

O FUTURO DAS BIO GRAXAS

LUBRICANTS AND GREASES CLASSIFIED AS EAL



BIODEGRADABLE



MINIMALLY
TOXIC



NOT
BIOACCUMULATIVE

III Encontro Internacional com o Mercado de Graxas da América do Sul
24 de outubro de 2023

FATORES CHAVES

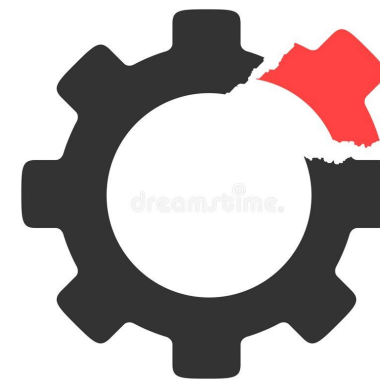


- As graxas de base biológica são um segmento de mercado muito pequeno, mas crescente.
- As preocupações ambientais e a conformidade regulatória são a principal motivação para o uso de graxas de base biológica.
- O diferencial de desempenho e preço entre graxas de base biológica e minerais está diminuindo.

O atrito e a oxidação são onipresentes em sistemas mecânicos lubrificados



PRINCIPAIS FALHAS DA INDÚSTRIA METAL MECÂNICA



FALHA **01**

DESGASTE

A maioria dos elementos de máquina falharam devido ao excesso de desgaste.

FALHA **02**

LUBRIFICAÇÃO

Redução dos intervalos de trocas dos lubrificantes usados devido a degradação acelerada.

EFEITO **03**

POLUIÇÃO

Emissão de gases de efeito estufa (GEE) aumentando a temperatura do planeta e prejudicando a qualidade do ar

EFEITO **04**

CONTAMINAÇÃO

do solo e da água devido a vazamentos ou descarte incorreto de lubrificante usado

A relação carga / lubrificante vem aumentando

PRINCIPAIS COMPONENTES DA GRAXA



Base Oil	Disadvantages
hydrocarbons	non-renewable feedstock, toxicity, environmental damage, price and supply fluctuations
triglyceride oil	thermal and oxidative instability, cost
diesters and polyol esters	diesters can degrade elastomer seals, high cost for polyol esters
polyglycols (e.g., polyethylene glycol, polypropylene glycol)	can degrade seals, paints
poly-alpha-olefin (PAO) oils	high-viscosity forms have varying degrees of biodegradability

~ 75% de óleo básico

Thickener	Disadvantages
simple soap (e.g., lithium or aluminum)	limited temperature and performance range; can stiffen after extended use
complex soap (commonly based on lithium, aluminum, or calcium sulfonate)	can be water-sensitive; may harden if overheated
organo-clay	may form residues in the housing after extended use; incompatible with most other grease types
polyurea	difficult to manufacture; toxic ingredients; some types are incompatible with most other greases
fumed silica	polar additives can disrupt the silica particle network

~ 20% de espessantes

Additive	Disadvantages
Zn dialkyl dithiophosphates (ZDDP); Mo, Sb, or Pb dialkyl dithiocarbamates (DTC); Pb naphthenate	toxicity, environmental effects, can accumulate in mechanisms and cause wear
Bi naphthenate	active sulfur co-EP agents can increase wear scarring at high speeds
MoS ₂ , graphite	particles can accumulate in components and cause wear
dodecylene succinic acid and other succinate derivatives	not as effective in preventing corrosion on cast iron or lead

5 a 10% de aditivos

https://www.stle.org/files/TLTArchives/2014/05_May/

ÓLEOS DE BASE VEGETAL

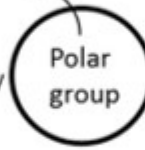


H = C - O (líquido polar)

Functional groups and polarity ↑

- ✓ Viscosity
- ✓ Tribofilm adhesion
- X Pour point (increase)
- X Thermo-oxidative stability
- X Chemical wear

Glicerol
C₃H₈O₃



Numbers of branching ↑

- ✓ Load-carrying capacity
- ✓ Pour point (decrease)
- ✓ Oxidative stability
- ✓ Thermal stability
- X Tribofilm adhesion

Degree of unsaturation ↑

- ✓ Pour point (decrease)
- X Tribofilm adhesion
- X Oxidative stability
- X Thermal stability

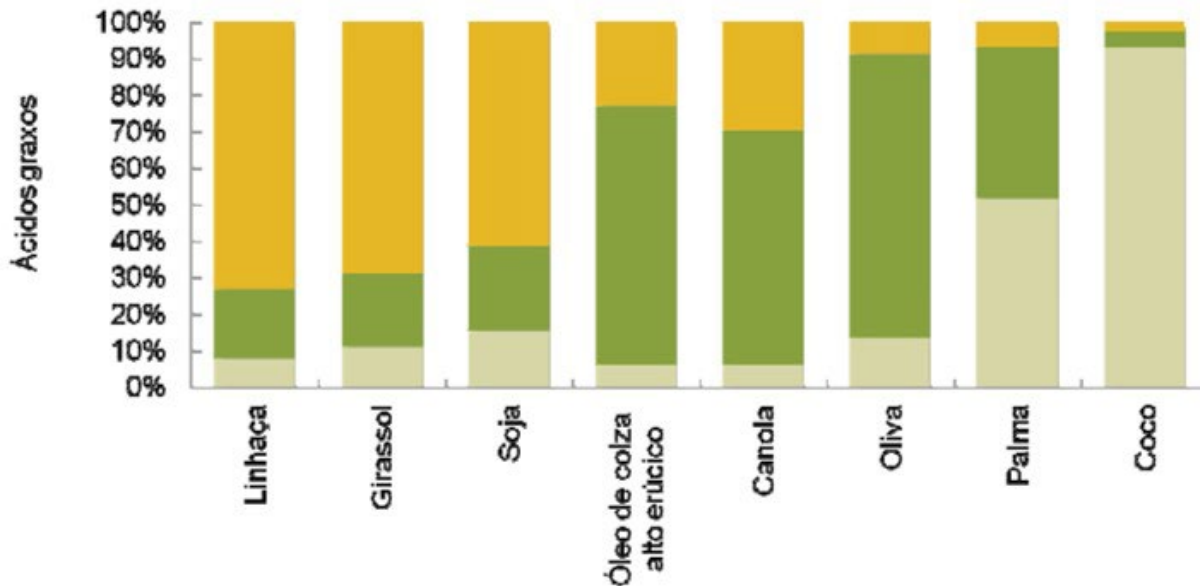
Carbon chain length ↑

- ✓ Viscosity
- ✓ Viscosity index
- X Pour point (except for molecules with steric hindrance)
- X Oxidative stability

