EFEITO DA PRESENÇA DE ETANOL NA LUBRIFICAÇÃO DE MOTORES COM UTILIZAÇÃO FLEXÍVEL DE COMBUSTÍVEIS ("FLEX-FUEL")

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Outline

- Motivation and objectives
- Lubrication of automotive engines
- Effects of ethanol on EHD film thickness and friction
  - Methodology
  - Example result
- Effects of ethanol on formation and stability of tribofilms
  - Methodology
  - Example result
- Interaction of ethanol with friction modifiers
  - Methodology
  - Example result
- Concluding remarks

Motivation - Brazil

- Brazil: Flex-fuel engines (2000´s)

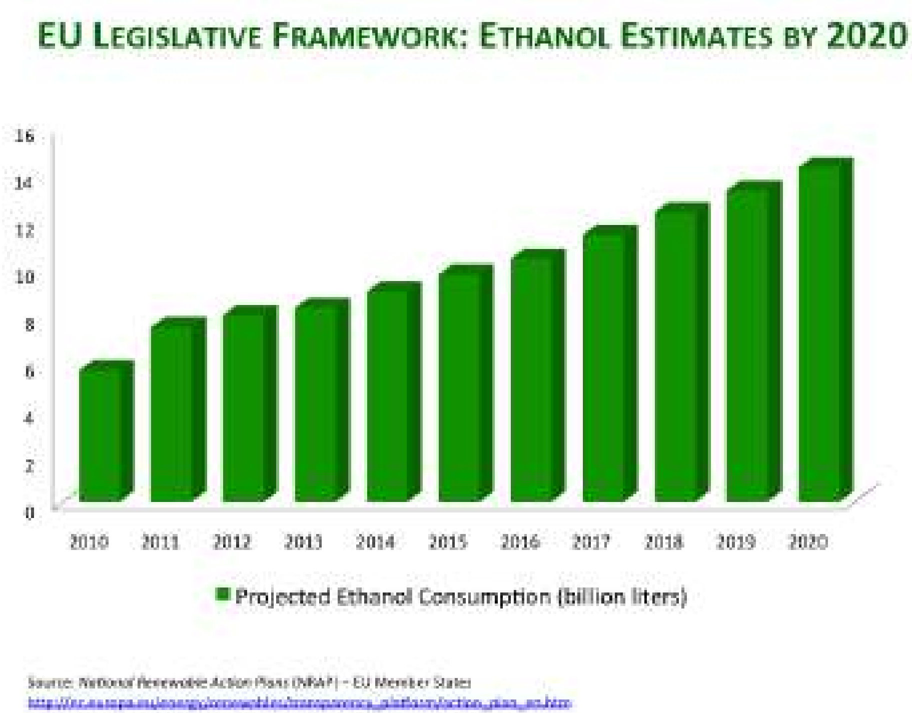
- Electronic system monitors the lambda probe signal
- Composition of the exhaust gases
- Identify fuel

- Anfavea: 85.7% in 2014
- 50% of combustibles in automobiles is renewable
- use of fuel hydrated ethanol in Brazil increased by 60%

Motivation - USA

- 13.5 billion US gallons of ethanol produced in US in 2010 (more than twice from Brazil)
- Ethanol was 10% of gasoline supply in 2011
- 11 million vehicles with bi-fuel engines using 85% ethanol in gasoline (E85) in 2013
- Most vehicles use 10-15% ethanol (E10)
- Energy Independence and Security Act of 2007 requires 36 billion US gallons of renewable fuel use by 2022
- Anhydrous ethanol (no water) since water not soluble in gasoline

Motivation - Europe



- Most current gasoline contains 5% ethanol
- So about 4% of current gasoline used is actually ethanol
- Currently imported or made mainly from sugar beet, wheat and corn
- Strong programs is some countries (Sweden, Belgium)
- Much research to produce ethanol from non-food sources (cellulose)

Motivation –tribological challenges

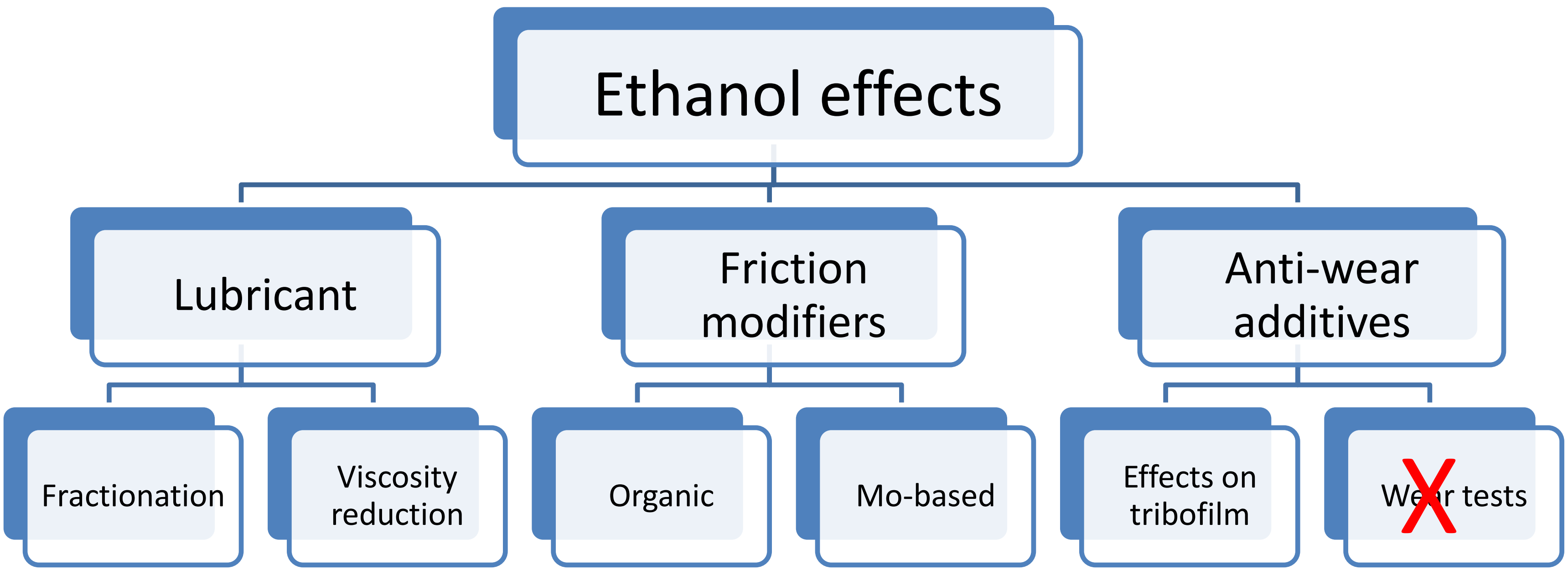
- Ethanol can accumulate in the lubricant (less volatile than gasoline/diesel)
- Especially in urban driving: can reach 5-10% wt.
- Reduction in viscosity?
- Corrosion?
- Wear?

- Interaction of ethanol with the base fluid?
- Interaction of ethanol with friction modifiers?
- Interaction of ethanol with detergents?
- Interaction of ethanol with antiwear additives?

Main goal:

-Help to understand severe wear commonly observed in flex-fuel engines

Specific goals:



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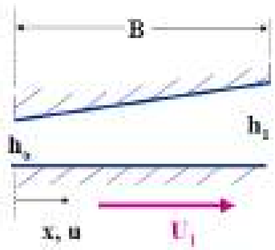
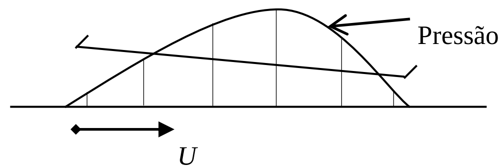
Lubrication of automotive engines

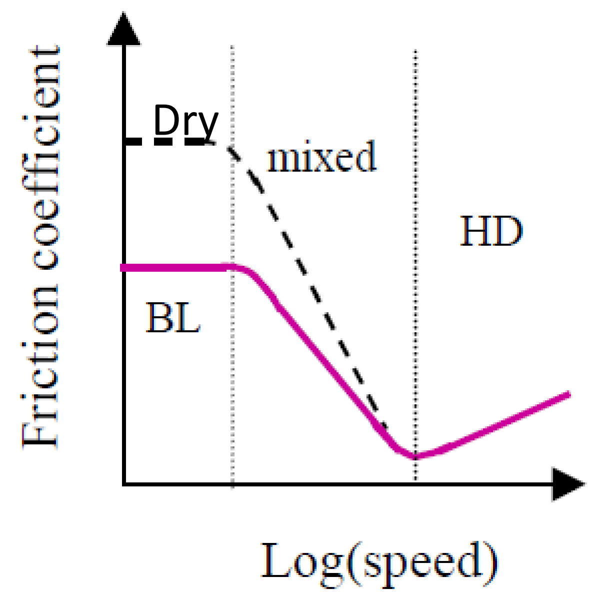
- Stribeck curves

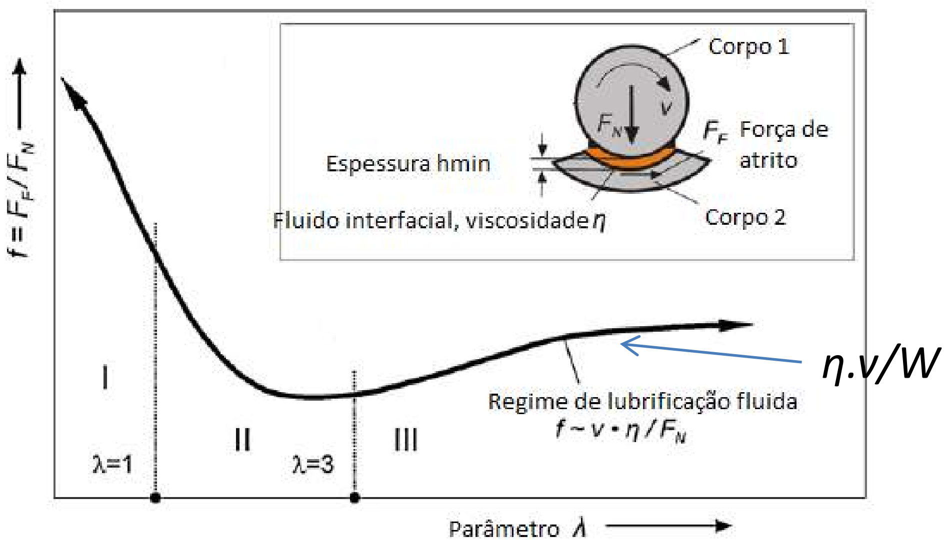




$$\frac{dp}{dx} = -6\eta U\left(\frac{h-h^*}{h^3}\right)$$

Effect of boundary films:





Lubrication of automotive engines

-Óleo base (95%)
-Aditivos (5%)

Minerais x sintéticos

25 a 45 átomos de C / molécula

- Grupo I
- Grupo II
- Grupo III?

- Grupo IV
- Grupo V

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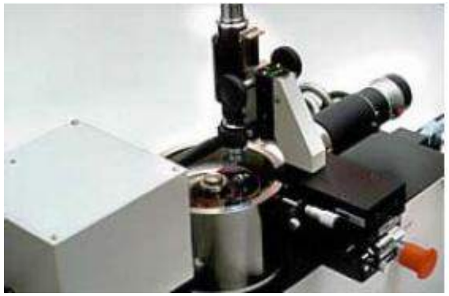
Lubrication of automotive engines

Categorias de óleos base automotivos (API)

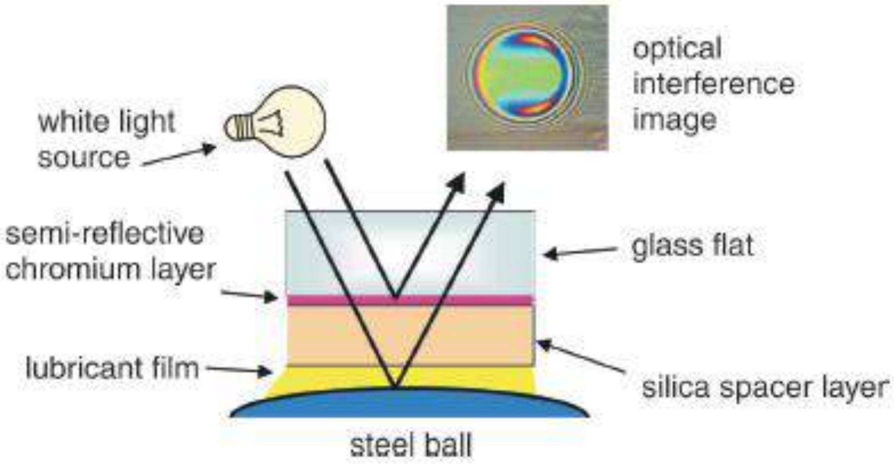
Grupo I	**% saturados < 90** **e/ou % S > 0.05%** **80 < VI < 120**
Grupo II	% saturados > 90 e %S < 0.03 80 < VI < 120
Grupo III	% saturados > 90 e %S < 0.03 e VI > 120
Grupo IV	Polialfaolefinos (PAOs)
Grupo V	Todos os demais

