Fuel and Lubricant Solutions

Marine Lubricants – Trends and products

BASF
We create chemistry

Naples May 5th, 2016 – T. Rühle

Agenda

- **Legislation**
- Suitable base stocks for marine lubricants
- Suitable additives for marine lubricants
- Example: Marine cylinder oils
- Examples: Biohydraulics
- Example: A new renewable biopolymer as lubricant additive
- Summary and Conclusions

Regulatory requirements for Marine Lubes

BASF
We create chemistry

Two Key regulations in place:

OSPAR – Convention for the protection of the marine environment of the North East Atlantic. Defines applications that can lead to discharge to sea. Black list of prohibited chemicals. Products require approvals -complex test protocols for approvals

EPA with VGP 2013 – Protection of USA Costal Waters. Defines conditions for EALs (mandated for oil to sea interfaces)

Other regions do not have strong environment protection

OSPAR

OSPAR COMMISSION
Protecting and conserving the North-East Atlantic and its resources

BASF
We create chemistry

Process OSPAR Chemical registration

1. Complete HOCNF Form
2. Submit to CEFAS who will send to OCNS team. (MSDS in English and Dutch)
3. OCNS will process data and generate a template and place chemical on definitive ranked list of registered products. Certificate lasts 3 years. Normally takes 8 weeks to process from submission of forms.

Data Needed

1. Full chemical name, molecular weight, CAS #, EINECS/ELINCS/REACH registration number
2. Biodegradability & Bioaccumulation (log Pow) data: results of >60% biodegradation in 28 days and Log Pow <3, or Bioconcentration factor (BCF) ≤100 and the molecular weight is ≥700
3. Ecotoxicity data results (algae, Crustacean, fish, sediment dweller, expressed as EC50 (Effective concentration) or LC50 (Lethal concentration)

VGP affected Marine Lubricant Market Vessel General Permit Legislation

BASF
We create chemistry

- The **US Environmental Protection Agency (EPA)** has published the **Vessel General Permit (VGP)** which came into force in Dec 2013.
- VGP requires an environmental **acceptable lubricants (EAL)** for all ship equipment having an interface with seawater and applies to all vessels (>79 feet in length) entering US waters, unless technically infeasible.
- Environmentally acceptable lubricants (EALs) according to VGP definition are lubricants that are
  - Biodegradable: Organization for Economic Co-operation and Development Test Guidelines 301 A-F (>20% but <60% biodegradation after 28 days), 306, and 310, and International Organization for Standardization 14593:1999.
  - Minimally-toxic: means a substance must pass OECD 201 , 202, and 203 for acute toxicity testing, or OECD 210 and 211 for chronic toxicity testing: LC50 of fluids must be at least 100 mg/L and the LC50 of greases, two-stroke oils, and all other total loss lubricants must be at least 1000 mg/L
  - Not bio accumulative: means the partition coefficient in the marine environment is log KOW <3 or >7 using test methods OECD 117 and 107, molecular mass > 800 Daltons, molecular diameter >1.5 nanometer, BCF or BAF is <100 L/kg, using OECD 305, OCSPP 850.1710 or OCSPP 850.1730, or a field-measured BAF or polymer with MW fraction below 1,000 g/mol is <1%.
- Alternatively, lubricants that are labelled under OSPAR, Blue Angel, European Eco label, Nordic Swan and Swedish Standard SS155470 are regarded as acceptable EALs.

Agenda

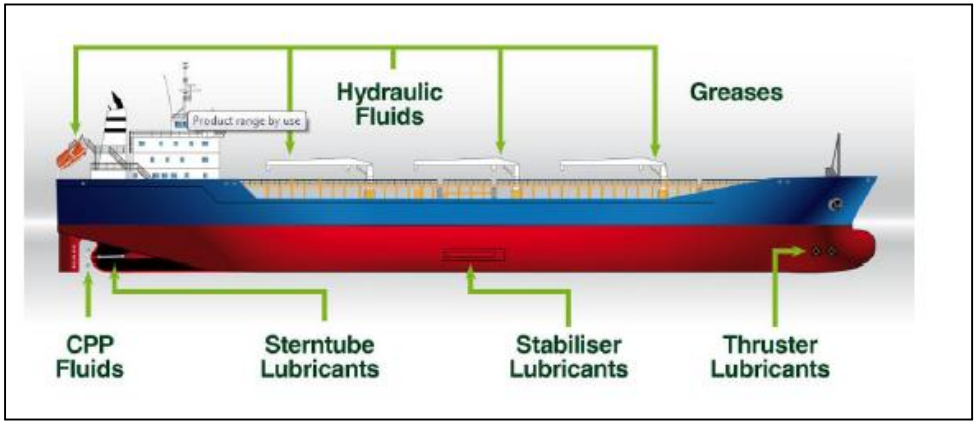
- Legislation
- **Suitable base stocks for marine lubricants**
- Suitable additives for marine lubricants
- Example: Marine cylinder oils
- Examples: Biohydraulics
- Example: A new renewable biopolymer as lubricant additive
- Summary and Conclusions

