FUNCTIONAL HF-
Biobased Hydraulic Fluid Packages

February 2021

Biobased Hydraulic Fluid

- Different targets:
  - **Biodegradable** – >60% by OECD, CEC, ASTM, etc.
  - **Environmentally acceptable lubricant (EAL)**
    - biodegradable plus low aquatic tox, non-bioaccumulative
    - VGP, Ecolabel, Safer Choice/DftE
  - **Biobased** – varying % minimum
    - **USDA Biopreferred** – >44% biobased carbon content
    - **Ecolabel** – >25%

FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

Recent HF History

- HF-580
  - 2.5wt% treat
  - Industrial package using components not limited by EAL approval
  - Sulfur / Phosphorus / Ester chemistry

- HF-590
  - 5.4wt% treat, obsolete after the 2018 Ecolabel rewrite
  - Ecolabel package using components applicable to European Ecolabel

- HF-595
  - 2.2wt% treat, Ecolabel listed
  - Low treat Ecolabel package designed as a starting point
  - Ca / Sulfur / Ester chemistry

HF-595 as Starting Point

- HF-590
  - 5.4wt% treat was ‘fully formulated’ for vegetable oil hydraulic fluids
  - High treat of antioxidants and custom defoamer/demulsifier blend

- Redesign for HF-595
  - New thinking
  - A general-purpose low treat EAL HF package that will go into veg oil, PAO, PAG, synthetic ester, etc.
    - Different base fluid chemistries need different types and levels of AO, defoamer, demulsifier

FUNCTIONAL HF

	Ecolabel?	Treat Level	Chemistry	Elements	Needs… *
HF-580	No	2.5 wt%	Ashless	Sulfur / Phosphorus / Nitrogen	None
HF-595	Yes	2.2 wt%	Low Ash	Sulfur / Calcium (0.19%)	Defoamer Demulsifier
HF-5XX	Yes	1.5 wt%	Mid Ash	Calcium (2%) / Sulfur	Defoamer

* Some EAL HF packages are formulated without defoamer or demulsifier since various EAL base fluids will require different DF/DM

FUNCTIONAL DF

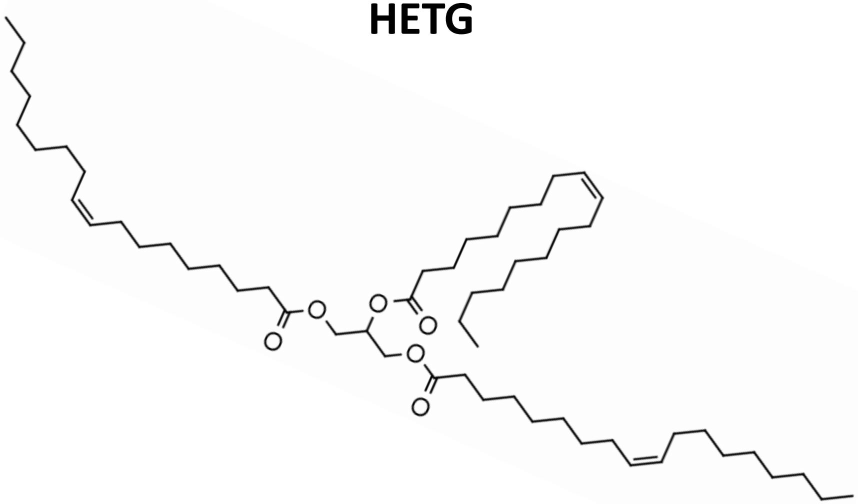
- Portfolio of EAL and sometimes NSF HX-1 defoamers
  - Low flammability for worker safer
  - No kerosene
  - No aquatic toxicity

- **FUNCTIONAL DF-400** is silicone-based defoamer for most base fluids
  - Ecolabel LuSC and NSF HX-1

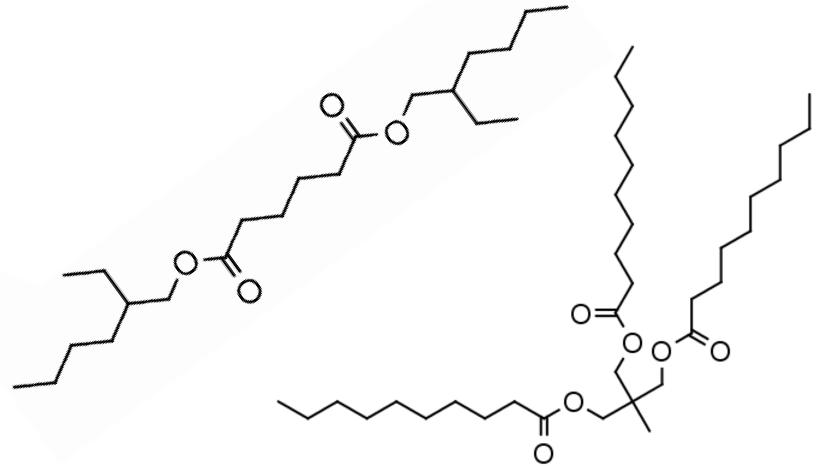
- **FUNCTIONAL DF-500** is acrylate-based defoamer for veg oils, fatty esters
  - Ecolabel LuSC

EAL Base Fluid Structures

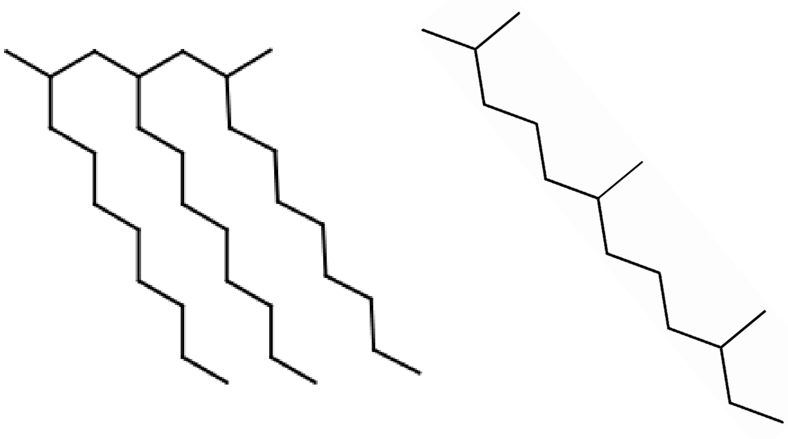
HETG



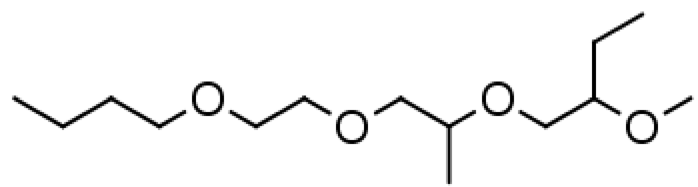
HEES



HEPR



HEPG



WS = EO/PO
WI = PO
OS = BO

Specific Needs of EAL Fluids

- ISO 15380 specifies four categories of EAL base fluids for HF
- Ranking: 4 is best; 1 is worst
  - Based on typical product datasheets and literature, not official

	Oxidative Stability	Hydrolytic Stability	Biodegradable	% Biobased	Low Temp	Cost	Anti wear	Foam	Demulsibility	Viscosity Grades Produced
Vegetable Oil (HETG HF)	1	1	4	4	1	4	4	1	2	1 (only 32)
Synthetic Ester (HEES HF)	3	2	3/2	3/2	3/4	1/2	3	2	3	2 (22
PAO (HEPR HF)	4	4	1	2/3	4/3	3	1	3	4	3/4
PAG (HEPG HF)	2	3	2/3	1	2	2/1	2	4	1	4/3

