CHEMEON TCP as a Room Temperature Seal for Anodized Aluminum

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Basic Aluminum Facts

- Lightweight
  - 1/3 less than iron, steel, copper, or brass
- Strength approaches that of steel for some alloys
  - High strength/weight
- Many applications
  - Automotive, aerospace, commercial, aviation

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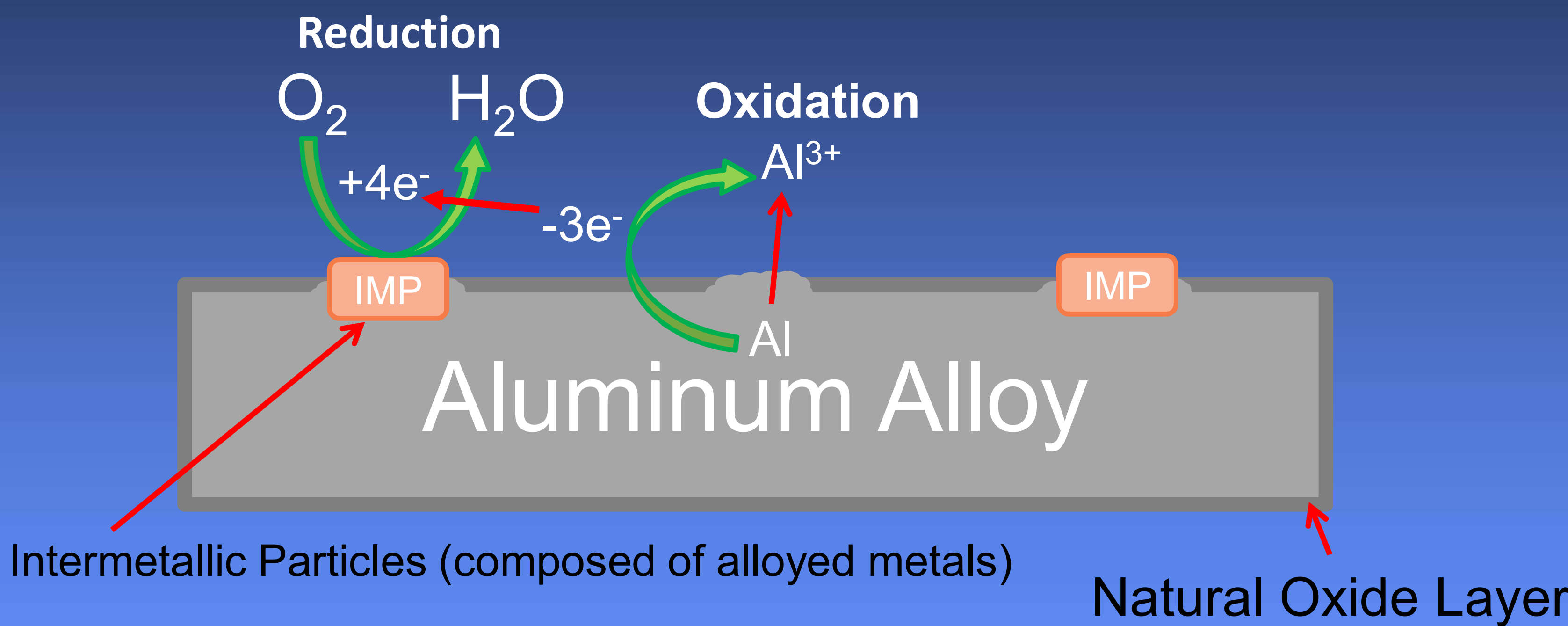
More Aluminum Benefits

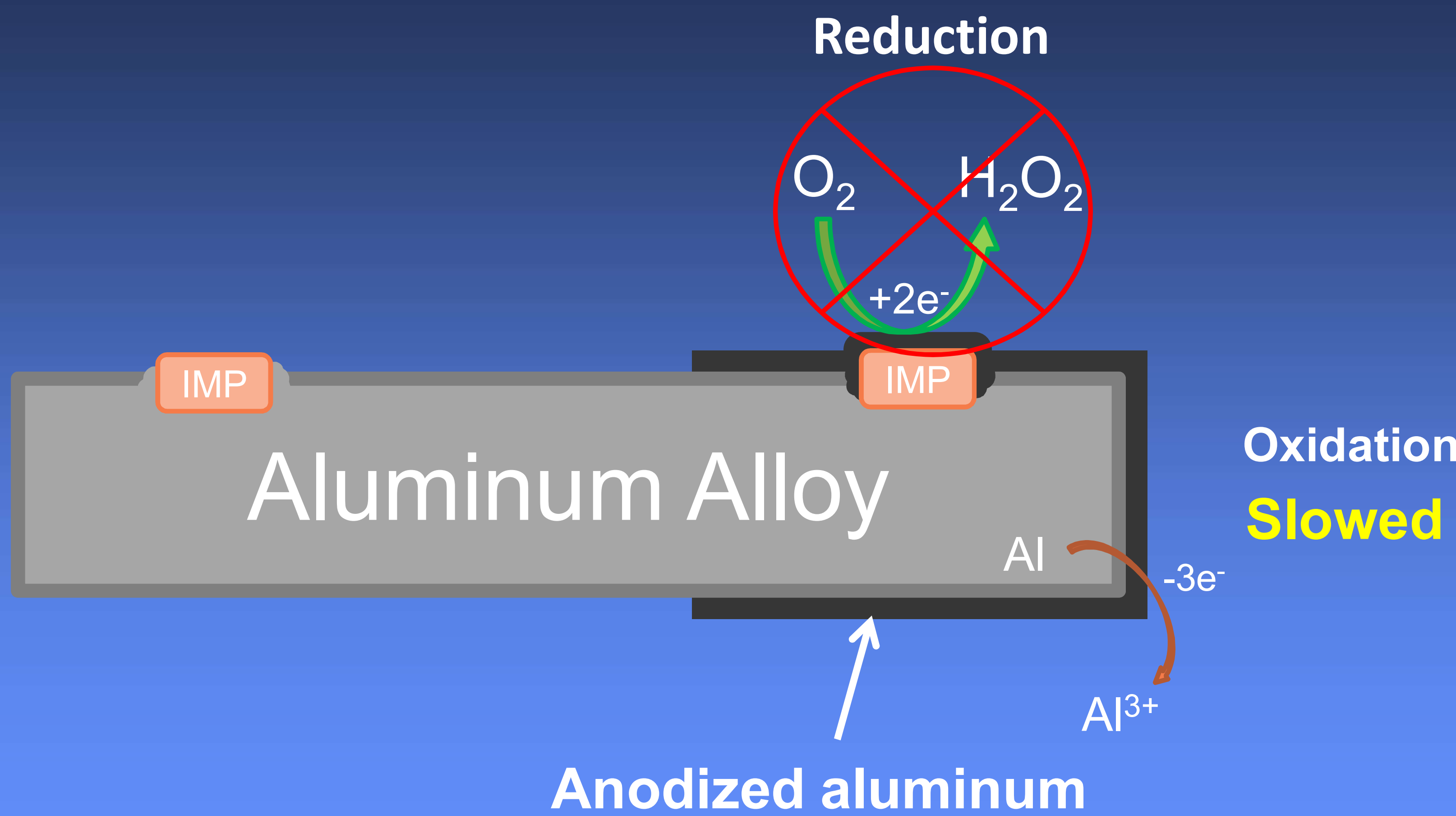
- Excellent thermal conductor
- Non sparking
- Conducts electricity
- Non magnetic
- Is recyclable