VGP affected Marine Lubricant Market Vessel General Permit Legislation

BASF
We create chemistry

- EALs are required for all ship equipments having an interface with seawater. The VGP specifically identifies applications that have the potential for an oil-to-sea interface as:

  - ✓ Stern Tubes
  - ✓ Controllable Pitch Propeller
  - ✓ Thruster Hydraulic Fluids
  - ✓ Paddle Wheel Propulsion
  - ✓ Thruster Bearings
  - ✓ Stabilizers
  - ✓ Rudder Bearings
  - ✓ Azimuth Thrusters
  - ✓ Propulsion Pod Lubrication
  - ✓ Wire Rope
  - ✓ Mechanical equipment subject to immersion (e.g. dredges, grabs, etc)



- Synthetic esters are the main base oils used in the EAL formulations:

  - ✓ Unsaturated oleate ester,
  - ✓ Saturated polyol ester.
  - ✓ Saturated diester

Examples
Esters for Marine Lubricants Base Stocks

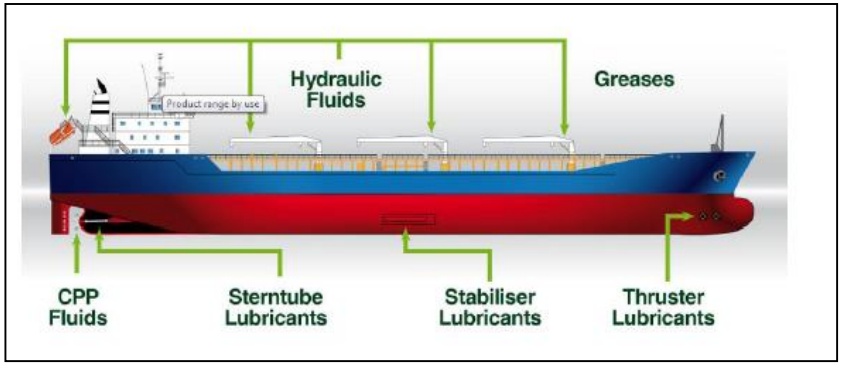
BASF
We create chemistry

Market information

Application: Applications with oil-to-see interface

Customer Industry: Marine Industry

Market: Global



Differentiation potential

- Friendly EHS profile
- Superior lubrication performance
- Excellent resistance to oxidation
- Good hydrolytic stability
- Good low temperature performance
- Broad range of available viscosities

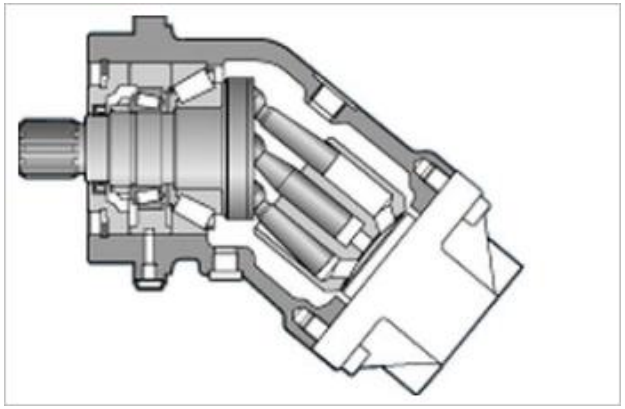
Sustainability performance

- Reduces negative impact on the aquatic environment
- Excellent biodegradability (ultimately/readily biodegradable)
- Low aquatic toxicity and high renewable content of >90%
- Enables EU Ecolabel and OSPAR listing for formulated lubricants
- Fulfill EPA requirements defined under Vessel General Permit (VGP)

