ASPHALT EMULSION MANUFACTURERS ASSOCIATION

International Bitumen Emulsion Federation

ISAET ‘21
7th International Symposium on Asphalt Emulsion Technology

High Float Emulsion Residue: Its Unique Rheology and Microstructure

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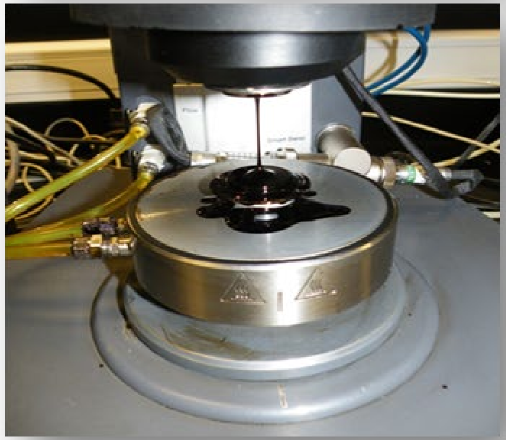
Part 1 (2014-2015)

- BACKGROUND
- RHEOLOGY
- TECHNIQUES & EXPERIMENTATION
- RESULTS & INTERPRETATION

Part 2 (2015-2021)

- BACKGROUND
- TECHNIQUES & EXPERIMENTATION
- RESULTS & INTERPRETATION
- SUMMARY

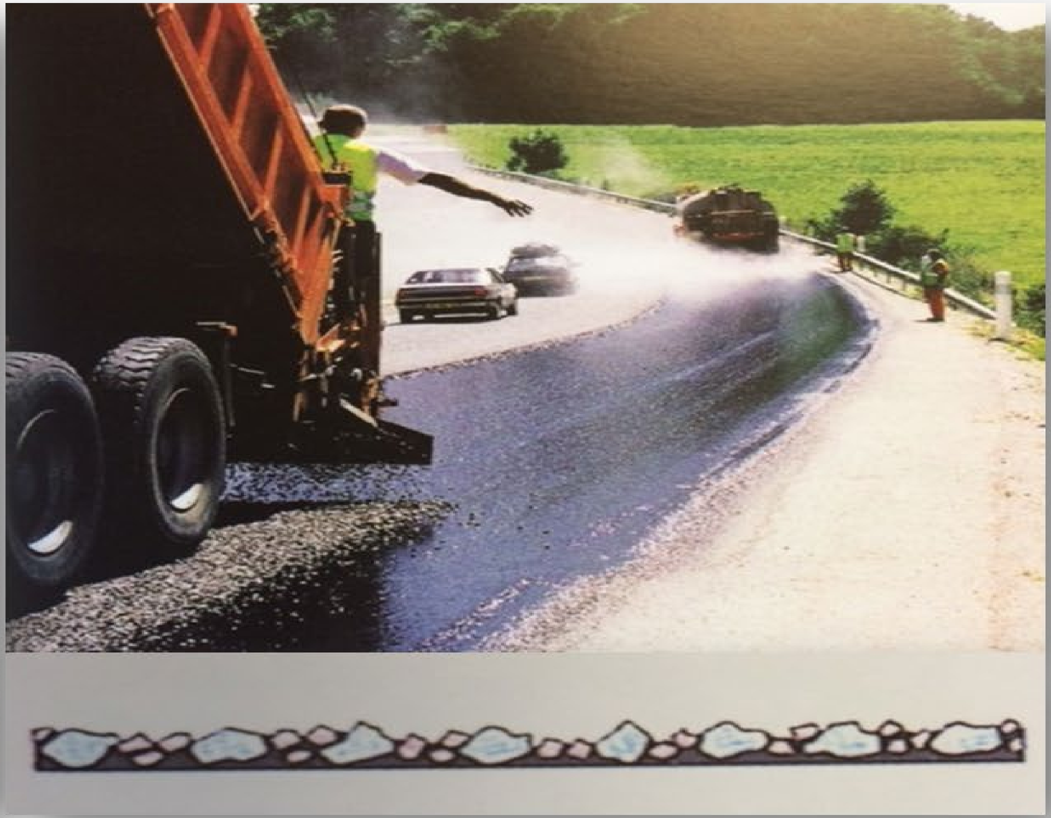


BACKGROUND

- In Canada, the paved public road network exceeds 400,000 km
- *Maintenance becoming a concern*
  - *Budgets*
  - *VOC constraints*
- Need to optimize next-gen pavement preservation materials

BACKGROUND

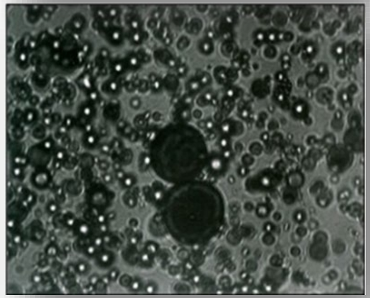
Pavement Preservation



BACKGROUND

3 major ways to liquefy “glue”:

- *Heating up bitumen (asphalt) - common in hot mix asphalt application (HMA)*
    - *Energy intensive*
- *Cutbacks – mixture of bitumen and petroleum solvents*
    - *Problem with VOC emissions*
- *Emulsions – mixture of bitumen, water and emulsifying agent*
    - *Environmentally responsible*
    - *Most cost effective*



BACKGROUND

Advancement in Emulsion Formulation

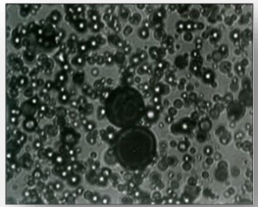
- *Select and specify bitumen emulsion for surface treatments*

Current Testing Framework

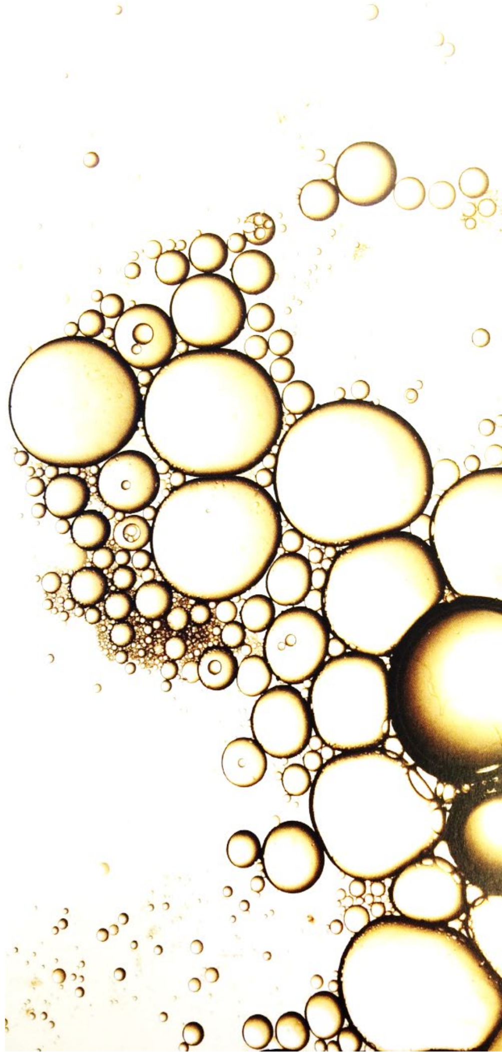
- *Does NOT consider all service conditions and performance characteristics*
- *Requires knowledge of basic science that underlies emulsion systems*

BACKGROUND

Emulsion Composition



- *Bitumen*
  - *SARA fractions, inorganic heavy metals*
  - *Inherent composition yields its "viscoelasticity"*
- *Water*
  - *Typically softened water*
    - *Favourable for addition of surfactants*
- *Emulsifier (surfactant)*
  - *Allows mixing of two immiscible liquids*
  - *Typically a chemical*
  - *Can add performance characteristics in residue*



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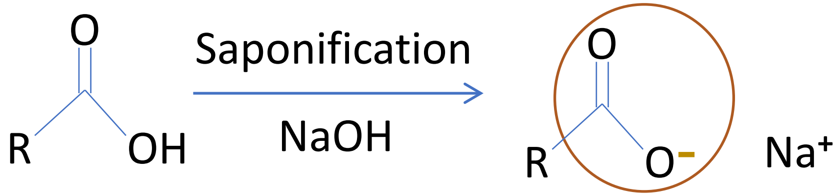
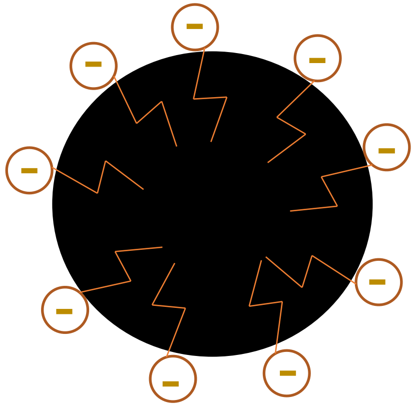
BACKGROUND

Identity of Emulsion

- *Dictated by the emulsifier*
  - *Cationic (+)*
    - *Fatty amines*
  - *Anionic (-)*
    - *Fatty acids*
  - ***High float (-)***
    - *Crude tall oil*
    - *Special type of anionic i.e. HF-100S*