Effects of ethanol on EHD film thickness and friction

PCS Instruments, EHD2



Lubricant film thickness measurements

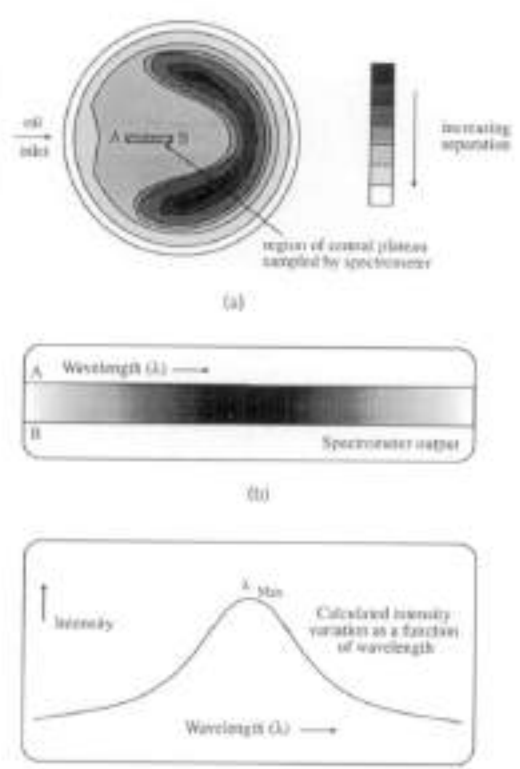


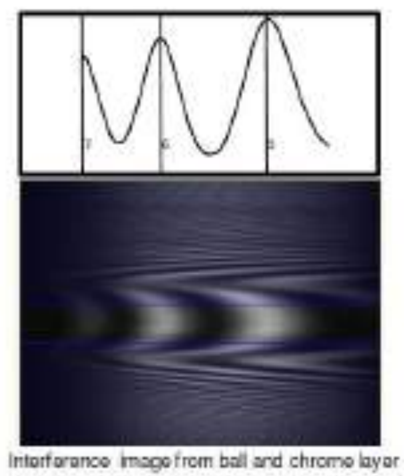
$$n_{oil}h_{oil} + n_{sp}h_{sp} = \frac{\left(N + \frac{1}{2} - \phi\right)\lambda}{2\ \mathrm{Cos}\ \theta} \qquad N = 0,1,2,$$

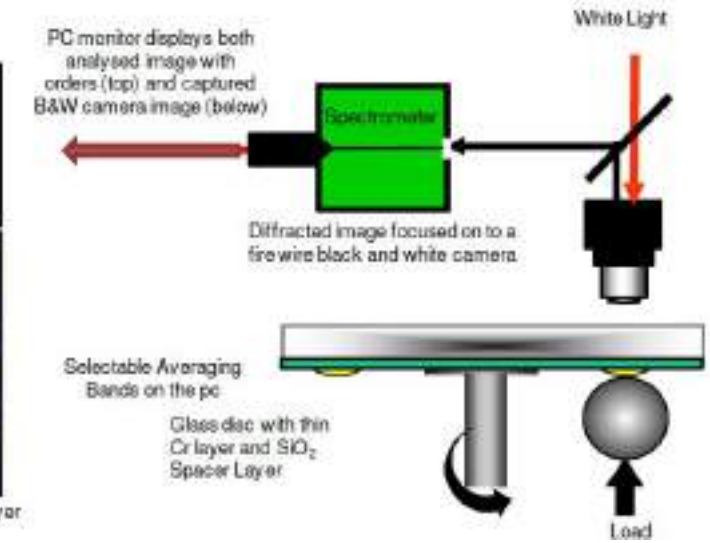
G. J. Johnston , R. Wayte & H. A. Spikes (1991): The Measurement and Study of Very Thin Lubricant Films in Concentrated Contacts, Tribology Transactions, 34:2, 187-194

Effects of ethanol on EHD film thickness and friction

Lubricant film thickness measurements







- Range: 1 to 500 nm
- Resolution: 1 nm

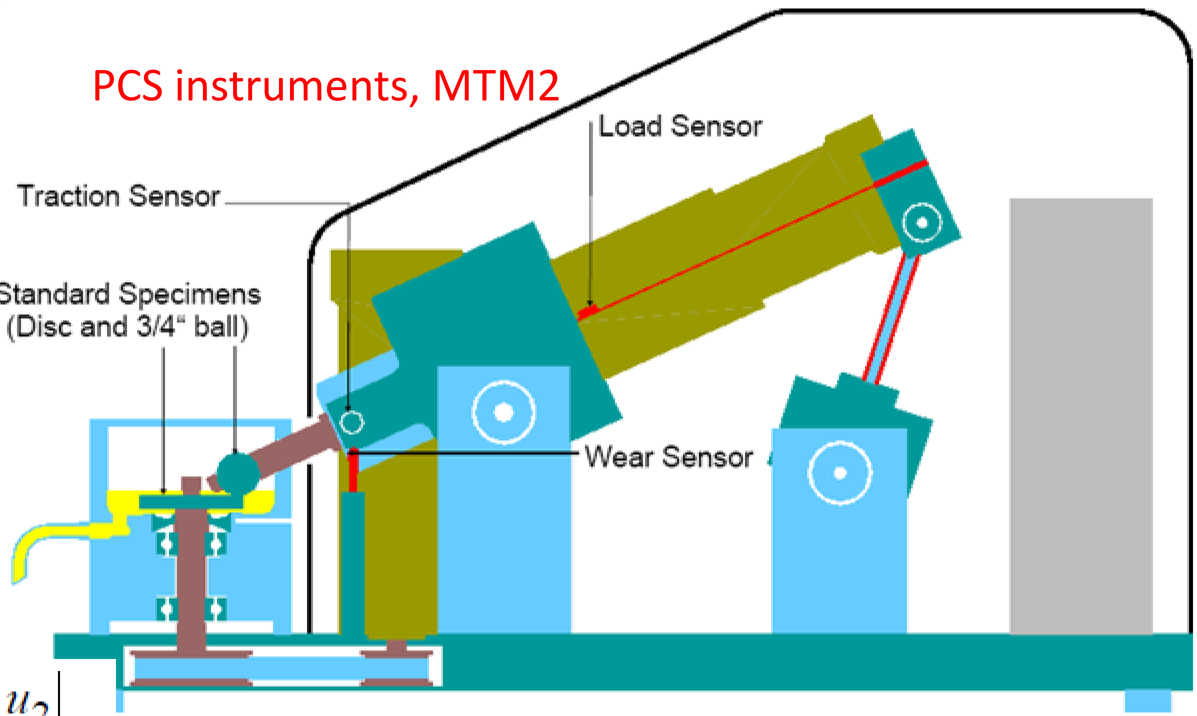
G. J. Johnston , R. Wayte & H. A. Spikes (1991): The Measurement and Study of Very Thin Lubricant Films in Concentrated Contacts, Tribology Transactions, 34:2, 187-194

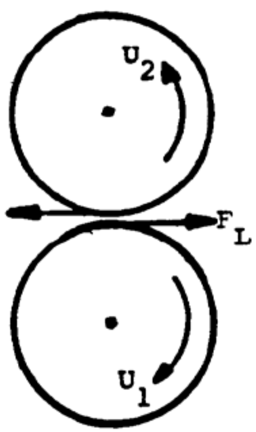
Effects of ethanol on EHD film thickness and friction

Friction mesurements: Stribeck curves

Mini-Traction Machine (MTM)

PCS instruments, MTM2





$$SRR = \frac{\Delta u}{U} = \frac{|u_1 - u_2|}{(u_1 + u_2)/2}$$

http://www.pcs-instruments.com/mtm/mtm.shtml#page=page-1

Effects of ethanol on EHD film thickness and friction

Materials

Base oil Group I

Formulated oil Group I (without friction modifiers)

Metal	Formulated oil SL B	
	Spectroil	X Ray
Ca	1630	1831
Mo	1	<1
Na	1	
P	720	786
Pb	1	<10
S		4300
Zn	987	954

Effects of ethanol on EHD film thickness and friction

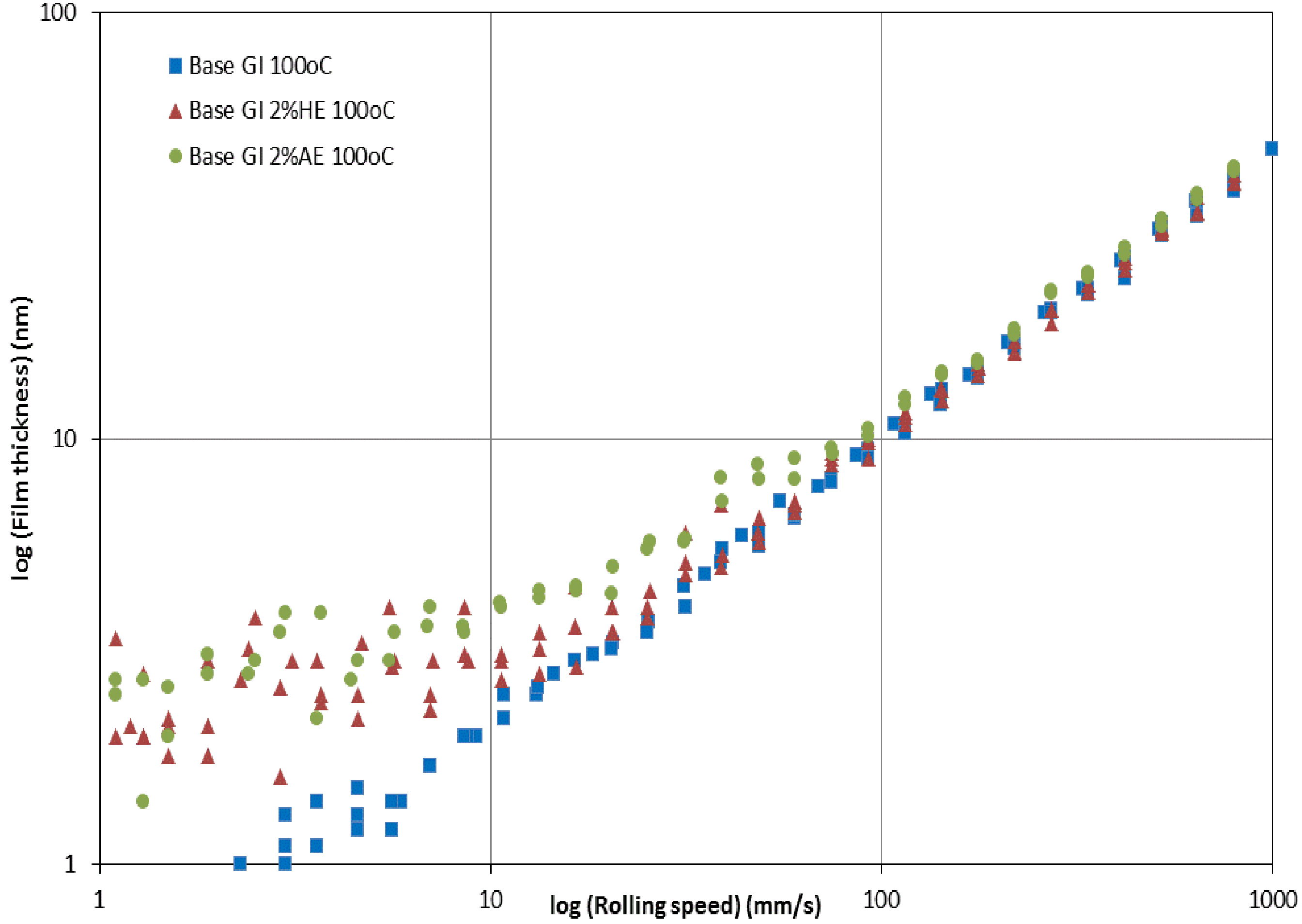
Lubricant film thickness measurements

- Viscosities and densities: SVM3000 Stabinger viscometer (40°C, 70°C and 100°C)

Oil	ρ at 15°C (g/cm³)	η at 40°C (mm²/s)	η at 70°C (mm²/s)	η at 100°C (mm²/s)	VI
Base	0.874	28.698	10.515	5.092	104.8
Base+2% AE	0.871	23.773	8.7069	N.M.	N.M.
Base+2% HE	0.873	27.218	9.6789	N.M.	N.M.
Base ZDDP	0.877	30.545	10.758	5.254	102.6
Base ZDDP 5%HE	0.873	25.999	8.440	N.M.	N.M.
Base ZDDP 5%AE	0.871	20.860	7.620	N.M.	N.M.
SLB	0.8701	97.16	30.809	13.621	141
SLB+5% HE	0.866	89.237	24.803	N.M.	N.M.
SLB+5%AE	0.865	70.259	20.732	N.M.	N.M.

