### HARIMA CHEMICALS, INC. www.harima.co.jp/en





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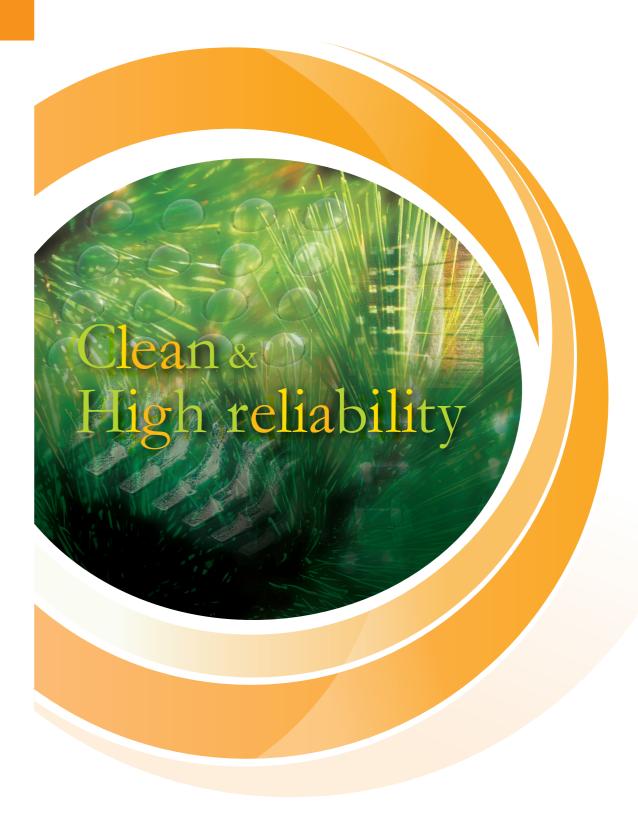
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### HARIMA CHEMICALS, INC.

Concept & Electronic Materials

# Solution Contents



Solder paste for automobile P10

Fine pitch printing solder paste

for automobile P11

Copper paste for through-hole P24

Electronic control unit(ECU)
Advanced driver assistance system(ADAS)
Vehicle-mounted camera and censor
Mechanically/electrically-integrated device

Highly durable solder paste P8-9

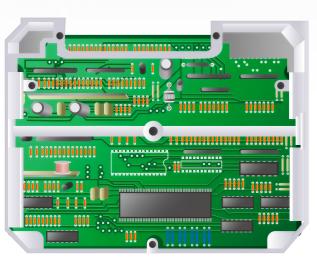
Solder paste for automobile P10

Fine pitch printing solder paste for automobile P11

 Residue crack resistance halogen free solder paste

P12

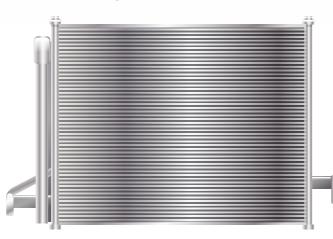
Clean type solder pasteP13





### Condenser, evaporator

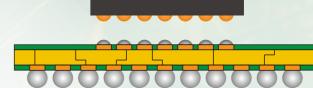
Brazing MaterialsP21-23



### LED Lamp

Highly durable solder paste P8-9

High thermal conductive paste P26



### **Semiconductor mounting board**

Solder paste for electronic packaging application P19



### **Surface mounting board**

Halogen free solder pasteP14-15

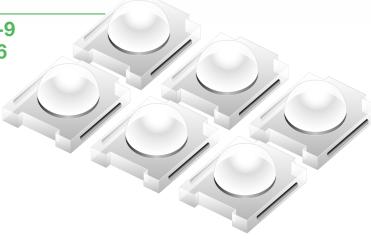
Low-silver lead-free solder paste P16

• 0201 chip compatible solder paste P17

Sn-3.0Ag-0.5Cu lead-free solder paste P18

Copper paste for electronic parts electrode P25

High Adhesive Nano Paste®
 P27



### Global Network

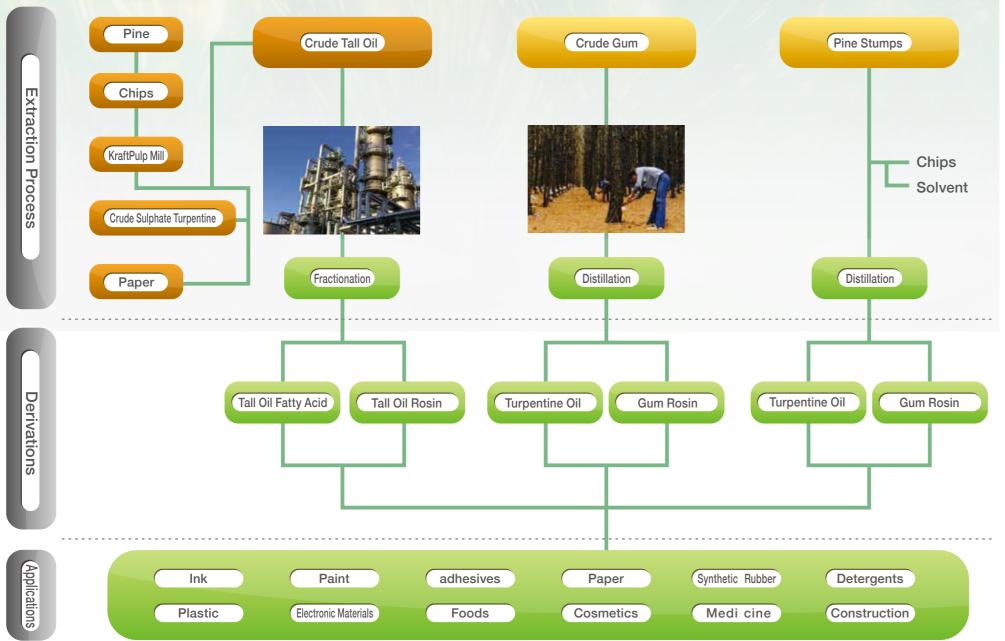
### Harima Chemicals Group's Network Meeting Global Customer Needs



# Clean & High reliability

Lead-edge through Environment Friendly

"Clean and High reliability" is Harima Chemicals' Philosophy to pursue the leading-edge technology in harmony with the natural environment.



