Overcome the Challenges of Cleaning Aluminum

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

More Info
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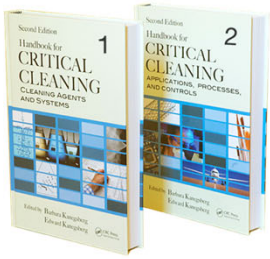
Hosts: The Product Quality Cleaning Workshop Team

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

- BFK Solutions - Consultants in Critical Cleaning
- Authors and Editors of the two-volume CRC Handbook for Critical Cleaning
- Independent evaluations and recommendations
- 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 and formulates cleaning chemistries
- williams@shsu.edu

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PQCW – Workshops for Terrific Products

- "While I would prefer to have been at in-person laboratories so I could have hands-on experiences with cleaning processes, **I really liked the two-week virtual PQCW**.
- "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

Mike Valenti – Director of Cleaning Technology

- A graduate of the University of Georgia
- Over 25 years of experience in specialty chemical development and product management
- Involved in the development and sales of specialty chemicals, detergents and cleaners, and metal finishing products.
- First with Milliken Chemical, and then with Hubbard-Hall, his experience has included recommending cleaners – both aqueous and solvent cleaning processes – non-ferrous surface preparation, equipment, and testing protocols for a wide range of the requirements for critical metal finishing operations.

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Overcome the Challenges of Cleaning Aluminum

Mike Valenti
Director of Cleaning Technologies
Hubbard-Hall

BFK Solutions LLC
Critical Cleaning Consulting

product quality cleaning workshops

Sam Houston State University

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Session Topics

1. Some Basics About Aluminum
2. What Does Clean Aluminum Really Mean?
3. Aluminum Cleaning Chemistry
4. Common Process Issues
5. Industry Examples
6. Measuring Cleanliness of Aluminum
7. Questions

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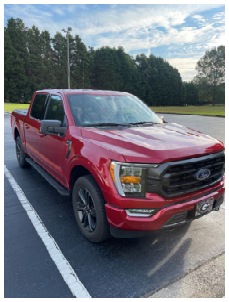
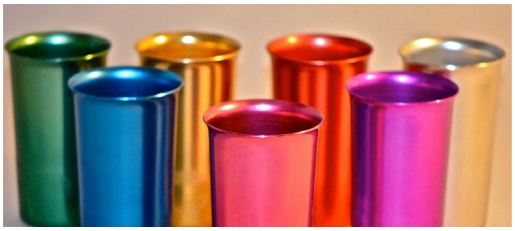
Why Aluminum……..

13
Al
26.98
Aluminum

- Lightweight, but alloys are strong as steel
- Excellent Conductor, Heat and Current
- Corrosion Resistant
- Easily Formed, Machined
- Sustainable – Easily Recycled Many Times
- Highly Decorative





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But…. Aluminum Is a Process Challenge

13
Al
26.98
Aluminum

Highly Reactive

$$4Al\,(s) + 3O_2(g) \longrightarrow 2Al_2O_3\,(s)$$

Aluminium (Metal) + Oxygen (From air) → Aluminium oxide (Amphoteric oxide)

$$2Al(s) + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2(aq) + 3H_2(g)$$

Sodium meta aluminate

The reactivity of Aluminum can make cleaning Aluminum parts difficult, but we can also use it to our advantage in preparing surfaces for other finishing processes

