



Bench Screening of Novel Anti-Wear Alternatives to ZDDP

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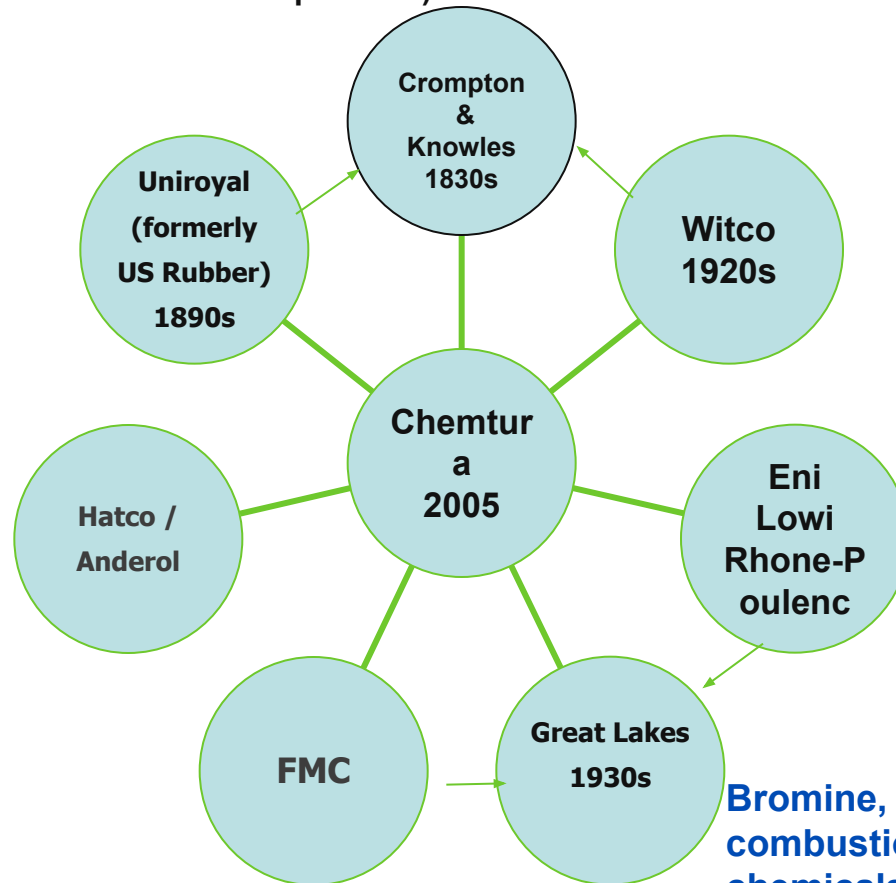
Our History

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;
Calcinat™, 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

