HALOGEN-FREE DEBATE ON SOLDERPASTE: IPC CLASSIFICATION AND APPLICATION

Christine Poon, Audrey Long, James Wang

Kester Components Pte Ltd

ABSTRACT

Halogen-free requirement[1] in PCBA and in related materials has been gaining momentum in recent months. Major computer manufacturers had made announcements about intentions to go bromine-free in the next two years[2, 3]. Halogen-free started from RoHS banned substances on PBB[4] and PBDE[5] initially, however, it has evolved to a broader coverage of detectable halogen level per IEC 61249-2-21[6], JPCA-ES-01-2003[7], and IPC-4101B[8] specifications. Currently, solderpaste formulation is classified by IPC J-STD-004A[9] standard, with permissible and declared halogen/halide level. This paper compares and contrasts the current IPC, J-STD-004A standard and the impact of halogen-free requirements on the classification. A study is also done to examine whether solderability of halogen-free solderpaste formulas is lowered versus halogenated formulas.

Key Words: halogen-free, solderpaste

INTRODUCTION

Brominated flame retardants (BFRs)[10] are effective flame-retardants. They are added to plastics used in electrical and electronic equipment to slow down or prevent ignition of fire. Some brominated flame-retardants are considered persistent organic pollutants known to bioaccumulate consequences are not well-known, although the environmental consequences of some, e.g. PBDEs are known.

Solderpaste is a physically mixture of solder powder and paste flux, typically 90%wt solder and 10% wt of paste flux. The solder powder is purely metallic and doesn't contribute to the halogen content. No-clean paste flux formulations are typical rosin-based or resin-based and the compositions are predominantly organic chemicals. The main task in paste flux in solderpaste during reflow is to remove the tarnish films from surfaces, protect surfaces from reoxidation and to promote wetting of solder onto the surfaces. The rosin/resin is often used as a base, though the fluxing activity of the rosin alone is limited. The major purpose of adding activators is to increase the capability of flux in promoting wetting and removing of oxide films. One family of activators that are commonly used is covalently bonded chlorine and/or bromine organic compounds.

J-STD-004A, "Requirements for Soldering Fluxes" classifies fluxes per composition and activity levels and recognizes the usage of halides used in the paste flux formulations. J-STD-004A identifies the halide content in formulas by assigning the absence (0) or presence (1) of halides in the flux. 0.0% halide is defined by < 0.05% by weight in flux solids and may be known as halide-free. The test method per IPC-TM-650, 2.3.28.1 is per extraction of the paste flux in the solderpaste into solvent and the solvent will be injected into ion chromatography column, whereby chloride (Cl^-) and bromide (Br^-) will be detected and quantified. Table 1 summarizes the detailed classification of soldering fluxes.

Table 1: Flux Identification System

Materials of Composition	Flux/Flux Residue Activity Levels	% Halide (by weight)	Flux Type	Flux Designator
Rosin (RO)	Low	0.0%	L0	ROL0
		< 0.5%	L1	ROL1
	Moderate	0.0%	M0	ROM0
		0.5%-2.0%	M1	ROM1
	High	0.0%	H0	ROH0
		> 2.0%	H1	ROH1
Resin (RE)	Low	0.0%	L0	REL0
		< 0.5%	L1	REL1
	Moderate	0.0%	M0	REM0
		0.5%-2.0%	M1	REM1
	High	0.0%	H0	REH0
		> 2.0%	H1	REH1

The standard bodies that have defined halogen-free are summarized in Table 2. Note that the standards adopt similar specifications, thus, we commonly refer to IEC standard for easy reference.

Table 2: Substance restriction for halogen-free products and components

Standards Bodies	JPCA (Japan Electronics Packaging and Circuits Association)	IEC (International Electrotechnical Commission)	IPC (Association Connecting Electronics Industries)
Specification No.	JPCA-ES-01-2003	IEC 61249-2-21	IPC-4101B
Cl	<0.09wt% (900ppm)	<0.09wt% (900ppm)	<0.09wt% (900ppm)
Br	<0.09wt% (900ppm)	<0.09wt% (900ppm)	<0.09wt% (900ppm)
Combined Cl and Br	Nil	1500ppm maximum	1500ppm maximum

Note: Fluorine, iodine, astatine (other Group VIIA halogens) are not restricted in the industry definition of halogen-free.

Table 3 compares and contrasts between IPC J-STD-004A and IEC 61249-2-21, test methods, sample types and sample preparation.