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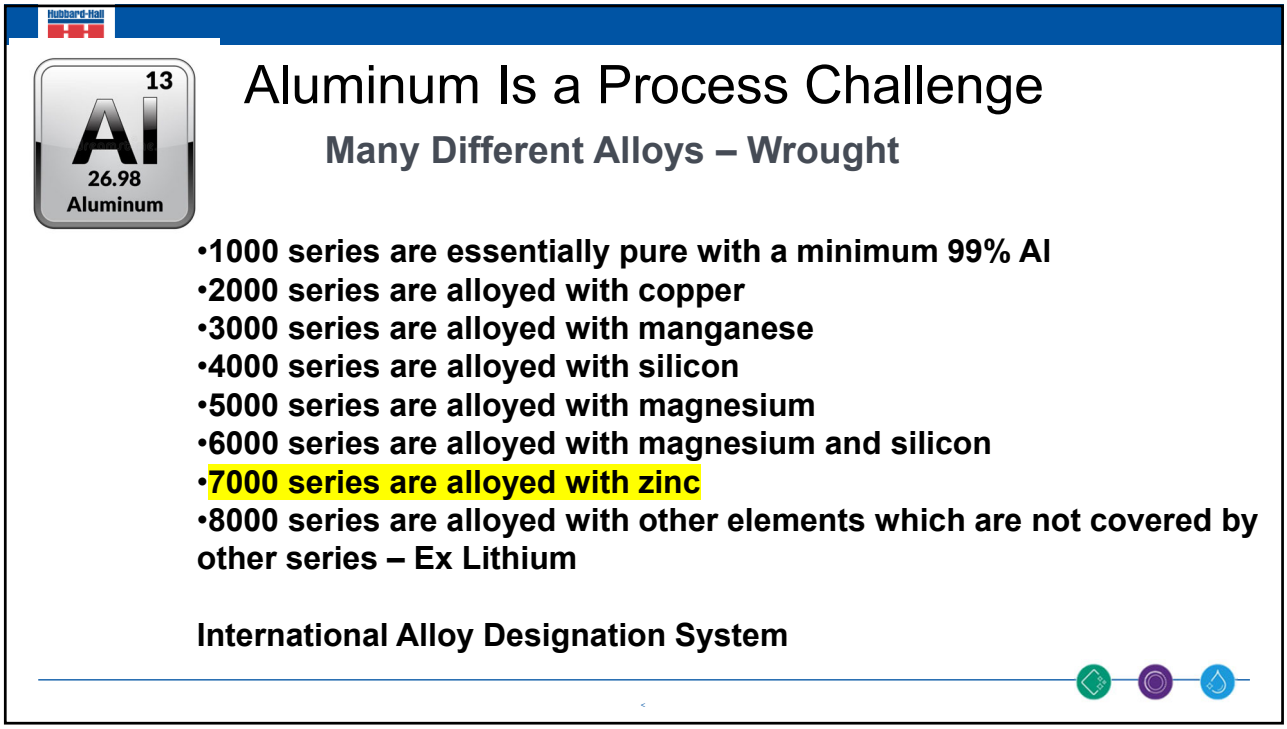
Hubbard-Hall
13
Al
26.98
Aluminum
Aluminum Is a Process Challenge
Many Different Alloys – Wrought
•1000 series are essentially pure with a minimum 99% Al
•2000 series are alloyed with copper
•3000 series are alloyed with manganese
•4000 series are alloyed with silicon
•5000 series are alloyed with magnesium
•6000 series are alloyed with magnesium and silicon
•7000 series are alloyed with zinc
•8000 series are alloyed with other elements which are not covered by other series – Ex Lithium
International Alloy Designation System