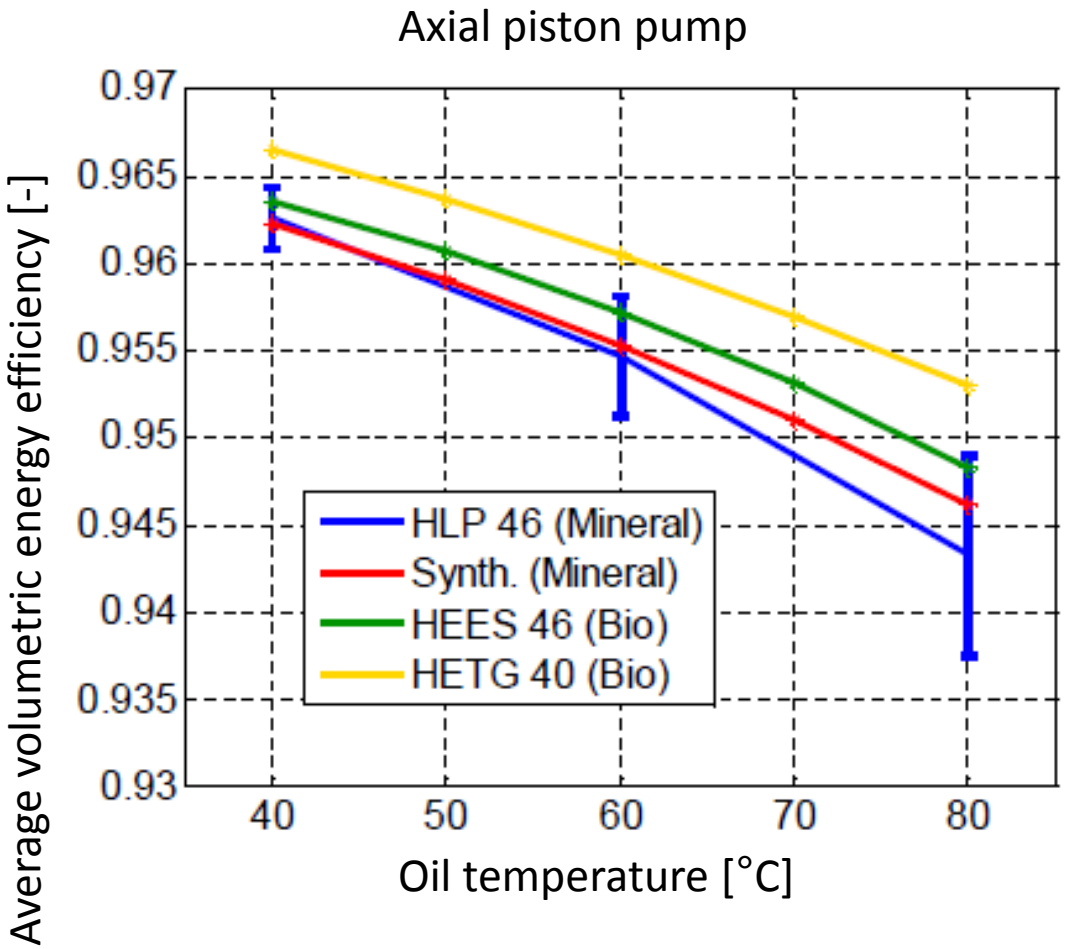
High performance esters for environmentally acceptable lubricants for the marine industry

Influence of Hydraulic Fluids on the Energy Efficiency

Source: Bosch Rexroth



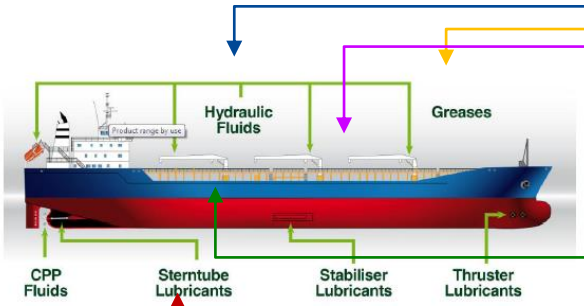
Wirkungsgraduntersuchung
Otto, Theissen RWTH Aachen IFAS



Agenda

- Legislation
- Suitable base stocks for marine lubricants
- **Suitable additives for marine lubricants**
- Example: Marine cylinder oils
- Examples: Biohydraulics
- Example: A new renewable biopolymer as lubricant additive
- Summary and Conclusions

