



# Indium8.9HF Halogen-Free Solder Paste

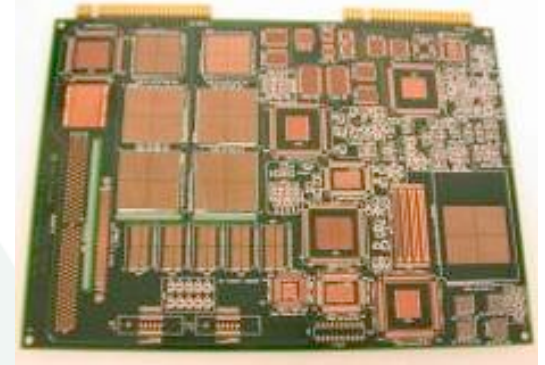
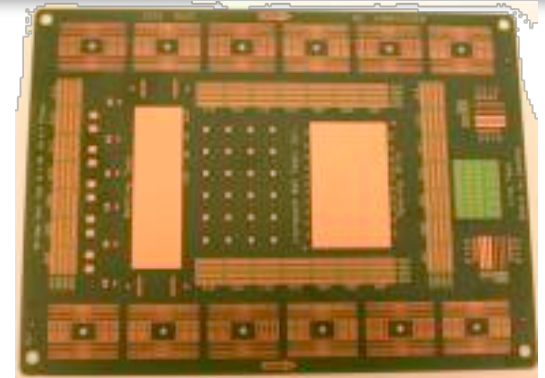
# Technology Drivers

- High reliability
  - Server, telecommunication, automotive
- Miniaturization
  - Multi-Functionality
    - PDA, Cell Phone, IPOD
  - Board Real Estate is a Premium
  - Components Continue to “Shrink”
- High Density on Large Boards
  - 0201 on Servers
  - CSP on Motherboards



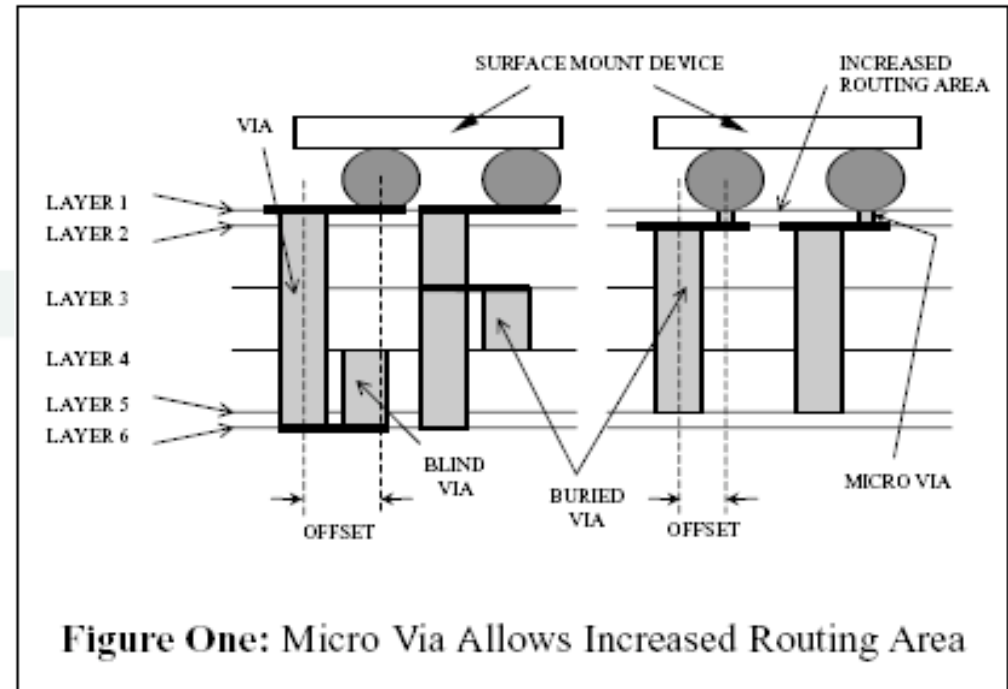
# Materials & Applications Development Primary Goals

- Full Product Characterization
  - Prior to Release
- Shared Projects & Test Vehicles
- Joint Projects with Industry Leaders
- Research & Development
  - Assist in Product Characterization
  - New Product Design Challenges
- Quality Assurance
  - Testing Methods & Criteria
- ***Verify Indium Materials exceed Industry & Customer Requirements!***



# New Solder Paste Technology Performance Requirements

- Printability
  - Area Ratio's below 0.66
  - High Slump Resistance
- Voiding
  - Micro Via-in-Pad
  - BGA
  - QFN (leadless)
- Wetting
  - Pb-Free Finishes
  - R-Nets & QFN's
  - Long Air Profiles
- Residue
  - Halogen-Free
  - Color
  - Probe-ability



# Halogen-Free vs. Halide-Free

## Halogen-Free

- It does not contain Cl, Br, F, I, At (although most just looking at Cl and Br)
- Concern is Environmental
  - Uncontrolled incineration
  - Dioxin formation
- No legislation around halogen elimination
- Flame Retardants
- Issues:
  - Do the halogen free PCB's impact end product reliability?

## Halide-Free

- Should be halide ion free as it is defined in electronics as not containing ionic halides.
- Concern is Reliability
  - Corrosion
  - Dendritic Growth
- Activators in flux
- Issues:
  - Is halide free actually more reliable than halide contained?
  - How do you test fluxes for halide content?

