QUALITY WORKS.

Exploring additive interactions in complex lubricant formulations

Reducing tribological losses and failures – Workshop and panel discussion - STLE Toronto section

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November 14, 2018

LANXESS
Energizing Chemistry

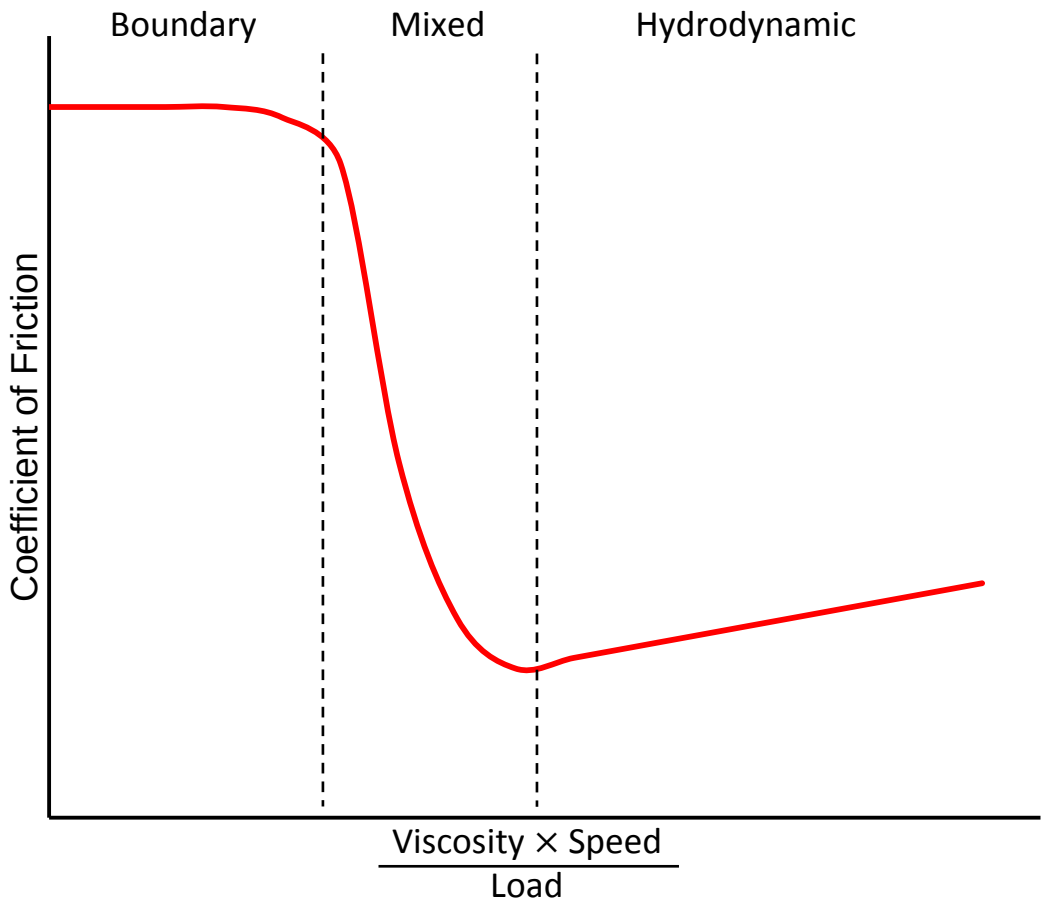
Friction and wear

- Wear mechanisms
  - Adhesion
  - Abrasion/Erosion
  - Corrosion
  - Surface fatigue
  - Fretting

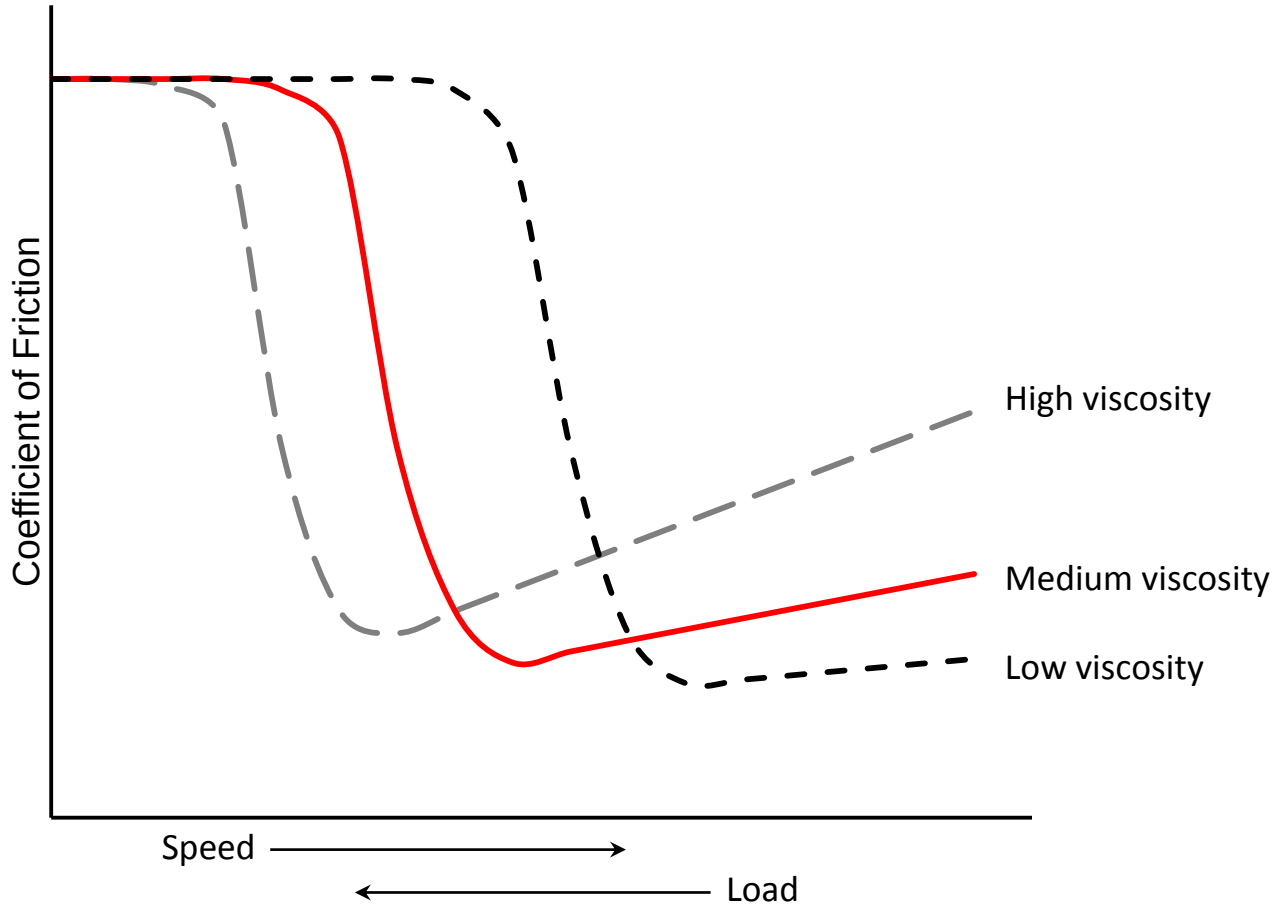
- Friction is caused by interactions at the surfaces of two parts.
  - Coefficient of friction is equal to friction force/normal force.