Comparison

- Formulating requires solving different challenges in performance and cost
  - Each EAL type will make certain challenges easier and others harder

	Key Advantages	Biggest Obstacles
Vegetable Oil (HETG HF)	Easy to meet 'readily biodegradable' and any % biobased for any ISO VG Lowest cost EAL base fluid by big margin	Hard to improve on oxidative stability Extra additives to make performance competitive can add cost
Synthetic Ester (HEES HF)	Wide variety of base fluids to suit specific needs	Hard to find one ester with all the properties you want ("iron triangle")
PAO (HEPR HF)	Great oxidative and hydrolytic stability and low temp fluidity Easy to translate know-how from industrial PAO HFs	Hard to meet 'readily biodegradable' above ISO 32
PAG (HEPG HF)	Easy to meet antiwear performance High biodegradability at ISO 46	Additive incompatibility, foam Hard to demulsify water Low to no % biobased content

Other Considerations

- Seal compatibility
  - PAO can shrink seals
  - PAG or synthetic ester can swell seals

  - And compatibility with hoses, paints, coatings, etc.

- Viscosity grades available

- Number of sources available (dual source possible?)

HETG Stocks

- Vegetable Oils
  - Canola oil is far better than soybean oil on stability
- High Oleic (HO) Vegetable Oils
  - HO Soybean Oil is best compromise on cost and performance for HO

- Most veg oil stocks will be 31-36 cSt @ 40C
  - Needs a thickener or viscosity modifier to reach ISO 46, 68, etc.
  - FUNCTIONAL V-521

- Requires 0.5-1.0wt% of veg oil PPD for low temp fluidity and storage stability

- RPVOT used as lab scale oxidation testing
  - Typically 50 minutes
  - Up to 150-200 minutes with high oleic stocks
  - Tend to need 1.5 – 2.0wt% antioxidant to optimize RPVOT

HETG Nuances

- High Oleic (HO) Vegetable Oils
  - HO Soybean Oil is best compromise on cost and performance for HO
  - HO Canola Oil tends to perform like normal canola oil
  - HO Sunflower is most stable but even more expensive than HO soy

- Look at the % oleic, % linoleic, % linolenic
  - Some high oleic veg oil producers blend harvests of varying quality
  - A few % of polyunsaturated fatty acids can ‘spoil’ a high oleic stock

- Pour points
  - Soybean oil:
  - Canola oil:

HETG Fatty Acids

- Oxidation rate increases exponentially with more unsaturation
  - Oxidized polyunsaturates catalyze the oxidation of saturates and oleic
  - A few % of C18:3 can spoil a high oleic veg oil

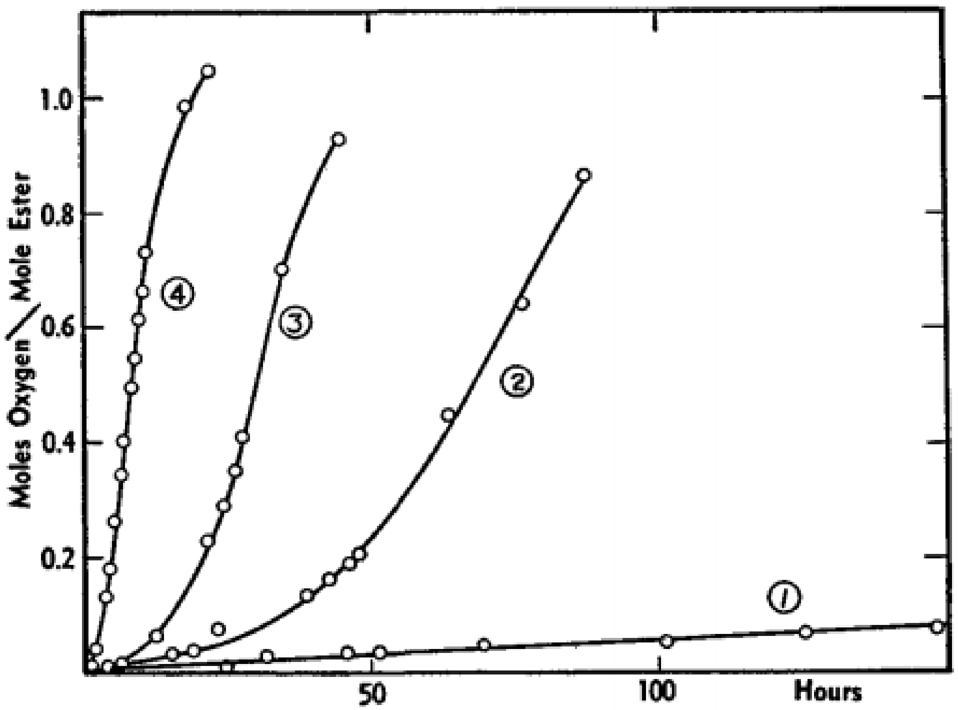
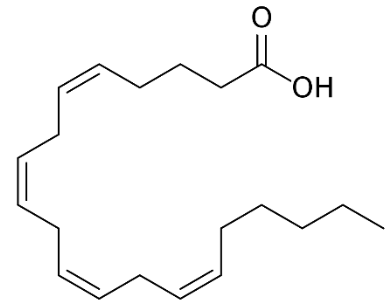
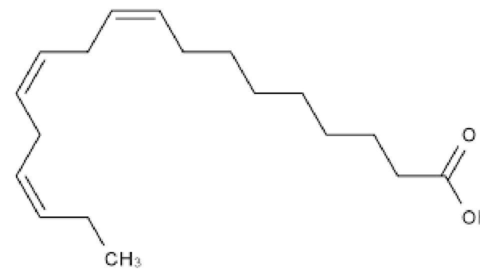
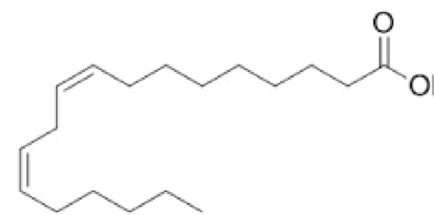


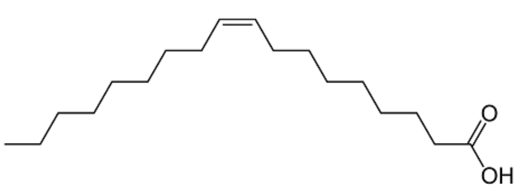
FIG. 1. Autoxidation of fatty esters in air at 37°C.