Aluminum Alloy Corrosion



Element (Weight %)	Cu	Fe	Mg	Mn	Si	Zn	Ti	Cr	Al
7075-T6	1.2-2	0.5	2.1-2.9	0.3	0.4	5.1-6.1	0.2	0.18-0.28	87.2-91.4
2024-T3	3.8-4.9	0.5	1.2-1.8	0.3-0.9	0.5	0.25	0.15	0.1	90.9-93.7

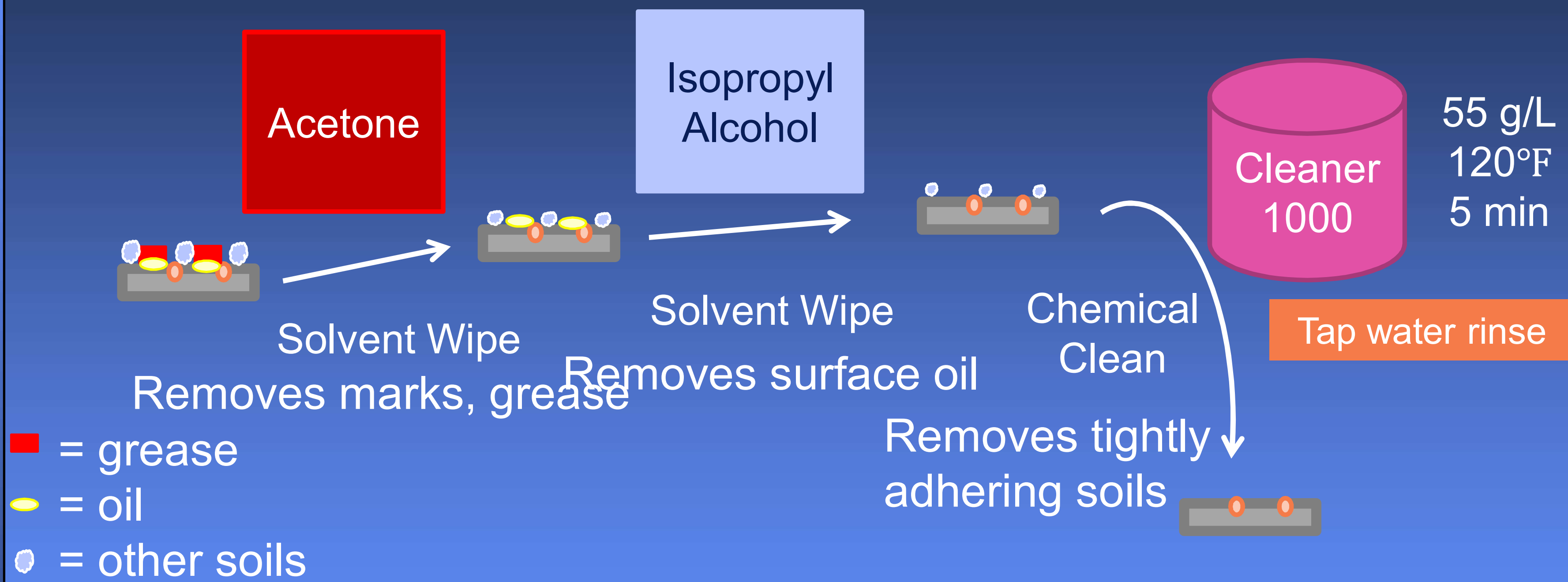
Anodize to Prevent Corrosion



Anodized Aluminum

- Produces a uniform strong, durable surface that dyes easily
- Applied to many consumer products requiring consistent finish and color
  - Cookware, cell phones
- Protects against corrosion for building materials exposed to harsh conditions
  - Façade of Sears (now Willis) Tower in Chicago, Illinois

Anodize Preparation Steps

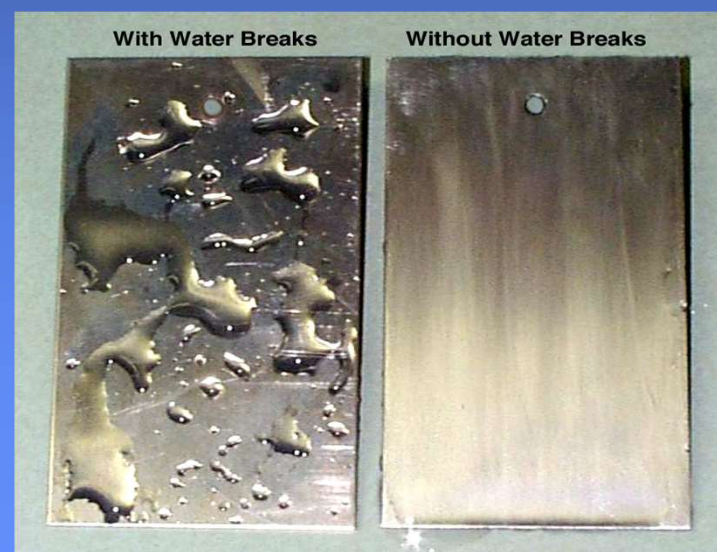


Cleaning

- **Prepare the part for anodize - remove soils**
- **Need different cleaners for different soils**

How to Determine Cleanliness

- Desire a chemically and physically clean surface
- Rule of thumb: water break-free surface