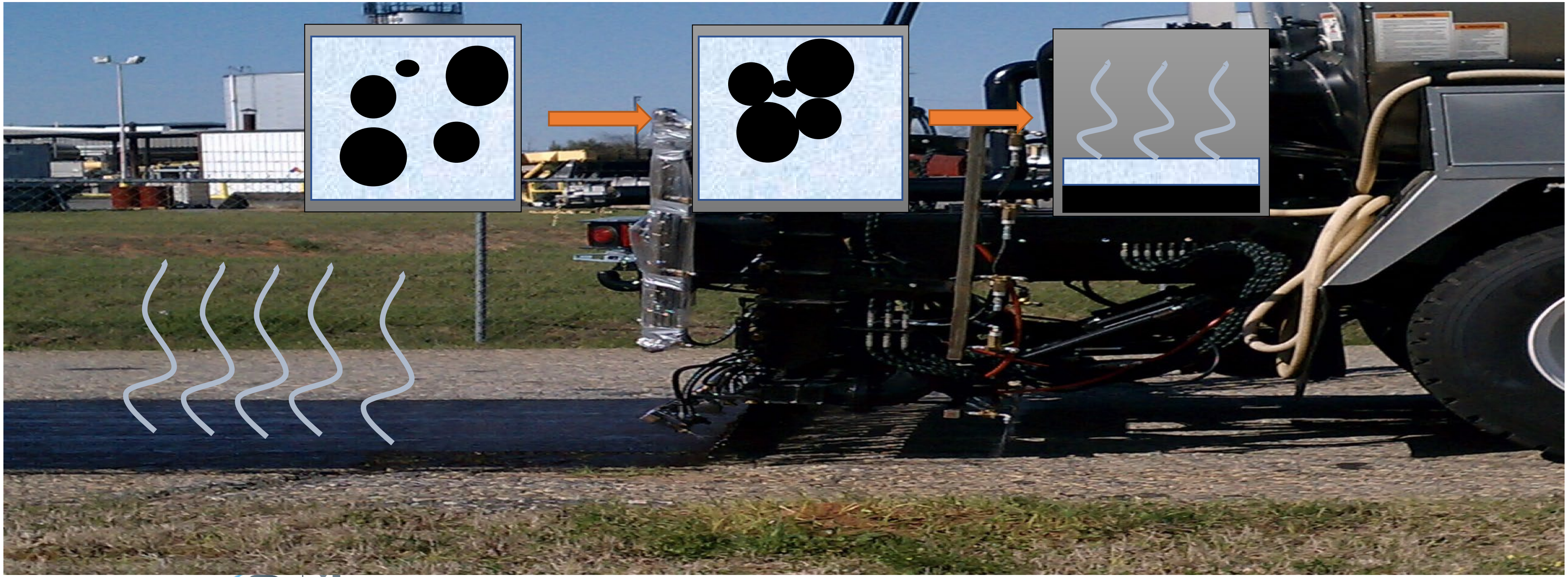




Surfactant adsorption at the bitumen-water interface

BACKGROUND

Emulsion Residue Formation



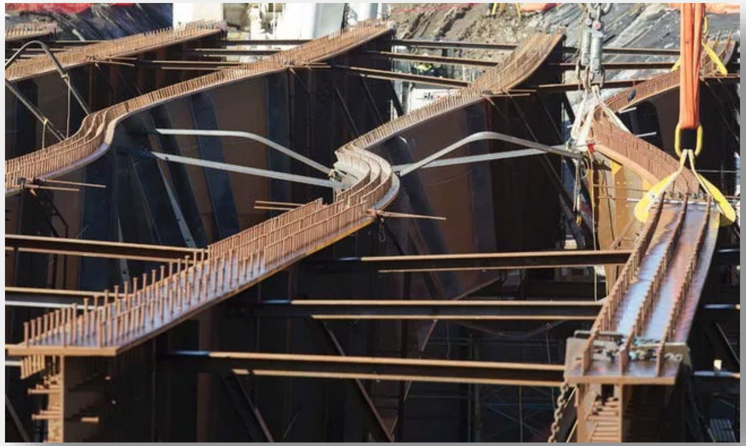
BACKGROUND

$t = 0$ $t = 1\ \text{hr}$ $t = 8\ \text{hr}$

Yield Stress???

BACKGROUND

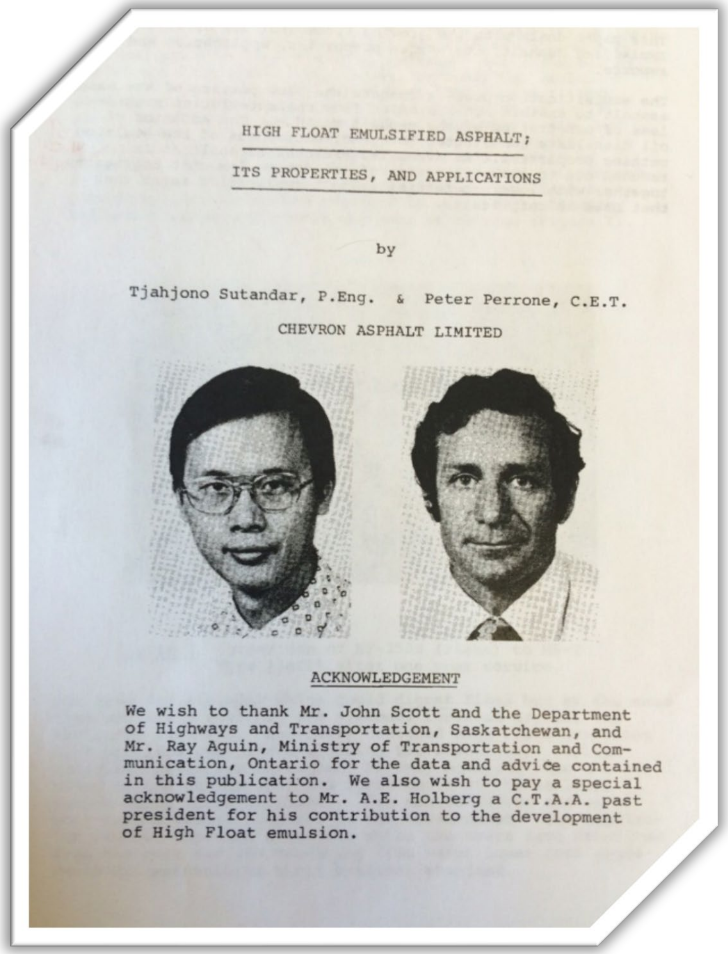
Materials with Yield Stress



BACKGROUND

- *1980 paper by Sutandar and Perrone claimed structure was characterize by **Bingham plastic flow behaviour***

- *Implied concept of yield stress*
  - *However, there is no rigorous way to quantify*
  - *Mechanism is not fully understood*



HIGH FLOAT EMULSIFIED ASPHALT;

ITS PROPERTIES, AND APPLICATIONS

by

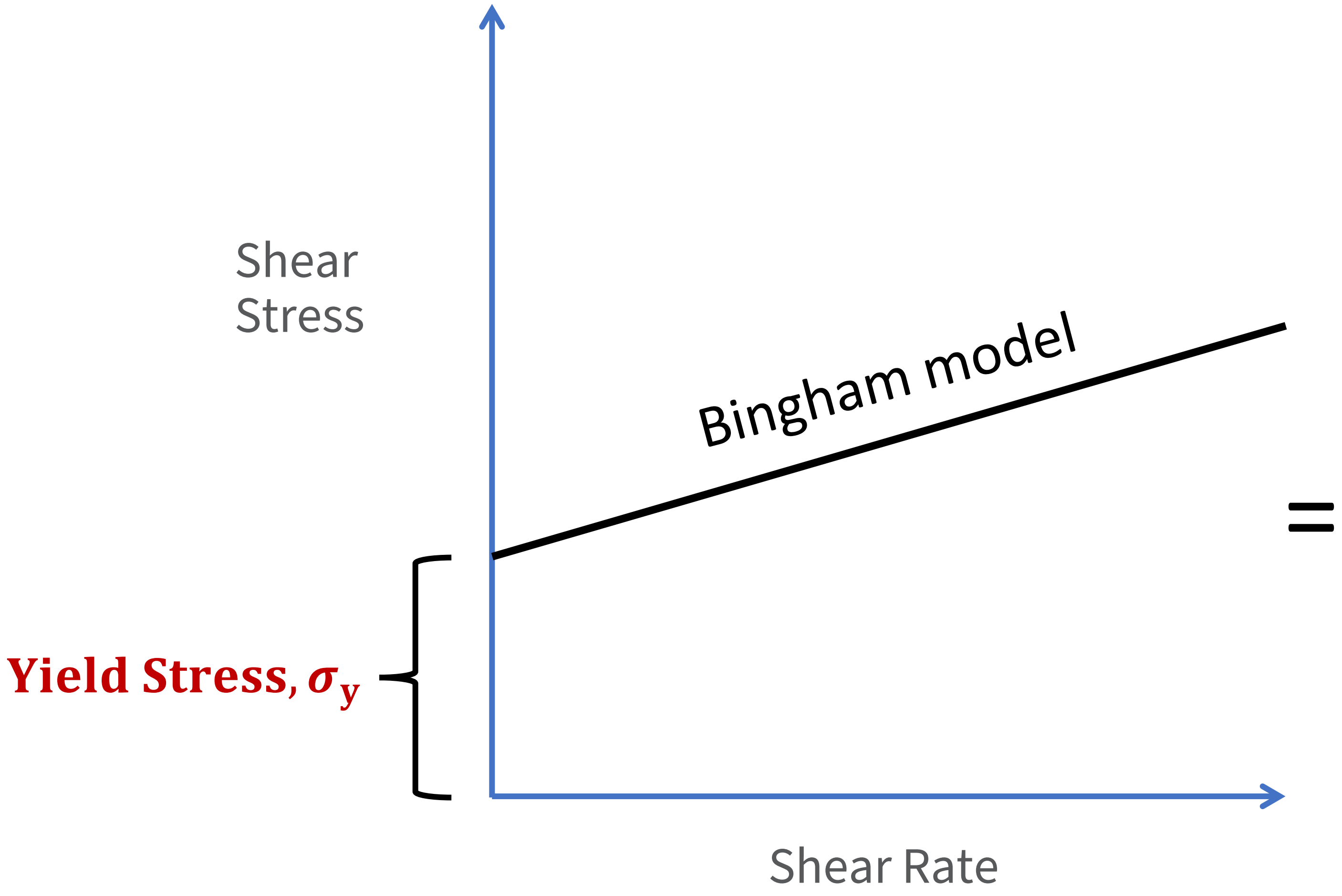
Tjahjono Sutandar, P.Eng. & Peter Perrone, C.E.T.

CHEVRON ASPHALT LIMITED

ACKNOWLEDGEMENT

We wish to thank Mr. John Scott and the Department of Highways and Transportation, Saskatchewan, and Mr. Ray Aguin, Ministry of Transportation and Communication, Ontario for the data and advice contained in this publication. We also wish to pay a special acknowledgement to Mr. A.E. Holberg a C.T.A.A. past president for his contribution to the development of High Float emulsion.