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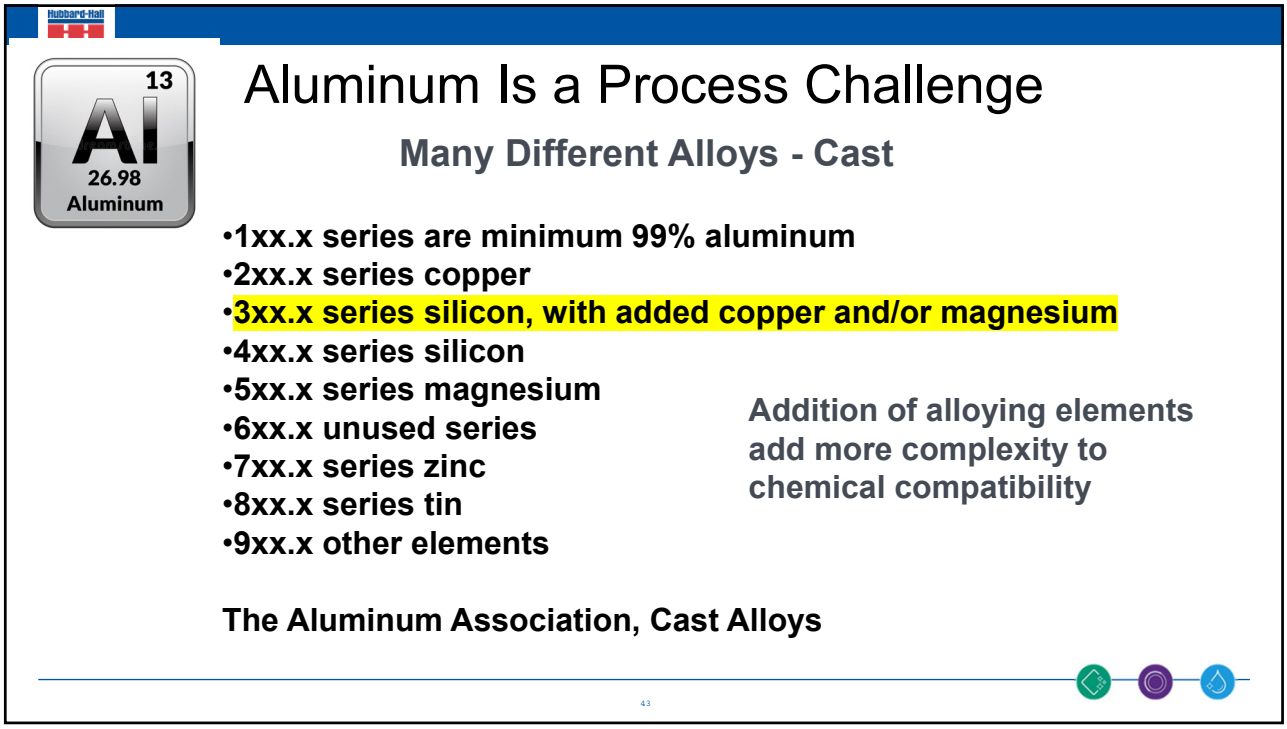
Hubbard-Hall
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Al
26.98
Aluminum
Aluminum Is a Process Challenge
Many Different Alloys - Cast
•1xx.x series are minimum 99% aluminum
•2xx.x series copper
•3xx.x series silicon, with added copper and/or magnesium
•4xx.x series silicon
•5xx.x series magnesium
•6xx.x unused series
•7xx.x series zinc
•8xx.x series tin
•9xx.x other elements
Addition of alloying elements add more complexity to chemical compatibility
The Aluminum Association, Cast Alloys

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What Does Clean Mean?

We are really talking about a pre-treatment process

In most aluminum finishing processes we must remove not only the organic soils(lubes, compounds) but the inorganic soils as well(surface oxides, corrosion products, scales)

- **Degreasing – Removes Organic Soils**
- **Etching – Removes Oxides, Elemental Impurities, Improves Adhesion, Removes Stock(Metal)**
- **Deoxidizing – Removes Oxides without removing stock, activation**
- **Desmutting – Removes the smut that can form from etching process**
- **Non-Etch surface also desirable for bright finish**

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What Does Clean Mean?

We are really talking about a pre-treatment process

In most aluminum finishing processes we must remove not only the organic soils(lubes, compounds) but the inorganic soils as well(surface oxides, corrosion products, scales)

- **Anodizing**
- **Chem Film(Cr+ Conversion Coatings)**
- **Plating, Electroless Ni**
- **Powder Coat**
- **Electrolytic Coloring**

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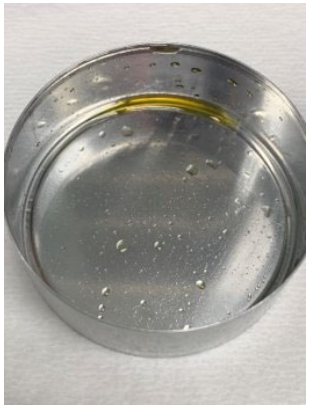
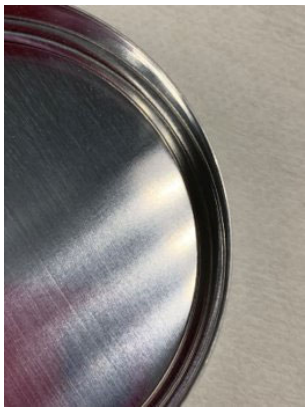
What Does Clean Mean?

We are really talking about a pre-treatment process





Degrease Only

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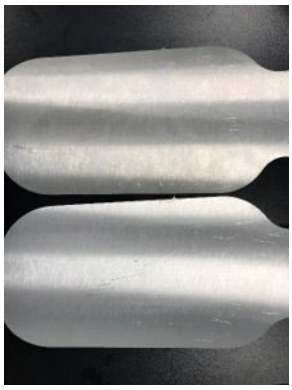
What Does Clean Mean?