Table 3: Comparison between J-STD-004A and IEC 61249-2-21

	J-STD-004A	IEC 61249-2-21
Halide Free	<0.05%Cl^-+Br^- (per solid content of paste flux)	
Halogen Free		< 0.09wt% Cl < 0.09wt% Br < 0.15wt% Cl+Br (per weight)
Test Method	IPC-TM-650 2.3.28.1	IEC 61189-2 Test 2C12
Specified Sample Type	Solder paste, paste flux, liquid flux, extracted solder perform flux or cored wire	Rigid or flexible base materials
Sample Preparation method	Extraction	Combustion flask
Analysis	Ion chromatography	Ion chromatography
Summary of Test Method	Detects free halide only	Detects halogen and free halide

IEC 61249-2-21 also uses ion chromatography to quantify chloride (Cl^-) and bromide (Br^-), however, it introduces an additional combustion flask test before ion chromatography which combusts and convert all halogenated compounds into free halides. The test method per IEC 61249-2-21 is also specifically written for rigid or flexible base materials. A specific sampling method for solderpaste method has not been written.

In first part of study, the quantification of the detected halogen versus the various sampling sizes of solderpaste is being conducted, per IEC 61189-2 Test 2C12 method. Second part of the study compares the solderability performance of a typical halogenated no-clean solderpaste formula versus the latest halogen-free no-clean solderpaste formula, to evaluate whether halogen-free no-clean solderpaste formulas have decreased solderability and narrower process window in SMT production.

EXPERIMENTAL

Part I

Halogenated no-clean Solderpaste A (SnAgCu alloy, 10.5%wt flux) was submitted to 2 external, certified test laboratories and tested per IEC 61189-2 Test 2C12 method, with different sampling sizes of 50mg to 300mg per test. Halogenated no-clean Solderpaste B (SnAgCu alloy, 10.5%wt flux) was subjected to the same test methology to confirm the consistency of results.

The solderpaste/paste flux specimen was wrapped in the flag-type filter paper (same filter paper used as a fuse/flame starter in the bomb flask) so that the solderpaste/ paste flux was supported and not dropped into the absorbent solution.

Part II

The solderability properties of a halogenated no-clean Solderpaste C and a halogen-free no-clean Solderpaste D are compared. Both are mature solderpaste formulas available in the market and conform to J-STD-004A no-clean requirements. Their properties are listed in Table 4.

Table 4: Summary of Properties of Paste C and Paste D

Sample	Solder Paste C, 11.5% SAC solder paste	Solder Paste D, 11.5% SAC solder paste
Halide % IPC-TM-650 2.4.38.1	0.45%	0.0%
IPC Classification Per J-STD-004A	ROL1	ROL0
Cu Mirror (IPC-TM-650 2.3.32)	Pass "L"	Pass "L"
Cu Corrosion (IPC-TM-650 2.6.15)	Pass "L"	Pass "L"
SIR (IPC-TM-650 2.6.3.3)	Pass	Pass
ECM (IPC-TM-650 2.6.14.1)	Pass	Pass
Halogen (Paste flux) per IEC 61189-2 2C12	Cl: ND* Br: 10427ppm	Cl: ND* Br: ND*
Comments	Halogenated	Halogen-free

*ND: Not detected (detectable limit: 50ppm)

Solderability comparison was done under a standard reflow in Heller 1800 Convection Oven, air reflow, as described in Table 5.

Table 5: Reflow profile (air)

Ramp rate 40-110 degC (^{o}C/sec)	Preheat 110-150degC (sec)	Soak 150-220degC (sec)	>220degC (sec)	Peak (^{o}C)
1.58	65	100	65	245

Joint Appearance

Solder pastes were first printed on the 20mils QFP copper traces and then went through the reflow oven.

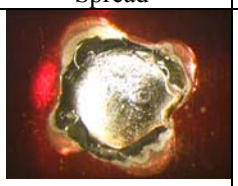
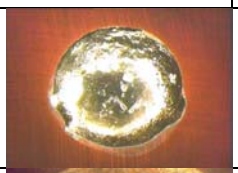
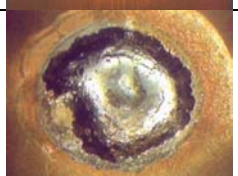
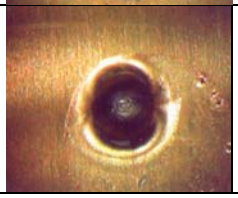
IPC Solderball Test