BACKGROUND



Float Test

BACKGROUND

Understanding of high-float emulsion is rudimentary

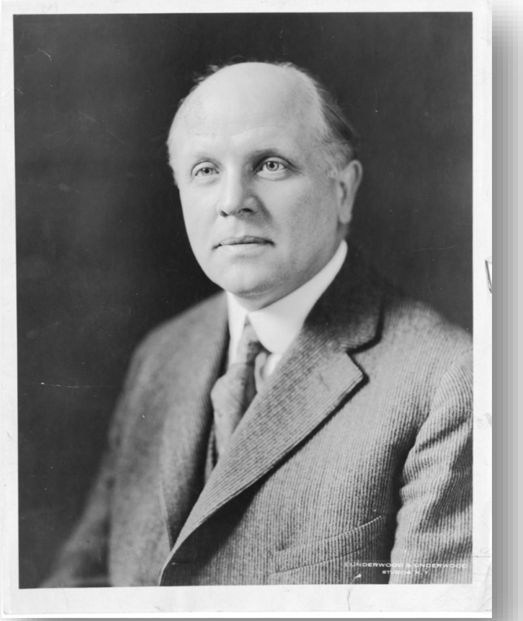
- *NO rigorous characterization of performance*
  - *Only semi-quantitative float test for "resistance to flow" behavior*

Our Strategy (2015):

1. Study the rheology of HF residues
2. Develop a rheological model
3. Quantify inherent yield stress - rigorous rheology
4. Propose an alternative to float test

RHEOLOGY

- *Viscoelastic materials led to the study of rheology*
- *Coined by Eugene Bingham*
- *Flow and deformation of materials when subjected to a stress*

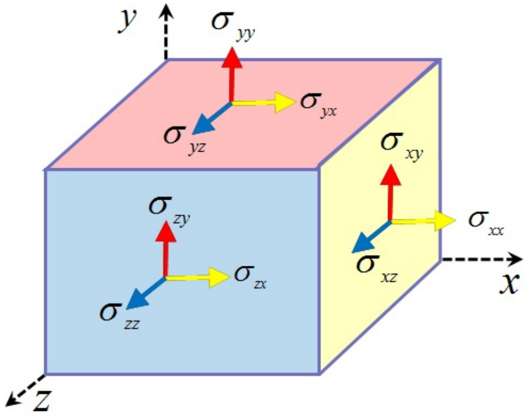


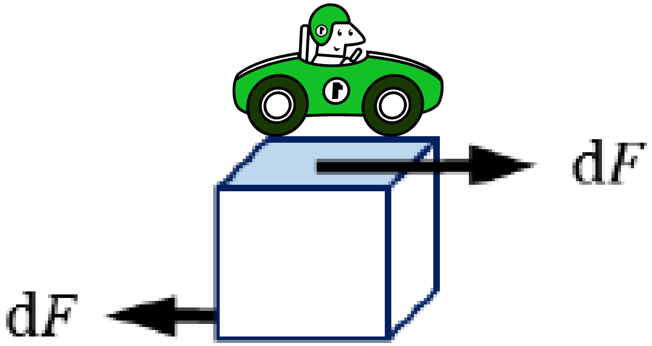
Eugene Cook Bingham
(1878-1945)

RHEOLOGY

Quantification Using Stress (σ) and Strain (ε)

- *Expressed as tensors for all modes of deformation*
- *Only need to consider one component:* ***Pure shear***





RHEOLOGY

Basic rheological models defined with stress and strain:

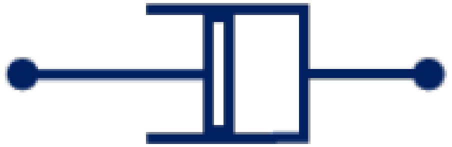
Hookean Solid

$$\sigma = G\varepsilon$$

- *Most common type of elastic behavior*
- *G is the "shear modulus"*

Newtonian Fluid

$$\sigma = \mu\dot{\varepsilon}$$

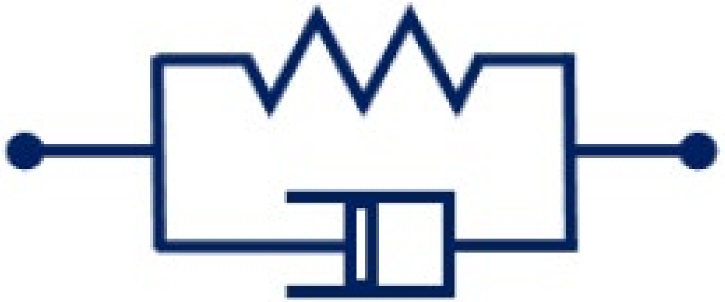


- *No resistance to deformation*
- *$\dot{\varepsilon}$ is the rate of strain, μ is viscosity*
- *Viscosity is the rate of deformation through mechanical energy into heat*

RHEOLOGY

Kelvin-Voigt Solid

$$\sigma = G\varepsilon + \mu\dot{\varepsilon}$$



- *Elastic and viscous elements are in parallel*
- *Internal dissipation within material but will complete recoil*

Maxwell Fluid

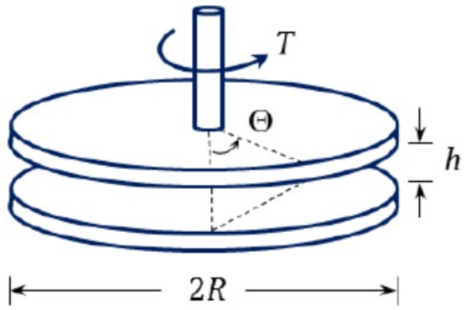
$$\dot{\varepsilon} = \frac{\dot{\sigma}}{G} + \frac{\sigma}{\mu}$$

- *Elastic and viscous elements are in series*
- *Flows like a liquid under constant force*

RHEOLOGY

Pure shear on Dynamic Shear Rheometer (DSR)

- *Sample is placed between two parallel plates*
- *Torque T is applied and used to calculate shear stress*
- *Angle of rotation Θ is used to calculate shear strain*



Setup of DSR. T is used to calculate "shear stress" and Θ is used to calculate "shear strain."

RHEOLOGY

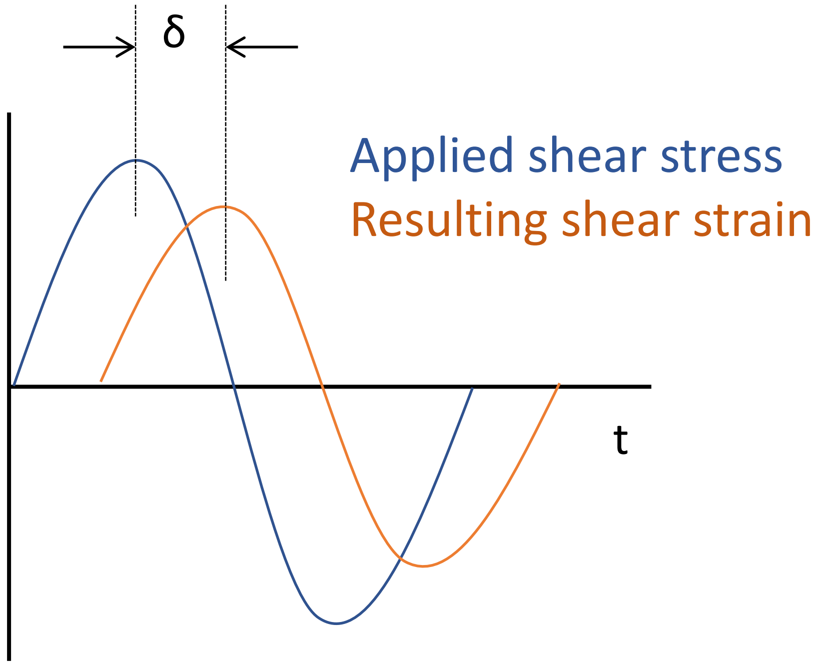
Response to Time-Varying Excitation

- *Sinusoidal Excitation*
  - *Oscillatory excitation*
  - *Phase angle δ denotes "viscoelasticity"*
  - *Used in paving industry to define rutting parameter:*

$$|G^*|/sin\delta \geq 1.00\text{kPa}$$

Problem:

- *Only measured at one frequency*
- *Does NOT characterize non-linear viscoelastic material*
- *What if material was similar to K-V material???*



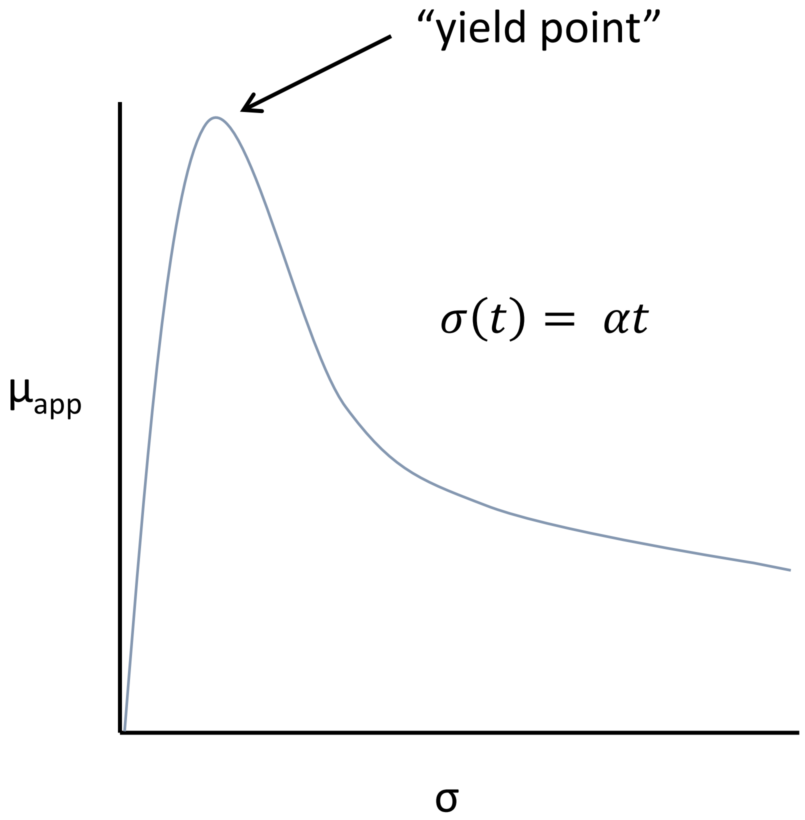
RHEOLOGY

Stress Ramp Excitation

- *Stress increases linearly with time at a constant rate* α
- *Most commonly reported is apparent viscosity:*

$$\mu_{app} = \sigma / \dot{\varepsilon}$$

- *Materials with inherent yield point's* (σ_y) *will undergo obvious physical changes*



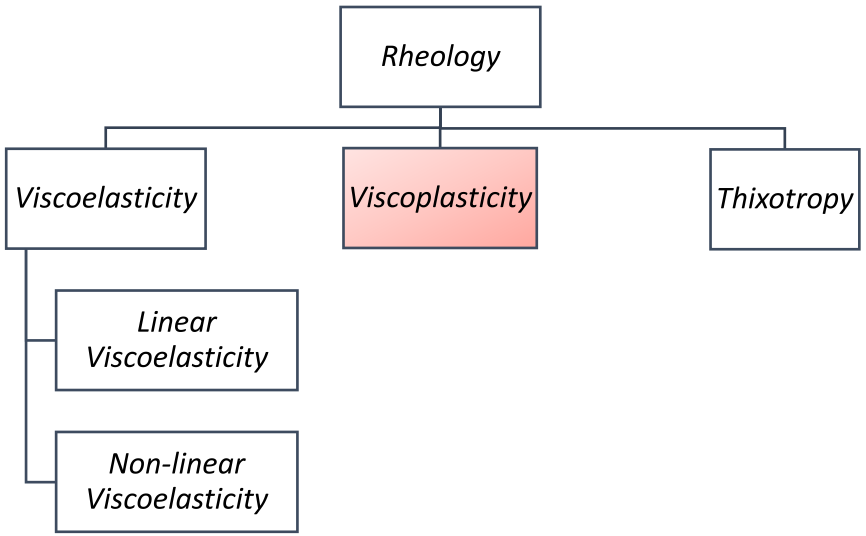
RHEOLOGY

Materials with a yield stress (viscoplastic)

- *When* $\boldsymbol{\sigma} < \boldsymbol{\sigma_y}$, *material behaves like a* ***solid***
- *When* $\boldsymbol{\sigma} > \boldsymbol{\sigma_y}$, *material behaves like a* ***fluid***
- *Most general model is the Herschel-Bulkley fluid:*