### **Contents**

### Solder Paste

	8
High joint reliability Lead-free solder paste, having excellent joint strength and durability after 3,000 thermal cycles test.	
Solder paste for automobile GSP	
Newly developed 'GSP' achieved all required features of in-car electronics standards, such as high reliability, good ability of soldering and excellent capability of operating.	
Fine pitch printing solder paste for automobile CLR	
'CLR' realized high speed and fine-pitch printability, in addition to the required reliability for auto-	mobi
Residue crack resistance halogen free solder paste HC	•
Residue crack resistance using flexible synthetic resin, having excellent solder wetting without have	aloger
Clean type solder paste VHICS	
Having the long-time use results and superior washing characteristics, solder past washing type with a few voids for junction.	e of
Halogen free solder paste NH	14-
Environment-friendly halogen free solder paste, reducing voids and achieving highly reliable sold	er joir
Low-silver lead-free solder paste HLS	
Low silver type solder paste which balanced with high reliability and low cost.	
0201 chip compatible solder paste FC	
Newly developed 0201 chip compatible lead-free solder paste contributing to the functionality and miniaturization of electronic devices and modules.	high
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Solder paste for electronic packaging application SS,SAC-N,SAC-U	-
Solder paste for electronic packaging application SS,SAC-N,SAC-U Lead-free solder paste for the package inner-bump which is applicable for the super-fine-pitch	
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### **LSP**Series

### ~ Highly Durable Lead-free solder paste ~





Due to high functionality and electronic controls of automotive features, highly durable solder joint is a must. Considering all usage conditions, a new lead-free solder alloy (LSP) with superior durability performance is developed.

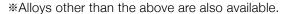
### **Characteristics**

- High joint reliability at harsh installation conditions
- High durability on different boards (glass epoxy/flexible/metal)
- •High reliability after soldering, required for automotive applications
- •No flux residue crack, and no whisker generation due to complete halogen free

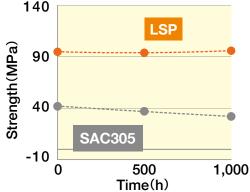
### **Alloy Composition** <Patented>

- Two times stronger than SAC305
- No deterioration of strength at 150°C

	LSP	SAC305
Composition	Sn-3.2Ag-0.5Cu-4.0Bi -3.5Sb-Ni+Co	Sn-3.0Ag-0.5Cu
Melting point	223℃	219℃
Strength	95MPa	42MPa
Elongation	20.4%	33.7%
Young's modulus	51GPa	52GPa



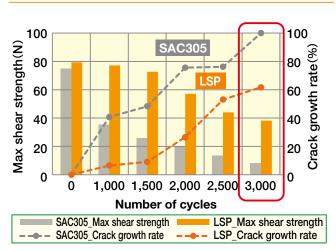




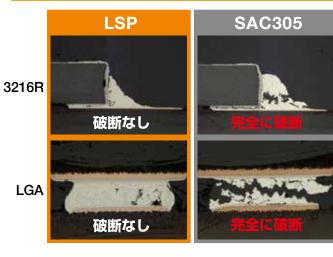
### Joint Reliability (Thermal fatigue characteristics (-40⇔+150°C × 3,000 Cycle)

- Controls the progress of crack, and maintains high strength after 3,000 cycles
- Effective for solder joints of electronics parts (LGA.QFN) where stress is applied

### Crack growth rate and max shear strength

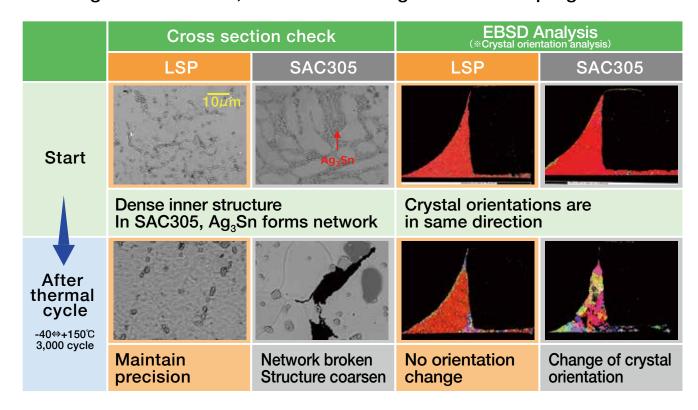


### Joint cross section (3,000 cycle)



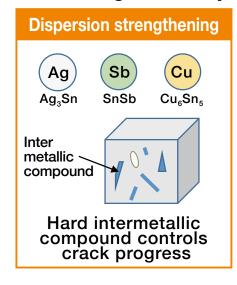
### **Check cross section**

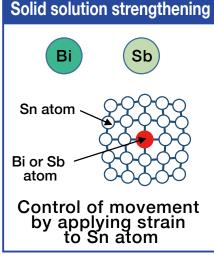
- For LSP, minimal internal structure (intermetallic compound) change Maintains strength, prevents crack growth and progress
- •For SAC305, coarser internal structure and crystal orientation change Strength deterioration, influences crack generation and progress

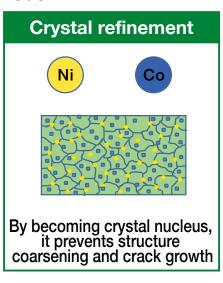


### **Durability improvement mechanism**

Realize high durability with 3 strengthening methods









### ~ Automotive Standard Solder Paste ~



GSP was developed in collaboration with Toyota, Denso and Denso Ten (Fujitsu Ten). For automotive applications, GSP has excellent electrical and mechanical reliability, even under very severe operating conditions.