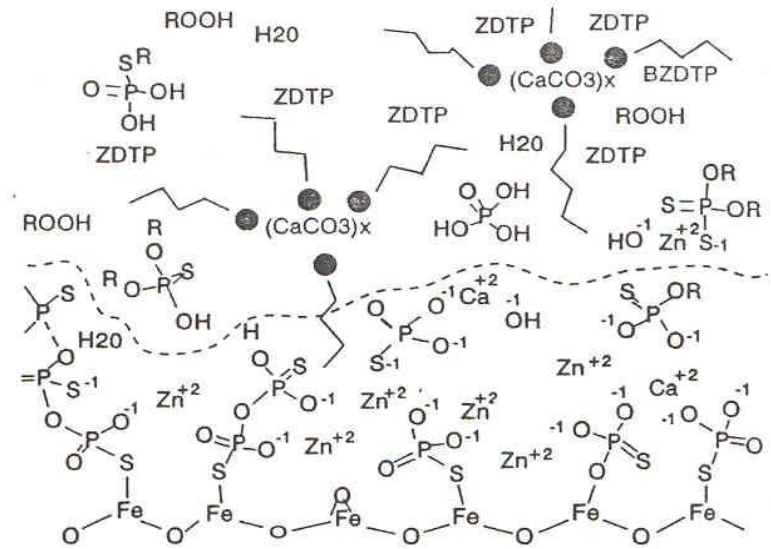
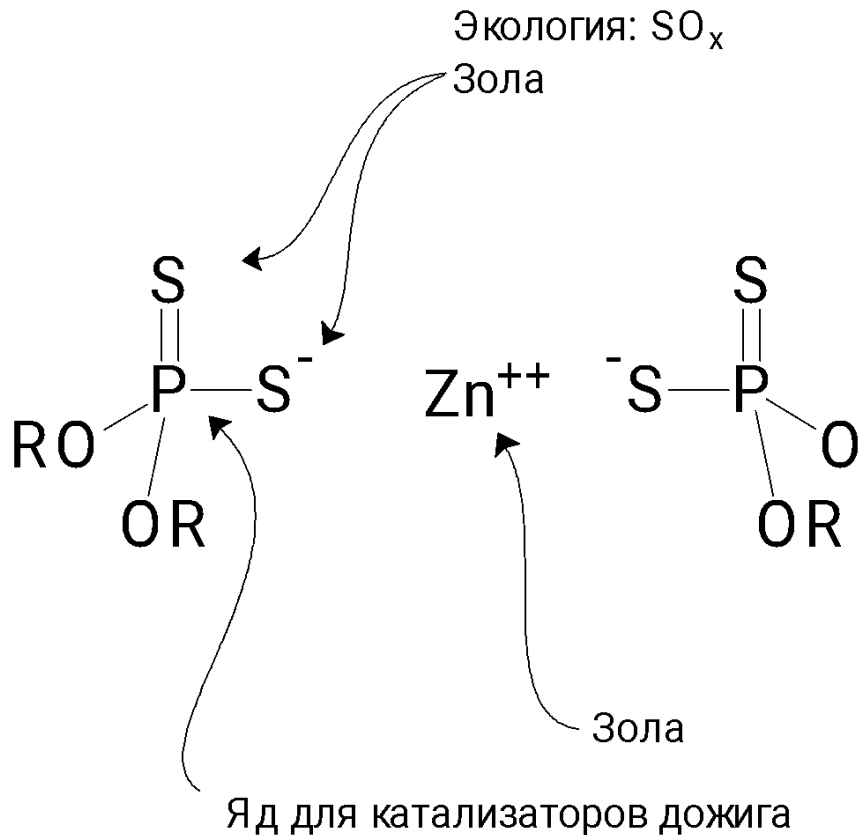