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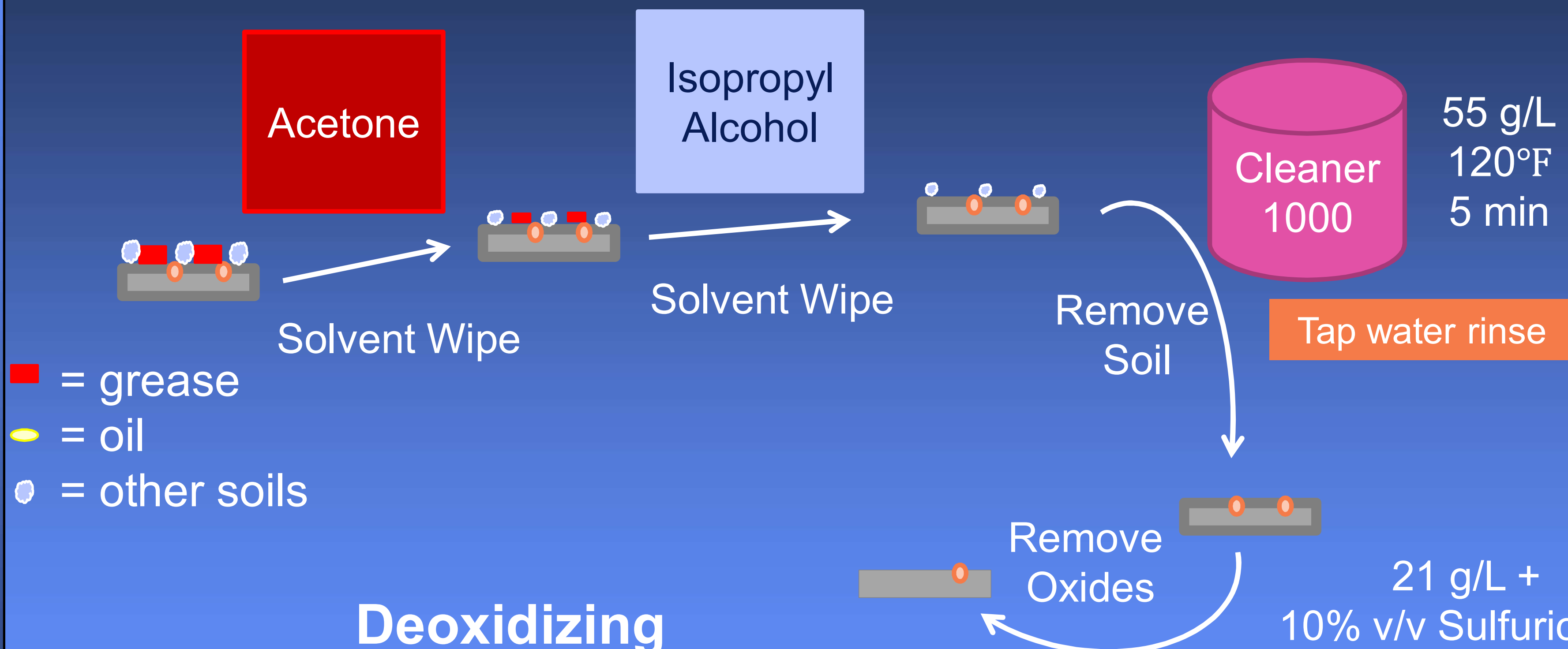
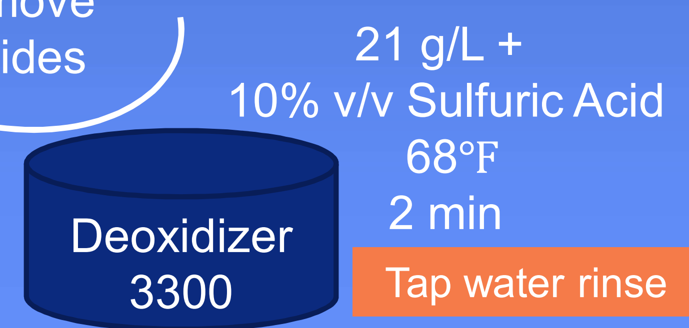
Anodize Preparation Steps





Deoxidizing

- **Remove smut left by etching or cleaning**
- **Removes oxides, some intermetallics**
- **Leaves an active surface to anodize**

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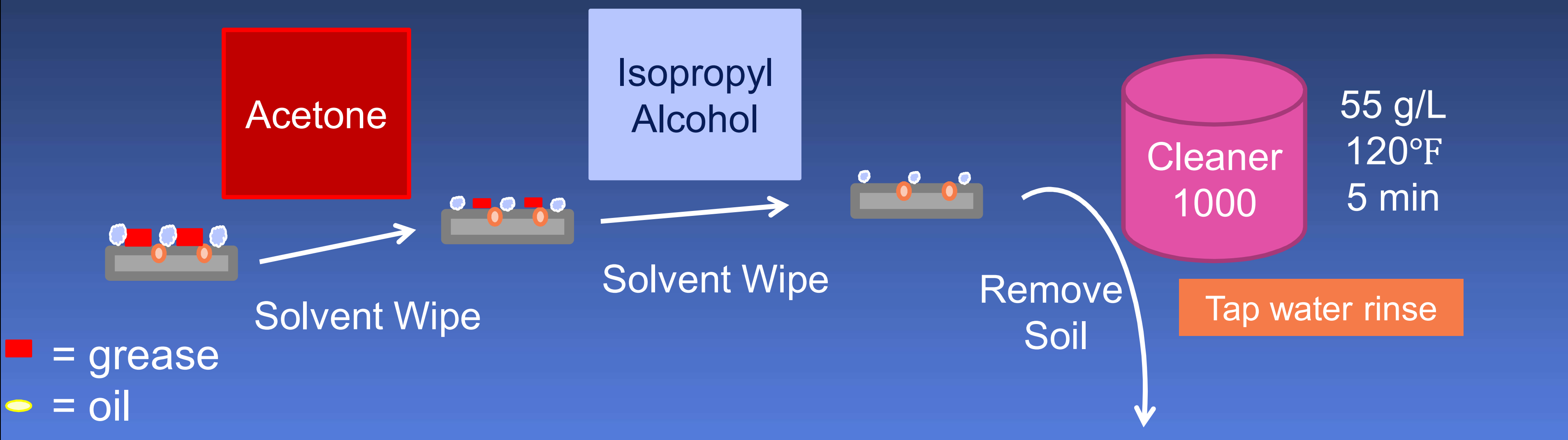
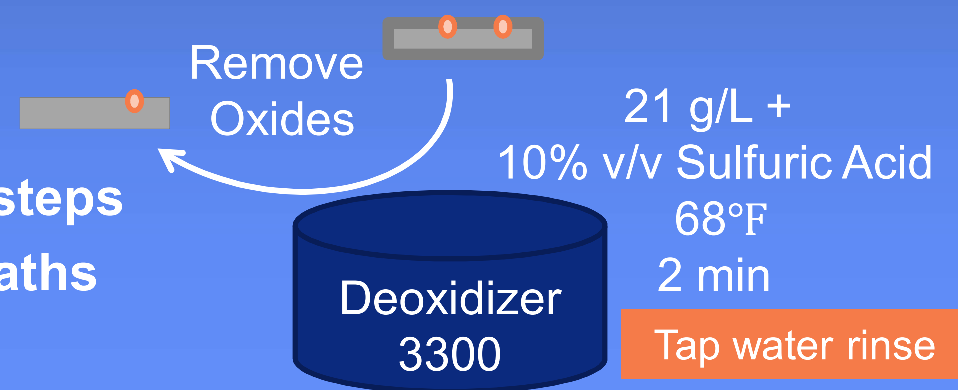
Anodize Preparation Steps





