



# Bench Screening of Novel Anti-Wear Alternatives to ZDDP

Victor Bakunin, Trade and Technical representative, CIS  
Moscow, Russia

Cyril Migdal, Director, Petrochemical Additives  
Middlebury, CT, USA

CHEMTURA – a new brand at the Oils and Additives market



**The *chemical*  
company  
of the *future***

**Chemistry+Future**

Chemistry+Future

Chemistry+Future

Chemistry+Future

Chemistry+Future

Chemistry+Future

Chemistry+Future

**Chemtura**

A. F. I. L. I. N. G. M. E. N. T. Crompton and Great Lakes have bonded into Chemtura: the world's largest plastics additive company and one of America's largest specialty chemicals companies. "We'll know us best by the size of our ideas and the success of our service." - Bob Wood, CEO

For all our enquiries, visit [www.chemtura.com](http://www.chemtura.com). THE FUTURE IS CLEARER THAN YOU THINK.

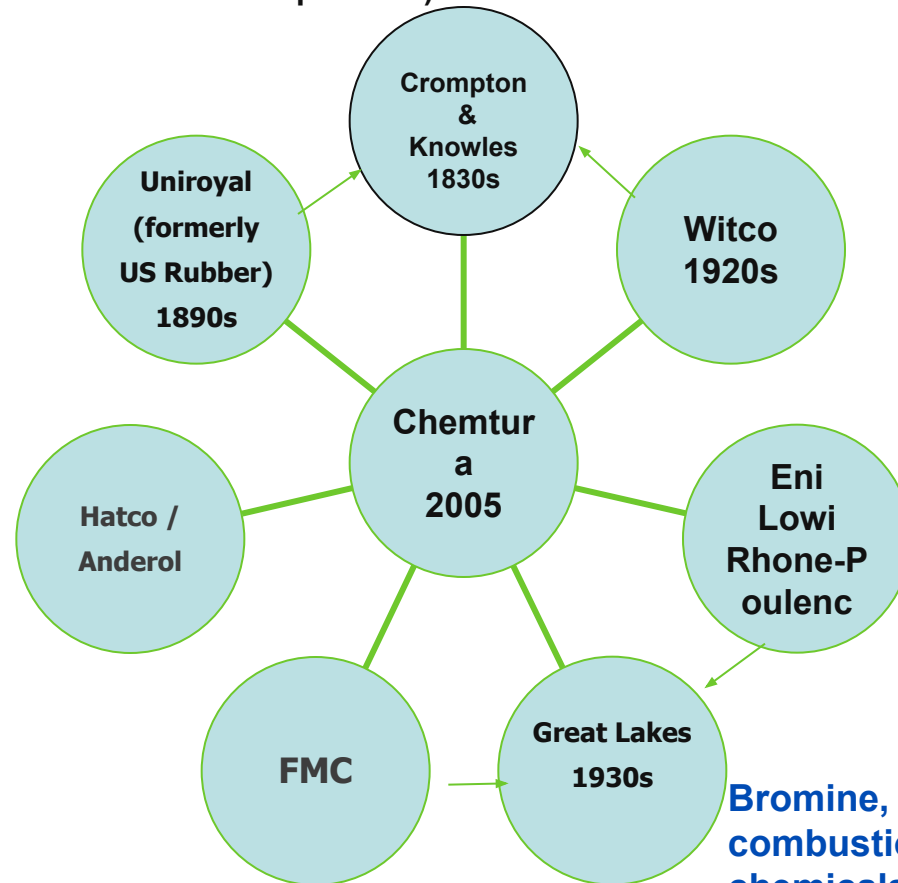
# Our History

Textile machinery, dyes,  
polymer additives,  
lubricants, agricultural  
chemicals, urethanes....  
Specialized chemicals



Rubber, rubber  
components,  
industrial rubber  
products,  
footwear, tires,  
synthetic rubber,  
agricultural  
chemicals

(Crompton  
Corporation)



Carbon for tires,  
plasticizing agents,  
stearates, stabilizers,  
silicones ...  
Specialized  
chemicals

Kaufmann Holdings  
was acquired in 2007.  
Ester lubricants –  
ester polyols +  
ready-to-use synthetic  
fluids

