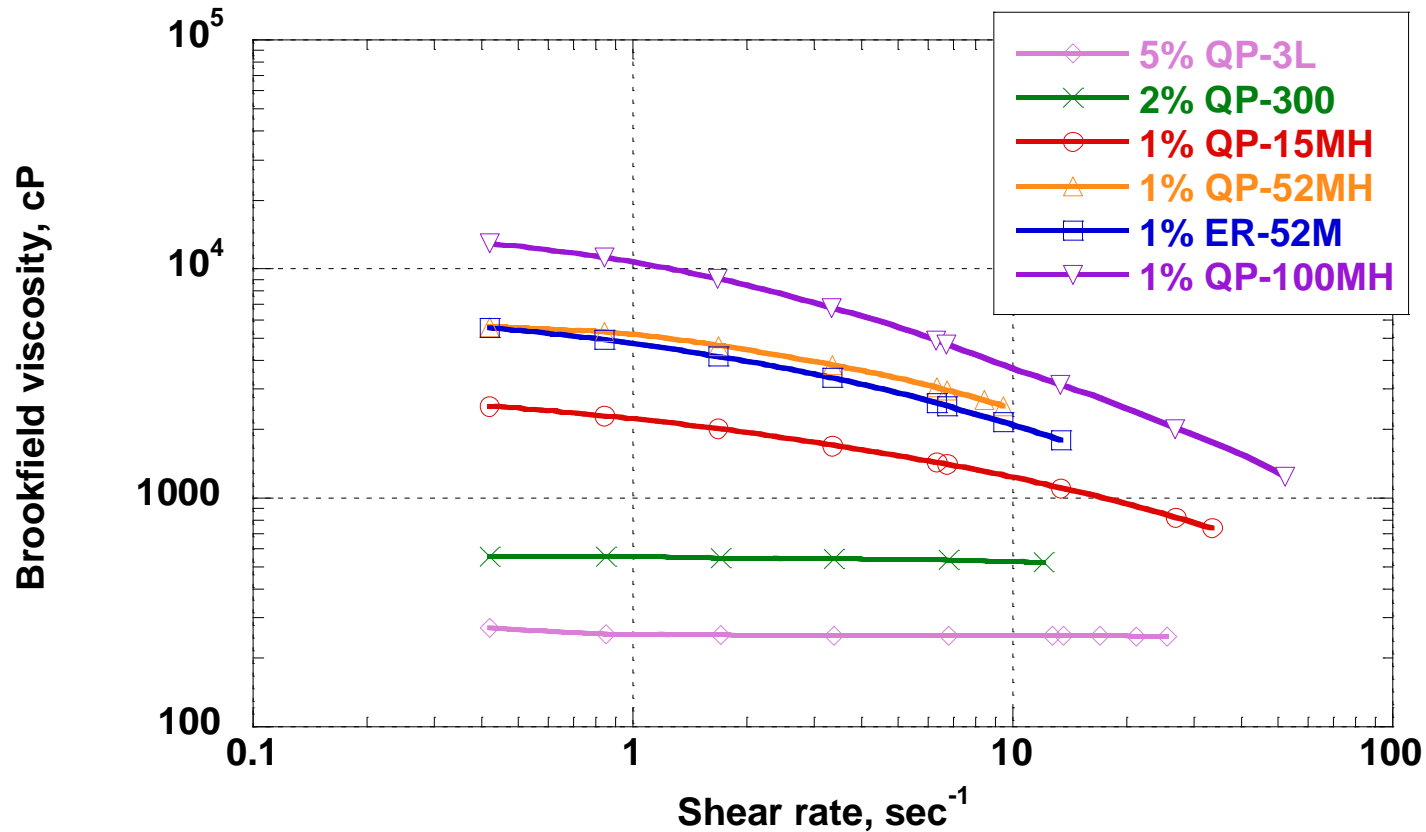
R & H: Acrysol RM-8 W, RM-2020

Cellulosics

- Hydroxyethyl cellulose (HEC)
- Ethyl Hydroxyethyl cellulose (EHEC)
- Methyl Hydroxyethyl cellulose (MHEC)
- Methyl cellulose (MC)
- Hydroxypropylmethyl cellulose (HPMC)
- Carboxymethyl cellulose (CMC) and its sodium salt (Na-CMC)
- Mechanisms: solution (hydration), high degree of molecular entanglement (increases with increasing MW) and hydrogen bonding
- Advantages: Dissolve/disperse easily, low foaming, efficient thickening ability, good flow and leveling.
- Disadvantages: Prone to biological attack, cause water sensitivity, may cause pigment flocculation, higher MW grades are more efficient, but give too much structure.

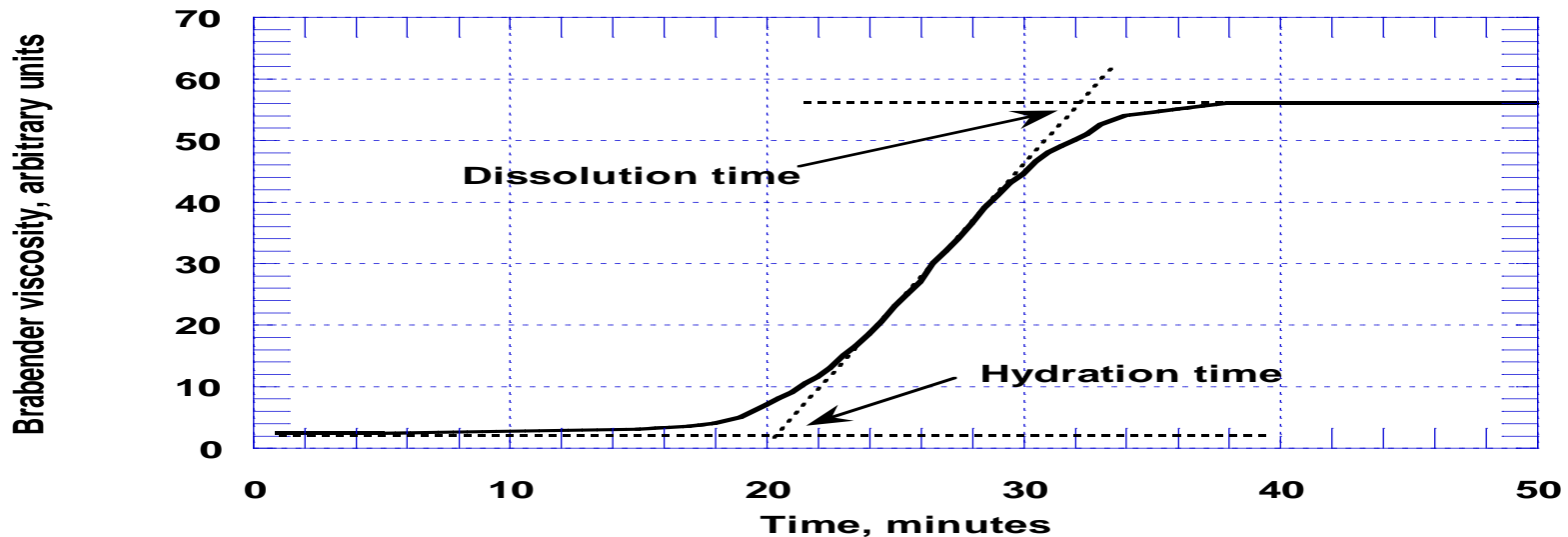
Types of HEC

Effect of shear rate on the Brookfield viscosity of aqueous solutions of CELLOSIZ HEC



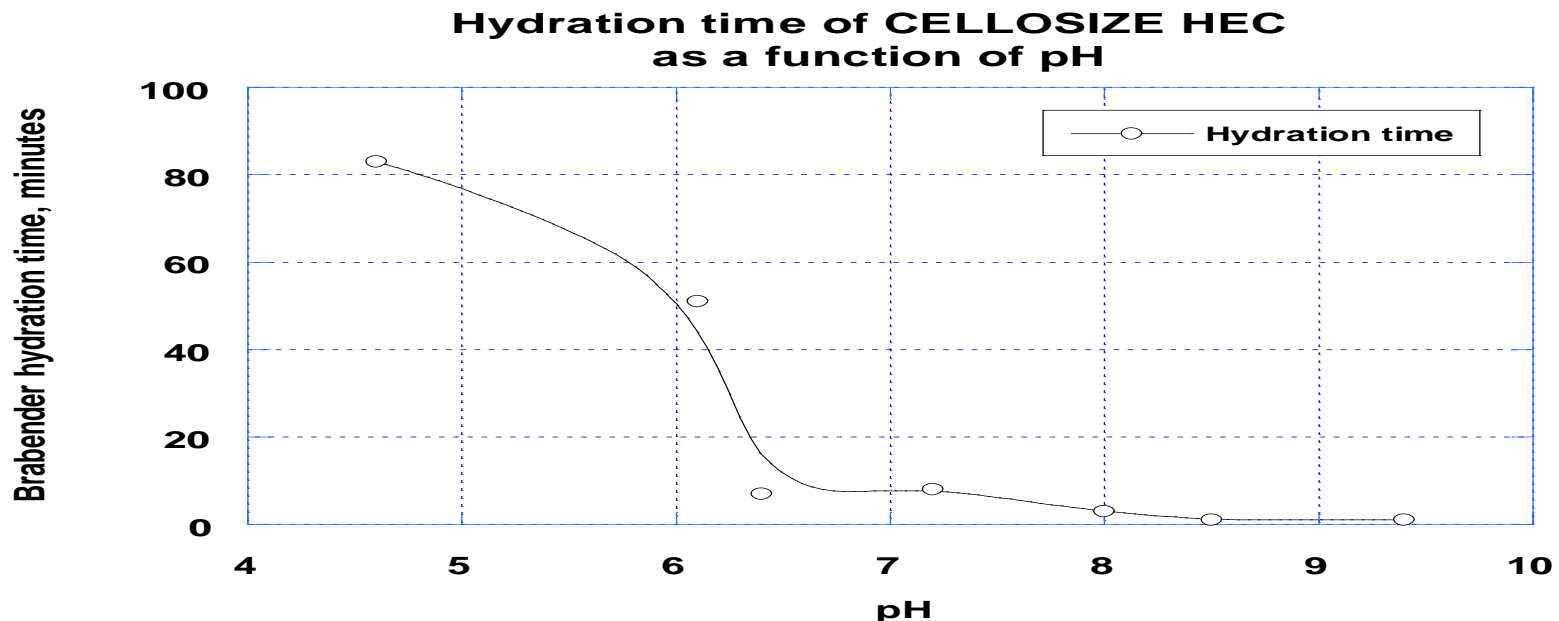
Hydration time of HEC

- Hydration time is the time to the onset of dissolution (viscosity build, e.g., T1)
- Hydration time measured by Dow using Brabender viscometer at 25°C and pH 7.2 buffer
- Error estimate for test method is $\pm 10\%$, or about ± 1 minute at 10 minutes
- Similar method are used by manufacturers of competitive cellulose ethers
- Dissolution time is the time to equilibrium viscosity (complete dissolution of polymer, e.g., T2)



Effect of Solution pH on Hydration Time of HEC

- $\text{pH} > 7$, CELLOSIZ HEC hydrates quickly
- $\text{pH} < 6$, CELLOSIZ HEC hydration time does not vary much with pH
- Steepest part of curve is between pH 6 & 7
- Adding CELLOSIZ HEC to water at $\text{pH} < 6$ = product will dissolve slowly
- Adding CELLOSIZ HEC to water at $\text{pH} > 8$ = product will tend to form gels.
- What are best ways to dissolve HEC?