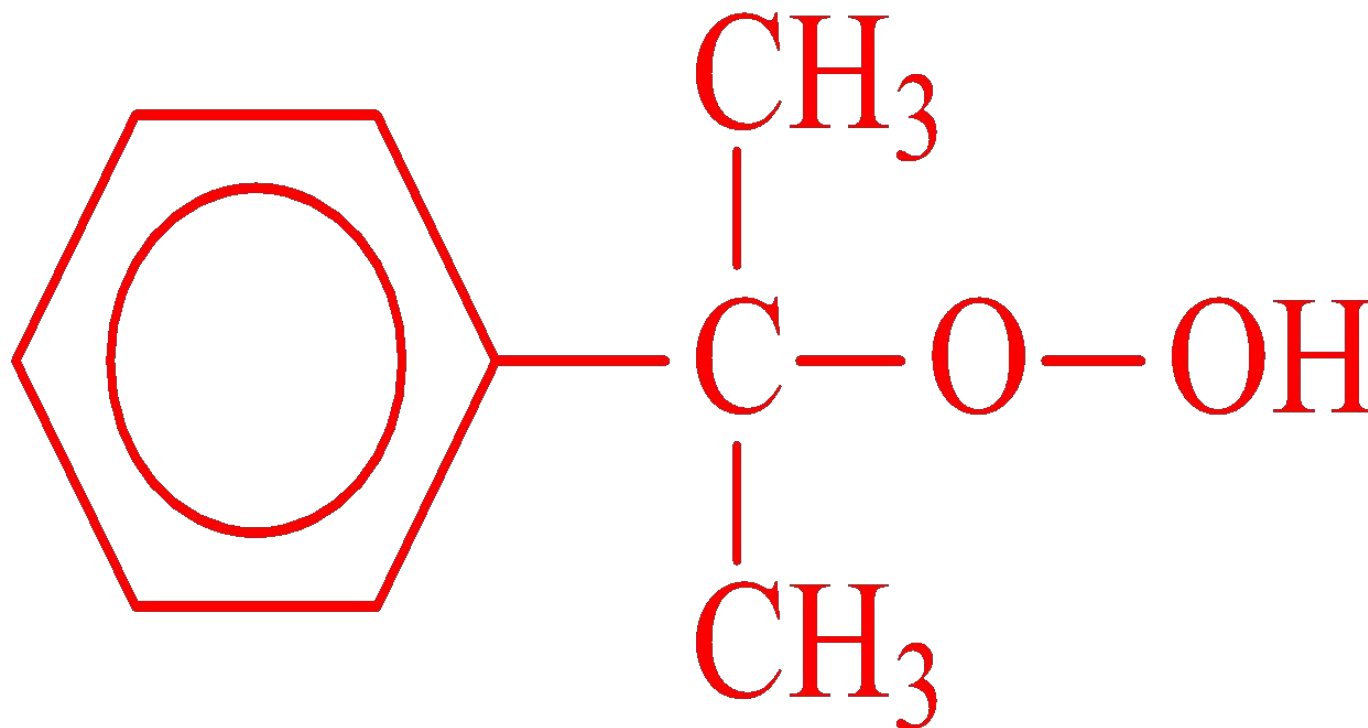