Example: Lubricant Additives for Marine Lubricants



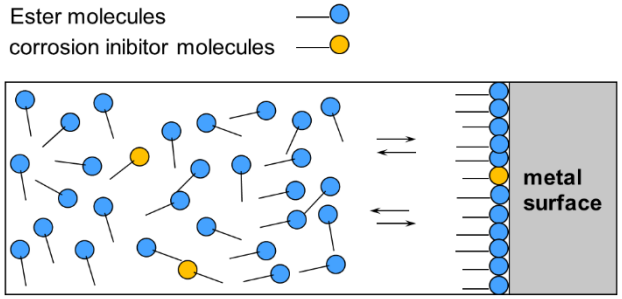
Additives

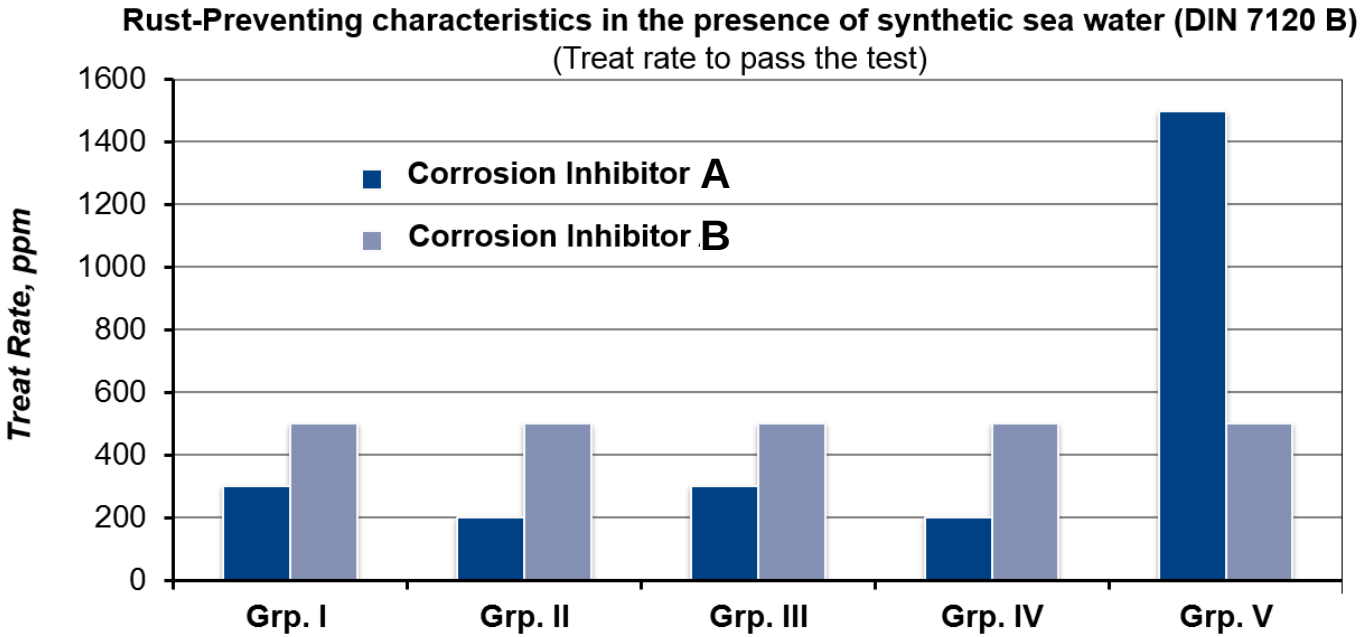
	EEL Categories				
	I: Hydraulic fluids and tractor transmission oils	II: Greases and stern tube greases	III: Stern tube oils chainsaw oils, concrete release agents, wire rope lubricants and other total loss lubricants	IV: Two-stroke oils	V: Industrial and marine gear oils
Antioxidans					
Phenolic Antioxidants	√	√	√	√	√
Aminic Antioxidants	√	√	√	√	√
Antioxidant blends	√	√	√	√	√
Secondary antioxidants	√	√	√	√	√
Antiwear additives					
Alkylphosphites	√	√	√	√	√
Thiophosphonates	√	√	√	√	√
Dithiophosphates	√	√	√	√	√
Amine dithiophosphates	√	√	√	√	√
Alkylphosphates	√	√	√	√	√
EP additives					
Sulphurized esters	√	√	√	√	√
Sulphurized triglycerides	√	√	√	√	√
Sulphurized olefines	√	√	√	√	√
Corrosion inhibitors					
Succinic acid esters	√	√	√	√	√
Sarcosine	√	√	√	√	√
Amine neutralized phosphoric acid ester	√	√	√	√	√
Metal Deactivators					
Benzotriazoles	√	√	√	√	√
Tolyltriazoles	√	√	√	√	√
Thiadiazoles	√	√	√	√	√
Industrial Additive Packages					
Circulating oil package	√	√	√	√	√
Turbine oil packages	√	√	√	√	√

EU Ecolabel
www.ecolabel.eu

http://www.ivam.uva.nl/wp-content/uploads/2014/11/LuSC-list-30062015-no-track.pdf

Example: Interaction of Corrosion Inhibitors in an Ester Base Stock





Source: T. Rühle. M. Hof, S. Seibel: A new corrosion inhibitor with unique performance advantages for industrial lubricant applications. Proceedings of the OilDoc Conference & Exhibition 2013, Rosenheim 22. -24.01.2013.

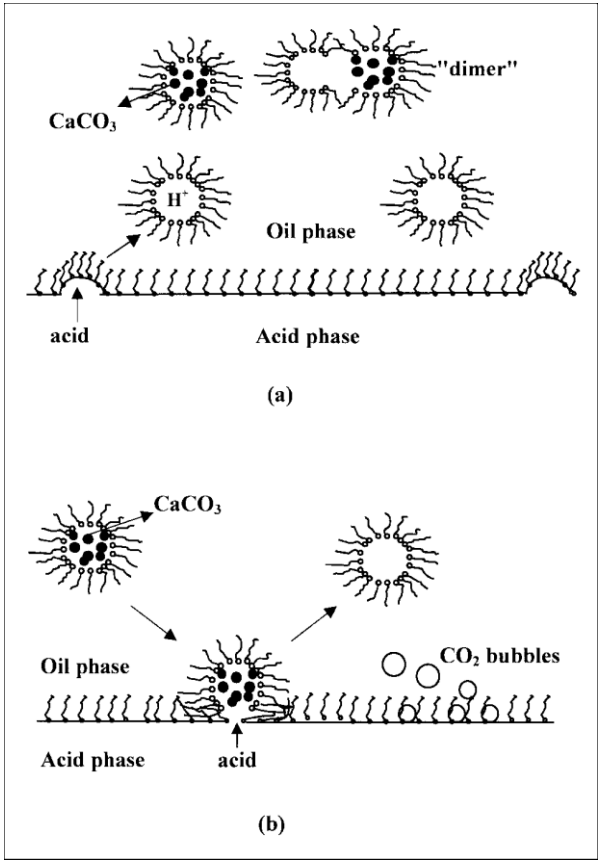
Agenda

- Legislation
- Suitable base stocks for marine lubricants
- Suitable additives for marine lubricants
- **Example: Marine cylinder oils**
- Examples: Biohydraulics
- Example: A new renewable biopolymer as lubricant additive
- Summary and Conclusions

Marine Cylinder Oils: Neutralization of Sulphuric Acid by overbased Detergents

BASF
We create chemistry

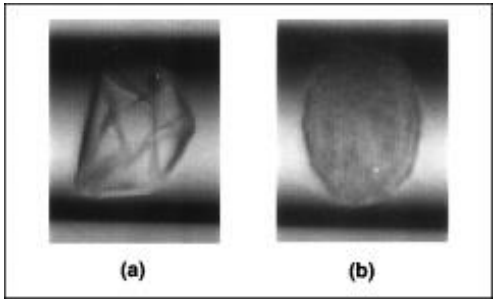
Mechanism of neutralization reaction in lubricating oil.



