

# Meeting Selectivity Needs with Unique Corrosion Inhibitors in Cleaning and Surface Finishing Practices

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LEVITRONIX *Ultrapure Fluid Handling and  
Wafer Cleaning Conference*

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Slide #1

# Agenda

- **Inhibitor Types**
- Inhibition by Chemisorption
- Ex. Performance (Cu, Al, Sn)
- In-Tool Processing
- Applications
- PQA Program
- Summary

# Inhibition Types

- Chemisorption (e.g. triazoles, silicates, etc.) react with the substrate to form a protective layer, thickness can be monolayer or continues to coat to excess
- Coating (e.g. organic protective film) barrier to reactive species
- Other - solution additives exist to tie-up reactive species or produce a “reducing” environment



# Factors Affecting Corrosion

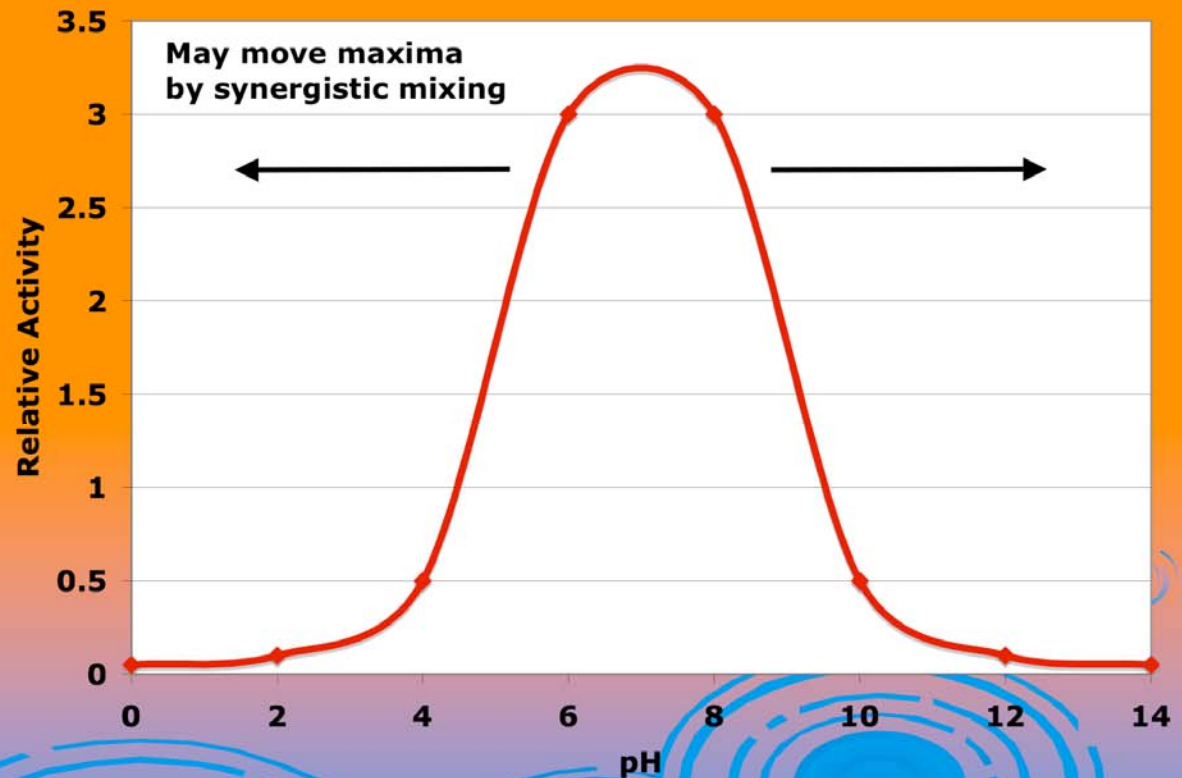
- Chemistry
- Conductivity
- Heat
- Agitation
- Other - current density, dissimilar metals
- Aluminum Oxidation
- $\text{Al}_{(s)} \Rightarrow \text{Al}^{+3} + 3e^{-}$   
 $E = 1.66\text{v}$
- Strong bases & acids

# Inhibitor Activity

Most inhibitors have max and min activity regions dependent upon the media (i.e. acid/base)

Certain inhibitors may operate well in corrosive media while others may exhibit synergism

Optimization is needed



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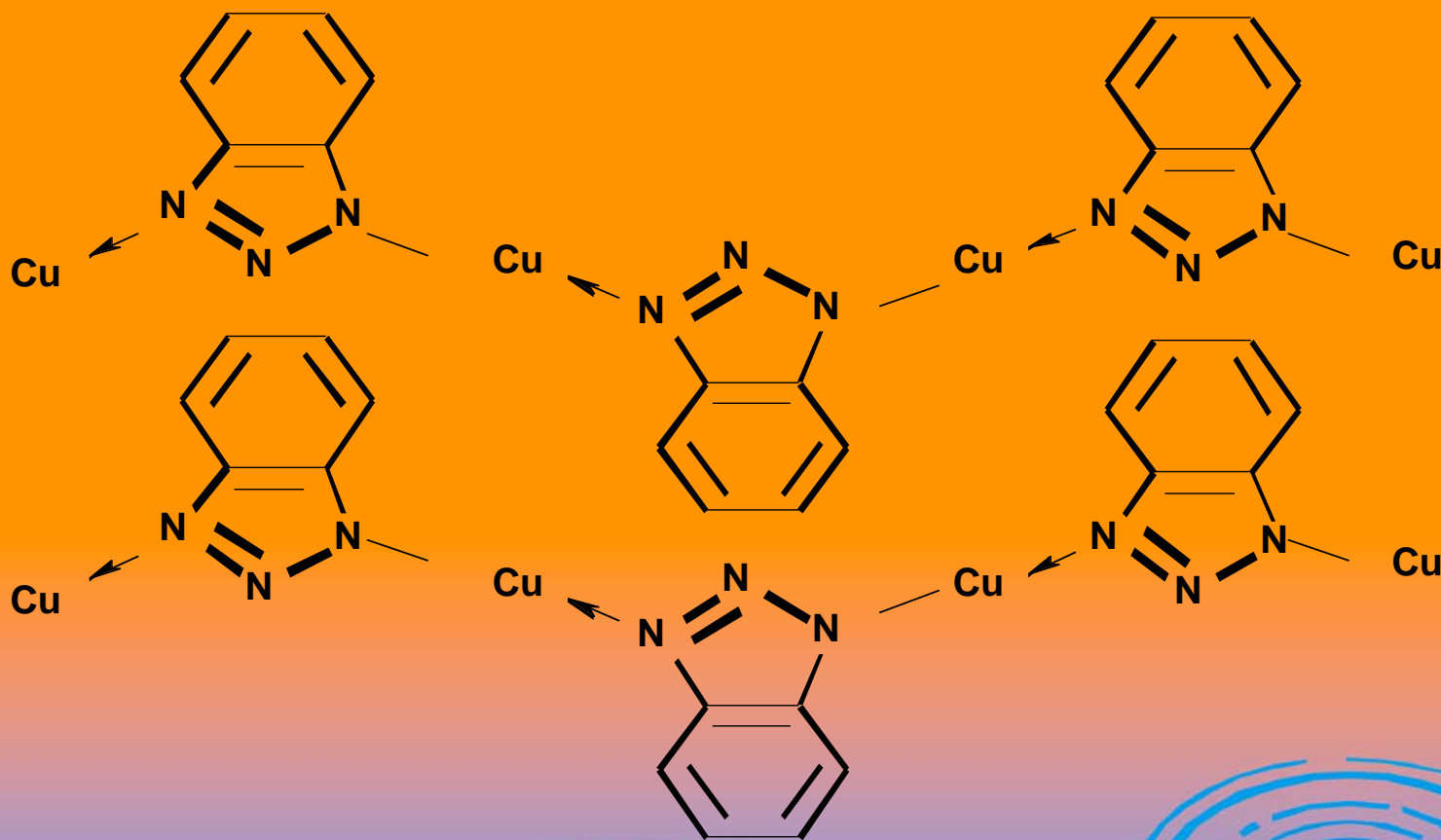
# Chemisorption Inhibitors

- Triazoles - good for Cu, prone to residue
- Borates, phosphates, iodics, silicates, carboxylics, nitrites, sulfites, amines, specialties & organometallics, surfactants
- Blends may achieve synergism
- Buffering/leveling for maximum activity



# Inhibition by Chemisorption

## Ex. Cu-Triazole, network formation

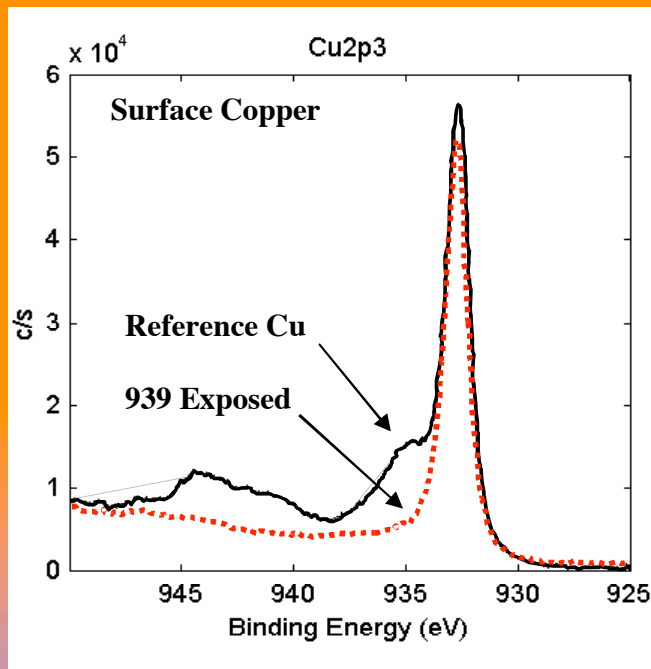




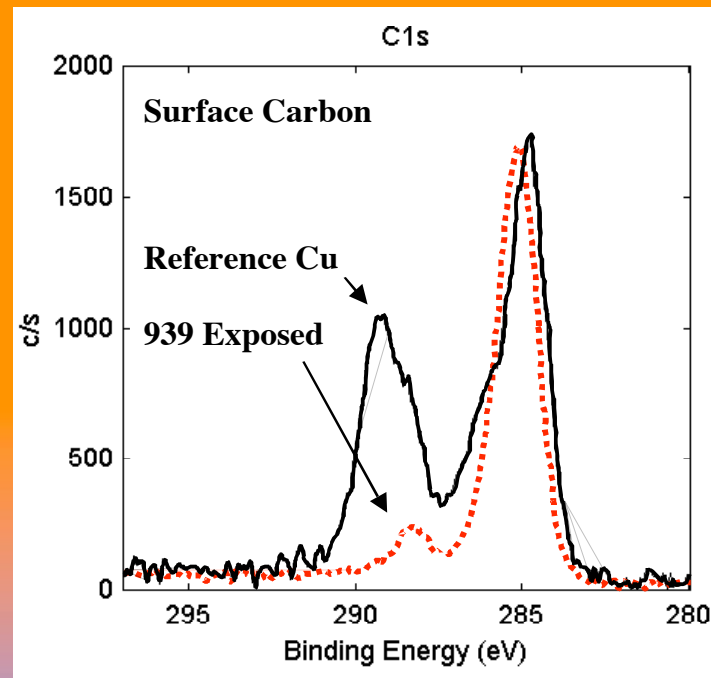
# Inhibition by Chemisorption

## Cu/Triazole - XPS Surface Analysis

Convert reactive  
Cu(2) to inert Cu(1)