Ordinary and  
specialized  
phenolic  
antioxidants

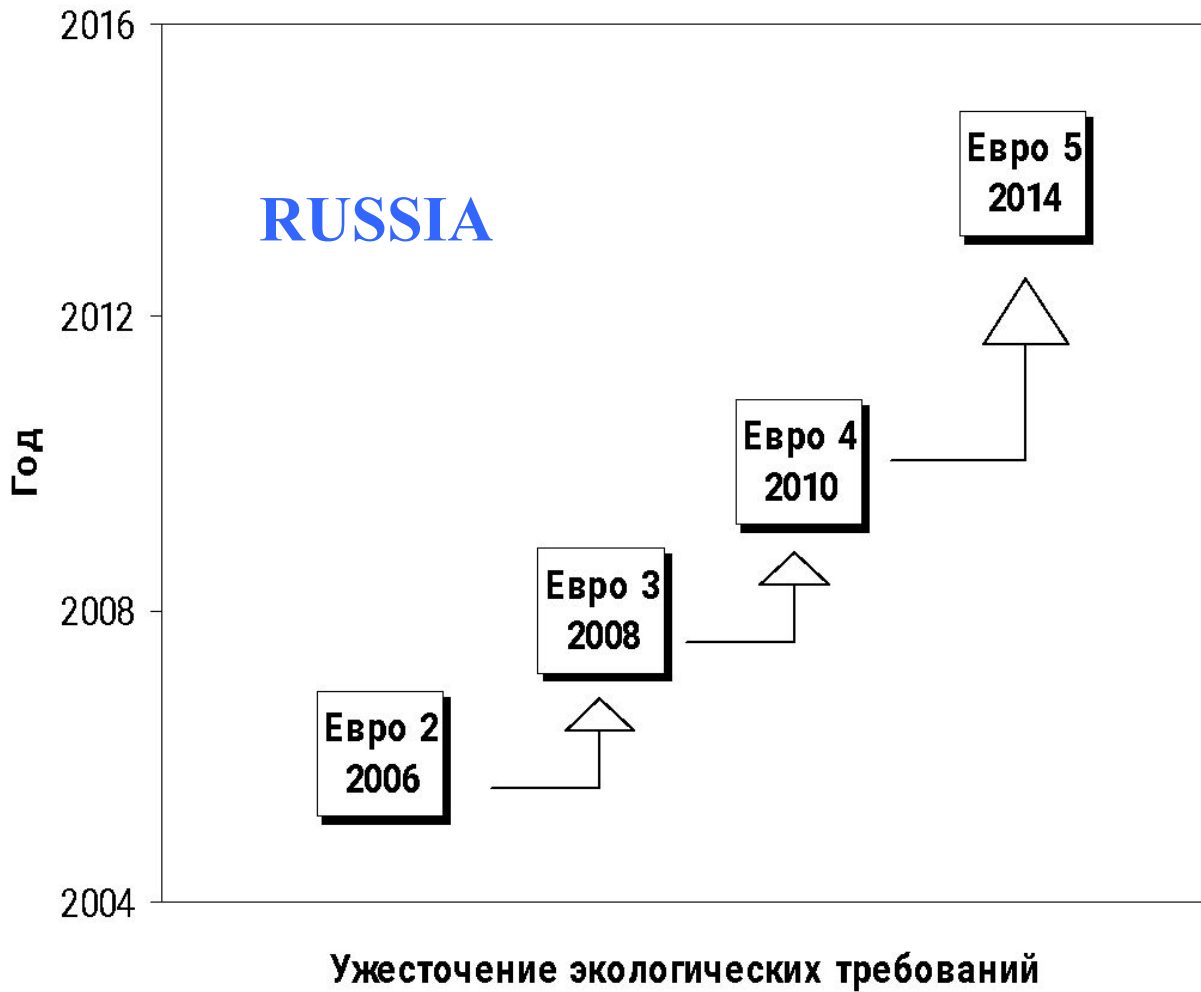
Phosphates –  
non-combustible  
fluids (formerly Ciba)

Bromine, bromine derivatives,  
combustion inhibitors, agricultural  
chemicals, polymer additives, pool  
chemicals, household chemicals,  
fluorine derivatives, optical  
monomers

# Our Additives Trademarks



Naugalube® and Naugard® antioxidants;  
Calciate™, Hystrene® and Industrene® anti-wear agents;  
Lobase®, Hybase® and Petronate® sulfonate detergents;  
Synton® high-viscosity polyalphaolefins (PAO);  
G-2000™ high-quality lubricants;  
Durad® additives based on organic phosphates;  
Reolube® non-combustible lubricants and fluids (phosphates);  
Reomol® and KP-140® special additives (phosphates);  
ANDEROL®, AOSyn®, PQ® special lubricants;  
Hatcol® esters and ester lubricants (ready-to-use and basestocks);  
Royco® aircraft lubricants.



## EUROPE

Standard	Approval Date
Euro 1	October 1993
Euro 2	October 1996
Euro 3	October 1999
Euro 4	October 2005
Euro 5	Октябрь 2008 October