$$u = \frac{f_F}{f_N}$$

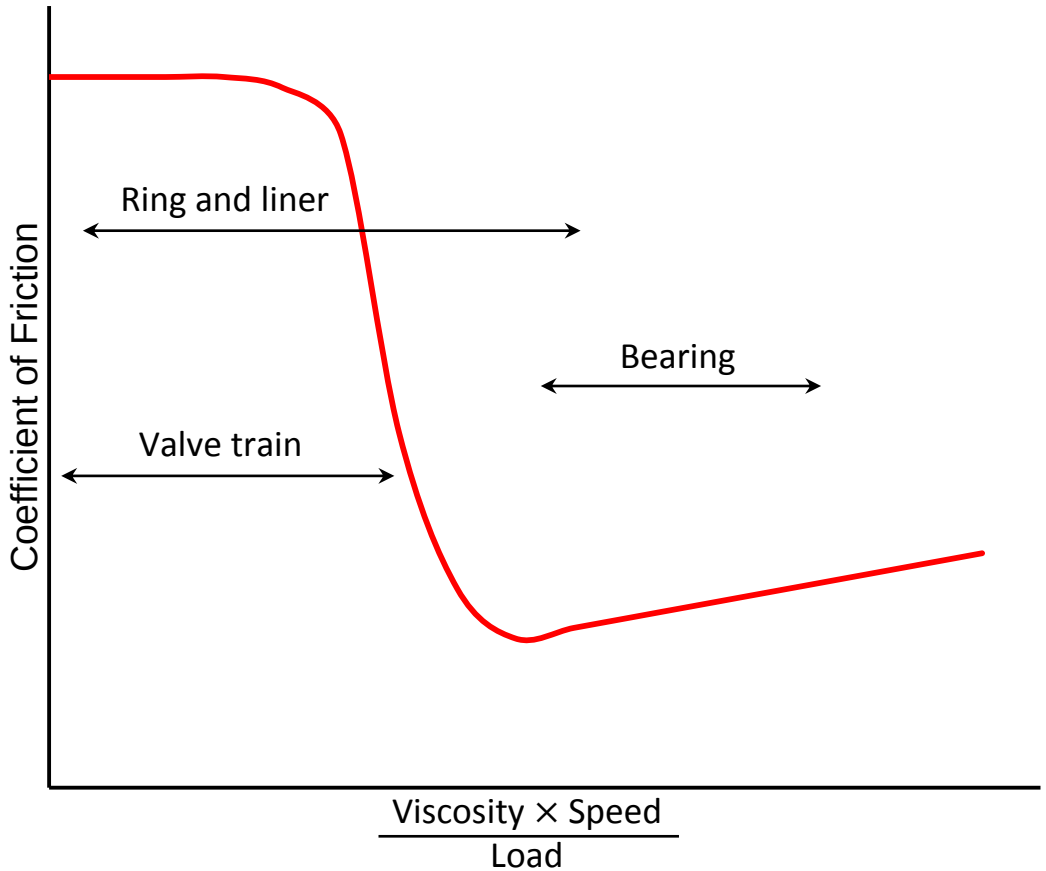
Stribeck curve



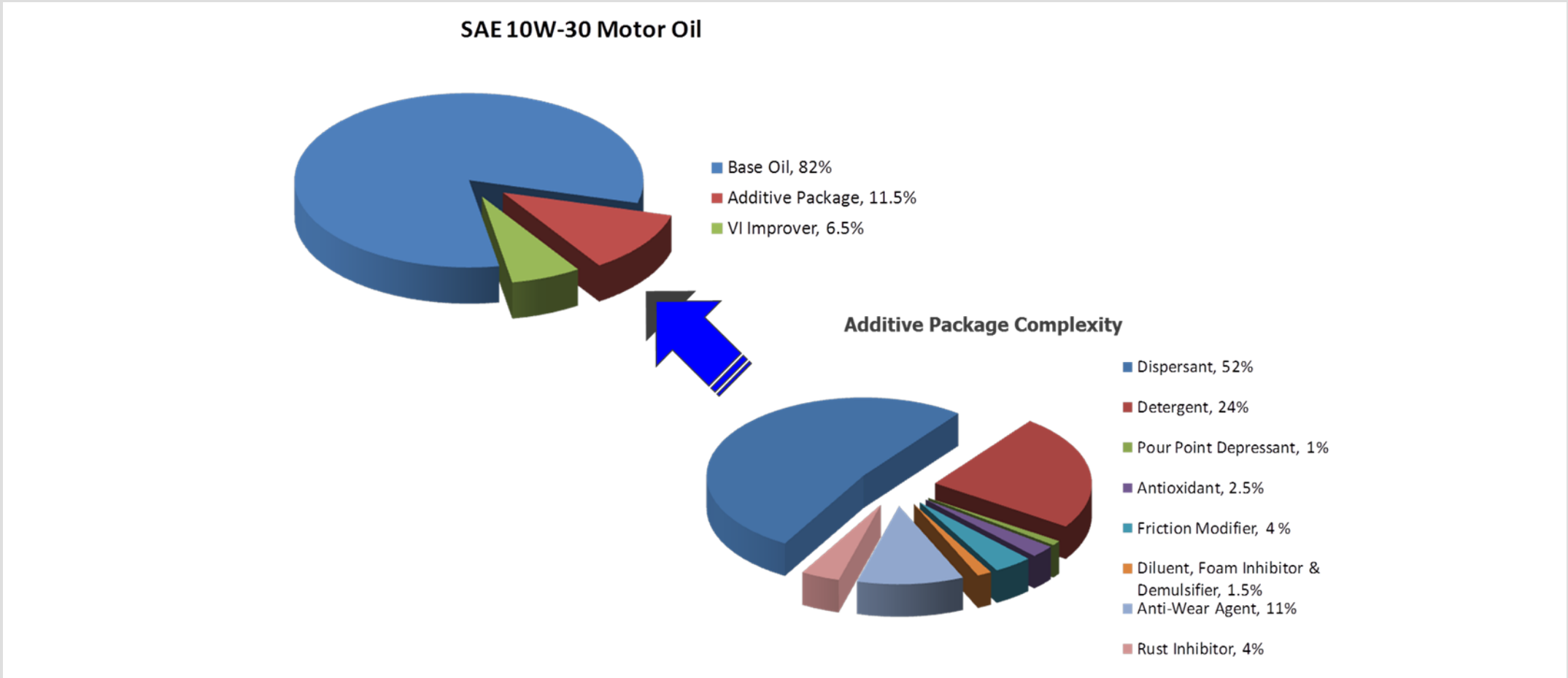
Lubricant viscosity effects



Stribeck curve regimes in an engine

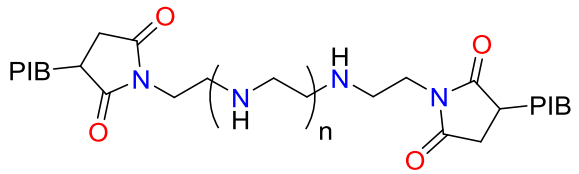


Engine oil composition

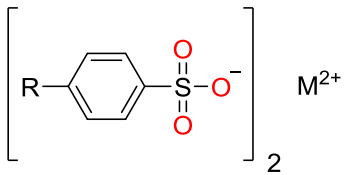


Additives chemistry

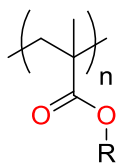
- Dispersants
  - Eg. polyisobutylene succinimide



- Detergents
  - Eg. low-base and high-base Ca and Mg alkylbenzene sulfonates



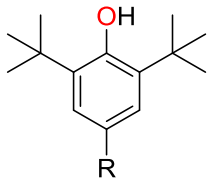
- Viscosity index (VI) improvers
  - Eg. polymethacrylates, ethylene-propylene copolymers
- Pour point depressants
  - Eg. polymethyl methacrylates

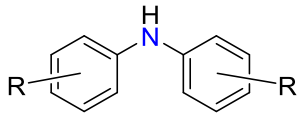


- Foam inhibitors
  - Eg. polysiloxanes

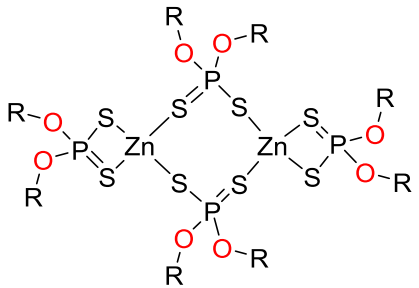
Additives chemistry

- Antioxidants
  - Eg. Hindered phenols and diphenyl amines

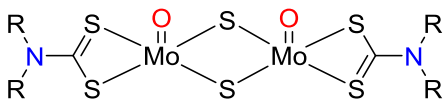


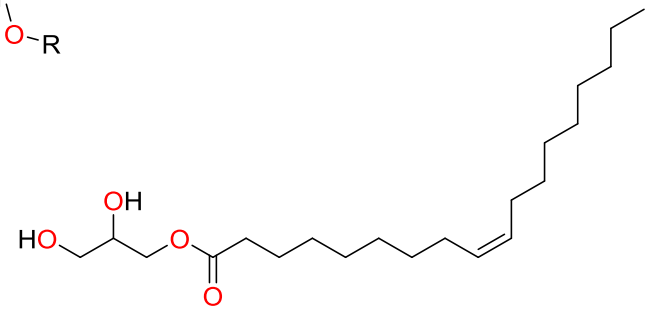


- Anti-wear additives
  - Industry standard: zinc dialkyldithiophosphates (ZDDP)

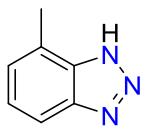


- Friction modifiers
  - Eg. Mo dithiocarbamates, Glycerol monooleate (GMO)





- Corrosion/rust inhibitors
  - Eg. tolyltriazole



Types of Antioxidants

Antioxidant Classification

Primary Antioxidants

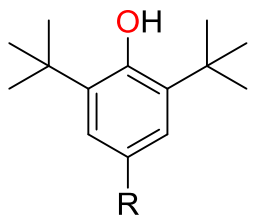
- ❑ Function as peroxide radical scavengers in oils.
- ❑ React with free radicals to form stable molecules that do not lead to further oxidation.
- ❑ Aromatic Amines – e.g. alkylated diphenylamines.
- ❑ Hindered Phenols – e.g. BHT.

Secondary Antioxidants

- ❑ Act by decomposing hydroperoxides.
- ❑ React with hydroperoxides to form stable alcohols without generation of additional reactive radicals.
- ❑ Phosphites, Sulfides, thiocarbamates, metal dithiocarbamates, zinc dialkyldithiophosphates (ZDDP's).

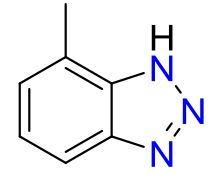
Tertiary Antioxidants

- ❑ Minimize the formation of catalyst species (oxidized metal or metal surfaces such as Fe, Co & Cu, dirt).
- ❑ Typically added as metal deactivators.
- ❑ Function as ferrous and non-ferrous metal passivators .
- ❑ Supplement the performance of antioxidants.
- ❑ Aromatic triazoles (TTA), substituted thiadiazoles and azoles.