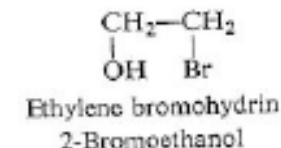
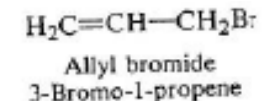
# Ionic vs. Covalent Halides

- Ionic halide bonds are typically easily broken; creates free halide to react with moisture to cause corrosion at room temperature
- Covalently bonded halides are much more stable at room temperature; bonds not easily broken
  - At elevated temperatures (such as solder temps) the covalent bonds are broken and halide can react with oxide

**Some Ionically Bonded Halides**

Name	Structure	Melting point (°C)
Dimethylamine hydrochloride	$(\text{CH}_3)_2\text{NH}\cdot\text{HCl}$	170
Diethylamine hydrochloride	$(\text{C}_2\text{H}_5)_2\text{NH}\cdot\text{HCl}$	227
Diethylamine hydrobromide	$(\text{C}_2\text{H}_5)_2\text{NH}\cdot\text{HBr}$	218
Aniline hydrochloride	$\text{C}_6\text{H}_5\text{NH}_2\cdot\text{HCl}$	196
Pyridine hydrobromide	$\text{C}_5\text{H}_5\text{N}\cdot\text{HBr}$	200d
Pyridine hydrochloride	$\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$	145
Ethanolamine hydrochloride	$\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}\cdot\text{HCl}$	84
Diethanolamine hydrochloride	$(\text{HOCH}_2\text{CH}_2)_2\text{NH}\cdot\text{HCl}$	liquid
Triethanolamine hydrochloride	$(\text{HOCH}_2\text{CH}_2)_3\text{N}\cdot\text{HCl}$	177

**Some Covalently Bonded Halides**



Ref: Lee, NC; *Reflow Soldering Processes and Troubleshooting: SMT, BGA, and Flip Chip Technologies*; 2004

# Testing For Halogen Content

- Silver Chromate Paper Test (qualitative)
  - Changes color in the presence of  $\text{Cl}^-$  or  $\text{Br}^-$
  - Does not detect Covalently bonded halides
- Titration (quantitative)
  - Solution titrated to endpoint and  $\text{Cl}^-$  equivalent is calculated
  - Only detects ionic halides and many chemicals can cause false positive results
- Ion Chromatography (quantitative)
  - Separation of ions and polar chemicals to quantify the amount of halides in a flux
  - Only detects ionic halides and many chemicals can cause false positive results
- Oxygen Bomb + Ion Chromatography
  - Flux is burned at high temperature breaking covalent bonds, volatilizing organics and leaving behind only halide and inorganics in the ash
  - Ion chromatography is run on the ash providing a “true” identification of halide content.

# Indium8.9HF Halogen Summary

- Silver Chromate Paper Test (qualitative)
  - Changes color in the presence of  $\text{Cl}^-$  or  $\text{Br}^-$
  - Does not detect Covalently bonded halides
  - **Indium8.9HF: PASS**
- Ion Chromatography (quantitative)
  - Separation of ions and polar chemicals to quantify the amount of halides in a flux
  - Only detects ionic halides and many chemicals can cause false positive results
  - **Indium8.9HF: PASS**
- Oxygen Bomb + Ion Chromatography
  - Flux is burned at high temperature breaking covalent bonds, volatilizing organics and leaving behind only halide and inorganics in the ash
  - Ion chromatography is run on the ash providing a “true” identification of halide content.
  - **Indium8.9HF RAW FLUX: PASS**
  - **Indium8.9HF FLUX RESIDUE: PASS**



# Indium 8.9HF: 3<sup>rd</sup> Party Oxygen Bomb Testing



TEST REPORT  
THE REPORTED TEST RESULTS RELATE  
ONLY TO THE ITEM(S) TESTED



NSL Lab No: 0821541

Sample ID: 8.9HF(F)

Tests	Results/Units	Methods
Br	<0.001%	Parr Bomb followed by Ion Chromatography
Cl	<0.001%	Parr Bomb followed by Ion Chromatography
F	<0.001%	Parr Bomb followed by Ion Chromatography

NSL Lab No: 0821542

Sample ID: 8.9HF(FR)

Tests	Results/Units	Methods
Br	<0.001%	Parr Bomb followed by Ion Chromatography
Cl	<0.001%	Parr Bomb followed by Ion Chromatography
F	<0.001%	Parr Bomb followed by Ion Chromatography

**Legend**

- (F) Signifies Raw Flux
- (FR) Signifies Flux Residue

Reporting Officer: 