1.) Ethyl oleate
2.) Ethyl linoleate
3.) Ethyl linolenate
4.) Methyl arachidonate





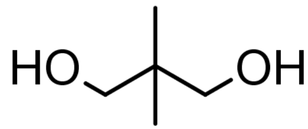
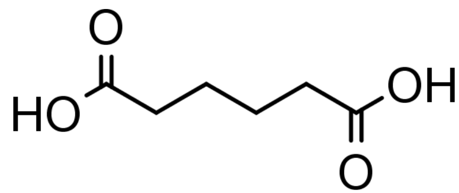
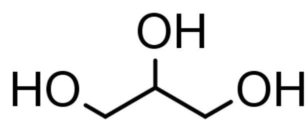
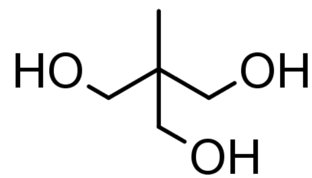
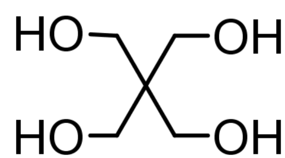
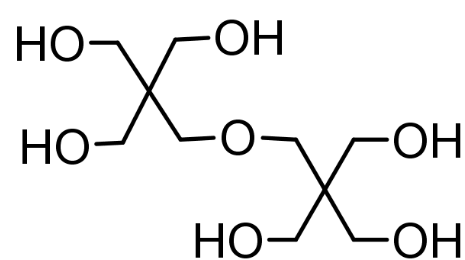


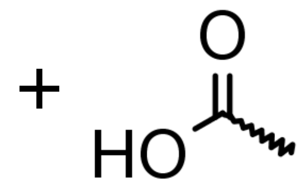


Ralph T. Holman; Otto C. Elmer (1947). *The rates of oxidation of unsaturated fatty acids and esters. , 24(4), 127–129.*

HEES Stocks

- Diesters (adipate) and polyol esters
  - TMPTO very popular but essentially a low temp version of veg oil

- Neopentyl glycol (NPG) 
  - Adipate / diester 
    - Glyceride 
      - Trimethylolpropane (TMP) 
        - Pentaerythritol (PE) 
          - Dipentaerythritol (DPE) 



1 Carboxylic Acid per -OH

HEES Nuances

- Many excellent HEES options to suit specific applications or performance areas – very few options that do everything well

  - “Iron triangle” in synthetic ester structure vs. properties
    - Saturated vs. unsaturated
      - Saturated gives better lubricity and stability
      - Unsaturated gives better low temp fluidity
    - Short (<C13) vs. long (C18+)
      - Short gives better low temp fluidity
      - Long gives better lubricity and flashpoint
    - Less groups (diester, TMP) vs. more (PE, DPE)
      - Less gives better additive compatibility
      - More gives better stability

HEPR Stocks

- PAO (decene/docene) and mPAO (octene)
- Biobased PAO (farnesene)

- Tricky to get ISO 46 with biodegradability >60%

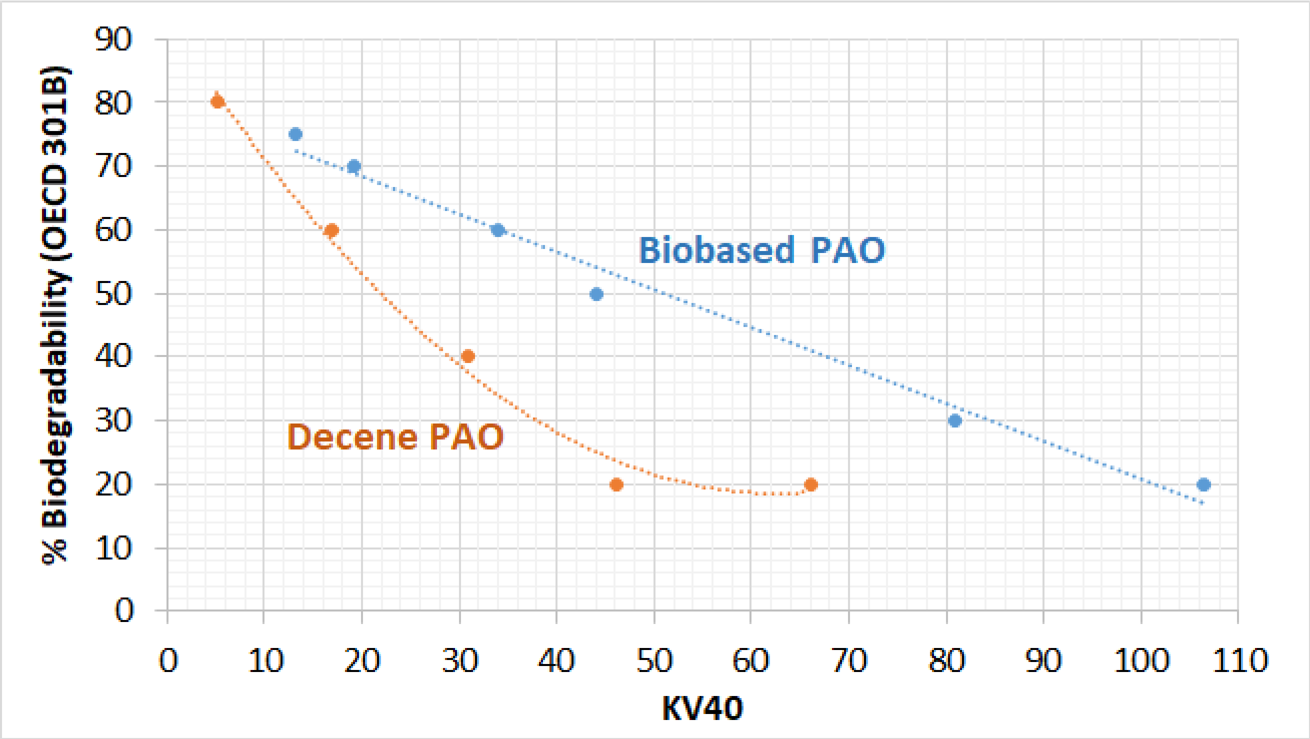
- Biodegradability is dependent on viscosity grade
  - PAO 2 about 80%
    - Carries aspiration and acute inhalation toxicities
    - Low flashpoint and seal compatibility are concerns
  - Biobased PAO

- Biobased PAO is single-sourced right now
  - Viscosity grades and raw materials subject to change

Comparing PAOs

- Decene PAO readily biodegradable at ISO 22 or lower
- Biobased PAO (Novvi) readily biodegradable at ISO 32 or lower

- No easy answer for how to get to readily biodegradable ISO 46 either way



HEPG Stocks

- Polyalkylene glycols
  - Water insoluble (WI)
    - 100% propylene oxide
    - Water soluble (ISO <32)
    - Partially water soluble (ISO 32-100)
  - Oil soluble (OS)
    - 100% butylene oxide
- Properties are highly dependent on type and ISO VG
- Excellent oxidation stability as finished lube with 1-2wt% aminic antioxidant
  - Poor ox stability by itself

HEPG Nuances

- Even if 100% PO or BO monomer, many variations possible
  - Initiator can be various alcohols or diols
  - Can be functionalized with end groups

- Difficult to convert a system from mineral oil to HEPG – fluid incompatibilities are most significant of all four EAL fluids

- Check SDS
  - Higher viscosity grades from some producers may carry residual monomer (EO or PO) which have extra hazard labeling

Viscosity Modifiers

- Most EAL fluids will be < ISO 46 and require a thickener

	FUNCTIONAL viscosity modifier	Alternatively…
Vegetable Oil (HETG HF)	FUNCTIONAL V-521	FUNCTIONAL PD-585
Synthetic Ester (HEES HF)	FUNCTIONAL V-508M (canola base) FUNCTIONAL V-508A5 (adipate base)	FUNCTIONAL V-521 for low temp
PAO (HEPR HF)	FUNCTIONAL V-160P2	FUNCTIONAL MG-1860
PAG (HEPG HF)	FUNCTIONAL V-508M (canola base)	

Ecolabel LuSC

- European Ecolabel lubricants
  - LuSC (lubricant substance classification) List
    - Whitelist of components to be used in Ecolabel lubricant formulating
  - Inconsistent rulings on whether you need a production site or just a distributor/rep in Europe to make Ecolabel branded products
    - Implementation of Ecolabel is country-by-country with each country having its own organizing body

US EPA VGP Certification

- Self certification
  - Boat owners/operators report the lubricants used annually for inspection or on maintenance logs
  - Must choose “VGP” marked lubricants or explain why a ‘technical infeasibility’ requires them to use a non-EAL lubricant