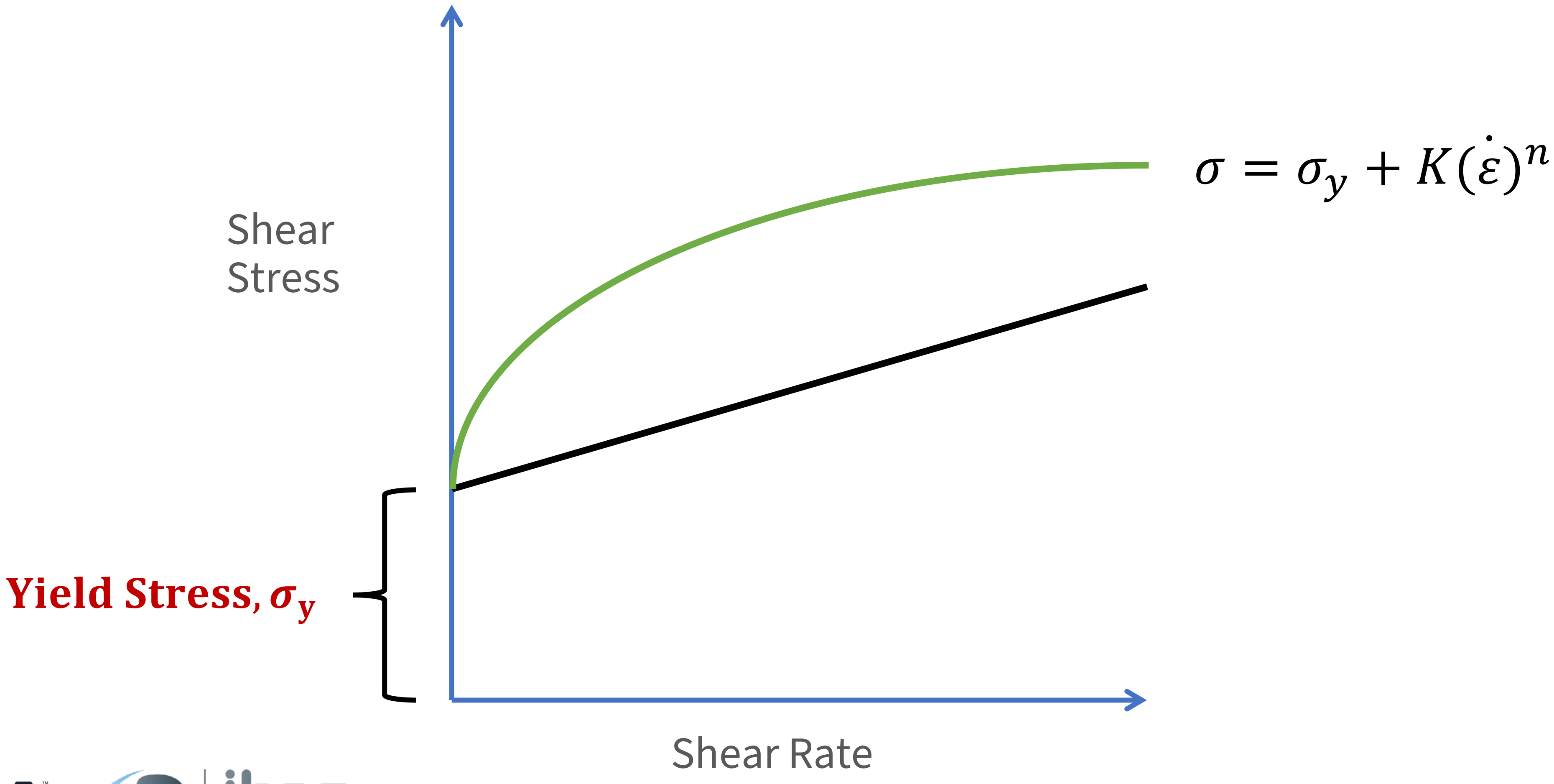
$$\mathit{When}\ \sigma < \sigma_y : \dot{\varepsilon} = 0$$

$$\mathit{When}\ \sigma > \sigma_y : \sigma - \sigma_y = K(\dot{\varepsilon})^n$$



Rheology and its Different Branches of Study

RHEOLOGY



Shear Stress
Shear Rate
Yield Stress, σ_y
$\sigma = \sigma_y + K(\dot{\varepsilon})^n$

RHEOLOGY

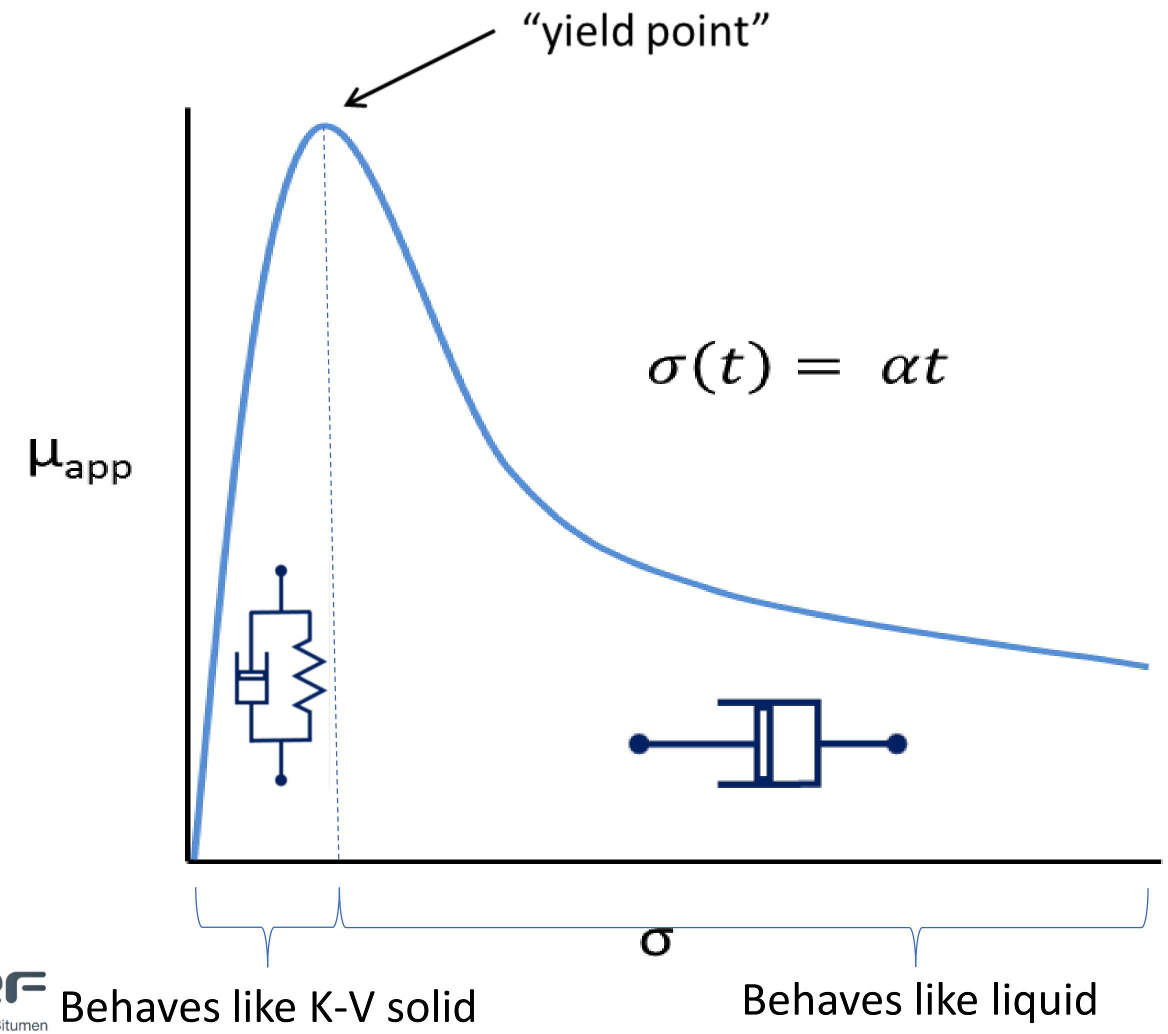
Consideration of Rheological Behavior when $\boldsymbol{\sigma} < \boldsymbol{\sigma_y}$

- *Experimental evidence indicates that the material must be allowed to deform as a solid*
- *New elastic parameter for* $\sigma < \sigma_y$ *regime:*

$$\sigma = \boldsymbol{\sigma_e} + \mu\dot{\varepsilon}$$

“elastic stress”

RHEOLOGY

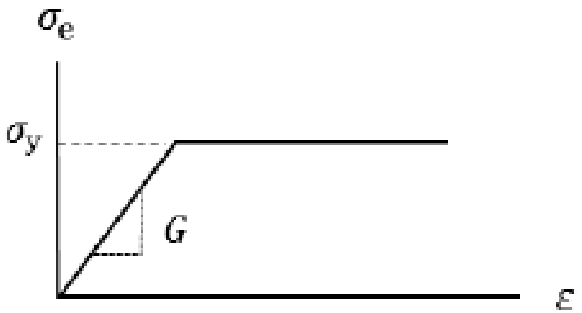


"yield point"
$\sigma(t) = \alpha t$
μ_{app}
σ
Behaves like K-V solid
Behaves like liquid

RHEOLOGY

Given that elastic stress has two parameters, G and σ_y, σ_e in terms of ε can be expressed as:

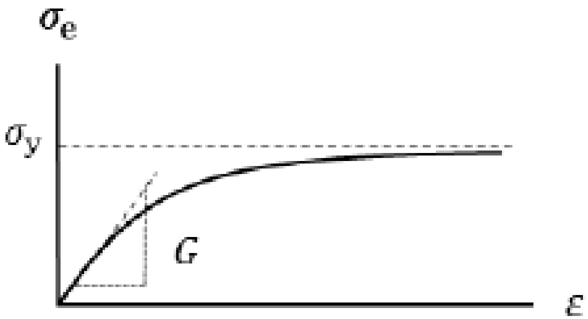
$$\sigma_e = \begin{cases} G\varepsilon;\ \varepsilon < \sigma_y/G \\ \sigma_y;\ \varepsilon > \sigma_y/G \end{cases}$$