# Zinc dialkyldithiophosphate (ZDDP)

## - more than simply anti-wear protection

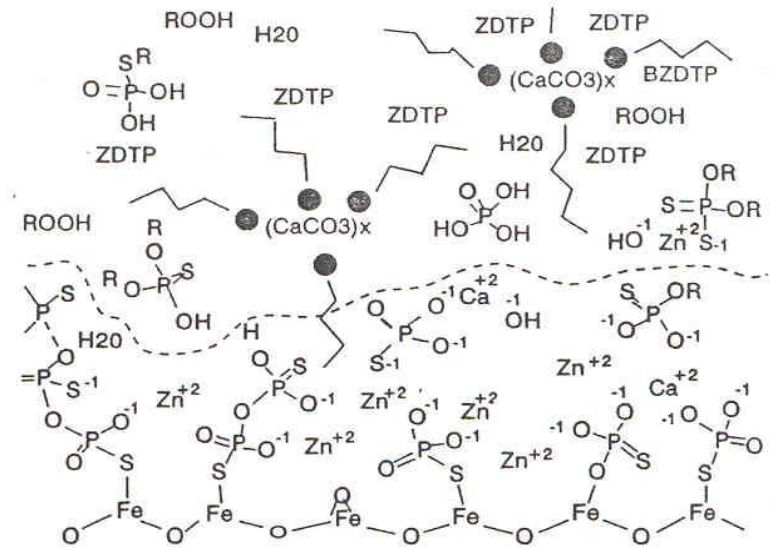
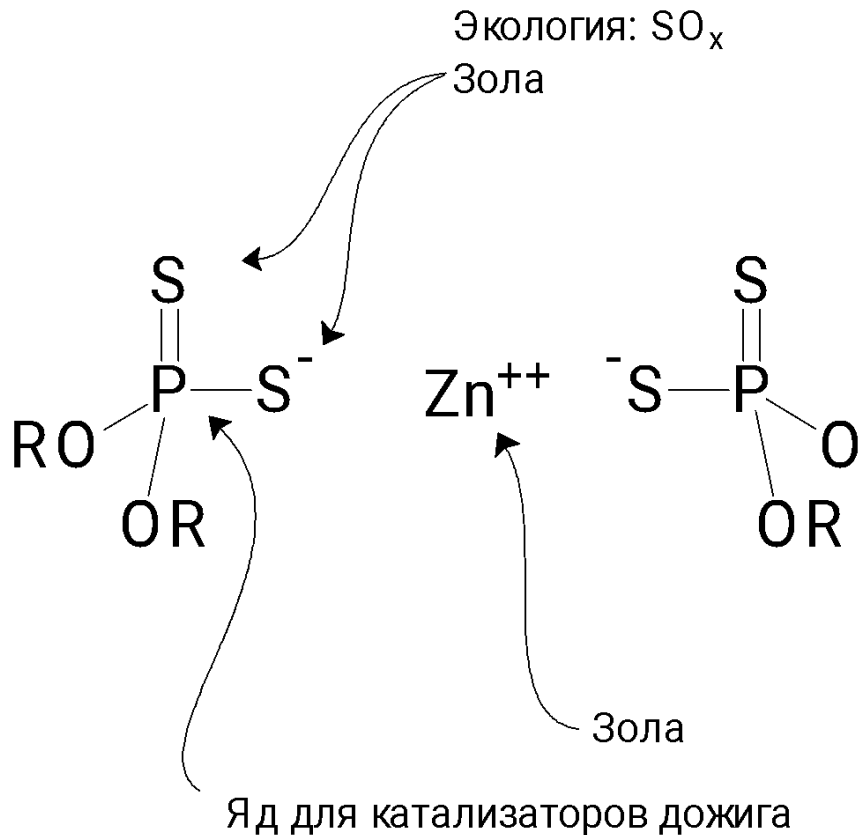
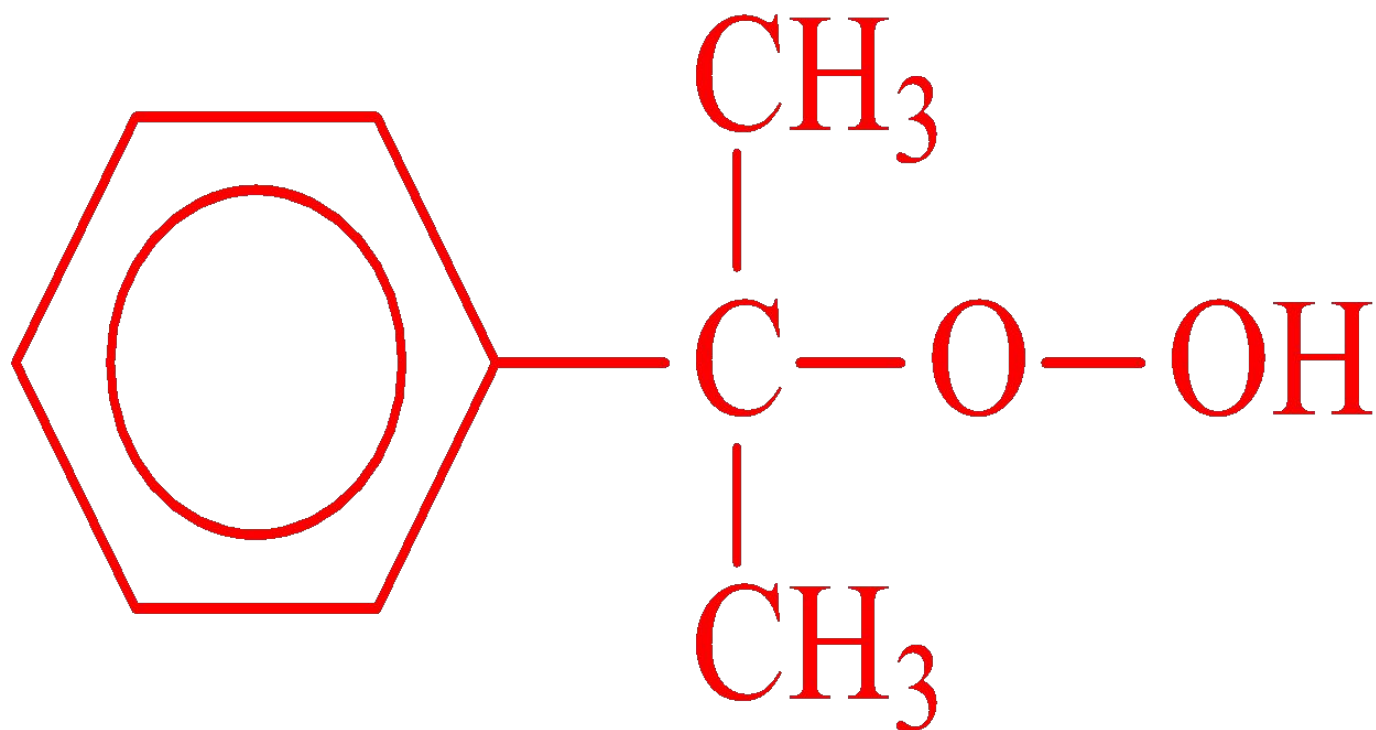