- 2013 US EPA VGP states an EAL program or ‘self certification’ may be used
  - Design for the Environment (DftE) now “Safer Choice”

VGP Self Certification Guide

- Base fluids
  - Use anything from EAL white lists including:
    - US EPA Safer Choice Ingredient List (SCIL)
      - Includes white oil
      - List is focused on consumer products
    - European Ecolabel LuSC list
      - List is focused on lubricant additives
  - Must be 60%+ biodegradable by ASTM D7373 math or tests like OECD
- Additives
  - Use VMs, packages, additives from Ecolabel LuSC list
  - Some odds and ends from US EPA SCIL (defoamers or demulsifiers)

Basic Performance - Wear

- Things to get right before the pump tests:
  - Antiwear (D4172) – 40kg
    - < 0.6 mm wear scar diameter (WSD) at a max
    - < 0.5 mm wear scar diameter more typical
    - $\leq$ 0.4 mm ideally
  - Extreme Pressure (D2783)
    - 160 kg weld load
    - Relatively low EP compared to gear oils, performance is likely residual from the AW chemistry used

Basic Performance - Corrosion

- Turbine Oil Rust (D665A and D665B)
  - A – distilled water; B - brine

- Copper Strip Corrosion (D130)
  - 3 hrs at 100C but some running 24 hrs at 100C
  - Most looking for 1b, some specs accept a 2a/b/c

  - For esters, look at the color of the test fluid and mass loss of strips

    - Fatty acids can continuously dissolve copper oxide on the surface
      - Gives a 1a copper strip in a blue-green fluid
        - Copper strips weigh less, change in dimensions

- Corrosion inhibitors also passivate metals and prevent metals from catalyzing the oxidative breakdown of lubricants

Basic Performance - Oxidation

- Aminic and phenolic AO
  - Aminic tends to be safer for humans (HX-1 options)
    - Synergizes well with PAG and esters
  - Phenolic tends to be safer for aquatic life (EAL)
    - BHT commonly used but toxic to humans (targets the kidneys)
    - Liquid or high MW phenolics preferred
  - Both carry varying levels of Acute and Chronic Aquatic Toxicity

- Sulfur sources can reactive with O_2 to form SO_x and prevent oxidation of hydrocarbons

- RPVOT (D2722), TOST (D943)
  - Dry TOST for veg oil HETG HF

- AO can affect and even improve wear testing vs. no AO

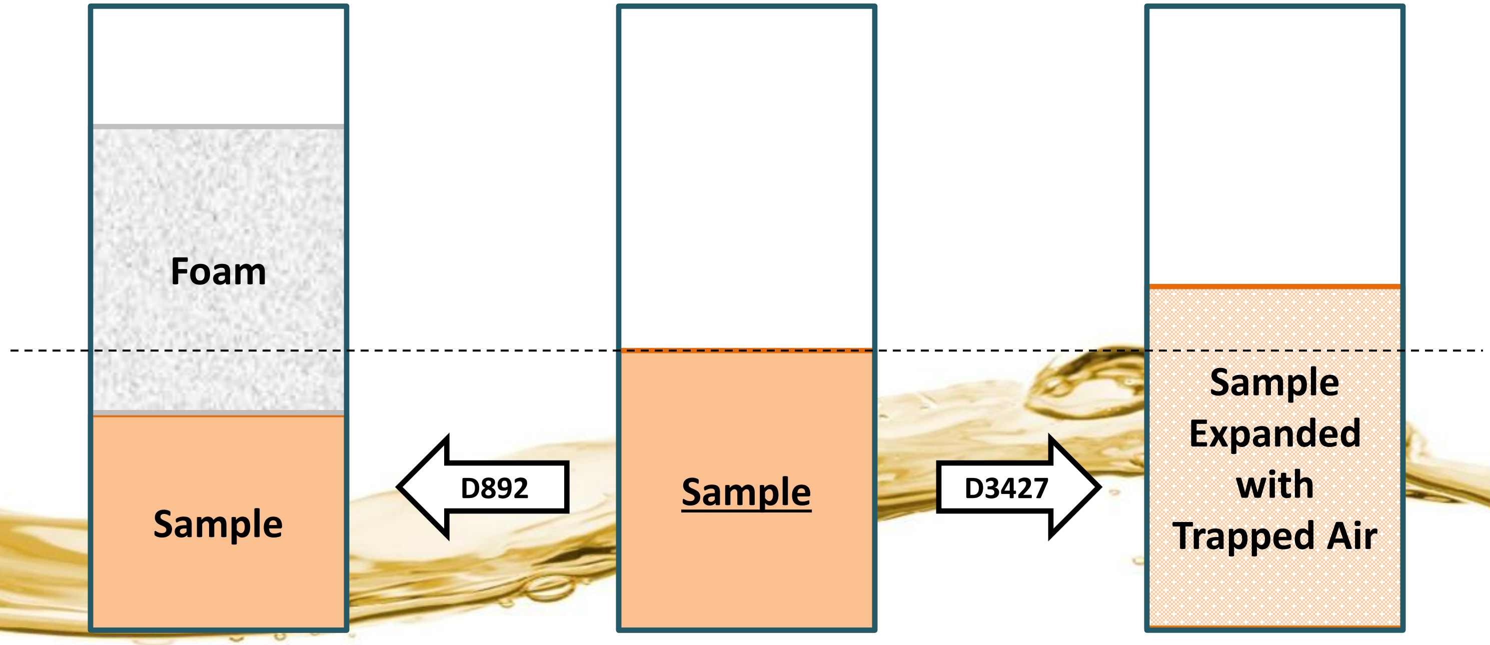
Basic Performance – DF/DM

- Air trapped in HF can't transmit power and can produce damaging cavitation
  - Foam (D892) – sequence I/II/III
    - Specs may be 80/0 to 150/0 but most people expect 50/0 or 30/0
  - Air Release (D3427)
    - Measures entrainment of air as bubbles rather than a fine foam
    - Sample will be murky with dispersed air bubbles in the fluid
    - < 9 cSt @ 40C = 25°C; 9 - 90 @ 40C = 50°C; >90 @ 40C = 75°C
- Separation of HF and water
  - Demulsibility (D1401)
    - 40/40/3 to 40/40/0 in 30 minutes

D892 vs. D3427

- D892 foam tendency/stability
  - Sample is clear with a layer of white foam on top of the fluid
  - Measure formation of foam over 5 minutes and collapse after 10 minutes

- D3427 air entrainment
  - Sample is murky with bubbles suspended in the bulk fluid
  - Measure density of the fluid before bubbling and then how long to return to within 98% of the original density



Basic Performance – Low Temp

- Pour Point (D97)
  - Varies, mineral oil specs typically call for <-12C

- 72hr Gel Test
  - For biobased, hold the samples at -20C for 72hrs and check for flow
    - Esters can have a tendency to form gel upon standing for long time

- Pumpability or dynamic viscosity
  - cP @ -20C / -30C / -40C if required

Basic Performance – Shear

- High end HF specifications (DIN 51524-3 HVLP) may call for testing the shear stability of the viscosity and VI improvers

  - 20hr KRL tapered roller bearing test (CEC L-45-A-99)
    - May be:
      - Report
      - Shear in grade
      - < 15% viscosity loss

  - Sonic shear (D2603 / D5621) was supposed to replace vane pump shear stability test methods like D2822 but is typically superseded by KRL and only old mil spec HF might use it

Higher End Testing

- After all the basic testing is done, many specs call for a few test rigs

- Vickers Vane Pump (V104C, ASTM D7043)
  - Most basic pump test, run by a few labs
  - $2700, 10 gallons of sample, 100 hrs