Typical Usage (0.1% - 1.5%)

- Aminic for higher temperatures (> 120 °C), phenolic for lower temperatures (< 120 °C).
- Amines + phenols can give synergistic antioxidant effects.
- Primary + secondary can give synergistic antioxidant effects.



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ZDDP – A multifunctional additive

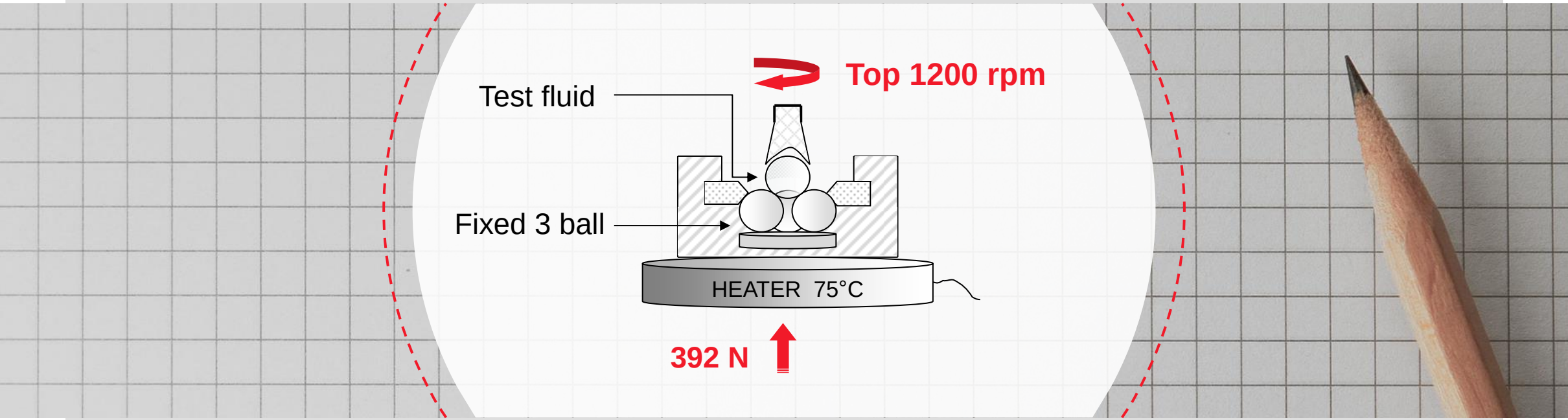
- Anti-wear properties
  - Protective tribofilm is formed during operation.
    - Tribofilms form at rubbing points of contact as a result of thermal degradation of the ZDDP.
    - Tribofilms are composed of Zn and Fe phosphates and polyphosphates.

- Secondary antioxidant properties
  - ZDDP also acts as a secondary antioxidant.
    - Peroxide decomposer.
    - Oxidized by-products are no longer effective anti-wear additives.

Spikes, H. *Tribology Letters* **2004**, *17*, 469-489.

Bench tribology testing: Four ball wear

ASTM D4172 (Average wear scar test)



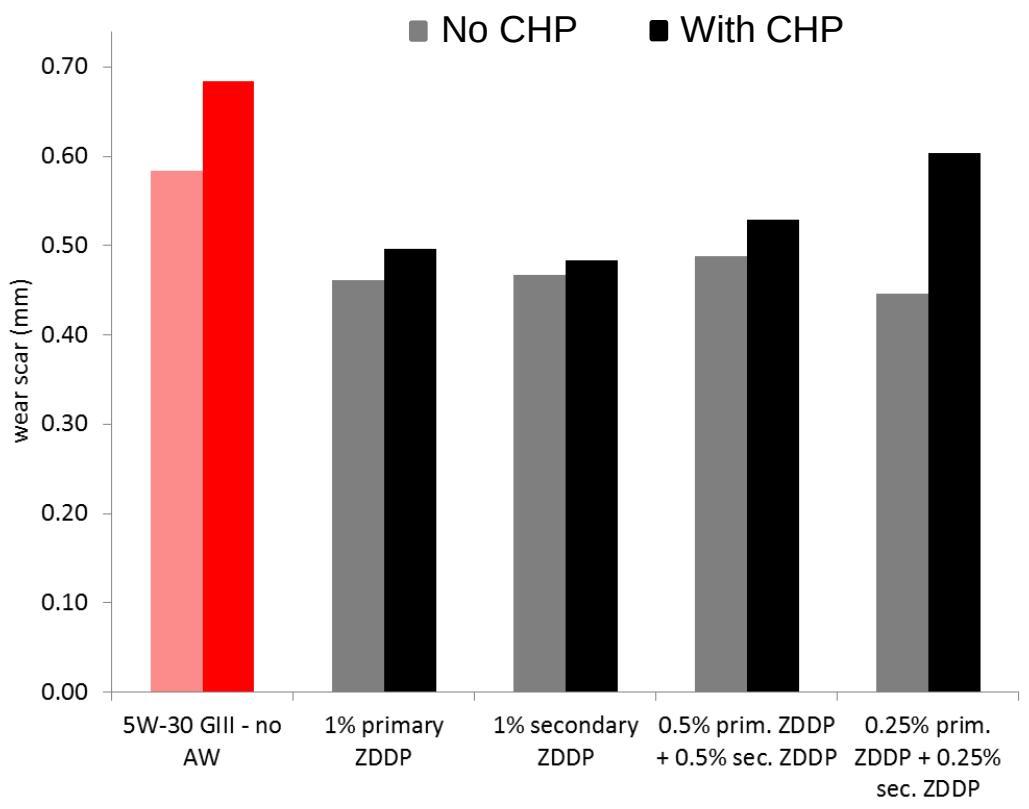
Test conditions				
Load: Newtons (N), kg	**Temperature (°C)**	**Rotation rate (rpm)**	**Test-time (h)**	**Measurement (mm)**
392 N, 40 kg	75 °C	1,200 rpm	1.0 h	Average wear scar over 3 balls, 2 dimensions

CHP impact on anti-wear performance

4 ball wear test

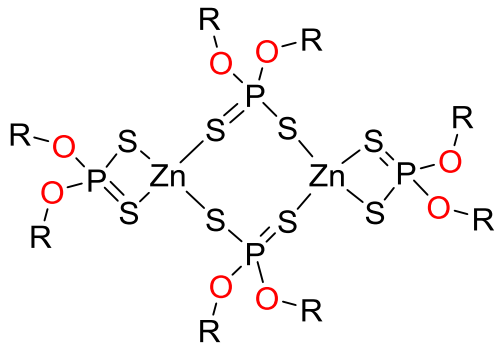
- SAE 5W30 test oil with no anti-wear additives.
- Conditions:
  - 40 kg load, 75 °C, 1200 rpm, 1 h.
  - Optional pro-wear reagent.
    - Cumene hydroperoxide (0.615 wt %)
- Cumene hydroperoxide (CHP) is used to simulate oil aging.

Comparison of ZDDPs

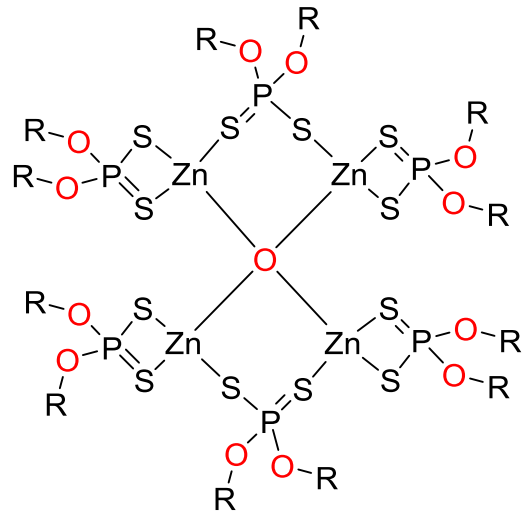


ZDDP structures

- ZDDP solution structures:



'neutral'
bimetallic
P:Zn ratio = 2:1



'basic'
tetrametallic
P:Zn ratio = 3:2

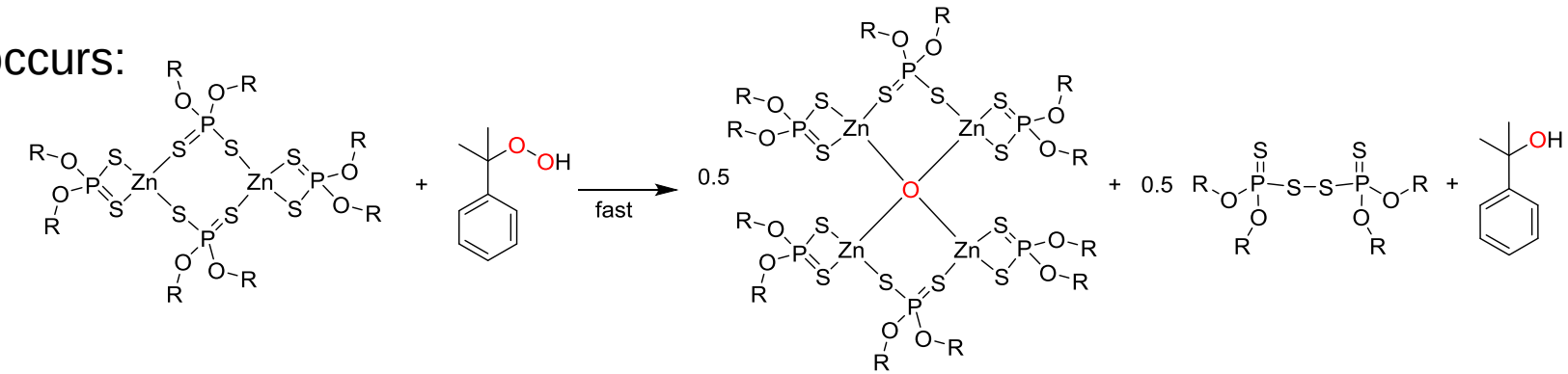
- Commercial products are typically a mixture of neutral and basic.
  - Typically R = primary and secondary alkyls (C_3 to C_8).