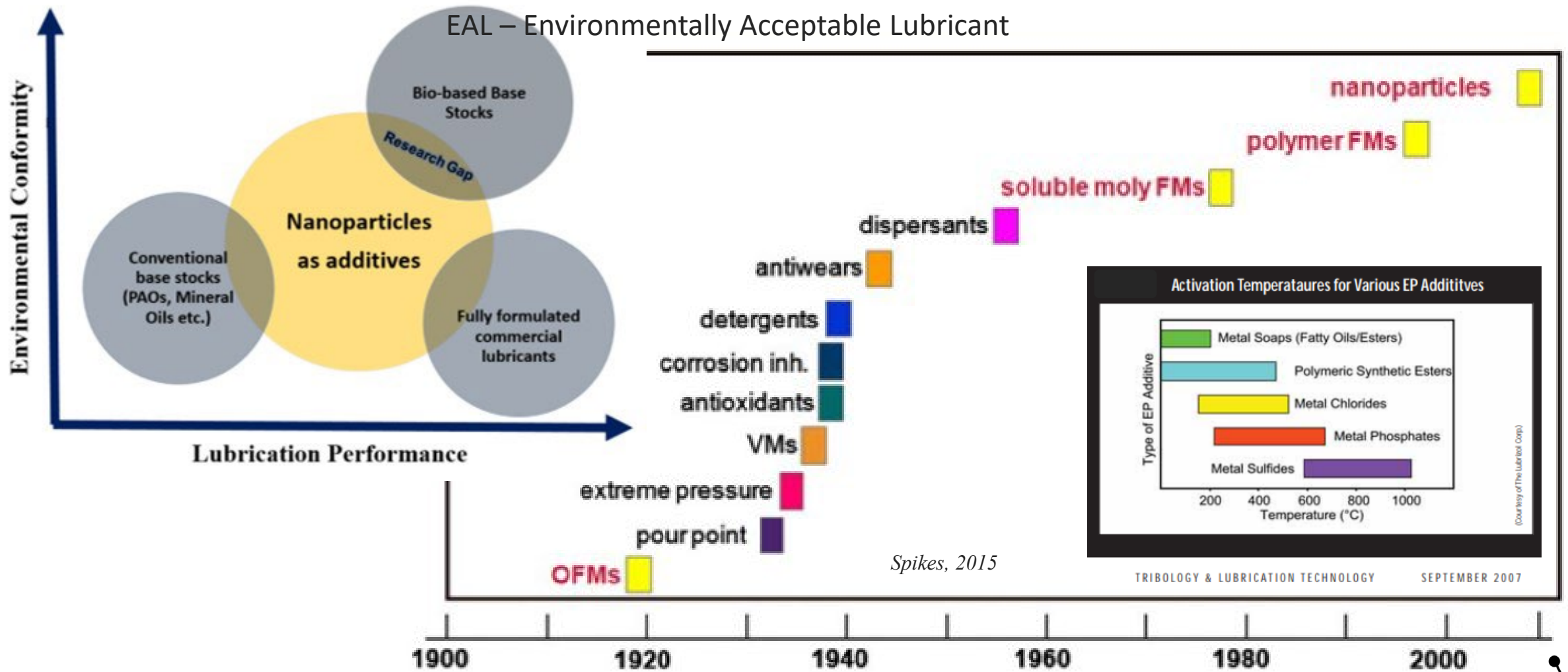
Ácidos Graxos

- ✓ Pros
- X Cons
- R carbon chain

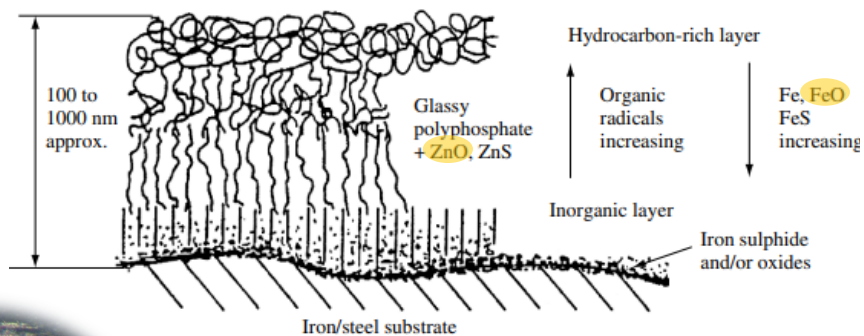
■ Saturados (C16:0, C18:0) ■ Monoinsaturado (C18:1) ■ Poliinsaturados (C18:2, C18:3)



A EVOLUÇÃO DOS ADITIVOS



TRIBOFILME ZDDP



(A) superfície original iniciando ação tribológica



(B) adsorção química ocorrendo na superfície



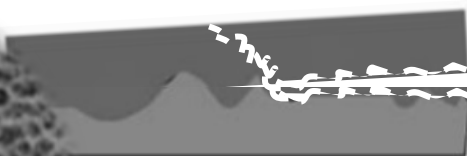
(C) reação formando tribofilme devido a ação tribológica



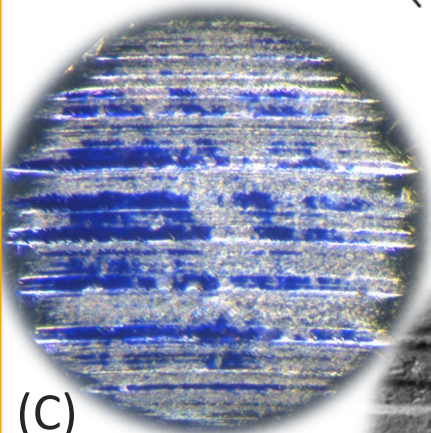
(D) ação contínua de crescimento do tribofilme



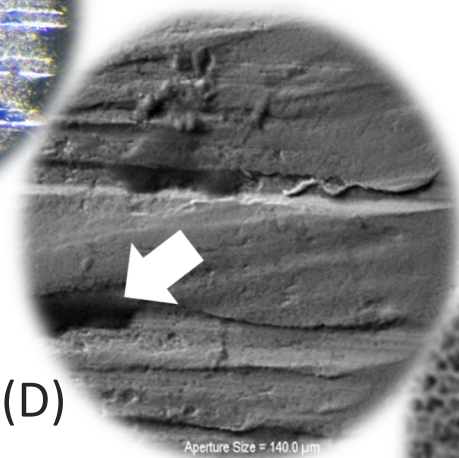
(E) diferença de potencial iniciando corrosão da superfície



(F) delaminação do tribofilme através de fadiga superficial

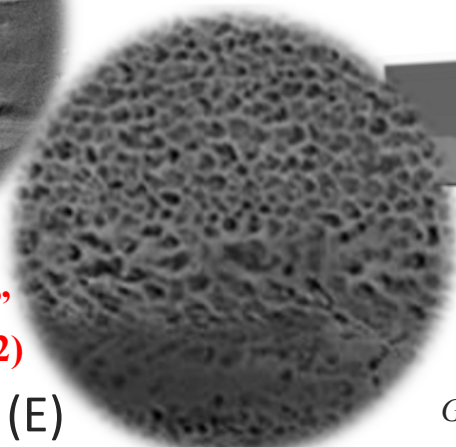


(C)



(D)

Aperture Size = 140.0 μm



(E)

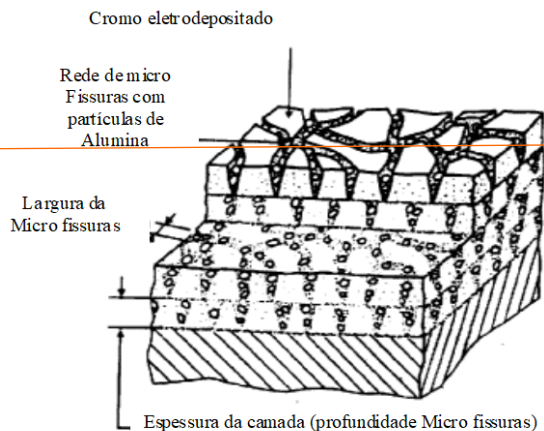
Garcia, 2014

geração de fragmentos para o tribosistema

“Será que o ZDDP, nunca será substituído?”
Tribology & Lubrication Technology (Jan/2022)

LUBRIFICANTES SÓLIDOS

Revestimentos Superficiais



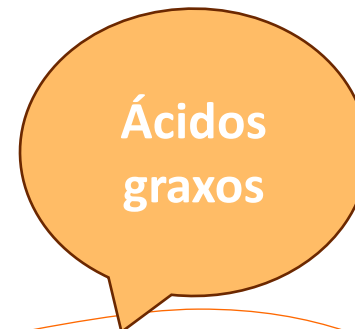
SIMPLES

BUCK

Lamelares
Polímeros
Metais
Óxidos
Compósitos
NTC

NANO

HIBRIDOS



Sais metálicos (ZDDP, WS2)