Mechanism of crystal formation

Stage	Phenomena
1. Reverse micelle moves close to the interface of acid droplet	
2. Aqueous acid transports into the core and contacts the $CaCO_3$ particles	
3. $CaCO_3$ reacts with acid, and nucleus of hydrated calcium sulfate is formed, together with CO_2	CO_2 bubbles
4. Once the nucleus is formed, the crystal grows	

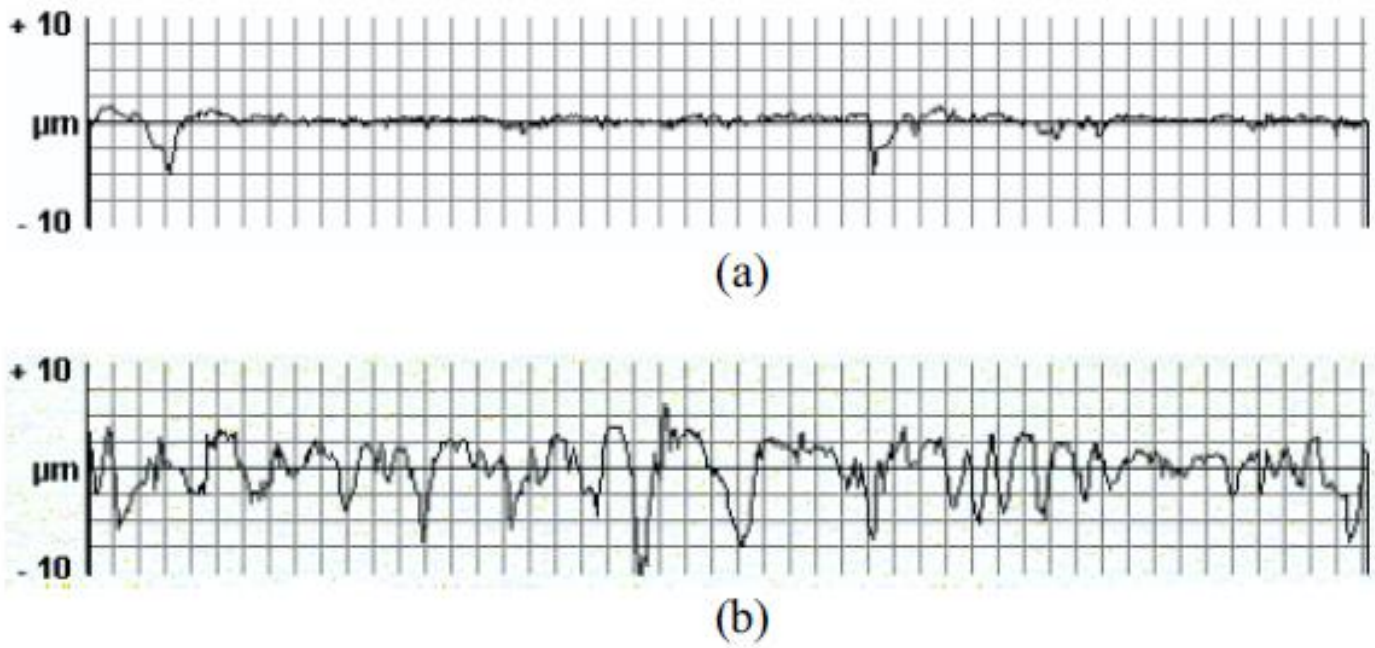
Visualized crystals in the neutralization reaction.



Source:

Rong Chang Wu, Kyriakos D. Papadopoulos, Curt B. Campbell: „Visualization Test for Neutralization of Acids by Marine Cylinder Lubricants“ in: AIChE Journal September 1999 Vol. 45, No. 9, 2011.

Marine Cylinder Oils: Effect of Deposits



Surface trace of typical liner surface. (a) without deposit (b) same surface with deposit.