Fig 3 Artist's conception of growing film and ZDDP-rich region

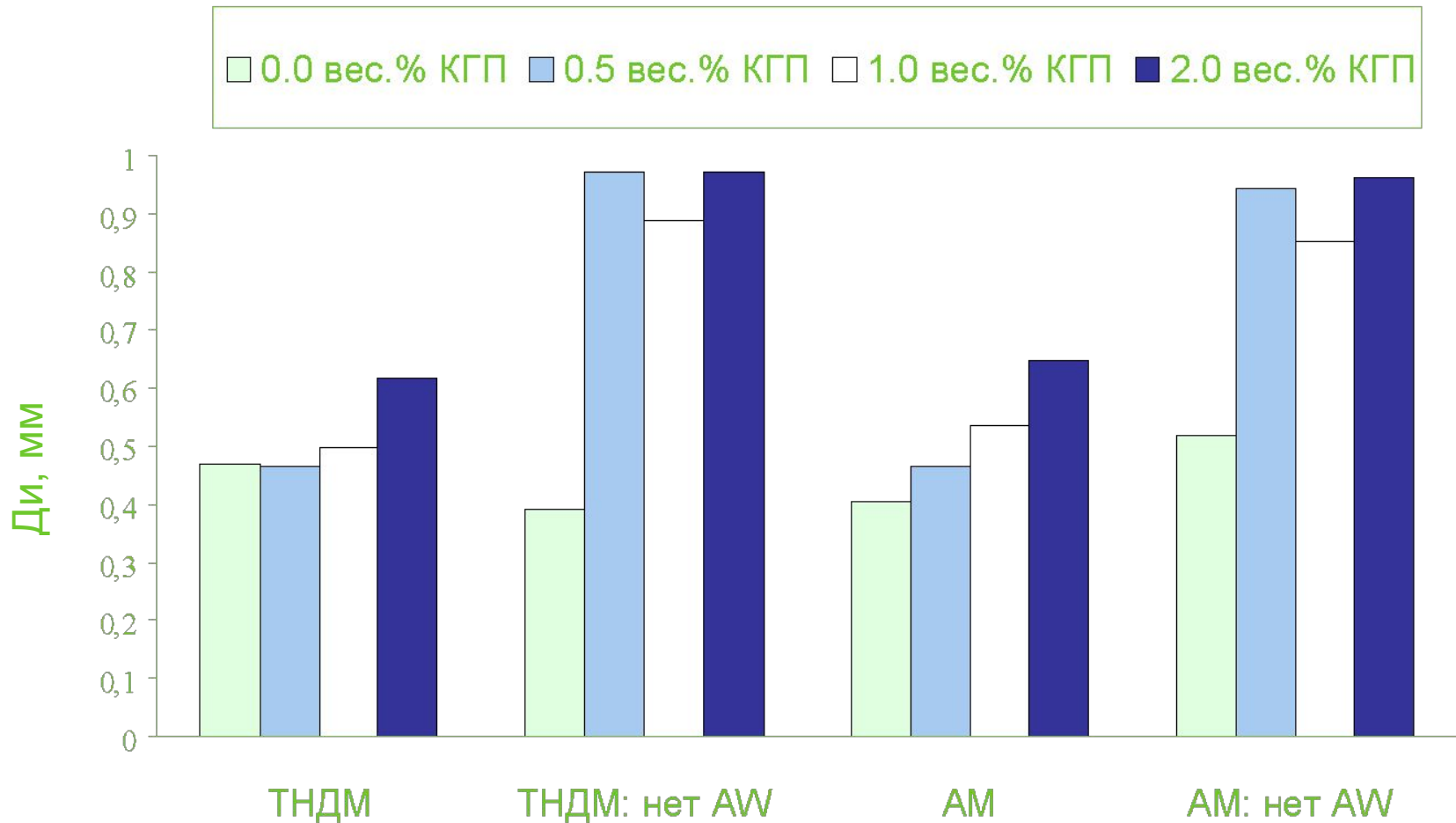
Willermet et al, Trib. Inter., 5/95

- Zinc is the base for the formation of tribolayers (Zinc Polyphosphate)
- ZDDP is an antioxidant
- ZDDP is a synergist for Mo-containing additives