Copolímeros, silicones, PMMA

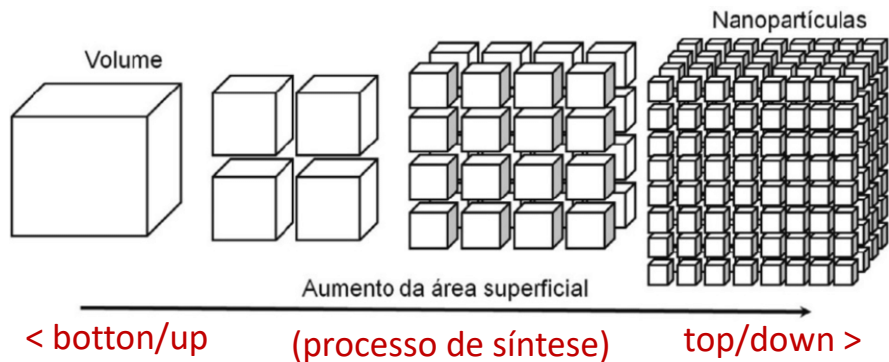
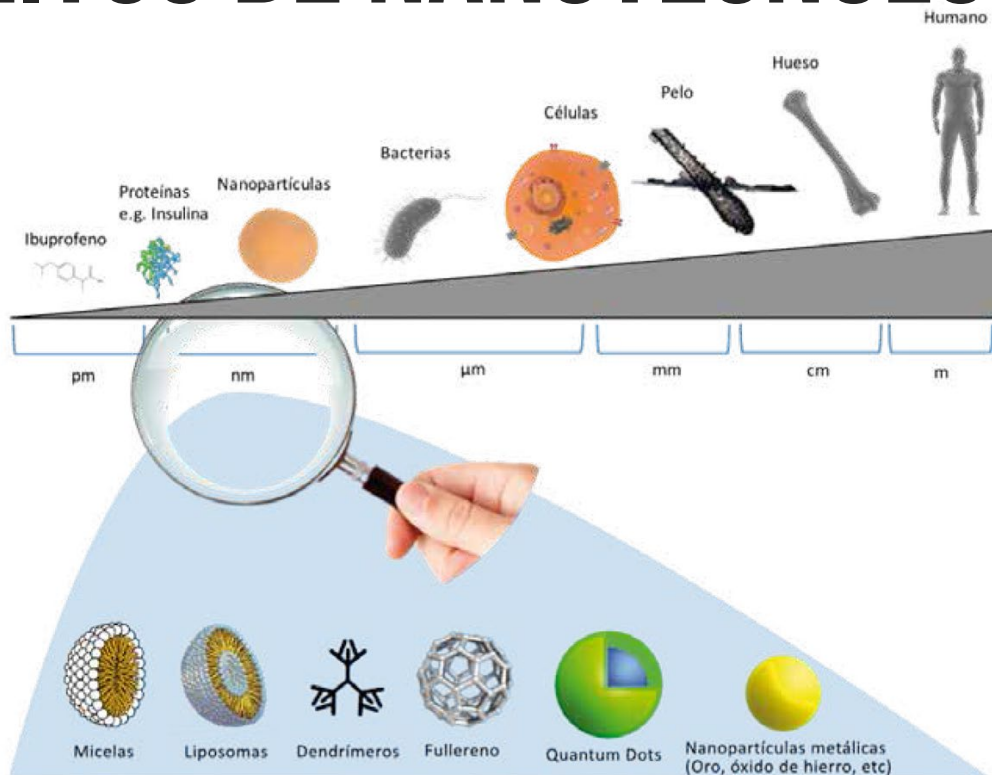
Tratamento Superficial	Cr Comp (Al ₂ O ₃)	Mo (MoC)	Nitret (Cr ₃ C ₂)
Desgaste do anel	●	○	○
Desgaste do cilindro	●	○	●
Resistência ao Scuffing	●	●	○
Durabilidade	●	○	●
Controle de óleo	●	●	●
Controle de emissões	●	●	●
Controle de Blow by	●	●	●
Economia de combustível	●	●	●
Agressão ao meio ambiente	○	●	●
Disponibilidade	●	●	●