HMHEC

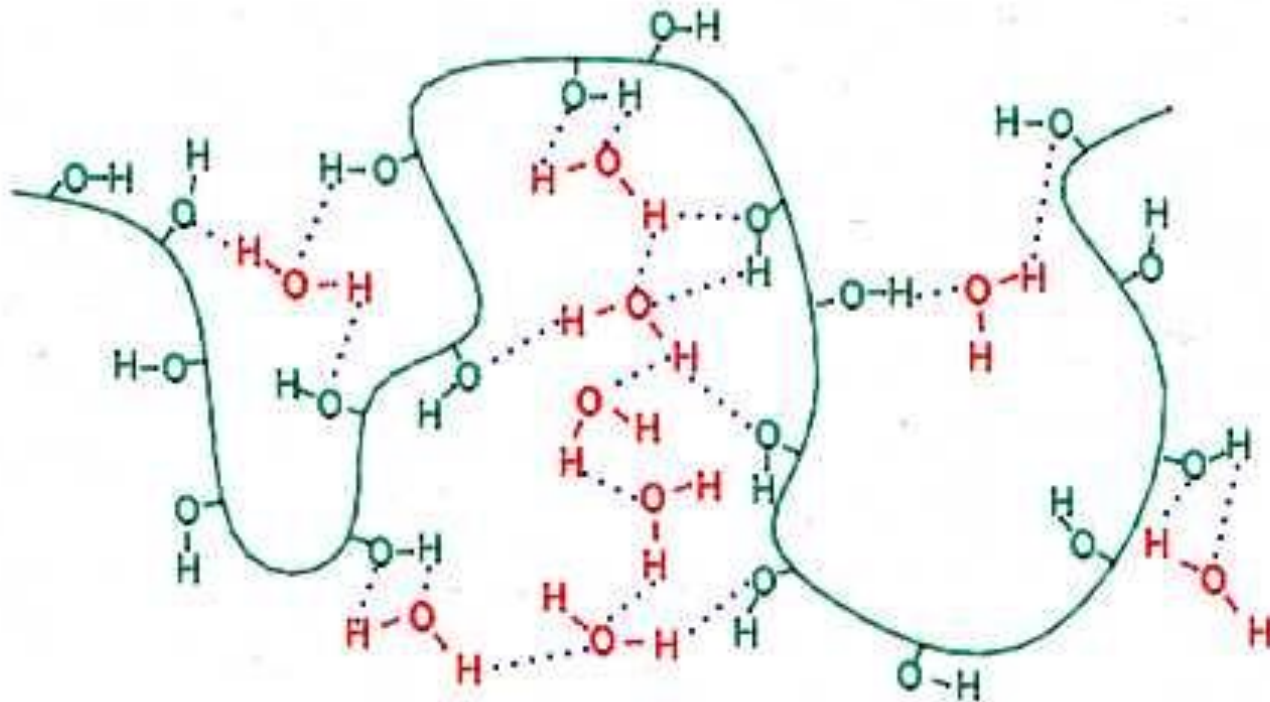
- HMHEC Not only thickens the aqueous phase by hydrogen bonds but also by interaction with latex particles and pigments
- PS and oil absorption of extenders have a great influence on the performance of HMHEC.
- Surfactants modify the rheological properties. Anionic surfactants increase the viscosity.
- Anionic surfactants with low HLB improve efficiency of thickening and leveling. The HLB of non ionic surfactants do not have influence in the thickening efficiency of HMHEC.

HEC Hydrophobically Modified

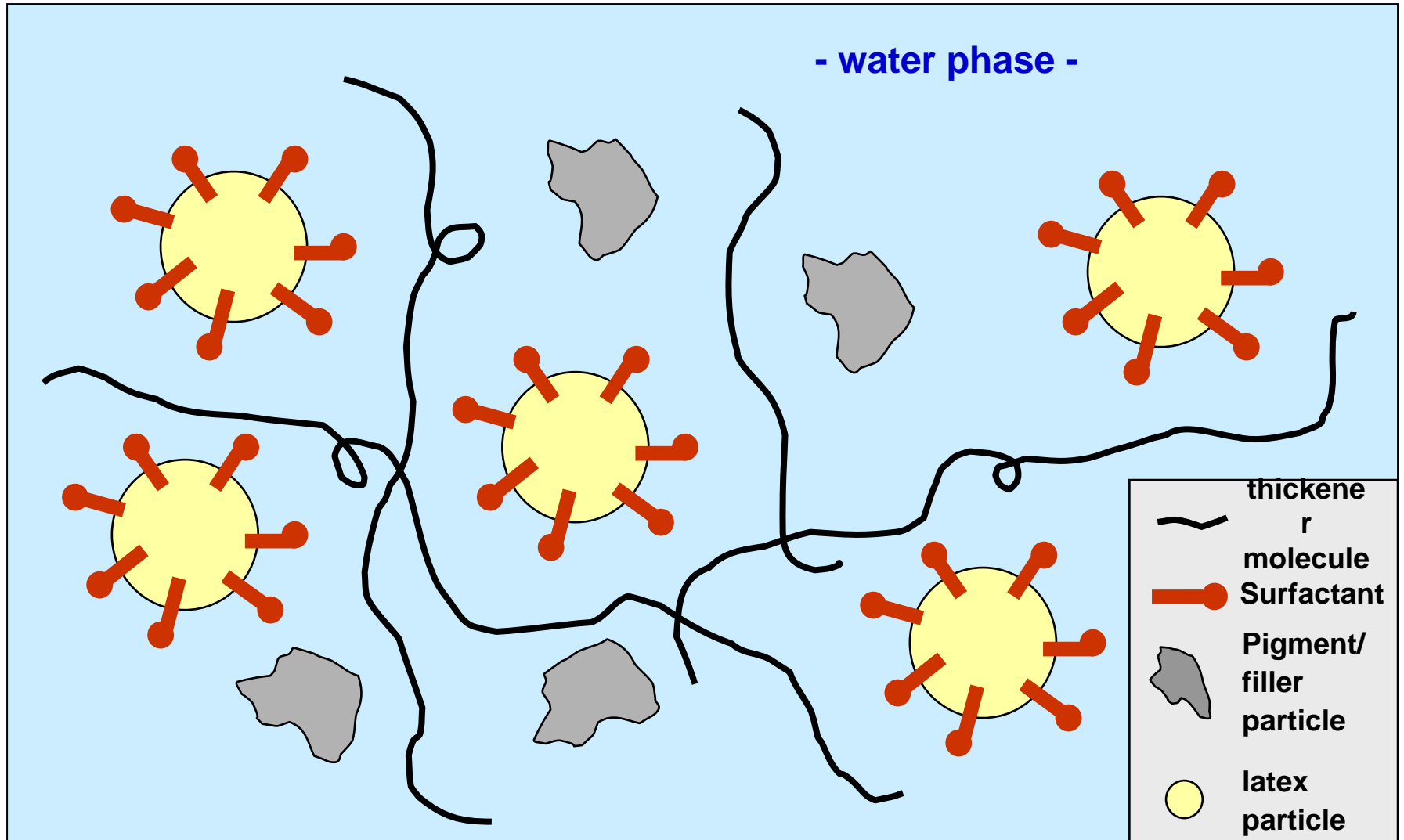
- Advantages
- Stable viscosity
- Compatibility with colorants
- No ionic
- Water retention
- Excellent spatter resistance
- Good ICI viscosity
- Good Levelling

Thickening mechanism

a) hydration of the cellulose molecules



Mechanism of Thickening with HEC



Water Soluble Polymers

- Poly(ethylene oxide)s $X-(O-CH_2-CH_2)_n-Y$
 - low MW – Carbowax polyethylene glycol
 - high MW – Polyox
- Advantages: Easy to incorporate, fairly efficient, good flow and leveling (if low MW).
- Disadvantages: Water sensitivity, not as effective as HEC, high MW grades give elastic solutions, high extensional viscosity (\rightarrow roller spatter, poor flow and leveling))

Clays

- Types of Clays: Bentones (Montmorillinite), Laponite (Hectorite), Attagel, Sepiolite
- Composed of platelets that expand and interact to form networks rather than dissolve. Work well in combination with soluble thickener.
- Long before they were used in w/b paints, clays were very common in s/b paints. Multi layer platelets expand and interact to form networks.
- Advantages: Fairly efficient, good for preventing pigment settling.
- Disadvantages: Difficult to incorporate, can be surfactant/dispersant sensitive, may hurt gloss.

Solvents as Thickeners (Swelling Agents)

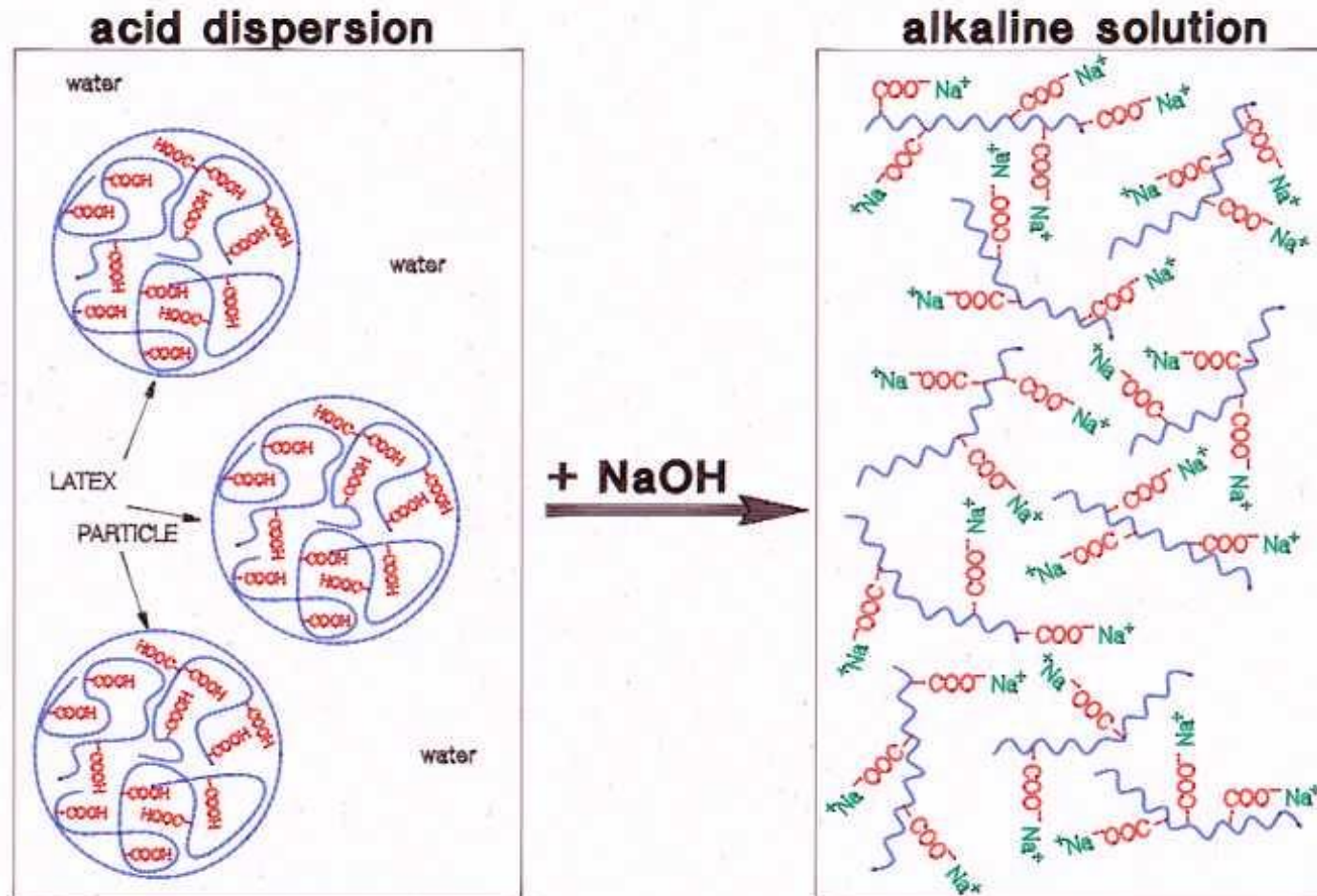
- Some solvents that have low water solubility swell latex particles and dispersion micelles and raise viscosity.
- Examples: ethylene glycol monohexyl ether (2-hexyloxyethanol), ethylene glycol phenyl ether (2-phenoxyethanol), Texanol ester alcohol

Acrylic Thickeners

- Polyacrylic acid and its salts – water soluble.
- High acid number acrylic copolymers – not water soluble, but are alkali soluble, i.e. dissolve on neutralization with suitable base.
- Partially crosslinked copolymers – thicken by swelling. Work well in combination with alkali-soluble acrylic.
- Advantages: Easy to incorporate, enzyme and bacteria resistant, good flow and leveling.
- Disadvantages: Some are water sensitive, all work best in acrylic paints.

