

#### P- and Si- Free Staining Inhibitors for Lightweight Metals

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# Agenda

- Light weight metals market trend
- Aluminum Staining Root Cause
- Anti-staining Mechanism
- Staining Inhibitor Existing Technology
- Phosphorus and silicone free technology



## Lightweight Metals Market Trend

Lightweight Materials Market, By Region, 2015 - 2026 (USD Billion)



The global lightweight materials market is estimated to reach USD 237.1 Billion by 2026 with a CAGR of 7.9% - Polaris market research

#### Aluminum: More and more usage in various applications, especially in automotive industry







# Aluminum Staining Root Cause

Aluminum reacts with oxygen and forms a stable oxide layer



Normal corrosive presence of Alumium

# Al Corrosion Mechanism in Aqueous Solution



H2 bubble activity is distinguished into the following phases:

①formation, ② detachment from metal surface and movement,

③ arrival at droplet surface and growth, and ④ bursting of H2 bubbles.

# $Al + 3H_2O \longrightarrow Al(OH)_3 + \frac{3}{2}H_2$

#### **Electrochemical reactions**

Anode : oxidation of metal (corrosion)

 $Al \longrightarrow Al^{3+} + 3e^{-}$ 

Cathode : reduction of depolarizing agent

$$\frac{3}{2}O_2 + 3H_2O + 6e^- \longrightarrow 6OH^-$$



# Anti-Staining Mechanism

Three main mechanisms:

- Chemical absorption: inhibitors form a protective layer through chemical bonding on Aluminum surface
- Complex formation: inhibitos form a complex with corrosive agents to prevent them from staining the Aluminum surface
- Physical barrier: A protective film formed to protect the aluminum surface from staining



# Type of Staining Inhibitors

#### $\rightarrow \mbox{Technologies}$ in the market

- Phosphorus based ones- Most effective ones with wide working pH range
- Sulfonates- Poor solubility in base oil
- Carboxylic Acid/amine salts- Narrow pH effective range and hard water sensitive
- Polymers-not to be compatible in synthetic fluids
- Silicates–Not stable enough. Hydrolysis reaction. Tend to form undesirable, tacky residue on the workpiece or the machine tool



# Mechanism of Phosphate Ester as Inhibitors



The adsorption and binding of Phosphate ester on the metal surface take place in 3 steps:

- 1. Acid H-bonded to hydroxylated surface
- 2. Condensation process
- 3. Formation of a resonance stabilized phosphonate complex



## Phosphate Esters

Phosphate ester chemical structure varies and affects its performance





	Parameters	Properties	Feedstocks availability and renewak raw materials
Type of alcohols	- Natural or Synthetic - Degree of alkoxylation of alcohols: EO, PO - Length chain	Surface activity/oil solubility balance	
Phosphating agents	- P2O5 - Polyphosphoric acid - POCl3 - Hybrids	Monoalkyl/Dialkyl/Trialkyl Phosphates ratio	Hydrophilic/Hydrophobic balance
Synthesis process	Molar ratio Temperature Type of catalyst	- Monoalkyl/Dialkyl/Trialkyl Phosphates ratio - Purity	Performance: Foam, Staining, Tribology, etc.



#### Aluminum Staining Inhibition – Different Phosphate Esters

DI Water, pH = 9.5

0.5% additive - pH = 9.5 - DI Water /  $45^{\circ}$ C - 7 days



Lubrhophos® LF 800 and LF 832: Lauryl based phosphate ester

Lubrhophos<sup>®</sup> LF 832 provides the best staining inhibition across aluminium grades, even in hard water conditions

440ppm Hard Water, pH = 9.5

0.5% additive- pH = 9.5 - Hard Water (440 ppm) / 45°C - 7 days



AI 2024 T3 📕 AI 6061 T6 📕 AI 7075 T6

### P - and Si - Free Technology: Geropon AS 020

New type of chemistry providing anodic protection to Aluminum surface and prevent staining

Al coupons half-immerse test Additive 0.15%wt@Dl water-pH(MEA:TEA=1:3)=9.3, 96h@50°C								
Al 2024			Al 6061			Al 7075		
Blank	Geropon AS 020	Rhodafac AS 010	Blank	Geropon AS 020	Rhodafac AS 010	Blank	Geropon AS 020	Rhodafac AS 010
		4.253	4750 We	sight change,	ng	4800	1676	47-16
-	0.1	-0.7	-	0.4	0	-	-0.1	0.1



Geropon AS 020 dissolve in water to form a transparent aqueous solution

• Geropon AS 020 is an effective inhibitor like Rhodafac AS 010 to answer the rise in most of the Al(alloys) machining process at a low dosage level.

### P - and Si - Free Technology: Geropon AS 020

New type of chemistry providing anodic protection to Aluminum surface and prevent staining

Al coupons half-immerse test Additive 0.15%wt@200 ppm hard water-pH(MEA:TEA=1:3)=9.3, 96h@50°C								
Al 2024			Al 6061			AI 7075		
Blank	Geropon AS 020	Rhodafac AS 010	Blank	Geropon AS 020	Rhodafac AS 010	Blank	Geropon AS 020	Rhodafac AS 010
1215	4829		9107				2740	
Weight change,mg								
-	0.1	0.1	_	0.4	0.1	-	0.1	0.6



Geropon AS 020 can be disperble in water to form a stable hazy aqueous solution.

- Geropon AS 020 provides Al(alloys) surface with efficient protection at low dosage.
- Geropon AS 020 shows much better hard water stability than Rhodafac AS 010 in both dispersibility and Al surface protection.

#### Geropon AS 020: Higher Thermal Stability for Modern Machining



 Geropon AS 020 has almost 40°C higher thermal decomposition temperature than Rhodafac AS 010 and other P esters. Superior solution for modern machining.

\*Rhodafac AS 010-Alkyl Phosphate Type Aluminum Corrosion Inhibitor of Solvay.

#### Geropon AS 020: Foam Tendency



• The foam tendency of Geropon AS 020 could be suppressed by tiny amount of defoamer to a lower foam level.

\*Rhodafac AS 010–Alkyl Phosphate Type Aluminum Corrosion Inhibitor of Solvay.



#### Geropon AS 020: Foam Tendency



Cnomo test

- The foam tendency of Geropon AS 020 is higher than Rhodafac AS 010 but could be suppressed by tiny
  amount of defoamer to a lower foam level.

\*Rhodafac AS 010–Alkyl Phosphate Type Aluminum Corrosion Inhibitor of Solvay.

## Conclusion

- Light metals like Aluminum and its alloy are susceptible to staining during machining
- Aluminum staining root cause: Filiform, Galvanic and Poultice corrosion
- Anti-staining mechanism: Chemical absorption, complex formation and physical barrier
- Type of staining inhibitors: Phosphate esters, sulfonates, carboxylic amine, polymer, silicates, etc.
- Phosphate esters: chemical structure varies and affects its performance
- New P- and Si- free inhibitor: effective anti-staining additive, especially in hard water and higher temperature stability but needs to be combined with antifoam



# Thank You