We are really talking about a pre-treatment process



Degrease and Deoxidize

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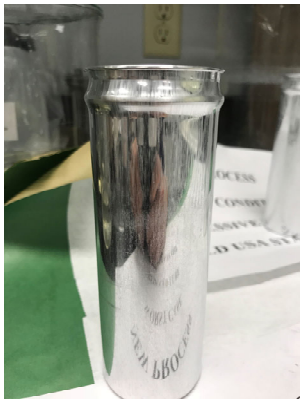
What Does Clean Mean?

We are really talking about a pre-treatment process



Non-Etch

Matte Etch

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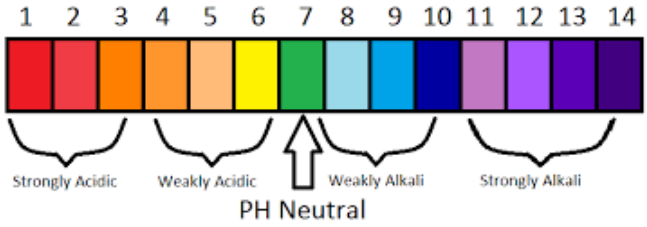
Pre-Treatment
pH is King



Do I use acid or alkaline based products?
It depends

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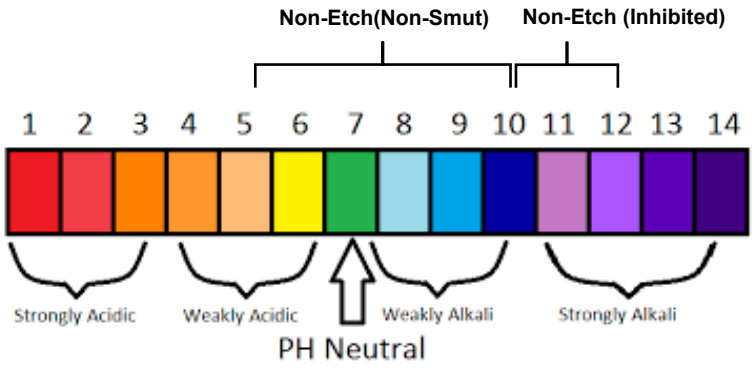
Pre-Treatment Cleaners



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Pre-Treatment – Cleaning Alkaline

- **Phosphates**
  No Etch(Can "Bite") Free Rinsing, Low Residue, Discharge Concerns
- **Borates(Borax)**
  Good No Etch, Cheap, Solubility Problems
- **Silicates(100%)**
  Better No Etch, Prone to Sludge(pH), Hard to Rinse(residues)
- **Fatty Acid Soaps**
  Best No Etch, Expensive, Acid Stability, Hydrophobic Film, Heavy Degreasing
- **Inhibited Caustic(Silicates)**
  No to Mild Etch, Cheap, Sensitive to Time and Temp(Etch and Smut) Sludge
- **Inhibited Caustic(Amines, Other)**
  Mild to Heavy Etch, Generally Require Post De-Smut Step

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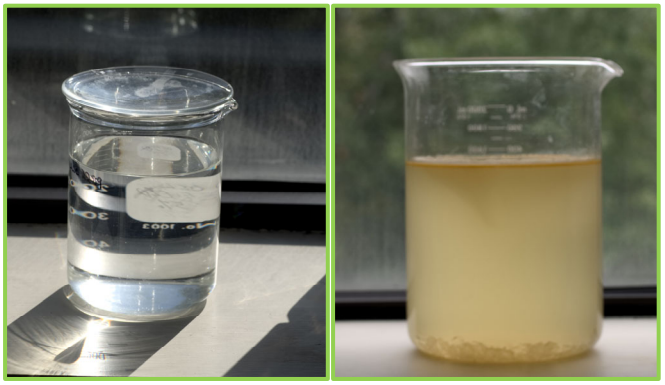
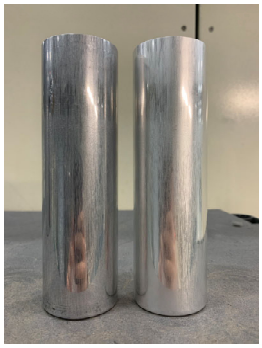
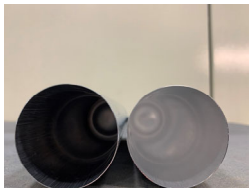
Borax Based Cleaner



