Post-machining Cleaning - an accelerated guide to nonionic surfactant chemistry in cleaning formulations

The PQCW offers practical, hands-on and independent, training in cleaning.
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Hosts: The Product Quality Cleaning Workshop Team

Barbara and Ed Kanegsberg – "The Cleaning Lady and the Rocket Scientist"

- BFK Solutions - Consultants in Critical Cleaning – established in 1994
- Authors and Editors of the two-volume CRC Handbook for Critical Cleaning
- Independent recommendations for process improvement
- Common sense expertise and industry involvement: JS3 (military), IPC, ASTM, U.S. ISO expert, EPA, FDA
- Co-chairs of the Product Quality Cleaning Workshops
- barbara@bfksolutions.com and ed@bfksolutions.com

Darren Williams – "The Professor"

- Professor of Physical Chemistry at Sam Houston State University
- Leader of the Cleaning Research Group
- Co-chair of the Product Quality Cleaning Workshops
- Performs cleaning trials, material compatibility studies, and models/tests cleaning chemistry formulations
- williams@shsu.edu

2

2

PQCW - Workshops for Terrific Products

- "People with different functions within our company, including Strategic **Sourcing**, Project **Management**, and **Manufacturing Engineering**, attended.

- "We learned a lot; and we have made changes. We are **refining our own cleaning** requirements and putting together training programs.
- "For example, we used the workshop to develop **black light testing and fixtures;** and we have already set up a one-hour **"Parts Washing 101"** training course.
- "The section about **EPA amended TSCA had useful, timely information."**
  - Christian Johnson, Engineer, Yaskawa, participant, PQCW21

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Our Speaker

Stephanie Cole

- Joined Clariant Corporation in July of 2019
- Sr. Formulation Chemist for the Industrial Lubricants business unit in North America.
- Bachelor of Science in Chemistry (marketing minor), University of Houston.
- Eight years of knowledge in the industrial lubricant field including:
  - industrial cleaning formulation and application
  - metalworking fluid formulation and application
- At Clariant Corporation she translates customer needs into technical solutions by understanding the application benefits of Clariant's portfolio through formulation and data generation.

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4

CLARIANT

Post Machining Cleaning

An Accelerated Guide to Nonionic Surfactant Chemistry in Cleaning Formulations

Stephanie Cole
Industrial Lubricants
ICS
01.03.2022

what is precious to you?

5

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Takeaways

Challenge the surfactant manufacturers and formulators to design molecules to address your pain points.

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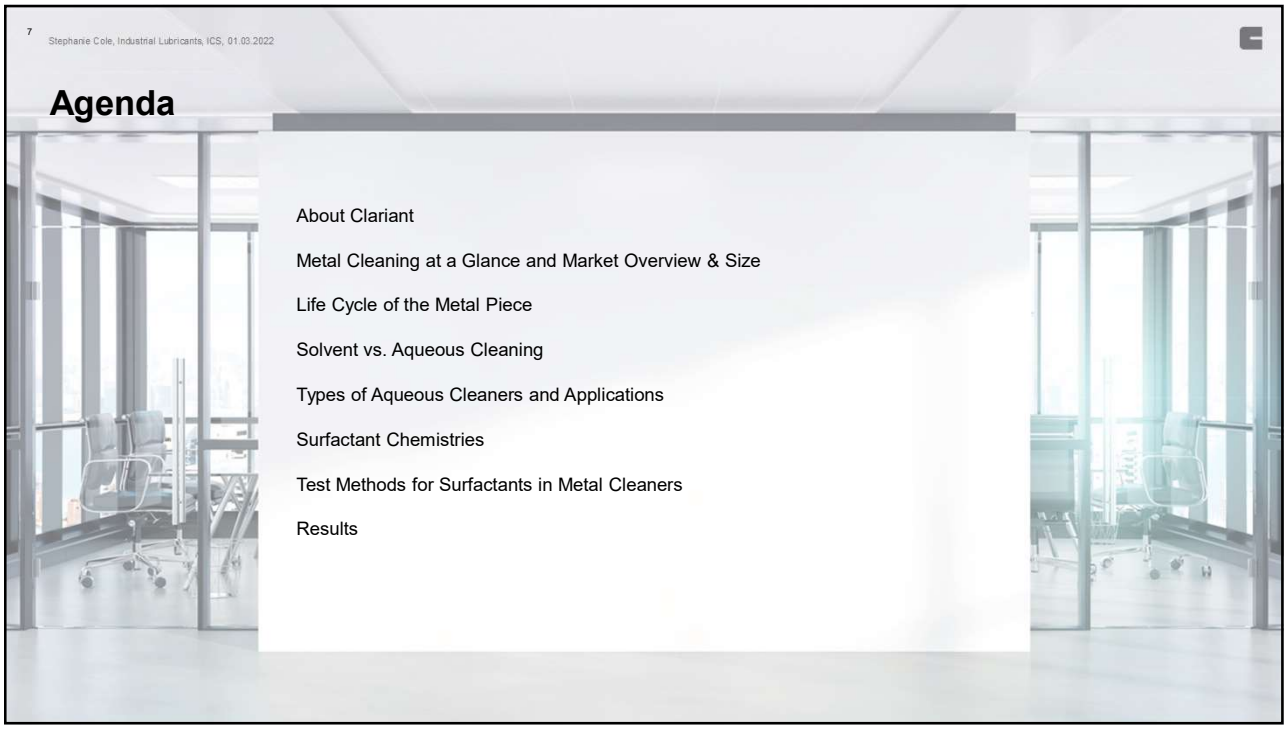
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Stephanie Cole, Industrial Lubricants, ICS, 01.03.2022
Agenda
About Clariant
Metal Cleaning at a Glance and Market Overview & Size
Life Cycle of the Metal Piece
Solvent vs. Aqueous Cleaning
Types of Aqueous Cleaners and Applications
Surfactant Chemistries
Test Methods for Surfactants in Metal Cleaners
Results