Goetze AG, 1989

Aditivos & Lubrificantes

CONCEITOS DE NANOTECNOLOGIA



Dimensões

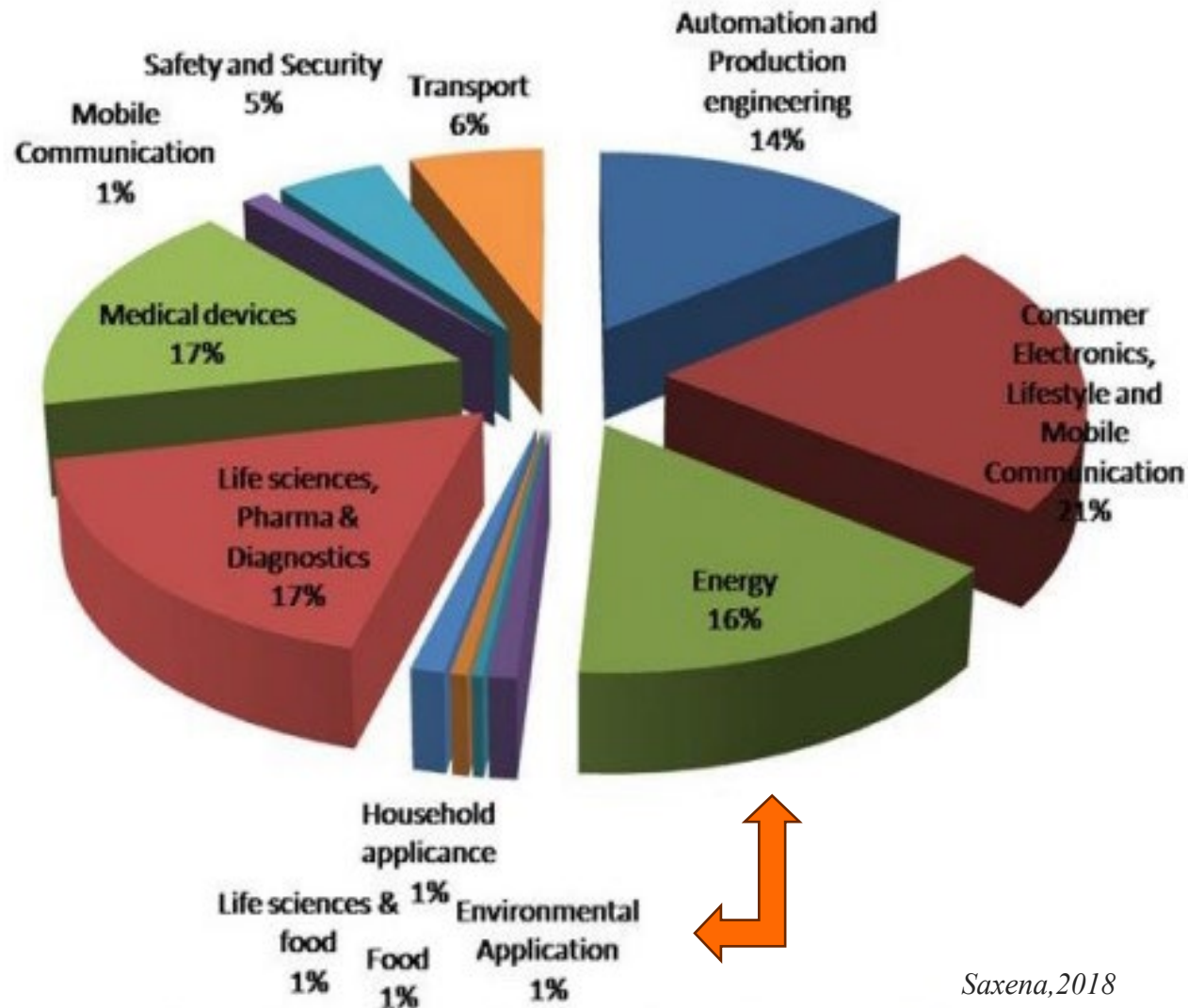
- 1D
- 2D
- 3D



Kotia, 2018



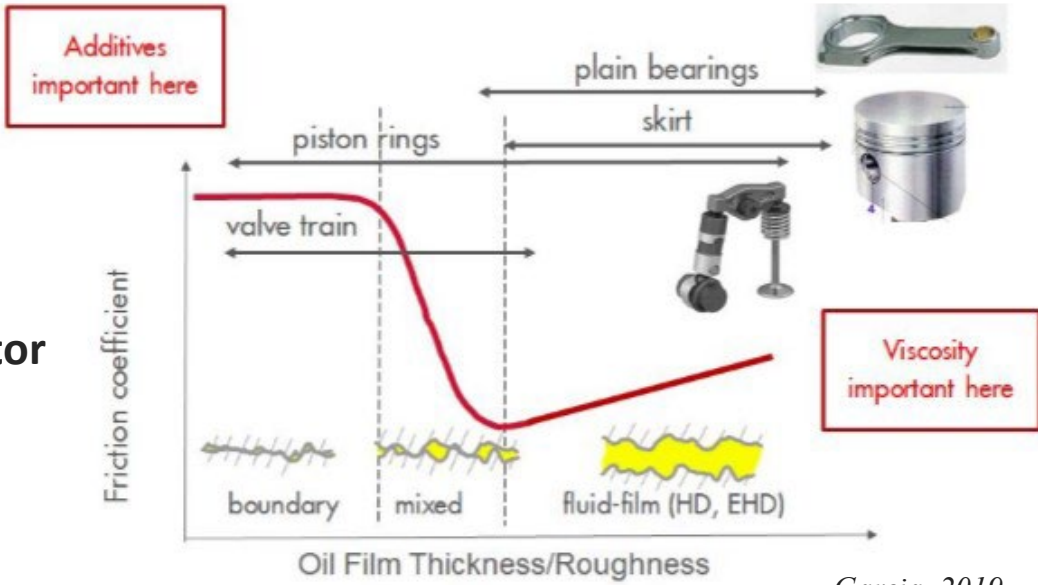
APLICAÇÕES DE NANO FLUÍDOS



Saxena, 2018

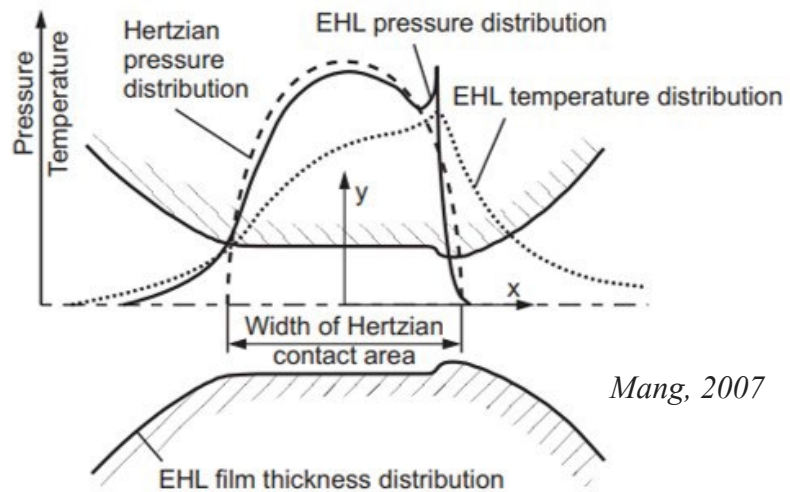
REGIMES DE LUBRIFICAÇÃO

Motor



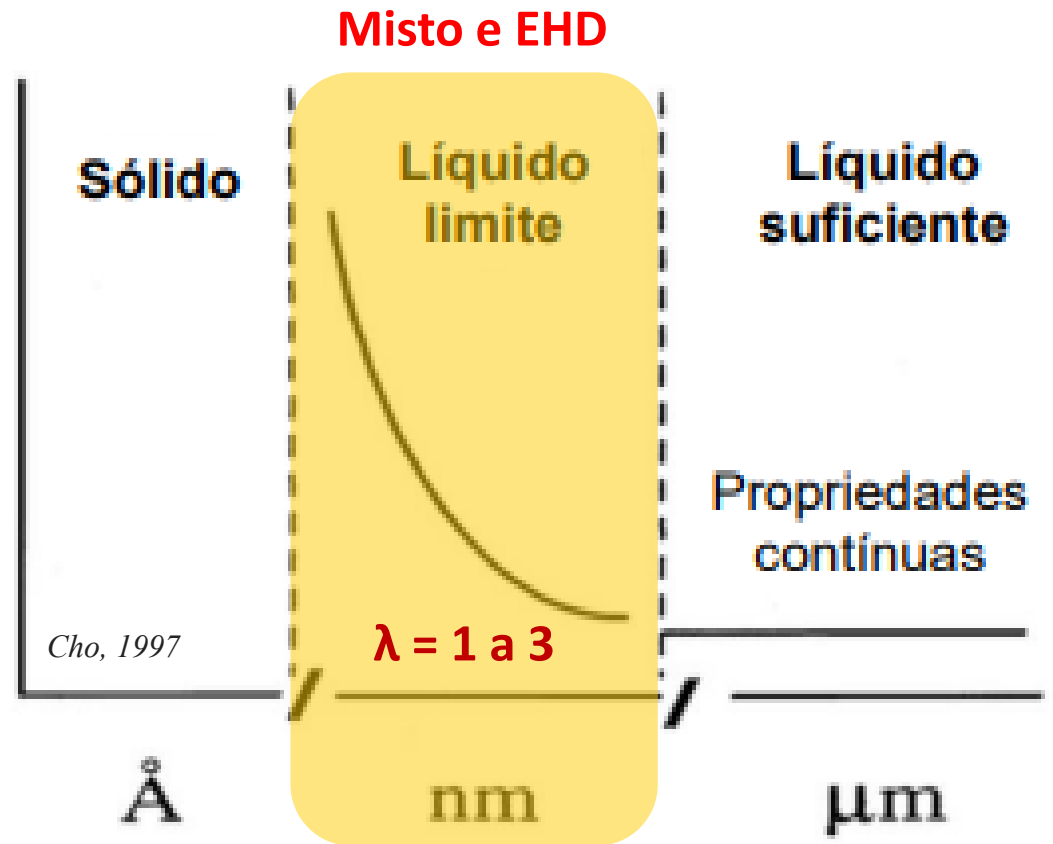