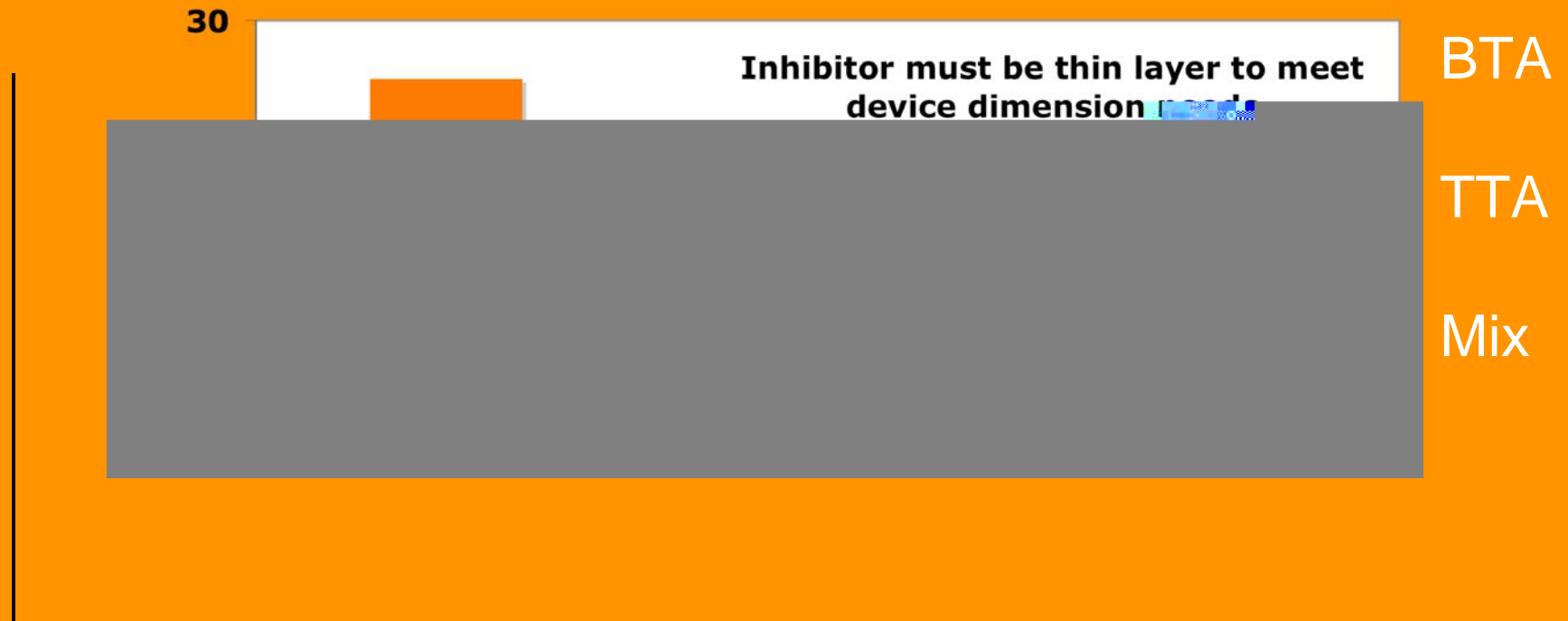


Convert C from  
oxidized to phobic



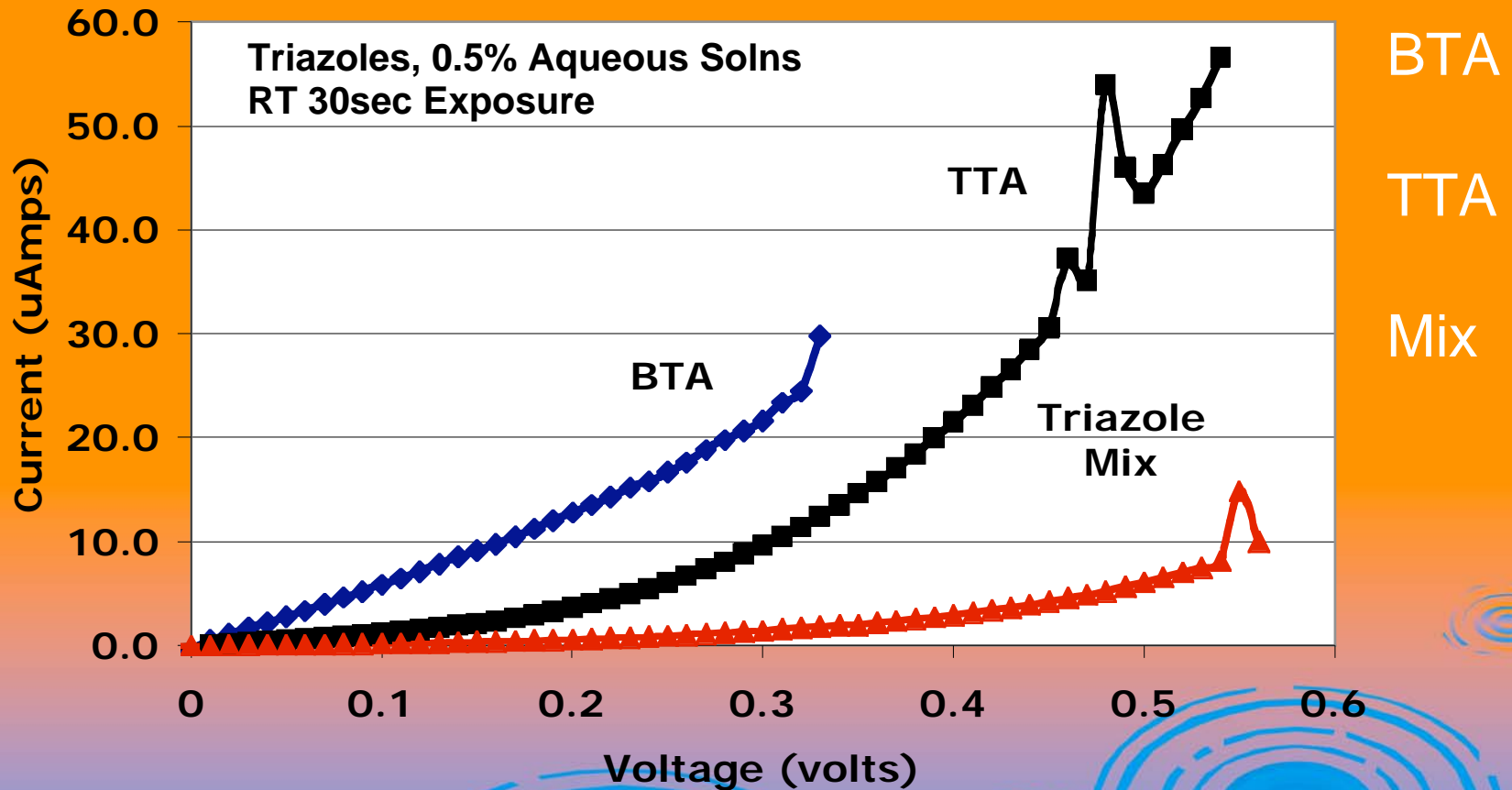
# Inhibition by Chemisorption

## Cu/Triazole - Ellipsometry



# Inhibition by Chemisorption

## Hg-Probe I-V Plots of Triazoles on Cu



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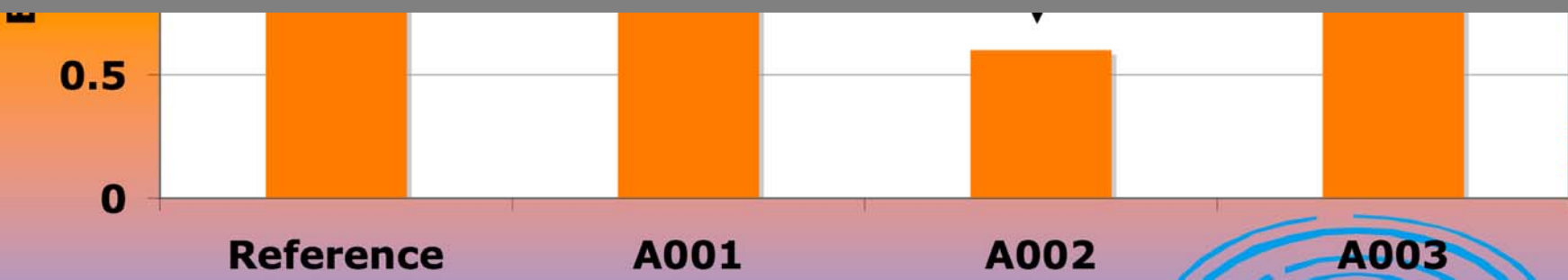
# Example Performance