Rinsing

Removes materials from previous steps

Prevents cross contamination of baths

Provide good agitation

Water changeover 1x per hour minimum

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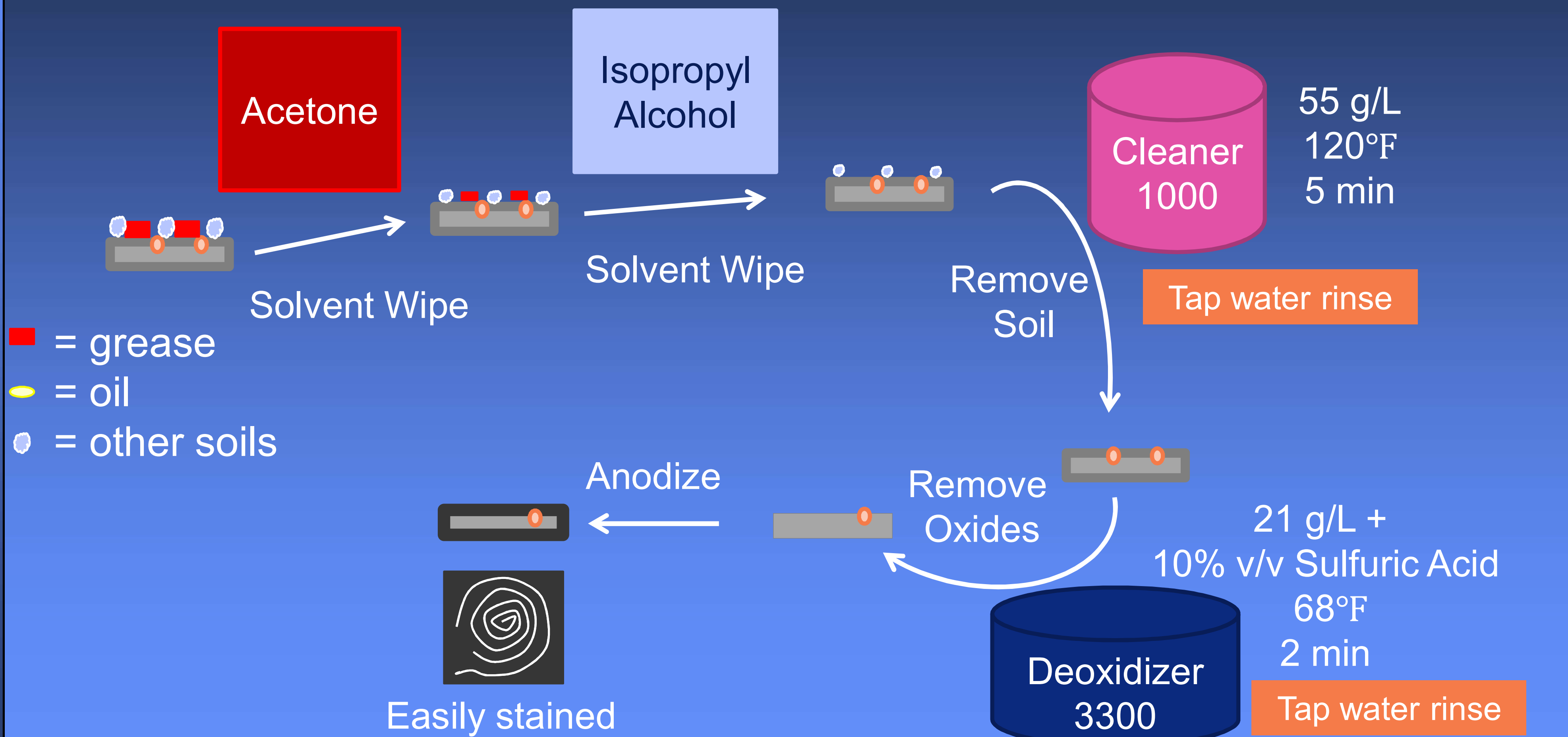
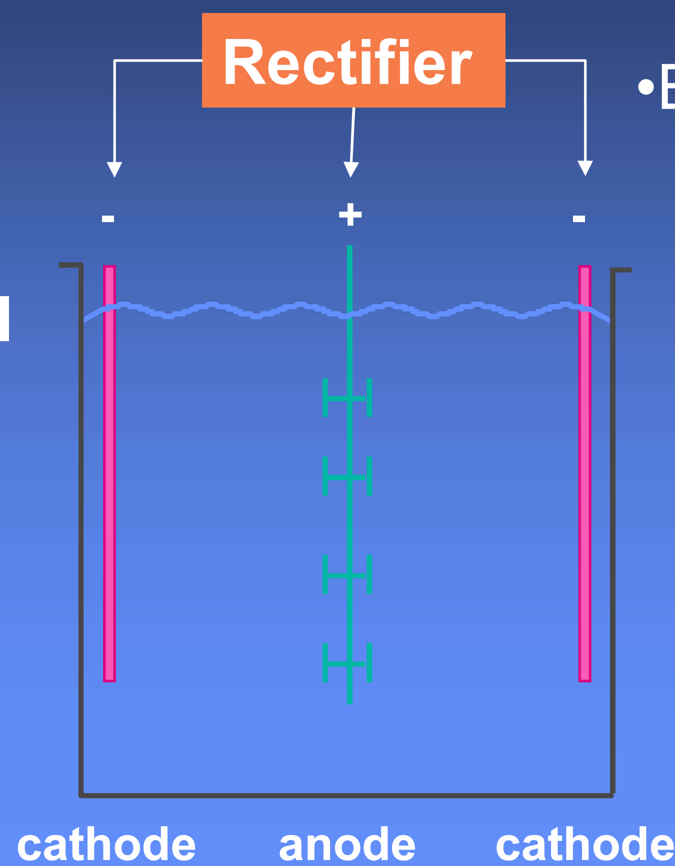
Anodize Preparation Steps



Process of Oxide Formation
Typical Anodize Tank Setup

- **Electrochemical oxidation of a metal to produce a stable oxide on the surface**



- Essential ingredients:
  - Aluminum anode - the part to be anodized
  - Suitable cathode - Al, Pb, C
  - Acid electrolyte - H_2SO_4 H_3PO_4, H_2CrO_4
  - Direct current

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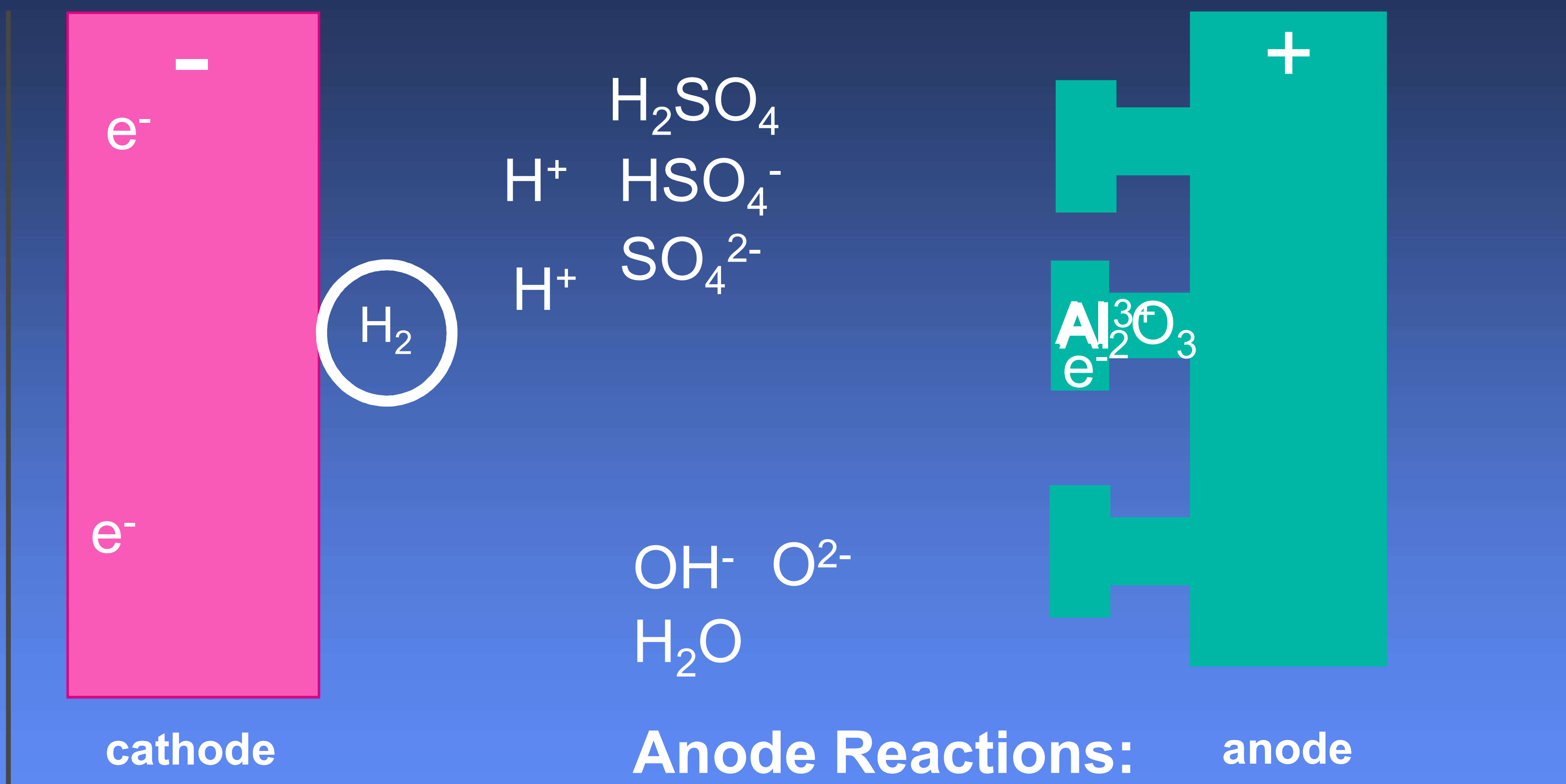
Anodize Barrier Layer Formation