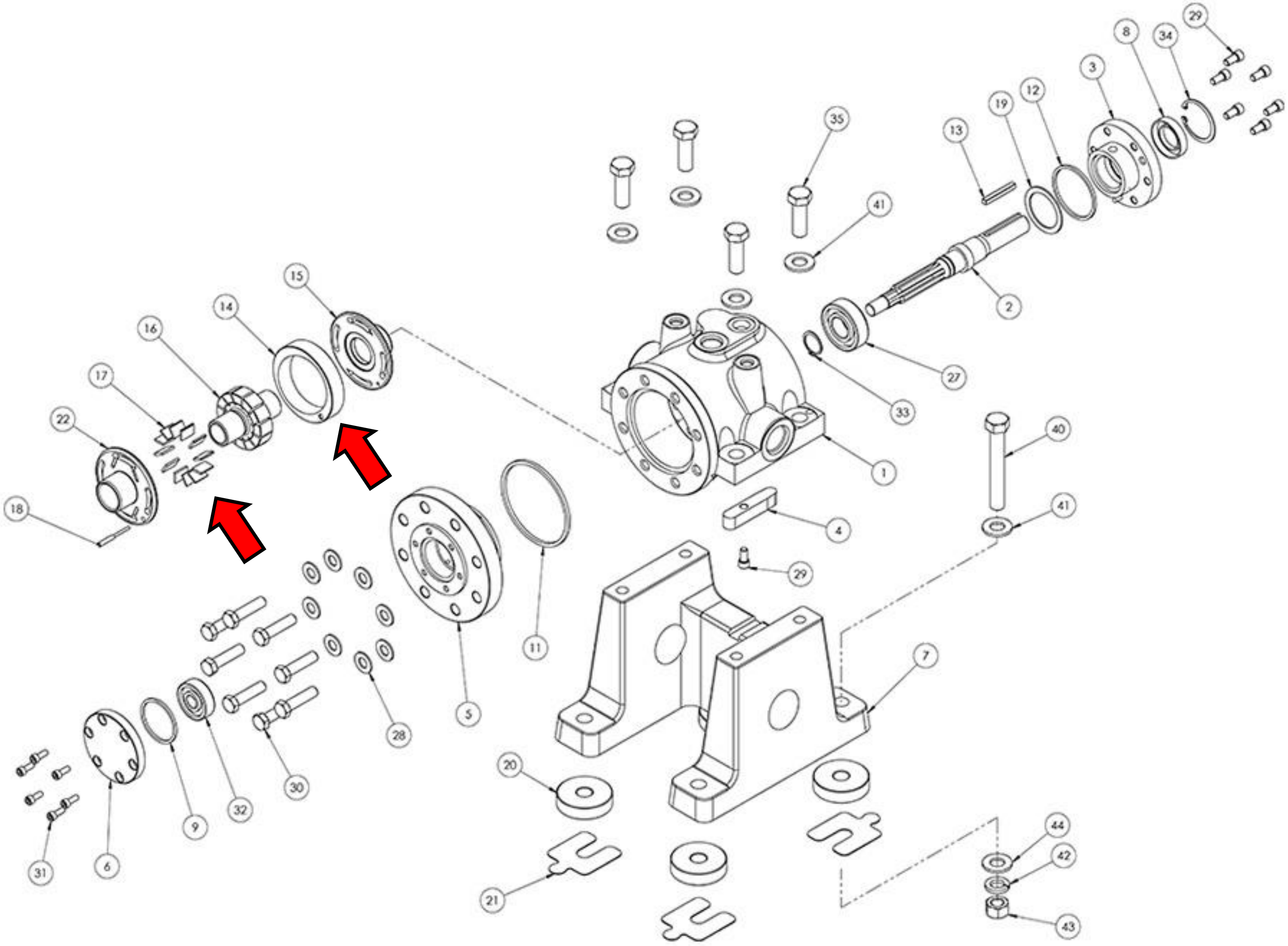
- FZG
  - Gear test method to measure scoring on the gears
  - 10 stage pass or better

- Other pump tests and higher test costs
  - Eaton 35VQ25A is displacing V104C test

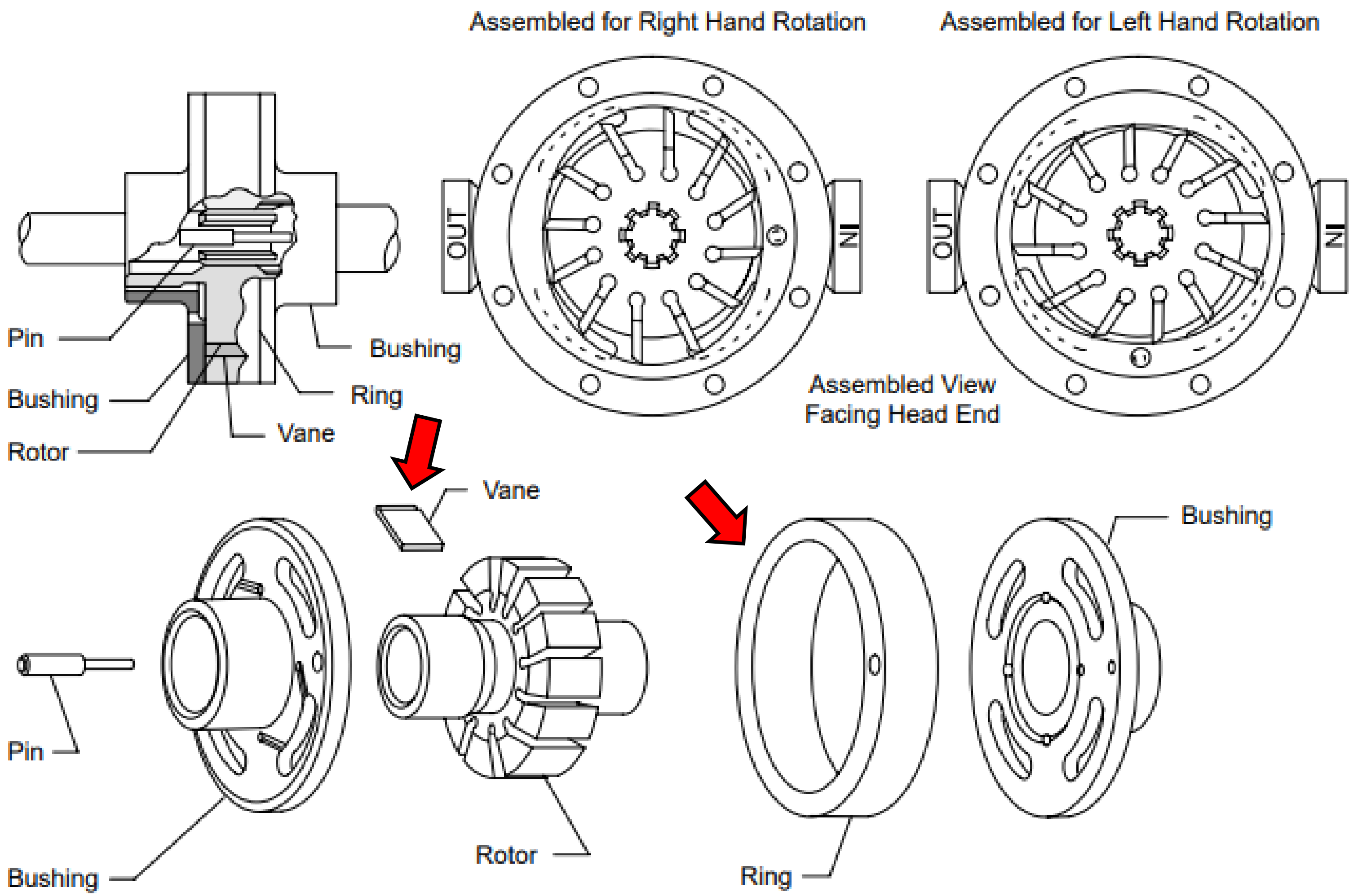
  - OEMS
    - Bosch Rexroth A4VG/A6VM piston pump testing - $60,000