Effects of ethanol on EHD film thickness

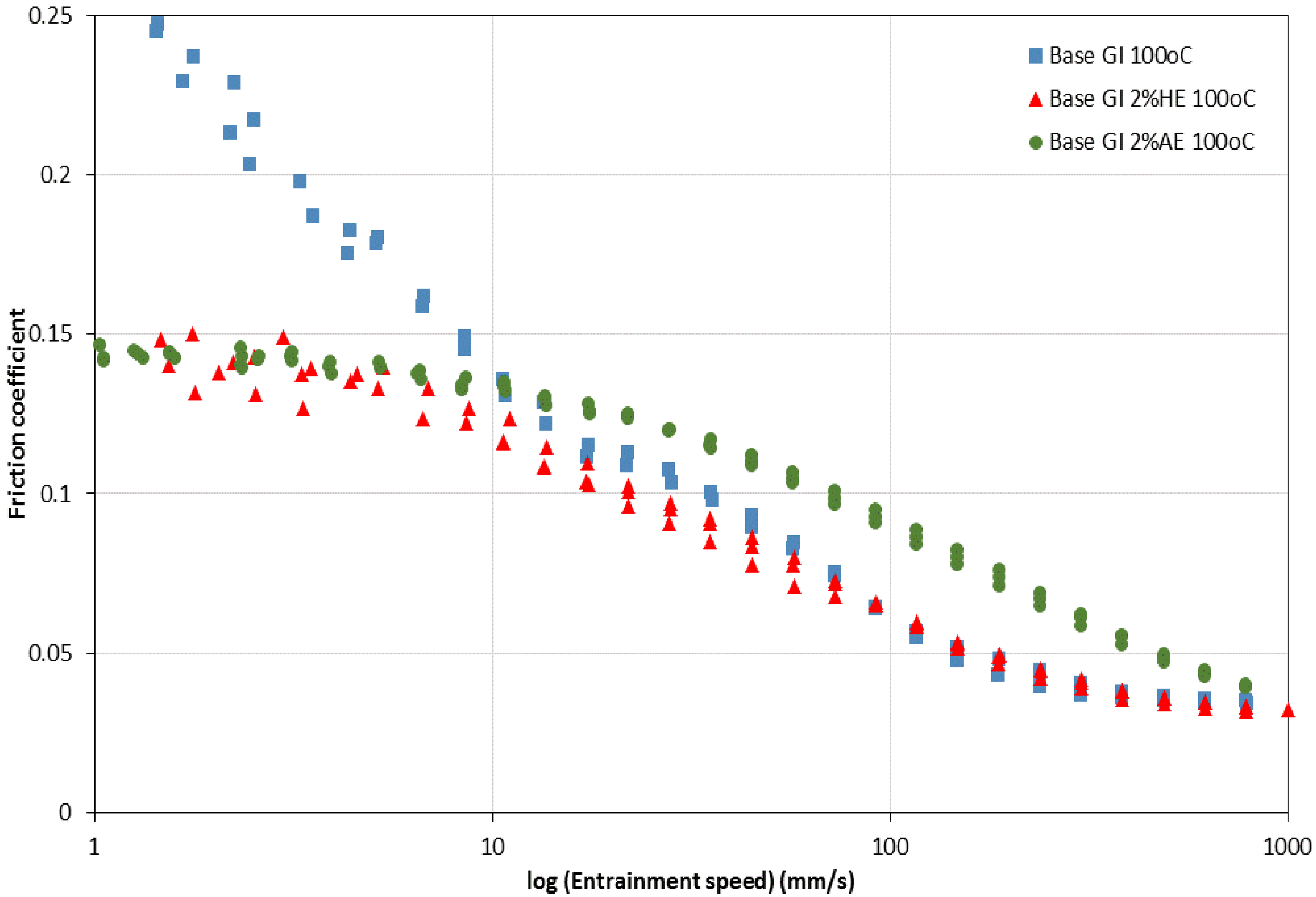
Example result



Base oil, 100°C

Effects of ethanol on friction (Stribeck curves)

Example result

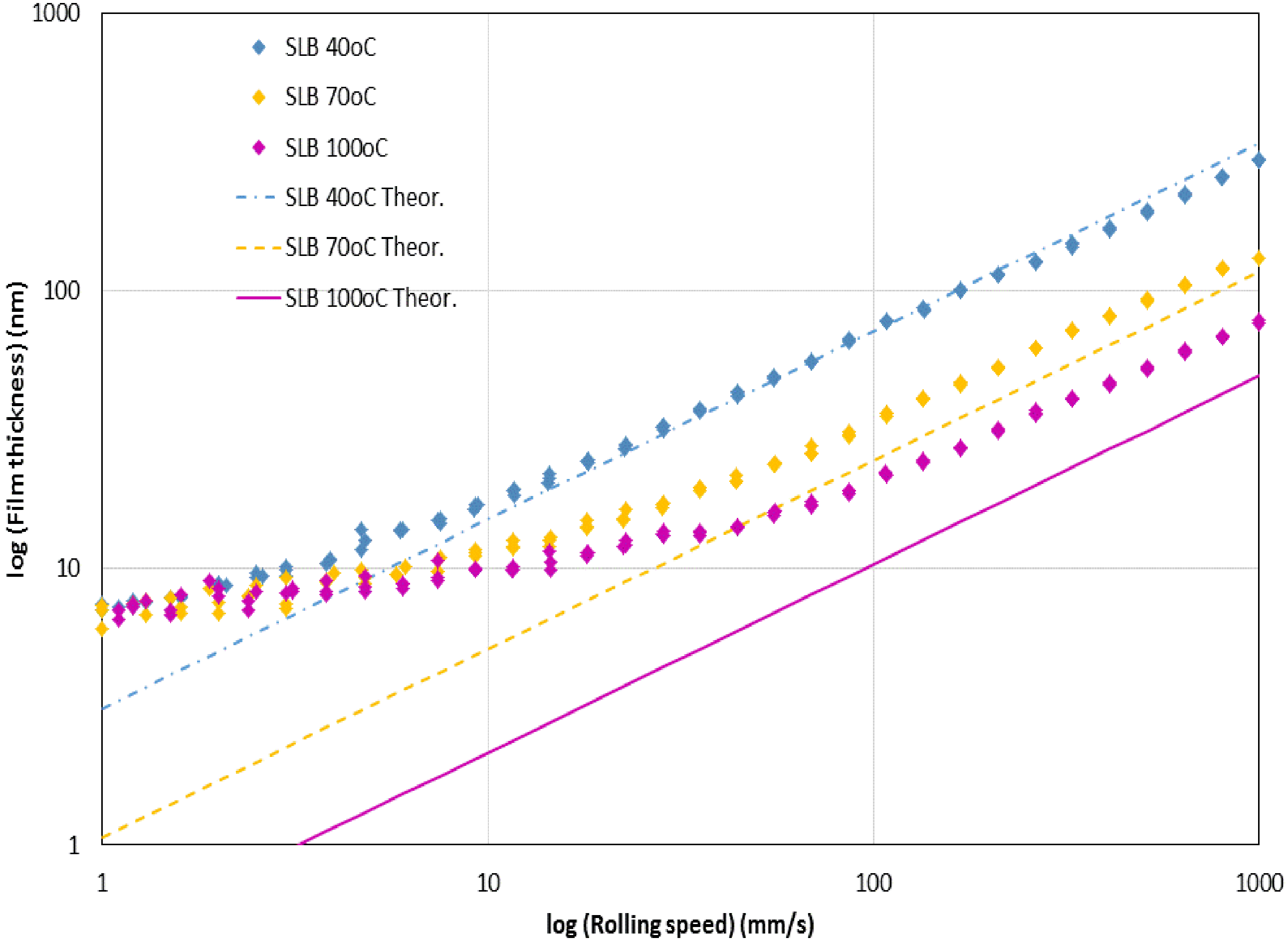


Base oil, 100°C

Effects of ethanol on EHD film thickness

Example result

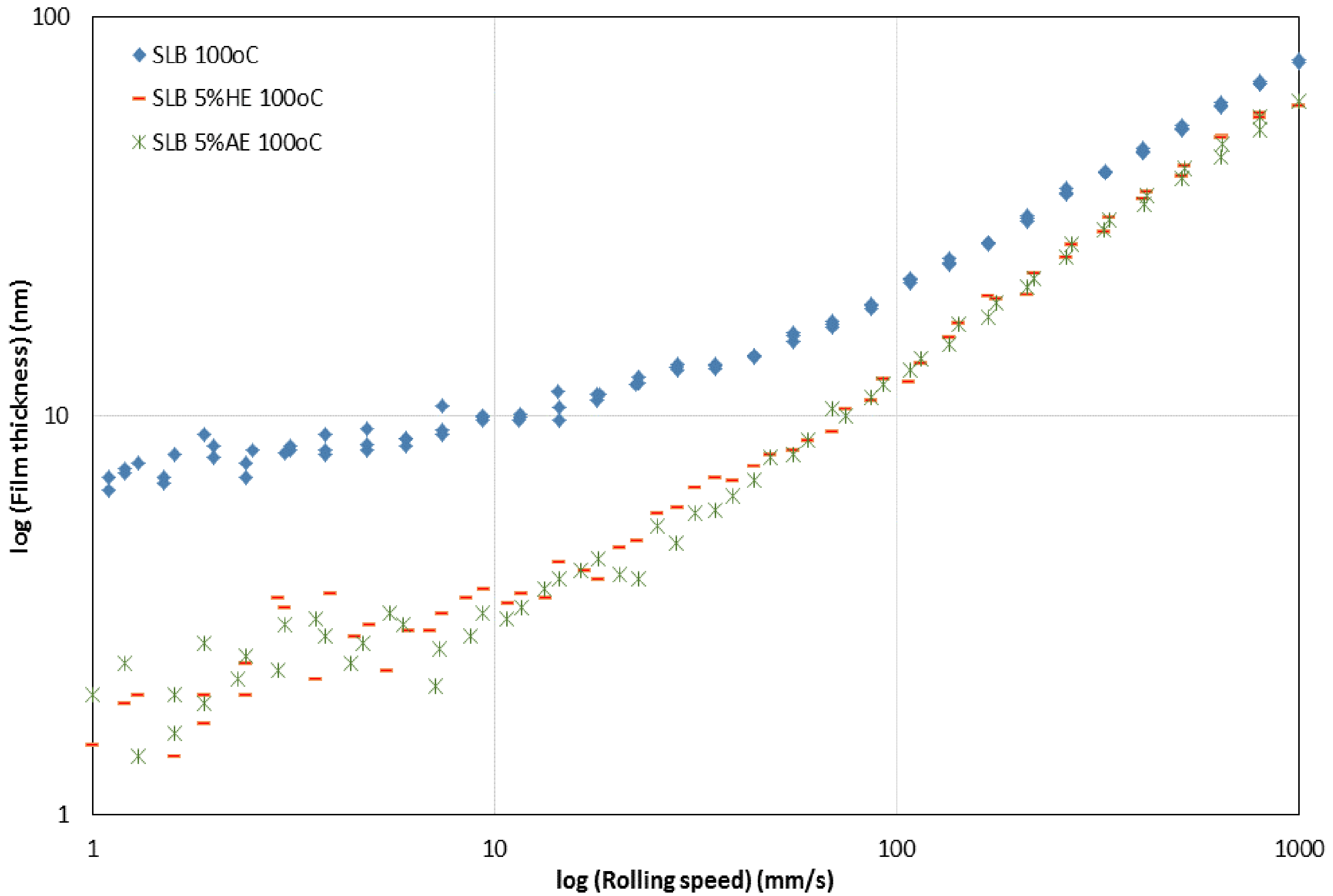
Formulated oil



Effects of ethanol on EHD film thickness

Example result

Effects of ethanol, 100°C

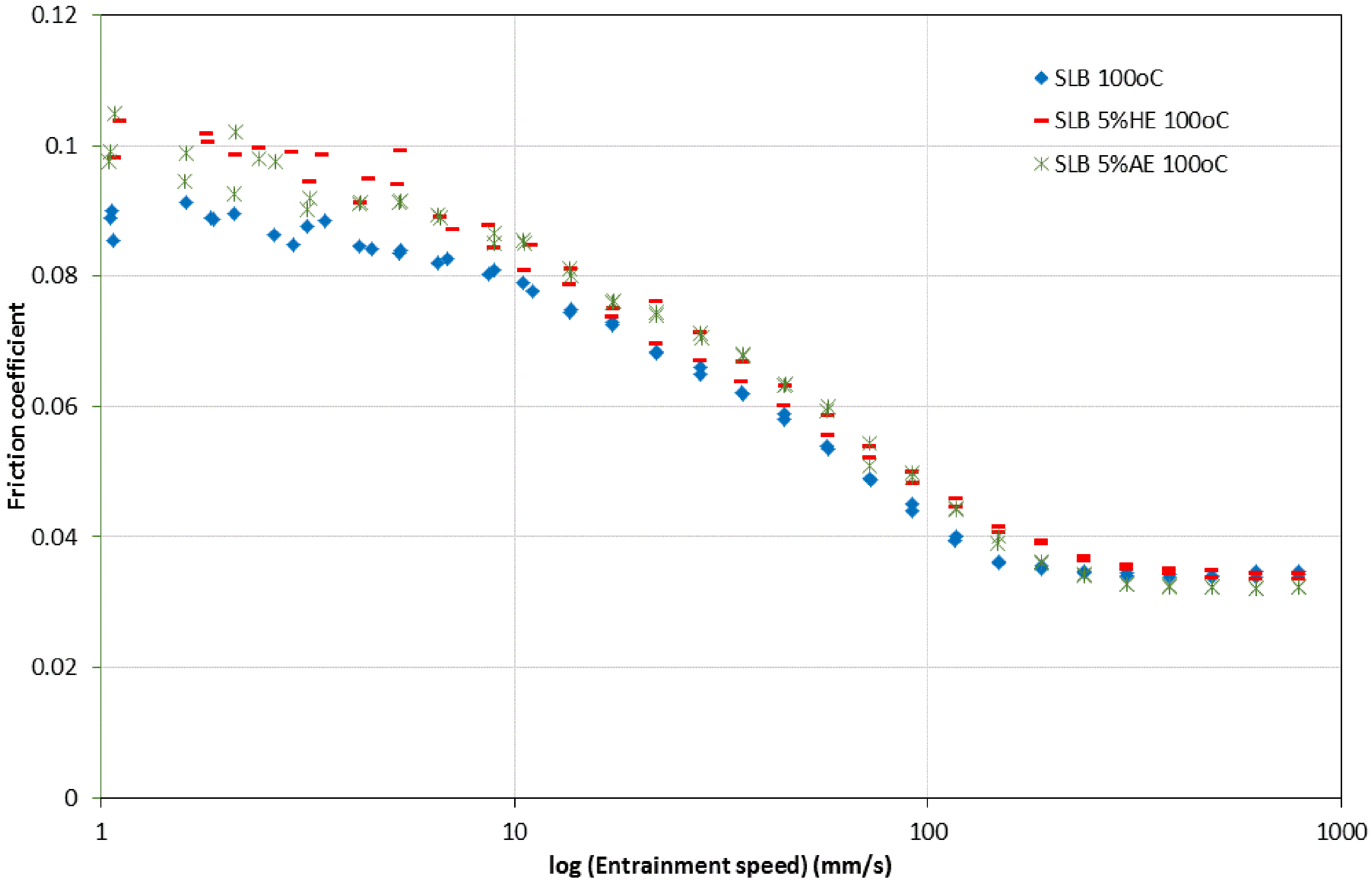


Formulated oil

Effects of ethanol on friction (Stribeck curves)