- Determined on metal film
- Extended period of time
- Dilute concentrations for “in-tool” mixing
- Elevated temperature - representative for etch residue & resist removal applications
- Benefit measured relative to baseline (I.e. no inhibitor)



# Copper Inhibitor Systems in H2SO4

Triazole.2 ..... Triazole.Mix ..... Triazole.1 .....  
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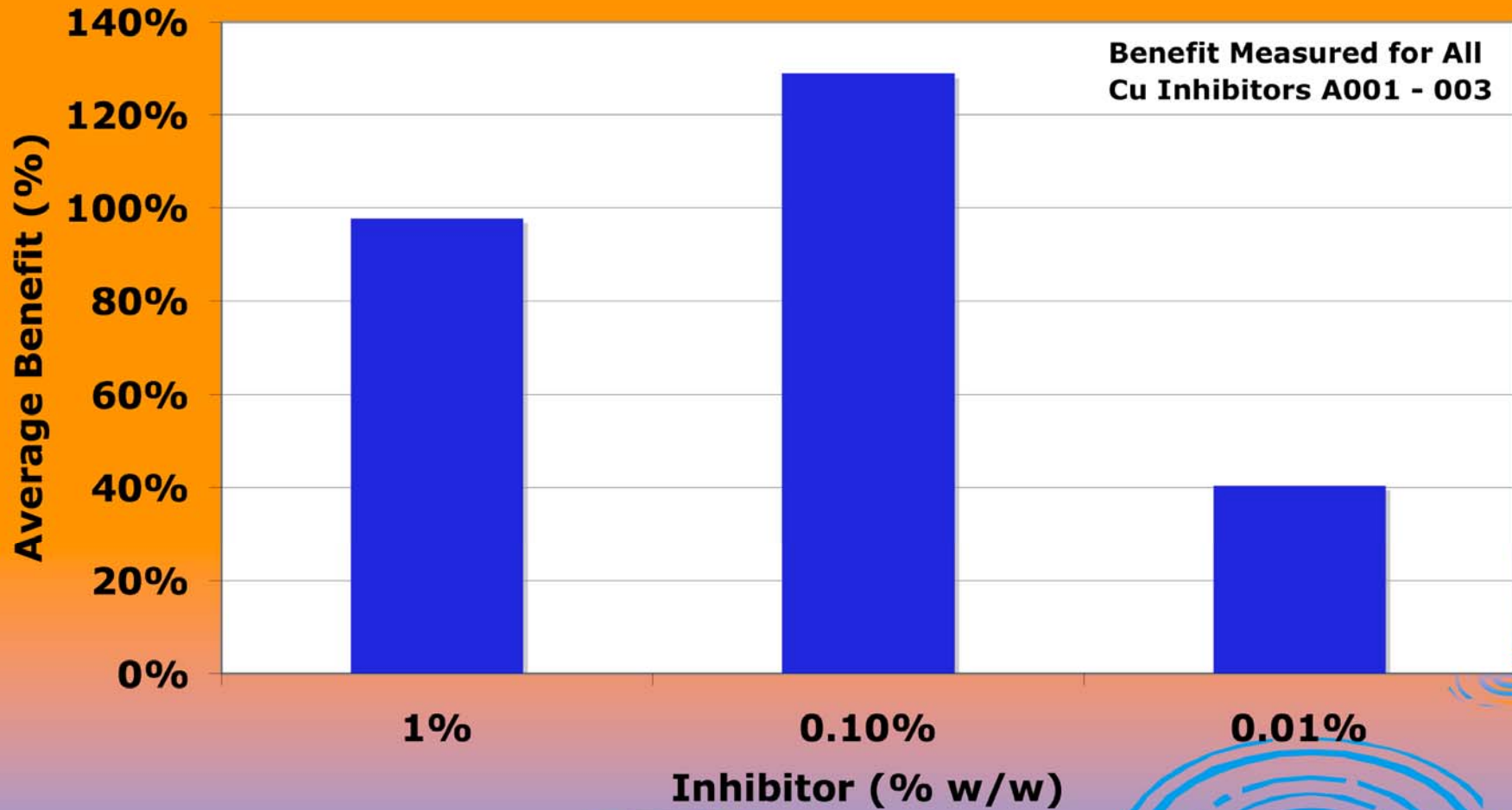
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# Copper Protection in H<sub>2</sub>SO<sub>4</sub>