Cathode Reaction:

$2H^+ + 2e^- \rightarrow H_2(g)$

Anode Reactions:

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

$2Al^{3+} + 3O^{2-} \rightarrow Al_2O_3$

$2Al^{3+} + 3OH^- \rightarrow Al_2O_3 + 3H^+$

Overall Reaction:

$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$

Anodize Growth and Pore Formation

Oxide Formation

$2Al^{3+} + 3O_2^- \rightarrow Al_2O_3$
$2Al^{3+} + 3OH^- \rightarrow Al_2O_3 + 3H^+$
$Al^{3+} + SO_4^{2-} \rightarrow Al_2(SO_4)_3$

VS

Oxide Dissolution

$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+}(aq) + 3H_2O$

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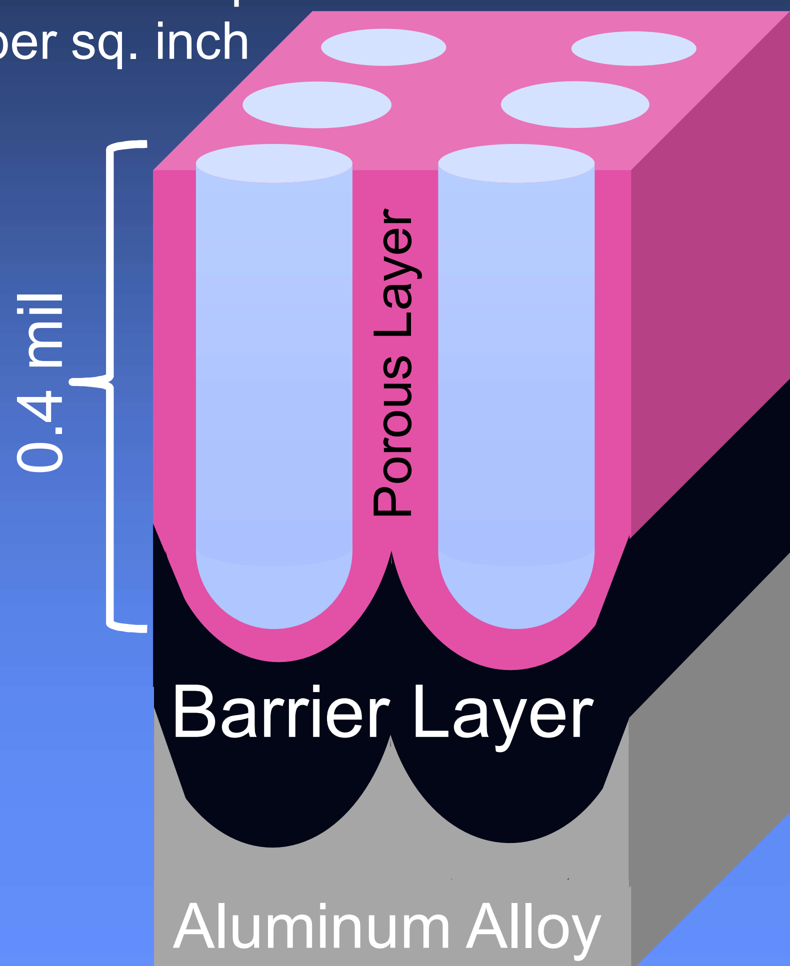
Characteristics of the Oxide

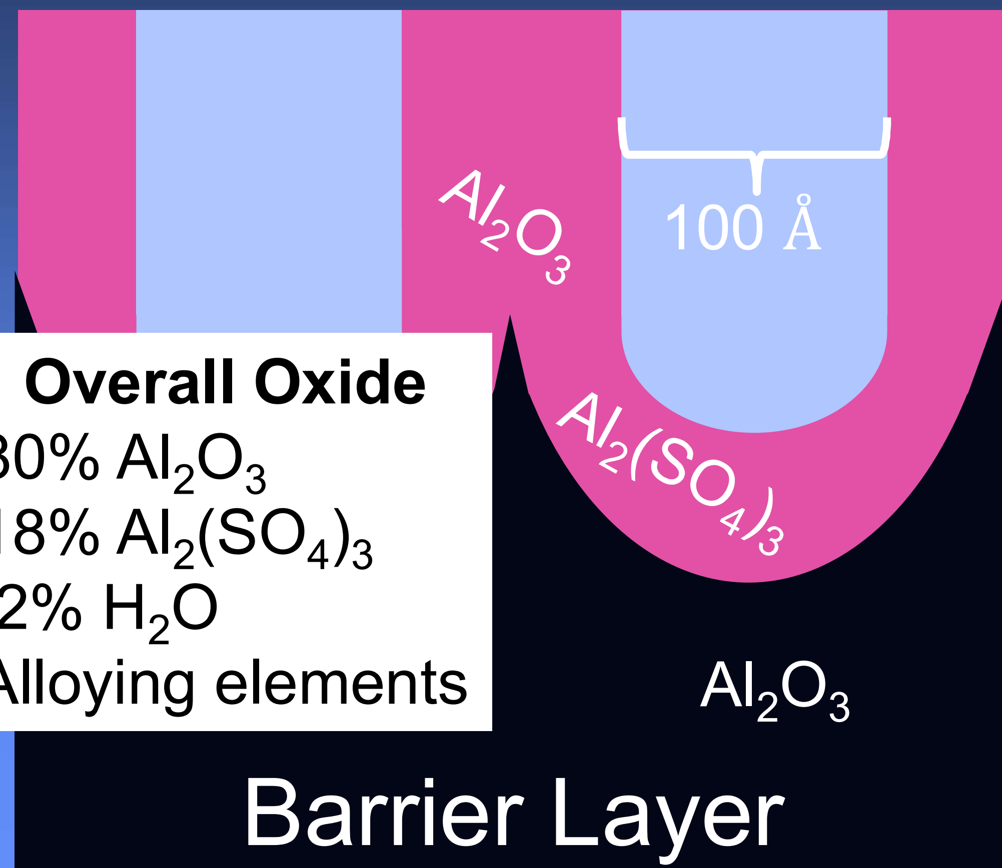
Typical Oxide Cell Structure

15% porosity
400 billion pores per sq. inch



Overall Oxide

80% Al_2O_3
18% $Al_2(SO_4)_3$
2% H_2O
Alloying elements



Wernick, S & Pinner, R & Sheasby, P.G. (2001). The surface treatment and finishing of aluminum and its alloys. ASM International, Materials Park. 5. 2-4.