Thickening mechanism

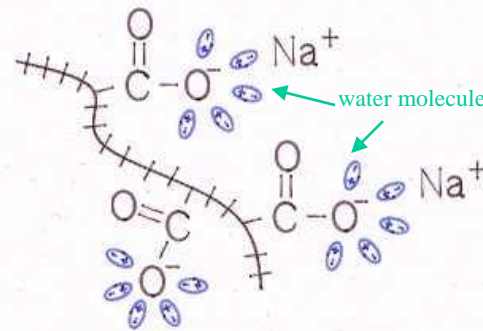
Thickening Mechanism on Neutralisation of ASE (Alkali Swellable Emulsion)



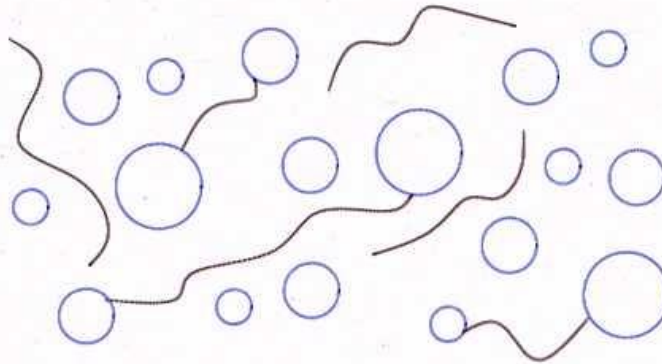
Thickening mechanism

Thickening Mechanism on Neutralization of Conventional Acrylate-Thickener

a) hydration



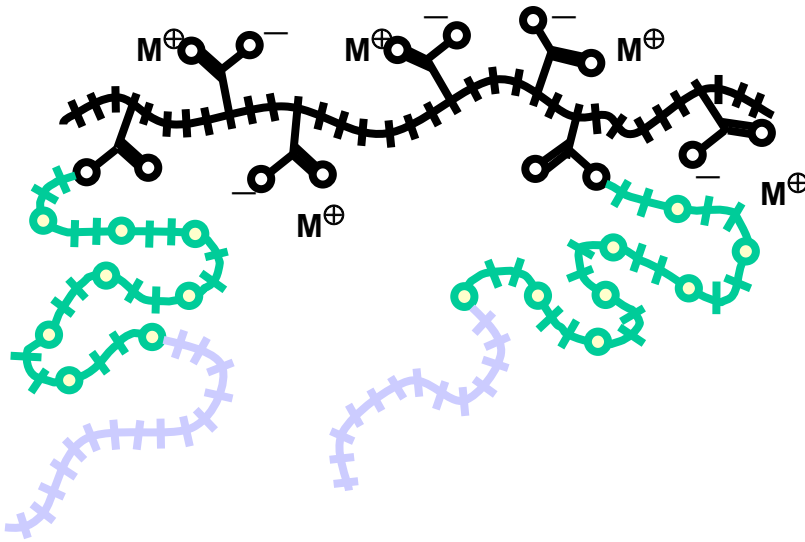
b) adsorption on Latex surface



Associative Thickeners

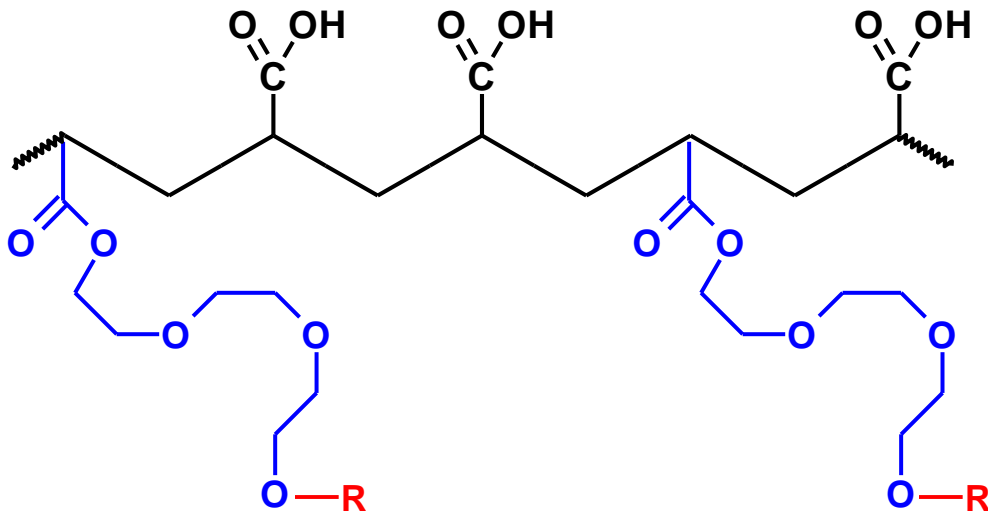
- Moderately low MW hydrophilic polymers with nonpolar groups spaced along the backbone.
- Examples:
 - Hydrophobe Modified Ethoxylate Urethanes (HEUR)
 - Hydrophobe Modified Ethoxylate Ureas
 - Hydrophobe Modified Alkali-Swellable/Soluble Emulsions (HASE)
 - HEC with hydrophobic chains
- Advantages: Reduce overspreading (higher high shear η), reduce roller spatter, excellent flow and leveling
- Disadvantages: Can be difficult to incorporate, most are less efficient than HEC, some are water sensitive, all are sensitive to surfactants.

Types of Thickeners



HASE
(**H**ydrophobically modified **A**lkali
Swellable **E**mulsion)

chemical structure:

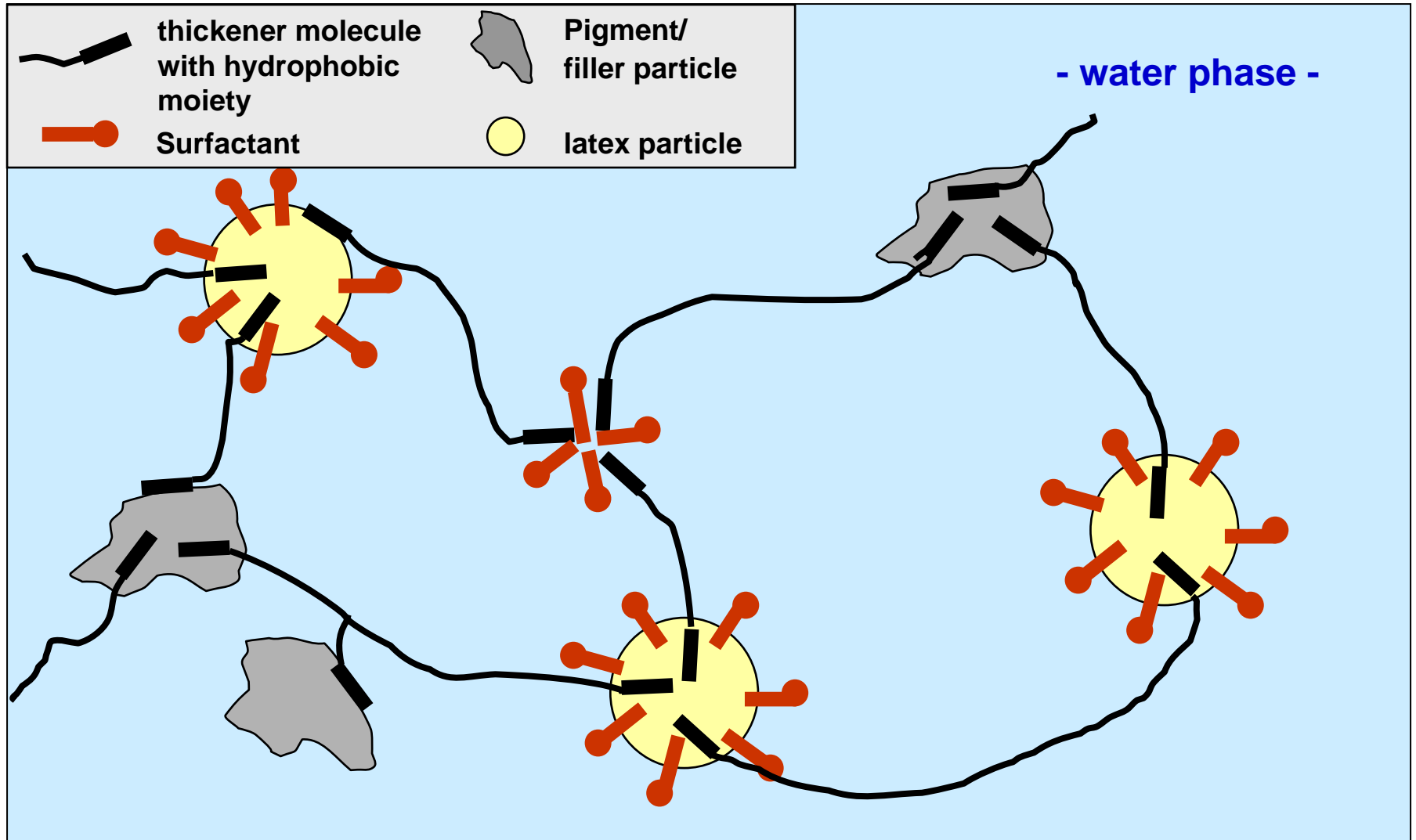


carbon chain with acidic groups

hydrophilic spacer

hydrophobic (e.g. alkyl) groups

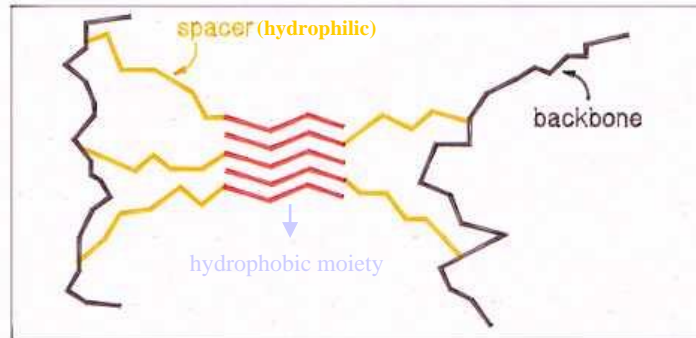
Mechanism of Thickening with HASE



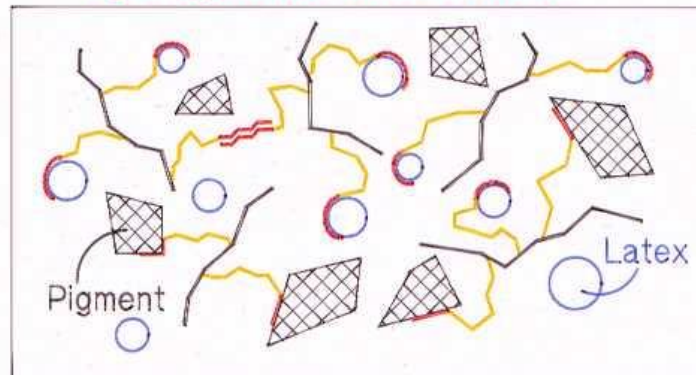
Thickening mechanism

Thickening Mechanism on Neutralization of associative Acrylate-Thickener

a) formation of micelle-like clusters



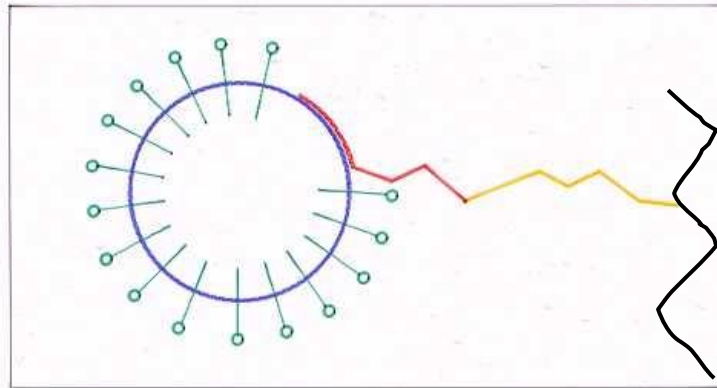
b) association and adsorption by hydrophobic interactions