Fig 3 Artist's conception of growing film and ZDDP-rich region

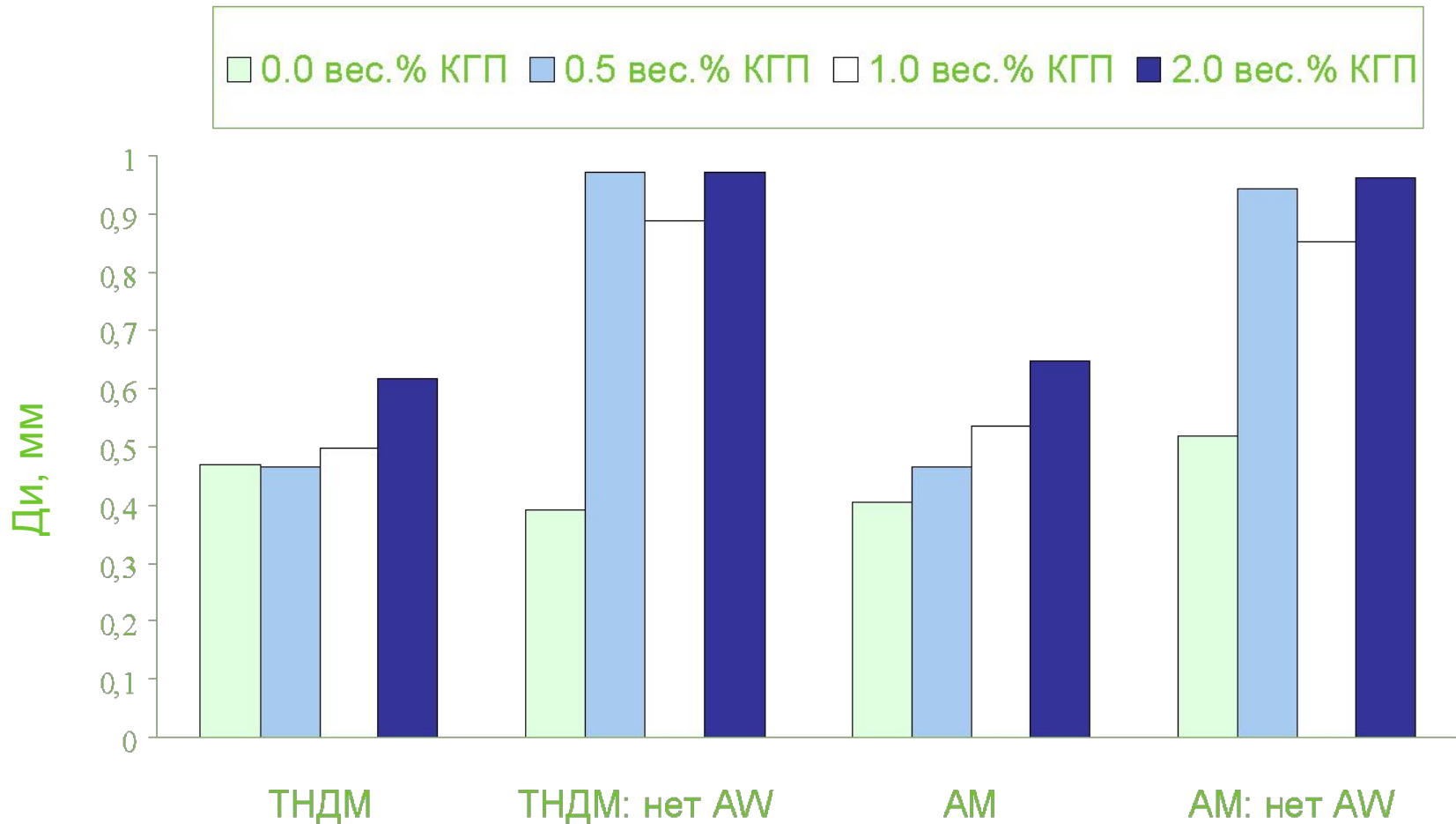
Willermet et al, Trib. Inter., 5/95

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

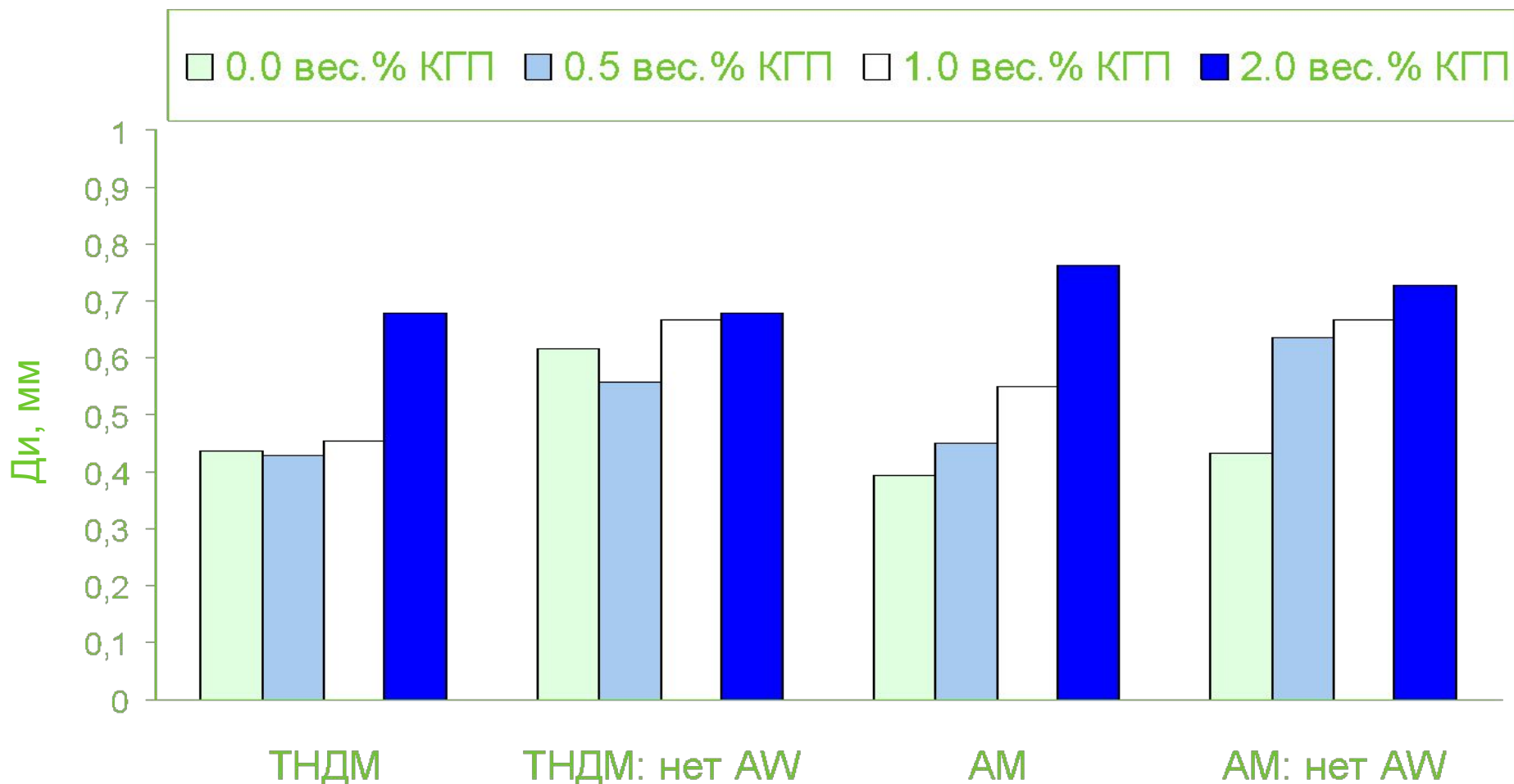
Cumylhydroperoxide (CHP)



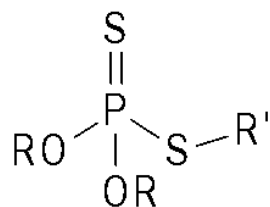
Effect of CHP on anti-wear properties of engine lubricants (four-ball test machine)