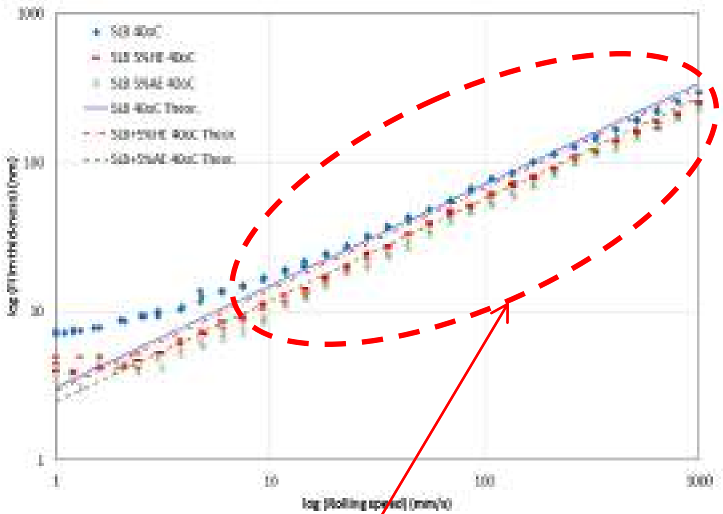
Example result

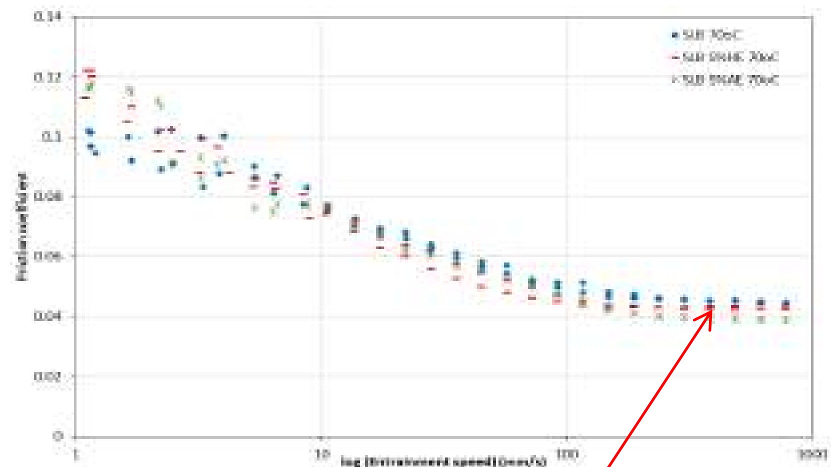
Formulated oil, 100ºC



Effects of ethanol on EHD film thickness and friction

Discussion: Mixed / Full film lubrication (base oil and formulated oil)





η PURE ETHANOL > η_{WATER}?
Hypothesis: water + ethanol → true solubility ↓
Ethanol: microemulsion
↓ influence on viscosity

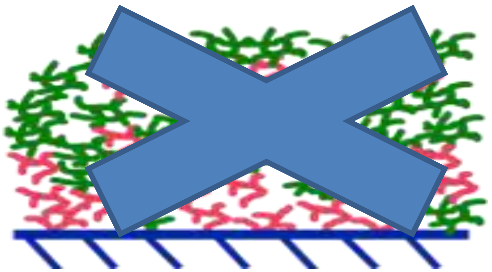
- friction levelling out at a relatively low value (μ_L)
- depends only on molecular structure of lubricant and its free volume

$\mu_{L\ AE} < \mu_{L\ HE}$

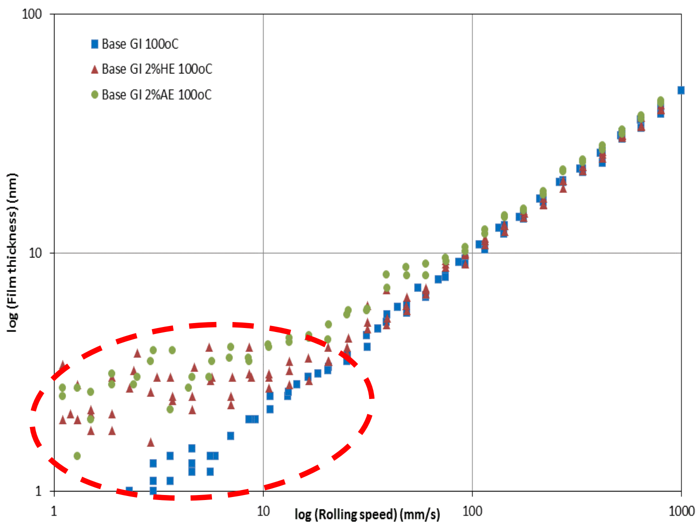
Effects of ethanol on EHD film thickness and friction

Discussion: Boundary lubrication (base oil)

Hypothesis:
Fractionation of ethanol



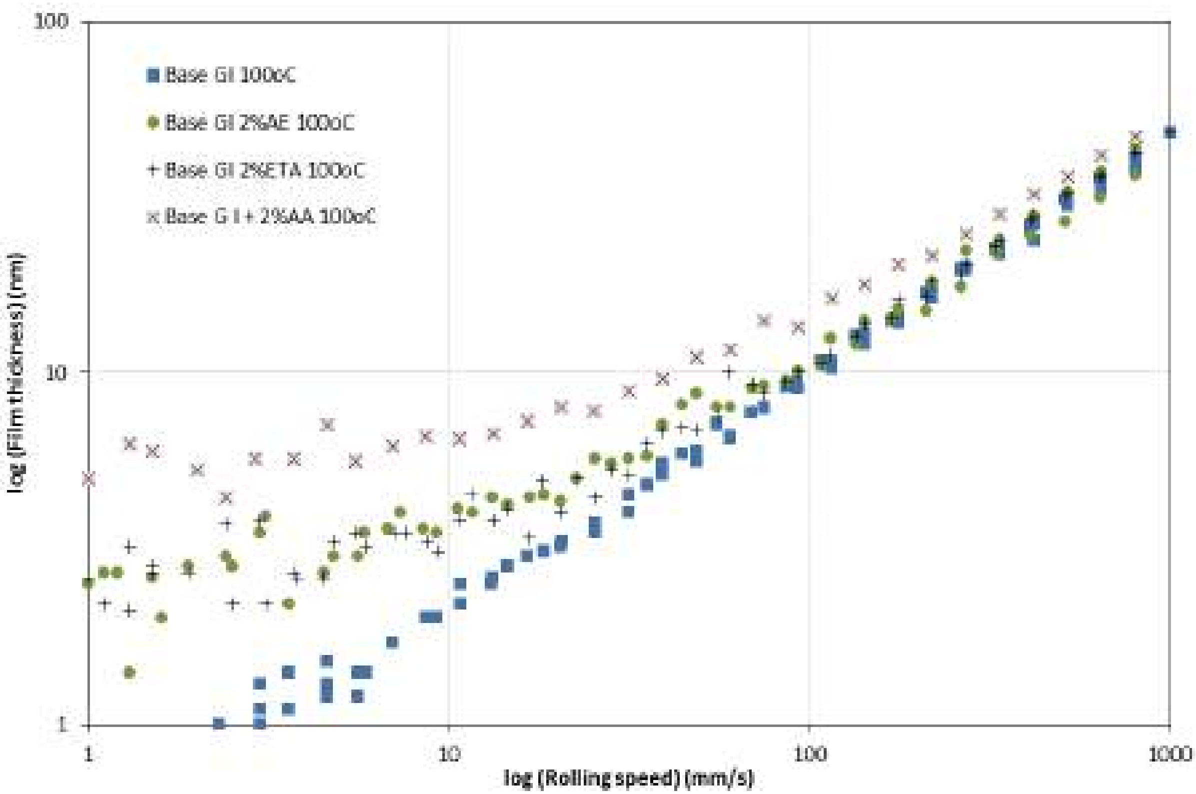
Guangteng, G. and Spikes, H. A. (1997), "The control of friction by molecular fractionation of base fluid mixtures at metal surfaces," Tribol T 40, 3, pp. 461-469.



- $\eta_{ETHANOL} < \eta_{OIL}$
- Boundary film in the presence of ethanol should be thinner!!!

Effects of ethanol on EHD film thickness and friction

Discussion: Boundary lubrication (base oil)



- Ethanal: 1st oxidation product
- Acetic acid: 2nd

- consecutive tests using same ball, disk and lubricant
- → film thickness ↑ continuously
- ball severely oxidized

Effects of ethanol on EHD film thickness and friction

Discussion: Boundary lubrication (Formulated oil)

- Absence of ethanol:
  - boundary, *ca* 9 nm, all temperatures
  - Solid-like: ↑film even at high speeds
  - Produced mechanically (adhesion and accumulation of overbased detergent particles)
  - Probably calcium carbonate

Topolovec-Miklozic, K., Forbus, T. R. and Spikes, H. A. (2008), "The film-forming and friction properties of overbased calcium sulphonate detergents," Trib. Letters 29, pp. 33-44.

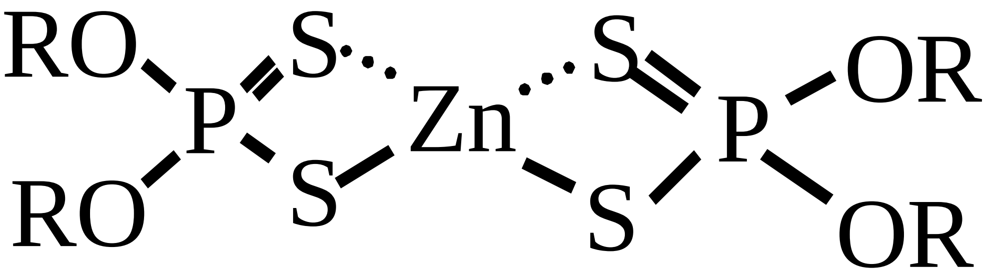
- Presence of ethanol:
  - Thinner boundary films
  - Higher friction in boundary regions
  - Prevents formation of thick, rough surface films.

Effects of ethanol on ZDDP tribofilms

Zinc dialkyldithiophosphate

ZnDTP **ZDP**

ZnDDP **ZDDP** **ZDTP**



- Aditivo anti-desgaste
- Anti-oxidante
- Inibidor de corrosão

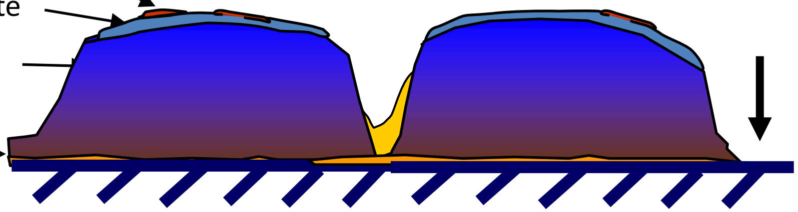
Effects of ethanol on ZDDP tribofilms

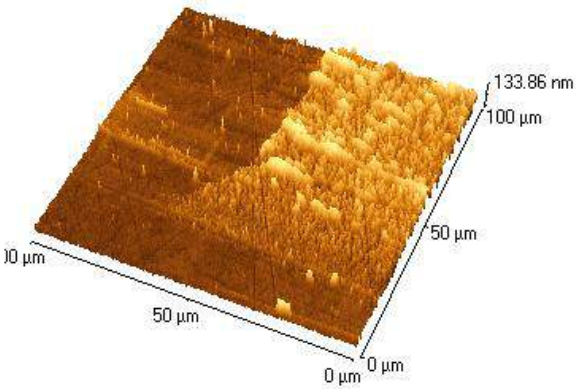
ZDDP tribofilms

Surface analysis

- Radiotracers
- IR
- XRF
- XPS
- AES
- SIMS
- EDAX,
- ECR
- EXAFS
- EELS
- TOF-SIMS
- STEM
- XANES
- XPEEM
- Mossbauer
- AFM
- FIBS

- Nature of tribofilm now reasonably well understood

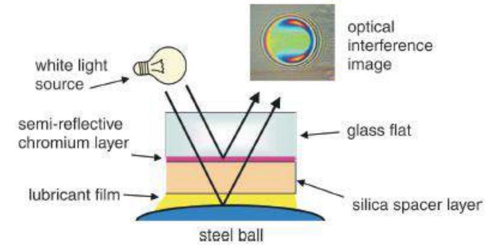




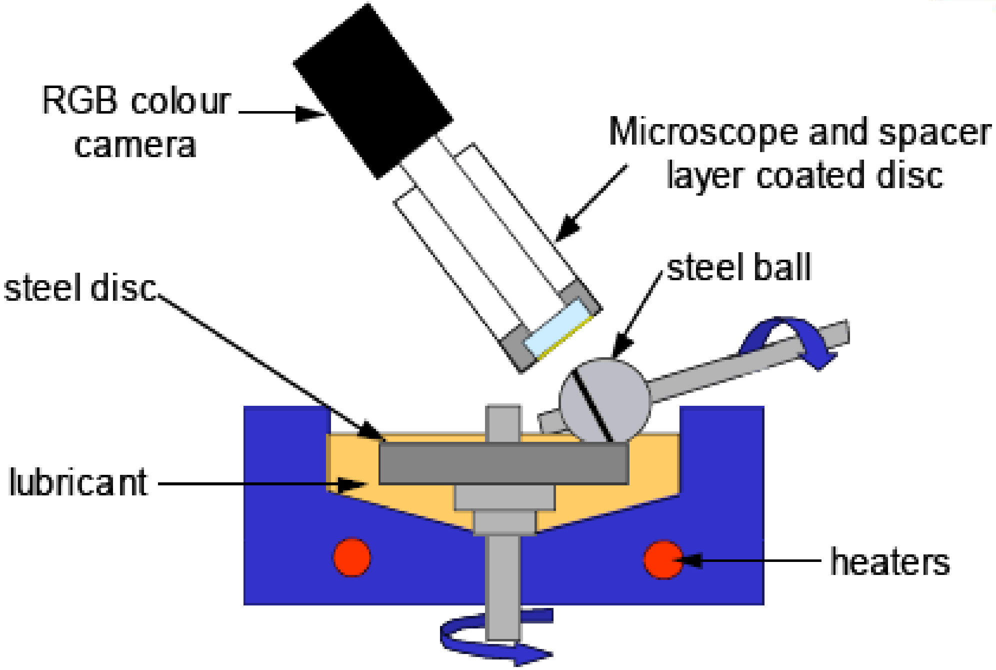
Effects of ethanol on ZDDP tribofilms

In-situ measurements?