Sulfuric Acid Anodizing

- First patented in 1927 in England
- MIL-A-8625 Type IC, II, IIB, III
- 10-20% w/w sulfuric acid in water
- Produces thick porous coatings 1-125 micron
- Abrasion resistant and hard
- Dyeable
- Most common– consumer, architectural, aerospace, military

Anodize Parameters

Anodize	Target Oxide Thickness	Anodize Time
Type II	0.36 mil	2024: 29.4 min
		7075: 26.7 min
Type IIB	0.18 mil	2024: 17.0 min
		7075: 12.7 min

Anodize
Type II
Type IIB

Anodize Time
2024: 29.4 min
7075: 26.7 min
2024: 17.0 min
7075: 12.7 min

Anodize Coating Weight

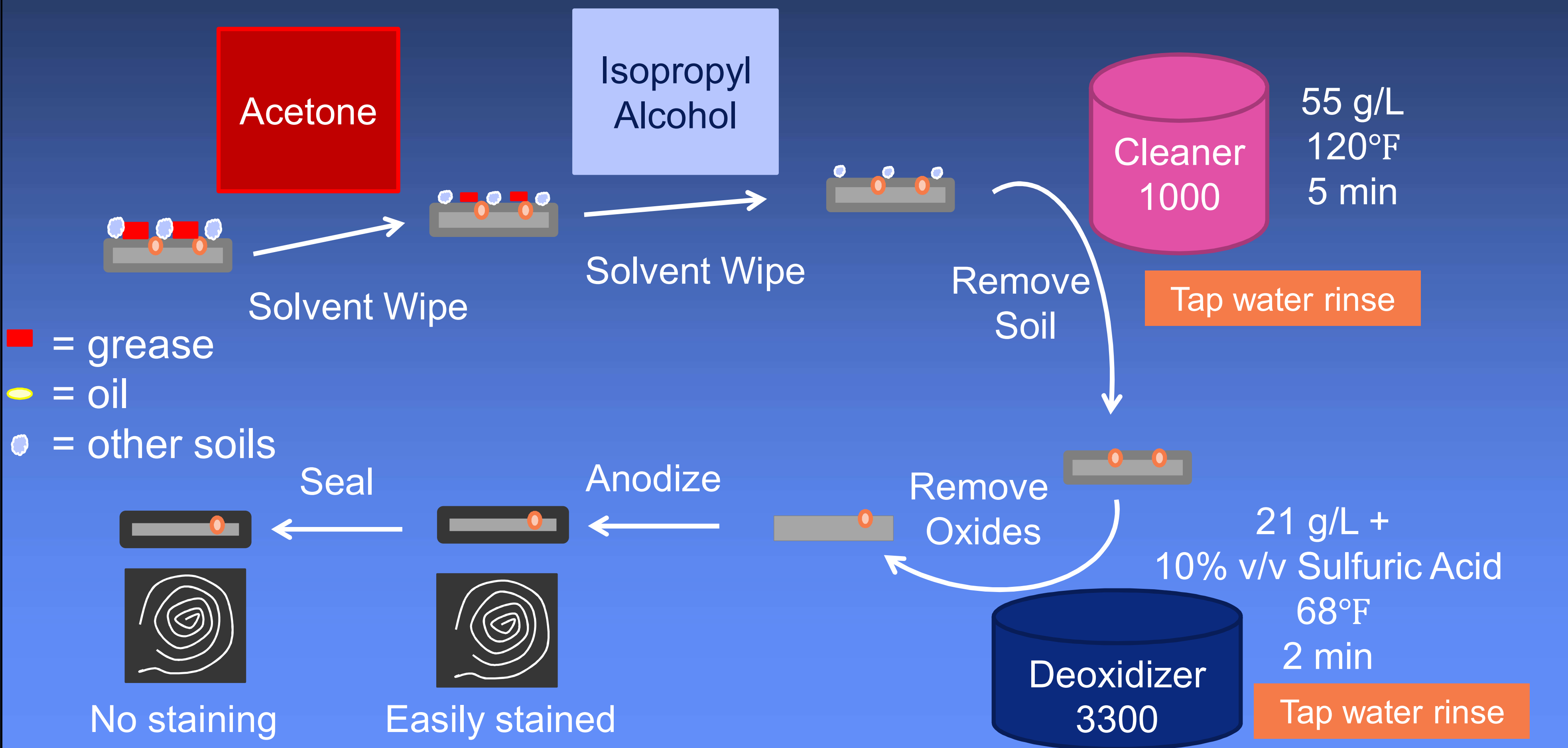
Designation	Alloy	Panel I.D.	Mil-A-8625F Requirement (mg/ft^2)	Average Coating Weight (mg/ft^2)
Type II	2024	HF8 – HF10	1,000 minimum	**1456.3**
	7075	HF18 – HF20		**2015.7**
	2024	NP28 – NP30		**1464.8**
	7075	NP38 – NP40		**2014.9**
Type IIB	2024	HF48 – HF50	200-1,000	**870.1**
	7075	HF58 – HF60		**917.3**
	2024	NP68 – NP70		**877.6**
	7075	NP78 – NP80		**893.3**

Anodize Thickness

Targets:
Type II = 0.36 mil
Type IIB = 0.18 mil

Designation	Alloy	Panel I.D.	Avg. Oxide Thickness (mils)	Avg. Oxide Thickness (microns)
Type II	2024	HF1 – HF10	0.360 ± 0.01	9.1 ± 0.3
	7075	HF11 – HF20	0.353 ± 0.01	9.0 ± 0.3
	2024	NP21 – NP30	0.363 ± 0.01	9.2 ± 0.3
	7075	NP31 – NP40	0.354 ± 0.01	9.0 ± 0.3
Type IIB	2024	HF41 – HF50	0.180 ± 0.01	4.6 ± 0.3
	7075	HF51 – HF60	0.159 ± 0.01	4.0 ± 0.3
	2024	NP61 – NP70	0.181 ± 0.01	4.6 ± 0.3
	7075	NP71 – NP80	0.156 ± 0.01	4.0 ± 0.3