# Cumylhydroperoxide (CHP)

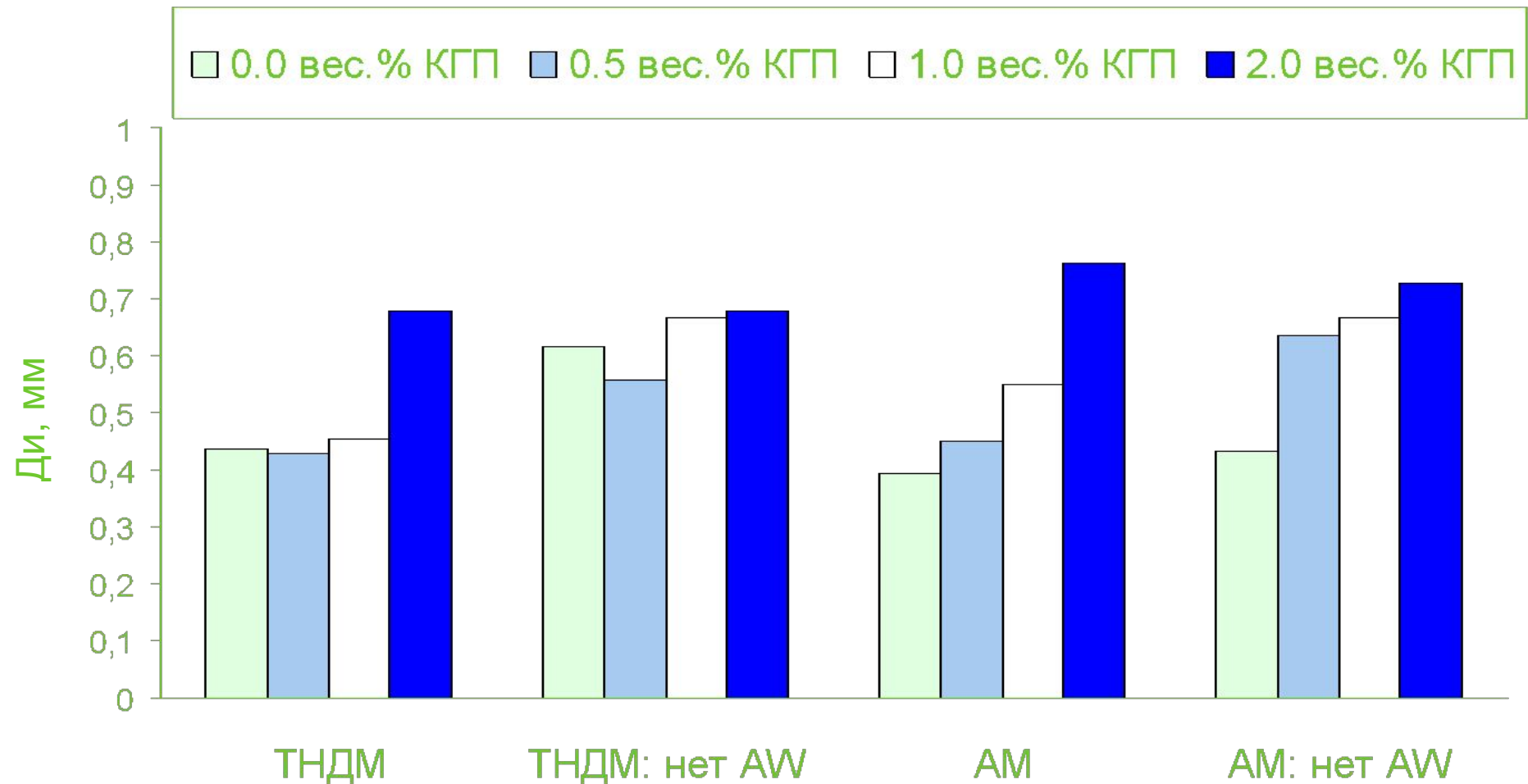


# Effect of CHP on anti-wear properties of engine lubricants (four-ball test machine)

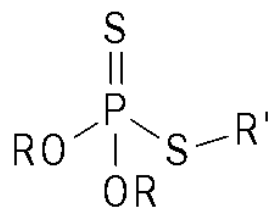




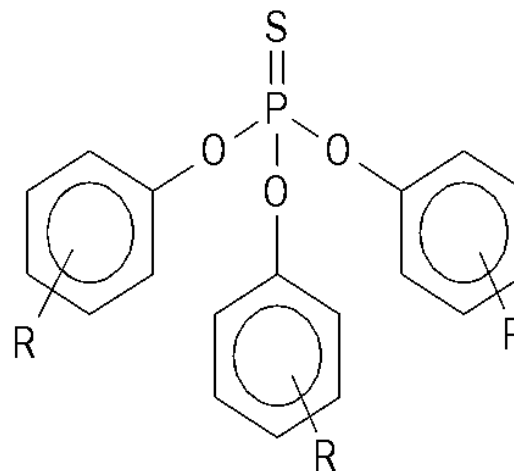
# Effect of CHP on anti-wear properties of engine lubricants (Cameron-Plint)



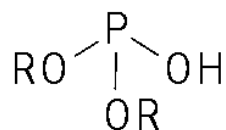
# Ashless P-containing additives



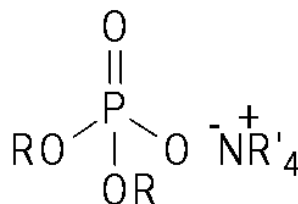
Ñë. ýò èðû äèèèî ô î ñô î ðí î é ê-òû



Òðèàðèèèèèèî ô î ñô àòû

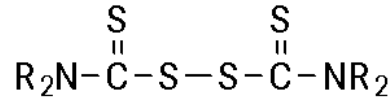


Ô î ñô èòû (í àò S)

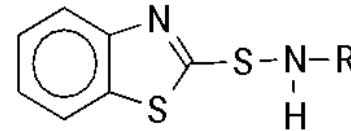


Ô î ñô àòû à ì ì î í èÿ (í àò S)

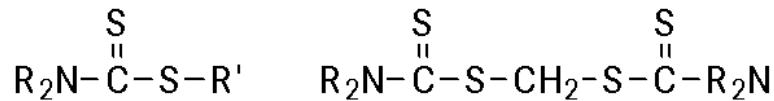
# Phosphorus-free additives (All contain sulfur - SOx, sulfate ash)



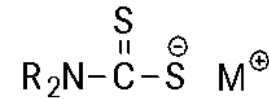
Òèóðàì äèñóëüô èäû



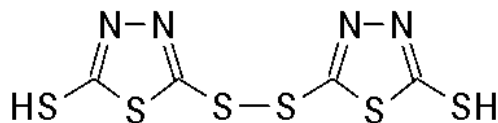
Ñóëüô áí àì èäû



Ýô èðû äèèèî èàðáàì èí î âî é è-òû



Äèèèî èàðáàì àòû  
(çî ëüí û á)