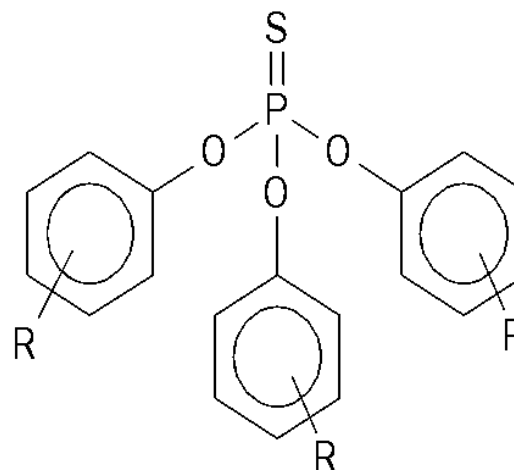
Effect of CHP on anti-wear properties of engine lubricants (Cameron-Plint)



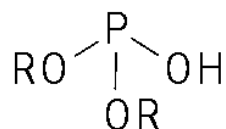
Ashless P-containing additives



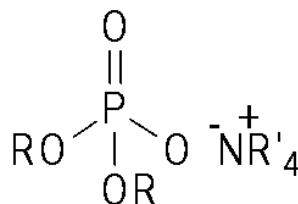
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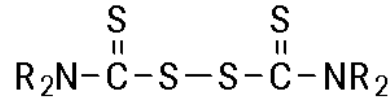