MTM-SLIM



?

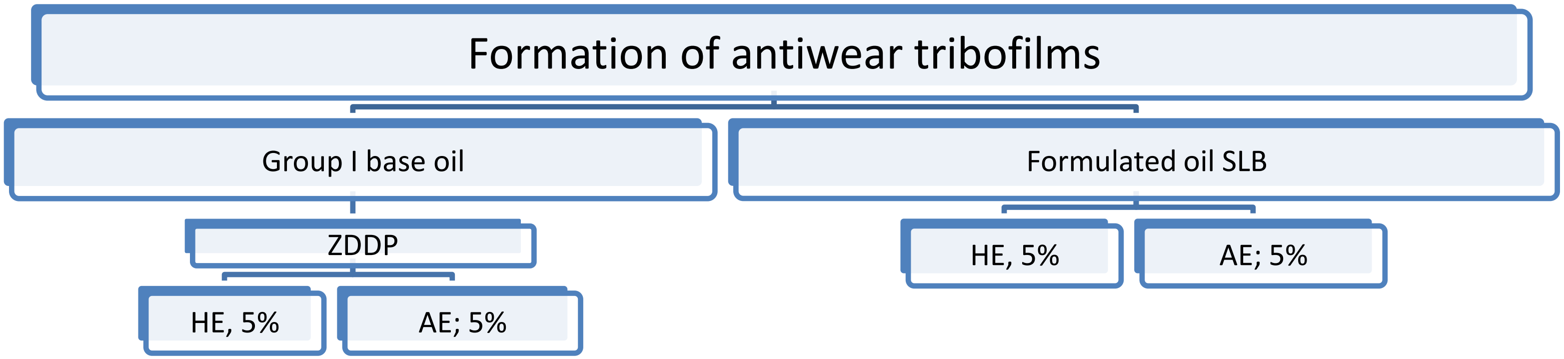


PCS Instruments, MTM-SLIM

H. FUJITA , R. P. GLOVNEA & H. A. SPIKES (2005) Study of Zinc Dialkydithiophosphate Antiwear Film Formation and Removal Processes, Part I: Experimental, Tribology Transactions, 48:4, 558-566

Effects of ethanol on ZDDP tribofilms

Description of the fluids



Metal	AW01	
	Spectroil	X Ray
Ca	0	500
Mo	1	16
P	89922	97300
Pb	6	<10
S	N.M.	180400
Zn	63503	17100

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MTM-SLIM – tribofilm formation

Clean new disc and ball

↓

Heat to test temperature (~15 min)

↓

Take interference image - Spacer layer thickness

↓

Take Stribeck friction curve: *SRR* = 50%, 0.95 GPa, *U* from 3500 to 7 mm/s

↓

A {

Take interference image

↓

Slow speed rubbing steel/steel: 1GPa, 50% SRR, 1GPa, 50 mm/s (h_{EHL} = 8 nm)

↓

Take interference image

↓

Take Stribeck friction curve

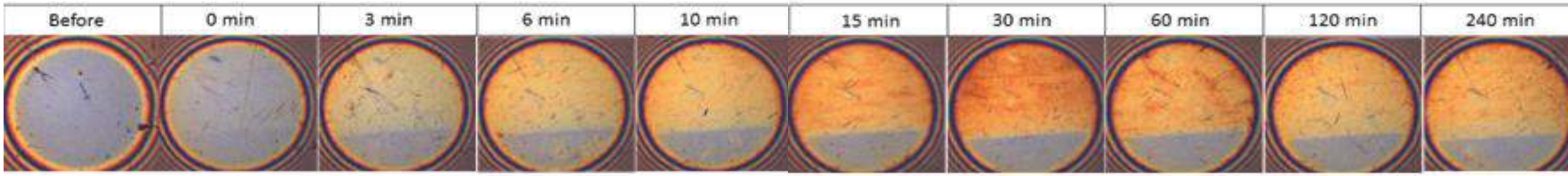
}

↓

Repeat **A** for increasing rubbing times

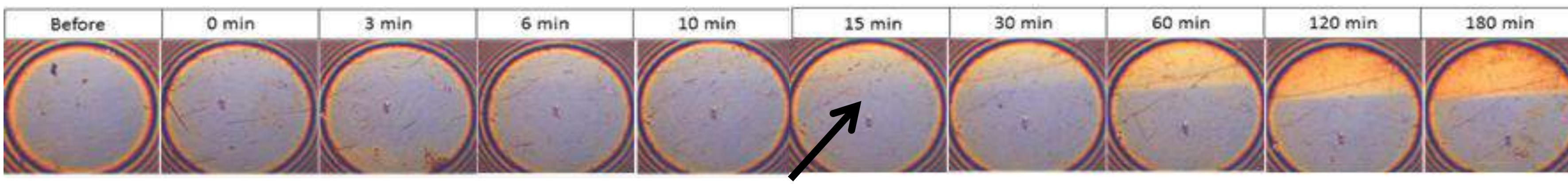
Effects of ethanol on ZDDP tribofilms

Formulated oil **70^{o}C** **Neat SLB**



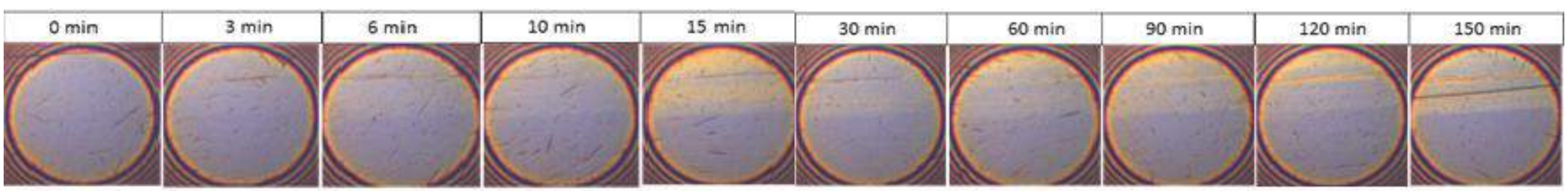
- Film formation delayed for 15 minutes

SLB + 5%AE



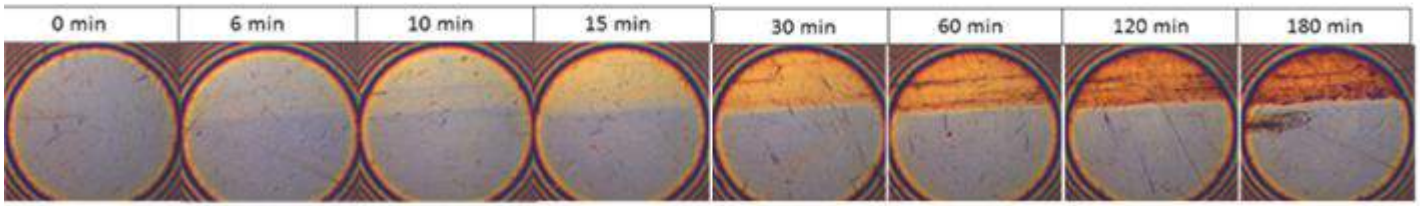
Ethanol has evaporated?

SLB + 5%AE, top-up, 70°C

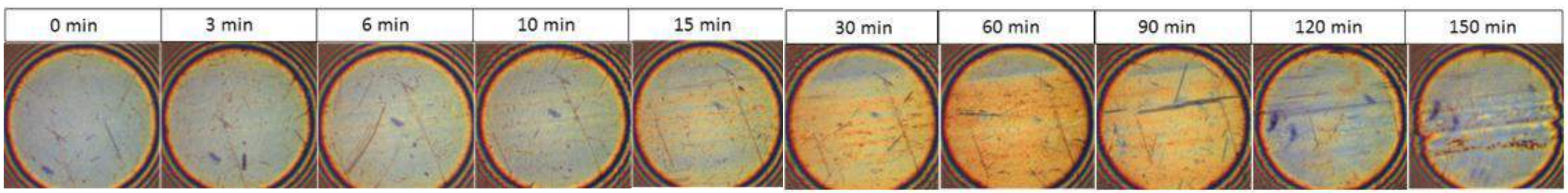


Effects of ethanol on ZDDP tribofilms

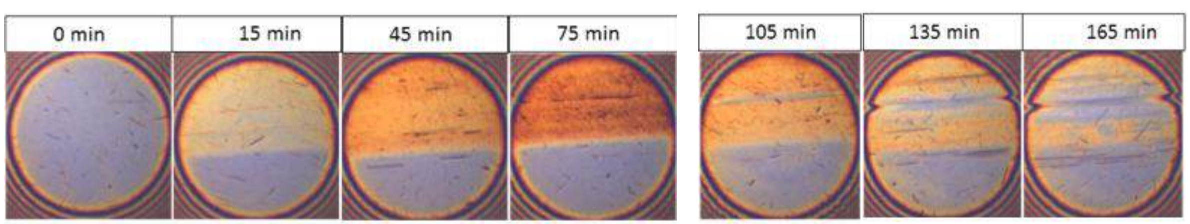
ZDDP solution, 70°C



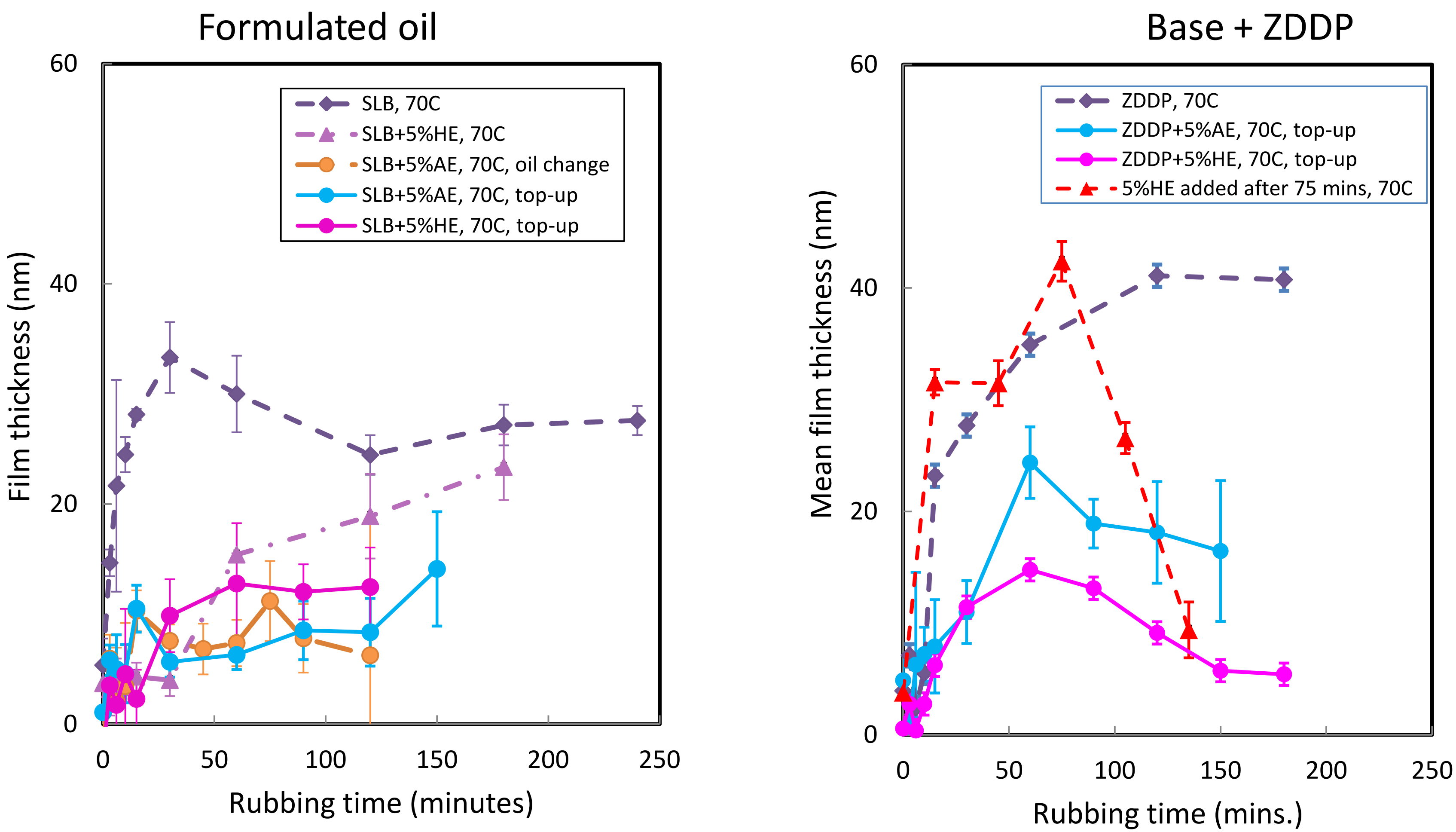
ZDDP solution + 5% HE, top-up, 70°C



ZDDP solution, 70°C, 5% HE added after 75 min.