OR

$$\sigma_e = \sigma_y[1 - \exp(-G\varepsilon/\sigma_y)]$$

- "softer" response



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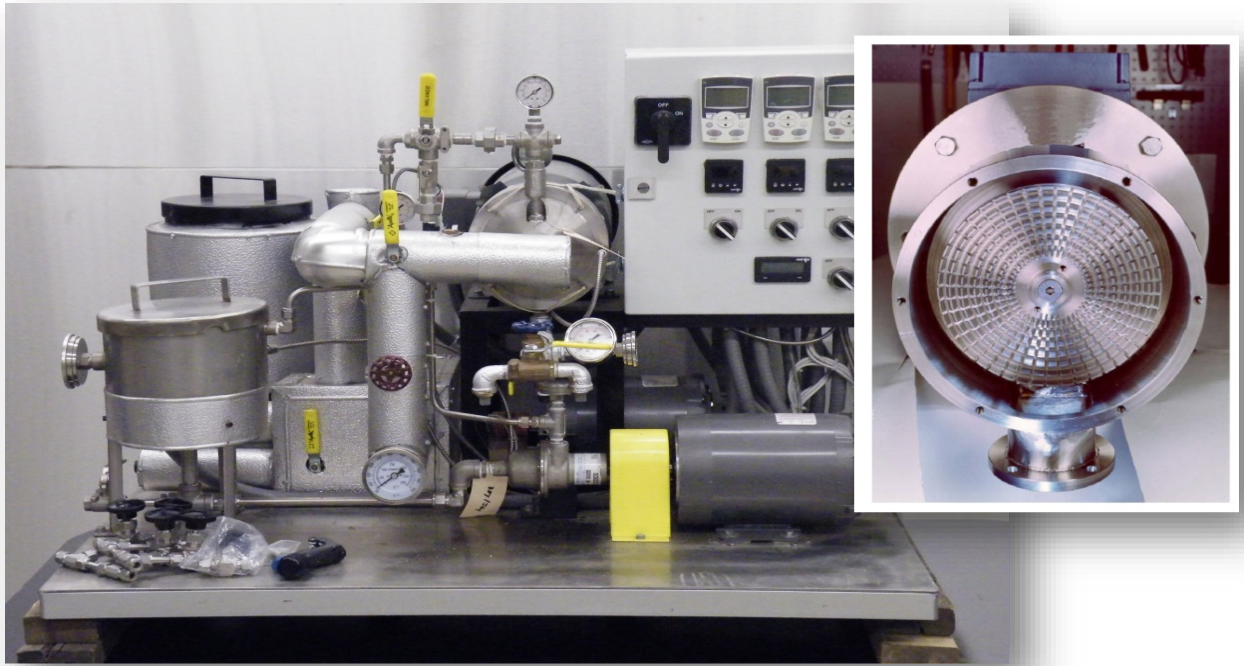
TECHNIQUES & EXPERIMENTATION

Emulsion Manufacture

- *Colloid mill*
- *Capability of rotating at 3450 RPM*
- *Provides mechanical energy to shear and disperse bitumen in aqueous phase*



TECHNIQUES & EXPERIMENTATION

Specimens

1. *Bitumen PG 58-28*
    - *Typical grade for CoE*
2. *Emulsion A (HF-100S)*
    - *Made with base PG 58-28*
3. *Emulsion B*
    - *Made with base PG 58-28*
    - *Designed to FAIL "float test"*

TECHNIQUES & EXPERIMENTATION

Emulsion Recipes

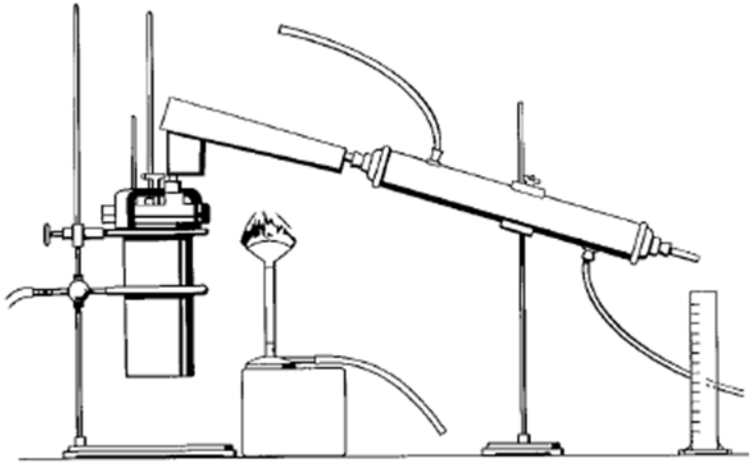
Emulsion	Base Bitumen	Bitumen (%)	CTO (%)	NaOH(s) (% by wt. CTO)	Water (%)
A	PG 58-28	62	2.2	10	35.8
B	PG 58-28	62	1.1	10	36.9

Emulsion B was specifically designed to FAIL the “float test” i.e. half the emulsifier (CTO) dosage of Emulsion A (recognized as HF-100S by industry standards).

TECHNIQUES & EXPERIMENTATION

Obtaining Residue by Distillation

- *ASTM D6997/ AASHTO T59*
- *Requires 200g of emulsion*
- *Water component distilled at 260°C over ~ 1 hour*
- *Residual testing performed on emulsions A & B (Residue A & B)*
  - *Float test, DSR*

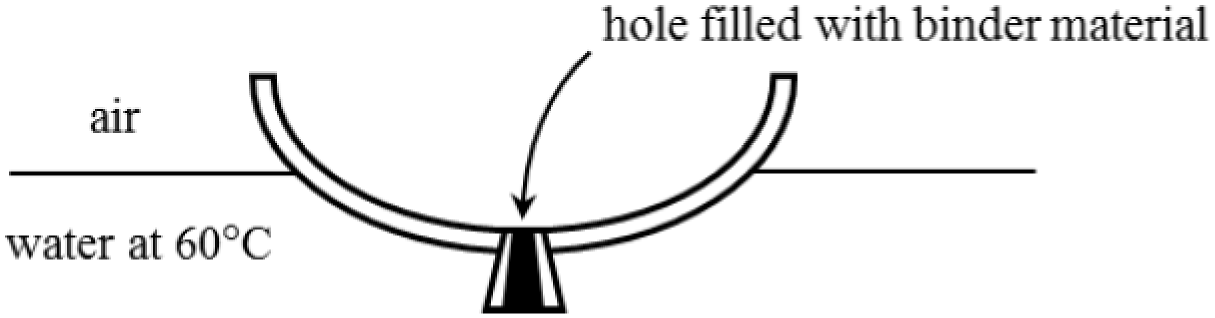


Distillation set up. This figure was taken from Asphalt Emulsions Manual Series no. 19 developed by AEMA, and Asphalt Institute.

TECHNIQUES & EXPERIMENTATION

Float Test

- *ASTM D139/ AASHTO T50*
- *Characterizes "consistency" by floating a plug of residue over a 60° C water bath*
- *Time required to float is 1200 sec*



RESULTS & INTERPRETATION

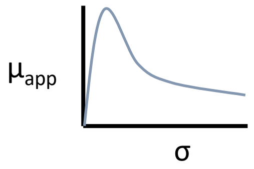
Float Test Results

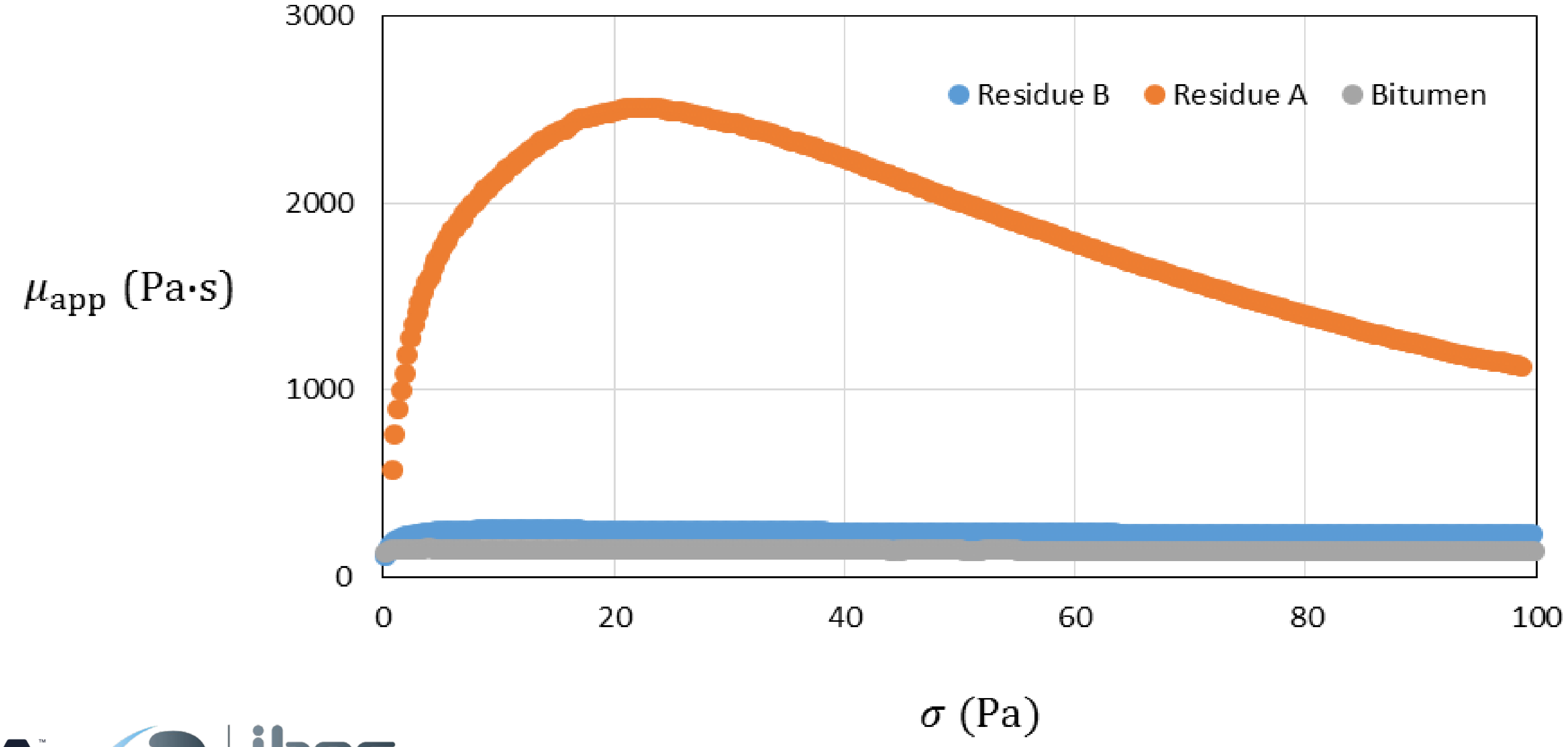
Material	Time (seconds)
PG 58-28	35
Residue A	1200+
Residue B	425

- Demonstration of the effect of emulsifier dosage (CTO)
- Residue A possess “high float” quality
    - Similar to K-V model