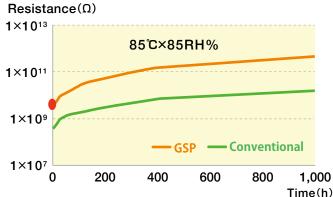
### **Characteristics**

- •High insulation resistance value (> 10 (E + 9)  $\Omega$ ) from start to 2,000 hours
- Resistance to flux residue crack (-40⇔+125°C,2,000cycle)
- Stable printing and solderability even after long time continuous printing
- Low solder ball generation even after long time continuous printing

### Reliability

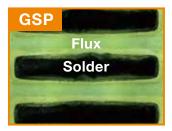
### **Insulation Resistance Value**

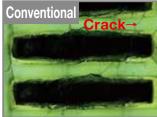
Maintain high insulation resistance from start



### Resistance to residue crack(after 2,000)

No crack flux residue





### **Evaluation Condition**

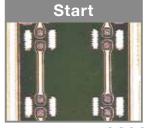
Cycle Condition :-40⇔+125°C 30 min
 Observation point :0.5mm Pitch QFP

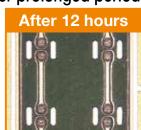
Observe by lighting from the back of the board

### Stability over long time usage

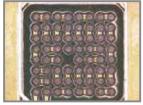
### **Continuous printing**

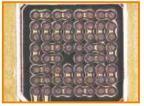
Stable printing after prolonged period





0603 chip

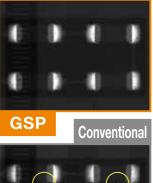


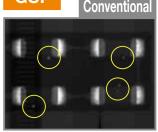


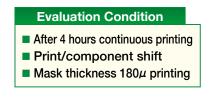
0.5 mm Pitch CSP

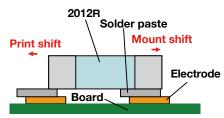
### Solder ball (after continuous printing)

Low solder ball even after continuous printing











### ~ Fine pitch printing solder paste ~



CLR® has excellent printability. In order to increase joint reliability, even with thicker stencil, enough solder paste can be printed for fine pitch.

### **Characteristics**

- To improve printability, new synthetic resin with enhanced water repellency is developed
- ■With mask thickness 150µm, stable printing is possible for 0.4mmQFP & 0.5mmBGA
- ■Excellent printability is achieved even at high speed printing (~100mm/sec)
- Resistance to flux residue crack (-40⇔125℃, 2,000 cycle)

### **Printability**

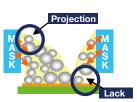
### Mechanism for improved printing performance

Strong

Less friction with metal mask opening, and as a result, fine pitch printing improved

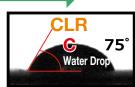
Metal mask

Adding water repellant material improved electrical reliability

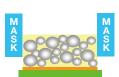








Weak

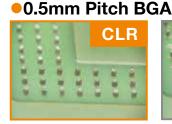


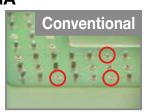
### Printing (Mask thickness:150µm)

- ■0.4mmQFP 0.5mmBGA mounting is possible with 150µm mask
- 0.4mm Pitch QFP



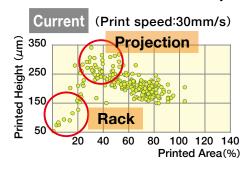


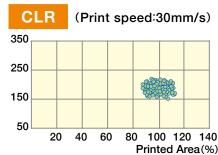


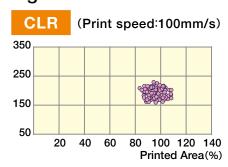


### High Speed Printing Mask thickness: 150μm Openting: Φ0.275mm

Maintain excellent printing at high speed printing (100mm/sec)









### ~ Residue crack resistance~ Halogen free solder paste

Residue Crack Prevention Halogen Free

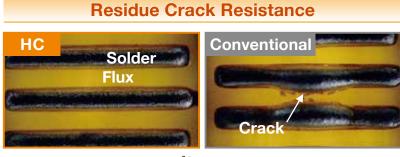
Residue crack resistance perfect halogen free solder paste

### **Characteristics**

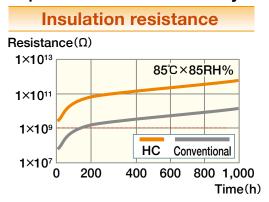
- Prevents residue crack by using flexible synthetic resin
- Ensures superior electrical reliability, high insulation resistance from start
- Controls whisker generation by using perfect halogen free flux

### Reliability

- •High crack resistance after thermal cycle
- High insulation resistance from start, and offers superior electrical reliability

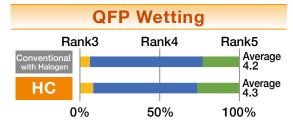


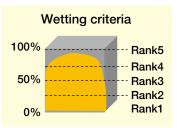


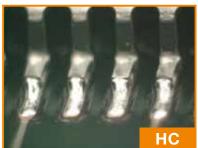


### **Wetting Characteristics**

Excellent wetting without halogen

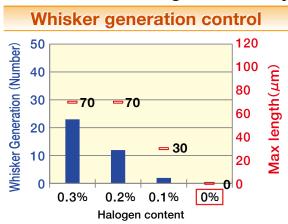






### Whisker prevention

Controls whisker generation by using halogen free flux





Due to high density component mounting space between components are getting narrower, and whisker generation may cause short circuit.