Garcia, 2019

Engrenagem

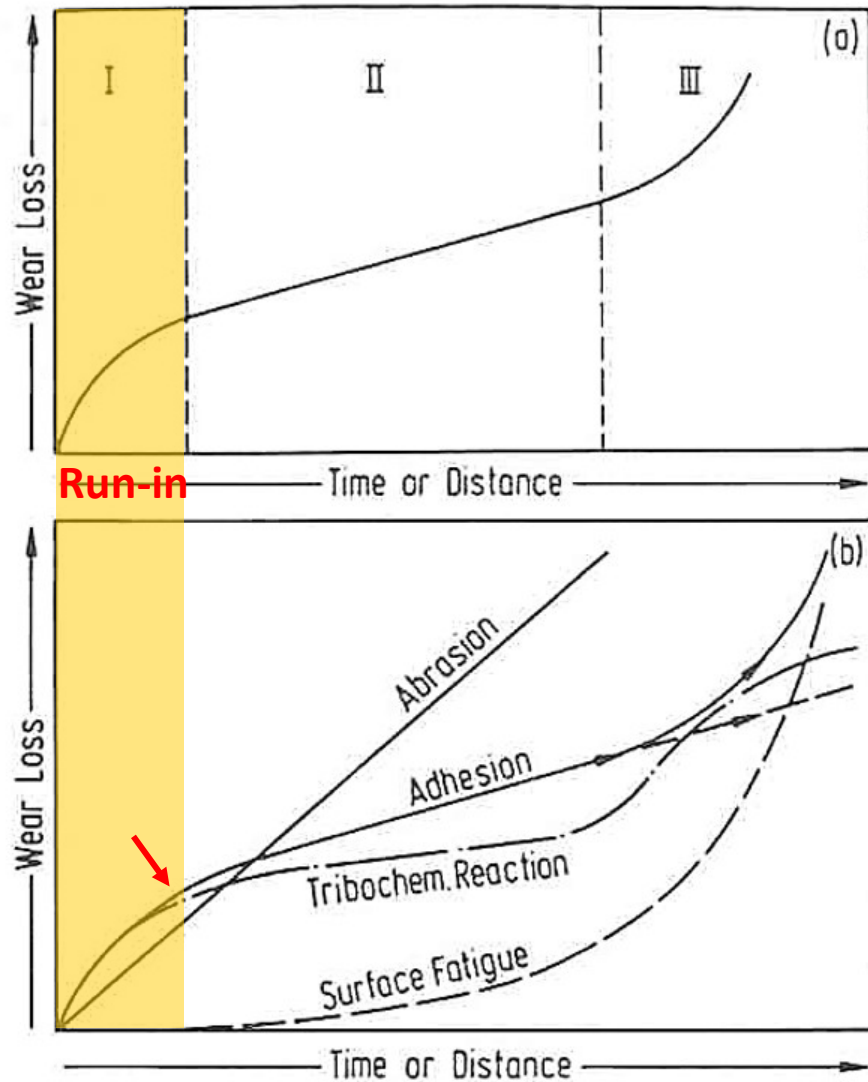


Mang, 2007

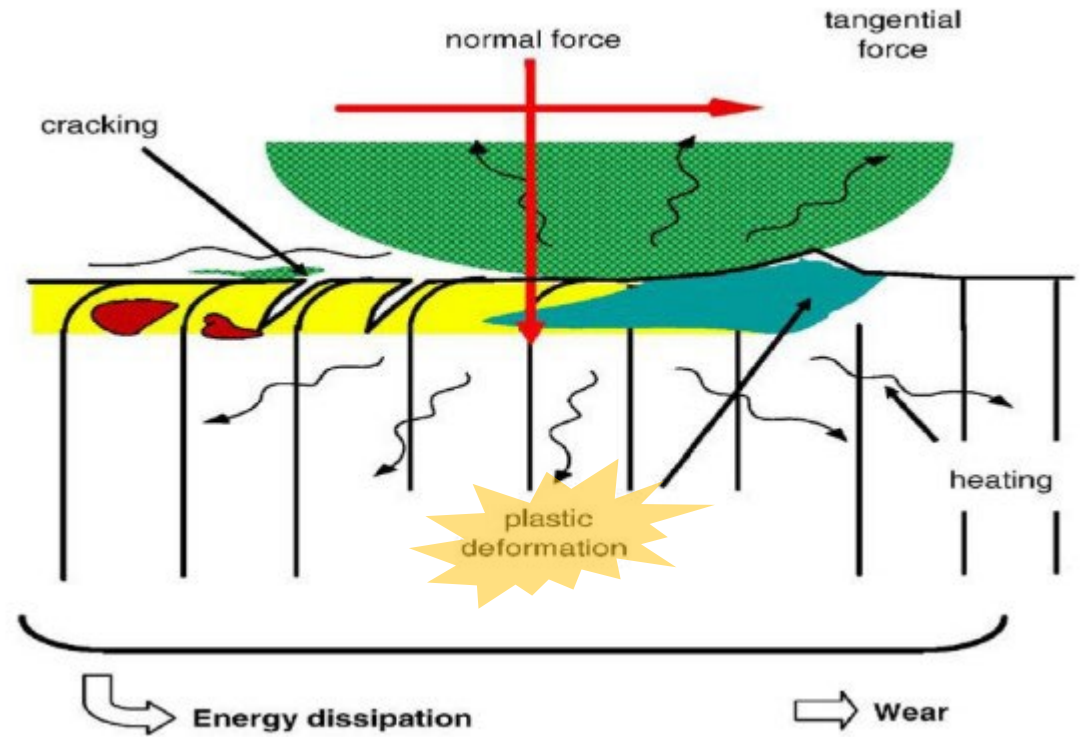
Coefficiente de Atrito



MECANISMOS DE DESGASTE

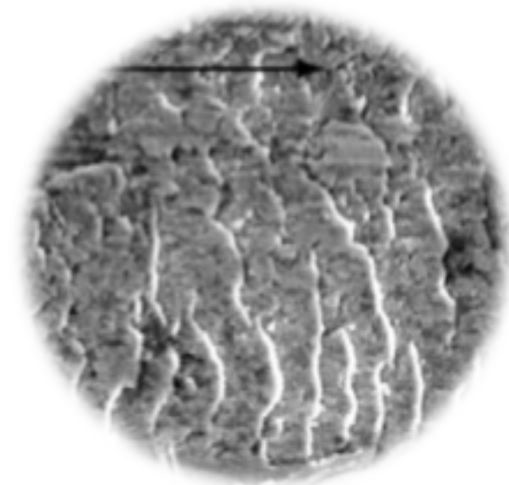


Zum Gahr, 1987



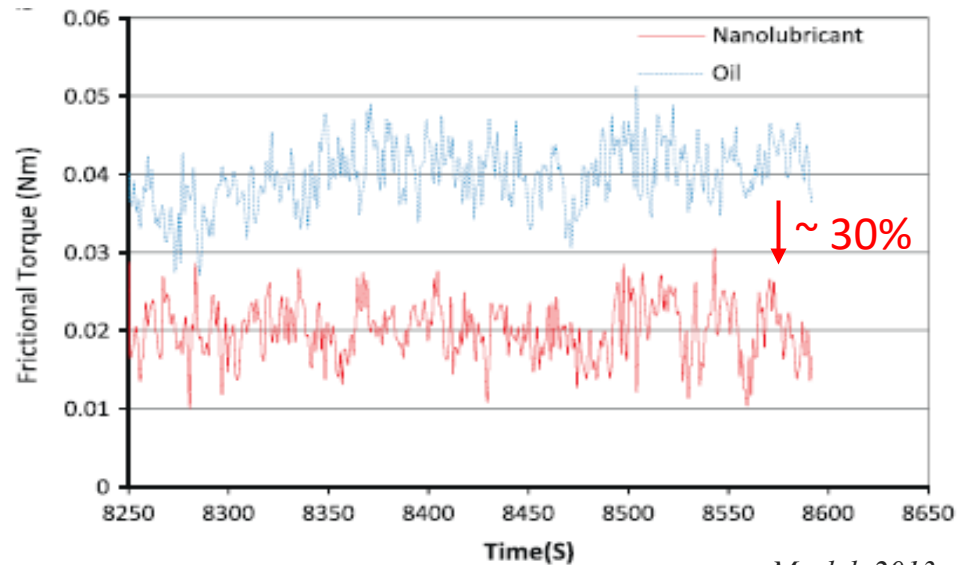
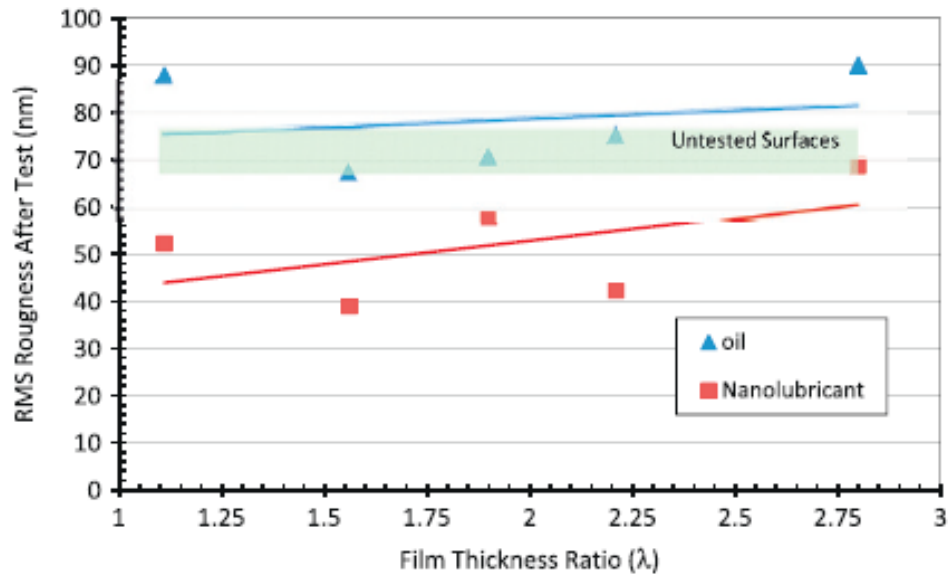
$$E_{total} = \mu \cdot F_n \cdot V$$