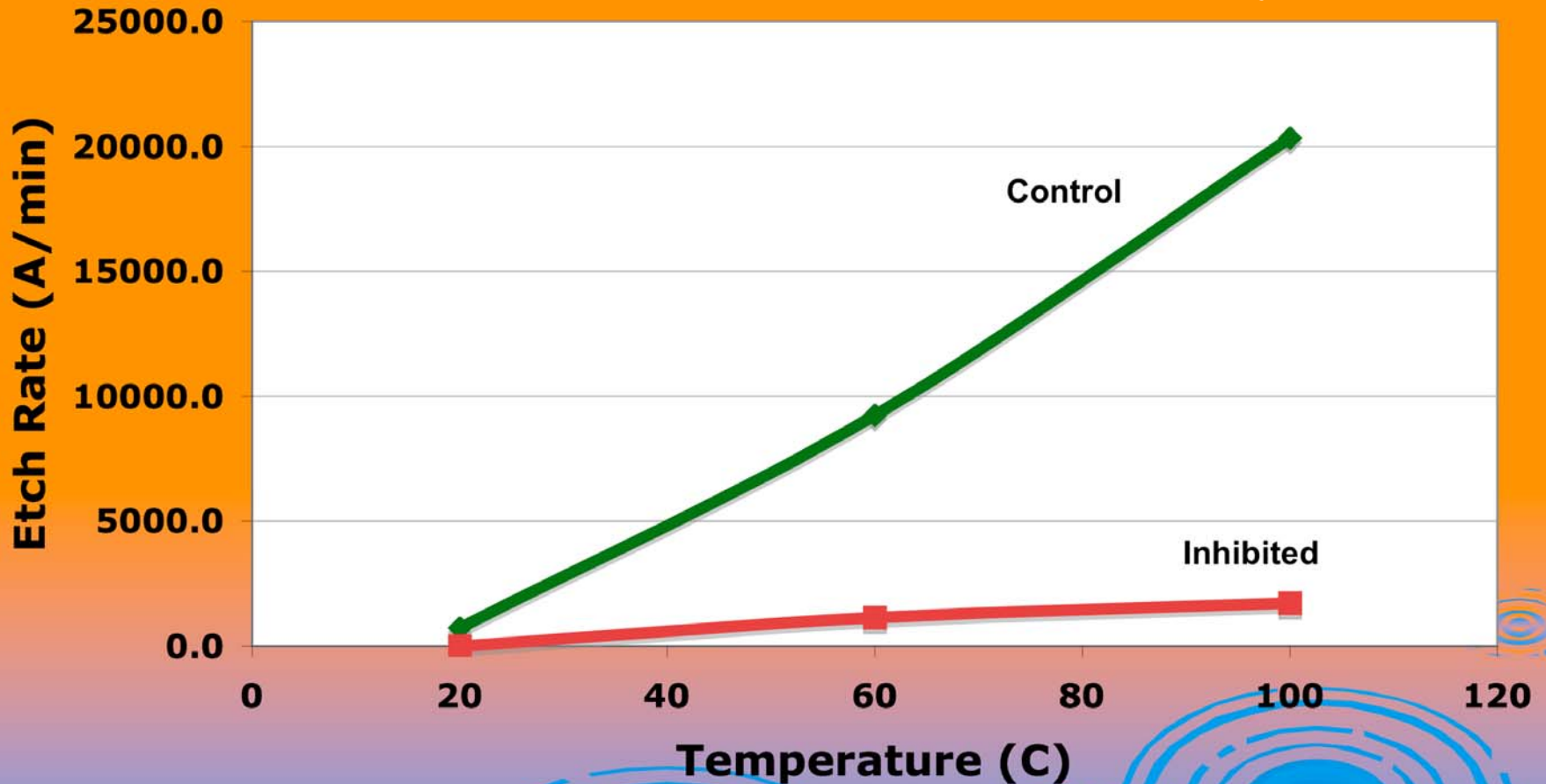
## Ave Benefit vs Concentration



# Aluminum Etch Rate vs Temperature 0.26N TMAH (pH = 14)

Control Inhibitor B

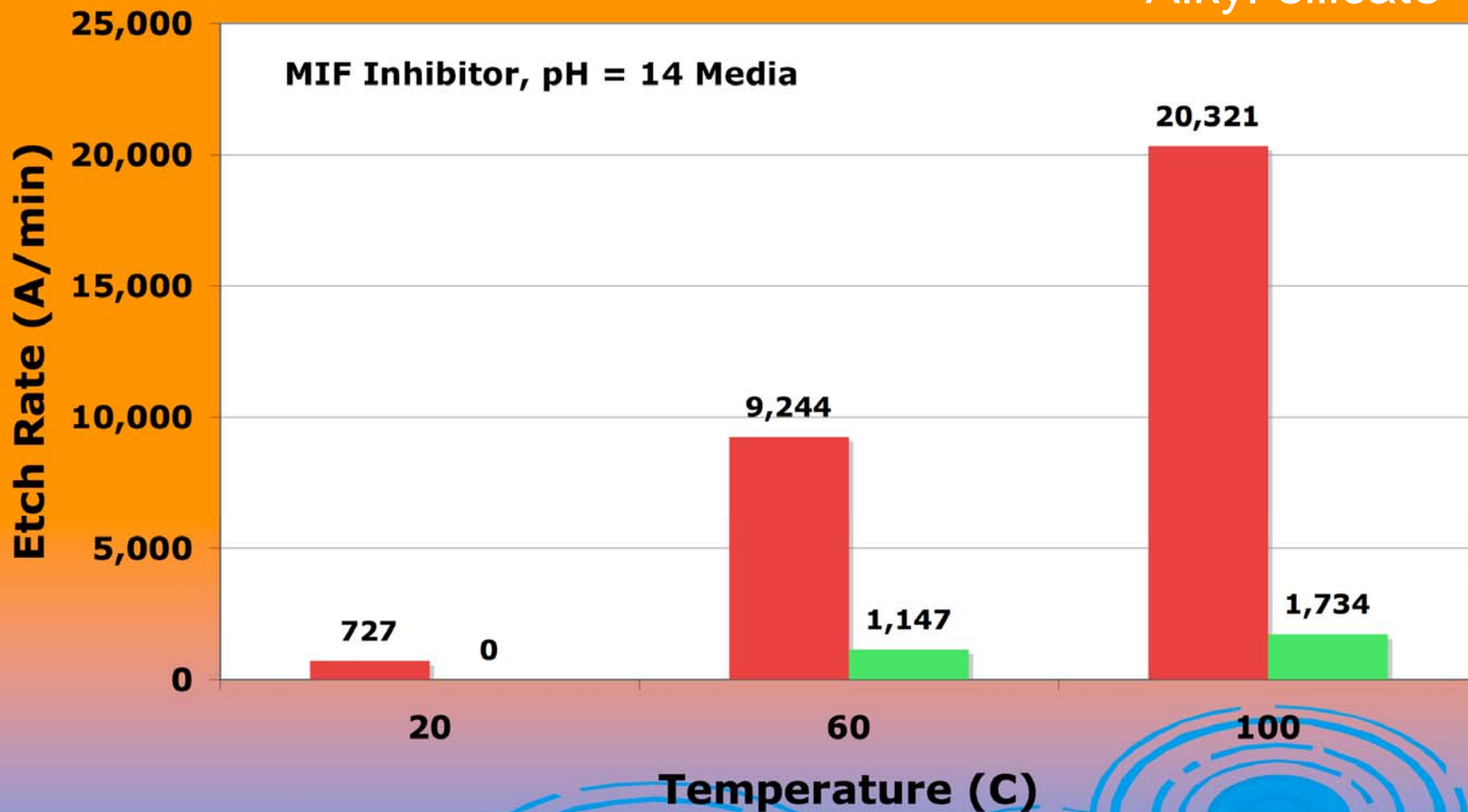
Alkyl-silicate



# Aluminum Etch Rate in Aqueous TMAH

Control Inhibitor

Alkyl-silicate

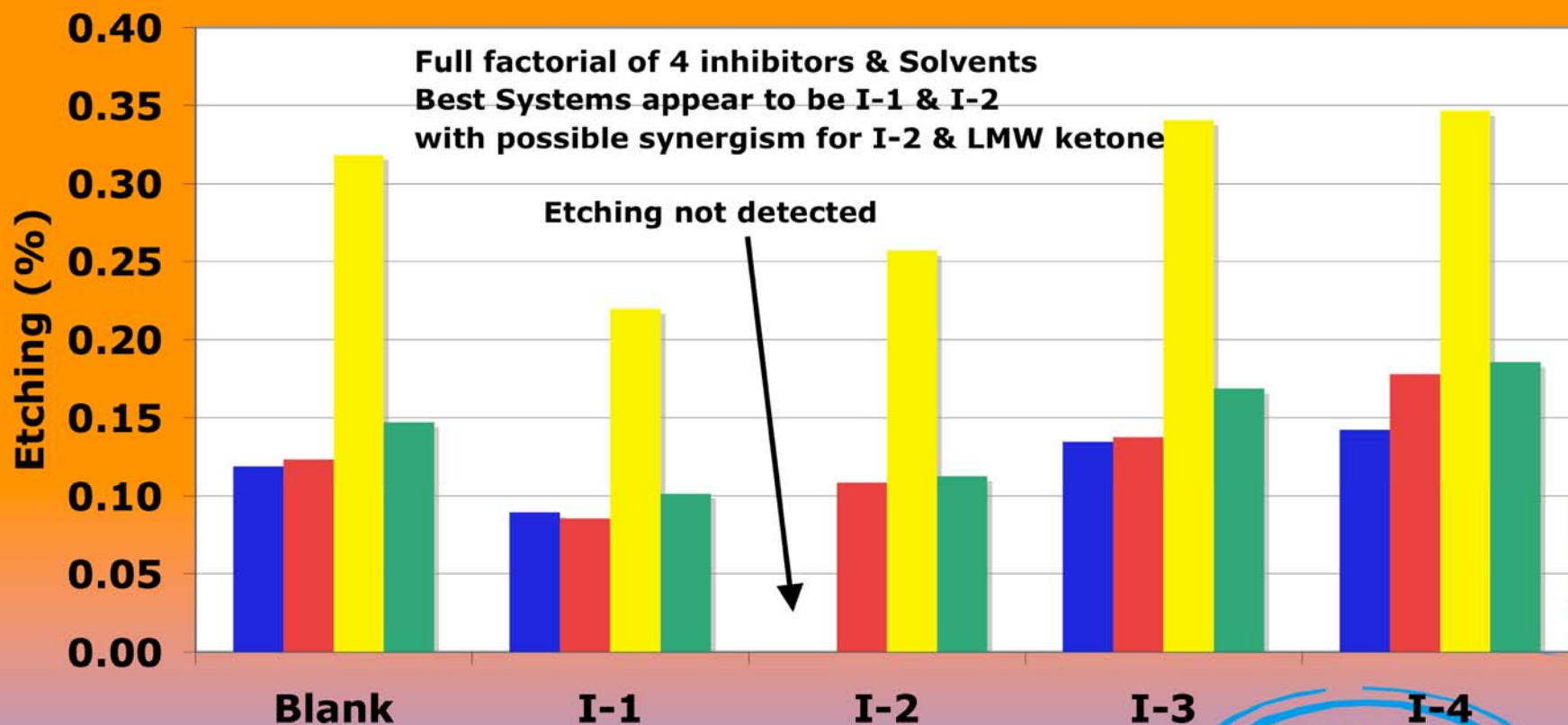


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## Tin Metal Protection In Stripper Media Choice of Solvent & Inhibitor

■ Ketone LMW ■ Ketone HMW ■ Sulfoxide ■ Amide



Inhibitors I1 - I4



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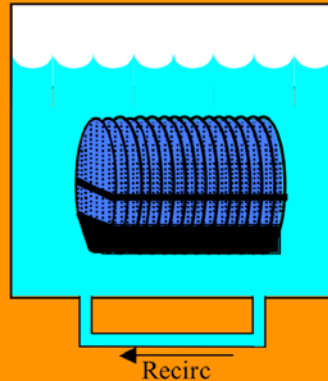


# Agenda

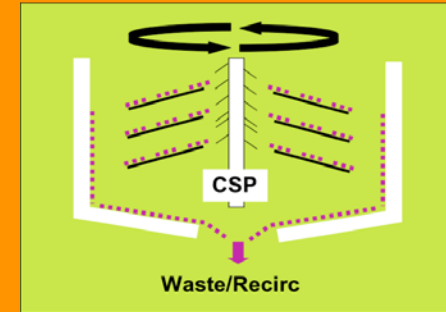
- Inhibitor Types
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# Review - Current Cleaning/Finishing

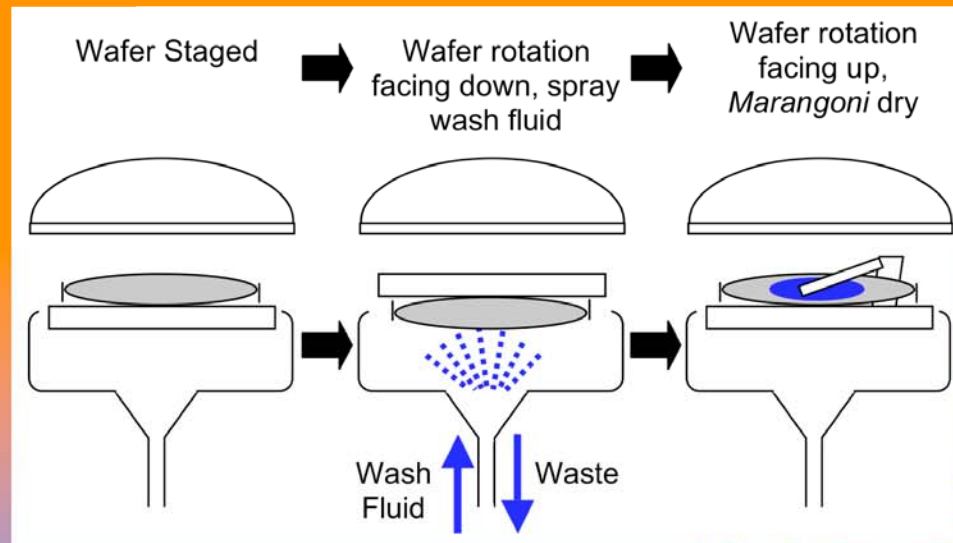
Immersion  
Removal by  
chemical  
interaction of  
the bulk fluid



Batch Spray  
Removal by  
Momentum-  
energy  
Transfer



Single Wafer  
Combination  
of spray  
principles and  
fluid control  
during drying





# In-Tool Liquid Controls

- Inhibitor designed for metal protection & rapid processing from cleans to rinsing
- Able to work in a range of chemical media for in-tool mixing
- Deliver reduced surface tension for improved wetting & rinsing
- No or low foam