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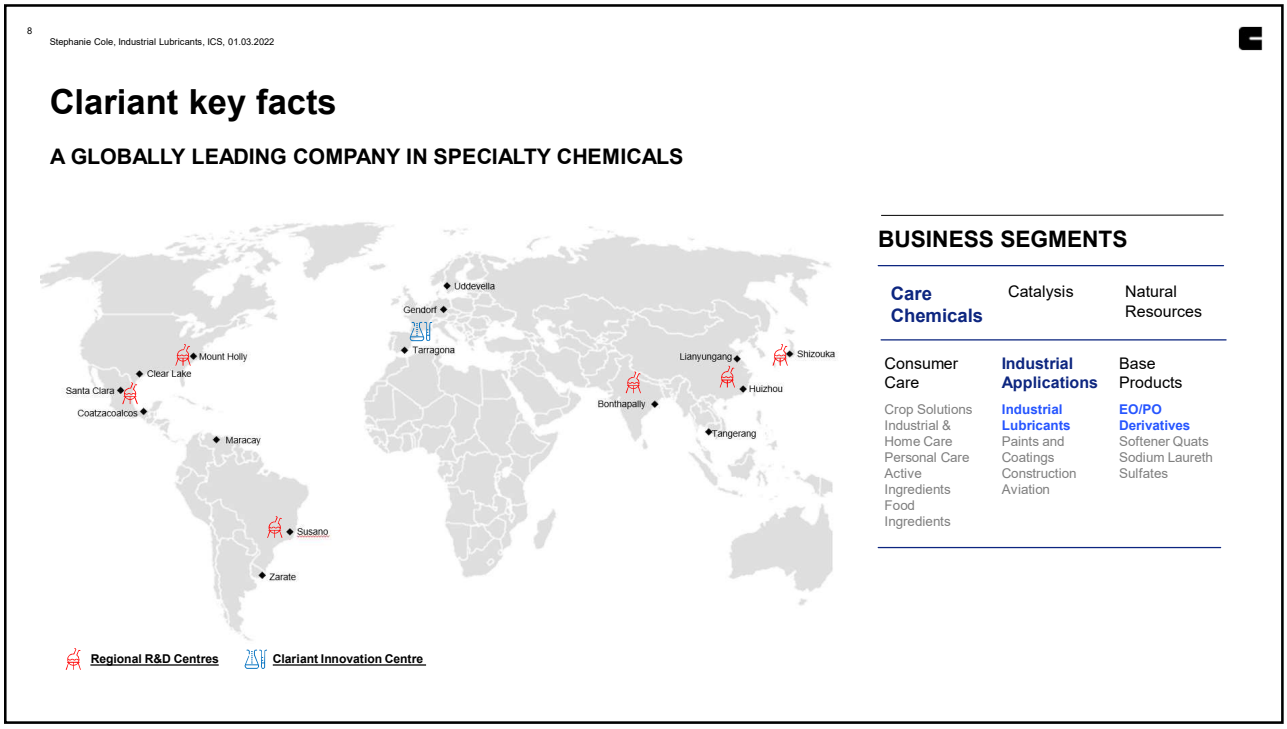
8
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Clariant key facts
A GLOBALLY LEADING COMPANY IN SPECIALTY CHEMICALS
Uddevella
Gendorf
Tarragona
Mount Holly
Clear Lake
Santa Clara
Coatzacoalcos
Maracay
Susano
Zarate
Lianyungang
Shizouka
Huizhou
Bonthapally
Tangerang
Regional R&D Centres
Clariant Innovation Centre
BUSINESS SEGMENTS
Care Chemicals
Catalysis
Natural Resources
Consumer Care
Crop Solutions
Industrial & Home Care
Personal Care
Active Ingredients
Food Ingredients
Industrial Applications
Industrial Lubricants
Paints and Coatings
Construction
Aviation
Base Products
EO/PO Derivatives
Softener Quats
Sodium Laureth Sulfates