V104C Vane Pump (D7043)

- 100 hrs, 1200 rpm, 66C -> measure wear on vanes and ring



V104C Cartridge



V104C Conditions

- Need to withstand physical wear over 100hrs
- Constant filtration of the fluid
- Possibility of cavitation from failure of defoamer (foam + air release)

TABLE 1—Comparison of Operating Conditions in the First Phase of Rig Testing

Parameter	V104C Vane Pump Test	35VQ25 Vane Pump Test	IUT AW-2 Test Rig
cam ring/disc sliding speed, m/s	4.2 – 5.2	10.4 – 11.4	9.4 (1800 rpm)
vane/pin oscillation frequency, Hz	48	80	6 (360 rpm)
contact load per unit length, kN/m	0 – 28	0 – 16	39 (load stage 7)
maximum Hertzian contact stress, GPa	0.02 – 1.60	0.17 – 1.70	0.78
inlet temperature, °C	65 (ISO VG 32)	90 – 96	55 – 60 (60°C at bath)

Smolenski, Donald J., et al. Tribology of Hydraulic Pump Testing. United States, ASTM, 1997.

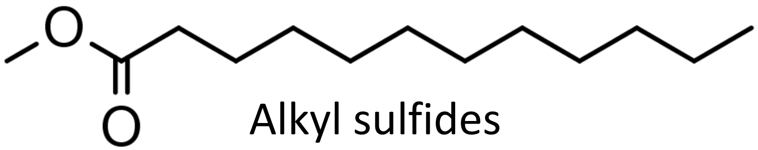
Standards

- Exact test methods will be prescribed by an ASTM / ISO / DIN test method
  - Some customers may also require additional testing
- Standards:
  - ISO 15380 (EAL)
  - ISO 11158 (mineral oil)
  - DIN 51524 (mineral oil)

Antiwear Chemistries

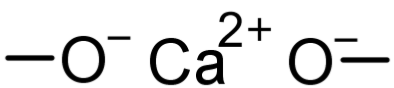
- *Excluding zinc and heavy metal complexes…*

Long chain fatty esters/alcohols/amides

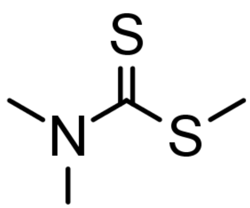


Alkyl sulfides

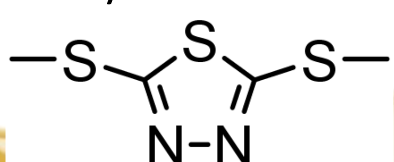
Neutral detergents



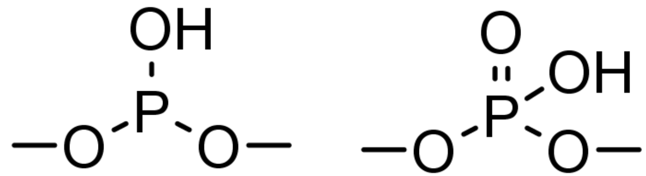
Ashless thiocarbamates



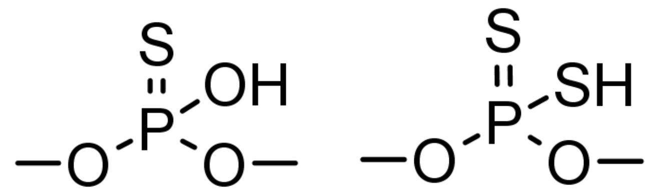
Alkyl thiadiazoles



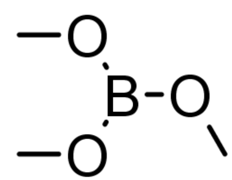
Phosphates / phosphites



Thiophosphates



Boron esters



Various alkyl/aryl substituents;
acids neutralized with variety of bases

Metal-based Antiwear

- Zinc complexes and zinc dialkylthiodiphosphate (ZDDP)
  - Movement to remove zinc and other heavy metals from lubricants

  - ZDDP is a core component of economic engine oil and HF
    - Excellent antiwear, modest EP, and antioxidant; synergy with adds.

  - Trace zinc is a nutrient
    - But in the environment zinc can accumulate in water bodies or in soil around spill sites and is then encountered at unsafe levels
    - Harms plant life and microorganisms; inhalation of zinc causes ‘metal fume fever’
    - Linked up increase lead uptake

https://www.atsdr.cdc.gov/phs/phs.asp?id=300&tid=54
https://www.nature.com/articles/7500286

Calcium

- Calcium is a far safer alternative to zinc where economy, wear performance, acid neutralization, and synergy with other additives are needed
  - Calcium sulfonates
  - Calcium carboxylates
  - Calcium overbases (nano to micro $CaCO_3$ particles)
- Is not ashless like sulfur/phosphorus chemistries
  - Ashless is required in engines with catalytic converts or particulate filters (diesel engine oil)
  - Metal salts can be hydrolyzed if emulsified with water
    - Emulsifying rock drill oil and metal working fluids
    - Not a concern with HF which contains demulsifiers

AW Optimization Struggle

- Antiwear chemistry balancing

Wear Scar

"We need to minimize damage between moving parts."

"But some wear polishes the surface smoother and reduces frictional heating…"

Coefficient of Friction

"We need lower CoF for lower startup energy and better efficiencies."

"Having a higher CoF wear-resistant surface also generates heat!"