Harrison, P. G.; Kikabhai, T. *J. Chem. Soc. Dalton Trans.* **1987**, 807-814.

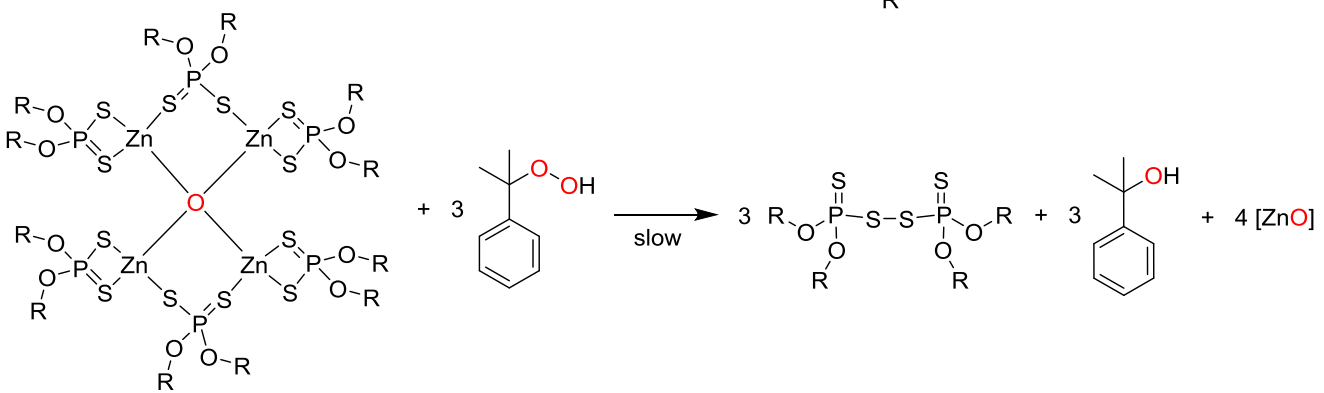
ZDDP oxidation

- ZDDP acts as a secondary antioxidant.
  - Hydroperoxide scavenger.
- A two-step reaction occurs:

Step 1:

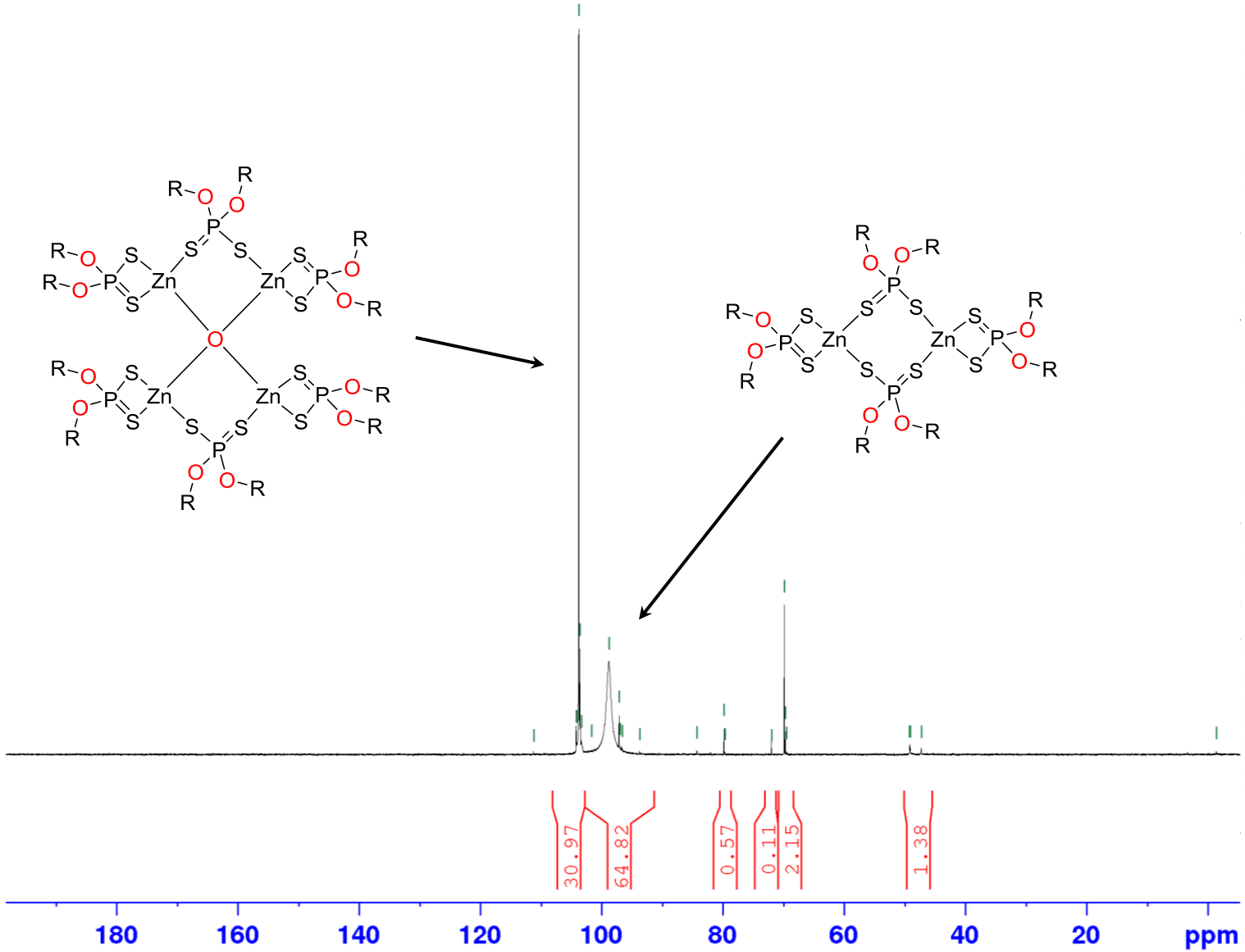


Step 2:



Spikes, H. *Tribology Letters* **2004**, *17*, 469-489.

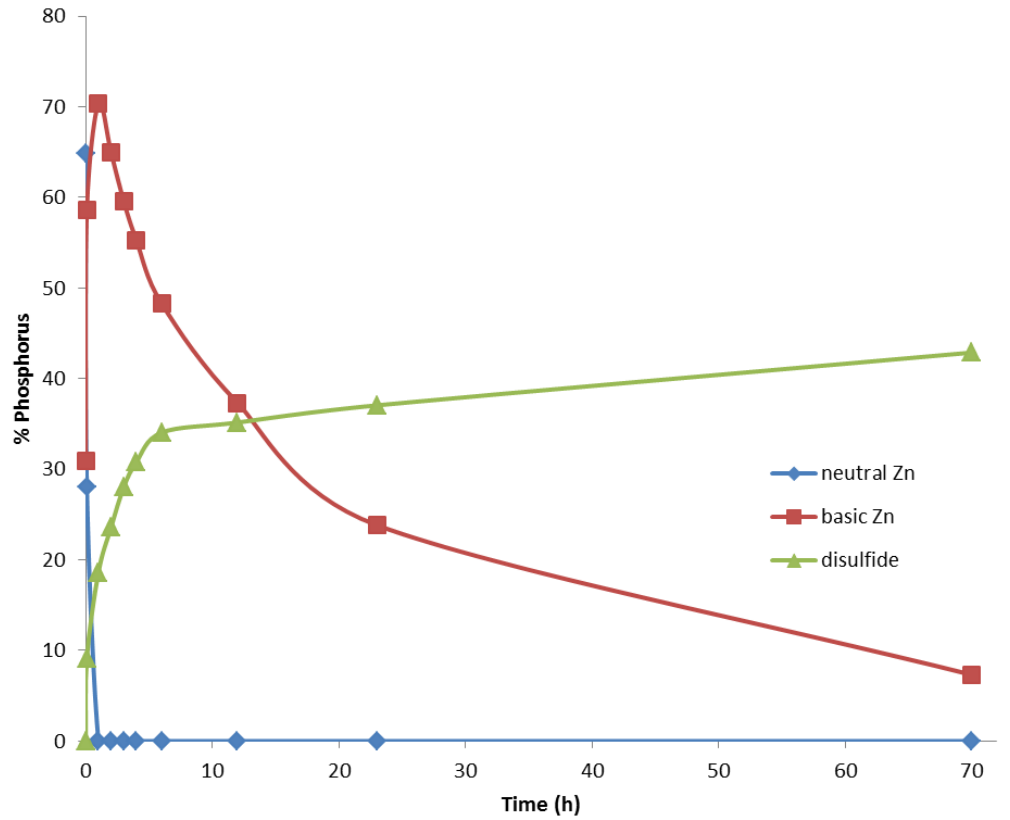
^{31}P NMR spectroscopic characterization of ZDDP



Reaction of ZDDP + cumene hydroperoxide

- Reaction of CHP/Zn with mole ratio of 2.5:1 monitored by ^{1}H and ^{31}P NMR.
  - ZDDP reacts with CHP in a 1:1 mole ratio.
  - Unreacted CHP remaining after 70 h.
    - Observed in ^{1}H NMR spectrum.
  - White ppte forms.
  - 'Neutral' Zn complex reacts rapidly with CHP.
    - Forms 'basic' Zn complex.
  - 'Basic' Zn complex reacts slowly.
    - Forms diphosphate disulfide complex and ZnO.