Abere, 2017



Deformação plástica superficial

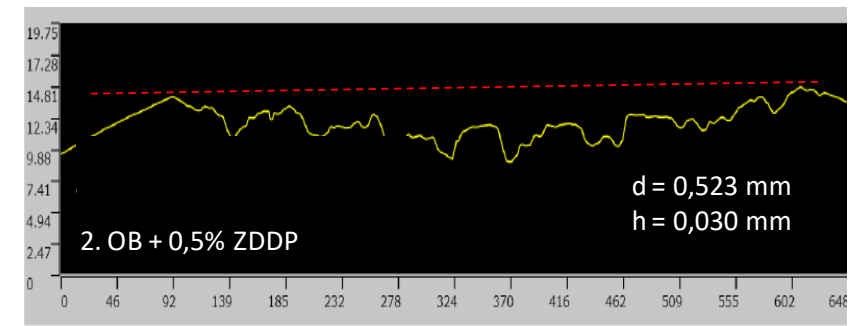
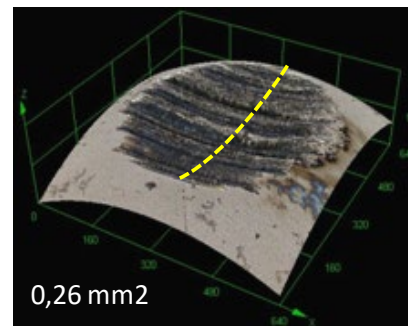
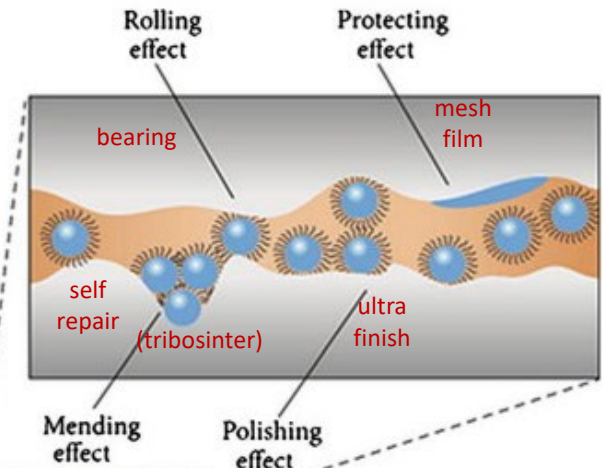
NANO MECANISMOS



Mosleh, 2013

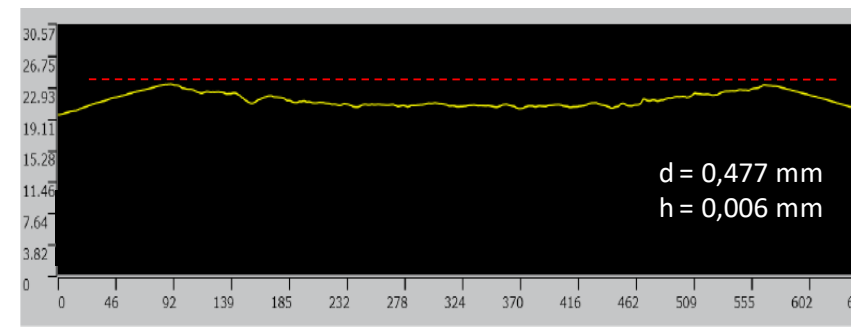
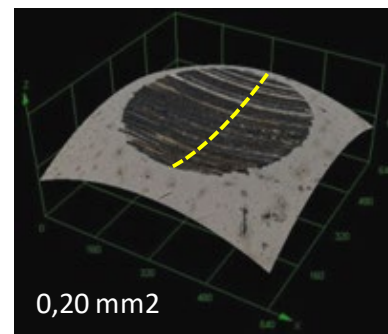
Ensaio Four Ball ASTM D4172

Lubrificante convencional



Garcia, 2014

Nanolubrificante



~ 25%

EXPERIMENTOS COM BIO GRAXA

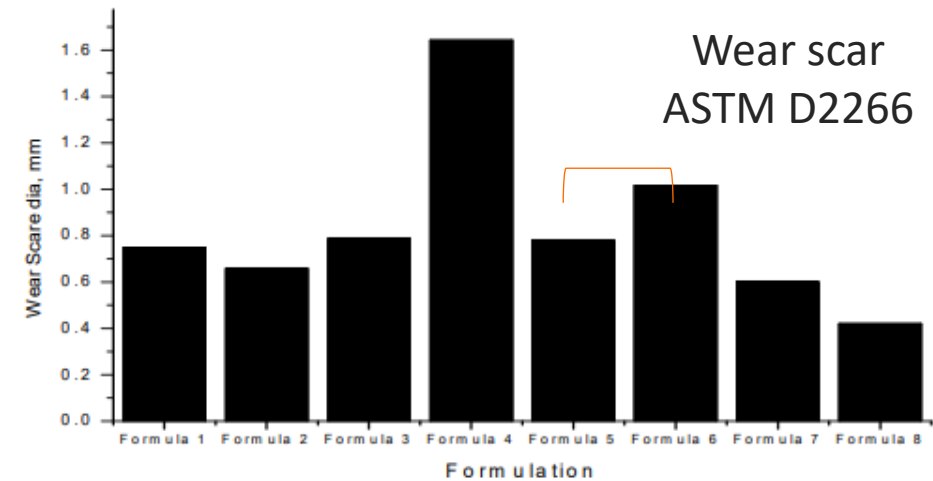
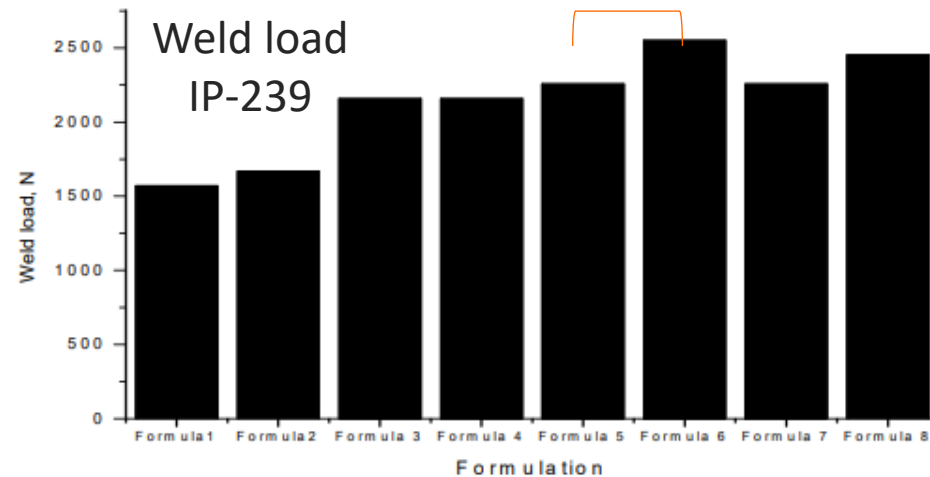
formulations of multipurpose grease with lithium stearate and oleato.

Serial Number	Component	Form. 1	Form. 2	Form. 3	Form. 4	Form. 5
1	Jatropha base oil	96	93.5	94	93.5	93.5
2	Lithium Stearate	3	3	5	5	5.5
3	Additive	1	1.5	1	1.5	1

(ZDDP)