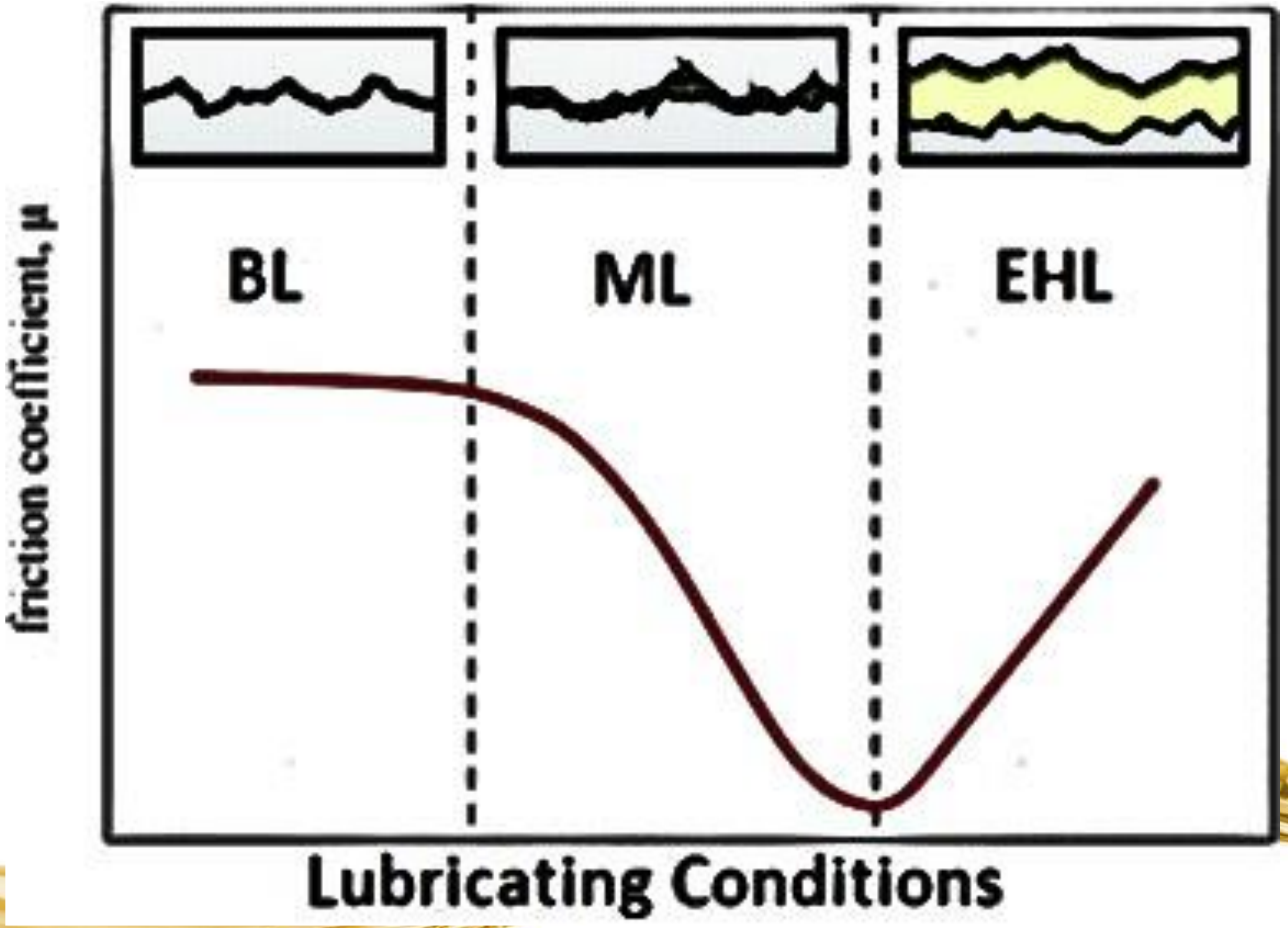
Heat Generation

"We need lower operating temps to extend the life of the oil and prevent overheat/melting of the metal."

"The act of polishing to create lower CoF generates some heat."

Stribeck Curve

- CoF and wear dependent on ‘lubricating conditions’
    - Speed, load, viscosity = film thickness
    - Surface asperities = surface roughness



https://www.tribonet.org/wiki/coefficient-of-friction/

AW vs. EP Struggle

- Balancing AW vs EP

4-Ball Wear (AW)
< 0.5 mm @ 40 kg

"The surface should be hard and slippery to prevent gradual wear under high speeds and low loads."

4-Ball EP
≥ 160 kgf weld load

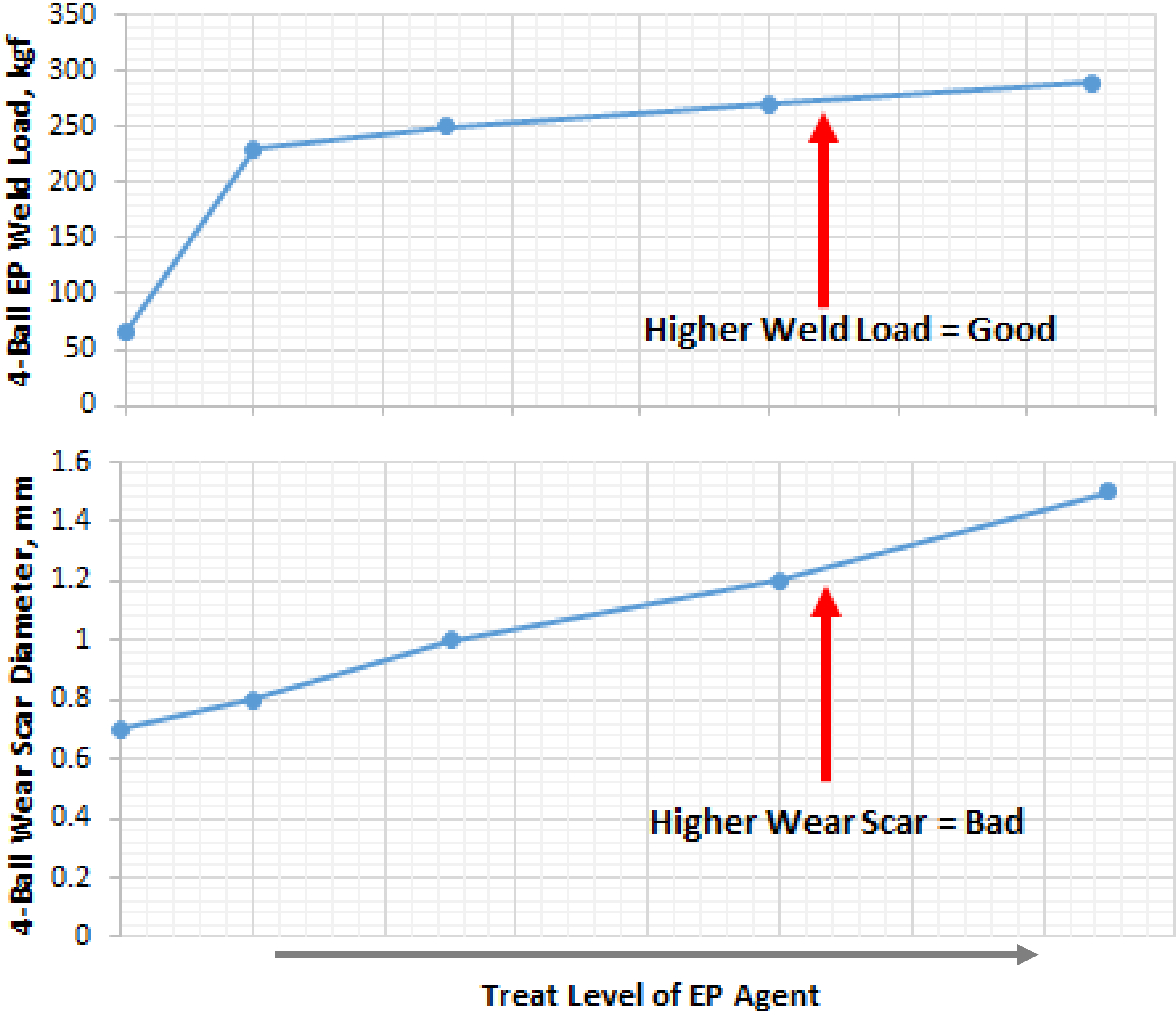
"The surface should be soft and flaky to provide a sacrificial layer to prevent high loads or impacts from causing damage."

Increase cost

Using more additive tends to improve both AW and EP but hurts economics and package competitiveness.