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Metal Cleaning at a Glance
Market Overview & Size

Cleaning metal and protecting it against rust or corrosion are important, whether the surface is to be painted or left uncoated

Metal has a reputation for being difficult to clean and a burden to maintain, but many specialized products are emerging to make metal-care tasks easier and more effective

The metal cleaning market is currently experiencing unprecedented growth; largely due to the rise of precision parts which require more critical levels of clean within more complex geometries

The global metal cleaning chemicals market size by value is project to reach

USD 16.5 billion by 2025

at a CAGR of 5.0%*

*Markets&Markets report

9

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Life cycle of the metal piece

Metal Lifecycle in Fabrication*:

Raw Metal	Shipping	Fabrication	Cleaning	Surface Prep	Drying	QC Check	Shipping/ Storage	Coating	Assembly	Post-Assembly
Pain Points	Corrosion	Part design Part Variance Corrosion Cutting Oils Metal Working Fluids Rust Preventatives Metal Oxides	Operator Safety Cleaner Chemistry Metal type Machine type Foam issues Contaminants Part Design Corrosion Water Quality Leaching of metals	Pre-Treatment Operator Safety Recontamination Corrosion	Recontamination Corrosion	Cleanliness Surface Finish Reproducibility Downtime Recontamination	Corrosion Outdoor factors Recontamination	Recontamination Corrosion	Downtime Recontamination Corrosion	

*complex lifecycle

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Solvent vs. Aqueous Cleaning

Solvent Cleaning

- Removal of soil and metal chips
- Higher cost
- Effective pre-cleaning
- Common solvents:
  - Aliphatic petroleum (ex: mineral spirits)
  - Halogenated solvents (Perchloroethylene)
  - Alcohols (Isopropanol)
  - Other (Acetone)

Aqueous Cleaning

- Removal of soil and to metal chips
- Cost effective
- Water dilutable
- Main component is water
- pH: from acidic, neutral, alkaline

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Types of Aqueous Cleaners and Applications

Mild Alkaline Cleaner	High Alkaline Cleaner	Neutral Cleaner	Acidic Cleaner	Rinse
Application Spray Dip Immersion Ultrasonic Initial Cleaning Step	**Application** Spray Dip Immersion Ultrasonic Initial Cleaning Step	**Application** Spray Dip Immersion Ultrasonic Initial Cleaning Step	**Application** Post Cleaning Step Preparation Step	**Application** Post Cleaning Step Preparation Step
Soils Waxes Oils Grease	**Soils** Waxes Oils Grease	**Soils** Surface Layer Soils	**Soils** Metal Oxides	**Soils** Removal of Cleaner
Substrate* Ferrous Non-ferrous	**Substrate*** Ferrous	**Substrate*** Ferrous Non-ferrous	**Substrate*** Ferrous Non-ferrous	**Substrate*** Ferrous Non-ferrous

*Formulation dependent

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Surfactant Chemistries

what is precious to you?

13

Solvent vs. Aqueous Cleaning

Solvent Cleaning

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  - Alcohols (Isopropanol)
  - Other (Acetone)

Aqueous Cleaning

- Removal of soil and to metal chips
- Cost effective
- Water dilutable
- Main component is water
- pH: from acidic, neutral, alkaline
- Formulation:
  - Mainly water
  - **Surfactants**
  - Alkaline/acidic components
  - Builders
  - Corrosion inhibitors

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15 , Surfactant Chemistries
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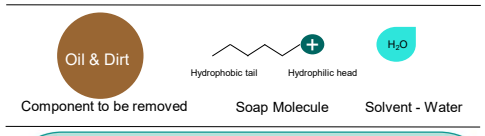
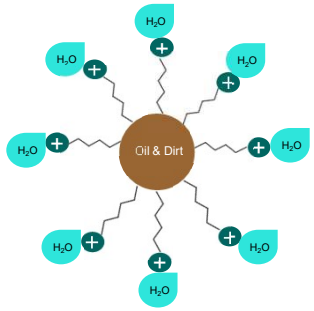
Surfactant Types

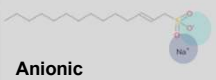
sur•fac•tant
/sərˈfaktənt/
noun
a substance which tends to reduce the surface tension of a liquid in which it is dissolved.