Lithium oleato

Form. 6	Form. 7	Form. 8
93.5	90	-
-	-	91
5	5	4
1.5	5	5



Nagendramma, 2015

*Jatropha, óleo vegetal não comestível conhecido como pinhão manso

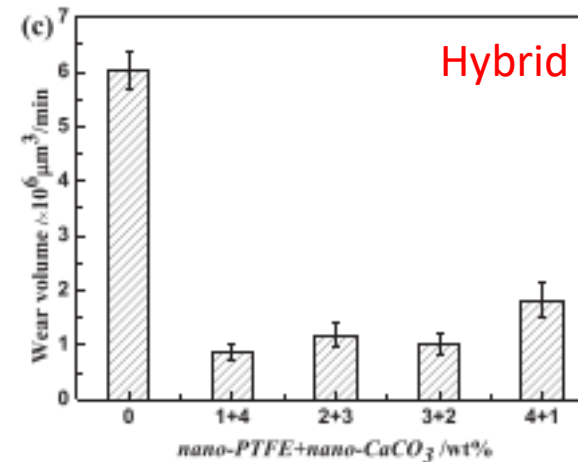
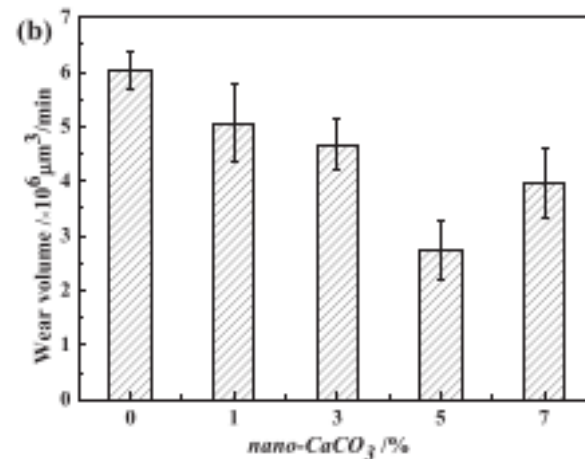
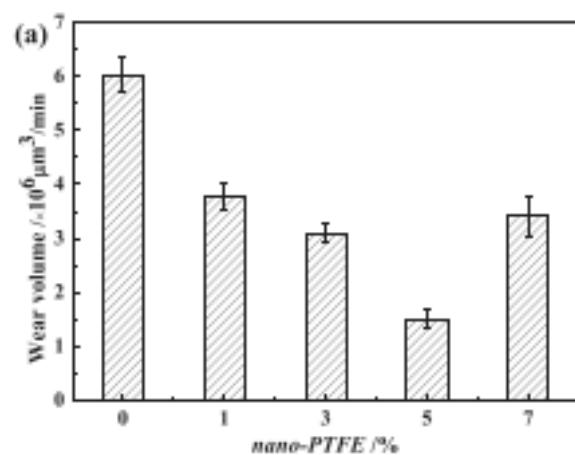
EFEITOS TRIBOLÓGICOS DOS NANOADITIVOS

Graxa de complexo de alumínio de qualidade alimentar

Suplementação

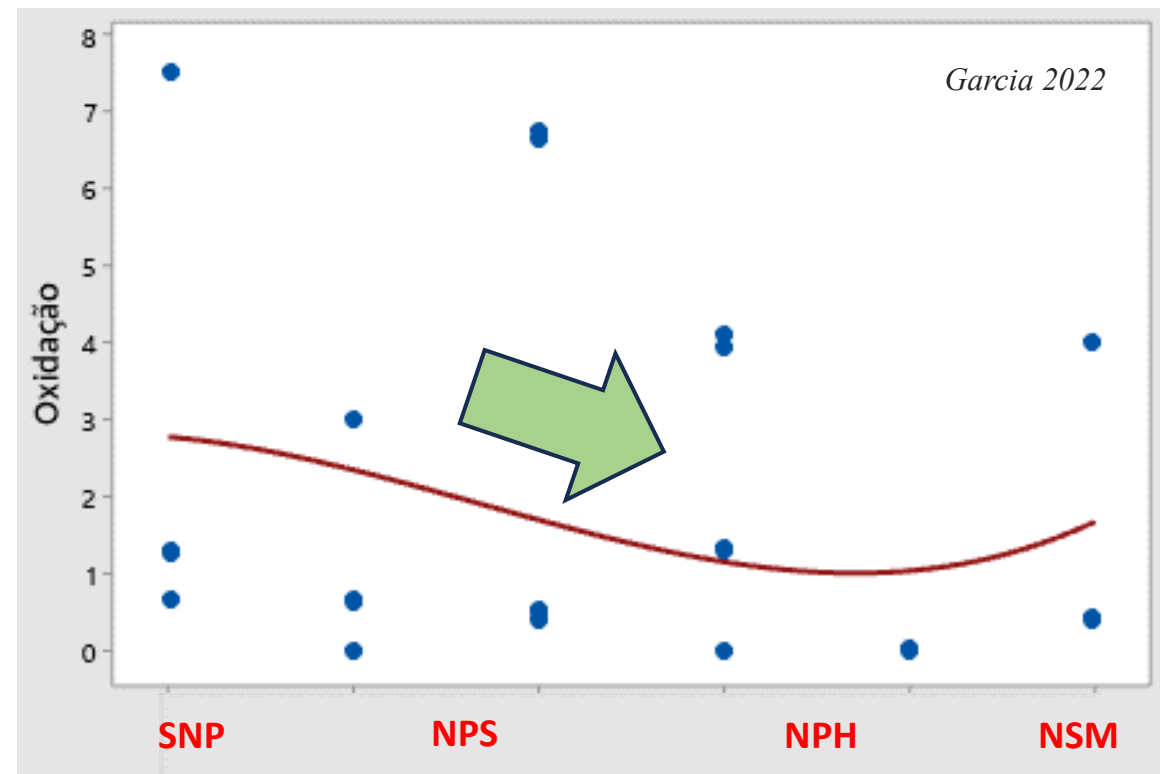
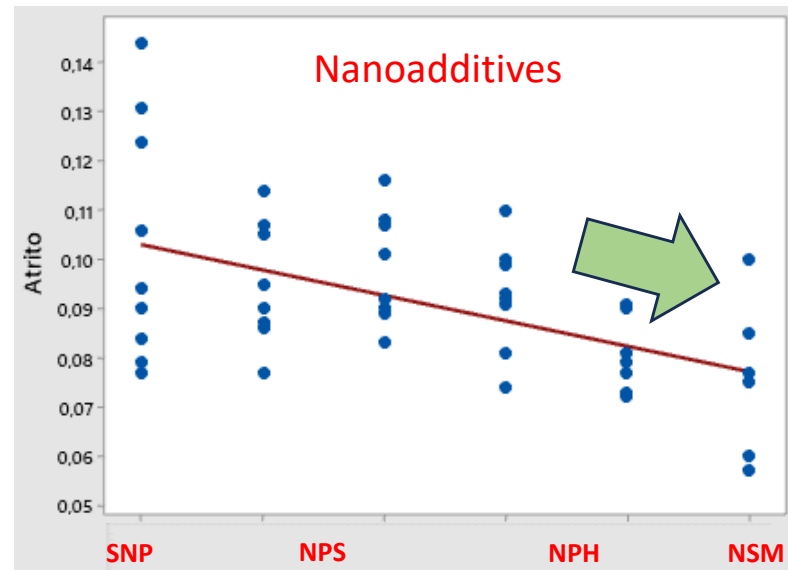
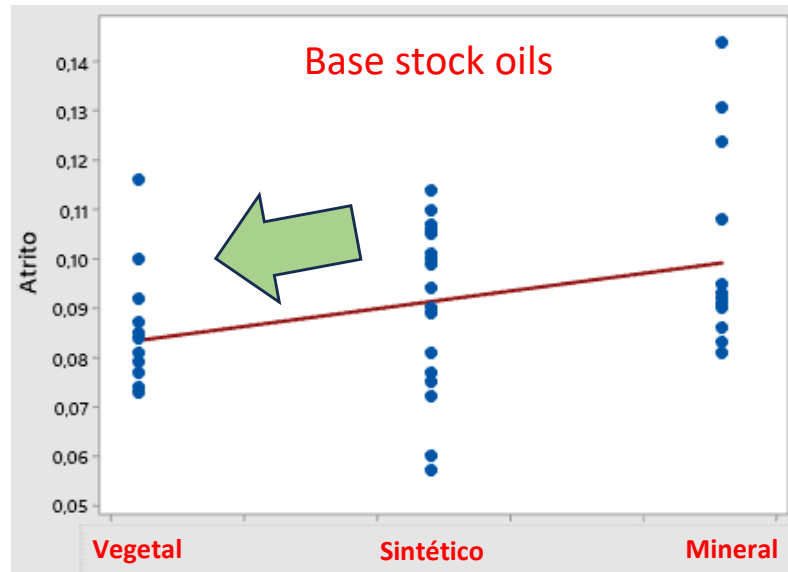
Tribological characteristics	NLGI 2 food safe grease	Same +5% WS ₂	Same +5% IF-WS ₂
Four ball wear, mm (ASTM D 2266)	0.59	0.39	0.45
Four ball weld, kg (ASTM D 2596)	315	670	540
Timken OK load, kg (ASTM D 2509)	18	30	24

Zhmud, 2013



Gong, 2021

EXPERIMENTOS NANOSTAR



SNP – óleos básicos sem nanoaditivo
NPS – nanoaditivos simples
NPH – nanoaditivos híbridos
NSM – nanoaditivo à base de sais metálicos