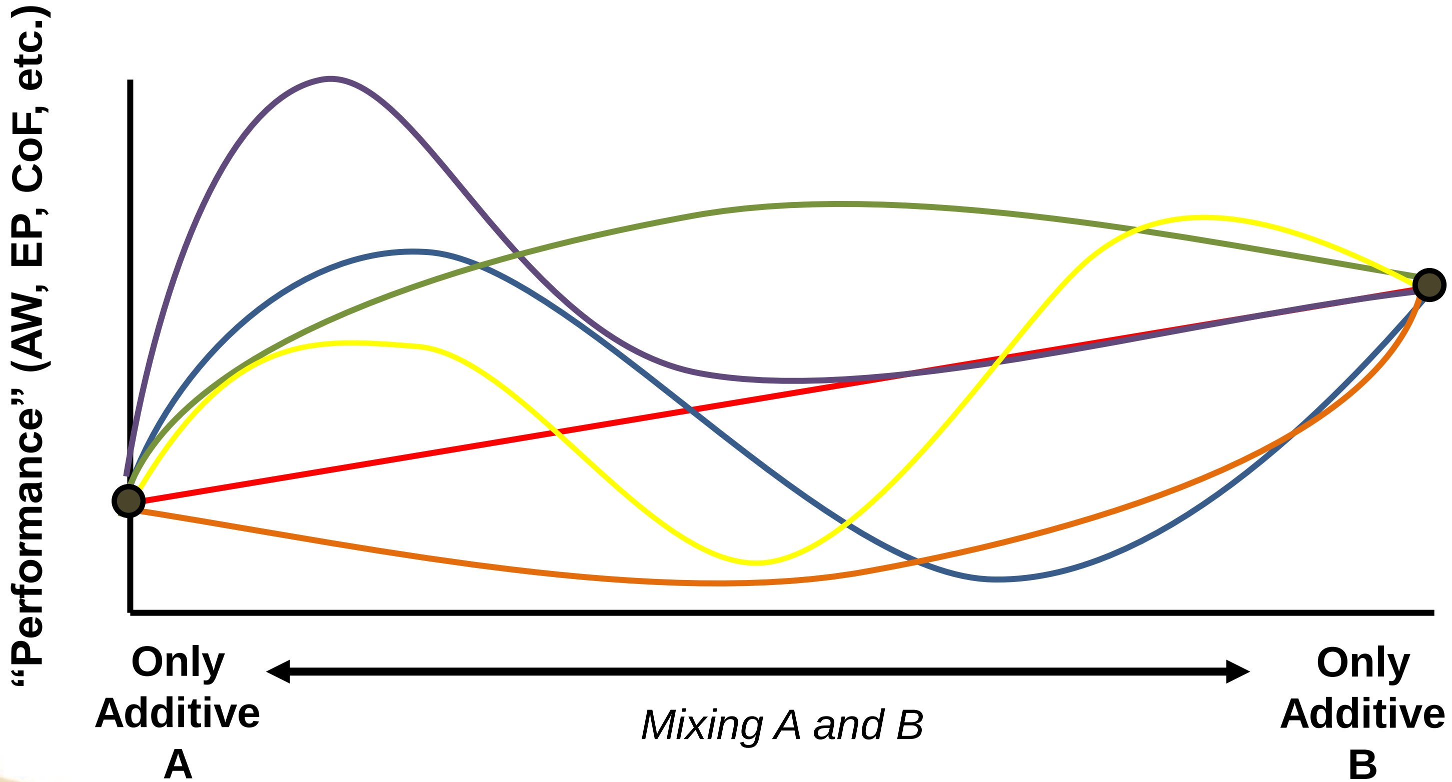
Example: EP vs. AW

- Varying concentration of one EP agent in one base oil



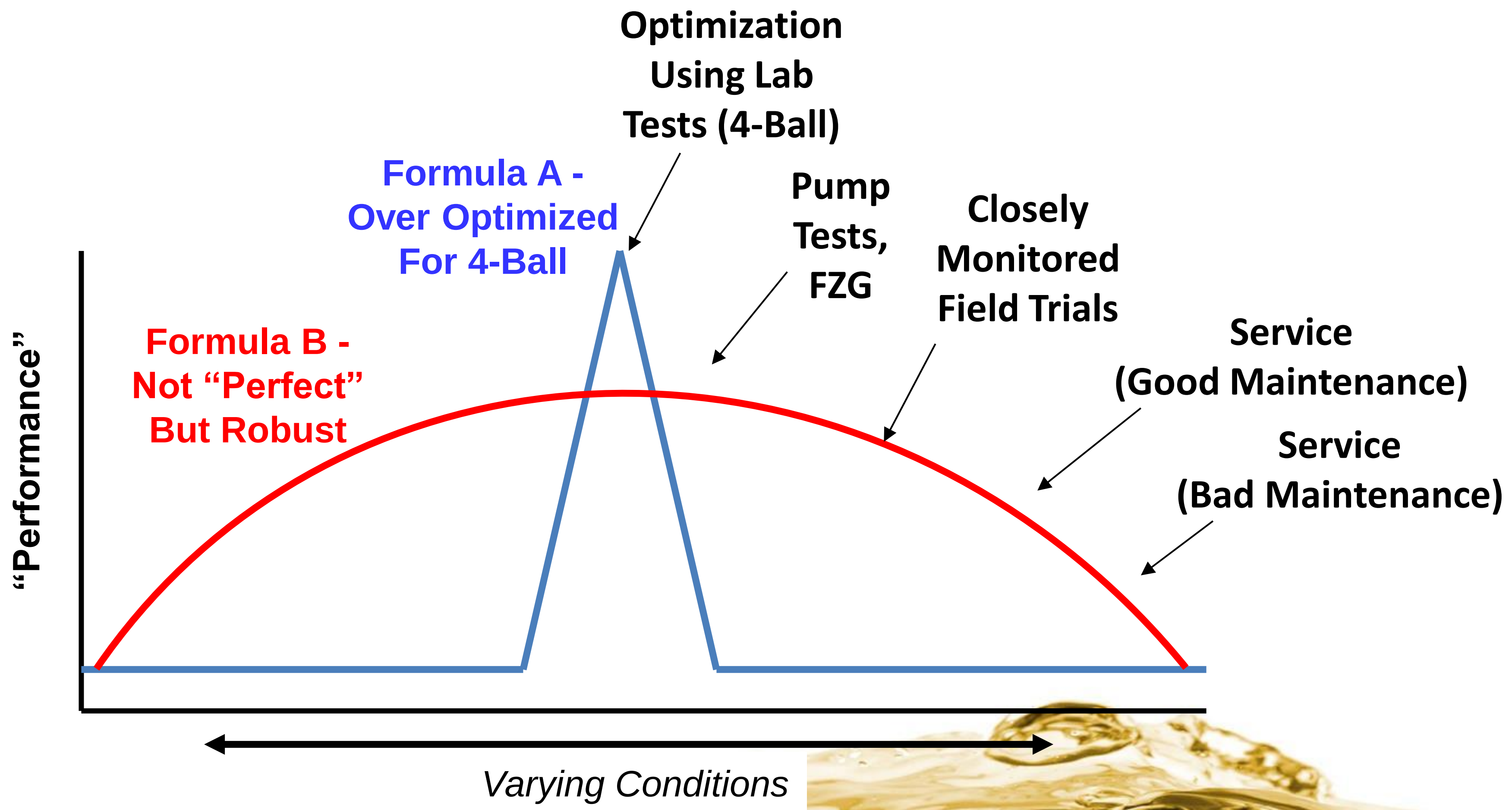
Combining AW and EP

- Using two or more additives with different chemistries and give/take between AW and EP performance can bend the 'iron triangle'
- Resulting effects of combining additives (A and B) can vary:



The Goal Is Robustness

- "Robust" means operating well when outside normal operating conditions
  - Though you can't account for everything you're certain to do okay



Summary

- Hydraulic fluid formulation is intensive
  - Low viscosity fluid requiring a robust set of additives
  - Fine balance of AW, EP, AO, defoamer, demulsifier, etc.

- FUNCTIONAL HF packages save you the work, go to market faster with proven HF additive chemistry tailored for your biobased or ecofriendly HF opportunities