### ~ Clean type solder paste ~



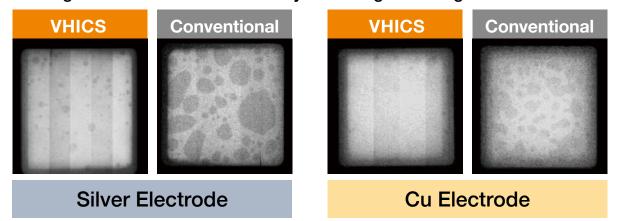
Low void generation of heatsink heat radiation bottom electrode, has superior residue cleaning characteristics

### **Characteristics**

- Regardless of electrode, low void generation of bottom electrode
- No alteration of flux after reflow heating, offers superior cleaning performance
- Controls solder or flux spattering in reflow

### Void

Void generation was controlled by choosing active agent suitable for electrode

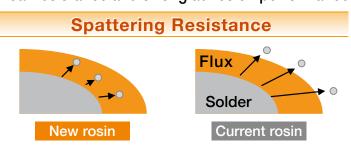


### Cleaning · Spattering Characteristics

- Control spattering by using strong adhesion rosin
- Use of newly developed rosin with superior heat resistance and strong adhesion performance



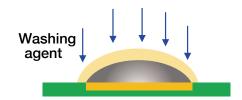




### **Cleaning characteristics**



«Cleaning solution, Clean though 750HS (by Kao Corporation)



Use of heat resistance rosin prevents oxidation, provides excellent cleaning performance



### ~Halogen free solder paste~



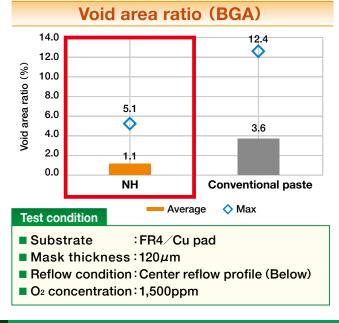
Does not contain environment polluting halogen such as Chlorine or Bromine, this is Sn-3.0Ag-0.5Cu halogen free solder paste.

### **Characteristics**

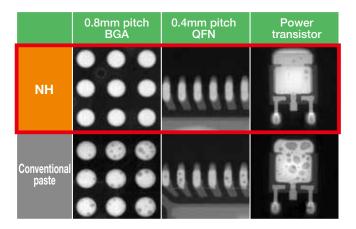
- Reduces voids, realizes highly reliable solder joint
- Applicable to wide range of reflow profiles, and products

### **Void performance**

Low void generation

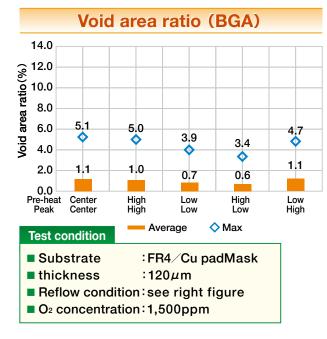


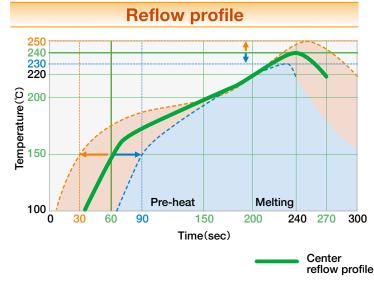
### Void results of each components (X-ray)



### Void performance for different reflow profiles

Applicable to wide range of profiles





### Wettability

Good wettability

φ250μm pad

NH Conventional paste

## NH Conventional paste

0.4mm pitch QFN

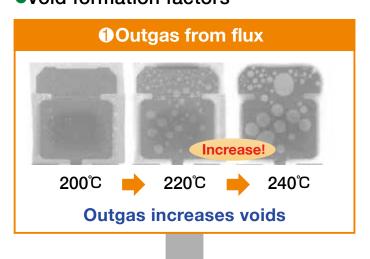
### Reliability

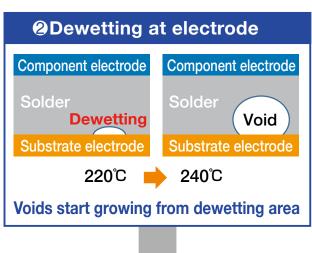
High insulation resistance and corrosion resistant

## Surface insulation resistance 85°C85%, 50V applying (Measure 100V) Resistance(Ω) 1×10¹¹ 1×10² 0 200 400 600 800 1,000 Time(h)

### Void improvement mechanism

Void formation factors





Achieve low void by reducing outgas and improving wettability



### ~Low-silver lead-free solder paste~





Developed highly reliable and low cost low silver alloy solder paste with excellent thermal fatigue and drop impact resistance properties

### **Characteristics**

- Realize higher joint strength and drop impact resistance with low silver alloys than SAC305
- Applicable to various reflow profiles of SAC305

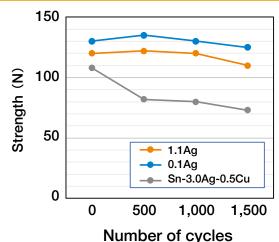
### Alloy composition <Patented>

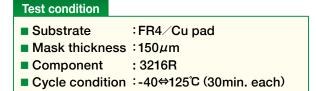
	Low 1.1% silver type	Low 0.1% silver type	SAC305
Composition	Sn-1.1Ag-0.7Cu-1.7Bi + α	Sn- <mark>0.1Ag</mark> -0.7Cu-2.0Bi +β	Sn-3.0Ag-0.5Cu
Melting point	223°C	225℃	219℃
Strength	64MPa	71MPa	42MPa
Elongation	35.2%	26.2%	33.7%