Nonionic
Neutral charge on their hydrophilic ends.

Purpose: Emulsification of oils, wetting



Anionic
a negative charge on their hydrophilic end.

Purpose: Lift and suspend soils

Cationic
positive charge on their hydrophilic end

Purpose: Antistatic

Amphoteric
simultaneously carrying the anionic and cationic hydrophilic group

Purpose: milder surfactant for personal care

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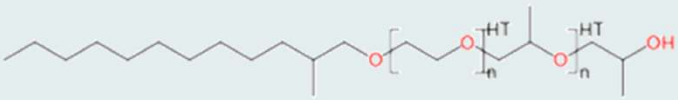
Nonionic Surfactants – Reaction Chemistry

Starting alcohol Ethylene oxide (EO) Propylene oxide (PO)

Nonionic Surfactant



Terminology	
Propoxylated	only adding propylene oxide
Ethoxylated	only adding ethylene oxide
Alkoxylated	adding both ethylene oxide and propylene oxide

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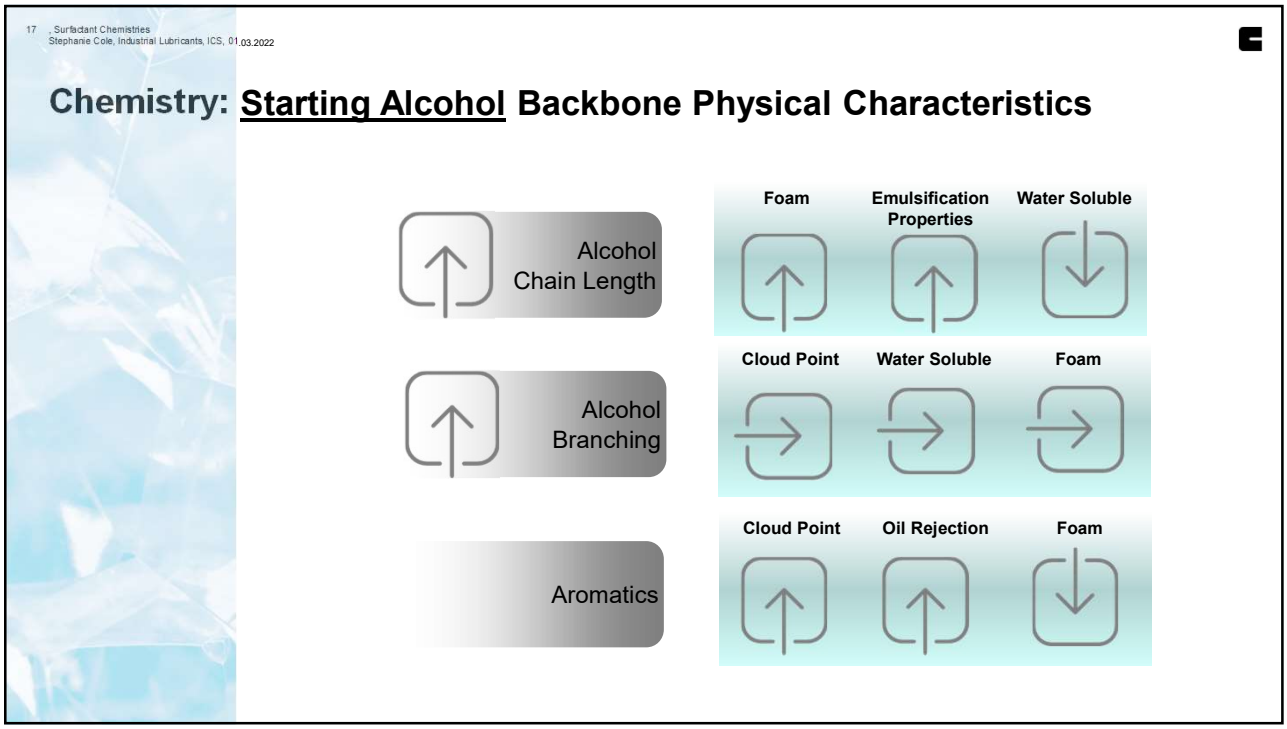
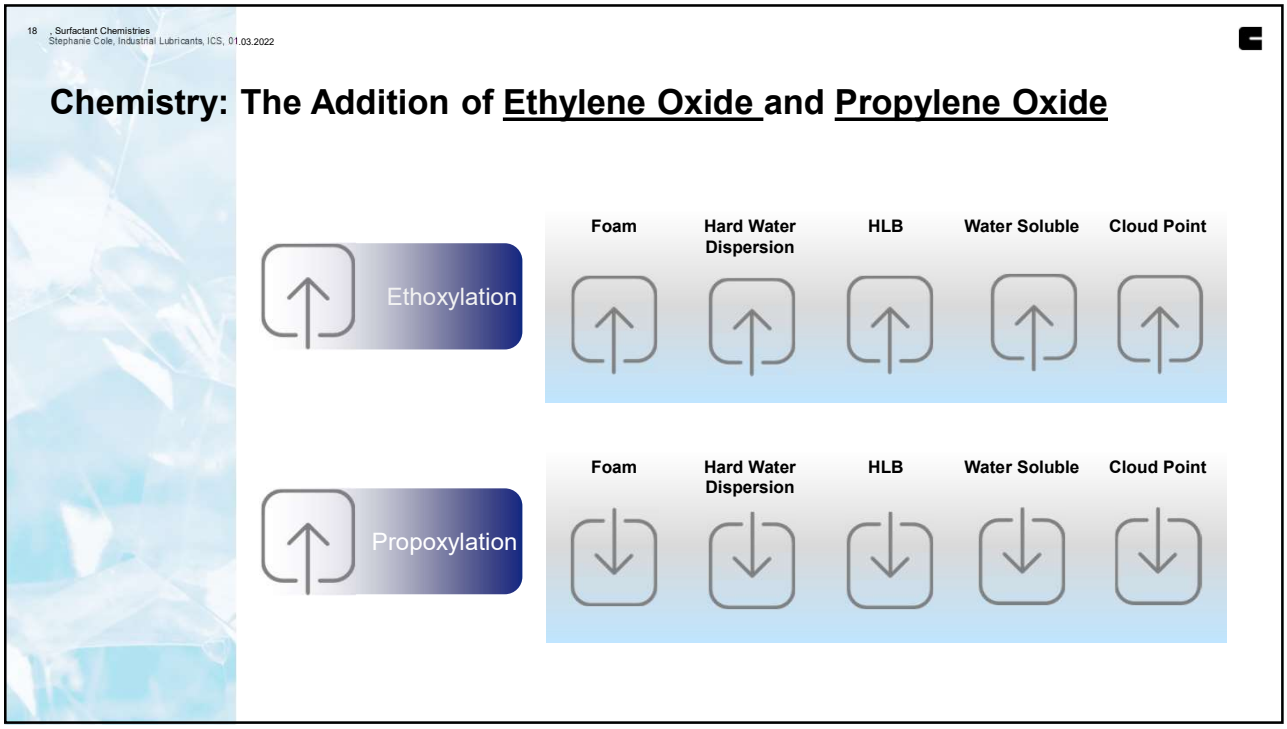

17 , Surfactant Chemistries
Stephanie Cole, Industrial Lubricants, ICS, 01.03.2022
Chemistry: Starting Alcohol Backbone Physical Characteristics
Alcohol Chain Length
Foam
Emulsification Properties
Water Soluble
Alcohol Branching
Cloud Point
Water Soluble
Foam
Aromatics
Cloud Point
Oil Rejection
Foam

17


18 , Surfactant Chemistries
Stephanie Cole, Industrial Lubricants, ICS, 01.03.2022
Chemistry: The Addition of Ethylene Oxide and Propylene Oxide
Ethoxylation
Foam
Hard Water Dispersion
HLB
Water Soluble
Cloud Point
Propoxylation
Foam
Hard Water Dispersion
HLB
Water Soluble
Cloud Point

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Test Parameters and Results

what is precious to you?