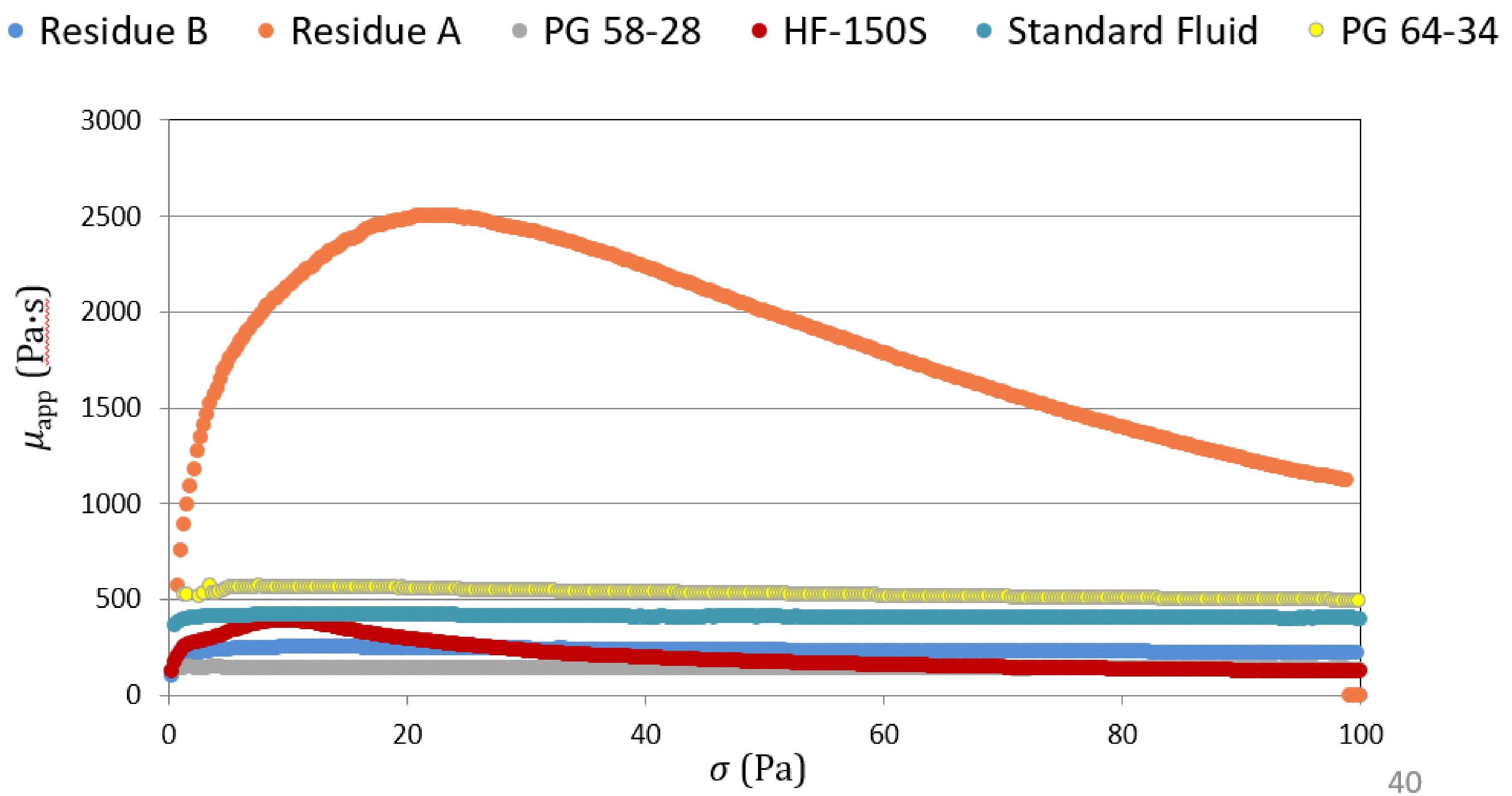
RESULTS & INTERPRETATION

DSR Test Results - Stress Ramp





RESULTS & INTERPRETATION



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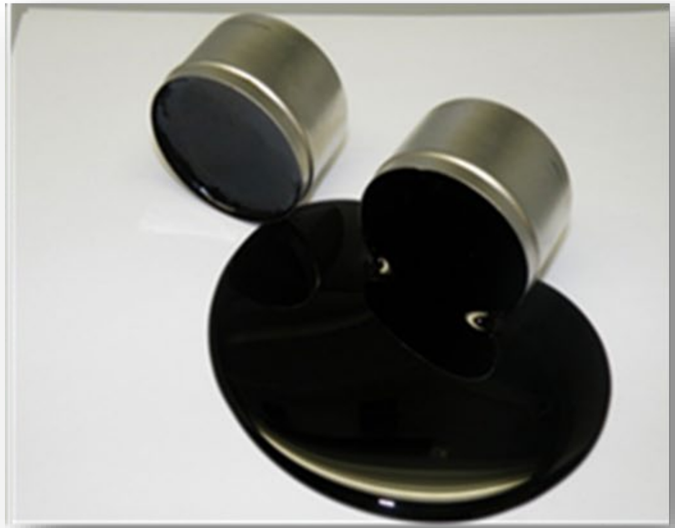
RESULTS & INTERPRETATION

Asphalt vs Mayonnaise:

Which one is “stronger” — when it comes to resisting bleeding or drainage?