### Joint reliability

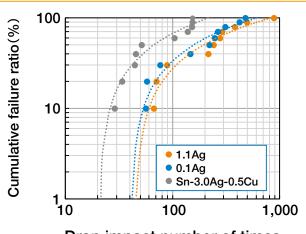
Excellent joint strength and drop impact resistance







### **Drop impact resistance**



Drop impact number of times

### Test condition ■ Substrate : FR4 / Cu pad ■ Mask thickness : 120 μm

■ Component : 0.5mm pitch LGA ■ Drop impact condition : JEDEC 1,500G

### ~0201 chip compatible solder paste~

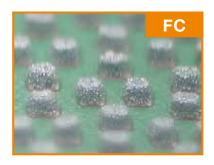


Developed 0201 chip compatible solder paste contributing to the high functionality and miniaturization of electronic devices and modules.

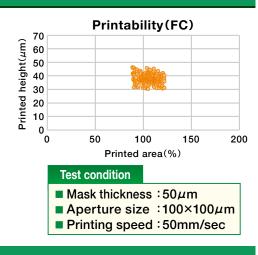
### **Characteristics**

- Excellent printing at small aperture, and good wetting characteristics
- •Small change of viscosity after continuous printing, can be used for a long period of time

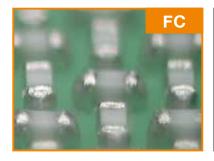
### **Printability**



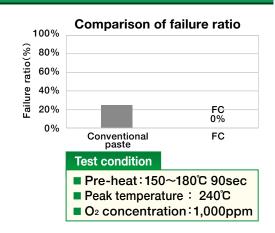




### **Mount wettability**

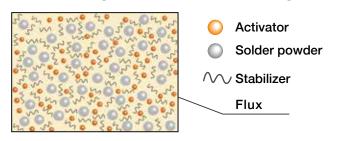


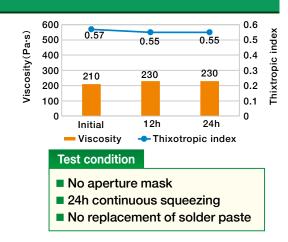




### Viscosity stability

- Suppress reaction between solder and activator by stable dispersion of flux ingredients
  - ▶Enable long time continuous printing





### ~Sn-3.0Ag-0.5Cu lead-free solder paste~

Sn-3.0Ag-0.5Cu generally better characteristic solder paste, contributing to higher productivity and low cost for commercial production

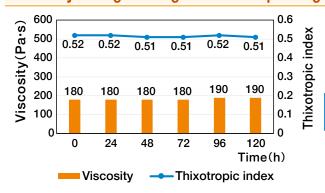
### **Characteristics**

- Realize stable printing and soldering, minimal performance change of paste in operation
- Reduction of waste paste amount by replenishment at continuous usage

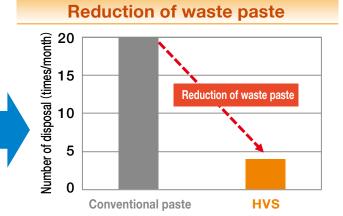
### Waste paste reduction

Small change of viscosity

### Viscosity change during continuous printing



### Waste reduction to 1/5



### **Test condition**

- No aperture mask
- 50% of paste replacement, every 12 hours

### Printability and wettability

### Stable printing and wetting

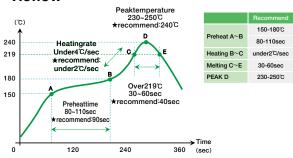
Otable printing and wetting					
	Printability	Wettabilty			
φ0.25mm Pad					
0.18×1.0mm Pad					
Test condition					
■ Mask thickn ■ O₂ concentra					

### **Recommended condition**

### Printing

	Recommend
Squeeze type	Metal, Urethane, Plastic
Printing speed(mm/sec)	30~80
Printing pressure (×10-2N)	20~50
Separation speed(mm/sec)	1.0~5.0
Separation mode	Constant speed

### Reflow

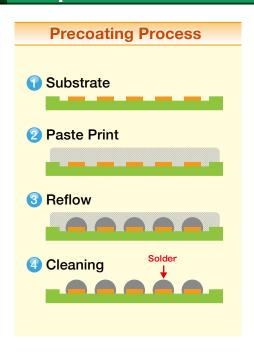


### Super Solder (SS) . SAC-N. SAC-Useries

~Lead-free paste for fine-pitch bump~

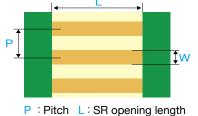
Fine-pitch soldering materials for peripheral substrate (Super Solder) and fine-pitch area array substrate (SAC-N, SAC-U series).

### Peripheral Substrate / Whole Surface Print Method



Precoating Examples*							
(unit:µm)							
Condition	1	2	3	4			
Electrode shape	Straight						
Arrangement	In-L	_ine	Stagg	gered			
Pitch, P	60	50	35	30			
Length, L	120	80 140 120					
Width, W	30	20	35	30			
Mean bump height	14 12 14 13						
STD	1.4	1.3	1.4	1.3			

\*)Representative values (not guaranteed)



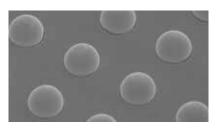


▲ 50 μm-pitch substrate Precoated Solder

### **Bump Formation: Fine-pitch Capability & Ultra Low-alpha Emission**

### Solder Bump Formation by SAC-U-330(150µm pitch Substrate)

W : Pad width



- Mean Bump Height : 35µm\*
- STD :2
- \*Representative values (not guaranteed)