# Reduced Surface Tension Processing Aids

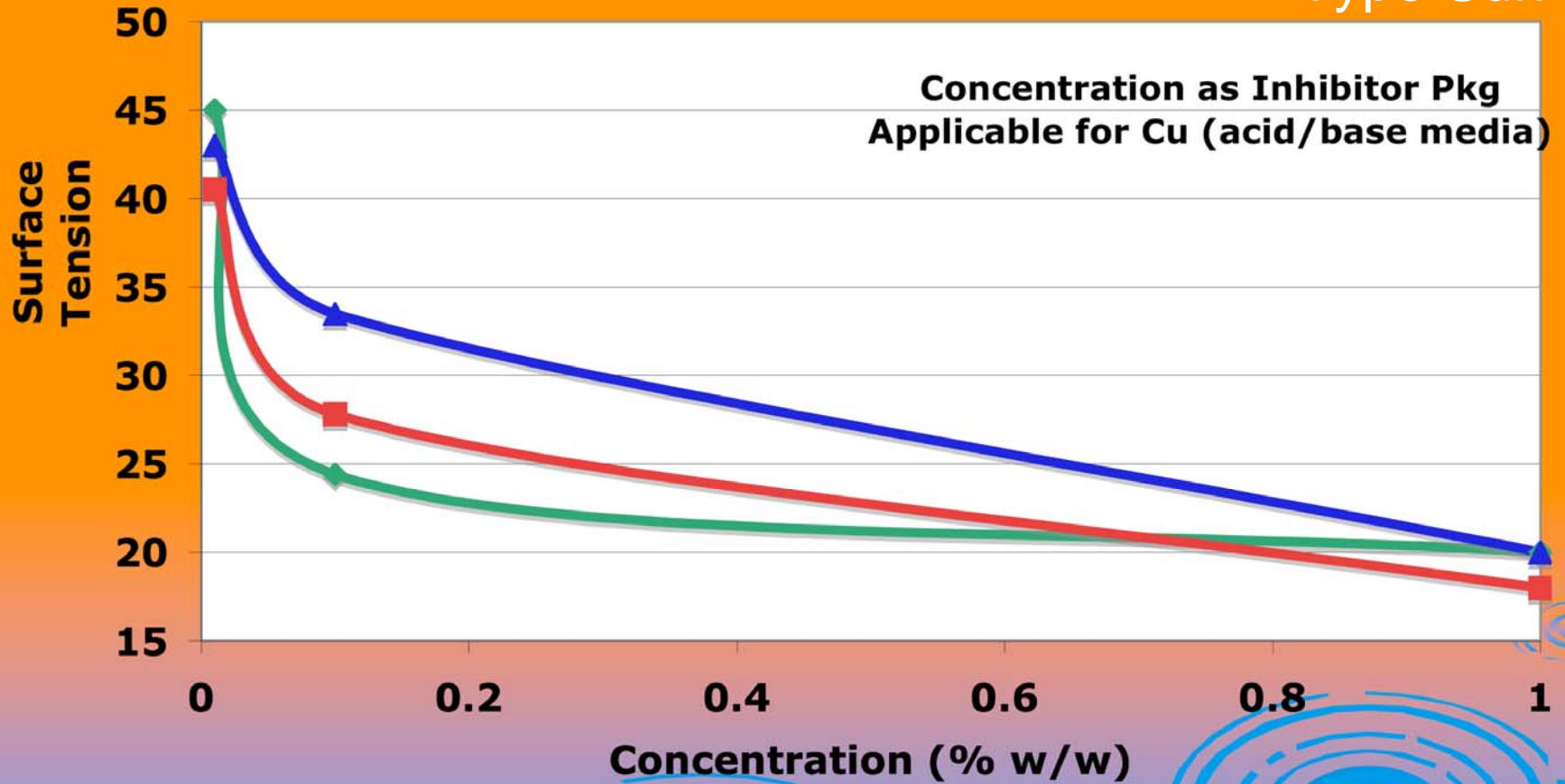
- Greater penetration to small areas
- Reduced redeposition
- Improved mixing during rinse cycle
- Low-foaming conditions

# Inhibitor Pkg for Spray Tools

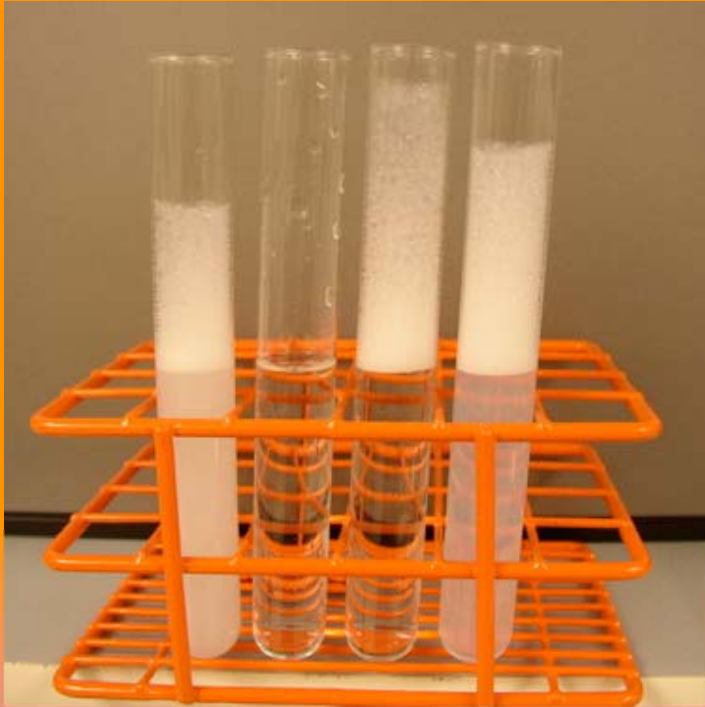
## Surface Tension vs Concentration

F +HC  
Type Surf

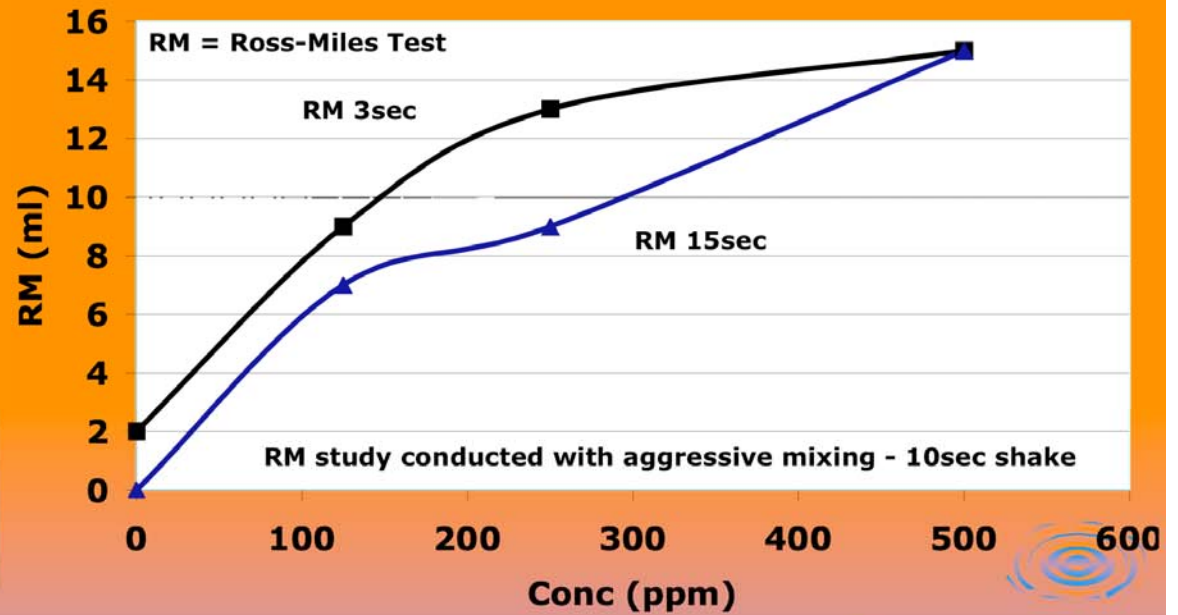
◆ A001 ■ A002 ▲ A003



# Screen for Foaming



Effects of Foaming of Surfactant  
Draves Foam Height vs Conc



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# Inhibitor Processing

- Pkg design for spray tools, immersion, etc.
- Dilute forms (I.e. most are  $\leq 1\%$ )
- Simple in-tool mixing and delivery
- Fast reaction - on contact
- Thin coating (I.e. monolayer)
- Low ST and non-foaming
- Easy water rinse





# Formulation for Processing

PR	Solvent	Active Agent	Tool	Process Issues
Novolac, FPD	BDG, DMSO	Monoethanolamine (MEA)	Conveyor/spray	Corrosion, foam, compatibility
Acrylic, bumping	DMSO	Tetramethylammonium hydroxide (TMAH)	Immersion	Corrosion, dissolution
PHost, Cu/Low-K	Sulfuric	Peroxide	Single Wafer	Corrosion
	Glycol + water	MEA	Single Wafer	Corrosion, rinsing

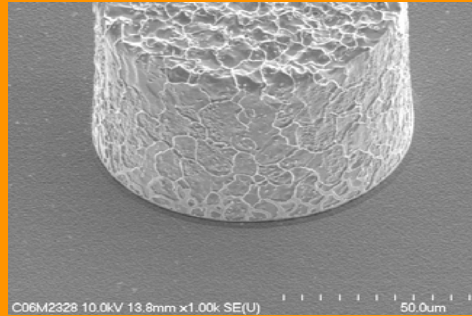
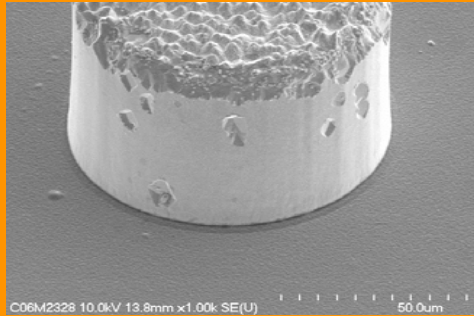
# Common Inhibitors

Metal	Stripper pH	Inhibitors*
Al	Alkali, acid	Silicate, citrate, phosphate, triazole, succinate, borate, catechol (EHS options)
Pb, Ag, Cu	Alkali, acid	Thiocyanate, triazole, EDTA, imidazole
Cu, Ti, Ta	Alkali, acid	Triazole, phosphate, citrate, resorcinol

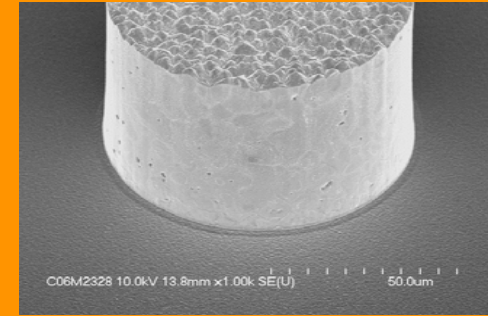
Solubility dependence on pH, organic content, salt level, and material form