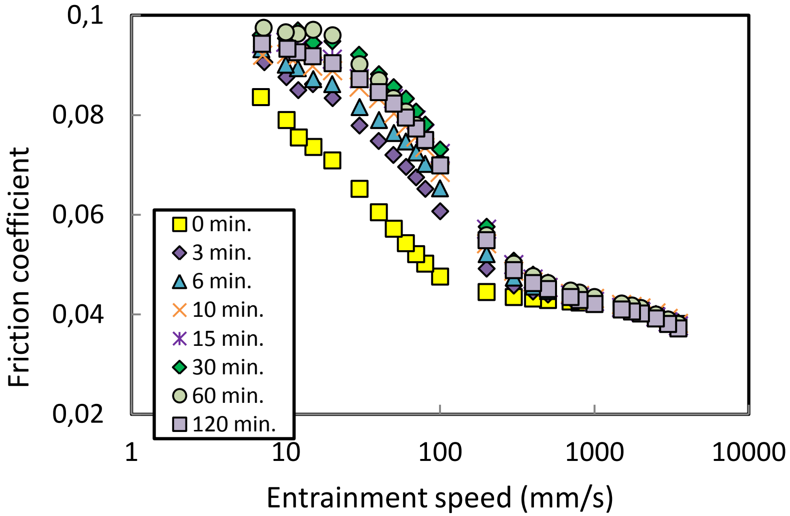


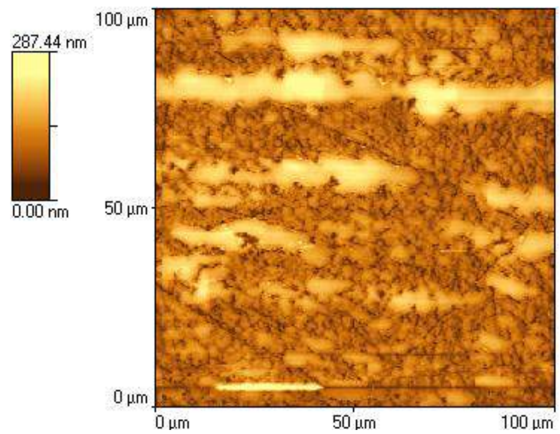
Effects of ethanol on ZDDP tribofilms



Effects of ethanol on ZDDP tribofilms

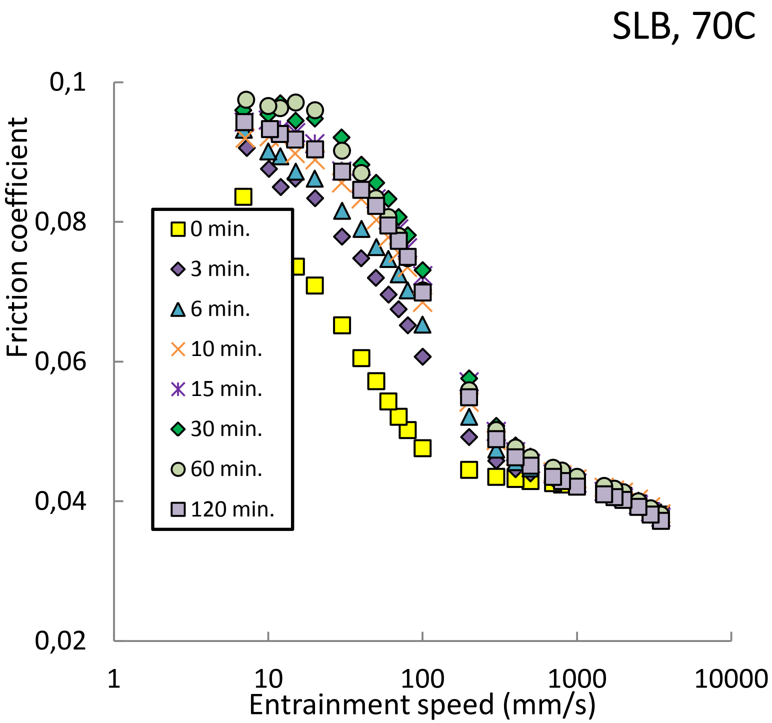
SLB, 70C

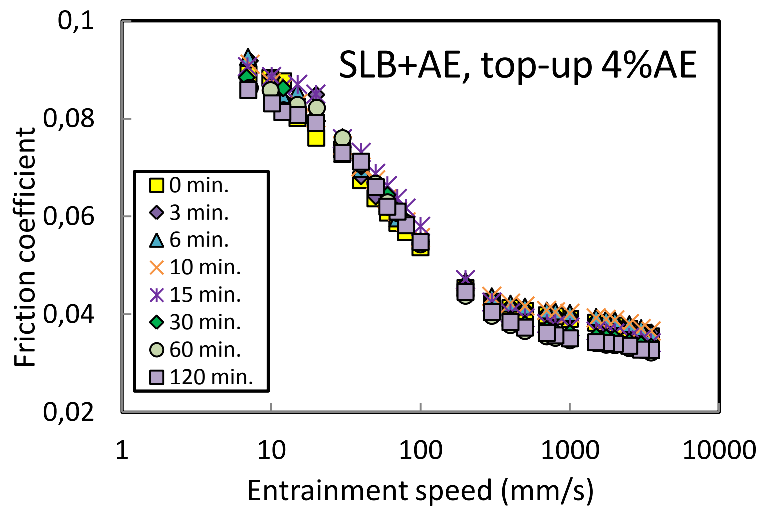


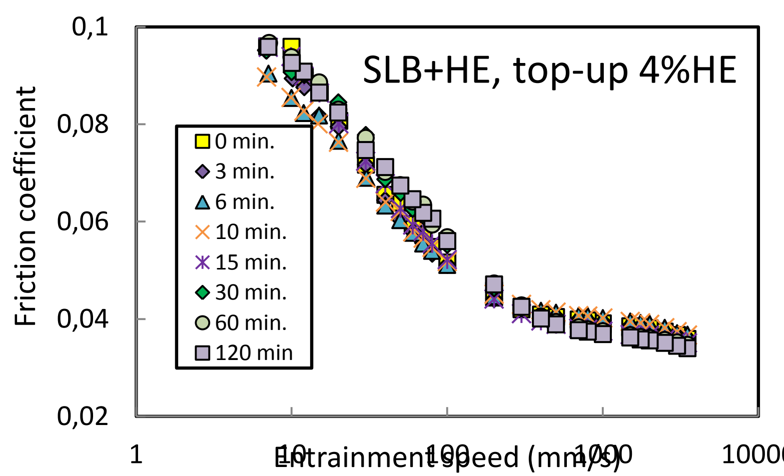


- ZDDP films produce high friction at intermediate speeds
- Probably due to very rough, pad-like ZDDP film

Effects of ethanol on ZDDP tribofilms







- AE and HE almost entirely suppress friction resulting from tribofilm formation

Effects of ethanol on ZDDP tribofilms

Slows down formation of tribofilm

Final tribofilm greatly reduced

Reduces (stops?) rightward shift of Stribeck curves

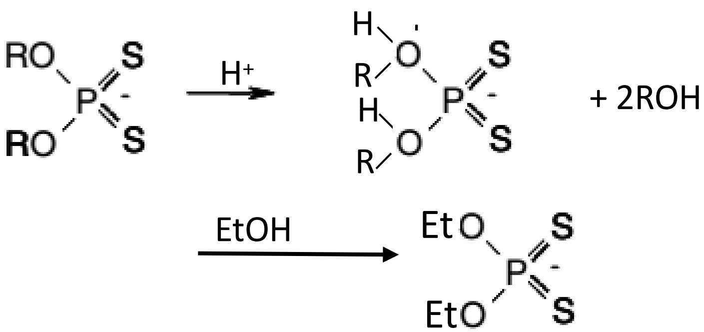
Effects of ethanol on ZDDP tribofilms

Discussion: Effects of ethanol

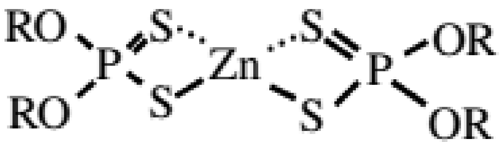
Ethanolysis? (suggested for methanol fuel)

Olsson, B., L. Mattsson, et al. (1991). Paper XVI (ii) A Model Study of Lubricant Additive Reactions in the Presence of Methanol. Tribology Series. C. M. T. D. Dowson and M. Godet, Elsevier. ***Volume 18:*** *429-437.*

- Presence of ethanol and acetic acid



- Not immediately obvious why this should so markedly reduce ZDDP film formation



More probably;

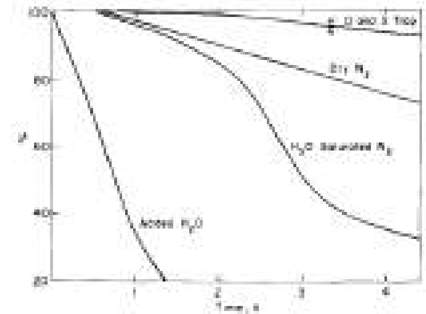
- ➢ **Ethanol blocks steel surface**
- ➢ **Ethanol stabilises, solubilises ZDDP reaction intermediates**

- Might help if we knew the ZDDP molecule to tribofilm reaction sequence in more detail!

Effects of ethanol on ZDDP tribofilms

Effects of water

Addition of hydrated ethanol gives 0.35% wt. H_20 but this may rise to 2% wt. during top-ups.



Spedding, Watkins. *Trib. Int.* 15, p. 9, (1982)

Breakdown/film formation by ZDDP is a hydrolytic process

Nedelcu et al.
Surf. Interface Anal. 2012, 44, p. 1219, (2012)

2% wt. water inhibits growth of ZDDP film and reduces length of poly-phosphate chain

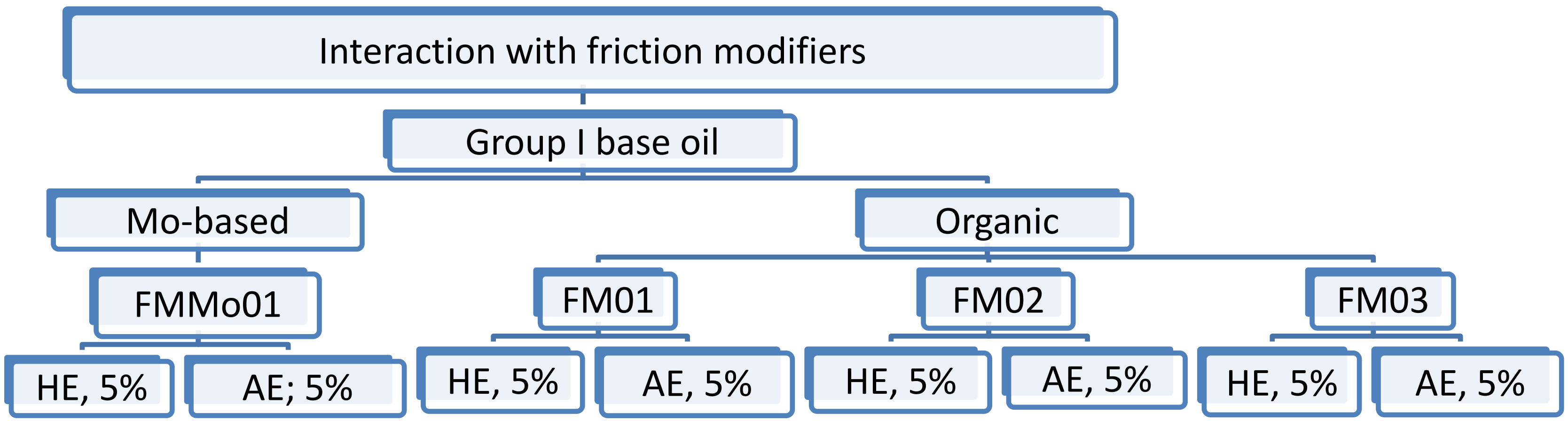
Initial water amount (wt%)	0	0.5	1	2
Zn/P	0.3	0.4	0.6	0.5
S(II)/P	0.3	0.4	0.7	0.6
P $2p_{3/2}$ binding energy (eV)	133.6	133.6	133.3	133.3
Layer thickness (min)	45	35	23	20