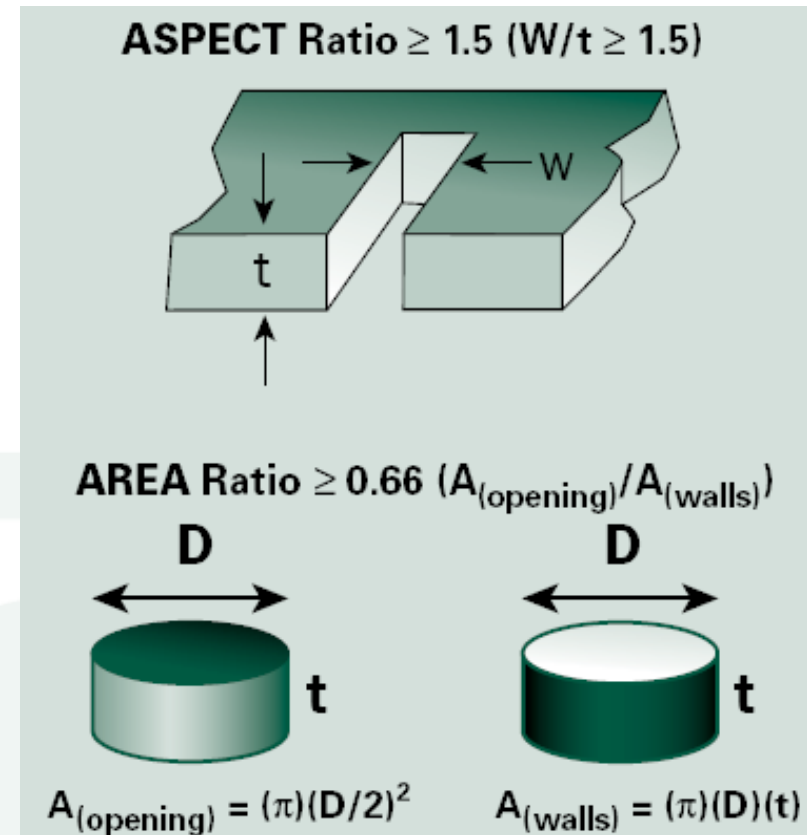
781

Cami D'Agostino, Wet Chem  
Supervisor

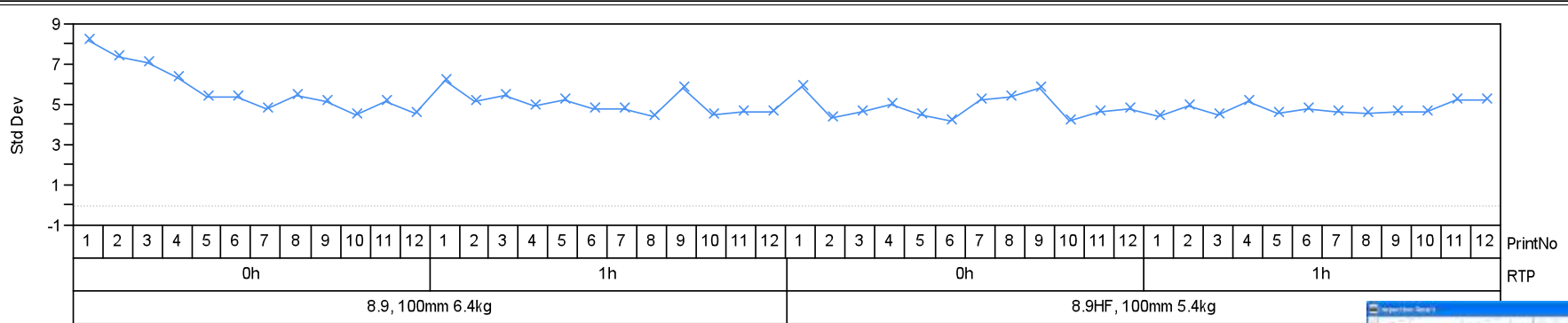
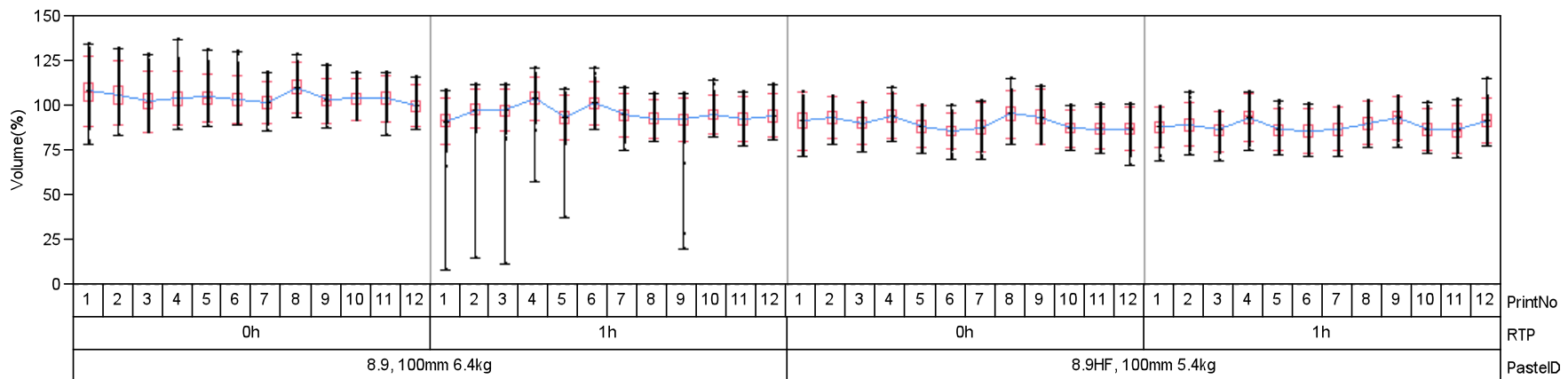


# Validation of Printability: Response to Pause

- Powder Sizes
  - Type 3
  - Type 4
- Stencil
  - 5 mil thickness
  - Laser-cut
  - No electropolish
- Aperture Pattern
  - Mask design pads (SMD)
  - Area Ratio
    - A.R. = 0.80 [16 mil circle (C16)]
    - A.R. = 0.60 [12 mil circle (C12)]
    - A.R. = 0.50 [10 mil circle (C10)]
- Motorola RTP
  - ZeroHr; OneHr; TwoHr; FourHr

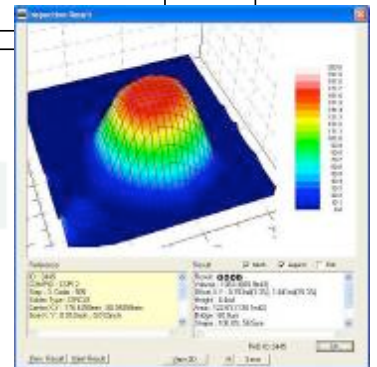


# Indium8.9HF: Transfer Efficiency vs. Indium8.9

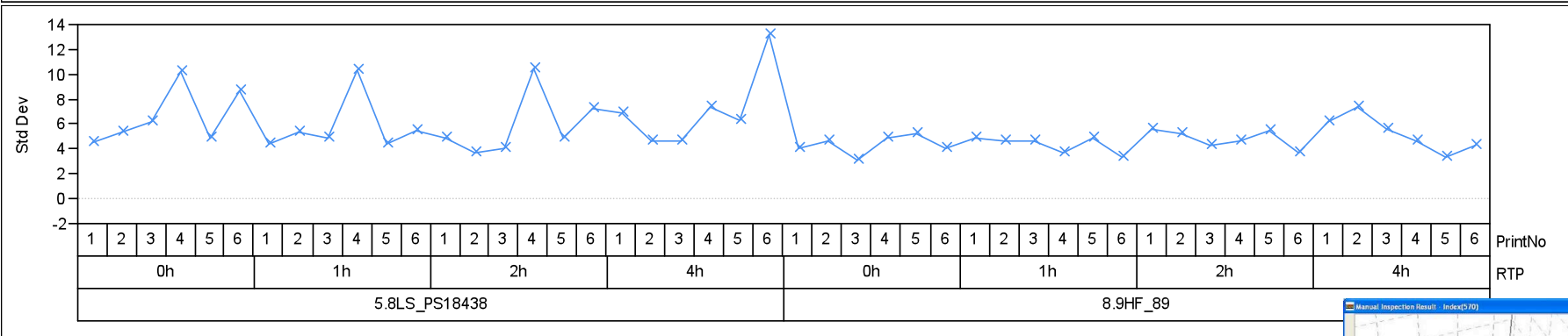
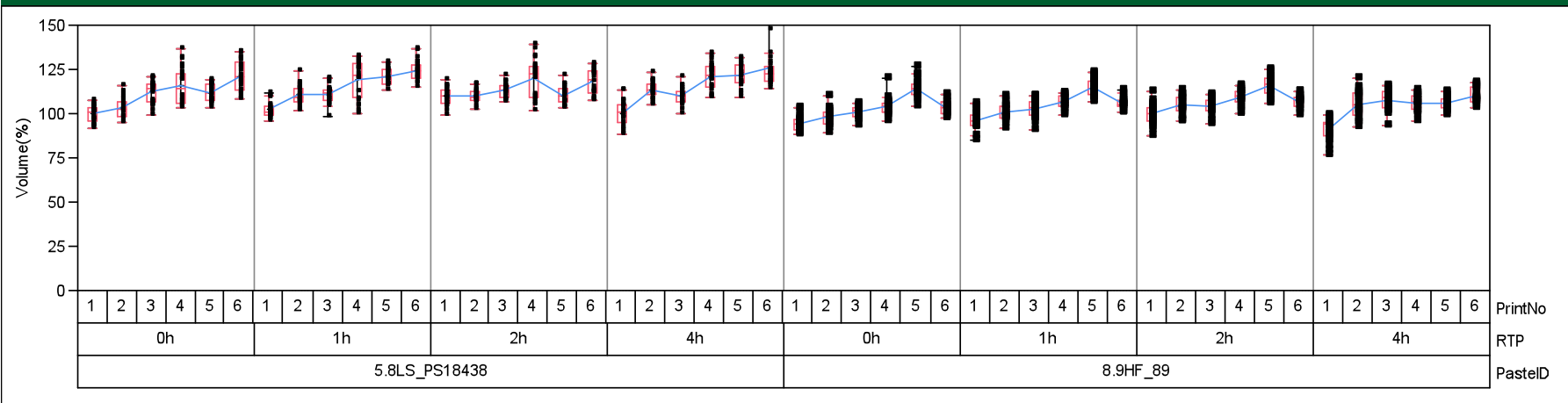