# Applications - Strippers

Bumping Chemistries w/No Inhibitor



w/Inhibitor

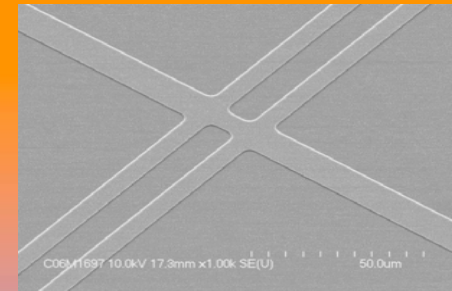


FPD Chemistries w/No Inhibitor

AI-based devices gross damage

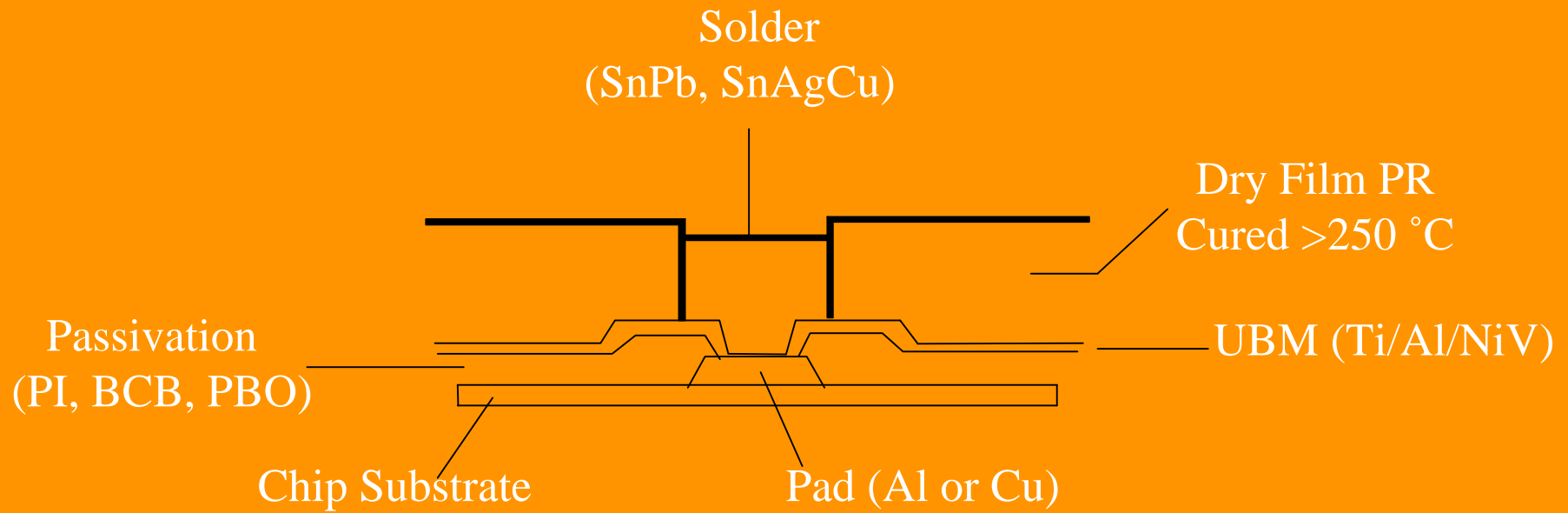


w/Inhibitor



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Mylar



Resist



Polypro



Suppliers  
DuPont Riston  
RHEM-Shipley  
Eternal  
Asahi (Sunfort)  
Hitachi

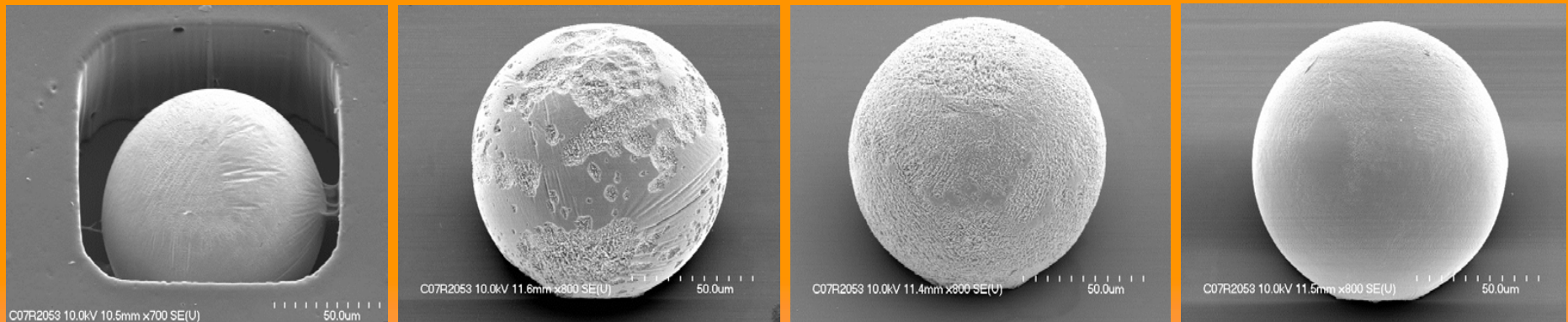


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# Strippers for FCT Bumping

Formula: Alkali  
Solvent  
Co-solvent  
Inhibitor



Ref

TMAH-H

TMAH-A

TMAH-A + I

Inhibitors: phosphates, succinates, imidazoles

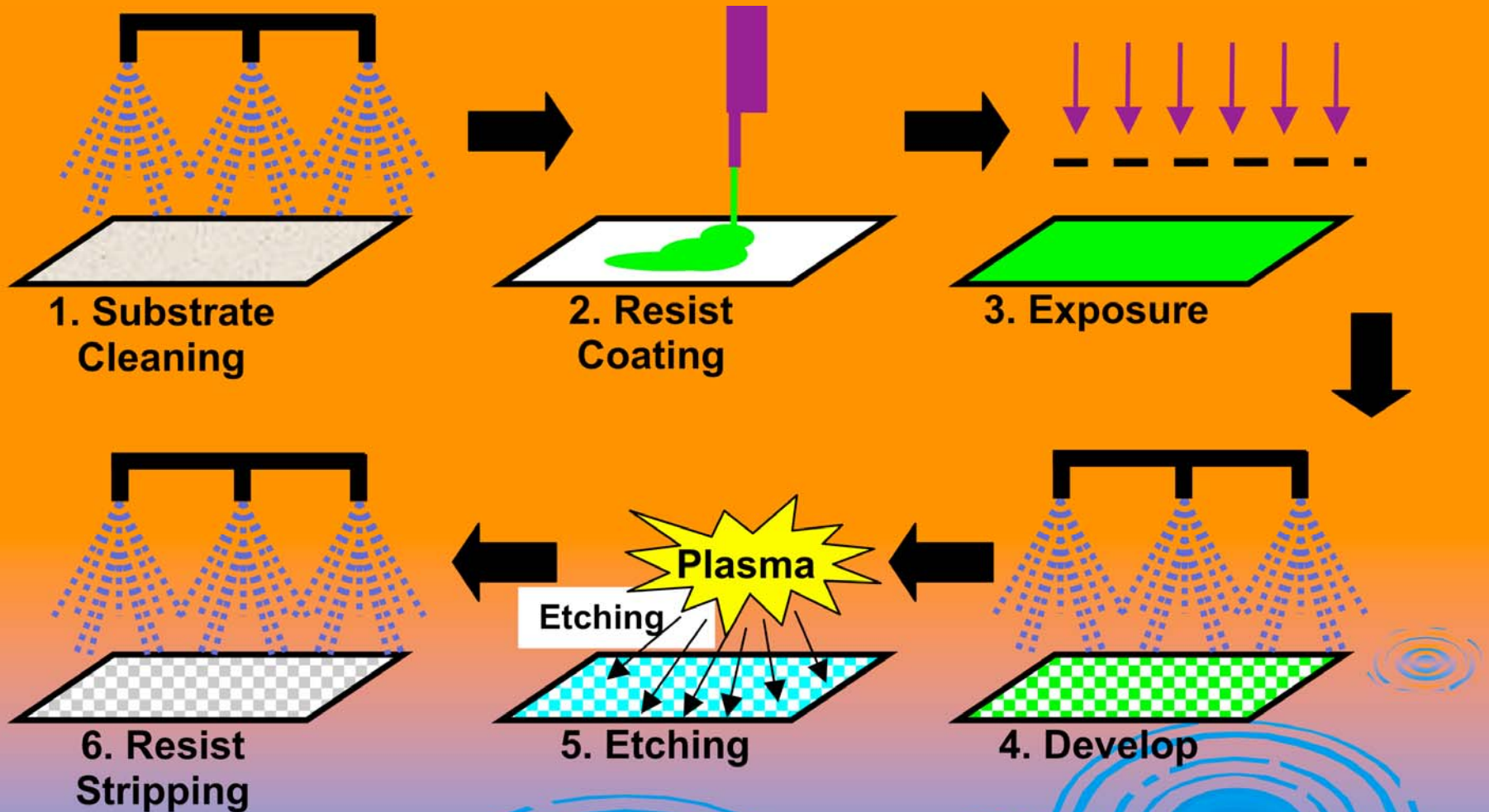


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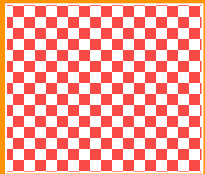
# Device Mftg Process