Inhibited Caustic/Silicated Cleaner





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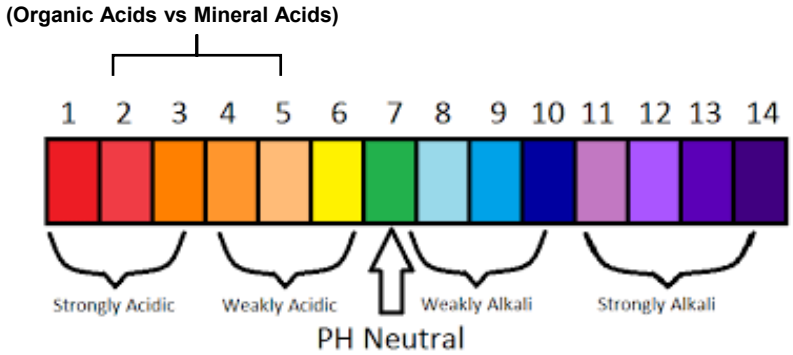
Pre-Treatment
Acid Cleaners



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Pre-Treatment – Cleaning Acids

- **Mineral Acids – Phosphoric, Fluoride Based, HF or Fluoroboric**
  All Deoxidize, Mild to Medium Etch, Fluoride Accelerates Etch
- **Organic Acids – Citric, Sulfonic Acids (DDBSA, MSA)**
  All Deoxidize, Used Properly Provide No Etch, Expensive
- **Not optimal for removing heavy soils, oils repel acids**
- **Very good at removing the stearate lube family**
- **Use can be alloy specific, so less flexibility**
- **Can't process other metals in process, ie Cu, Fe – Immersion Plating**
- **Equipment compatibility more limited, Materials of Construction**
- **Improved compatibility with many downstream Al processes**

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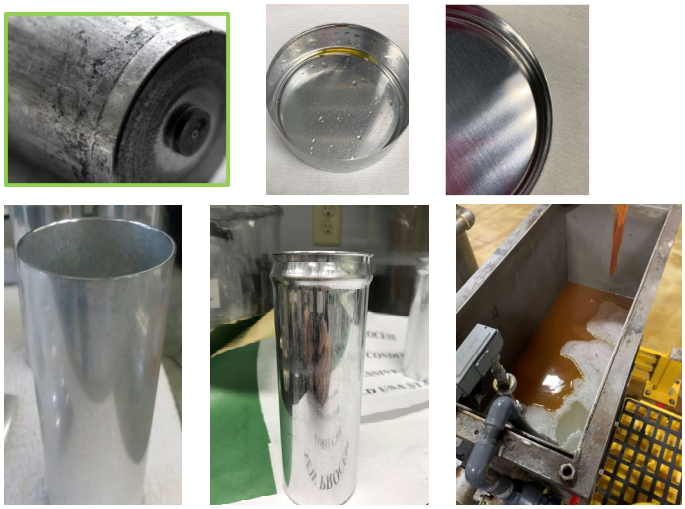
Organic Acid Based Cleaners



7075 – High Zinc Alloy
Pitting with Acid Cleaners

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Cleaning - Deoxidation Example

Example: Conversion Coating Pretreatment Study, Alloy 2024-T(High Copper), 6061-T6
Application: MIL-DTL-5541
Corrosion Test: ASTM B117
Materials Qualification: MIL-DTL-81706

Process:

- Acid based cleaner/deoxidizer #2
- Tap Rinse
- Tri-Chrome Seal(Cr+3)
- DI Water Rinse

Results:

Aluminum Alloy:	Set #	Immersion Time Clean and Deox Tri-Chrome Seal	Salt Spray Hours:	Pass/Fail:
2024-T3	Set #1	2.5 minutes / 5 minutes	504	Pass
2024-T3	Set #2	5 minutes / 5 minutes	168	Fail
6061-T6	Set #3	2.5 minutes / 5 minutes	1176	Pass
6061-T6	Set #4	5 minutes / 5 minutes	1176	Pass