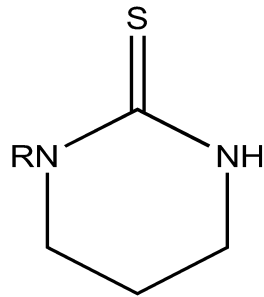


Òèàäèàçî ëû

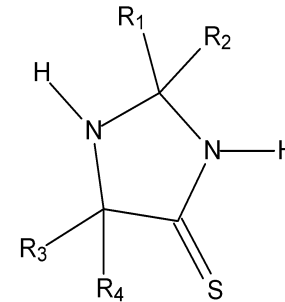
Î ñãðí áí í û á î èãò èí û

Î ñãðí áí í û á ñë. ýô èðû

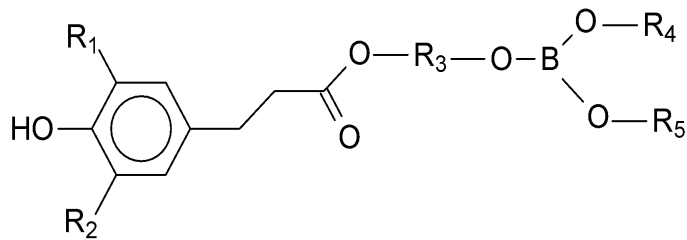
# New anti-wear additives



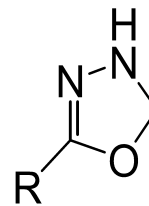
**Cyclic thiourea**



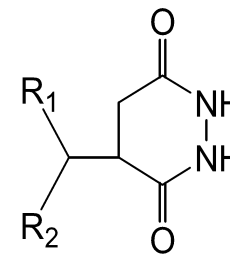
**Imidazolidine thion**



**Imidazolidine thion**

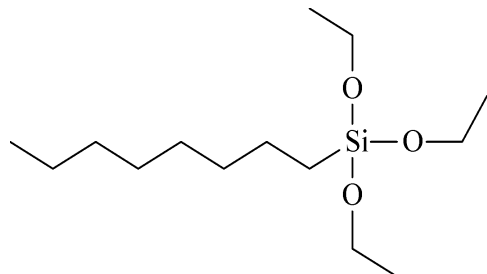


**Oxamide**

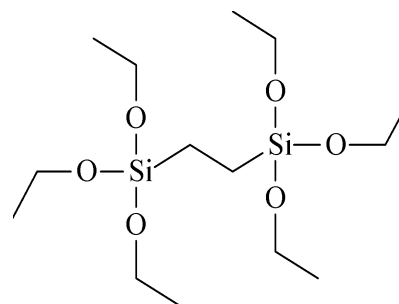


**Hydrazide of succinic acid**

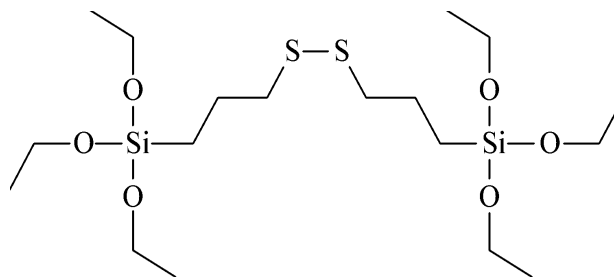
# Silicon-containing compounds: Silanes/Siloxanes



**Octyltriethoxysilane**



**Bis-(triethoxysilyl) ethane**



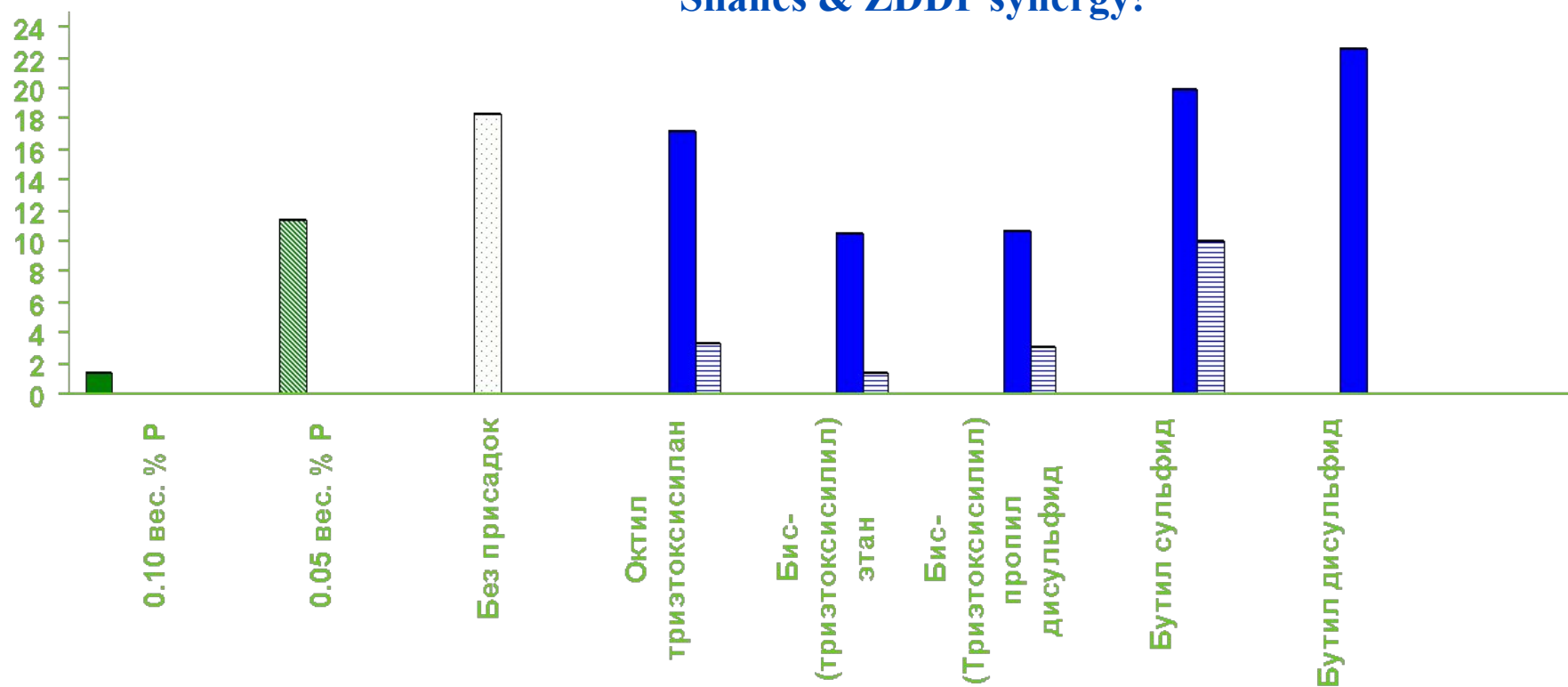
**Bis-(triethoxysilyl) propyl disulfide**