Source:
Øyvind Buhaug: „Deposit formation on cylinder liner surfaces in medium-speed engines“,
Faculty of Engineering Science and Technology, Norwegian University of Science and Technology. Trondheim, Sept 15, 2003

Marine Cylinder Oils: Effect of Deposits

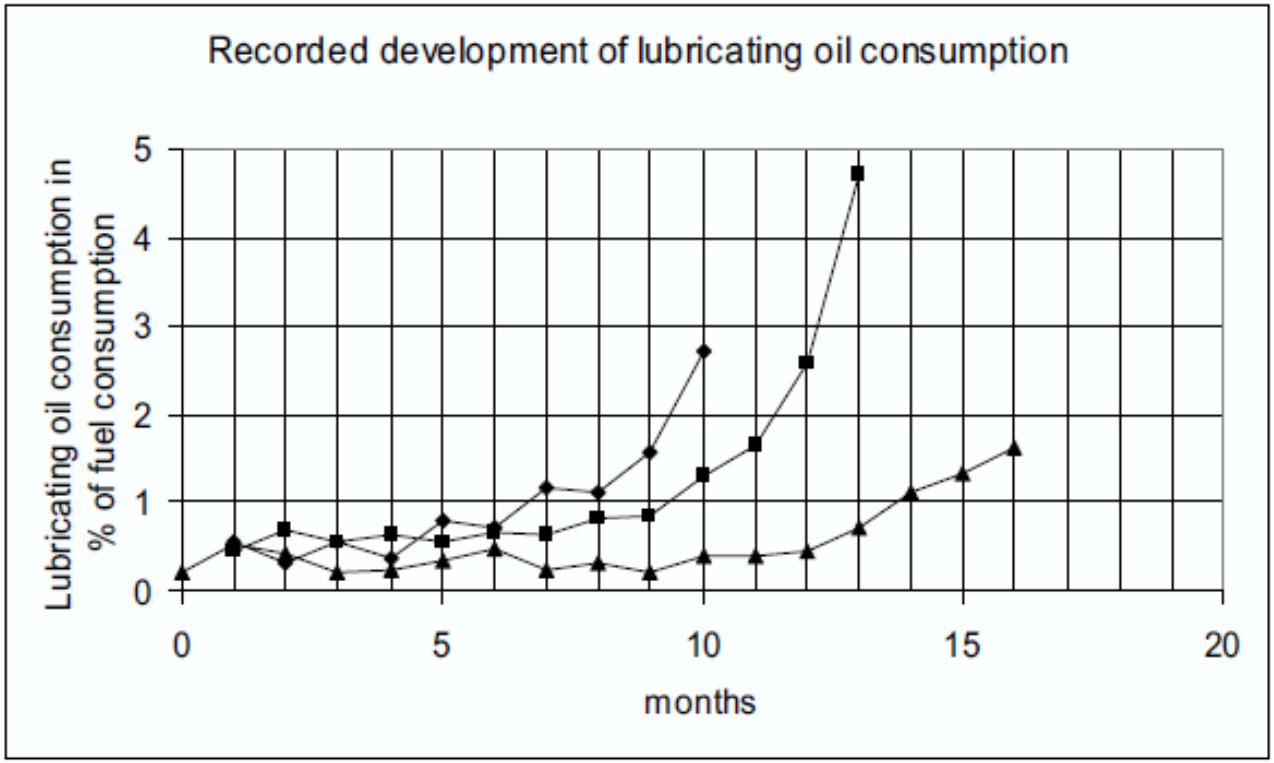


Figure 2 *Lubricating oil consumption in engines with liner deposits*

Source:
Øyvind Buhaug: „Deposit formation on cylinder liner surfaces in medium-speed engines“,
Faculty of Engineering Science and Technology, Norwegian University of Science and Technology. Trondheim, Sept 15, 2003

Examples
A new widely available Group V technology

Market information

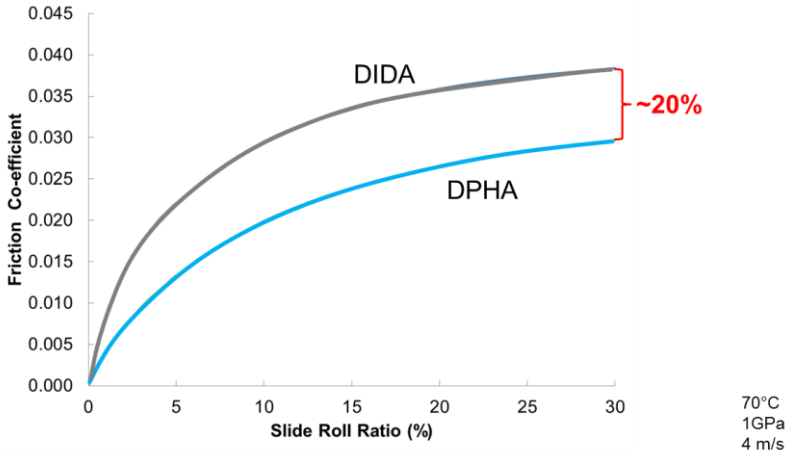
Application: Top tier automotive & industrial lubricants
Marine cylinder lubricants

Customer Industry: Various

Market: Global

Differentiation potential

- **Supply security:** several production sites worldwide plus complete backwards integration into all raw materials (already established world scale capacity)
- **Performance Benefits:**
  - Outstanding thermal and hydrolytic stability
  - Superior cold temperature properties
  - Low coefficient of friction
  - Cleaner operation offering – less deposits



Sustainability performance

- Friction reduction offering a potential for energy efficiency
- Sustainable supply security via backwards integrated raw materials