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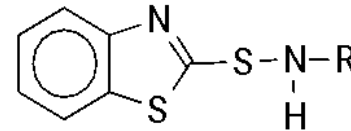


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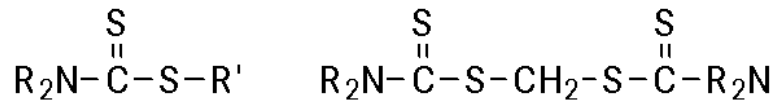
Phosphorus-free additives (All contain sulfur - SOx, sulfate ash)



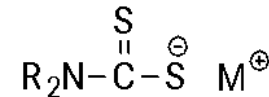
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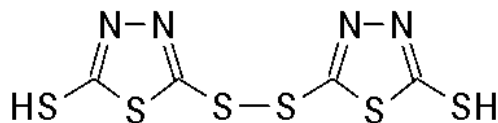
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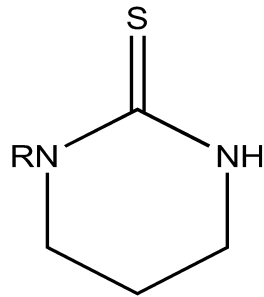


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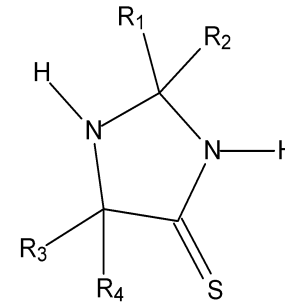
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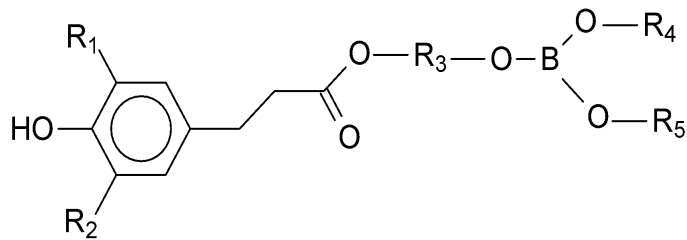
New anti-wear additives



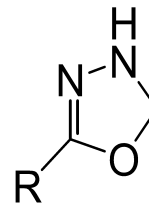
Cyclic thiourea



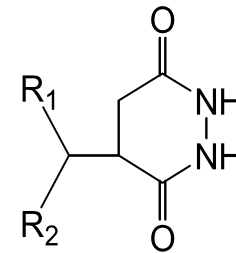
Imidazolidine thion



Imidazolidine thion

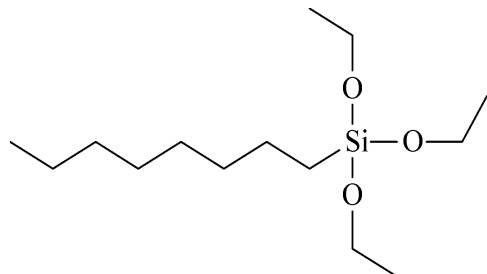


Oxamide

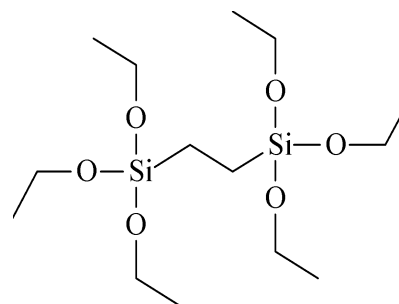


Hydrazide of succinic acid

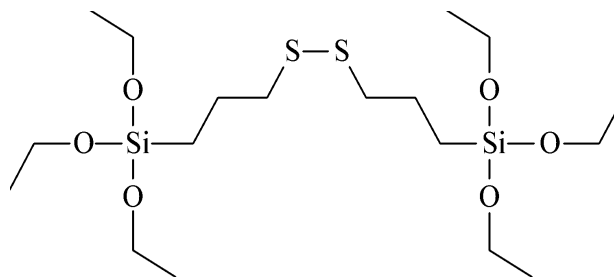
Silicon-containing compounds: Silanes/Siloxanes