Cen et al.
Trib. Int. 56, p. 47 (2012)

1% wt. water inhibits growth of ZDDP film and causes only phosphate chains to form. Little effect on friction but increases wear

Interactions of ethanol with friction modifiers

Description of the fluids



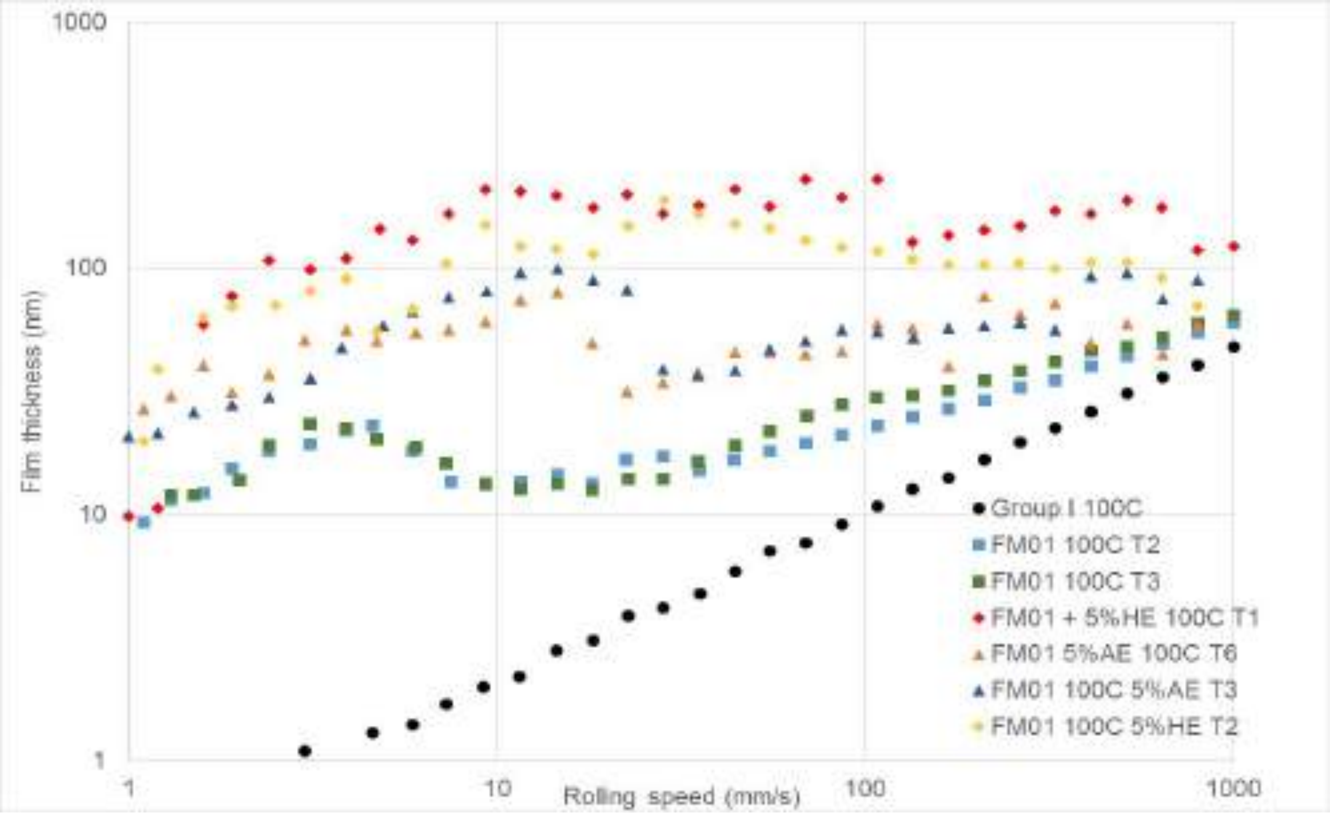
Metal	FMMo01	
	Spectroil	X-ray
Mo	14699	3767
P	196	1431
Pb	0	<10
S		149200

- **EHD measurements**
- **Stribeck curves**

Interactions of ethanol with friction modifiers

Example result: organic friction modifier FM01

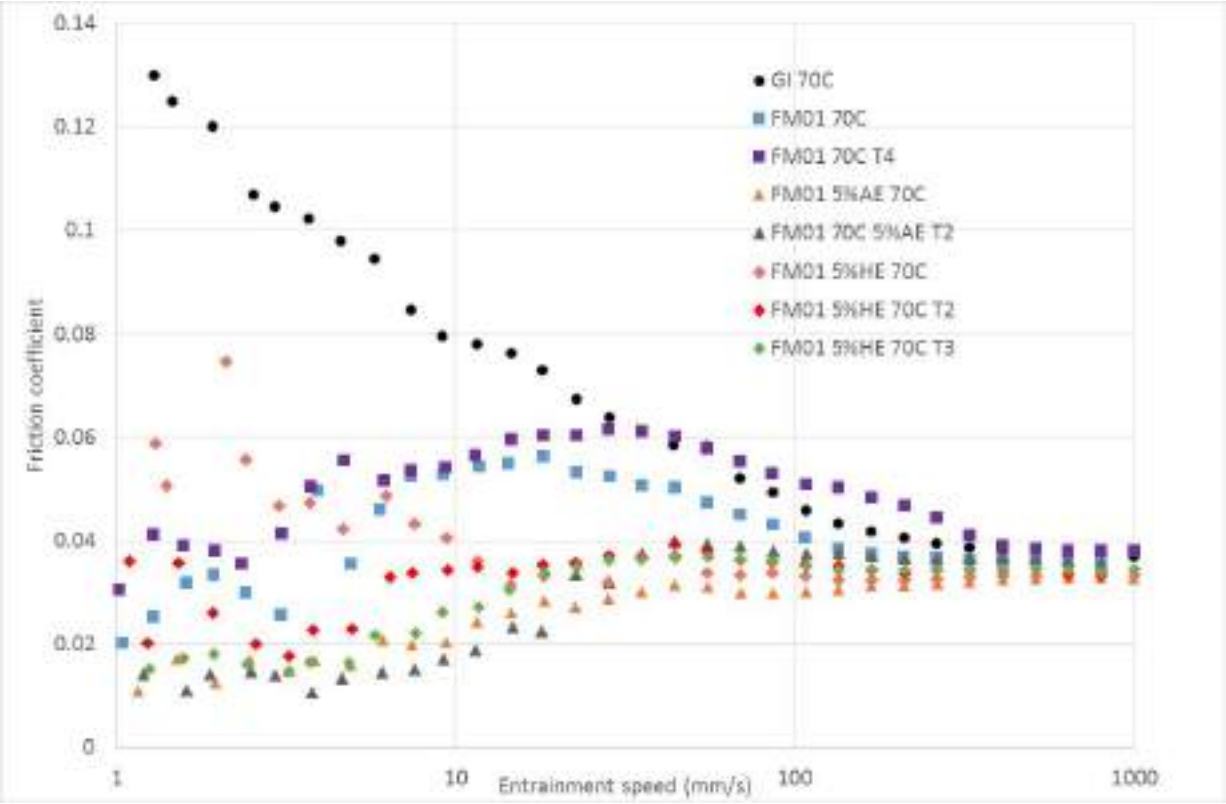
EHD film thickness



Interactions of ethanol with friction modifiers

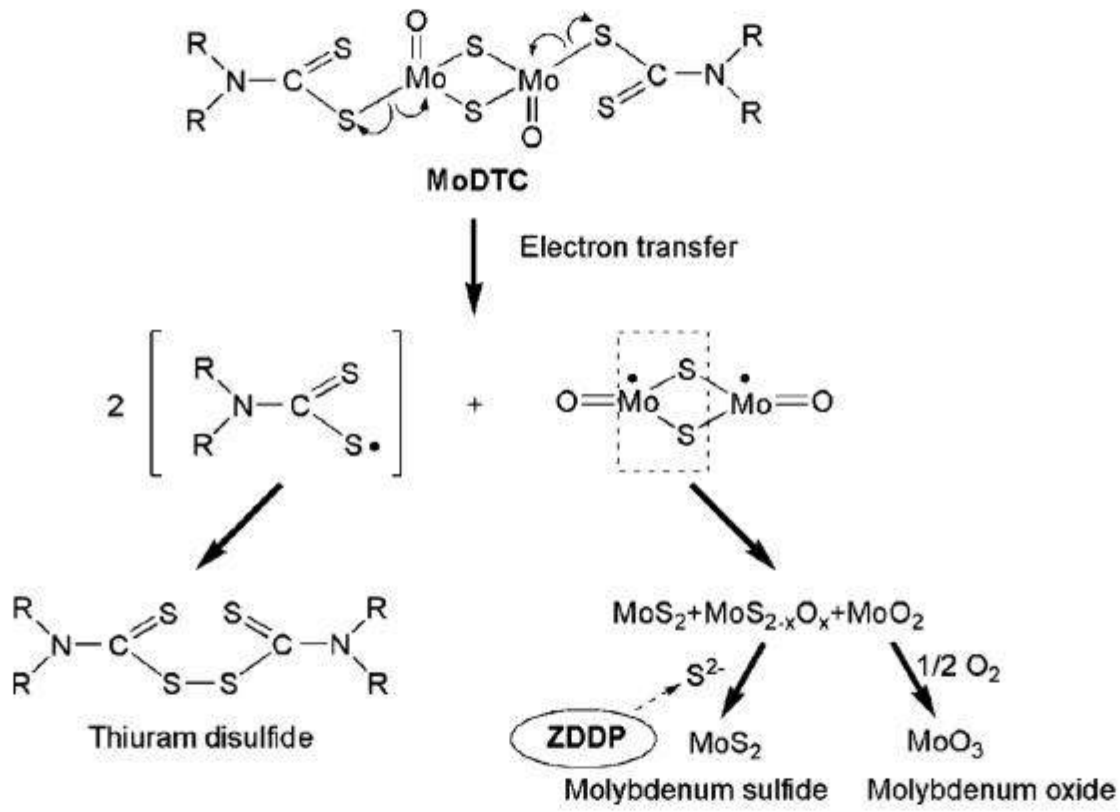
Example result: organic friction modifier FM01, 70ºC

EHD film thickness: addition of ethanol



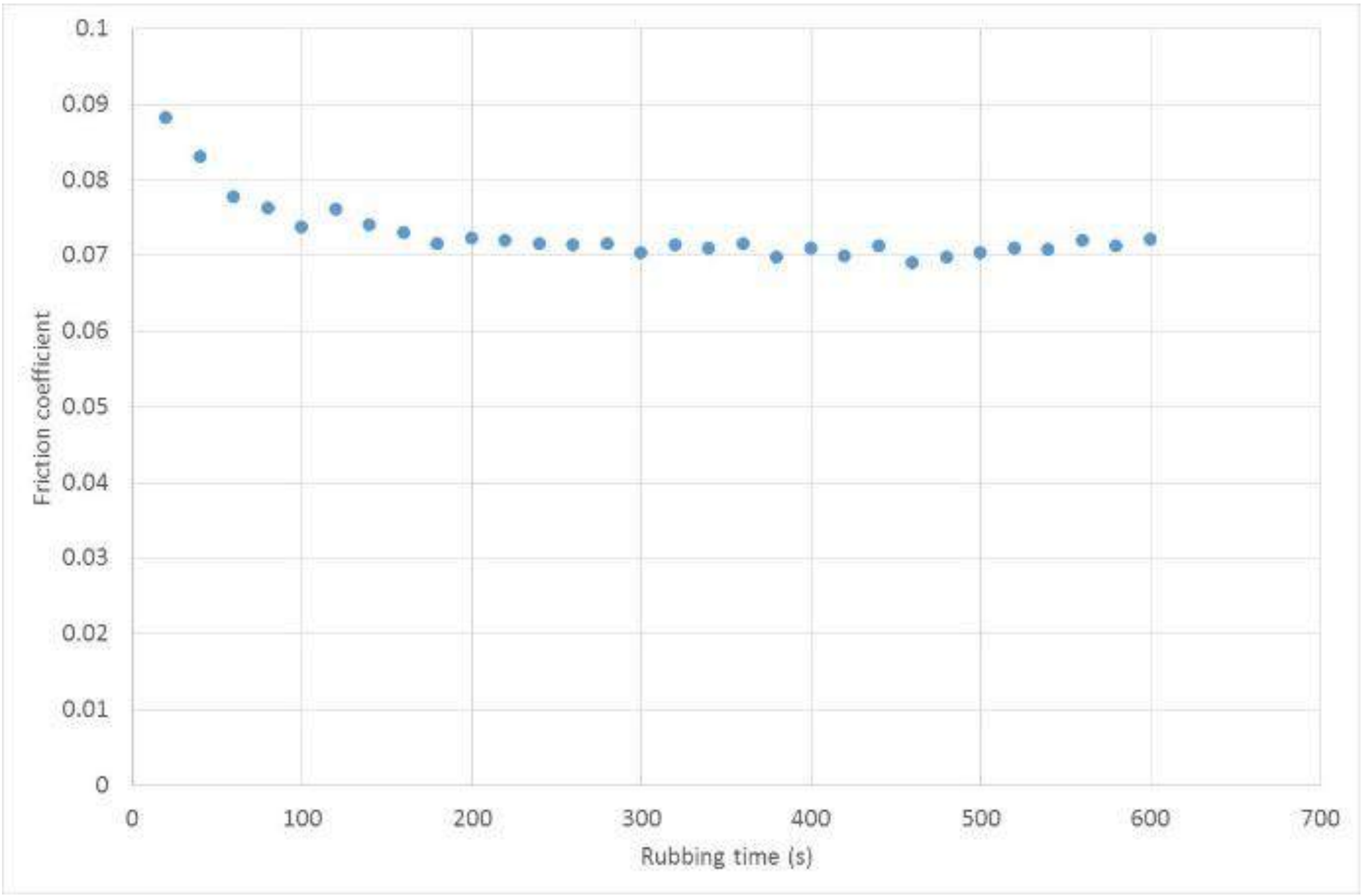
Interactions of ethanol with friction modifiers