Rxn in toluene at ambient temperature



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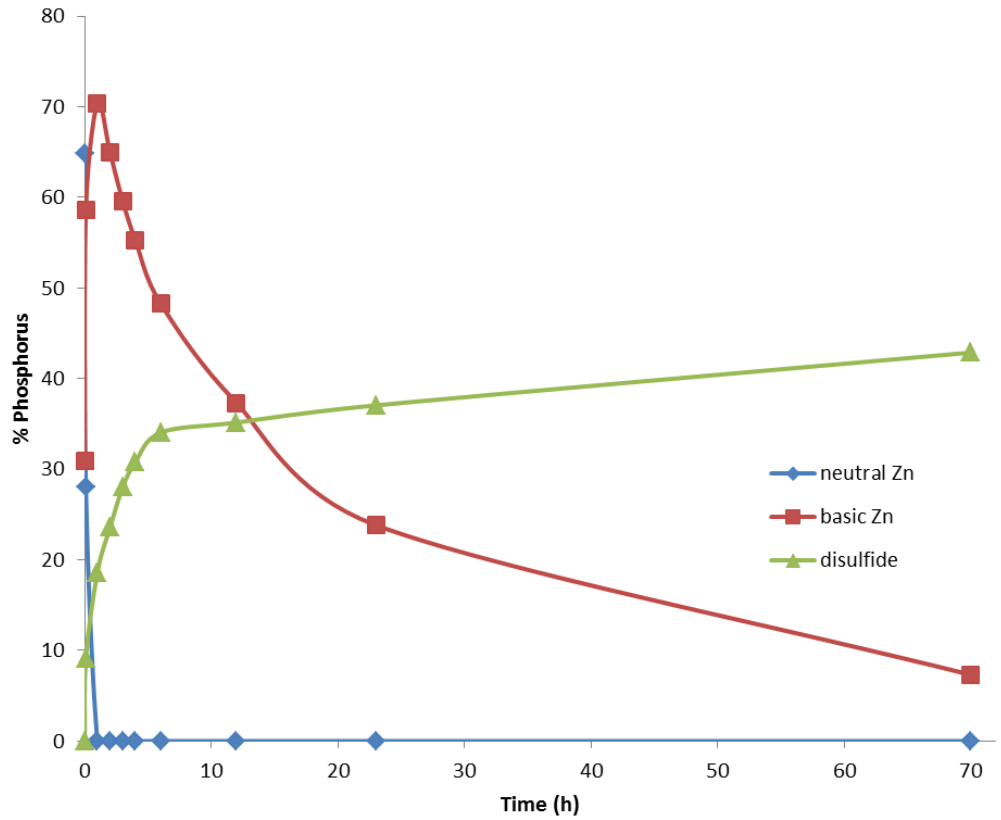
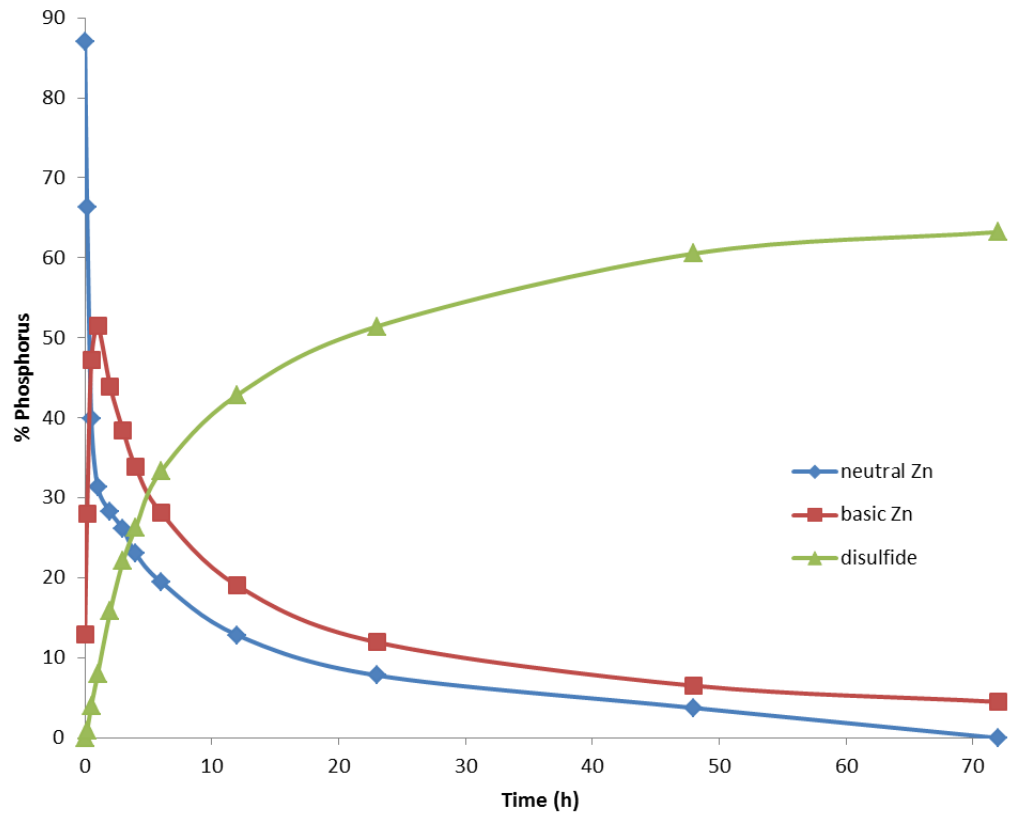
Oxidation of primary and secondary ZDDP