A novel fully saturated high performance ester base stock technology for various applications

Agenda

- Legislation
- Suitable base stocks for marine lubricants
- Suitable additives for marine lubricants
- Example: Marine cylinder oils
- **Examples: Biohydraulics**
- Example: A new renewable biopolymer as lubricant additive
- Summary and Conclusions

Examples
Premium Bio Hydraulic Fluid

BASF
We create chemistry

Market information

Application: (Marine) Hydraulic fluids

Customer Industry: Various

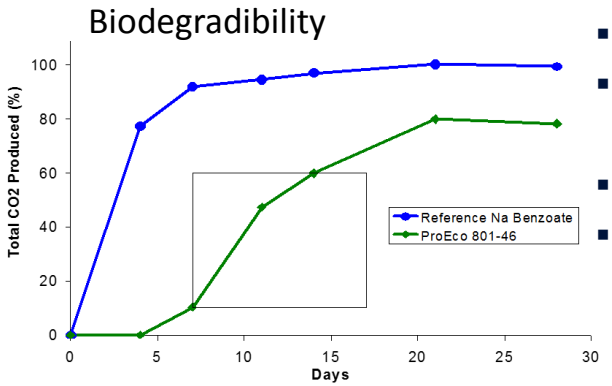
Market: Global

Differentiation potential

- **OEM Approvals:**
  - Bosch Rexroth RD90221-1
  - Eaton Vickers 35VQ25 / 104C
  - HAWE Hydraulic
  - ZF TE-ML 07G
  - Voith Turbo gears – list 120.00059010 (ISO-VG 32)
- **Standards:**
  - DIN ISO 15380

ProEco HE 801

- **Environmental Labels:**
  - EU Ecolabel
  - MIA Vamil
  - Swedish Standard SS 15 54 34
  - Japan EcoMark
  - USDA Bio Preferred