Octyltriethoxysilane



Bis-(triethoxysilyl) ethane



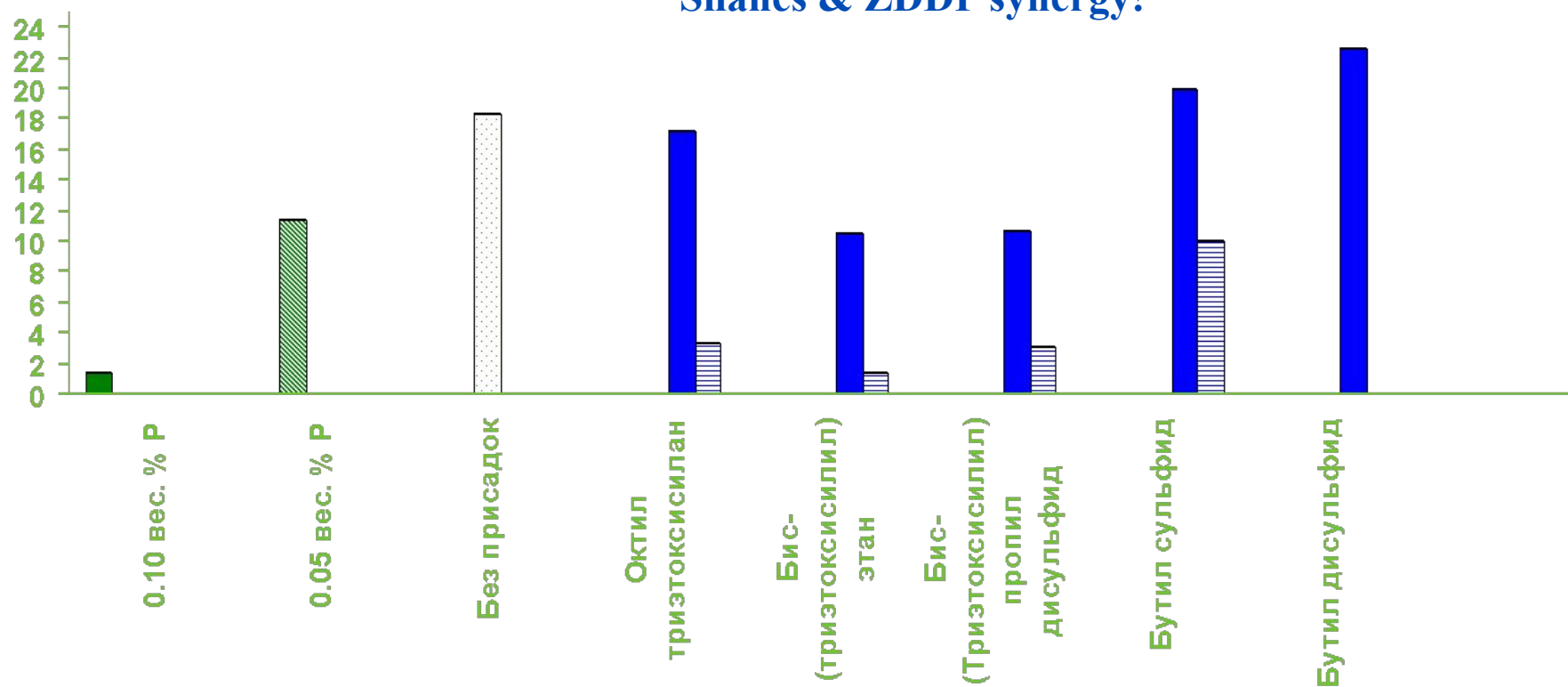
Bis-(triethoxysilyl) propyl disulfide