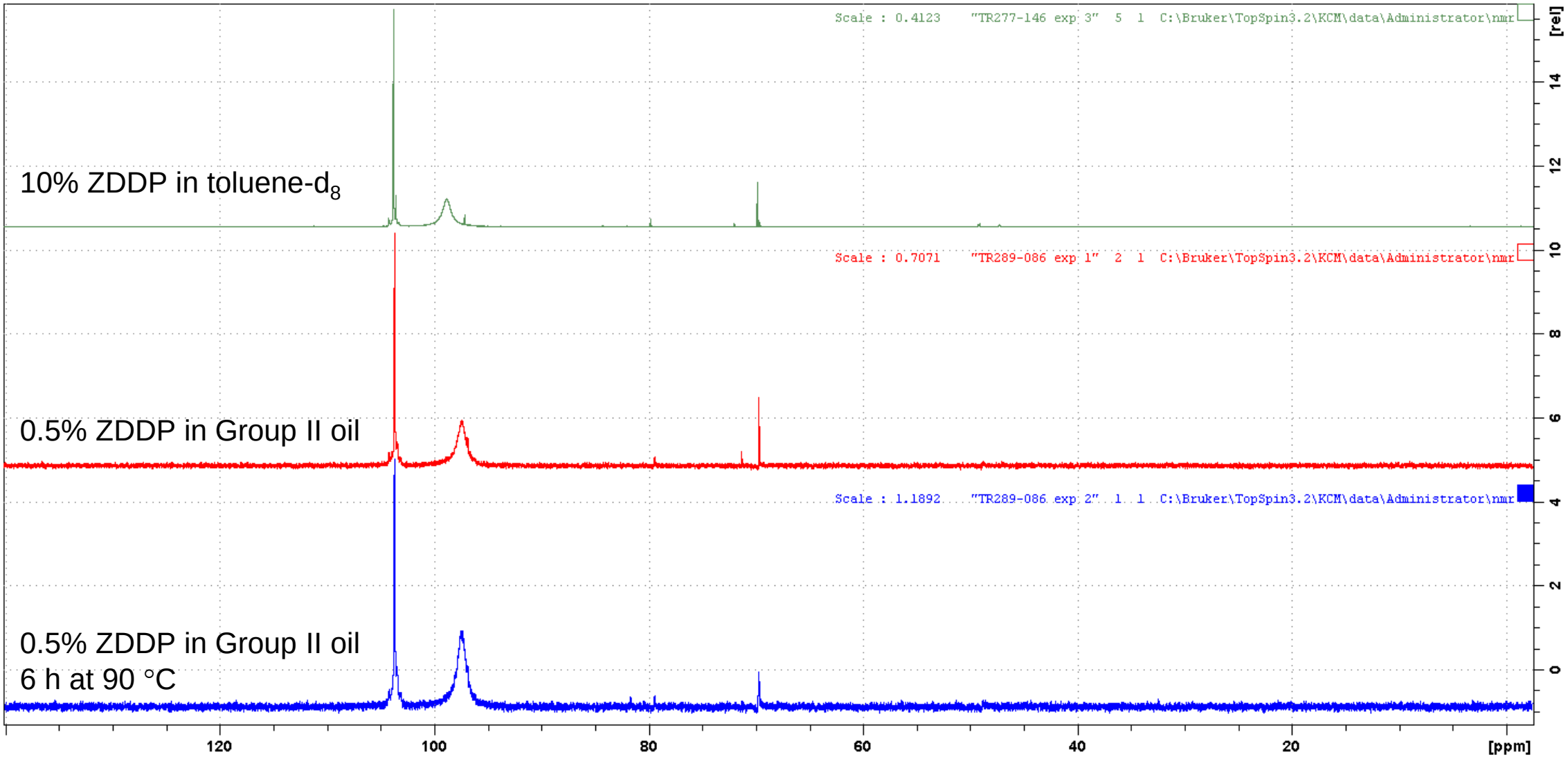
Primary alkyl ZDDP + CHP



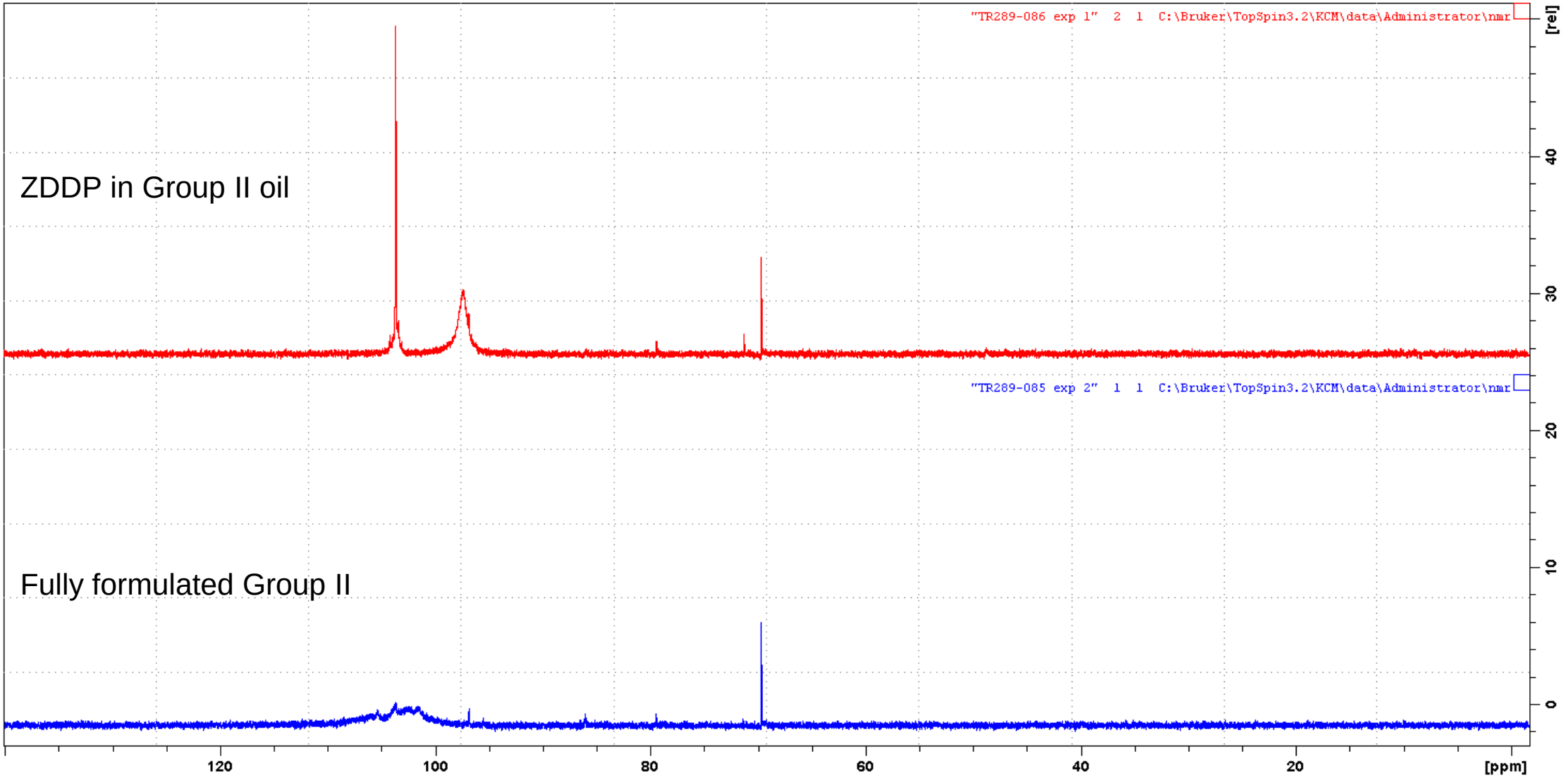
Secondary alkyl ZDDP + CHP



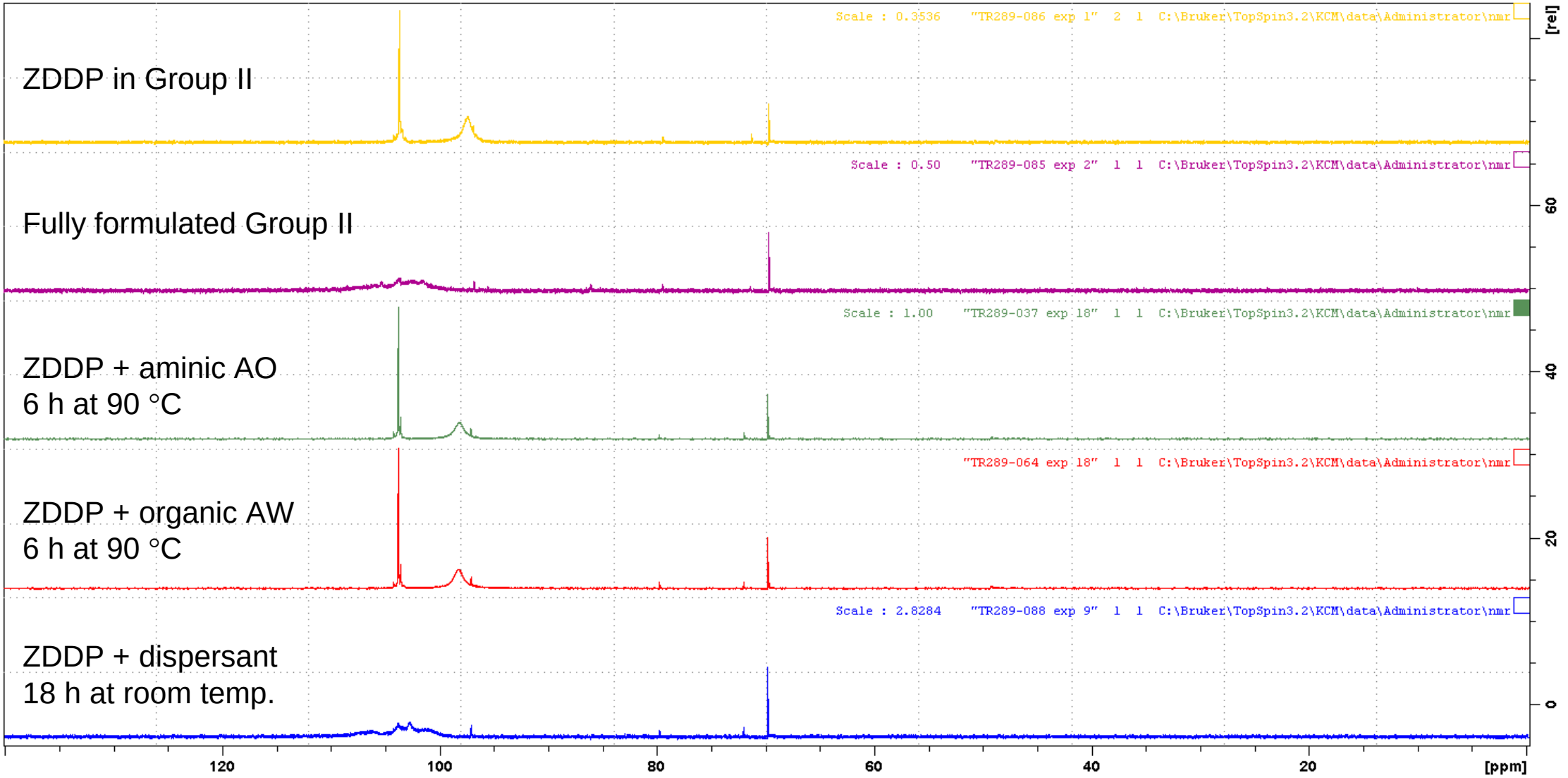
^{31}P NMR of ZDDP in oil



^{31}P NMR of ZDDP in fully formulated oil



Analyzing individual component interactions



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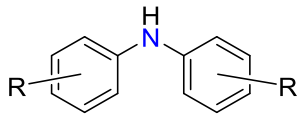
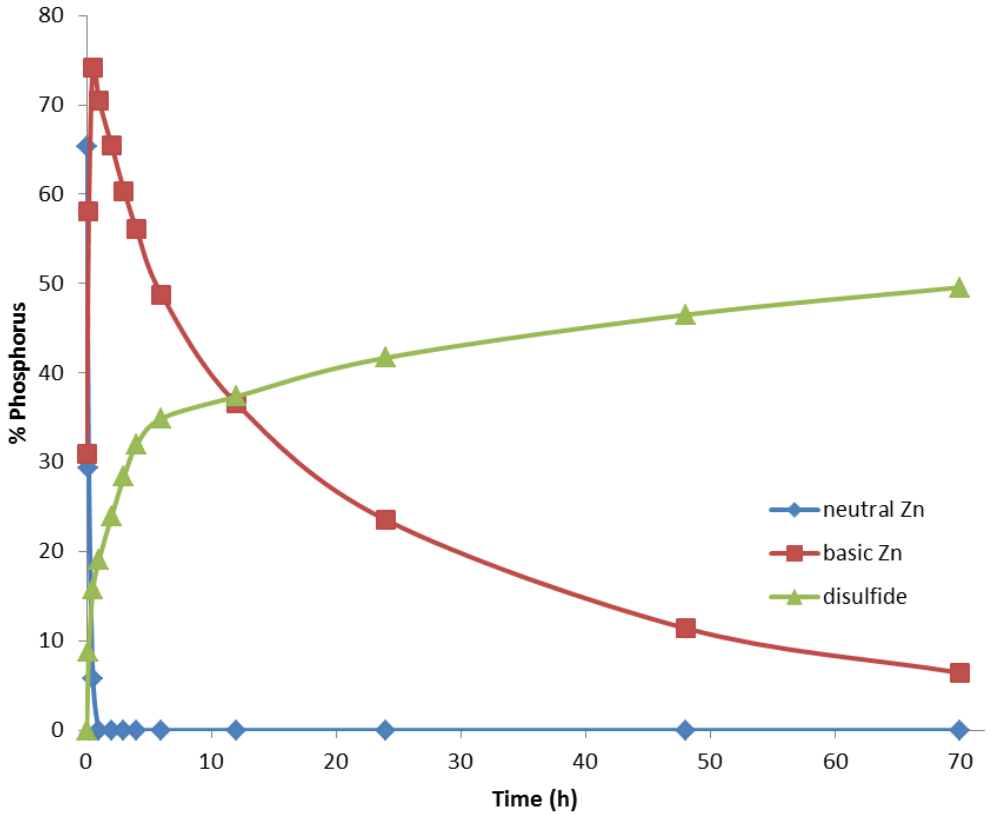
ZDDP + CHP in the presence of an aminic antioxidant



- Used wt. ratio 1:1:0.615 of ZDDP/AO/CHP.
  - Mole ratio ~ 1:2:2.5.
- No change in ZDDP oxidation in presence of AO.
  - Aminics are primary antioxidants.
- Approx. 50% unreacted CHP after 70 h.
  - CHP does not react directly with the aminic AO.

Rxn in toluene at ambient temperature