Anodize Preparation Steps



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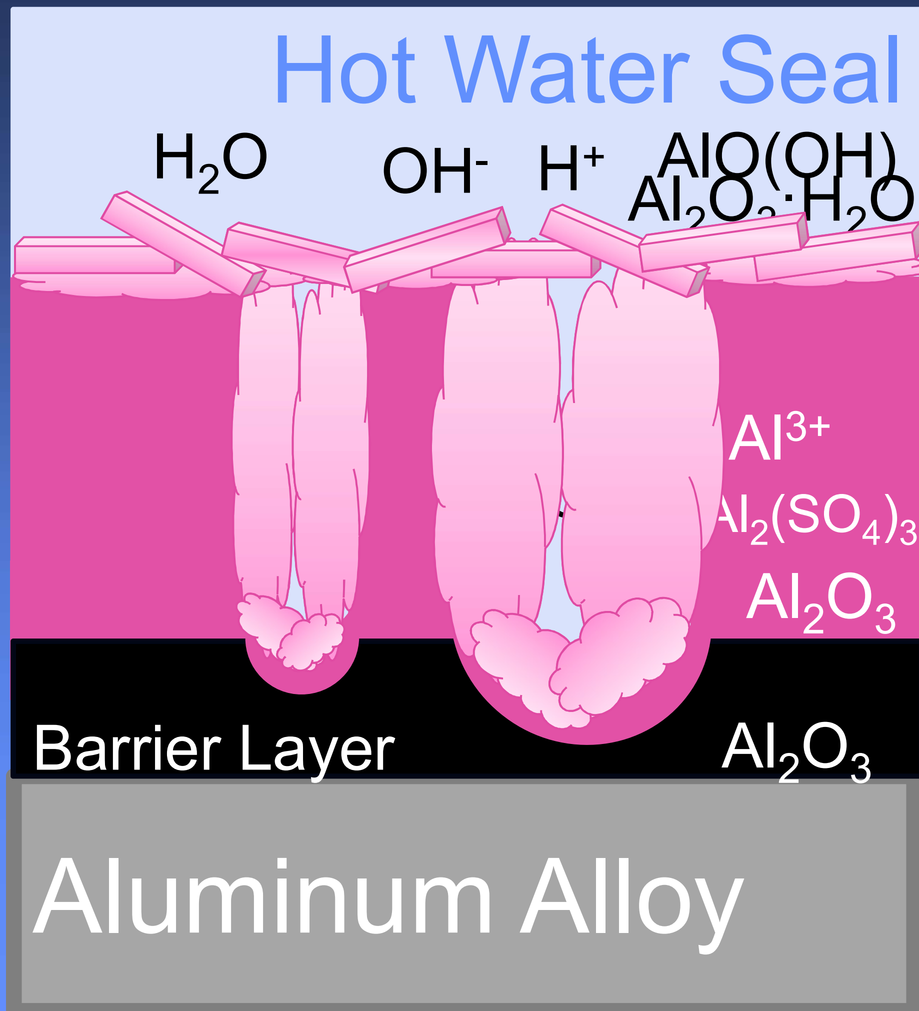
Hydrothermal Sealing Anodize



Chemical change of oxide

Oxide Composition

	Unsealed	Sealed
Al_2O_3	78.9%	61.7%
$Al_2O_3 \cdot H_2O$	0.5%	17.6%
$Al_2(SO_4)_3$	20.2%	17.9%
H_2O	0.4%	2.8%

Long seal times:
More crystalline oxide (boehmite)
AlO(OH) = seal smut

Wernick, S & Pinner, R & Sheasby, P.G. (2001). The surface treatment and finishing of aluminum and its alloys. ASM International, Materials Park. 5. 2-4.

Hot DI Water Seal

Temperature: 205-212ºF
pH: 5.5 - 6.5
Time: 15-20+ minutes

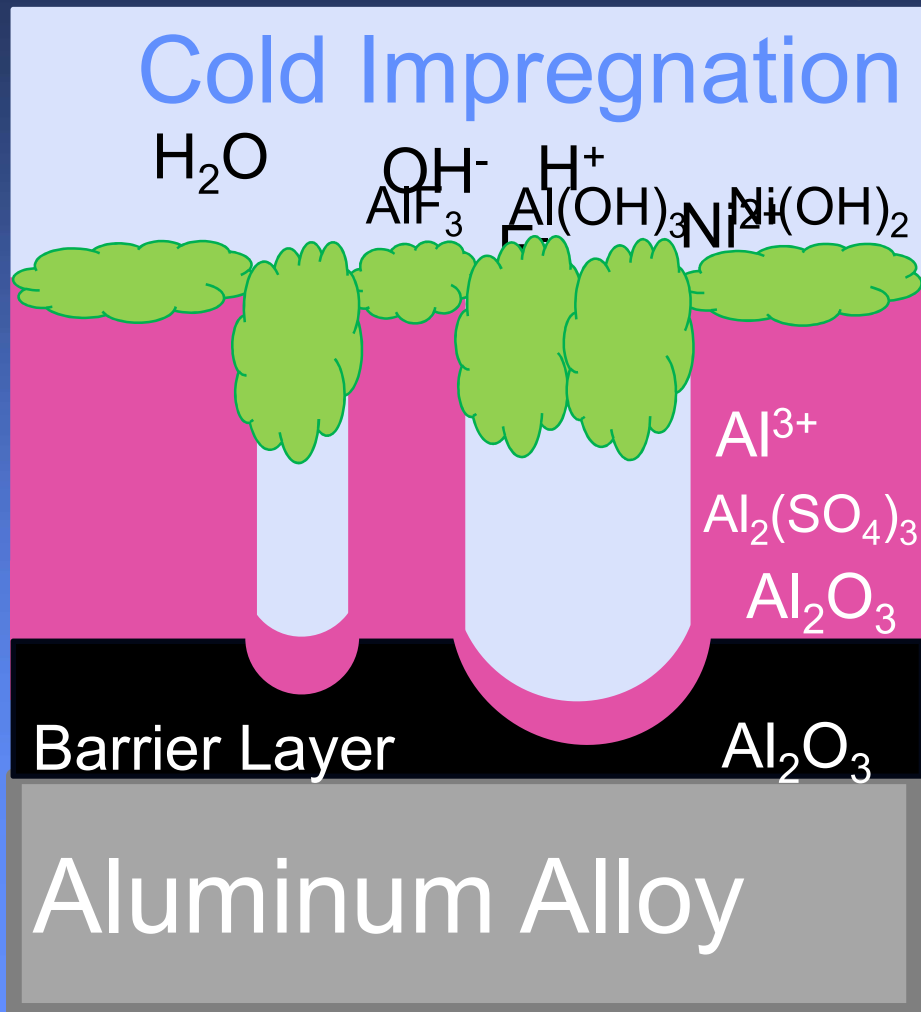
Advantages

- Inexpensive makeup
- Non-polluting
- Easily discarded

Disadvantages

- Easily contaminated
- pH difficult to control
- High energy usage
- Seal smut

Cold Sealing Anodize



Oxide plug fills pores

Oxide Composition

Cold Ni Seal
$Ni(OH)_2$
$Al(OH)_3$
AlF_3
All hydrated forms of the above oxides

Wernick, S & Pinner, R & Sheasby, P.G. (2001). The surface treatment and finishing of aluminum and its alloys. ASM International, Materials Park. 5. 2-4.