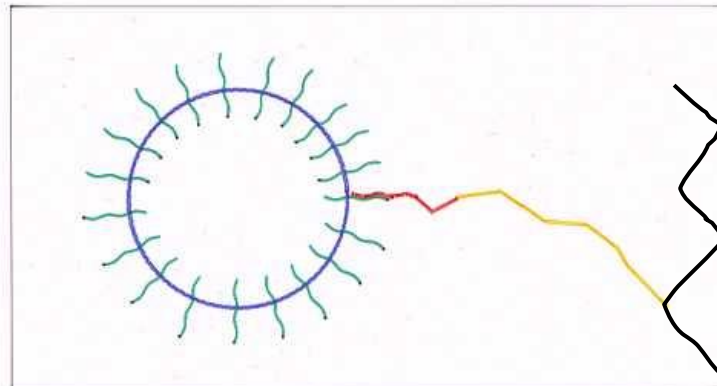
Adsorption of associative thickeners

Possibilities of adsorption of
associative-Thickener on the Latex

a) on free surface of the Latexparticle



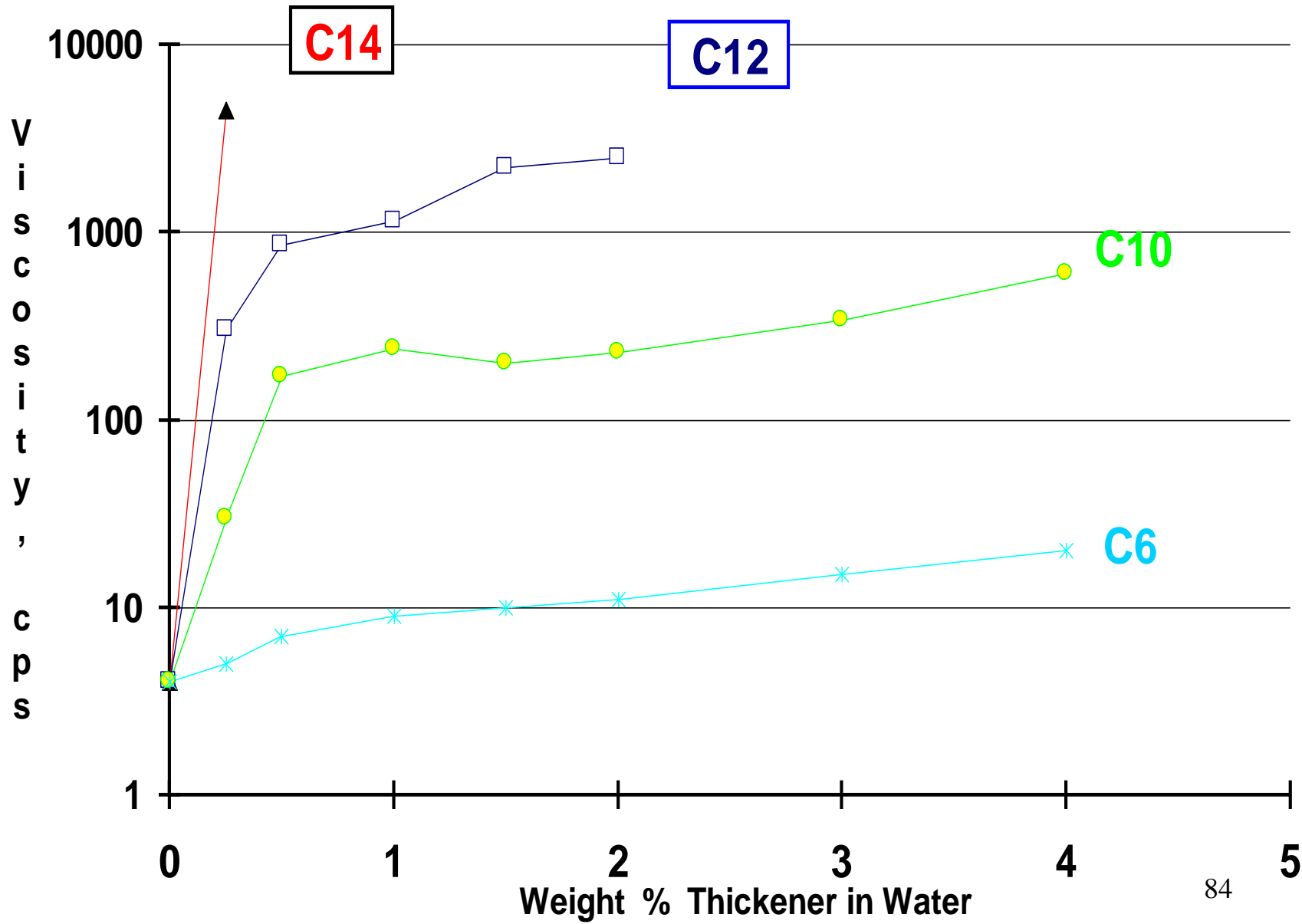
b) on the surfactant of the Latexparticle