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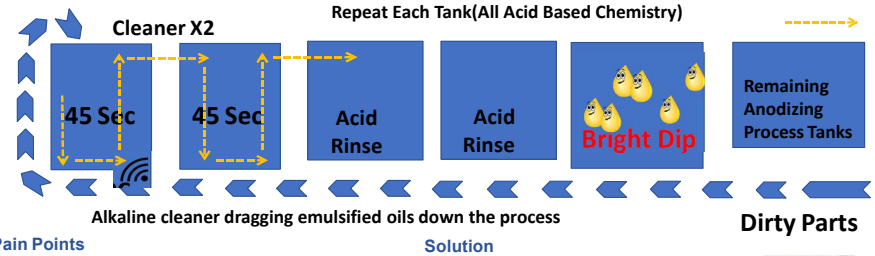
Story From The Field
In-Line Degreasing for Anodizing



Pain Points

- Poor Cleaning
- High Scrap Rate
- Business Demand
- "Poisoning" of the Bright Dip Tanks with Lube
- Bright Dip Eruptions
- Operator Exposure to Hazards, Rashes

Solution

- Change chemistry of cleaner(Acid)
- Improved compatibility downstream
- Improved chemical feeding
- Improved oil removal from tanks
- Overall cleaning improved
- Scrap reduced 5X

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Aluminum Cleaning Process Improvement

Example: Acid Cleaner for Deep Drawn Aluminum

Standard Process:

- Immersion Washer with Ultrasonics.
- Strong alkaline(base metal attack) and silicated cleaners not allowed.
- Hard to remove stearate lubes, neutral phosphate cleaners not effective
- Post heat treatment causes defects with improper cleaning

Improved Process:

- Acid based cleaner
- No base metal attack
- High solubility of stearate lubes
- Bright lustrous finish without attack or etch
- No post heat treat issues

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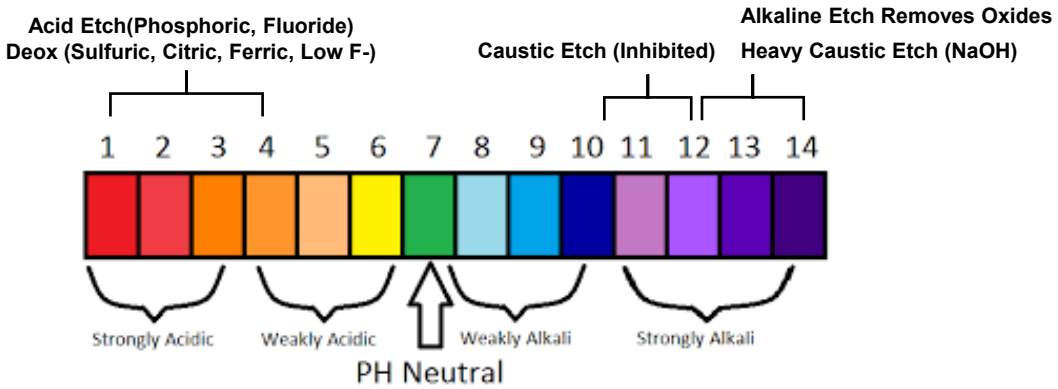
Pre-Treatment
Etching and Deoxidation



Etch = Remove Stock(Metal)
Deoxidation = Remove Surface Metal Oxides Only

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Pre-Treatment – Etch and Deoxidation

Etch

- **Caustic(NaOH)**
  Course Etch, Significant Stock Removal, **Generate Smuts**, High Sludge
- **Inhibited Caustic**
  Controlled Finer Etch, Less Stock Removal, Low to No Smut, High Sludge
- **Acid**
  Fine Etch, Short Immersion Times, 10x Less Stock Removed, Low to No Smut

Deoxidation

- **Caustic(NaOH)**
  Deox Happens as Part of Etch
- **Inhibited Caustic**
  Deox Happens as Part of Etch
- **Acids**
  Deox Can Be Accomplished Without Etch

Smuts are the reaction products, including intermetallic compounds, that become insoluble in the etch solution. These adhere to the metal surface and must be solubilized