The solder ball test was conducted per J-STD-005 IPC-TM-650, 2.4.43. Two test specimens were prepared by printing three solderpaste deposits of 0.65mm in diameter and 0.25mm thick onto a glass slide using a stencil. One set of test specimen was reflowed within 15 mins after printing. The other test specimen was stored at 25degC and 50%RH for 4 hours after printing and then reflowed. Both specimens were reflowed on a hot plat that was heated at a temperature of 25degC above the liquidus temperature of the solder alloy. As soon as the solder has melted, the specimens were withdrawn from the hot plate. The reflow should occur within 20 seconds after specimen was placed in contact with the hot plate.

Solderability (Ni and Brass Plates) Test

Two different metal plates, nickel and brass plates, were used to evaluate the wetting properties of the solder pastes. The substrates were polished by a Metal Polish from Autosol, followed by thorough cleaning with IPA prior to use. Solder pastes were printed on the substrates manually with a stainless steel stencil with hole diameter of 6.5 mm and a 8 mil thickness, and then went through reflow oven. The spread on the plates were graded as Table 6.

Table 6: Grading of spread on Ni and Brass plate

Grade	Spread	Inspection
1		Condition where the solder dissolved from the solder paste wets the test plate, and the wetted area becomes larger than the paste coated area.
2		Condition where all the solder paste coated part is wetted by the solder
3		Condition where almost all the solder paste-paste coated part is wetted by the solder (including the de-wetted)
4		Condition where no solder seems wetted, and the molten solder becomes one or more solder balls (non-wetting)

Solderability (Imm Sn board)

The immersion tin test coupon was preoxidized by one time reflow through the standard profile. Solderpaste was printed onto the test coupon and reflowed. The degree of spread on the solderable pads was compared and contrasted.

RESULTS AND DISCUSSION

Part I

The halogen test results are summarized in Table 7-9 as below.

Table 7: Halogen quantification of Solderpaste A

Sample	Sample Weight	Test Lab X	Test Lab Y
Solder Paste A 10.5% SAC solder paste	50mg	Cl: ND* Br: ND	
	100mg		Cl: ND Br: ND
	100mg		Cl: ND Br: 70ppm
	200mg	Cl: ND Br: 187ppm	
	300mg		Cl: ND Br: 175ppm
	400mg		Cl: ND Br: 130ppm
	500mg	Cl: ND Br: 180ppm	

*ND: Not detected (detectable limit: 50ppm)

Halogen is unable to be detected or inconsistent when the solderpaste sample size is below 200mg.

Table 8: Halogen quantification of Solderpaste B

Sample	Test Lab X		Test Lab Y	
Sample Weight	300mg		400mg	
Solder Paste B 10.5% SAC solder paste	Cl: ND* Br: 2143ppm	Cl: ND Br: 2100ppm	Cl: ND Br: 2300ppm	Cl: ND Br: 2250ppm

*ND: Not detected (detectable limit: 50ppm)

Solderpaste B was analyzed with sample weight of 300-400mg and the results were consistent between the 2 test labs and repeated sampling.

Table 9: Halogen quantification of Paste Fluxes (50mg sample size, Test Lab X)

Sample	Paste Flux A	Paste Flux B
Analyzed Results	Cl: ND* Br: 2097ppm	Cl: ND Br: 26327ppm
Calculated Value in Solderpaste (10.5% wt flux)	Cl: Nil Br: 200 ppm	Cl: Nil Br: 2597 ppm
Comments	Paste flux halogen level close to Solderpaste tesing for > 200mg sample size	Paste flux halogen level close to Solderpaste tesing for > 300mg sample size

*ND: Not detected (detectable limit: 50ppm)

The calculated halogen content per paste from the tested flux halogen data was quite close to the actual analyzed figures in paste flux. The key to a consistent halogen figure in solderpaste is to test more than 300mg of solderpaste. Thus, a small sampling size of < 100mg solderpaste will yield non-detected or lower halogen values, which is misleading.