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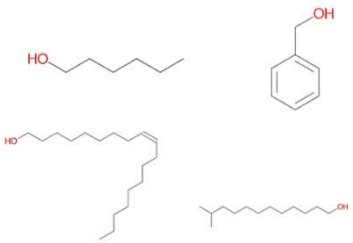
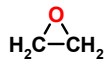
Surfactant Chemistries Tested

Starting Alcohol Backbone
Linear Alcohol
Branched Alcohol
Aromatic Alcohol

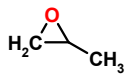


Alcohol Chain Length
C6-C18

EO (mol)	PO (mol)
2-20	0
2-20	4-20



Ethylene oxide (EO)



Propylene oxide (PO)

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Verification of Surfactant Properties
Test Methods

Water Soluble	Solubility in water
Cloud Point	1% in water 1% in a water glycol mixture
Formulation Synergy	Acid compatibility Base compatibility Can the surfactant correct a formulation (act as a coupler)
Degreasing	In house cleaning test (next slides)
Emulsification	Emulsification of foreign oils (next slides)
Foaming Characteristics	Apparatus that generates foam (next slides)

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Degreasing Test Procedure

Soil Formulation	
25-35%	Water displacing commodity chemical
25-35%	Anti-wear hydraulic oil (Ex: AW 32)
25-35%	Cutting, grinding fluid that is oil based (ex: honing oil)
1-4%	Carbon black
1-4%	Iron oxide

Cleaning Formulation	
70-80%	water
1-10%	Alkaline component (ex: NaOH or KOH)
2-10%	Coupling agents (Ex: acid base salt, glycol**)
2-10%	Surfactant

Equipment
304 SS 1"x3"x.032"
Stir bar
Stir plate – Take note of RPM
150 mL beaker

Experiment Steps/Considerations
1. Test will be completed twice
2. Cleaners are diluted to 5% with tap water; 115 g of soln is tested
3. Control is cleaning soln without surfactant
4. Clean coupon with IPA
5. Weigh coupon
6. Apply three coats of soil using a lip gloss applicator
7. Bake for 30 minutes at 40°C
8. Allow to cool, then weigh (this determines how much dirt was applied)
9. Gently place coupons in cleaner soln; do not allow magnet to touch coupon
10. Let stir for 30 min
11. Remove coupons and dip 3X in tap water
12. Allow to dry for 30 minutes in 105°C oven
13. Weigh coupons
14. Take photos of coupons after cleaning
15. Calculate Percent Removal

** Be careful when testing formulation with a coupler – the coupler can contribute to cleaning which may effect results

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23 , Test Parameters and Results
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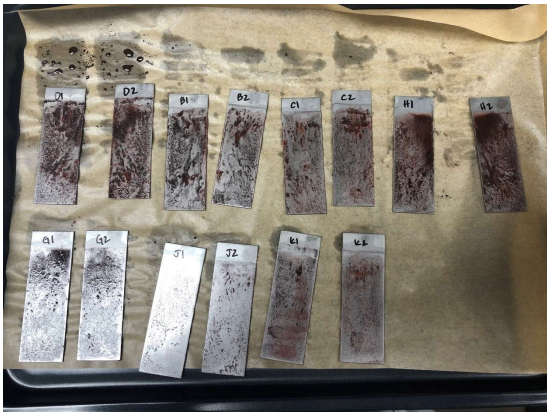
Degreasing Test



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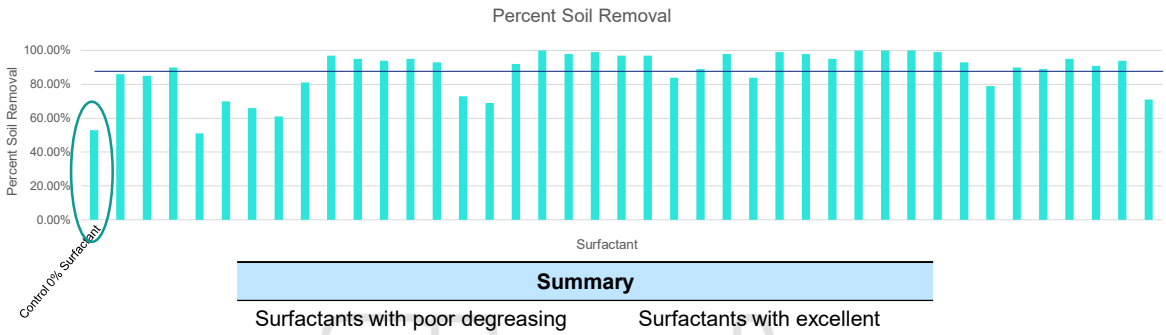
Degreasing Test Results



Summary	
Surfactants with poor degreasing properties	Surfactants with excellent degreasing properties
Aromatic alcohol More PO to EO Ratio Lower chain length linear alcohols	Higher chain length linear starting alcohol More EO to PO Ratio