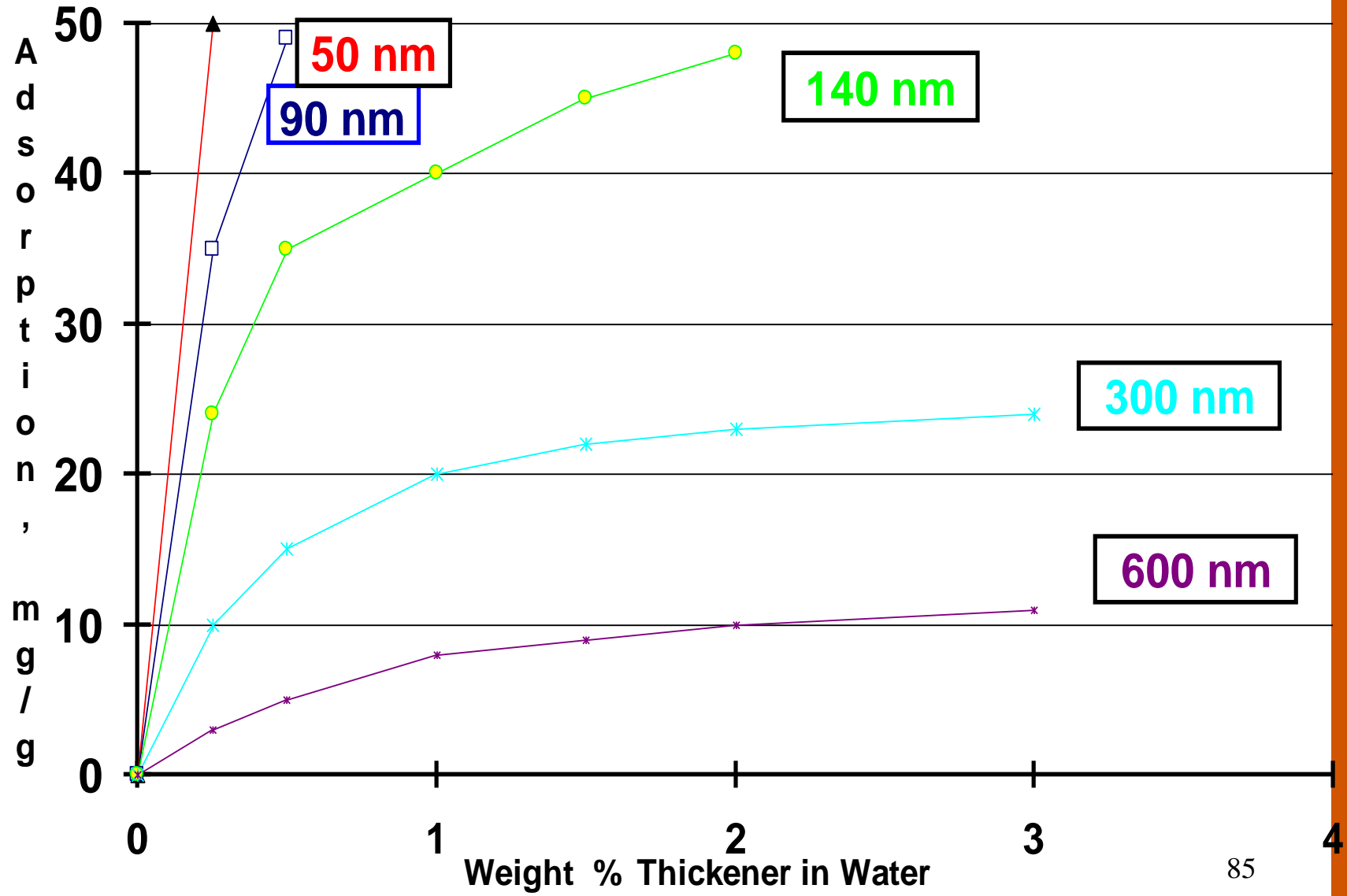
AT Properties affecting viscosity

- **Hydrophobe type**
- **Hydrophobe level**
- **Hydrophobe placement**

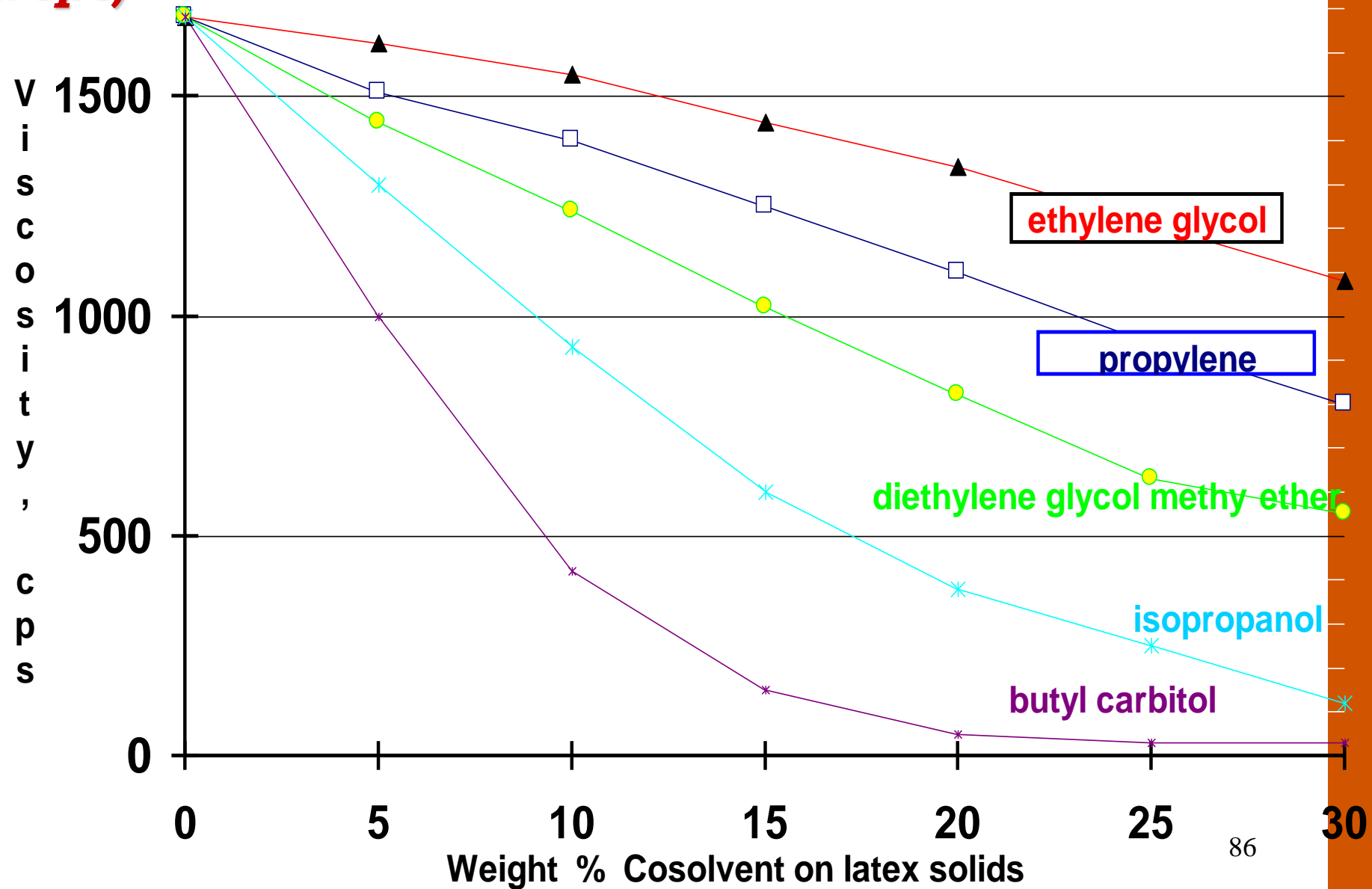
Effect of hydrophobe size on viscosity



Effect of latex particle size on adsorption



Effect of cosolvents on viscosity (drops)



Thickener Combinations

- Combination of two or more thickeners (or two or more MW grades)
 - better flow
 - greater stability
 - more efficient
- Good combinations
 - HEC + clay
 - HEC + associative thickener
 - soluble acrylic + swellable acrylic
 - low MW + high MW HEC

Pigments and Extenders

- Not usually thought of as rheology modifiers, but their level in the paint certainly influences viscosity.
- Adding more pigment increases viscosity by raising solids.
- Flocculated pigments give structure, tend to raise the low shear viscosity. Help prevent pigment settling.

Comparative Properties

HEC/Conventional Non-Associative Thickeners

☐ Thicken by chain entanglement-----bigger = more efficient

☐ Problems

- Very poor flow and leveling
- Poor roller spatter
- Flocculation hiding and gloss loss
- Biodegradation
- Handling a solid, dusting, preparation of solutions

☐ Strengths

- Very predictable performance
- Excellent color acceptance and development
- Excellent sag and syneresis resistance

☐ Price relative to other thickeners has been going up

Associative Thickeners

- ❑ **Thicken by association of hydrophobes--which adsorb onto latex**
- ❑ **Adsorption increases as latex particle size decreases**
- ❑ **Problems**
 - **Adsorption is selective and varies with properties of latex**
 - **Performance is less predictable**
 - **Cosolvents and surfactants can cause desorption**
 - **Viscosity stability thus a challenge (when tinted and heat aged)**
 - **Color acceptance is also more challenging**
- ❑ **Strengths**
 - **Excellent flow and leveling**
 - **Excellent application properties (brush and roller hiding)**
 - **Excellent film build**
 - **Excellent spatter resistance**
 - **Very good film properties (resistance and durability)**

Comparison between Cellulosic Ethers and HASE

Matt Paints

Cellulosic Ether Thickener

- longer open time
- improved scrub resistance
- no impact of pH-value
- expensive
- susceptible to bacteria

HASE Thickener

- short open time
- loss in pigment binding power
- strong impact of pH
- low price
- resistant to bacteria

Semi Gloss and Gloss Paints

Cellulosic Ether Thickener

- pseudoplastic rheology

high viscosity at low shear rates
low viscosity at high shear rates

HASE Thickener

- alkyd like rheological behaviour:

levelling similar to alkyd paints
improved brush drag

Comparative Evaluation

	<i>Celulosicos (HEC)</i>	<i>ASE</i>	<i>HASE</i>	<i>HEUR</i>
Thickening Mechanism	Liquid phase	Liquid phase	Liquid phase & association	Liquid phase & association
Viscosity Profile	pseudoplastic	pseudoplastic	Less pseudoplastic	Newtonian to pseudoplastic
Handling	+	++	++	+ / -
Bacteria Resistance	-	+	+	+
Cost	+	+ / -	+ / -	-
Application field	Interior/Exterior Paints	Interior paints	Interior /Exterior Paints. Less than 8 Lbs/100 gallons	Interior / Exterior Less than 8 Lbs/100 gallons



HEUR thickener can affect gloss development on paint formulations. Everybody knows that the surface of TiO_2 is positively charged in low pH solutions, neutral at the isoelectric point and negatively charged in high pH solutions. As a consequence of that it is expected that nonionic components with minimal proton donating functions should not be expected to adsorb on TiO_2 in an alkaline medium. This lack of adsorption is indeed observed. Neither the nonionic ethoxylated surfactants added to the paint formulation nor the HEUR thickener adsorbs on the surface of TiO_2 . Under alkaline conditions. Adsorption of anionic polyelectrolytes on a negatively charged pigment surface would also seem to be severely restricted by charge –charge repulsion

However high molecular weight polyacids show adsorption on TiO₂ at pH above the isoelectric point?

Two factors favor this type of adsorption. The first is the close proximity of pendant acid functions, which inhibits ionization of all of the carboxylate groups because of electrostatic repulsion. With repeating acid units, unionized carboxylated groups would be present to facilitate hydrogen-bond interaction with the pigment surface. The second factor favoring adsorption is that even with low enthalpies of interaction the detachment of most interacting acid segments from the TiO₂ surface do not occur simultaneously for statistical reasons.

It has been chemically demonstrated that in α -olefin / maleic acid dispersing agents the neighboring hydrophobe units lower the dielectric constant in the area around the carboxyls contiguous to the hydrophobic groups giving a structure where approximately 50 % of the carboxyl groups are unionized. An interaction between the hydrophobic segments of the HEUR and the dispersant could provide steric stabilization complementing the electrostatic forces and a greater barrier to flocculation of the pigment, improvement film gloss.

The primary mechanism for stabilization of disperse phases in a medium of low dielectric constant is steric and/or entropic, in ion containing water, electrostatic repulsive forces are generally too weak for particle stabilization.

The surface of TiO₂ with or w/o its inorganic surface treatment is higher in interfacial energy than any of the different latices (vinyl acrylics, acrylics and styrene acrylics). So, this high-energy inorganic surface is the most poorly stabilized in the crowded environment of water borne coating formulation. It means that if any disperse phase were prone to flocculate by a depletion layer or by suppression of the electrical double layer mechanism, that phase would be the high-energy pigment.

Dispersions stabilized by the hydrophobic diisobutylene / maleic acid dispersant with the HEUR thickener does not exhibit high complex viscosity at low oscillation frequencies. It means that the association between the dispersing agent and the HEUR reduces the flocculation via increased electrostatic/steric stabilization.

Also HEUR's tend to be very sensitive to other paint ingredients such as surfactants, colorants and co-solvents. The addition of a colorant to an HEUR/HEUR system may reduce the Stormer viscosity by as much as 15 KU. Today there is a new family of HEURASE thickeners, specially developed to avoid this inconvenience.

Alkali Swellable and Alkali soluble Thickeners:

Are carboxyl functional copolymers produced by the free radical polymerization of ethylenically unsaturated monomers. The copolymers are substantially insoluble in water at low pH, but exhibit thickening on swelling or dissolution in aqueous media at higher degrees of ionization. Conventional Alkali swellable thickeners can be modified with hydrophobes to construct an associative thickener.

The dominant mode of interaction of nonassociative thickeners with latex particles is 'volume restriction' or 'depletion' flocculation while the HEURASE and HASE thickeners act by swelling and Adsorption through the hydrophobes. Because of the similarities to surfactant molecules, complete desorption of the thickener was affected by the addition of a sufficient level of surfactant and the amount required increased with decreasing particle size of the binder latex. Water-soluble cosolvents were also effective in causing desorption, although larger amounts were necessary than with the surfactant. Another Important observation is that these associative thickeners are more markedly Newtonian.

The difference between nonionic associative thickeners (HEUR) and HASE or HEURASE is high at low shear rates. The low molecular weight nonionic (HEUR) associative thickener lost viscosity rapidly on desorption with surfactant while the much higher molecular weight HASE or HEURASE did not. The proposed reason for this result was that the hydrodynamic mechanism is still operational for HASE and HEURASE.

Adsorption was found to increase with decreasing particle size for both thickener types.

Because latices vary greatly in their particle size distributions and in the hydrophobicity of their particle surfaces, the choice of latex binder had a major effect on interactions with the anionic and nonionic associative thickeners. The type and particle size of pigments and extenders are not usually important because these particles are mostly hydrophilic. Solvents that are water miscible can change the solubility parameter of the aqueous continuous phase and these different solubility parameters altered the associative interactions. In contrast water insoluble coalescing agents showed little effect. On the other hand the lower MFFT observed for HASE and HEURASE associative thickeners (compared with HEUR types) is responsible for the improved gloss & wet scrub resistance obtained with these products.

The main difference between conventional HASE and HEURASE is the latest has an urethane bond between the Ethylene oxide moieties and the hydrophobe, while the HASE has an ester bond which can be hydrolyzed in alkaline conditions with the consequent lost in thickening efficiency. Likewise the polymerization process of HEURASE thickeners together with some chemical factors are responsible for the lower water absorption showed by this thickener family when they are compared with HASE types.

In addition, HEURASE associative thickeners show better-wet scrub resistance than the one showed by HASE type thickeners.

To avoid flocculation, which can be responsible for lower contrast ratio, wet scrub and gloss, co/polymeric hydrophobic dispersing agents are recommended (isobutylene/maleic acid).

Inorganic Thickeners

Organoclays, organically modified laminar silicates, are the most widely used inorganic thickeners and have found many applications in the paint- and coatings industry. Well-known laminar or phyllosilicates are hectorite and bentonite. Other important silica thickeners are the synthetic amorphous silicates. In this chapter, typical properties and applications of organoclays (also known as “organophilic clays

Organoclays

Nature has many mineral substances which have the ability to swell in water and can be turned into masses that are easily formed into shapes. Clays are a good example of such minerals. They give a heavy structure to loamy earth, and has been used for millenniums by mankind as raw material for the production of ceramic objects. In the mid-thirties of this century it was discovered that within this widebranched family, there is a group of minerals, the so-called smectites, that are capable of forming gel-like structures when exposed to sufficient shear forces within a suitable pH-range. The smectites have been analysed very intensively by X-ray diffraction spectroscopy, and they were found to generally have the morphological structure shown in Fig. 3.1-1. They are composed of silicates made up of layers of trimorphic (3-layered) sheets. The middle layer consisting of Al_2O_3 octahedra is surrounded on both sides with SiO_2 tetrahedra. These elementary modules are in turn stacked

as plates one above the other, like cards in a stack of playing cards (Fig. 3.1-2). The distance between two neighbouring layers is approximately 10- 15 Å. The thickness of such an elementary layer has been measured to be 9.6 Å. The smectite octahedral layers are not all constructed similarly, in contrast to other laminar silicates. The central, positively charged metal ion has partly been replaced in an isomorphous way by another ion of lower valency. This confers a negative charge on the entire crystal lattice, compensated for by absorbed cations on the basal surfaces (Fig. 3.1-3). Two smectites, montmorillonite and hectorite, have found extremely important practical applications.