Mo-DTC (Molybdenum dithiocarbamate)



Interactions of ethanol with friction modifiers

Mo-DTC: effect of rubbing time on friction

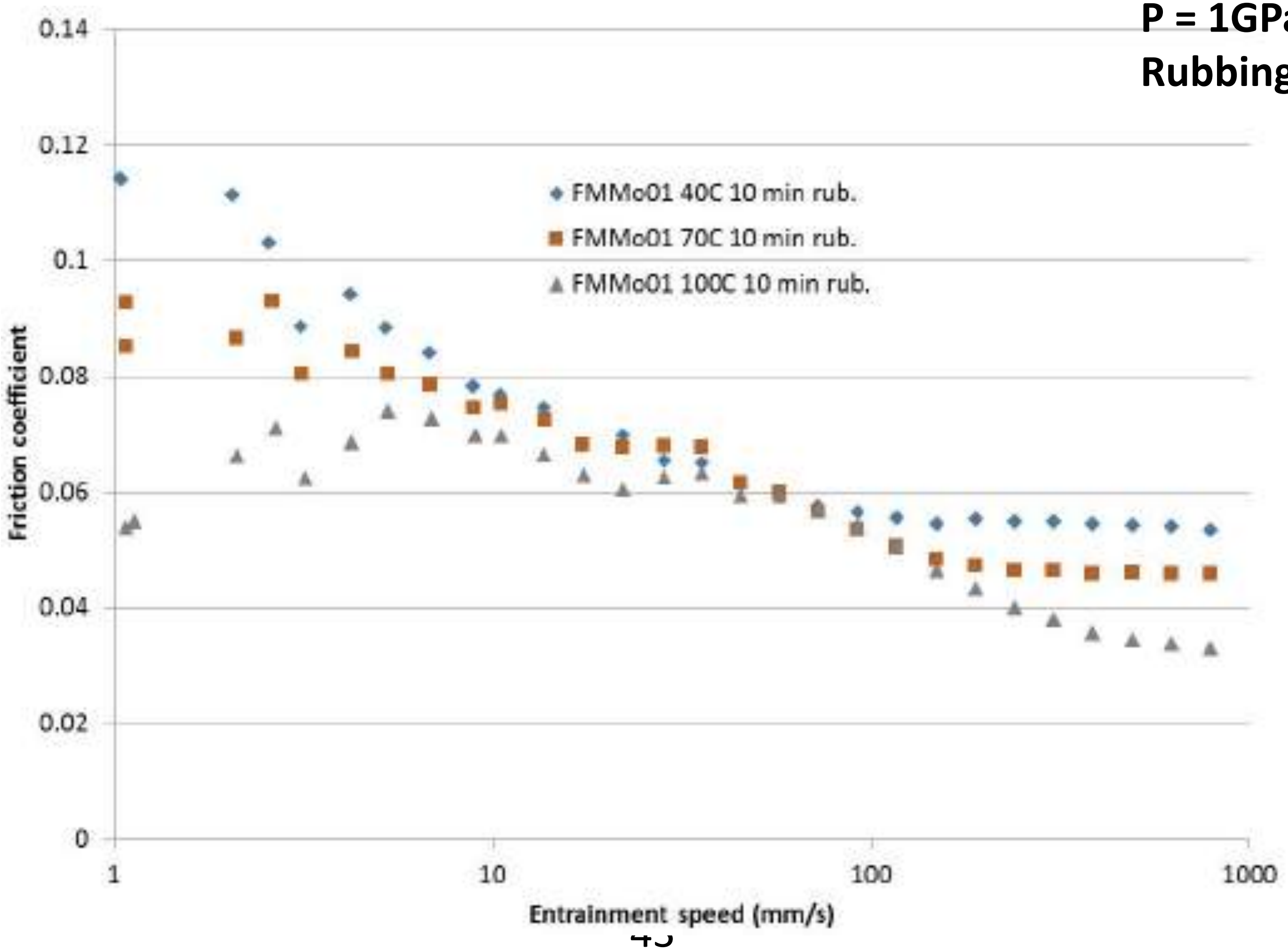


SRR = 50%
P = 1GPa
70^{o}C
20 mm/s

Interactions of ethanol with friction modifiers

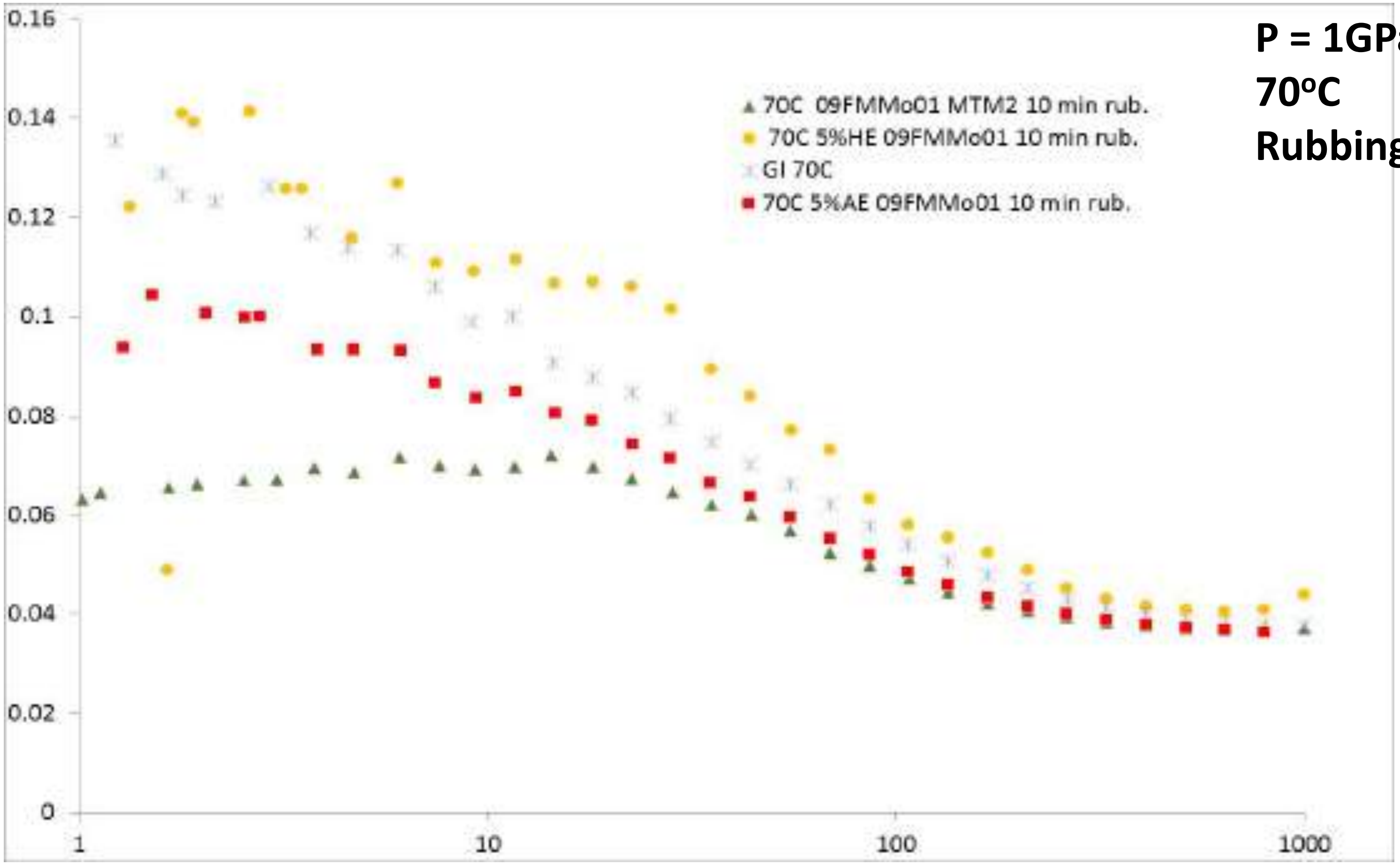
Mo-DTC

SRR = 50%
P = 1GPa
Rubbing = 10 min

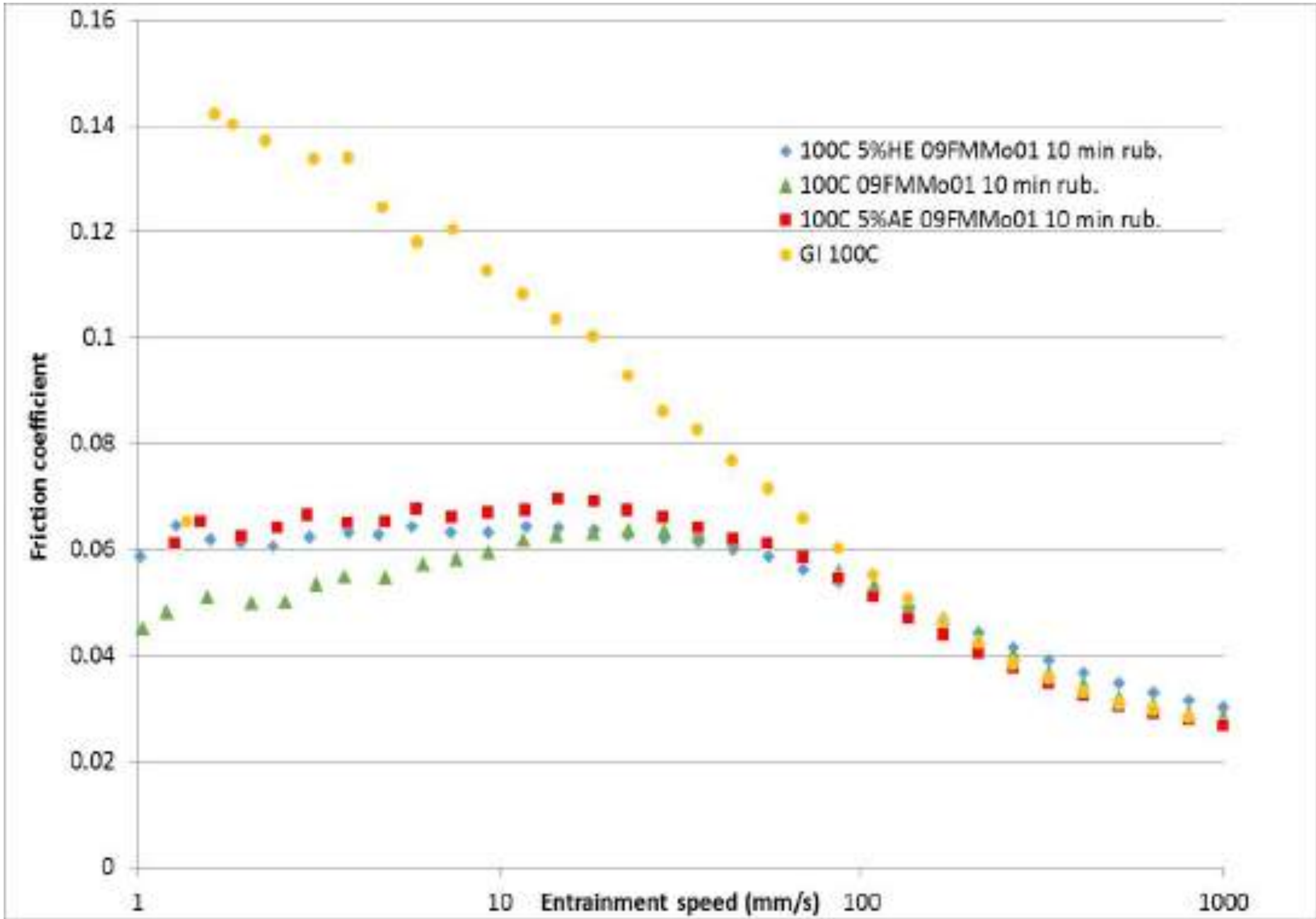


Interactions of ethanol with friction modifiers

SRR = 50%
P = 1GPa
70^{o}C
Rubbing = 10 min



Interactions of ethanol with friction modifiers



SRR = 50%
P = 1GPa
100°C
Rubbing = 10 min

Conclusions

- The addition of quite small proportions of ethanol reduces EHD film thickness and friction in the full film and mixed regimes.
- In the boundary regime, ethanol contamination of the base oil promoted the formation of a boundary layer , which seems to result from oxidation. In a formulated engine oil, the presence of ethanol reducing the thickness of the detergent boundary film from *ca* 9 nm to *ca* 2-3 nm.
- Ethanol reduces the stability and thickness of ZDDP tribofilms, which is more severe for HE than for AE
- The presence of ethanol did not seem reduce the efficiency of organic friction modifiers. In fact, it increased the thickness of the low friction boundary film and therefore increased range of speeds for which very low friction, below 0.06, could be achieved.
- The presence of ethanol reduces the efficiency of Mo-based friction modifiers.

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Questions?