**Test Details:** 12mil round CSP deposit analyzed; 5-mil laser cut stencil

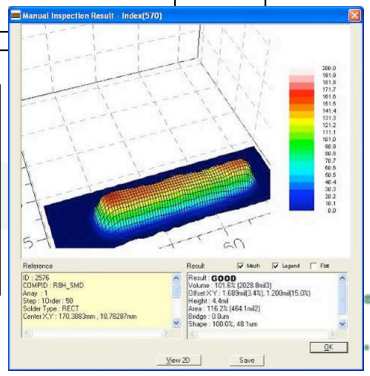
**Procedure:** Print 12 boards; pause 1-hour; print 12 boards



# Indium8.9HF: Transfer Efficiency vs. Indium5.8LS



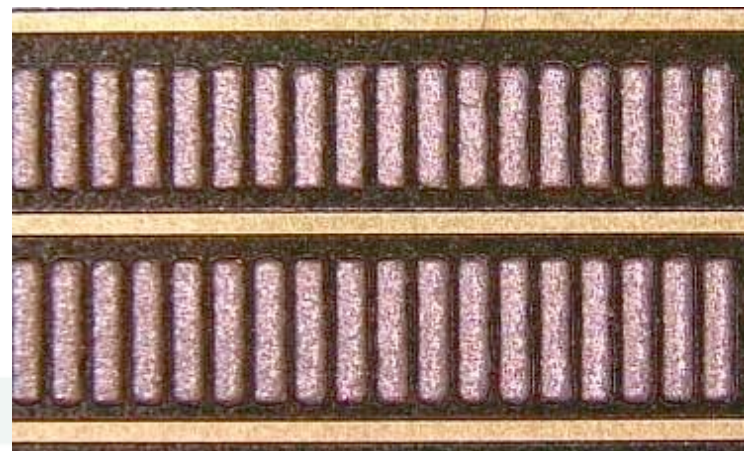
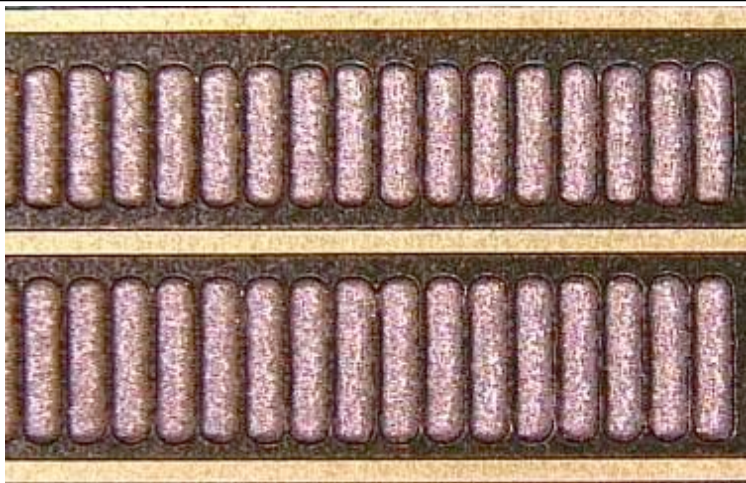
**Test Details:** 8x50-mil rectangle deposit analyzed; 5-mil laser cut stencil  
**Procedure:** Print 6; pause 1-hour; print 6; pause 1-hour; print 6; pause 2-hours; print 6