Nickel Room Temperature Seal

Temperature: 70-90ºF
pH: 5.5 - 6.5
Time: 5 - 10 minutes

Advantages

- Stable pH
- Offers good corrosion resistance
- Improves dye lightfastness
- Low energy consumption
- Long lasting bath

Disadvantages

- Contains heavy metals and fluorides
- [F-] must be controlled
- Expensive makeup
- Not easily discarded
- Sensitive to impurities, contamination
- Often must follow with mid-temp or hot DI seal to pass corrosion tests

Sodium Dichromate Seal
Hydrothermal and Plug Formation

Temperature: 205-212ºF

pH: 5.6-6.0

Time: 15-25 minutes

Advantages

- Seals well
- Good corrosion resistance

Disadvantages

- High energy consumption
- Contains hexavalent chrome
- Requires good ventilation

CHEMEON TCP Seal

Developed and patented by the US Navy after existing coatings failed to qualify for Navy use due to high cost and inferior performance

CHEMEON was the first licensee of the DoD

Non-carcinogenic

Passes >2,000 hr salt spray

Can replace sodium dichromate seals

Advantages

- Short immersion times
- No ventilation required
- Ambient (room) temperature
- No hexavalent chrome
- Very little smut or residue
- Long lasting bath

Disadvantages

- New method
- Unknown dye sealing abilities (TBD)

Seal Parameters

Seal	Concentration	pH	Temperature	Immersion time
TCP-HF	28.6% v/v	3.81	70°F	5 minutes
TCP-NP	0.53% v/v	3.81	70°F	5 minutes

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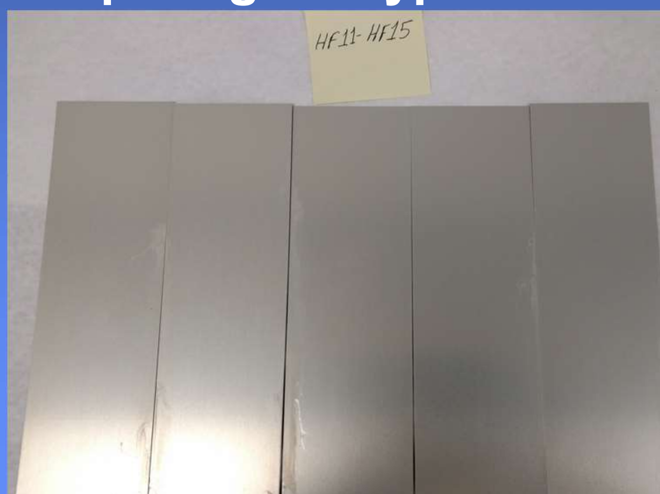
Neutral Salt Spray Corrosion Resistance Testing

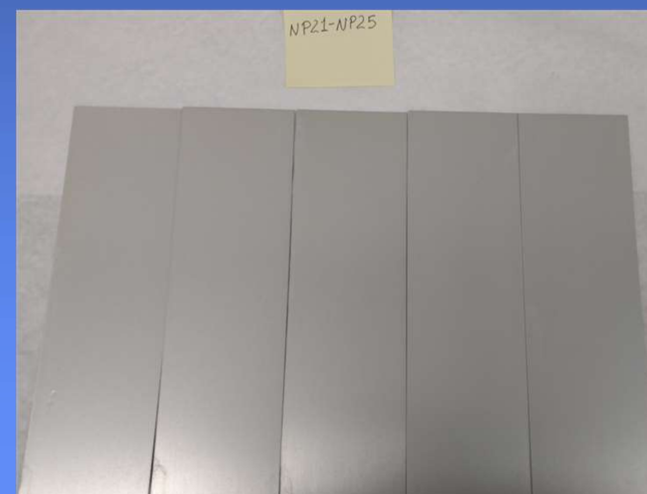
- **Tested at Atlas Testing Laboratories IAW ASTM B117 per MIL-A-8625F**
  - **Calls for 336 hours without pitting**
  - **Exceeded 2,000 hours with no pitting on Type II, minimal pitting on Type IIB**

TCP-HF
Before



TCP-HF
After **1,120 hours**

TCP-NP
Before



TCP-NP
After **1,120 hours**

Corrosion Resistance
Type II Anodize

Alloy	Seal	Panel I.D.	Pits and Results at 336 Hours Neutral Salt Spray		Pits and Results at 1,000 Hours Neutral Salt Spray		Pits and Results at 2,000 Hours Neutral Salt Spray	
2024	TCP-HF	HF1	0	**PASS**	0	**PASS**	0	**PASS**
		HF2	0		0		0	
		HF3	0		0		0	
		HF4	0		0		0	
		HF5	0		0		0	
7075	TCP-HF	HF11	0	**PASS**	0	**PASS**	0	**PASS**
		HF12	0		0		0	
		HF13	0		0		0	
		HF14	0		0		0	
		HF15	0		0		0	
2024	TCP-NP	NP21	0	**PASS**	0	**PASS**	0	**PASS**
		NP 22	0		0		0	
		NP23	0		0		0	
		NP24	0		0		0	
		NP25	0		0		0	
7075	TCP-NP	NP31	0	**PASS**	0	**PASS**	0	**PASS**
		NP32	0		0		0	
		NP33	0		0		0	
		NP34	0		0		0	
		Np35	0		0		0	

Corrosion Resistance
Type IIB Anodize

Alloy	Seal	Panel I.D.	Pits and Results at 336 Hours Neutral Salt Spray		Pits and Results at 1,000 Hours Neutral Salt Spray		Pits and Results at 2,000 Hours Neutral Salt Spray	
2024	TCP-HF	HF41	0	PASS	0	PASS	1	PASS
		HF42	0		0		1	
		HF43	0		0		1	
		HF44	0		0		1	
		HF45	0		0		3	
7075	TCP-HF	HF51	0	PASS	0	PASS	0	PASS
		HF52	0		0		0	
		HF53	0		0		1	
		HF54	0		0		1	
		HF55	0		0		2	
2024	TCP-NP	NP61	0	PASS	0	PASS	2	PASS
		NP62	0		0		2	
		NP63	0		0		3	
		NP64	0		0		3	
		NP65	0		0		3	
7075	TCP-NP	NP71	0	PASS	0	PASS	2	PASS
		NP72	0		0		2	
		NP73	0		0		3	
		NP74	0		0		3	
		NP75	0		0		3	

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Paint Adhesion

Designation	Alloy	Panel I.D.	Seal	Wet Tape Result
Type II	2024	HF6, HF7	TCP-HF	**PASS**
	7075	HF16, HF17	TCP-HF	**PASS**
	2024	NP26, NP27	TCP-NP	**PASS**
	7075	NP36, NP37	TCP-NP	**PASS**
Type IIB	2024	HF46, HF47	TCP-HF	**PASS**
	7075	HF56, HF57	TCP-HF	**PASS**
	2024	NP66, NP67	TCP-NP	**PASS**
	7075	NP76, NP77	TCP-NP	**PASS**

Results Summary

- Aim for **Type II** thickness = **0.36 mil**

  Actual thickness = **0.353 – 0.363 mil**
- Aim for **Type IIB** thickness = **0.18 mil**

  Actual thickness = **0.156 – 0.181 mil**
- Coating weight **Type II > 1,000 mg/ft^2**

  Actual coating weights = **1456.3 – 2015.7 mg/ft^2**
- Coating weight **Type IIB = 200 - 1,000 mg/ft^2**

  Actual coating weights = **870.1 – 917.3 mg/ft^2**
- Type II and IIB **pass** neutral **salt spray** testing for **2,000 hours**
- Type II and IIB **pass paint adhesion**

Performs up to MIL-A-8625 standards, comparable to hydrothermal and other cold seals

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Future Work

- Performance analysis at a variety of anodize thicknesses
- Performance analysis with dye
- Direct comparison to hot dichromate seal to show superior performance

Acknowledgements

- Dr. Sjon Westre
- Taylor Clarke
- Shay, Jason, Joe, Alec
- CHEMEON Surface Technology

Questions?

Process of Oxide Formation

Typical Anodize Tank Setup