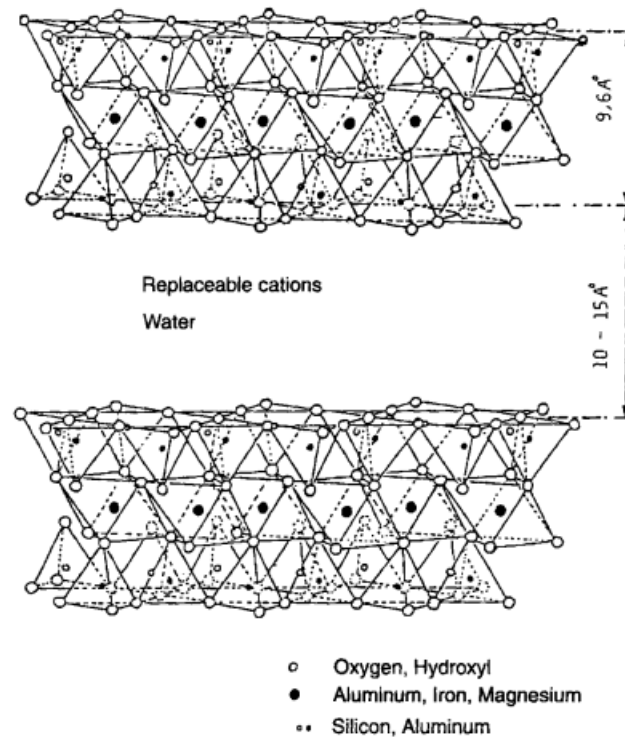


Figure 3.1-2. Smectite layers

Incorporation Procedures

Various methods may be considered for the incorporation of organoclays into a coating materials. However, the two basic methods are the powder method and the paste method.

Powder Method For this, the dry organoclay powder is dispersed in the system together with the pigment. Variations in the order of addition are possible, depending on the available quantity and quality of solvents/hinders in the formulation as well as the wetting properties of the binders and the dispersing equipment used. A polar solvent has to be added during the dispersing phase.

Paste Method With this method a master batch paste of the organoclay is produced first of all, e. g., as follows: - solvent: 90.0 parts by weight - organoclay: 7.5 parts by weight - dispersed over 5 min with a high-speed dissolver - polar solvent: 2.5 parts by weight - dispersed for another 5 min The quantity of organoclay within the paste may vary but it should not exceed 10 % as more concentrated pastes are difficult to work with and a good predispersion of the organoclay can then usually not be ensured. The master-batch paste is added to the milling paste or during the let-down procedure of the coating manufacture. It is possible to vary the time of adding, depending on the wetting properties of the binders and dispersing equipment used. However, it is important that the master-batch paste is subjected to an intensive shear load when it is worked into the coating system, if its full effectiveness is to be realized.

Viscoelasticity: an useful science

RHEOMETER GEOMETRY

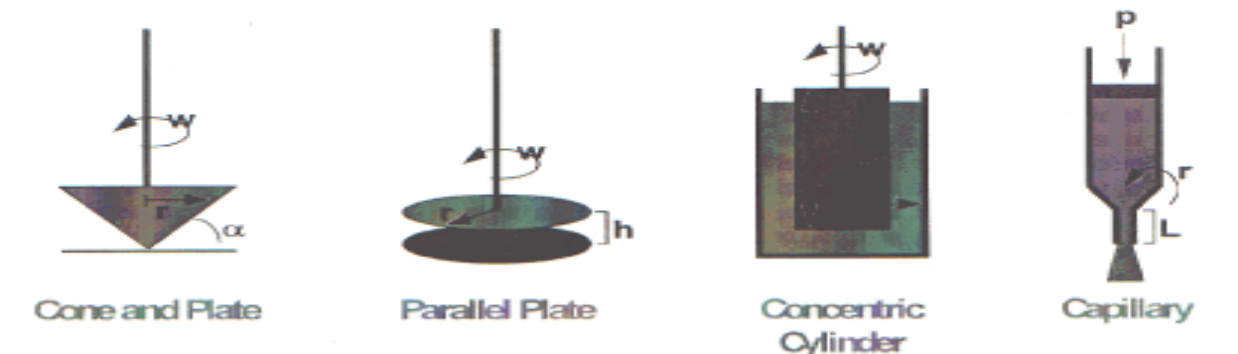


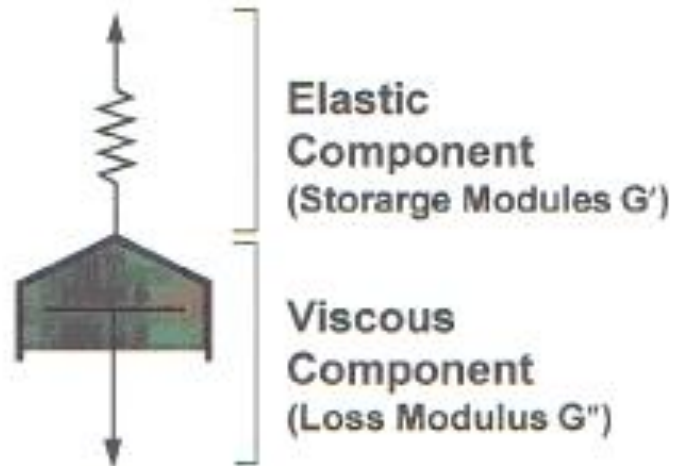
Figure 22

COMPARISON OF RHEOMETER GEOMETRIES

	<i>Strengths</i>	<i>Weaknesses</i>
<i>Cone and Plate</i>	Uniform Shear Good for Thixotropic Systems	Edge Effects Limited to Low-Medium Shear Small Gap at Center
<i>Parallel Plate</i>	High Shear Rates ($10^4 - 10^5 \text{ sec}^{-1}$) Narrow Gap \rightarrow Less Edge Effects	Non-Uniform Shear Rates Materials with Yield Stress
<i>Concentric Cylinder</i>	Uniform Shear if Gap Small Higher Shear Rates Greater Sensitivity Limits Sample Drying	Shear Heating Secondary Flows End Effects
<i>Capillary</i>	Wide Shear Rate Range Ultra High Shear ($10^5 - 10^6 \text{ sec}^{-1}$)	Non-Uniform Shear Requires Correction of Data

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VISCOELASTIC LIQUID (*Maxwell Element*)

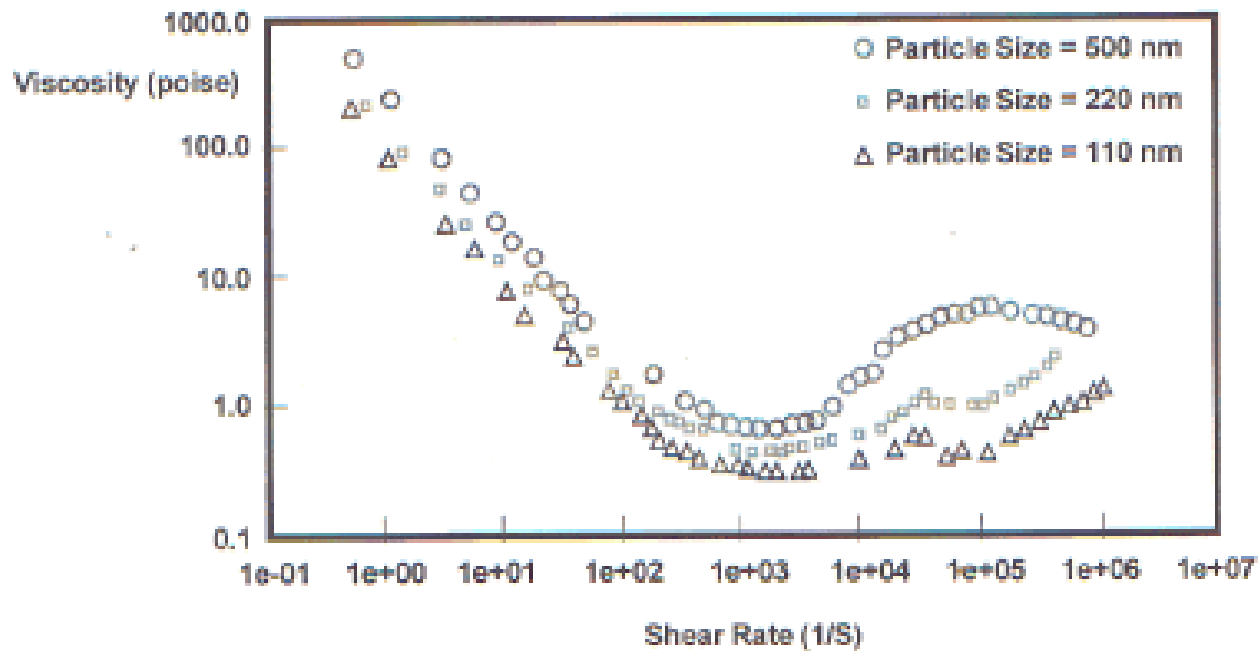


Properties Depend Primarily on Rate of Shear

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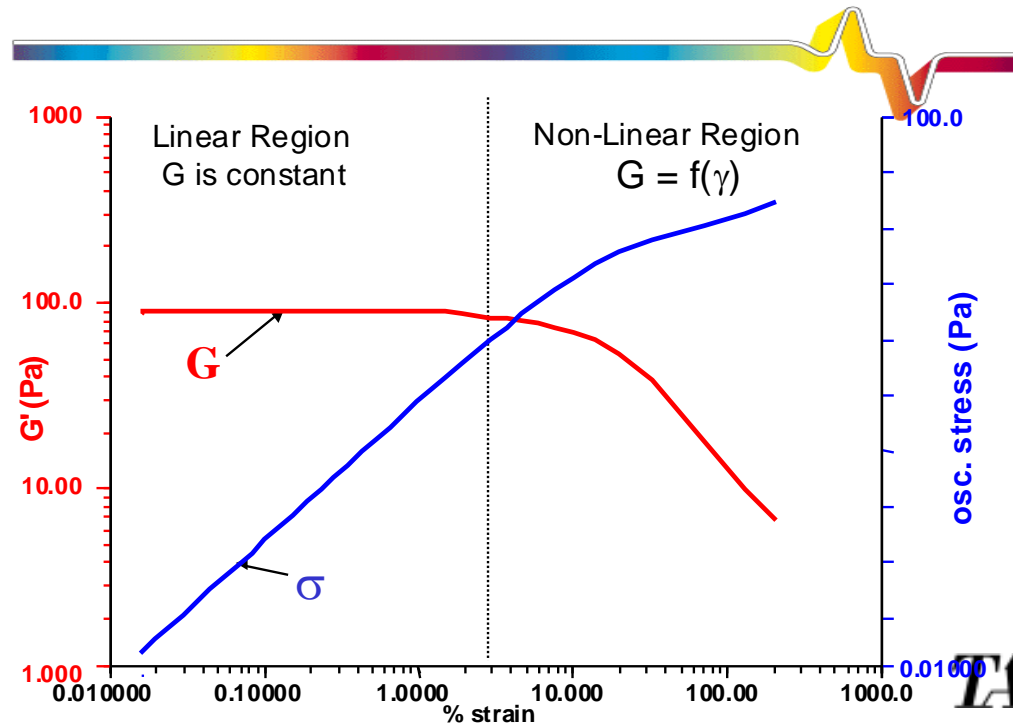
EFFECT OF LATEX PARTICLE SIZE ON VISCOSITY