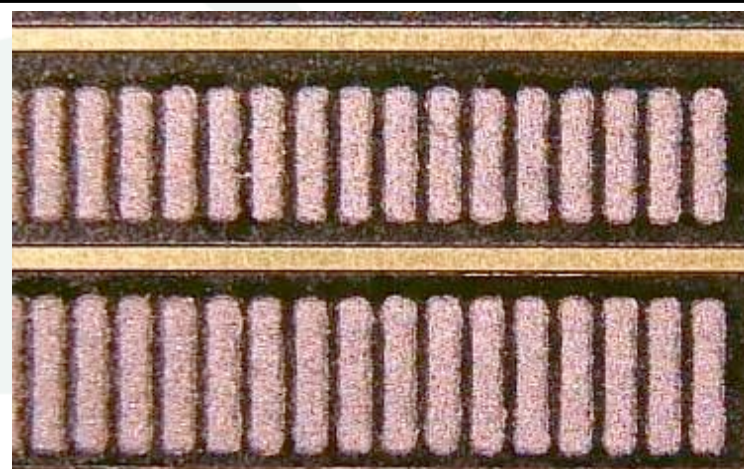
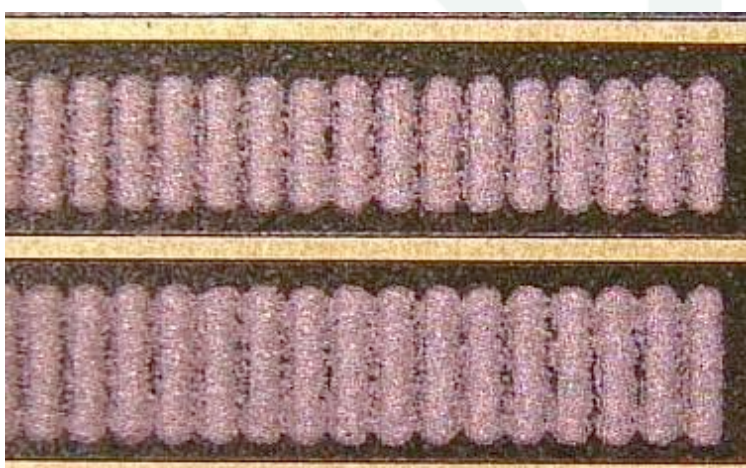
# Indium8.9HF: No Slumping

## Typical Paste

## Indium8.9HF

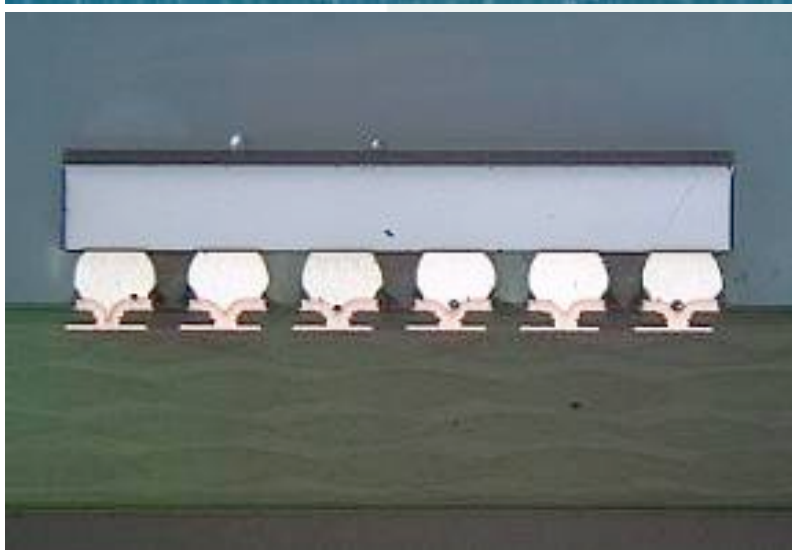
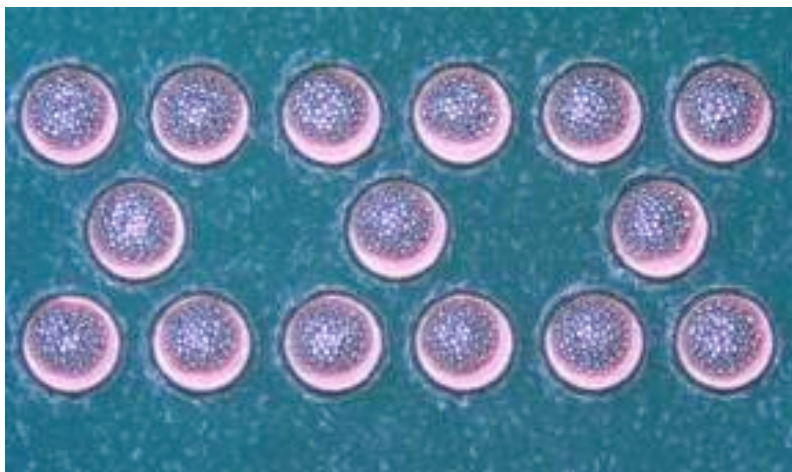


**Fresh**



**Hot Slump  
180 C**

# Indium8.9HF: Ultra-Low Via-in-Pad Voiding

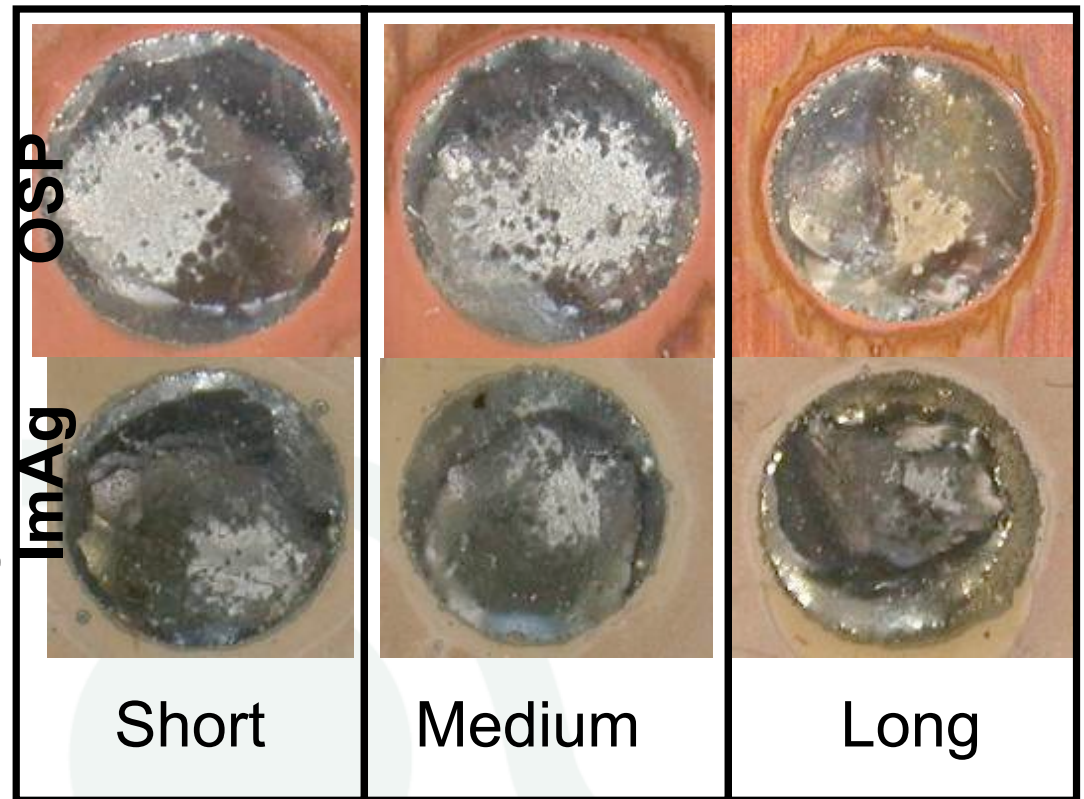
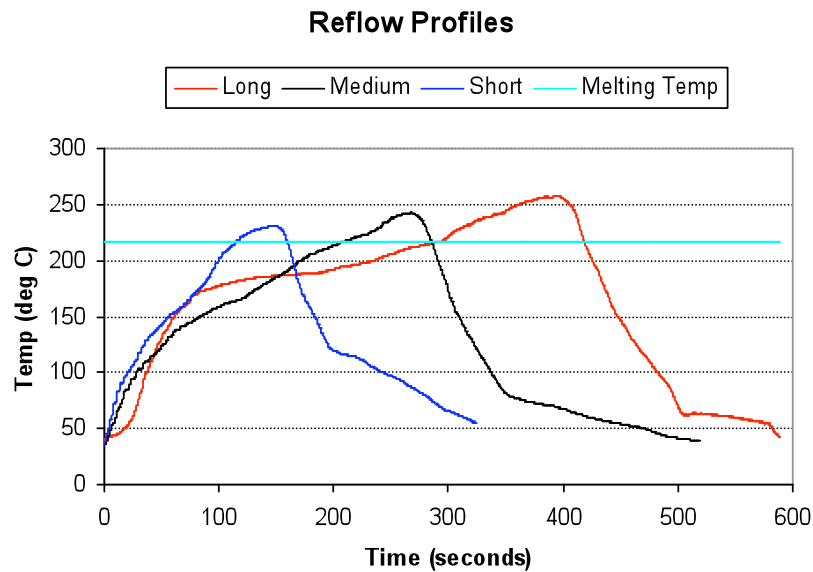