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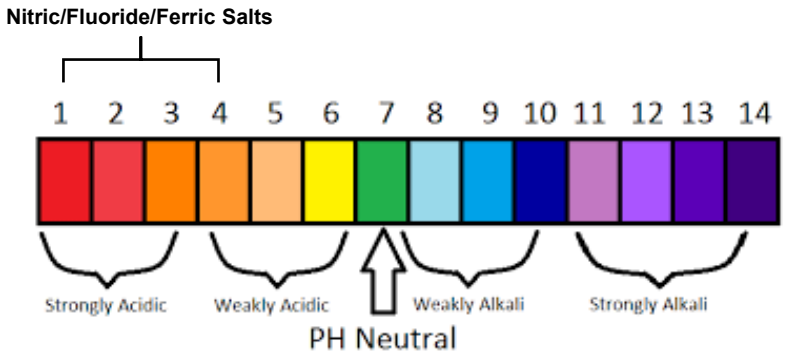
Pre-Treatment
De-Smutting



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Pre-Treatment – De-Smutting Acids

- **Mineral Acids – Nitric, HF(including fluoride salts), Ferric Salts**
- **Combo of All Three(3) Cover Most Alloys**
- **Some Sulfuric/Peroxide Based, Not Robust, Light Smuts**
- **Most Deoxidizers will De-smut, Not All De-Smutters will Deoxidize(HNO3)**

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Process Issues - Rinsing

The Dirty Rinse Tank

Exposing clean parts to a dirty rinse tank results in…..

Dirty Parts!

The Rinsing step in Aluminum Cleaning is more critical than with most other alloys

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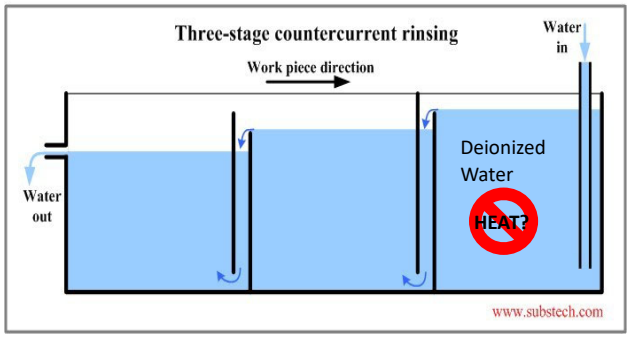
Poor Rinsing Example

Poor Rinsing, Residual Contaminates

In this example the residues from the cleaner tank remain on the surface and "burn" into the surface during a heat-treating step.



Simple Solution, Continuous Clean Rinse

Hot rinses can cause uneven surface oxidation

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Process Issues – Waiting to Clean

The longer you wait to clean Aluminum The more difficult your cleaning process will be

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Process Issues – Waiting to Clean
Example - Reactive Lubes

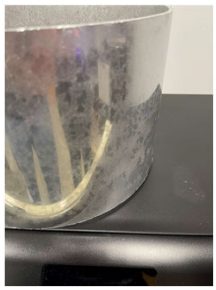
Reactive Surface Contamination

Sensitive Alloys, Aluminum, Copper, Brass, et al

Lubricants can permanently damage the surface of parts if not removed in a timely manner.

Oxidation, smutting, and chemical surface attack.

Amine based lube attack on 6061 Alloy



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Measuring Cleanliness of Aluminum

Water Break Test - Involves examination of a surface for the presence of a continuous water film that has no water breaks. If a water-break-free film of water is present, it is indicative of the absence of **hydrophobic surface contaminants**. Oils, greases, and water-insoluble organic compounds would be examples of hydrophobic contaminants. **The water break test does not confirm the presence or absence of hydrophilic contaminants or oxides.**

Tests based on **Surface Tension(Dynes Testing)** have been used to determine the cleanliness of surfaces. **Care must be taken to ensure the use of test solutions specific to the substrate surface.**

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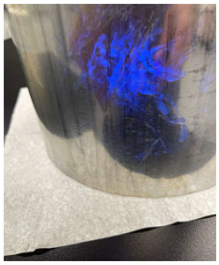
Practical Cleanliness Testing
UV Detection






UV Fluorescence @301 nm
Dr. Darren Williams, SHSU, Product Quality Cleaning Workshop

If soils are doped with compounds that **exhibit fluorescence**, exposure of cleaned parts to ultraviolet light will confirm the presence or absence of residual soils.