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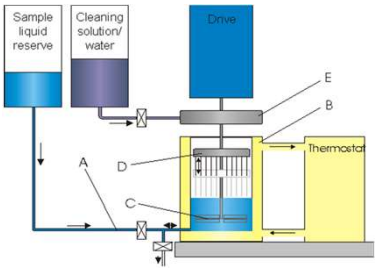
Foam Test Procedure

Testing Parameters	
Temperature	20 °C
Fill Volume	250 mL
Rotor Speed	1200 rpm
Foam Generator	
Stirring Interval	10 s
Number of Stirring Intervals	30 times
Foam Decay	
Measuring	30 s
Total Time	10 min
Surfactant Concentration	0.1 %



SITA Foam Analyzer: R-2000

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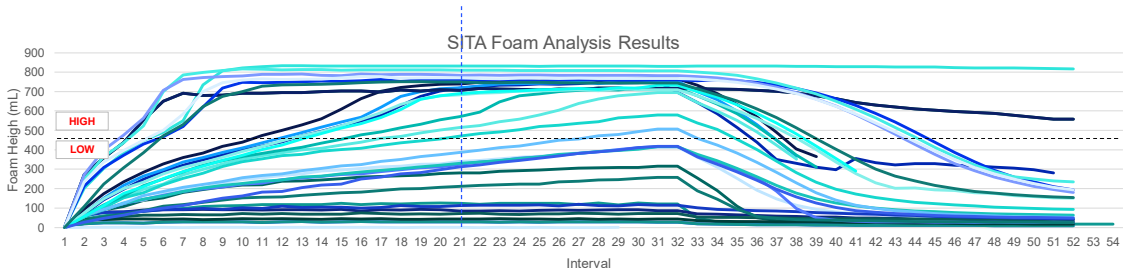
Foam Test



Summary	
Low Foaming Surfactant Characteristics	High Foaming Surfactant Characteristics
Aromatic alcohols with EO only Linear chain alcohols with EO and PO Lower chain length linear alcohols	Linear alcohols with EO only

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27 , Test Parameters and Results
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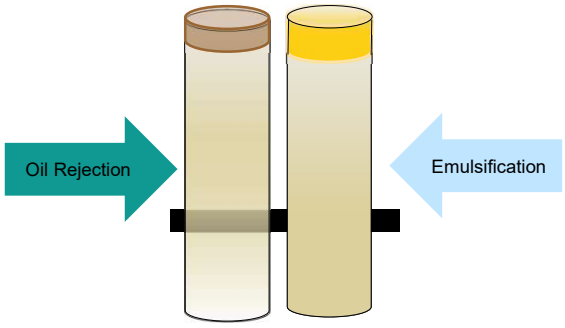
Emulsification/Oil Rejection Test

Procedure Concept
Introduce a foreign oil to the solution and record observations

Experiment Steps/Considerations
1. Prepare a 1% surfactant + DI water soln
2. Place into a 100 mL graduated cylinder
3. Remove 3 mL of soln
4. Add 3 mL of honing oil
5. Shake 10X
6. Allow to rest and recording
7. Record 1. Initial observation 2. 15 min 3. 30 min 4. 1 hour (final reading)

General Rules
If layer below oil rejection was clear – poor emulsification; good oil rejection
If layer below oil rejection was slightly hazy – moderate emulsification
If layer below oil rejection was opaque – excellent emulsification



Summary	
Oil Rejection Surfactant Characteristics	Emulsification Surfactant Characteristics
Shorter Chain Length Alcohols Aromatics	Carbon Chain Length >10 Higher EO content

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Metal Cleaning Surfactants
Genapol ®

what is precious to you?

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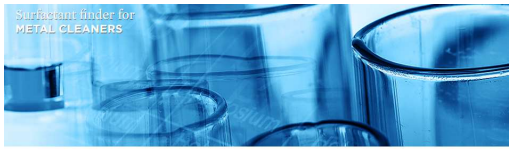
Surfactant Finder Tool



clar·i·fy
verb

1. to make a situation more clearly comprehensible

Clariant believes in offering simple solutions to complex formulations. Clarify is a digital selection tool designed to help you identify the ideal surfactant for your industrial cleaning innovations. Designed to easily guide you toward the best choice for your targeted performance attributes, Clarify will recommend the optimal product based on your input. The decision is yours but is now even easier.