Solids Level = 64%



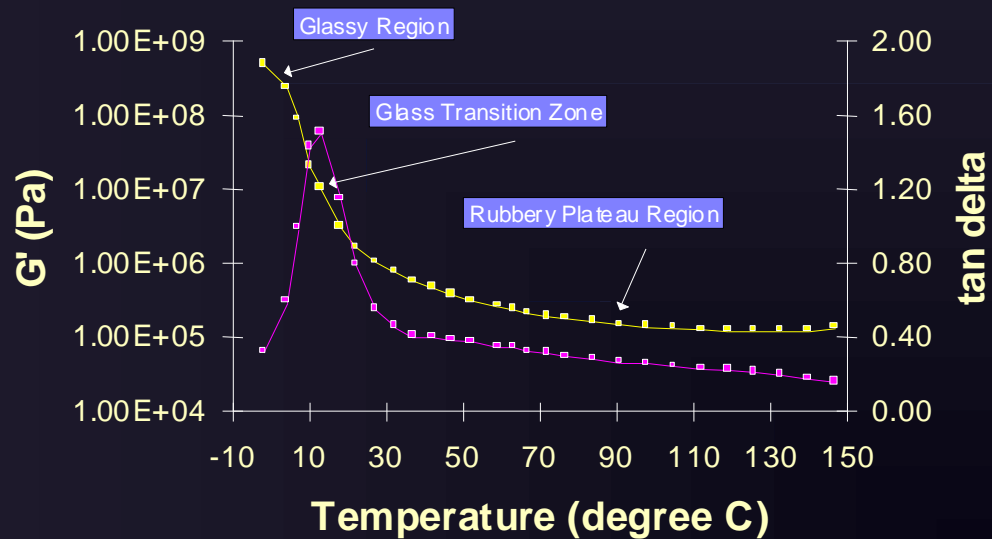
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Linear and Non-Linear Stress-Strain Behavior



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Dynamic Mechanical Spectrum of Polymer



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Tan Delta

Instrumentation:

AR-1000 Rheometer

Concentric Geometry (Cup and Bob)

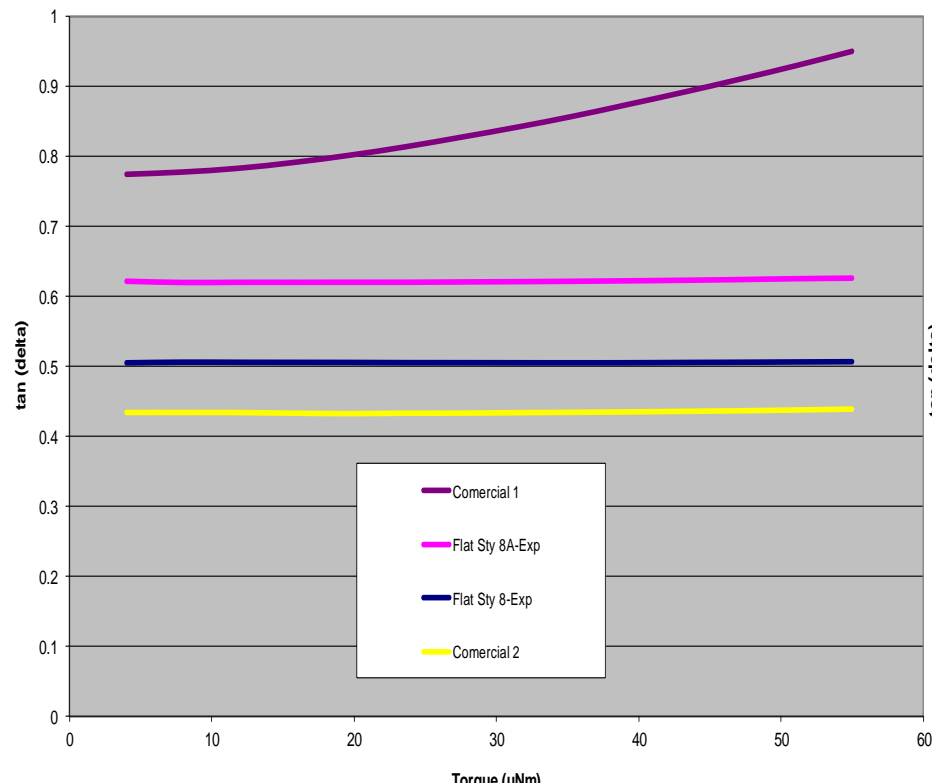
20 degree F constant temperature

10 Pa pre-shear for 30 sec. with 5min. equilibration

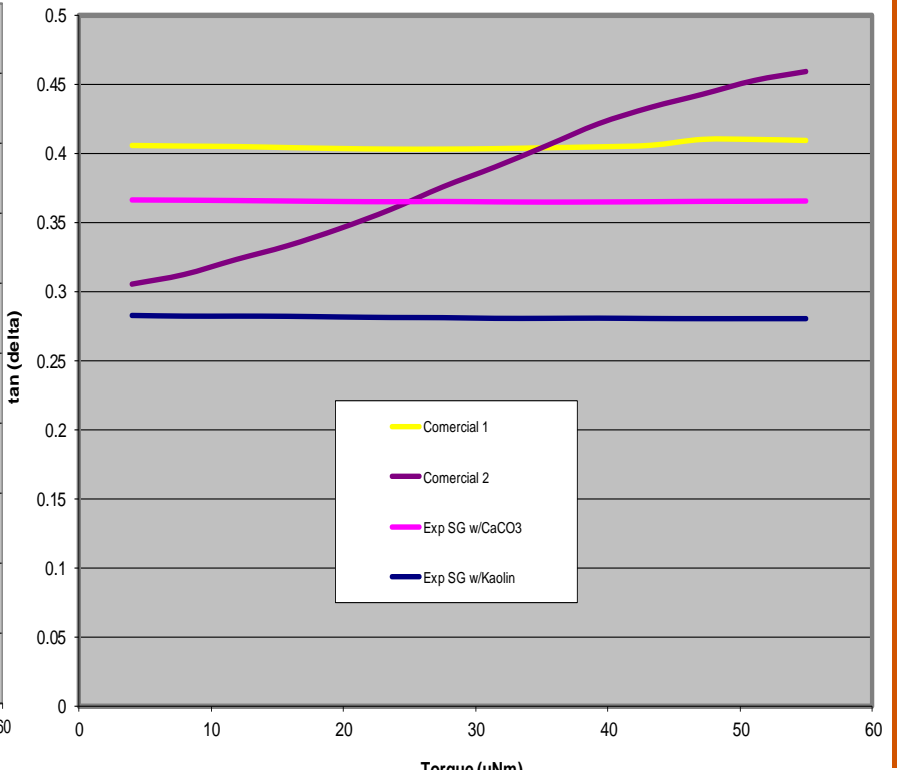
This experiment consisted of applying a torque sweep from 0 to 60uNm while recording the $\tan \delta$. $\tan \delta$ is the ratio of viscous (energy dissipation) to elastic (storage) behavior and values in the range of 0.5 to 1.5 are desirable for paint. A paint that has an increase in stress with increasing Torque suggests poor long-term stability such as pigment sedimentation or syneresis. Low $\tan \delta$ values can imply more structure and good non-drip properties. Where as, high $\tan \delta$ values suggest less structure or more fluid like behavior.

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Flat



semigloss

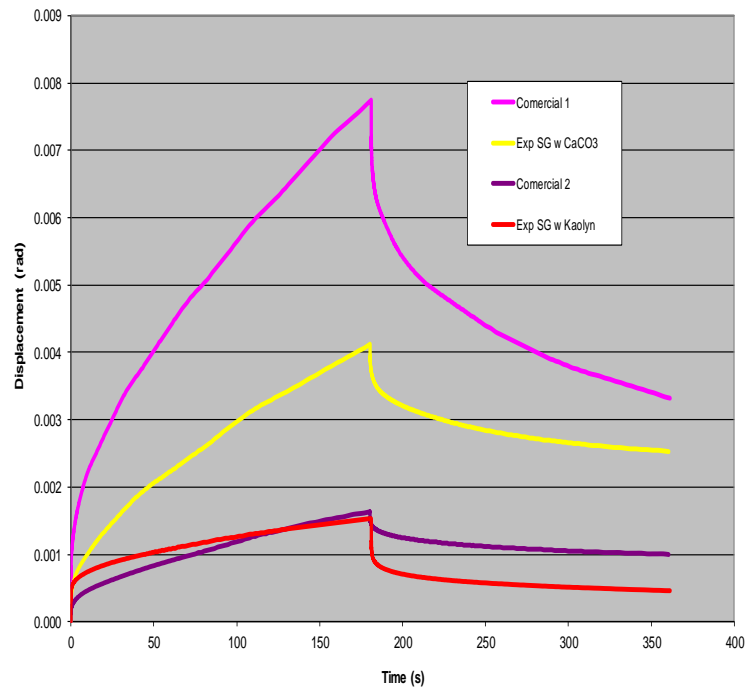
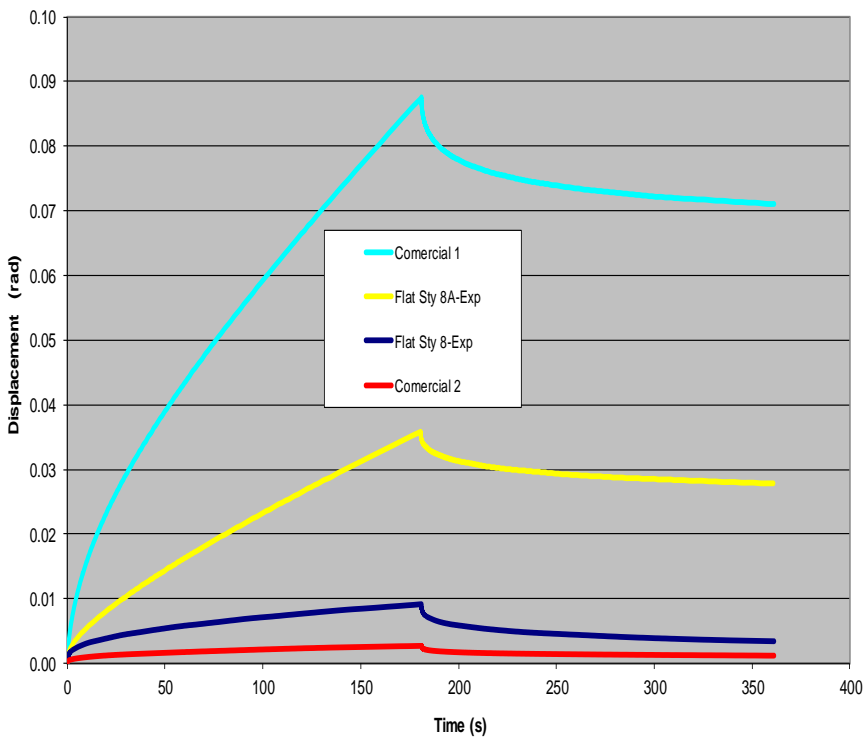


Viscoelasticity: an useful science

Creep Test

A constant force of 1.0 Pa is applied to the paint during a time of 180 seconds and then must be wait the recovery of the paint after the removal of the force by 180 minutes

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Viscoelasticity: an useful science

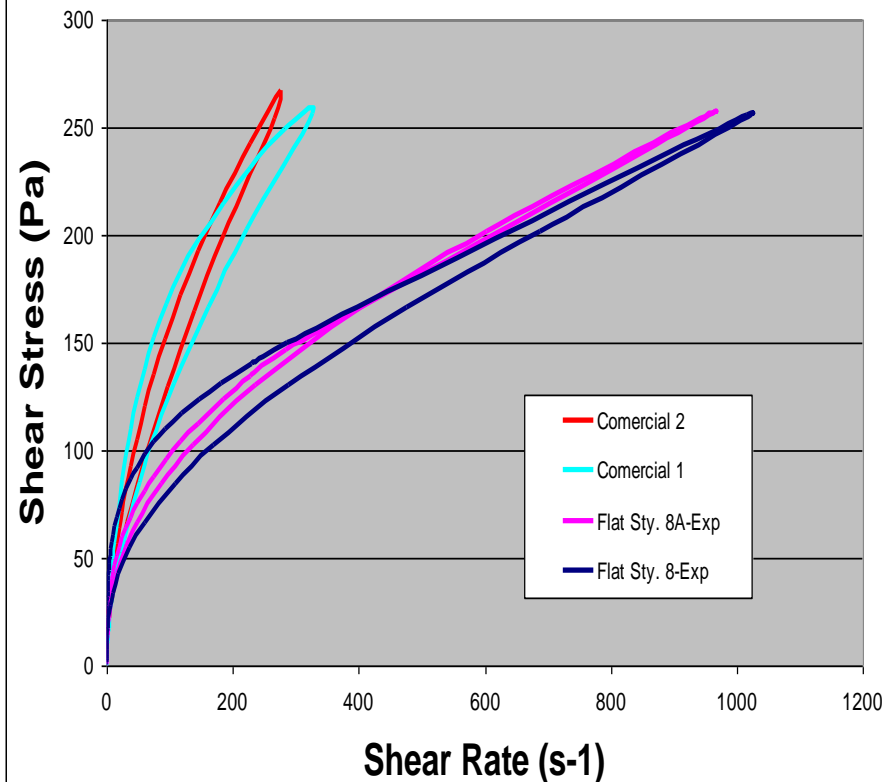
Flow Test

The paints were subjected to a controlled force (0 to 200 Pascal) and the resulting strain rates were measured. Flow mode is the best way to provide ease of application. Paints should always show a decrease in viscosity with an increase in shear rate for greater ease of application. A good viscosity for rolling is in the region of 0.1 to 0.5 Pascal seconds.