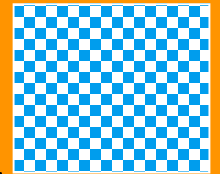


# FPD Process Strip & Rinse

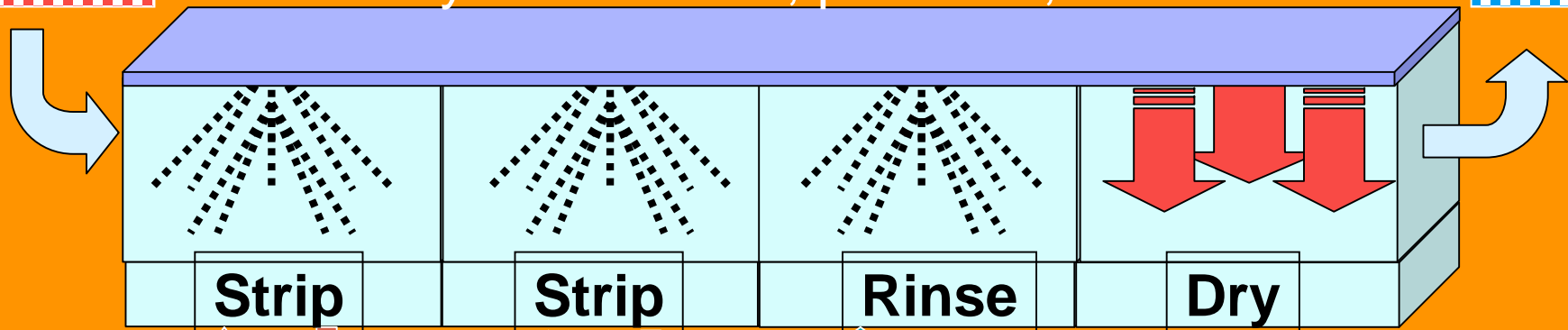
resist mask



Clean



Conveyor Tool: heat, pressure, time control



Strip

Strip

Rinse

Dry

Dirty Tank

Clean Tank

House  
DI Water

Hot N<sub>2</sub>  
Dry

On-site  
Treatment

Stripper

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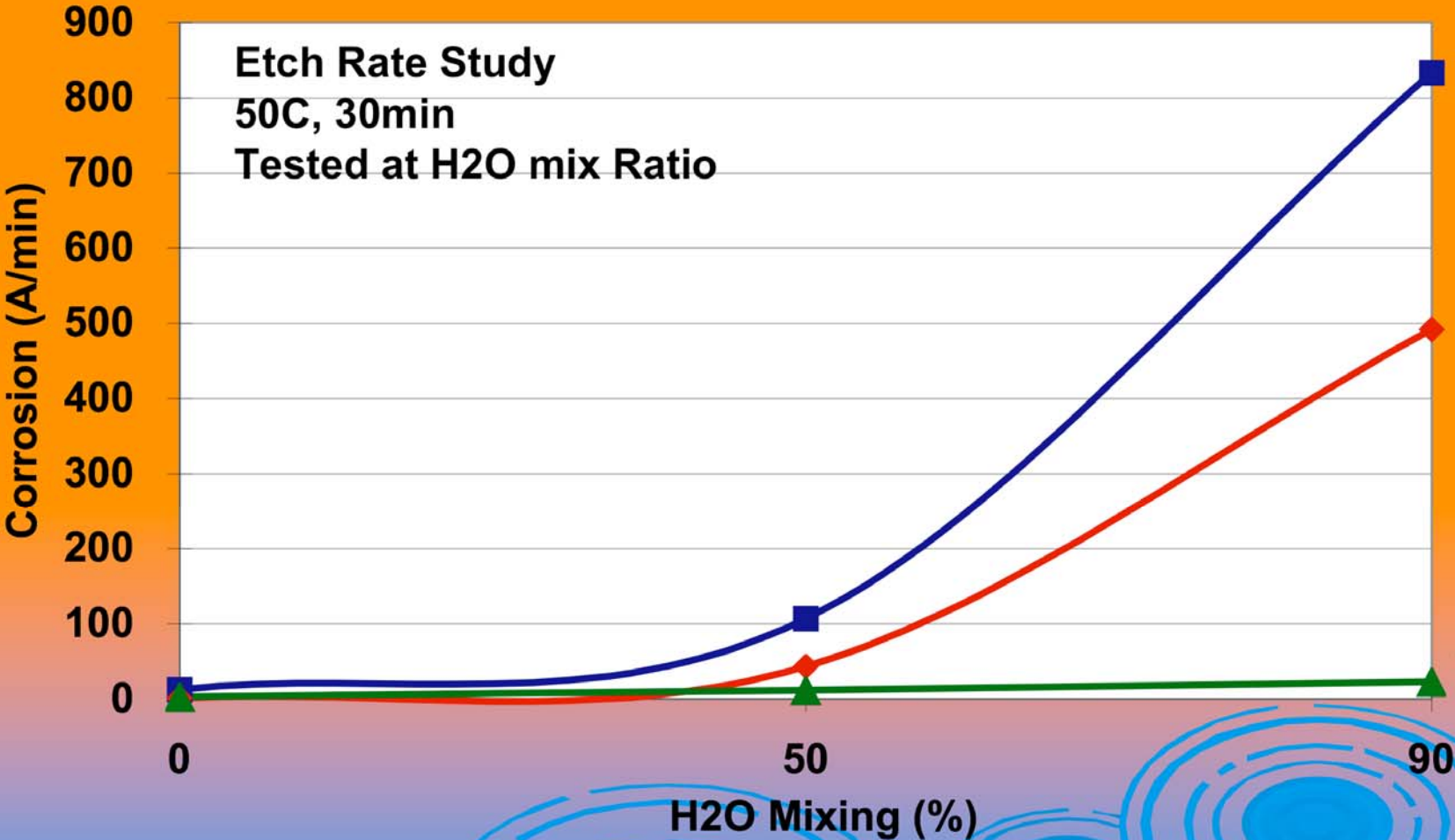
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# Demo on Alloy Blanket

Stripper	H <sub>2</sub> O 0%	H <sub>2</sub> O 10%	H <sub>2</sub> O 25%	H <sub>2</sub> O 50%	H <sub>2</sub> O 75%	H <sub>2</sub> O 90%	H <sub>2</sub> O 95%
PR Strip A	NC	NC	5min	5min	3min	2min	2min
PR Strip B	NC	NC	NC	NC	4min	3min	2min
PR Strip C Inhib.	NC	NC	NC	NC	NC	NC	NC

# Metal Etch Rate Measurement

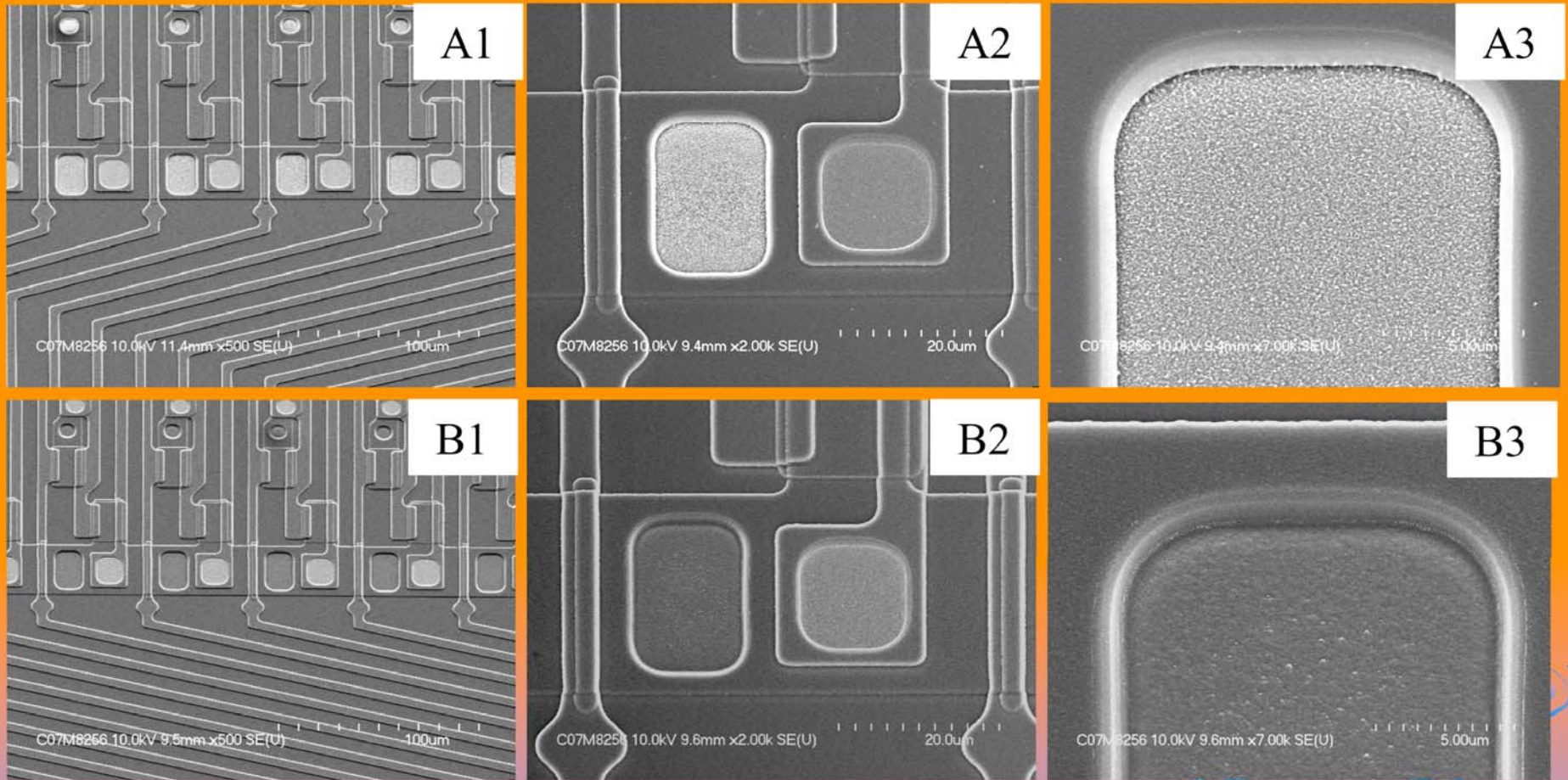
■ PR Strip A    ◆ PR Strip B    ▲ PR Strip C + Inhibitor



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# Panel Device After Process