Peak Temperature	Time Above Liquidus		
	60Sec.	70Sec.	80Sec.
229C	P1	P4	P7
237C	P2	P5	P8
245C	P3	P6	P9

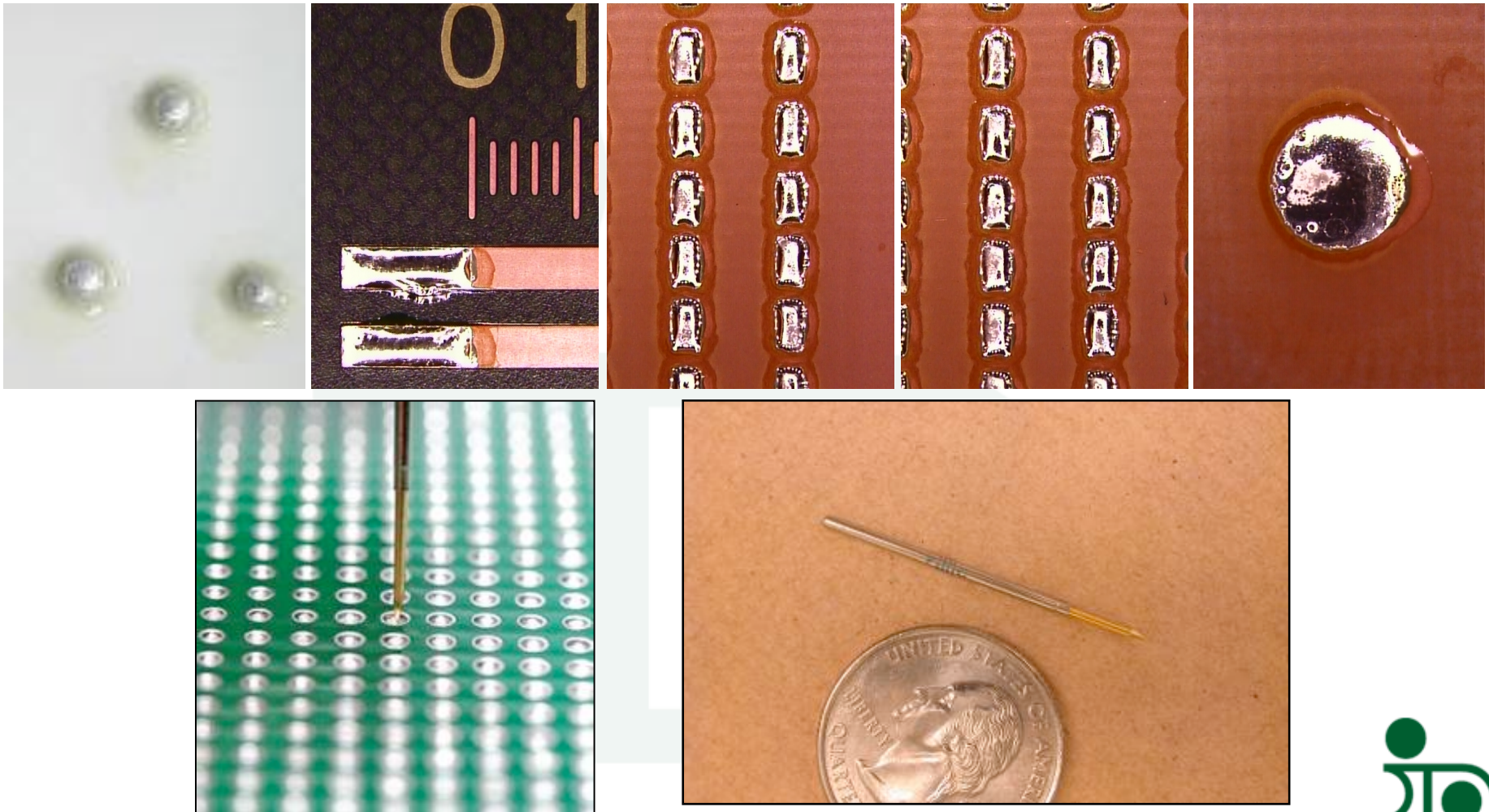
- Profiles P1, P5, and P9 targeted
- 4-mil microvia on a 12-mil Entek 106A OSP (11 mil aperture)