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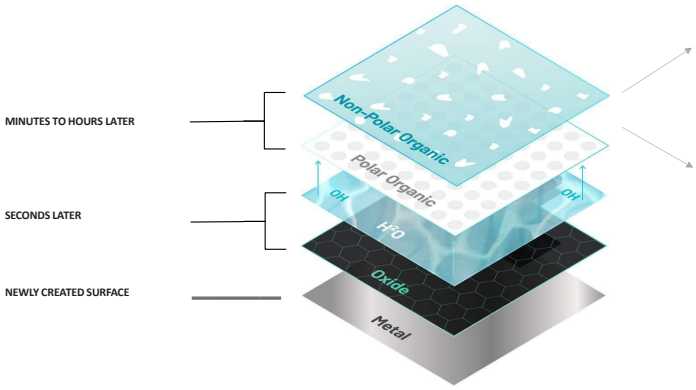
Measuring Cleanliness of Aluminum

BTG LABS

Fundamental Connection: Surface Science and Water Contact Angle



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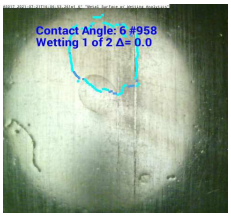
Practical Cleanliness Testing
Contact Angle

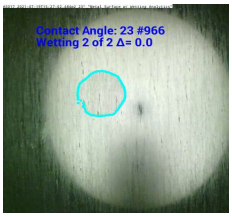
Example is standard Aluminum surface prep process



Dirty Dynamic Wetting*
Water Based Lube

Solvent Degreased

Residue Post Degreasing



Deoxidation

Chemical Etch

Contact Angle measurement can be easily correlated to the surface preparation steps to determine cleanliness

Contact Angle via Optical Measurement BTG Labs Surface Analyst

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Summary

1. **Aluminum Alloys are Highly Sensitive to the Chemistry used in Cleaning Processes**
2. **Cleaning is Really About Surface Preparation**
3. **Pre and Post Cleaning Steps Are Critical**
4. **There are Practical Tools Available to Monitor the Cleanliness and Surface Properties of Aluminum**

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Thank You! Questions?

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Aluminum Pretreatment

Challenges in Cleaning and Deoxidizing Aluminum

1. Aluminum parts can have difficult lubes, oxides, and finely divided aluminum that must be removed.
2. Heavy Alkaline or Mineral Acid based processes can lead to over etching or smut. Smut removal requires additional steps, Nitric Acid.
3. Silicates can reduce etch and smut, but contribute to scale build up and waste treatment problems.

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Aluminum Pre-Treatment Studies

Example: Conversion Coating Pretreatment Study, Alloy 2024-T(High Copper)
Application: MIL-DTL-5541
Corrosion Test: ASTM B117
Materials Qualification: MIL-DTL-81706

Process:

- Acid based cleaner/deoxidizer #1
- Tap Rinse
- Tri-Chrome Seal(Cr+3)
- DI Water Rinse

Results:

Aluminum Alloy:	Set #	Immersion Time Clean and Deox Tri-Chrome Seal	Salt Spray Hours:	Pass/Fail:
2024-T3	Set #1	2.5 minutes / 10 minutes	168	Pass, Failed 336-hr
2024-T3	Set #2	5 minutes / 10 minutes	504	Pass
2024-T3	Set #3	10 minutes / 5 minutes	336	Pass, Failed 504-hr
2024-T3	Set #4	10 minutes / 10 minutes	168	Pass, Failed 336-hr

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Aluminum Pre-Treatment Studies

Example: Anodizing Pretreatment Study, Alloy 2024-T(High Copper), 6061-T6
Application: MIL-A-8625
Corrosion Test: ASTM B117

Process:

- Acid based cleaner/deoxidizer
- Tap and DI Water Rinses
- Sulfuric Acid Anodize, (190 g/L sulfuric, 6.0g/L Al, 70 F, 0.42 mil thickness)
- Tap Water Rinse
- Tri-Chrome Seal(Cr+3) and Nickel Acetate Seal
- DI Water Rinse

Results:

Aluminum Alloy:	Anodic Seal:	Salt Spray Hours:	# Pits:	Pass/Fail:
2024-T3	Tri-Chrome	336	0	Pass
2024-T3	Nickel Acetate	336	0	Pass
6061-T6	Tr-Chrome	336	0	Pass
6061-T6	Nickel Acetate	336	0	Pass

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Overcome the Challenges of Cleaning Aluminum

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

More Info
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