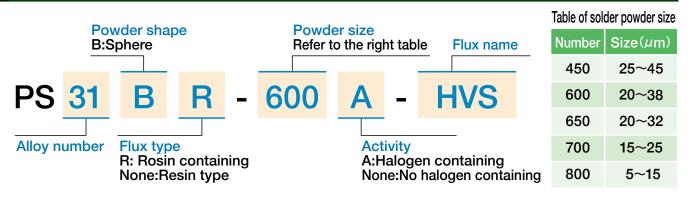
Application	Fine-pitch Are	ea Array Bump	Ultra- fine-pitch	Area Array Bump	
Product Name	SAC-N-400	SAC-U-600	SAC-N-110	SAC-U-330	
Ultra Low α	Non Compliant	Compliant	Non Compliant	Compliant	
α Emission Count	high $lpha$	< 0.002 cph/cm <sup>2</sup>	high $lpha$	< 0.002 cph/cm <sup>2</sup>	
Alloy Composition	Sn-3.0A	.g-0.5Cu	Sn-3.0Ag-0.5Cu		
Melting Point	220	O °C	220 ℃		
Particle Size	5-15	5 μm	1-10 µm		
Viscosity	280	Pa·s	300 Pa⋅s		

### Solder paste product lineup

### Solder paste product lineup

	Product name	Feature	Alloy composition	Powder size (µm)	Viscosity (Pa·s)
	GSP	Automotive for general purpose	Sn-3.0Ag-0.5Cu	20-38	160
	CLR	Excellent printability	Sn-3.0Ag-0.5Cu	20-38	220
	PS48BR-600-LSP	High durability	Sn-3.2Ag-0.5Cu-4.0Bi-3.5Sb-Ni-Co	20-38	220
Automotive	PS31B-600-HC1	Halogen free	Sn-3.0Ag-0.5Cu	20-38	200
	PS31BR-600A-VHICS	Washable and voidless	Sn-3.0Ag-0.5Cu	20-38	200
	PS10B-600A-ANI-1	Tin-lead for general purpose	Sn-37Pb	20-38	200
	PS60B-450A-TR5	Tombstone improved	Sn-36Pb-2Ag	20-38	200
	PS31BR-600A-HVS3 PS31BR-700A-HVS3	Lead-free for general purpose	Sn-3.0Ag-0.5Cu	20-38 15-25	180
	PS31BR-600-NH5		Sn-3.0Ag-0.5Cu	20-38	200
	PS31BR-600-NH11	Halogen free	Sn-3.0Ag-0.5Cu	20-38	170
Consumer electrronics	PS31BR-600A-LH1		Sn-3.0Ag-0.5Cu	20-38	200
	PS31BR-800-FC1	0201 chip soldering	Sn-3.0Ag-0.5Cu	5-15	210
	PS24BR-600A-HLS7	Low 1.1% silver	Sn-1.1Ag-0.7Cu-1.7Bi+α	20-38	180
	PS20BR-600A-HLS7	Low 0.1% silver	Sn-0.1Ag-0.7Cu-2.0Bi+β	20-38	180
	PS58BR-450A-KL1	Low melting point(SnBi)	Sn-58Bi	25-45	180

### Naming of solder paste product



### Solder alloy list

Classification	Alloy number	Alloy composition	Sn	Ag	Cu	ln	Bi	Sb	Pb		Melting point(°C)
Sn-Ag-Cu	31	Sn-3.0Ag-0.5Cu	Balance	3.0	0.5	-	-	-	-	-	219
Durability type	48	Sn-3.2Ag-0.5Cu-4.0Bi-3.5Sb-Ni-Co	Balance	3.2	0.5	-	4.0	3.5	-	•	223
Low 1.1% silver	24	Sn-1.1Ag-0.7Cu-1.7Bi+α	Balance	1.1	0.7	-	1.7	-	-	•	223
Low 0.1% silver	20	Sn-0.1Ag-0.7Cu-2.0Bi+β	Balance	0.1	0.7	-	2.0	-	-	•	225
Low melting(In)	37	Sn-3.5Ag-8.0In-0.5Bi	Balance	3.5	-	8.0	0.5	-	-	-	207
Low melting(Bi)	58	Sn-58Bi	Balance	-	-	-	58.0	-	-	-	138
Sn-Pb	10	Sn-37Pb	Balance	-	-	-	-	-	37.0	-	183
JII-FD	60	Sn-36Pb-2Ag	Balance	2.0	-	-	-	-	36.0	-	190

### **Brazing materials and their lineup**

We propose Brazing products to meet a wide variety of coating method.

Coating method	Coating method	Characteristics
Flux containing NHP-NV112	Spray <i>mmmmmm</i> coating	· Suitable for the bent or curved surface coating
Flux containing NHP-X1002-39F	Flow coating	· Make it possible to coat partially to the parts
Flux containing NHP-X1001-50F  Silicon containing NHP-X1003-50FS(EX)  Zinc containing NHP-X2200-50Z	Roll coating	<ul><li>Suitable for the flat surface coating</li><li>Good evenness</li><li>Good yield</li></ul>
Flux containing NHP-X109-50FG  Metal containing NHP-X1600	Dispense coating	<ul> <li>Make it possible to feed properly to the parts</li> <li>Good yield</li> </ul>

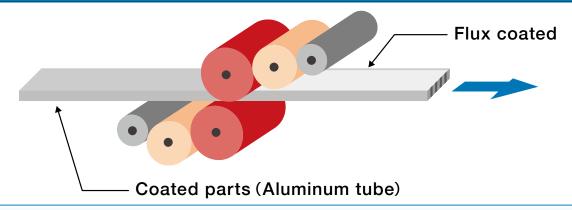
\*\*Handle a lot of brazing materials except the above.