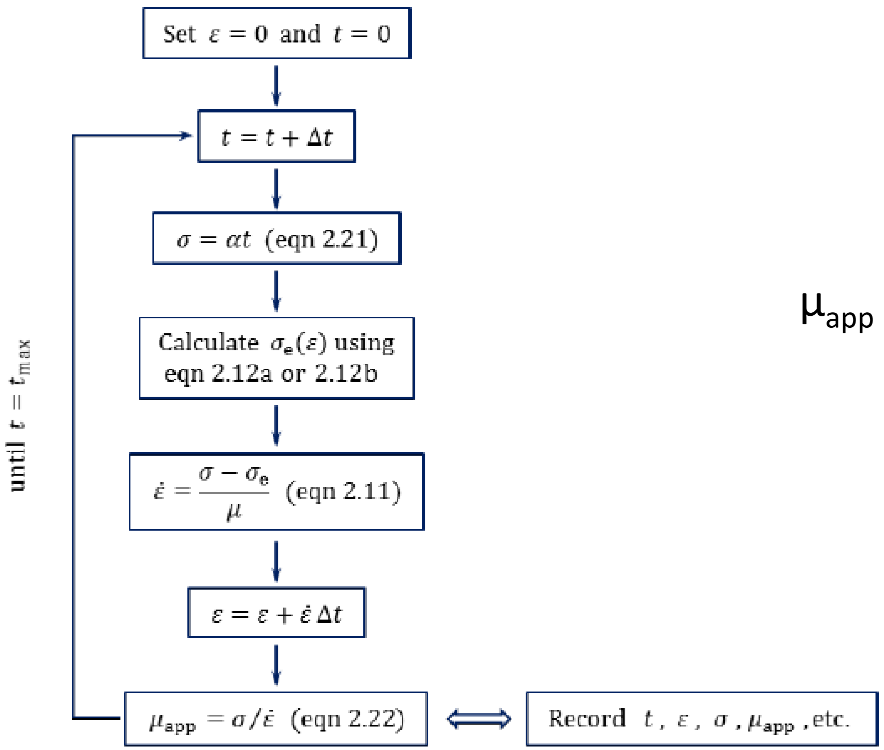


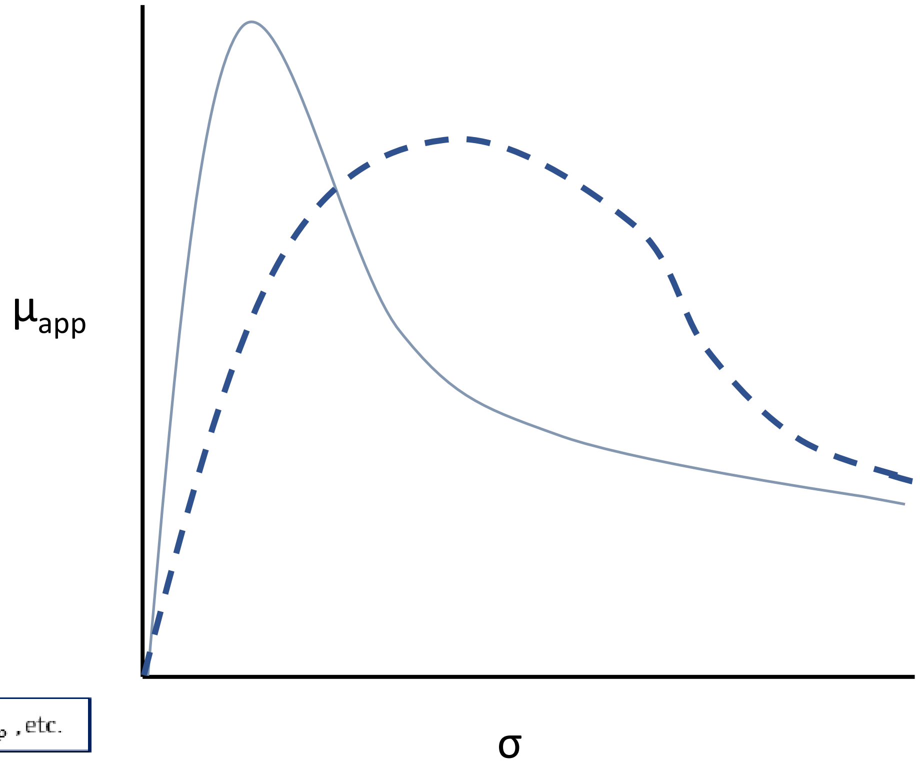
$t = 8\ \mathrm{hr}$

$t = 12\ \mathrm{hr}$

RESULTS & INTERPRETATION

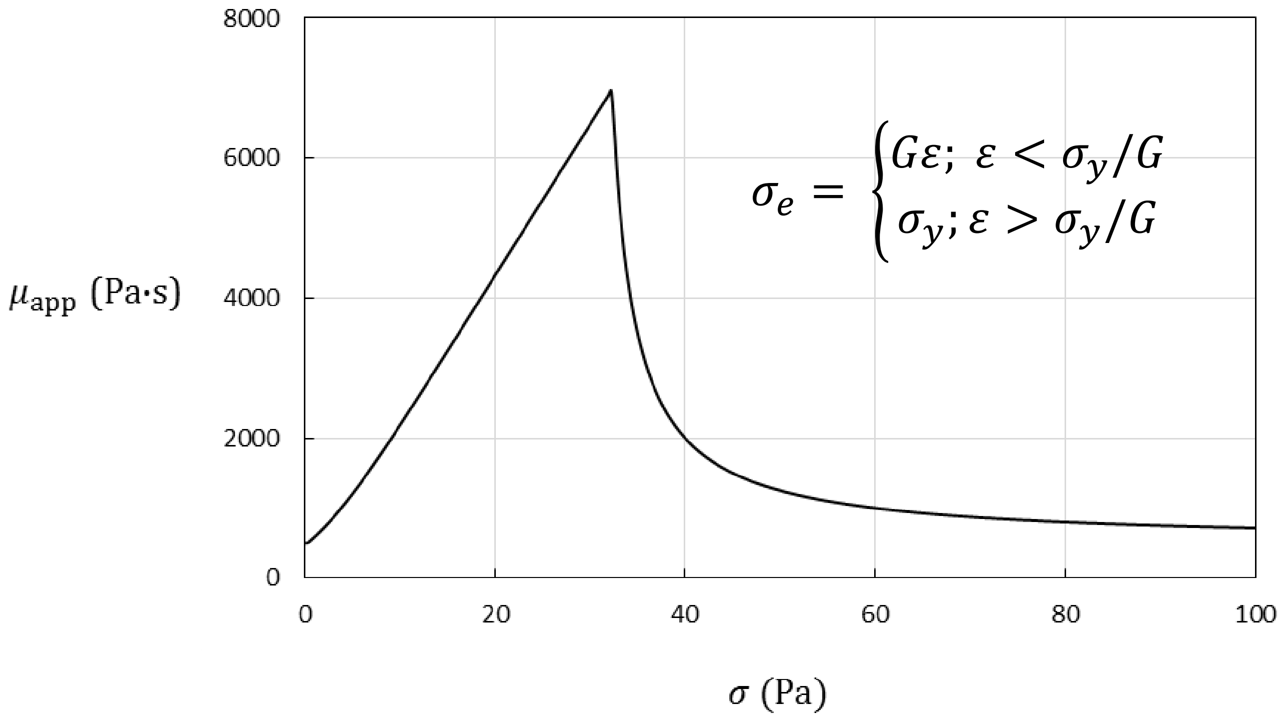
Numerical Simulation





RESULTS & INTERPRETATION

Numerical Simulation



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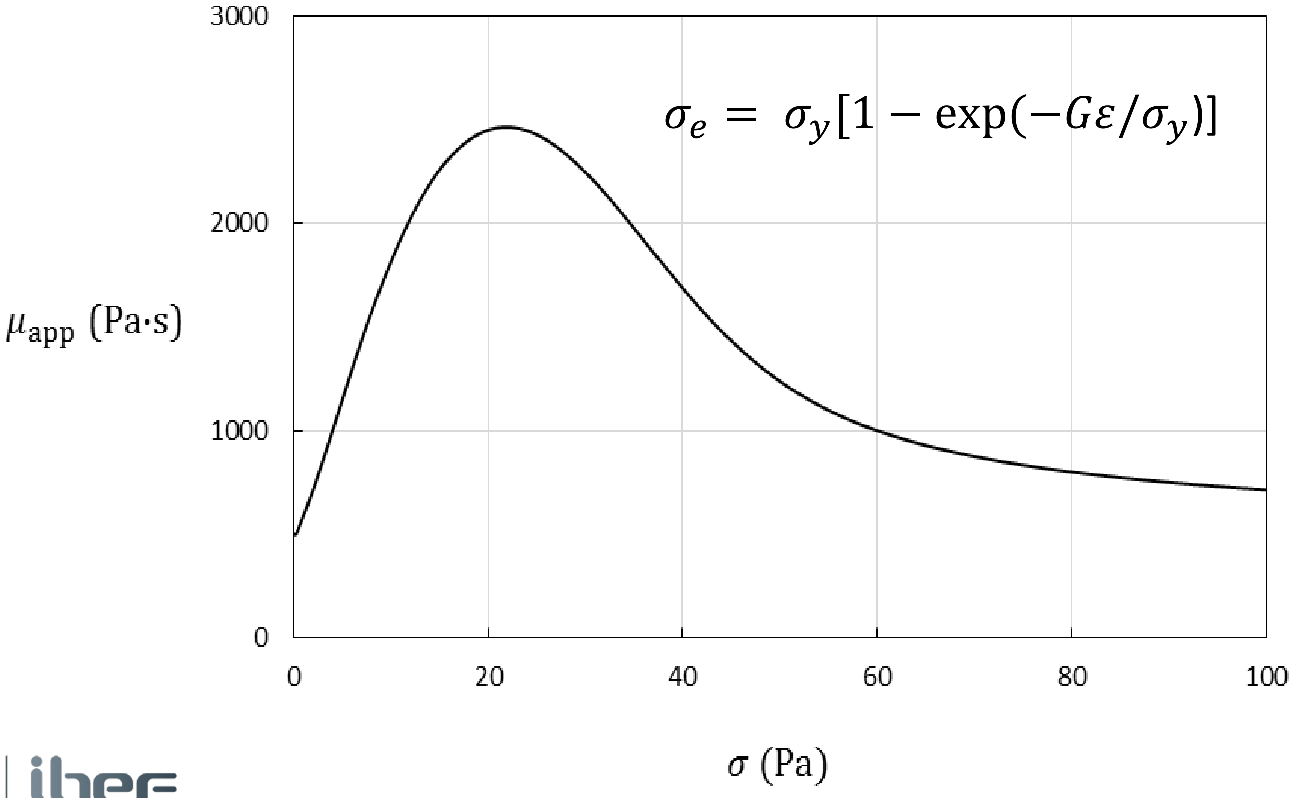
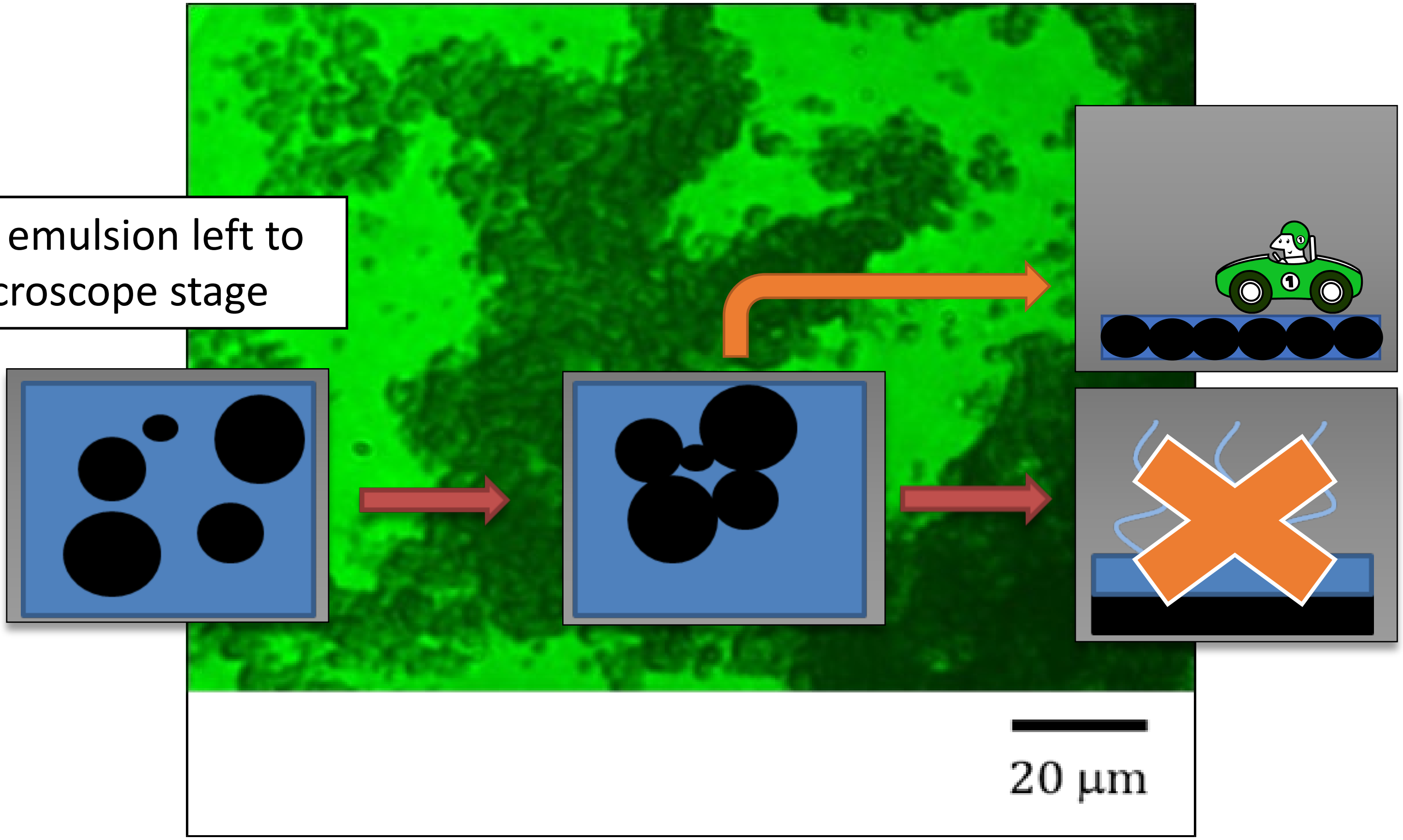
RESULTS & INTERPRETATION

Numerical Simulation



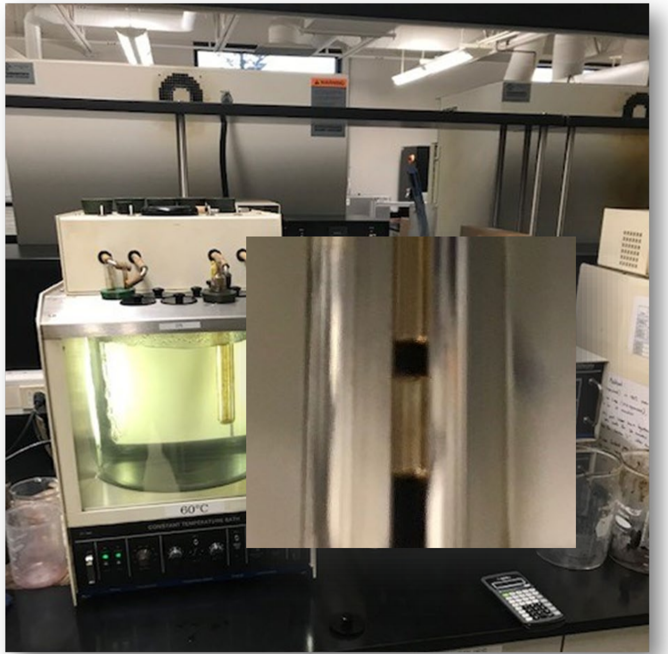
RESULTS & INTERPRETATION

High-float emulsion left to dry on microscope stage



2015 to 2021

Some time went by…



	ASTM D4957			DSR Flow Sweeps		
Product	Size of Tube	μ_{app}	$\dot{\varepsilon}$	μ_{app} @ min. $\dot{\varepsilon}$	μ_{app} @ max. $\dot{\varepsilon}$	μ_{app} @ D4957 $\dot{\varepsilon}$
HF-100S	100	191.04	1.36	229.10	163.80	198.70
HF-150P	200	587.76	0.86	206.90	171.30	184.65
HF-150S	100	103.35	2.52	117.40	87.30	92.60
HF-250S	100	46.20	5.63	39.70	36.60	34.20