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

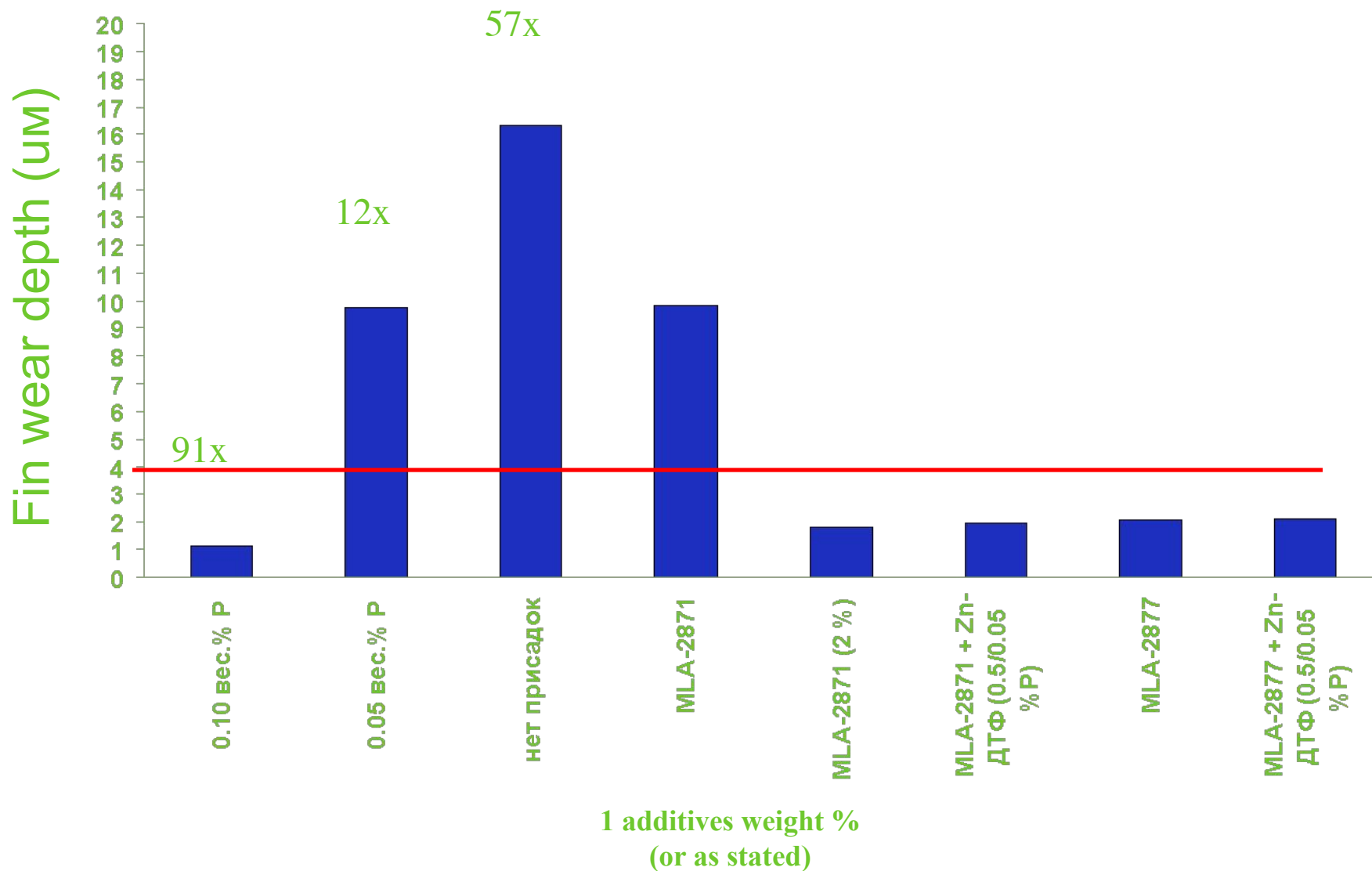
MLA-2871

- 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**