### **NHP**

### ~Paint flux for roll coating~

The paint flux provides good adhesiveness and excellent thermal decomposition derived from Harima developed binder.

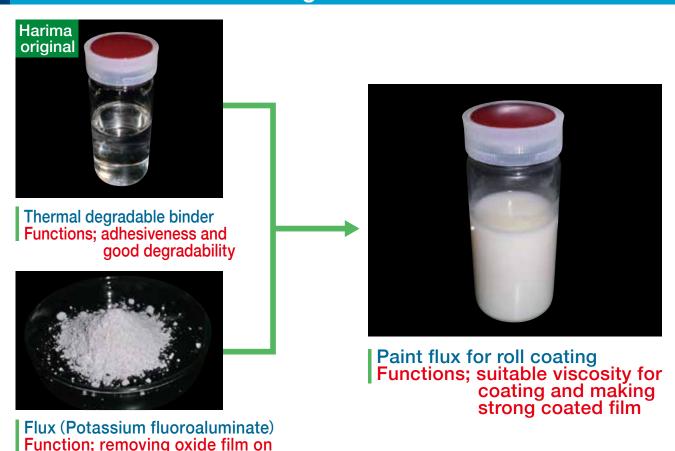
### What is roll coating?



The technology of making evenness coating by roll printing

### Paint flux for roll coating

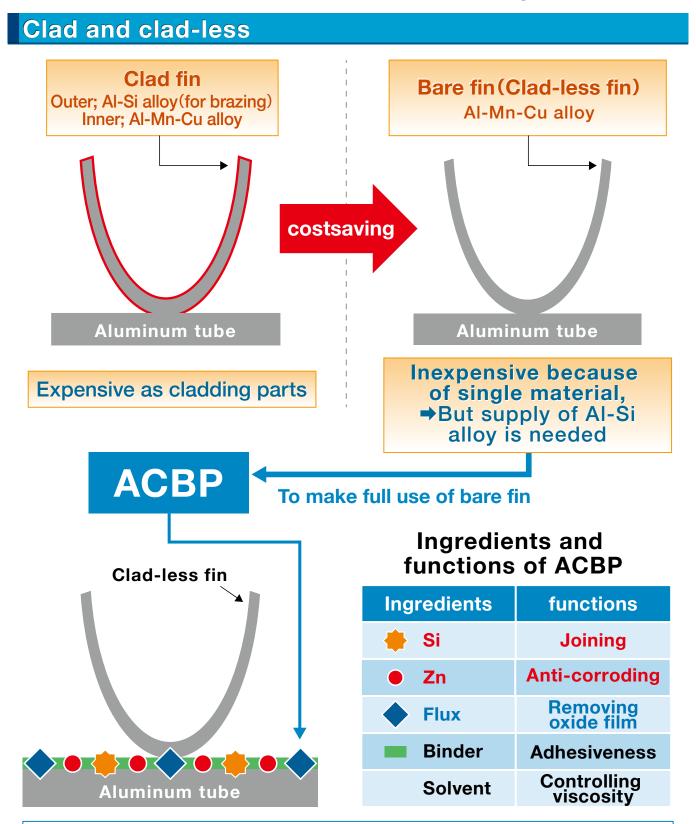
Aluminum surface



Paint flux for roll coating makes it possible to coat by optimum flux amount

### ACBP ~Anti-corroding clad-less brazing paint~

The brazing paint allows clad-less brazing as well as provides corrosion resistance on Al surface after brazing.



Make it possible to provide not only joining but also anti-corroding

### CP-800S,CP-1000S

~Copper paste for through-hole~

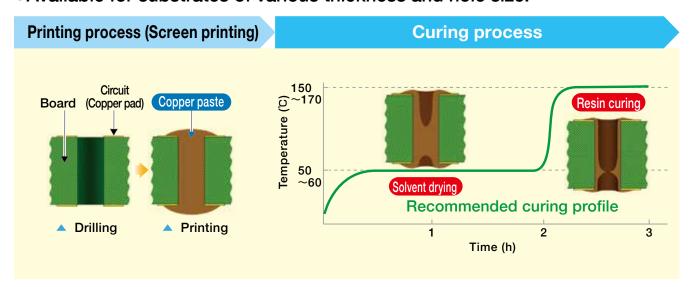
Highly-reliable copper paste for through-hole, available for automotive boards.

### **Features**

- Compared to copper plating or silver paste, copper paste can reduce production cost.
- •Available for small diameter through-hole and four-layer boards.
- Meets all the industrial standards of reliability evaluations required by electrical assembly field.
   Excellent electromigration resistance and available for wide range of board types, from for consumer to automobile.

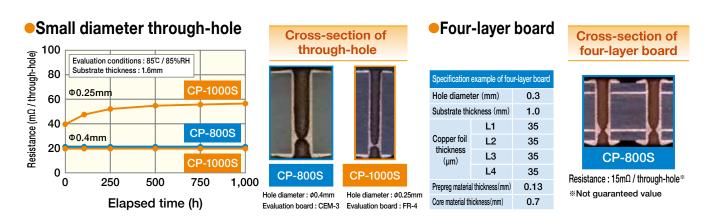
### **Printing and Curing process**

- Compared to plating, copper paste printing process is simpler and produces less waste.
- Available for substrates of various thickness and hole size.



### Application examples for small diameter through-hole and four-layer boards

- CP-800S used in various fields maintains high reliability even in the case of small diameter and four-layer boards.
- •We offer CP-1000S(developed product) applicable for Φ0.25mm diameter through-hole with 1.6mm substrate thickness.