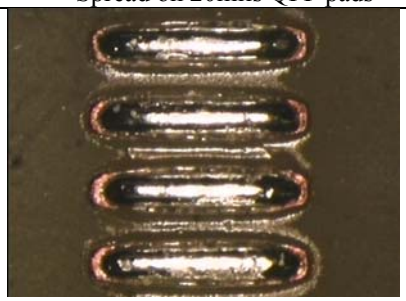
Part II

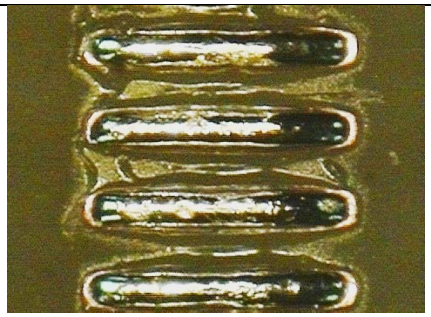
The halogen-free formulation of Solderpaste D was validated versus Solderpaste C in the solderability performance.

Joint Appearance

Table 10 showed the joint appearance of the halogenated paste versus the halogen-free solderpaste. There was no significant difference between the 2 formulas. Both were bright, smooth and shiny.

Table 10: Joint appearance of 20mils QFP pads

	Spread on 20mils QFP pads
Solderpaste C	 Smooth and shiny

Solderpaste D	 Good spread

IPC Solderballing Test

Solderballing was preferred for both formulas, meeting IPC requirements, as shown in Table 11.

Table 11: IPC Solderballing Test

Solderpaste C	 Preferred
Solderpaste D	 Preferred

Solderability (Ni and Brass Plates) Test

The spread of Solderpaste D was better on Nickel plate than Solderpaste C, as shown in Table 12.

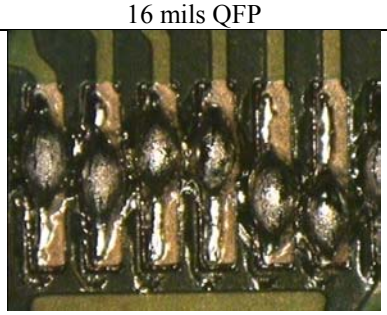
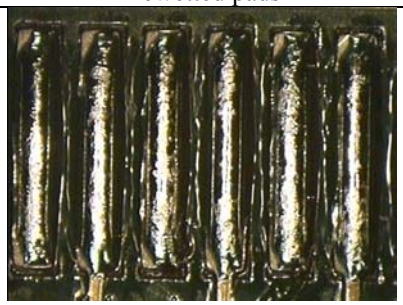
Table 12: Spread on Ni and Brass Plates

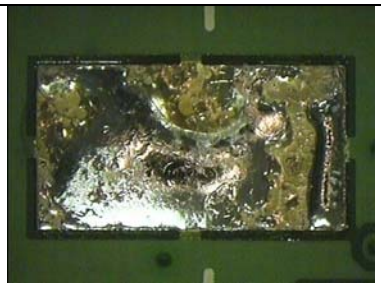
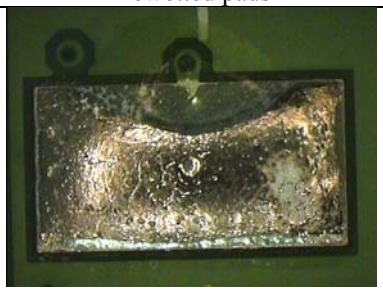
	Solderpaste C	Solderpaste D
Brass	2	2
Nickel	3	2

Solderability (Imm Sn board)

Solderpaste D had significantly better spread on preoxidized immersion tin board, summarized in Table 13.

Table 13: Solderability on immersion tin board (1x oxidized)

Location	16 mils QFP
Solderpaste C	 Dewetted pads
Solderpaste D	 Good spread

Location	1x reflowed Imm Sn board, Open pads, 4 x 8mm
Solderpaste C	 Dewetted pads
Solderpaste D	 Good spread

Solderpaste D had better solderability than Solderpaste C on various substrates. Thus halogen-free solderpaste formulas do not imply poorer solderability. It is dependent on the chemistry and the use of non-halogenated activators to formulate a SMT processible solderpaste with similar process window.

CONCLUSION

The recommended minimum quantity used for halogen-free analysis for solderpaste products is 300mg while the minimum quantity for paste flux is 50mg, so that the test value will not report lower than the true value. The industry needs to write a solderpaste specific test method with a fixed sample size.

Solderability of halogen-free, no-clean paste formulas can be similar to halogenated formulas, meeting the SMT requirements. Customers are able to evaluate and qualify halogen-free solderpaste formulas as per standard no-clean solderpaste qualification.

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Christine Poon, Audrey Long and James Wang can be contacted at lppoon@kester.com.sg, wslong@kester.com.sg and jameswang@kester.com.tw respectively.