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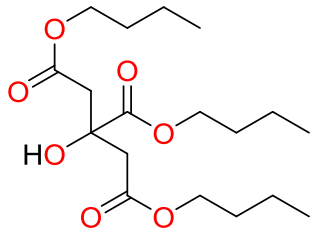
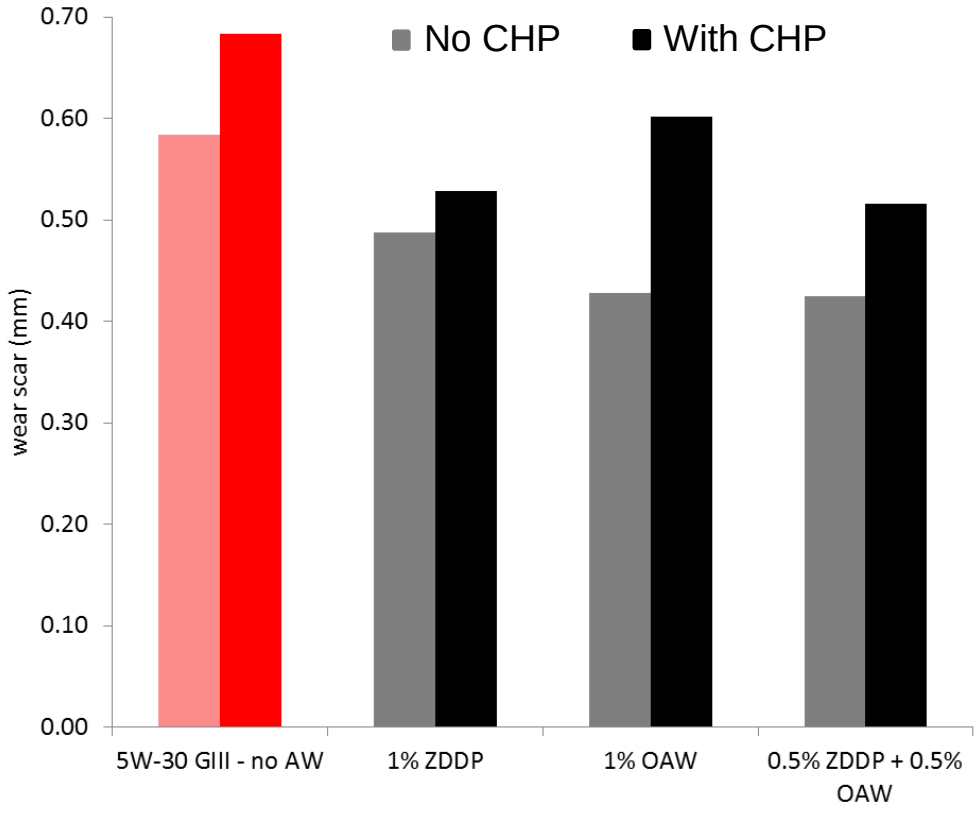
ZDDP combination with an organic anti-wear additive



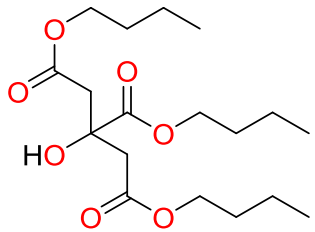
- Tributyl citrate organic anti-wear (OAW) additive.
  - No solution interaction with ZDDP observed by NMR spectroscopy.

- Conditions:
  - 40 kg load, 75 °C, 1200 rpm, 1 h.
  - Optional pro-wear reagent.
    - Cumene hydroperoxide (0.615 wt %)

4 ball wear test

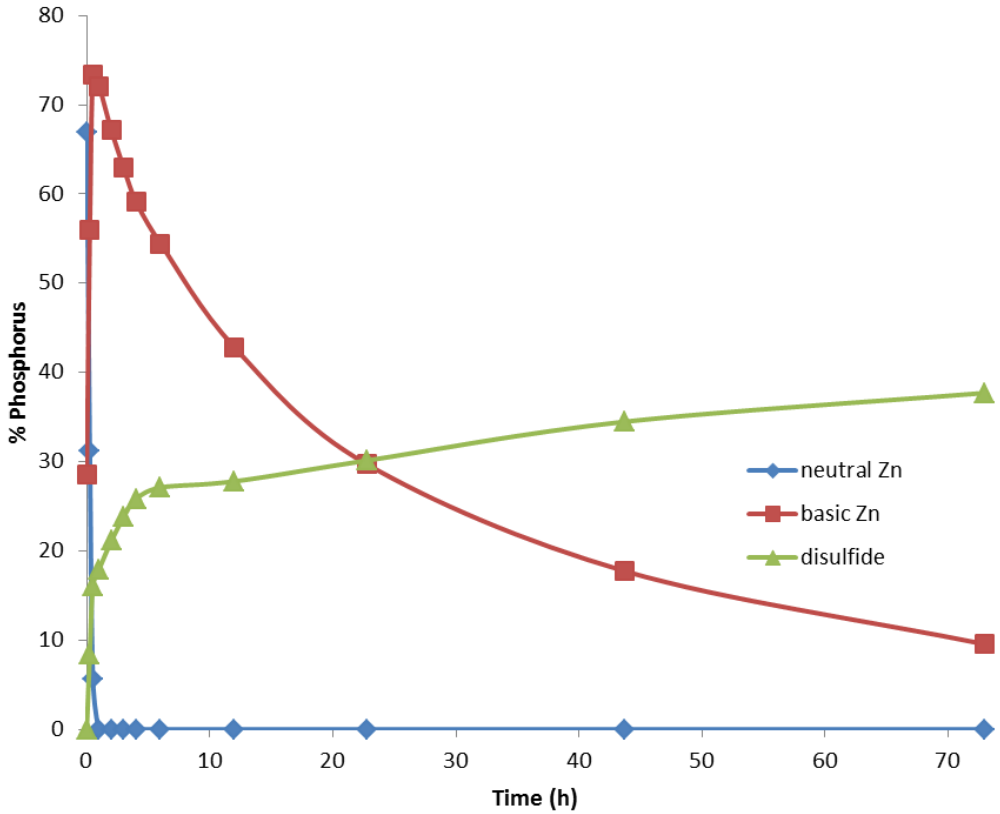


ZDDP + CHP in the presence of an organic anti-wear additive



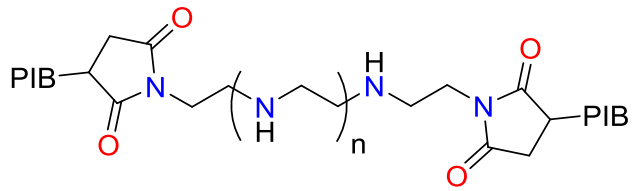
- Used wt. ratio 1:1:0.615 of ZDDP/OAW/CHP.
  - Mole ratio ~ 1:2:2.5.
- No change in ZDDP oxidation in presence of OAW.
- Approx. 50% unreacted CHP after 73 h.
  - CHP does not react directly with the tributyl citrate.