**Indium8.9HF solder paste exhibits less than 10% voiding across all profiles.**

# Indium8.9HF: Wide Profile Window

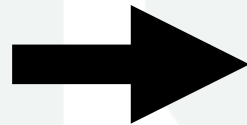
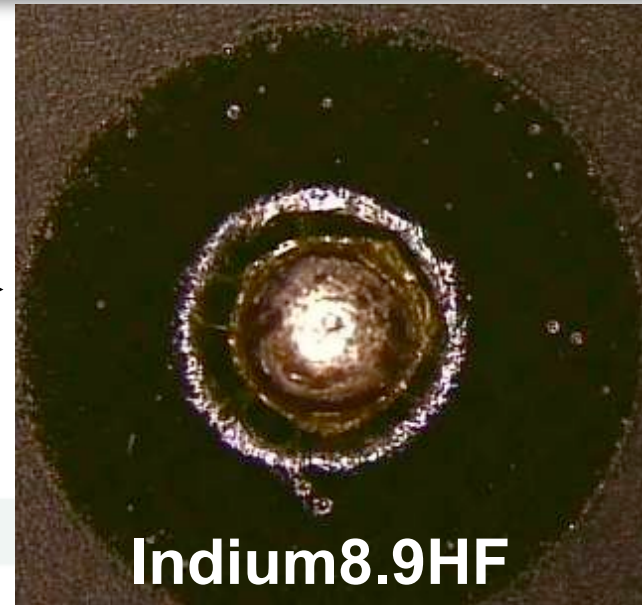
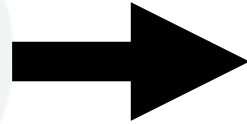
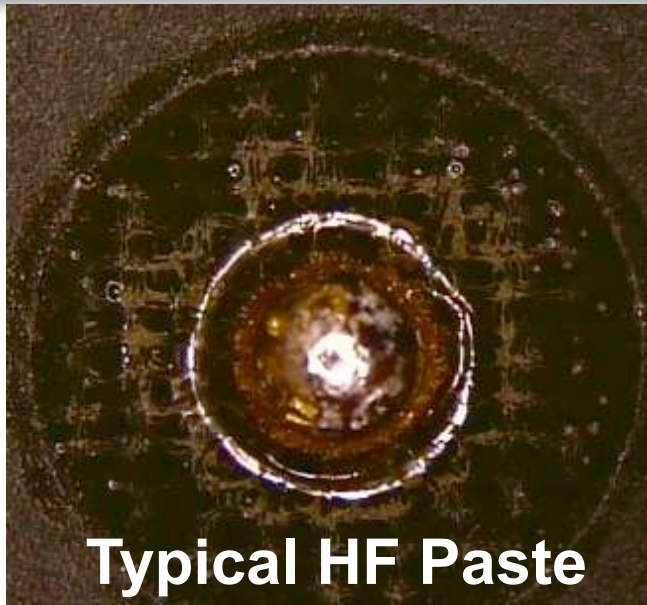