O FUTURO DAS BIO GRAXAS



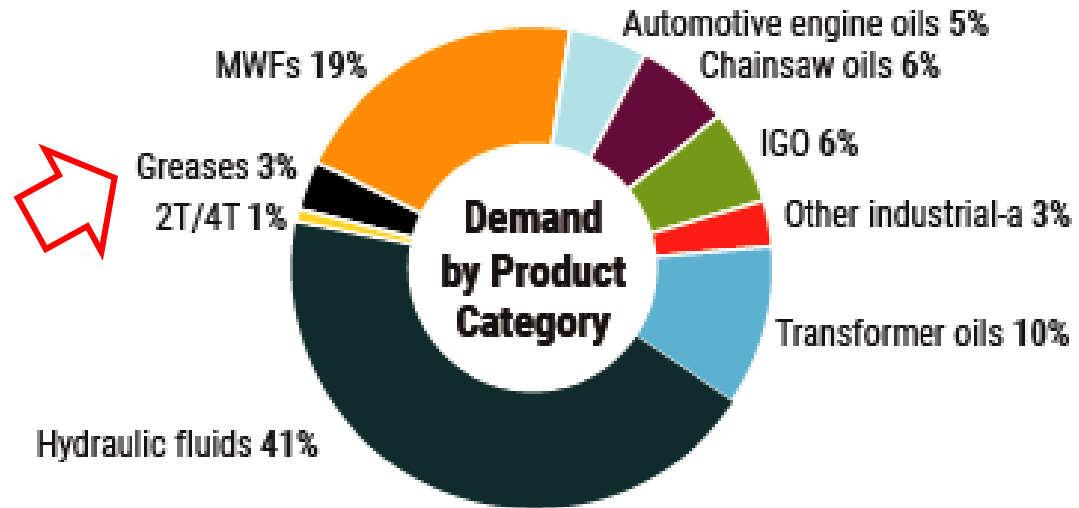
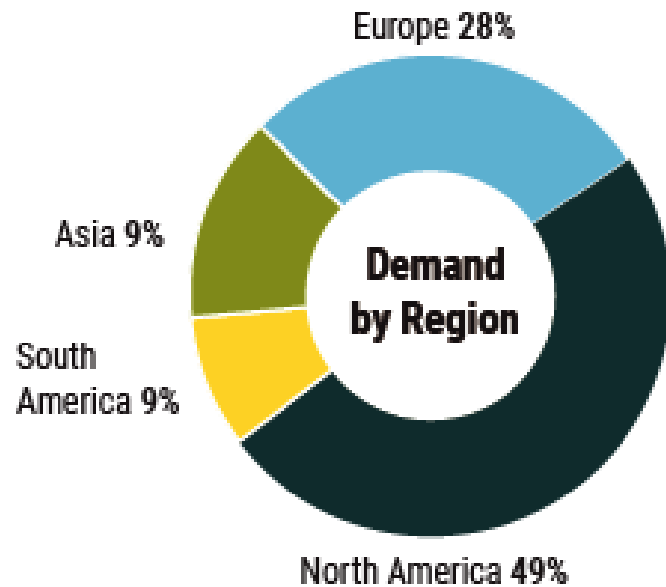
Lubricant Base Oil	Ratio of EAL cost to Conventional Mineral Oil Lubricant Cost
Mineral Oil	1
Vegetable Oils	1.2
Synthetic Esters	2 to 3
Polyalkylene Glycols	2 to 3

https://www3.epa.gov/npdes/pubs/vgp_environmentally_acceptable_lubricants.pdf

- As regulamentações ambientais continuarão impulsionando a mudança para produtos de **base biológica**, assim como aumentará a procura por **aditivos mais compatíveis**.
- Novos óleos básicos poderão entrar em jogo, utilizando óleos de plantas exóticas ou algas, ou ainda **misturas de óleos de base biológica com óleos minerais e sintéticos**.
- As flutuações nos preços do petróleo e os óleos de base biológica com **melhor desempenho** irão acrescentar mais incentivos para tornar a graxa ecológico.

https://www.stle.org/files/TLTArchives/2014/05_May/

MERCADO GLOBAL DE BIOLUBRIFICANTES

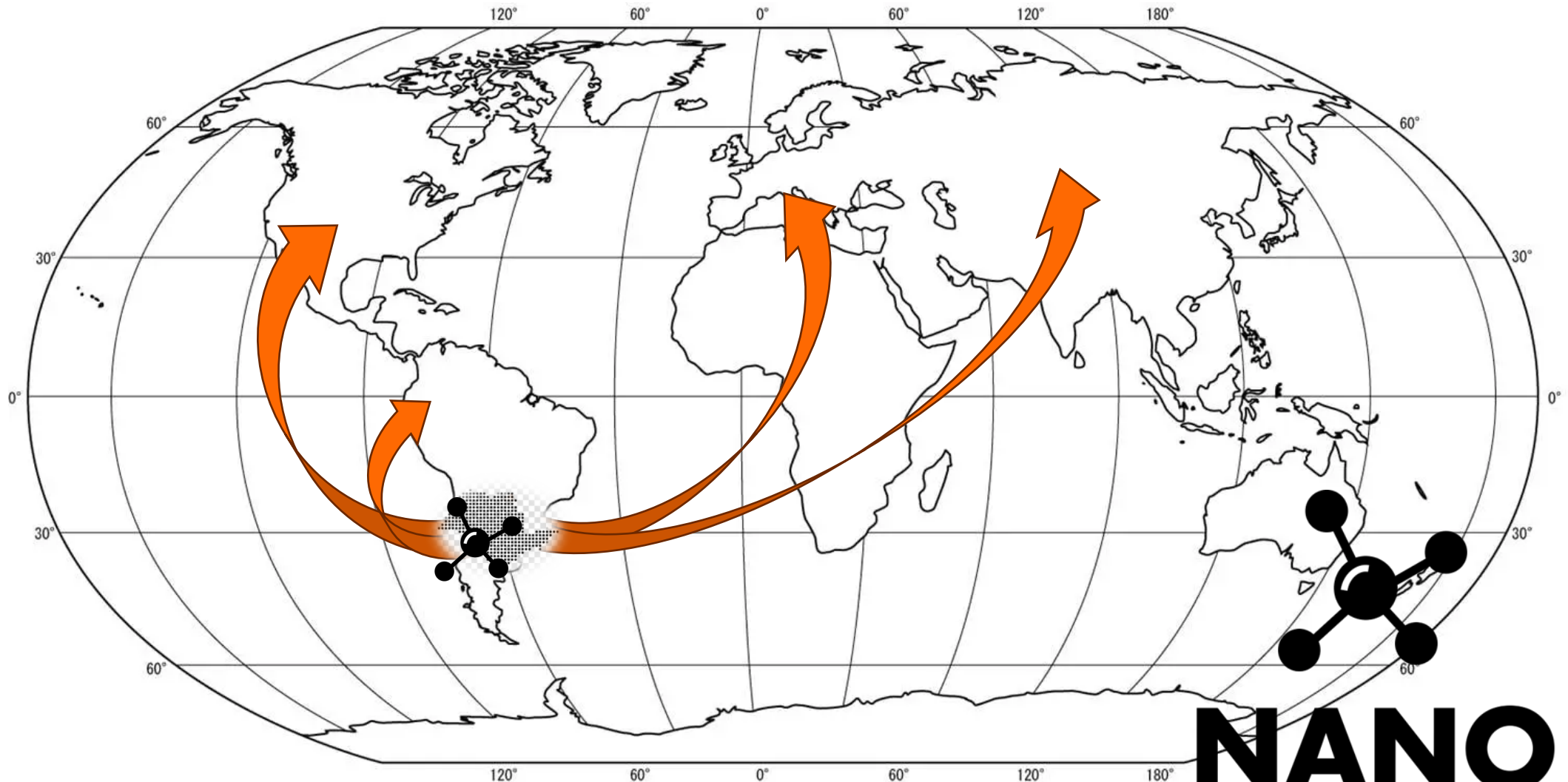


Source: Kline & Company, July 2020, Bio-Lubricants: Market Analysis and Opportunities
LubesnGreases.com

BIOLubrificantes
Mundo US\$ 3,5 BM
Brasil US\$ 206 MM
GMR Análisis 2023



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THE.NANOSTAR@GMAIL.COM

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