# Anti-wear properties of engine lubricants containing silanes (Cameron-Plint)



## Silanes & ZDDP synergy!

Max. fin wear depth (um)



# Anti-wear additives based on esters



- **MLA-2837**
  - Ashless, no S & P
  - Synergism with ZDDP
  - Free-flowing clear liquid
  - Non-corrosive

# Sulfur-containing anti-wear additives



## MLA-2877

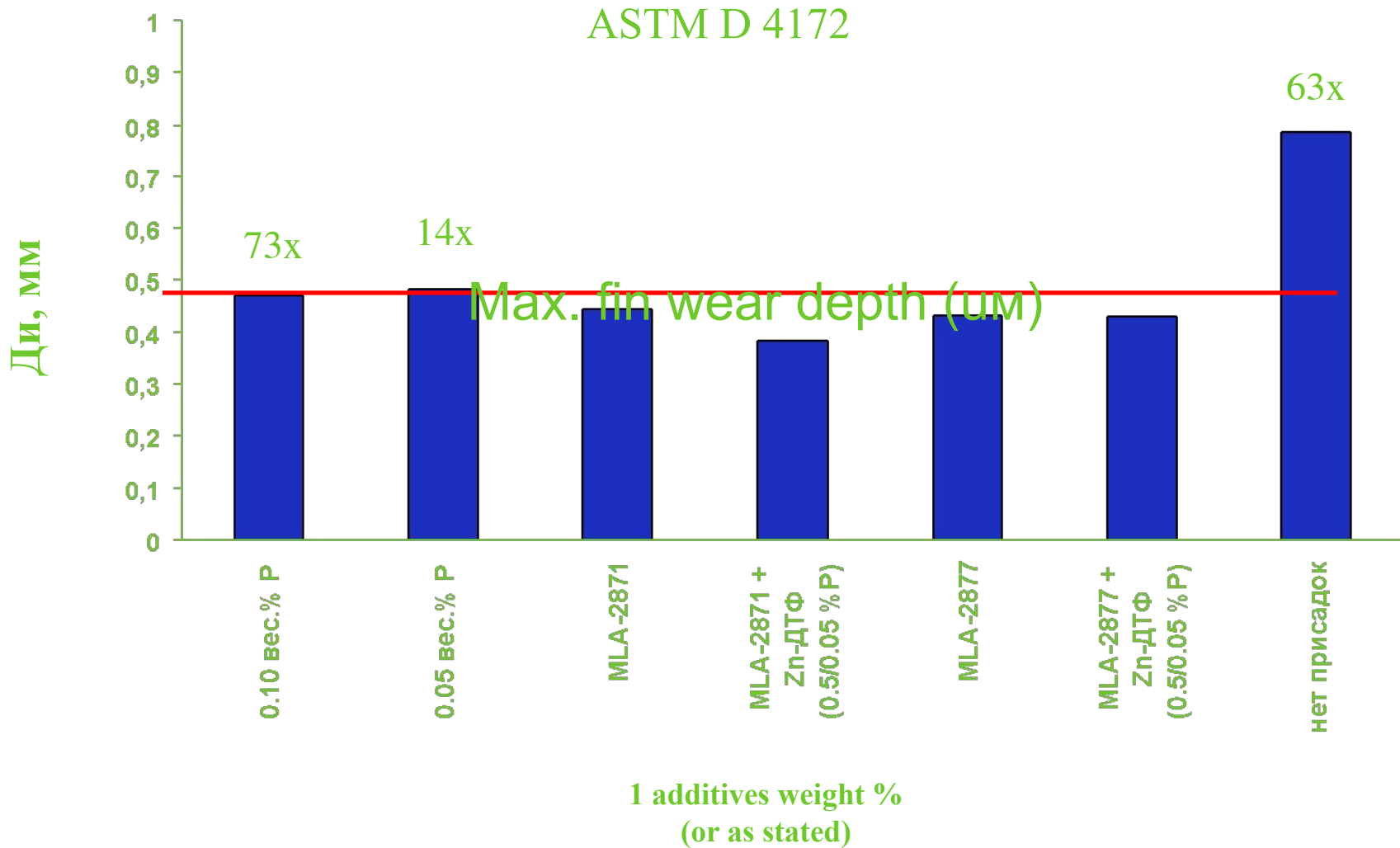
- Thiocarbamate derivative
- 12 % S
- Free-flowing yellow liquid
- Non-corrosive