### **CP-5000D**

~Copper paste for electronic parts electrode~

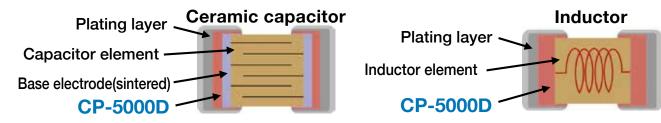
Resin cure type copper paste applocable for electrode of electronic parts.

### **Features**

- Replacing silver to copper reduces cost.
- Possesses the same performance as silver paste.
- Containing resin in copper paste ease the stress on components after mounted on the substrate.

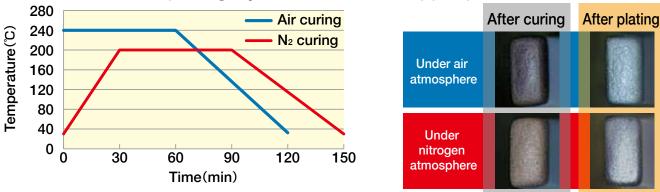
### Applicable position of copper paste for electronic component

Our copper paste is applicable for electronic component.



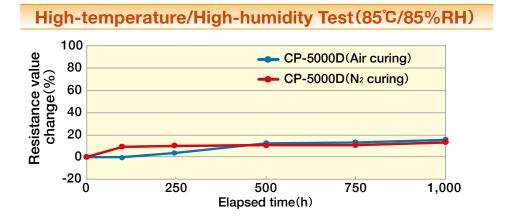
### **Curing profile**

 Our copper paste is curable under both air and nitrogen atmosphere, and able to form plating layer on the cured copper paste.



### Electric resistance value change of the cured copper paste

Our copper paste maintains high reliability.



### NH-3000D,NH-4000,SHB-200 ~High thermal conductive in

conductive paste~

These silver pastes have higher thermal conductivity than solder.

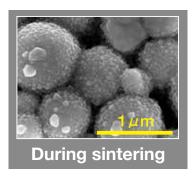
### **Features**

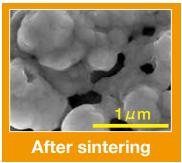
- These pastes have high joining reliability.
- •Due to mixing of silver nanoparticles and silver powder, dense sintered junction layer shows high thermal conductivity.
- •New sinter paste SHB-200 is available for direct joining with Ni under pressurized process. It has been applied for a patent

### Mechanism of high joining strength and high thermal conductivity

 Silver powder and silver nanoparticles sinter closely to show high joining strength, high thermal conductivity and low volume resistivity

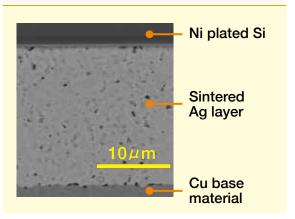
### **SEM** observation result of the particle surface





Silver nanoparticles promote fusion between silver powders to strengthen thermal and electronic moving pathways.

### SEM observation result of cross-section of joining part



### **Specification (typical data)**

Ite	ms	NH-3000D	NH-4000	SHB-200	additional notes
Curing o	ondition	190℃×90min	150 ℃×90min	150 ℃×90min 250℃×30min *)	
Joining	First	21 N/mm <sup>2</sup> *1)	20N/mm <sup>2</sup> *1)	40N/mm <sup>2</sup> *2)	Element type *1)2mm□Au plated Si、 *2)5mm□Ni plated Si
strength			-10%	0%	Aftre 1,000cyc. -55/+125℃, each 30 min.
Thermal co	onductivity	95W/m⋅K	65W/m⋅K	240W/m·K	laser flash method
Volume resistivity		12 <i>μ</i> Ω⋅cm	14 <i>μ</i> Ω·cm	14 $\mu\Omega$ ·cm 5 $\mu\Omega$ ·cm	
Eleme	nt size	2mm□以下	2mm□以下	5mm□以下	-
Minimum thickness		10µm	10μm 20μm		-
Available ba	ase material	Au, Ag	Au, Ag	Au, Ag,Cu, Ni	-

Above data are representative value, not a standard value.

### NPS-L,NPS-L-HB,NPG-J

~High Adhesive Nano Paste®

Due to the stability of the dispersion, our product shows excellent printing features, and it is a suitable material for printed electronics.

### **Features**

- Ensures high adhesion to variety of substrates.
- •Metal film can be formed with the wide range of thickness.
- •We also offer Gold Nano Paste® NPG-J for ink-jet printing.

### **High adhesion**

 Due to our original metal composite technology, high adhesion to variety of substrate was achieved. Patent registered

Adhesion to substrate of metal film of NPS-L and NPS-L-HB

Substrate	PET	Cu	Ni	Glass	Alumina
Heating condition (under air atmosphere)	120℃×1h	120℃×1h	120℃×1h	400℃×1h	400℃×0.5h
Adhesion*	Class 0				

<sup>\*</sup>Test method: Cross-cut adhesion test(Former JIS K 5400)

Classification of adherence : (Excellent) 0 · 1 · 2 · 3 · 4 · 5 (Poor)

### Specification(typical data)

 Since our product has favorable adhesiveness, it is able to form metal film on various substrates.

Item	NPS-L	NPS-L-HB	NPG-J
Component metal	Ag	Ag	Au
Heating condition	120℃×1h	120℃×1h	250℃×1h
Formable thickness	0.2~7μm	5~50µm	0.2∼1 <i>µ</i> m
Volume resistivity	10 <i>μ</i> Ω·cm	10 <i>μ</i> Ω·cm	12 <i>μ</i> Ω·cm
Pencil hardness	Н	2H	3H
Printing method	ink jet screen	screen	ink jet
Adhesible substrate	Au, Ag, Cu, Ni, PET, Glass, Alumina, etc.		Au, Ag

Above data are representative value, not a standard value.