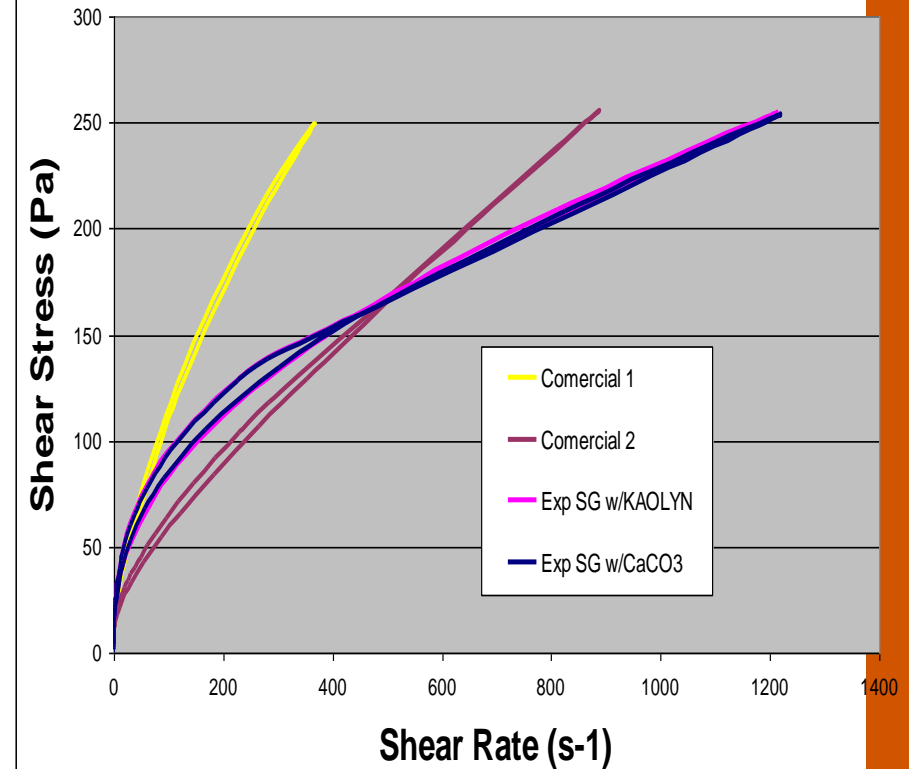
To measure the thixotropy of the paints, the force was increased from 0 to 200 Pascals and then decreased again to zero and the corresponding strain rates were measured.

Viscoelasticity: an useful science

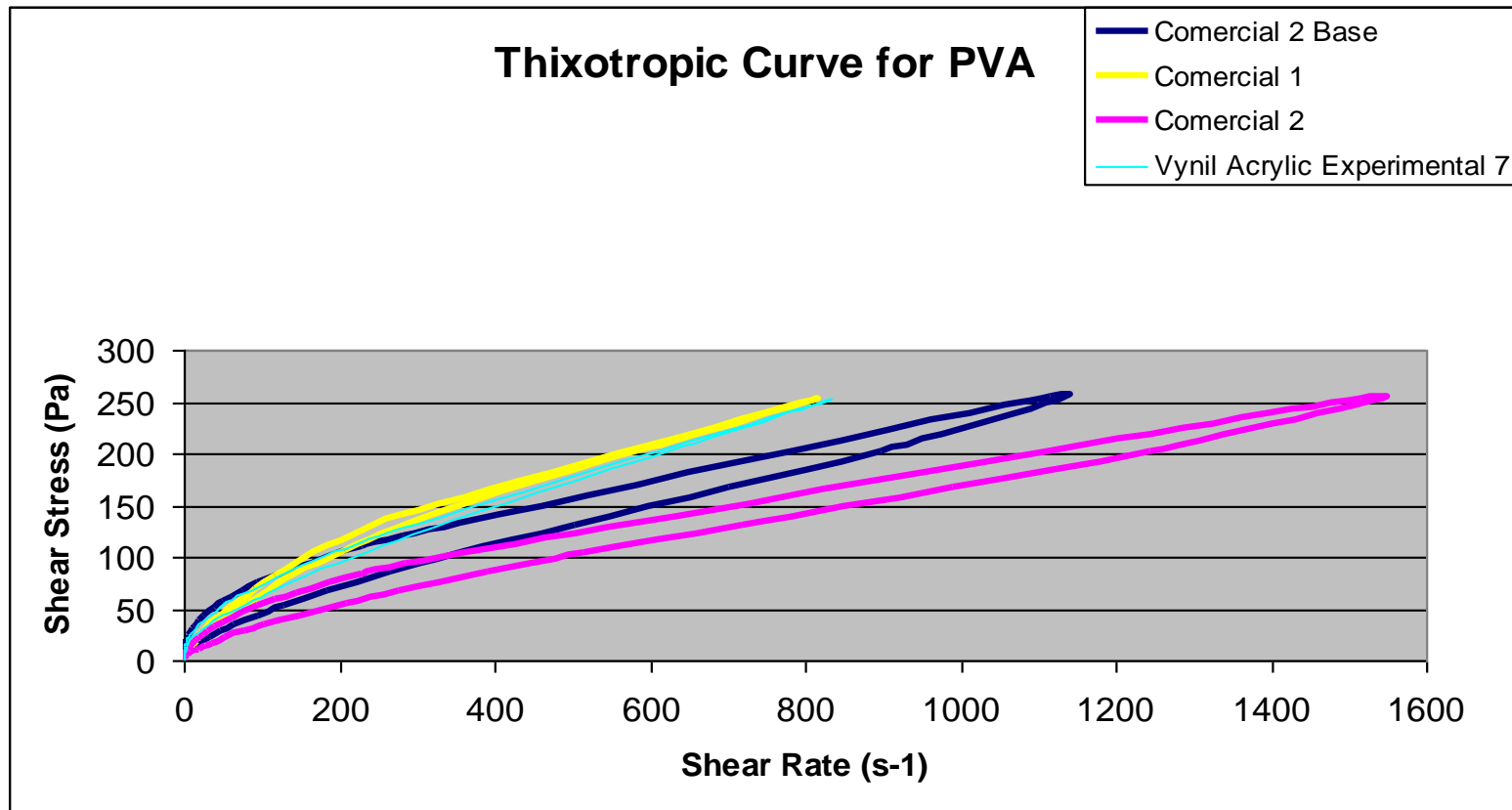
mate Thixotropic curves



Semi-brillo Thixotropic curves



Viscoelasticity: an useful science



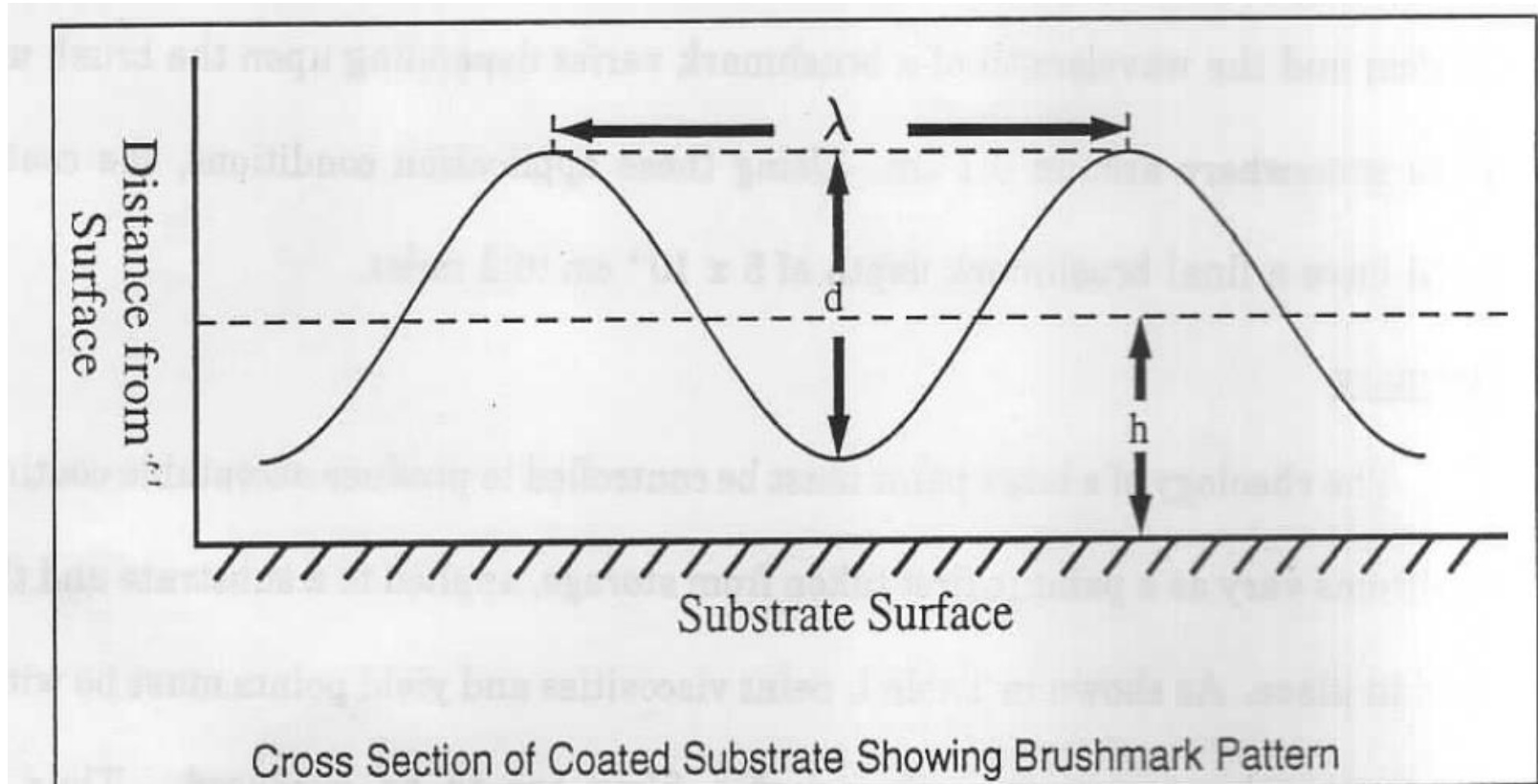
Rheology during the leveling process

- Leveling is controlled by two opposing forces. The driving force for leveling is the force produced by surface tension (surface tension) while on the other hand the force that resists leveling is viscosity.

$$d = \frac{\sigma_0 \lambda^3}{4\pi^3 \delta h}$$

- The brush mark d is proportional to the shear force threshold value and the wavelength of the brush mark (distance between ridges)
- The brush mark is inversely proportional to surface tension and application thickness

Rheology during the leveling process





Thanks !!

Questions ?

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