# Indium8.9HF: Clear, Pin Testable Residue

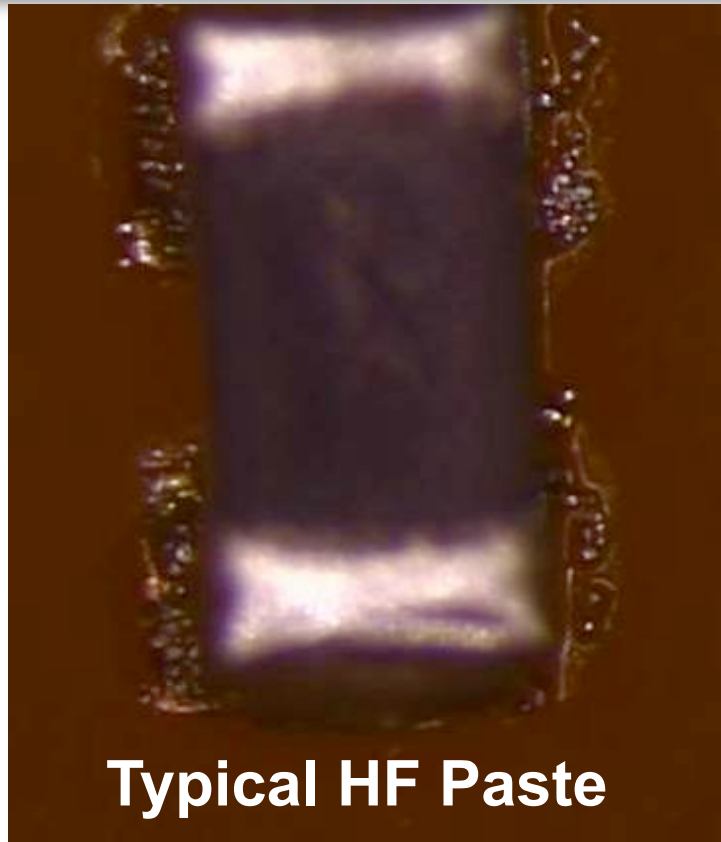




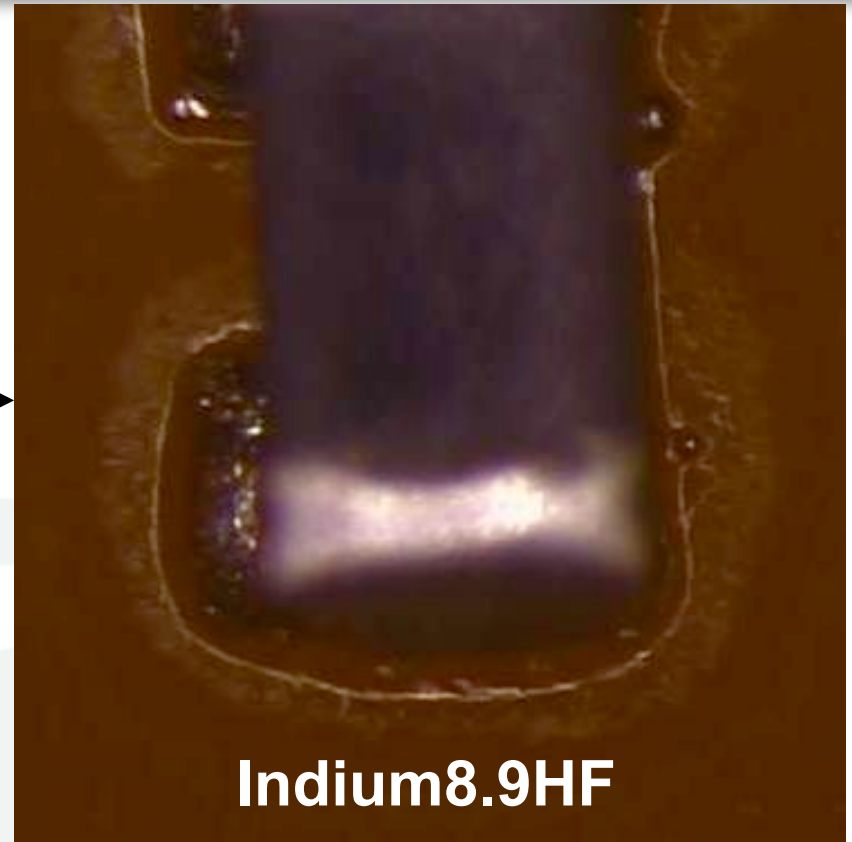
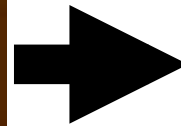
# Indium8.9HF: Wetting & Solder Balling



# Indium8.9HF: Harsh Profile Graping Improvement



Typical HF Paste



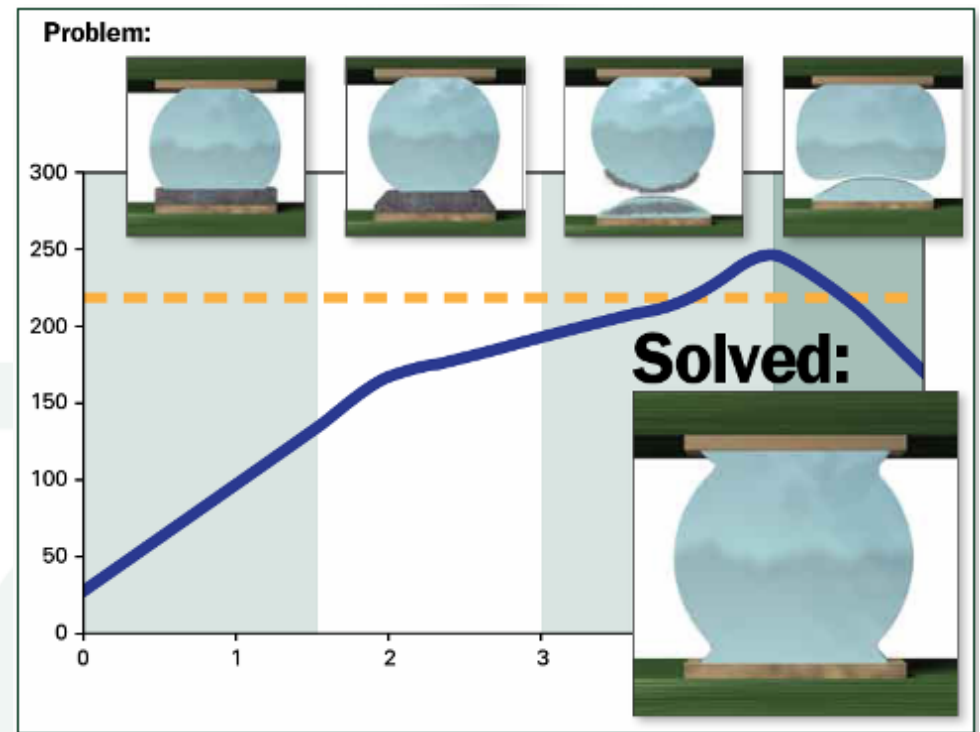
Indium8.9HF



# Indium8.9HF: Head-in-Pillow (HIP) Reduction

## Test Procedure

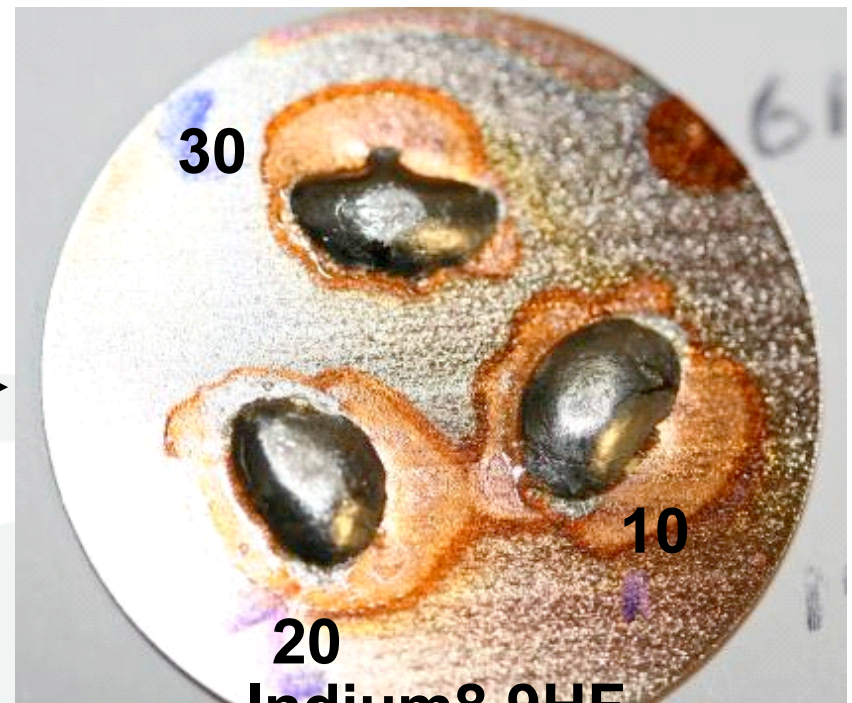
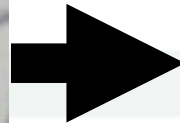
- Print paste onto Cu coupon
- Reflow paste on hot plate
- Drop sphere into molten solder at **10** second intervals beginning **10** seconds after going molten



# Indium8.9HF: HIP Reduction



Typical HF Paste



Indium8.9HF



# Discussion