## MLA-2871

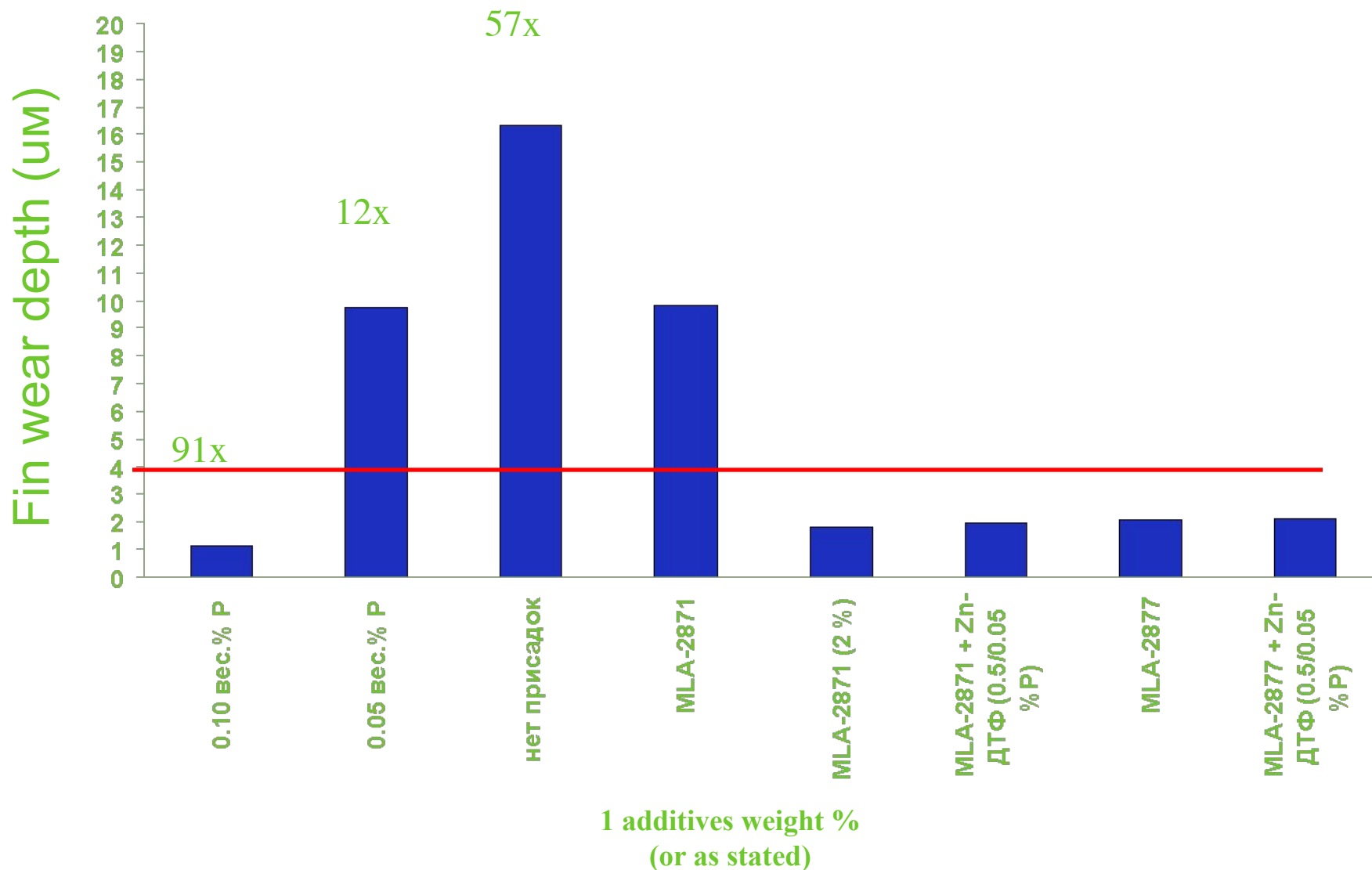
- S-containing heterocycle
- Synergism with ZDDP
- 22 % S
- Free-flowing yellow liquid
- Non-corrosive



# Four-ball friction machine



# Cameron-Plint tribometer



# Selection criteria



## Use conditions

- Activation temperature/ pressure

Price/Quality

Corrosive power

Volatility

Color

Solubility

Compatibility with sealants

Smell

Physical condition

Toxicity

Compatibility with packaging

Duration of action

Multifunctionality

- AO; AF; contribution to EP

# Conclusions



As an anti-wear catalytic agent, CHP reliably distinguishes among lubricants with respect to anti-wear qualities in tests on a four-ball friction machine and the Cameron-Plint tribometer.

By screening various compounds, it was possible to identify several quality classes of potential anti-wear additives for engine lubricants as replacements for zinc dialkyldithiophosphate:

- **Heterocycles with Sulfur/Nitrogen atoms**
- **Esters with Nitrogen atoms (CHON)**
- **Silanes/Siloxanes**