Matching products: 9 of 38 — Show results

Performance Characteristics
- ✓ Degreasing
- Emulsification
- Oil Rejection
- Wetting
- ✓ Low-Foaming

Application
- ✓ Spray
- Immersion
- Ultrasonic

Physical Characteristics
- Water Solubility
- Cloud Point (<20)
- Cloud Point (20-27)
- Cloud Point (28-40)
- Cloud Point (>40)
- Plant Based
- Label-Free

Formulation Compatibilities
- Neutral
- Potassium Hydroxide
- Sodium Hydroxide
- Phosphoric Acid
- Hydrochloric Acid
- Nitric Acid
- Sulfuric Acid

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Results — Change filters

Genapol EP 0244
LOW FOAMING SURFACTANT FOR INDUSTRIAL USES
Genapol EP 0244 is a low foam, nonionic, alkoxylated alcohol with hard water stability. Its excellent emulsifying and degreasing properties make it suitable for spray, immersion, and ultrasonic cleaning applications. Good compatibility with aqueous acids and bases makes it stable in a range of formulation types.
› READ MORE

Genapol EP 2484
LOW FOAMING SURFACTANT FOR INDUSTRIAL USES
Genapol EP 2484 is a low foam, nonionic, alkoxylated alcohol with hard water stability. Its excellent emulsifying and degreasing properties make it suitable for spray, immersion, and ultrasonic cleaning applications. Good compatibility with aqueous acids and bases makes it stable in a range of formulation types.
› READ MORE

Genapol 1585
LOW FOAMING SURFACTANT FOR INDUSTRIAL USES
Genapol 1585 is a low foam, nonionic, alkoxylated alcohol with excellent emulsifying properties making it suitable for spray, immersion, and ultrasonic cleaning applications. Good compatibility with aqueous acids and bases makes it stable in a range of formulation types.
› READ MORE

Genapol 1424
LOW FOAMING SURFACTANT FOR INDUSTRIAL USES
Genapol 1424 is a low foam, nonionic, alkoxylated alcohol with hard water stability. Its excellent emulsifying and degreasing properties make it suitable for spray, immersion, and ultrasonic cleaning applications. Good compatibility with aqueous acids and bases makes it stable in a range of formulation types.
› READ MORE

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Clariant's Low Foaming Surfactants

Properties	Genapol A 55	Genapol EP 2584	Genapol EP 2556	Genapol EP 2484	Genapol BA 040
Low Foaming	✓	✓	✓	✓	✓
Oil Rejection	✓				✓
Degreasing		✓	✓	✓	
Coupling Properties	✓				✓
Solvency Properties	✓				✓
Formulation Compatibility	✓	✓		✓	✓
Water Solubility	✓	✓	✓	✓	✓
Hard Water Stability	✓	✓	✓	✓	✓
Cloud Point °C (1% in water)	>40	39-40	23-35	39-42	>100

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Guide Formulations

what is precious to you?

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32 , Guide Formulations
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Example of Metal Cleaning Formulations for Formulators
A guide to aqueous cleaners

Multi Metal Alkaline Cleaner

Component	Percentage	Function
Water	60-90%	Carrier
Sodium Metasilicate	0.25-1.5%	Builder, corrosion protection for aluminium
Potassium pyrophosphate (TKPP)	0.5-3%	Builder
BDG (Diethylene glycol monobutyl ether)	1-10%	Coupler
Triethanolamine	2-12%	Alkalinity
Genapol ® EP 2556	2-10%	Surfactant
Genapol ® A 55	1-10%	Coupler
Genamin ® CH 020	0.5-4%	Alkalinity
Dodecanedioic acid	0.25-1.5%	Ferrous corrosion protection

Ferrous Metal Alkaline Cleaner

Component	Percentage	Function
Water	60-90%	Carrier
45% KOH	1-10%	Builder
BDG (Diethylene glycol monobutyl ether)	1-10%	Coupler
Triethanolamine	2-12%	Alkalinity
Genapol ® EP 2584	2-10%	Surfactant
Genapol ® A 55	1-10%	Coupler
Genamin ® CH 020	0.5-4%	Alkalinity
Dodecanedioic acid	0.25-1.5%	Ferrous corrosion protection

Do not try this formulation at home
This is a concentrate formulation that will be diluted at the end user location

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Questions?

Challenge the surfactant manufacturers and formulators to redesign molecules and modify formulations to address your pain points.

What are your pain points?

- Cloud point
- Foam
- Compatibility
- Hard water
- Corrosion

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Post-machining Cleaning - an accelerated guide to nonionic surfactant chemistry in cleaning formulations

Thank you for attending.

The PQCW offers practical, hands-on and independent, training in cleaning.

More Info
shsu.edu/pqcw
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Stephanie Cole
Clariant Corporation
stephanie.cole@clariant.com

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