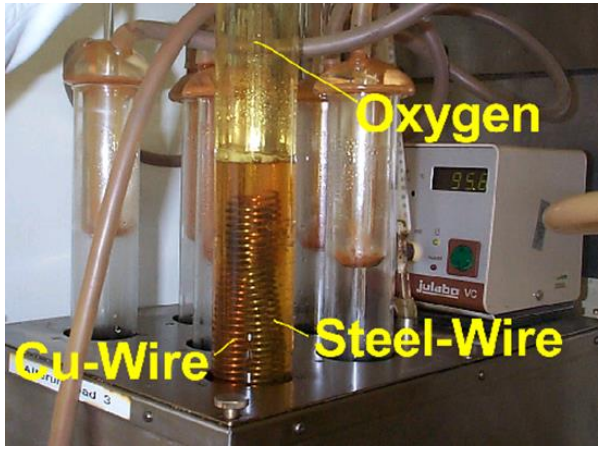


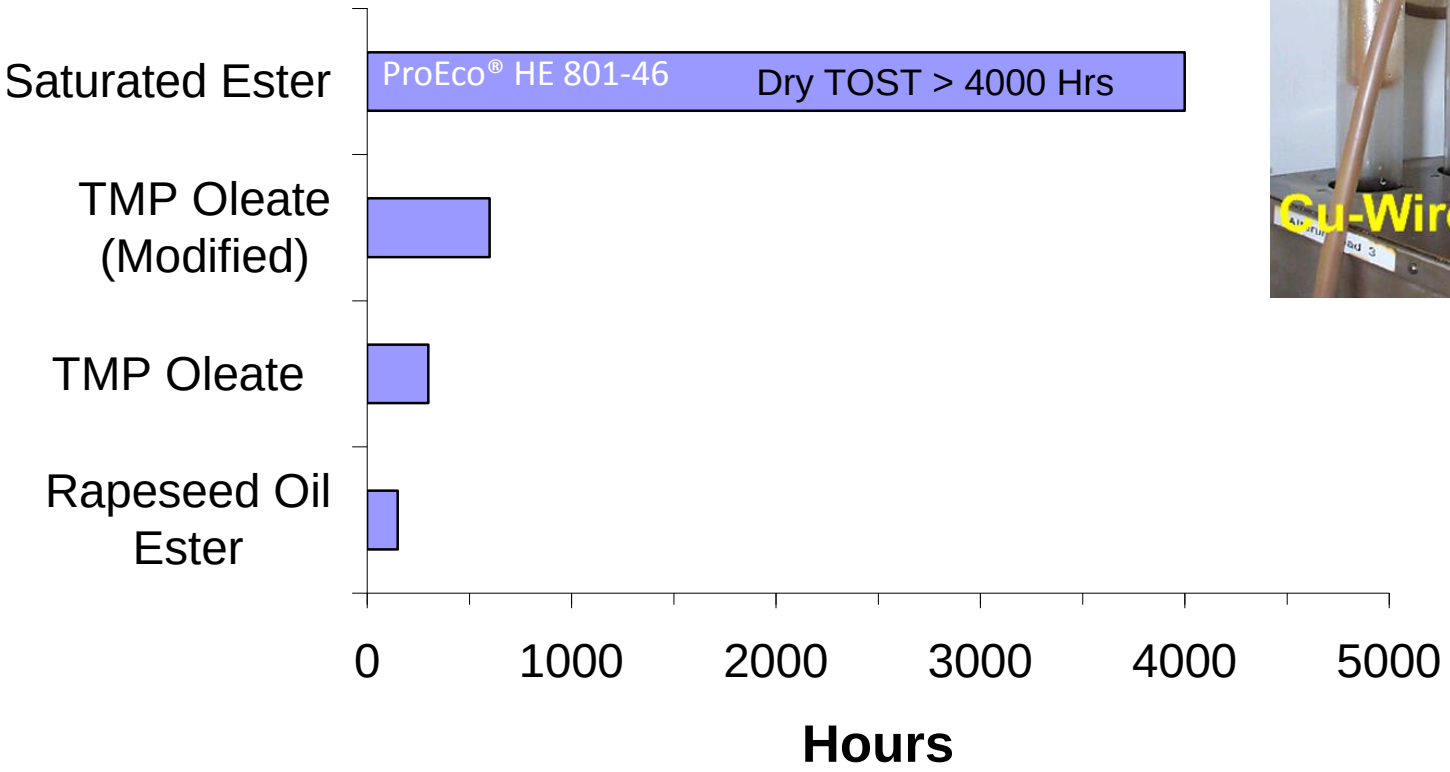
Sustainability performance

- Reduces negative impact on the aquatic environment
- Excellent biodegradability (ultimately/readily biodegradable)
- Low aquatic toxicity
- Enables OSPAR listing

Biodegradable hydraulic oil based on saturated synthetic esters HEES

Oxidation Test – Dry TOST – ISO 4263-3





Agenda

- Legislation
- Suitable base stocks for marine lubricants
- Suitable additives for marine lubricants
- Example: Marine cylinder oils
- Examples: Biohydraulics
- **Example: A new renewable biopolymer as lubricant additive**
- Summary and Conclusions

Examples: A New Renewable Biopolymer as Lubricant Additive

BASF
We create chemistry

Market information

Application: Industrial lubricants

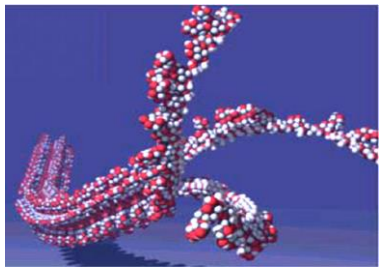
Marine lubricants

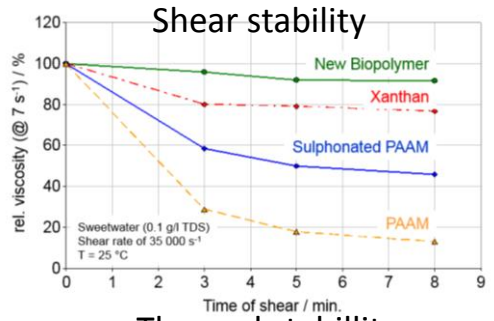
Customer Industry: Various

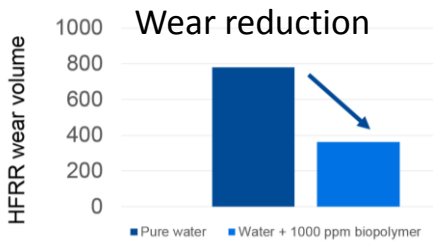
Market: Global

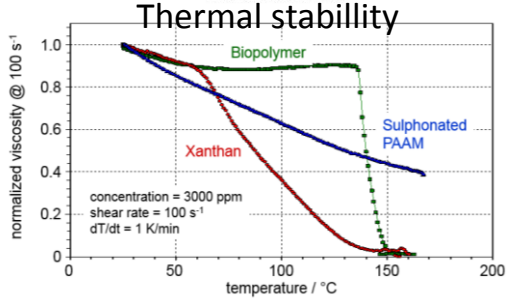
Differentiation potential

- **Performance Benefits:**
  - Outstanding shear stability
  - Outstanding thermal stability
  - Outstanding thickening efficiency
  - Reduction of wear and friction









Sustainability performance

- Reduces negative impact on the aquatic environment
- Excellent biodegradability
- Low aquatic toxicity and renewable content of 100%
- Enables EU Ecolabel and OSPAR listing for formulated lubricants

Health and Safety | Renewables | Biodegradability | Resource Efficiency

Agenda

- Legislation
- Suitable base stocks for marine lubricants
- Suitable additives for marine lubricants
- Example: Marine cylinder oils
- Examples: Biohydraulics
- Example: A new renewable biopolymer as lubricant additive
- **Summary and Conclusions**

Summary and Conclusions

BASF
We create chemistry

- Regulations trigger the increased use of biolubricants: OSPAR and VGP
- The most relevant base stocks are synthetic esters
- For esters base stocks, potential interactions with surface active additives should be considered
- MCL: calcium based deposits are a problem – use of metal free dispersants/cosolvents?
- Biohydraulic fluids with a premium technical performance are available for marine applications
- Future: Use of biobased additives ?

We create chemistry