Rxn in toluene at ambient temperature



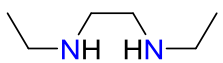
ZDDP combination with a succinimide dispersant

- PIB succinimide dispersants are well-known ZDDP antagonists.
  - Higher succinimide base number gives stronger interaction.
    - Leads to lower anti-wear performance.
  - Proposed Zn binding to the secondary amine.



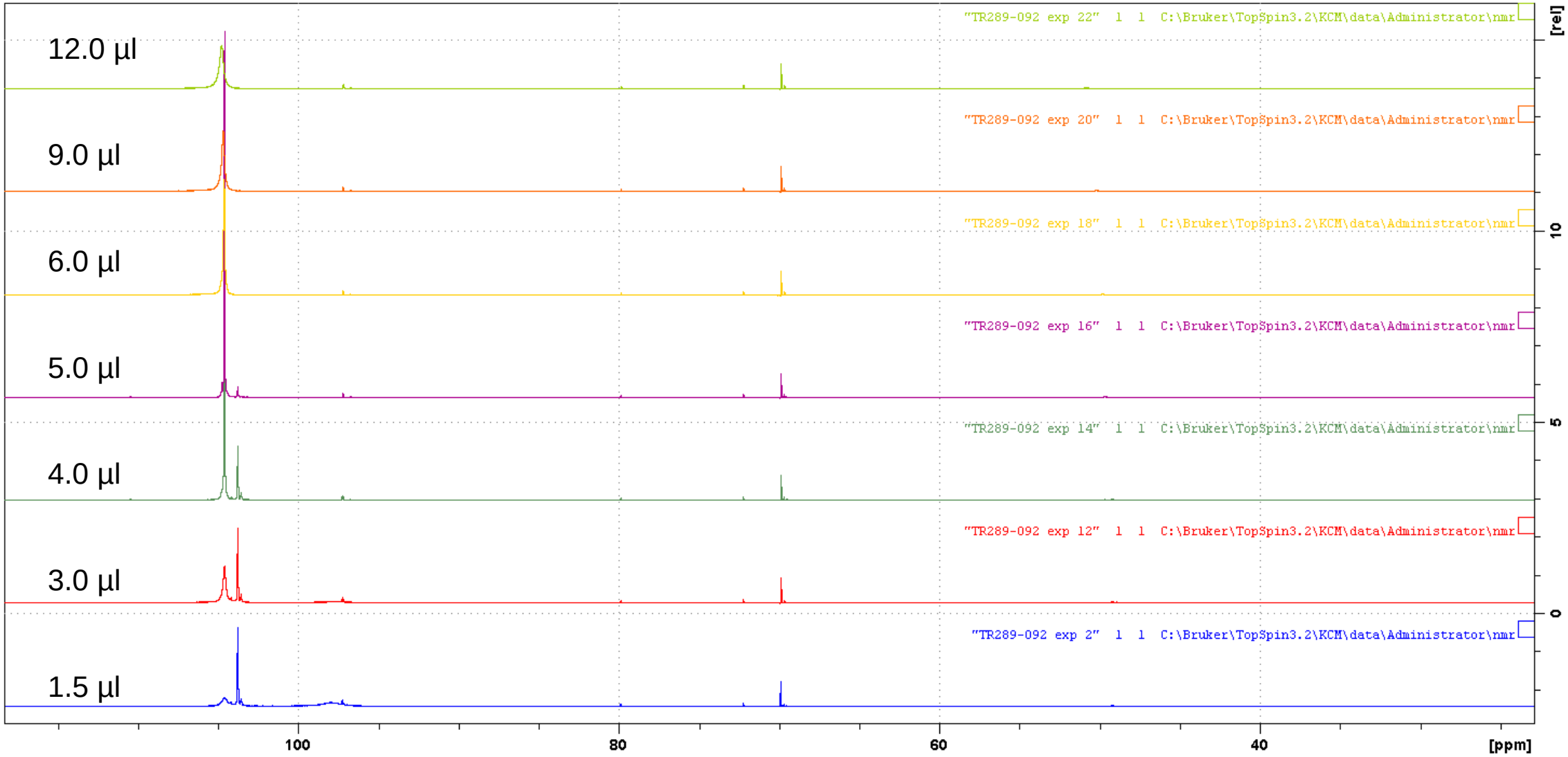
- Dispersant passivation is commonly used.
  - Eg. PIB succinimide reaction with boric acid.

- Difficult to evaluate ZDDP oxidation in presence of dispersant.
  - Dispersant is a mixture of amine compounds.
  - Model compounds are easier to study.
    - Eg. *N,N`*-diethylethylenediamine



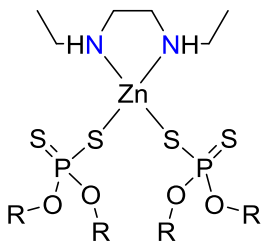
Bartha, L.; Deak, G.; Kovacs, M.; Kocsis, Z.; Vuk, T. *Lubr. Sci.* **1997**, *9*, 173-180.
Yamaguchi, E. S.; Onopchenko, A.; Francisco, M. M.; Chan, C. Y. *Tribol. Trans.* **1999**, *42*, 895-901.

^{31}P NMR of ZDDP + diamine

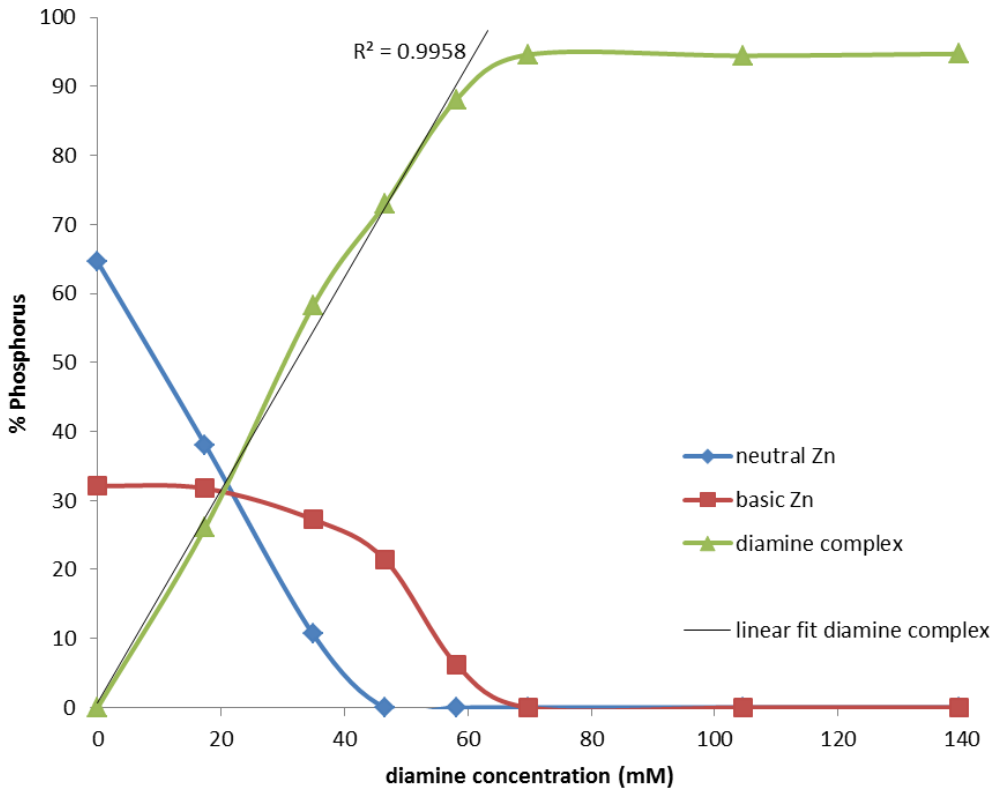


ZDDP + diamine

- Rapid binding is observed.
  - Reaction complete in < 30 min.
  - New peak in ^{31}P NMR at 104 ppm.
    - Assigned to the $Zn[(S_2P(OR)_2]_2$diamine complex.
- Neutral Zn complex reacts preferentially with diamine before basic Zn complex.
- Binding curve indicates 1:1 ratio of diamine/Zn.



Binding curve



Summary

- Additive interactions are common in complex lubricant formulations.
  - Understanding additive interactions allows for optimization of lubricant formulations.
- ZDDPs are a mixture of neutral and basic Zn structures in solution.
- Other additives can influence the ZDDP solution structures.
  - Eg. PIB succinimide dispersants.
- ZDDP performance can be influenced by other additives.
- ZDDP is oxidized by reaction with CHP at ambient conditions.
  - NMR spectroscopy is an effective way of monitoring oxidation of ZDDP.

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