Low

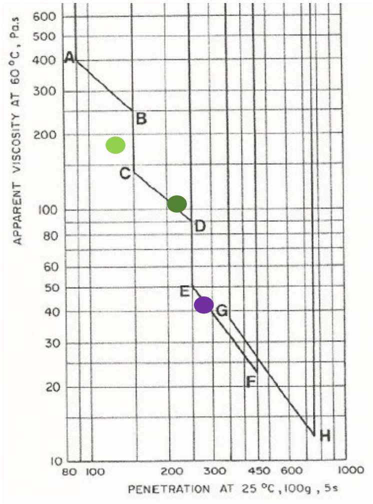
High

For a 100 modified Koppers Tube: Max shear rate is 3.2 s^{-1}; min. is 0.8 s^{-1}

For a 200 modified Koppers Tube: Max shear rate is 1.6 s^{-1}; min. is 0.4 s^{-1}

Passes, but likely due to a clog

Example of a rheogram



… started to question reliability of some our of HF residue results

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BACKGROUND (part 2)

Current HF Residue Testing in Canada

- *Float test (D139)*
  - ➢ *Resistance to flow*

- *Penetration test (D5)*
  - ➢ *Material consistency*

- *Viscosity test (D2171, D4957, Par. 6.2.5/A in CGSB Can2-16.5-M84)*
  - ➢ *Absolute and Apparent Viscosity*

All performed after Residue by Distillation ASTM D6997

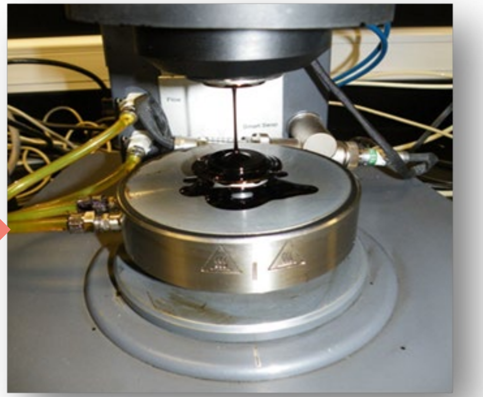
BACKGROUND (part 2)

HF Residue Characterization Using the DSR

- *Hinging on idea that the DSR can potentially measure reliable μ_{app} at various $\dot{\varepsilon}$, could we also replace the pen, and float tests by measuring viscosities below and above the yield stress?*

Penetration test

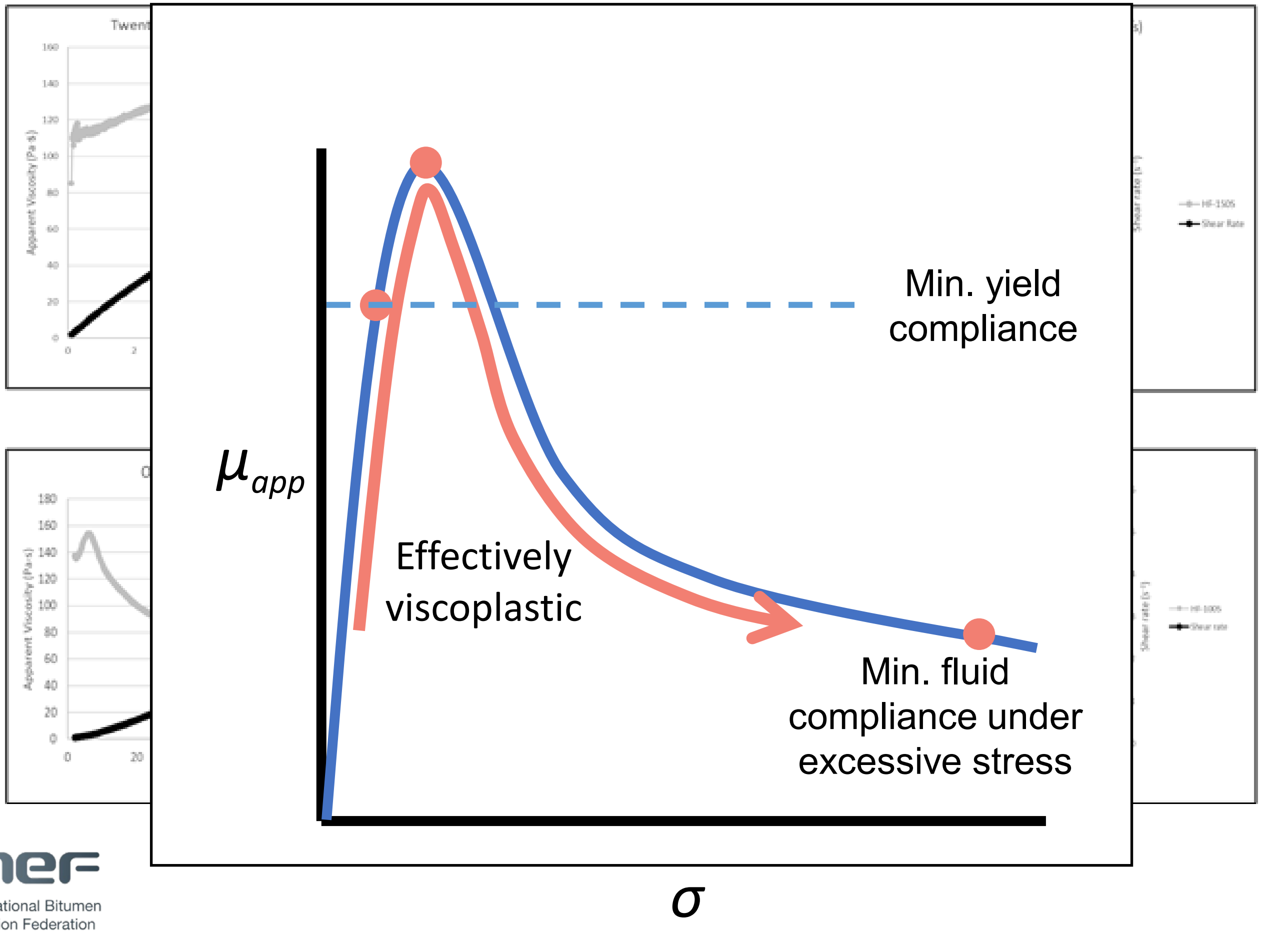
Float test



Flow sweeps on DSR

RESULTS & INTERPRETATION (part 2)

HF Residue Characterization Using the DSR



RESULTS & INTERPRETATION (part 2)

- *Key viscoplastic shear rates, $\dot{\varepsilon}$:*

➢ *Below σ_y, resistance to flow*
➢ *σ_y, maximum μ_{app}*

Metrics for HF residue susceptibility to flushing/drainage, replacing the float test

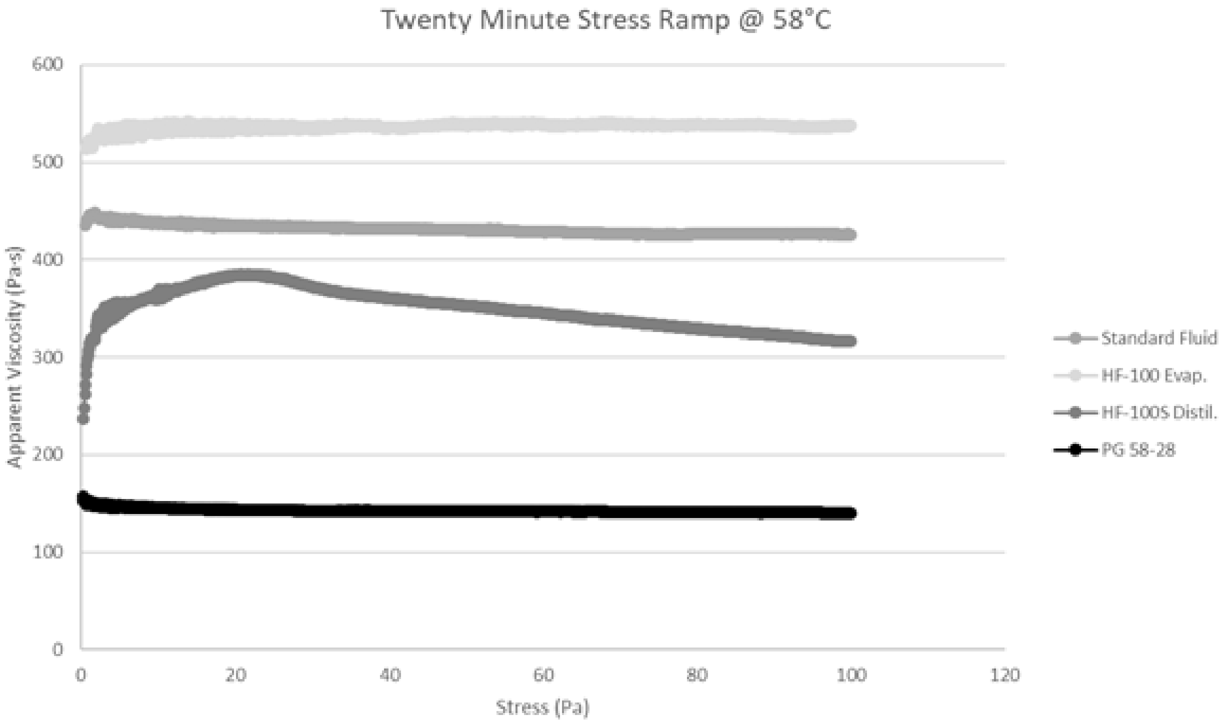
➢ *Above σ_y, steady-simple flow*

A better measurement of "consistency", replacing the pen. test

- *Shear rate considerations for measuring μ_{app} after 50 stress ramps*

➢ *HF-100S, 150S resistance to flow compliance, $\dot{\varepsilon} < 0.1\ s^{-1}$*
➢ *HF-250S resistance to flow compliance, $\dot{\varepsilon} < 0.05\ s^{-1}$*
➢ *Simple-fluid behavior for all HFs, $\dot{\varepsilon} > 1.0\ s^{-1}$*

RESULTS & INTERPRETATION (part 2)



Only considered Residue by Distillation, what about Residue by Evapouration?

- *High viscosity*
- *No yielding*
- *Behaves like a fluid*

RESULTS & INTERPRETATION (part 2)

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SUMMARY

- *Demonstrated that Residue A has different physical properties from original PG 58-28 bitumen*
- *High float residue possesses a yield stress*
- *Developed a new hybrid rheological model for high float residue*
- *Propose an alternative protocol to the Float Test (ASTM D139)*

SUMMARY (part 2)

- *Current HF residue testing is inadequate, and not equally understood*
- *It is still important to measure the apparent viscosity of an HF residue well beyond its yield*
    - Flow curve or stress ramp measurements could replace the current *vacuum capillary viscosity methods*

- *Evaporated specimens behave more like a viscous fluid and not like a viscoplastic fluid unless residue is NOT sieved*

IN THE FUTURE

- *Gather more data of varying HF grades to determine proper ramp rates and corresponding shear rates*

- *Look at alternative recovery techniques to adequately emanate field conditions*

- *Discuss with stakeholders about continuing our research to progress to more scientific, robust, performance-based testing*

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THANK YOU

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