A-series: baseline (no inhibitor), B-series: stripper + inhibitor

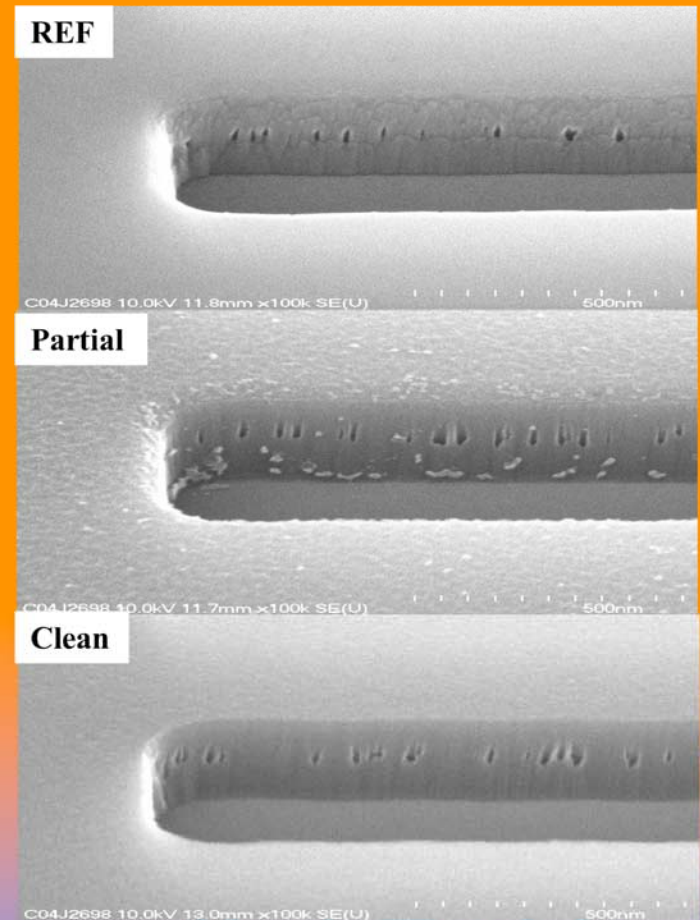
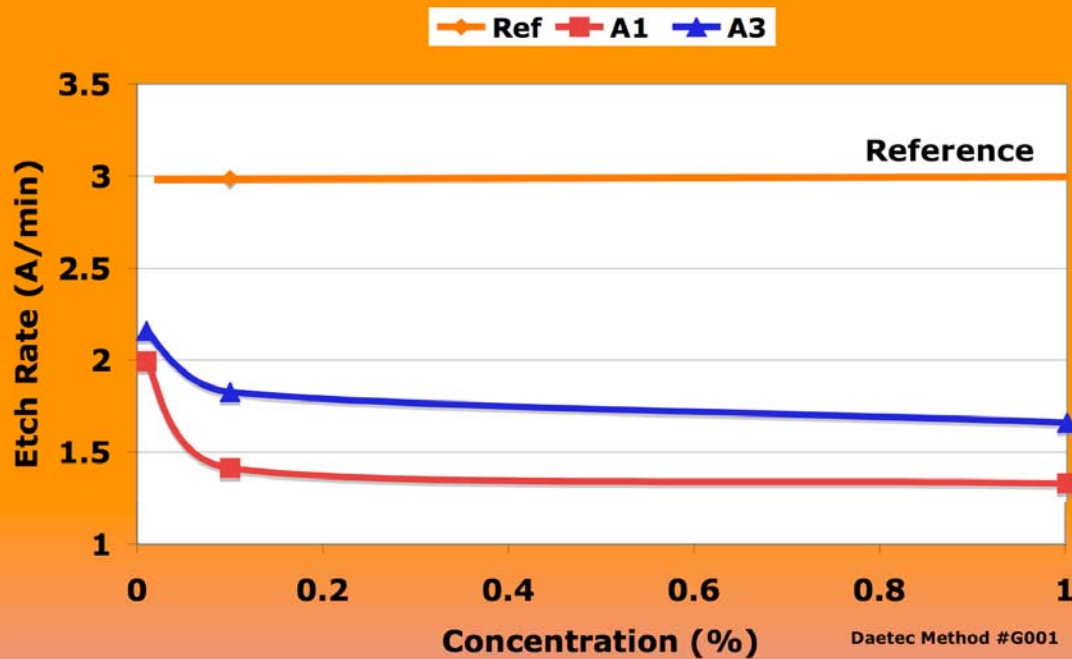


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# Cu/Low-K Residue Cleans

Cu Etch Rate in Dilute H2SO4



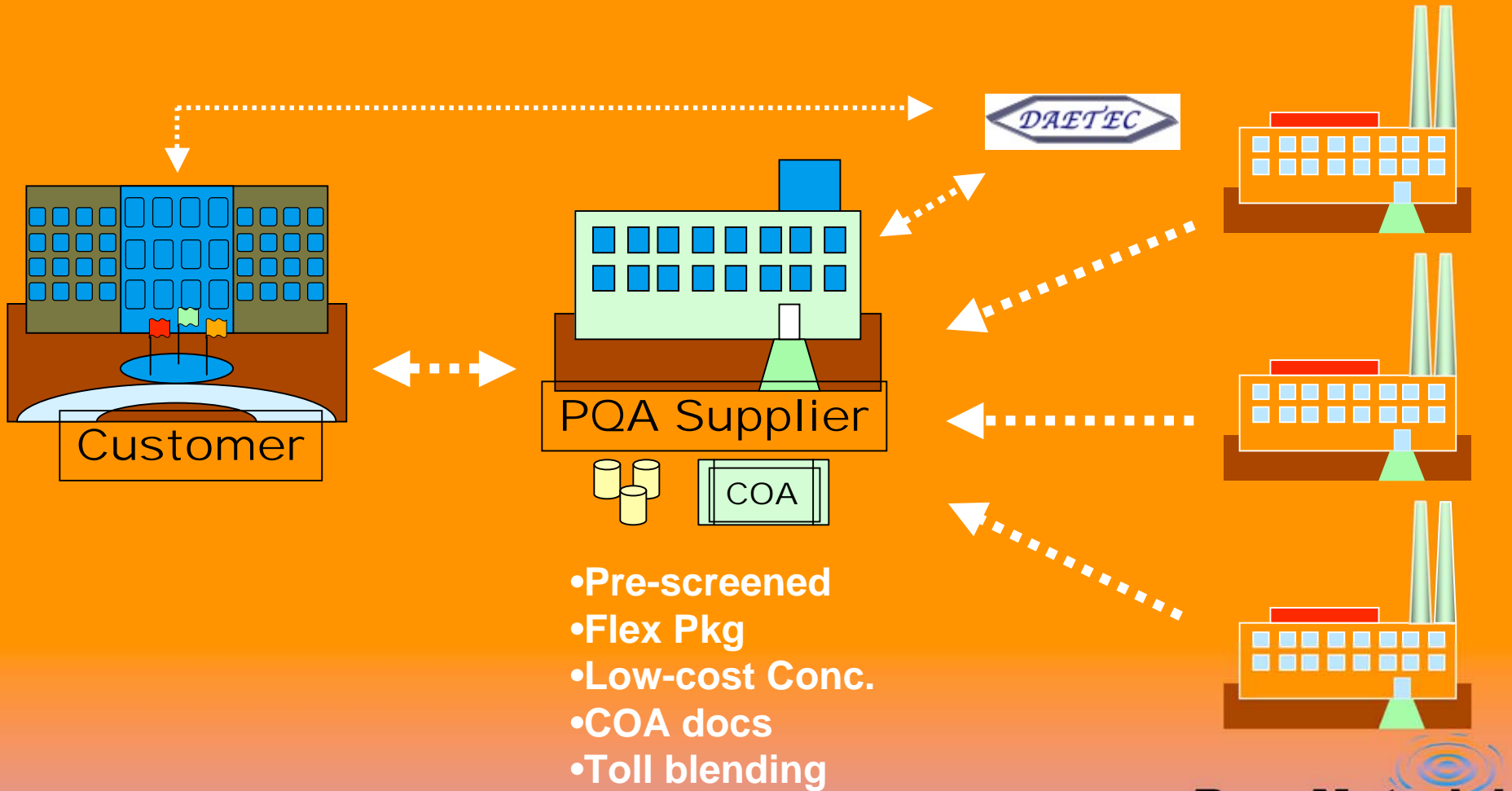


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# Chemical Industry

- \$2trn global enterprise
- 70,000 different products
- Several hundred large producers @  
@  $\geq$ \$1bn, thousands of small
- Triad locale: EU, N. America, Japan
- Not including pharma
- Many materials not included (I.e. final forms: metals, polymers, detergents)



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# Pre-Qualified Agents (PQA)

- Tested for performance - key benefits expected;
- Tested for media compatibility - limitations on pH, solubility, etc.;
- Tested for process integration - suggested use rates, properties per the industry, example formulary;
- Available in concentrate - low cost;
- Single source, ISO certified, flexible pkg.

# Pre-Qualified Agents (PQA)

- Formulators - reduces test requirements, accelerates new product development;
- Tool Companies - facilitates in-tool mixing, accelerates process development and new tool designs;
- End Users (Fabs) - allows feasibility and R&D on integration challenges for next generation devices.



# PQA Product Listing

- GaAs-safe solvents & amines
- Cu-safe amines
- Inhibitors for Cu, Al, and other metals
- Alkali agents, high TMAH content
- Surfactants for low ST and emulsification
- Viscosity modifiers (gels)
- Polymers - Coatings, HT applications
- Polymers - Coatings, aqueous wash applications & HT
- Polymers - Adhesives for wafer thinning
- Carrier solvents for coatings - high dep & low TTV

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# Summary

- Various inhibitors exist, chemisorption types may be preferred;
- Inhibitor pkg must be optimized for the media, sometimes aggressive chemistry, to ensure maximum activity, low residue, easy rinsing, etc.
- Pre-Qualified Agents available to accelerate product development;
- DAETEC offers development and technical support in a variety of business models

# Contact for More Information

- Pre-Qualified Agents for new product development:

DAETEC (805) 484-5546

[info@daetec.com](mailto:info@daetec.com) [www.DAETEC.com](http://www.DAETEC.com)

Applications include: etch residue, hard baked, & thick resist removal, high temp protective coatings, aqueous washable coatings, polymers for 3D-Pkg and wafer thinning.



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