Challenges toward Implementing a Halogen-Free PCB Assembly Process

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INTRODUCTION
The electronics industry continues to strive to provide more environmentally friendly products. This movement is partly due to legislation from various countries, partly due to public outcry from well publicized 3rd world recycling practices, and partly due to non-government organizations (NGOs) testing and publishing information on electronic devices regarding their content of various toxic materials. One set of materials targeted for reduction and eventual elimination are halogenated compounds. Halogens are found in plastics for cables and housings, board laminate materials, components, and soldering fluxes. Replacing these halogenated compounds can have a dramatic affect on the PCB assembly process. In this paper those challenges will be discussed as well as techniques and practices that will help ensure high end of line yields and continued reliability.

"GREEN" TRENDS
The enactment of RoHS on July 1, 2006 prohibited the use of two halogenated flame retardants: Polybrominated biphenyls (PBBs) and Polybrominated diphenyl ethers (PBDEs). Although there may be some remaining controversy, it appears there is general agreement that PBBs and PBDEs are environmentally unfriendly. Such compounds tend to bioaccumulate and can be found in humans, animals and the environment. In addition, when products containing these flame retardants are recycled, they place workers at risk.

Early in 2008 the OKO institute published and additional list of more than 40 substances to be considered for RoHS inclusion. RoHS was always intended to be a "living" document and hence will be modified with time. This proposed modification has been dubbed by some as RoHS 2. Tetrabromobisphenol A (TBBPA) and Hexabromocyclododecane (HBCD or HBCDD) were included in the above list of 40 or so substances. TBBPA is one of the most important flame retardants for PCBs. HBCDs are used in thermal insulating foams, so they are not of much interest to the electronics industry.

As we are writing this paper (mid December 2008), the EU has announced that no new substances will be banned under RoHS at this time. However, 10s of thousands of substances will be evaluated under the EU's REACH law including TBBPA. REACH (Registration, Evaluation, Authorisation and restriction of CHemicals), at 849 pages, is the "largest" law ever enacted by the EU. In comparison RoHS has only 6 pages. REACH requires that any chemical imported or manufactured by a company in the EU in quantities over 1 metric ton must be registered. After registration, the companies importing or producing each material must participate in cooperative evaluation of the material to demonstrate its safety. It is expected that this work will take decades to accomplish. However, sixteen substances will likely be designated as substances of very high concern (SVHC). These substances will require early evaluation and disclosure in any product where they are used. TBBPA is not on the list, but its flame retardant cousin HBCDD is.

Non-government organizations (NGOs) such as Greenpeace will likely have a growing influence on the "Greenness" of electronics. Their "Guide to Greener Electronics", see Figure 1 is an example.

One of the features of REACH is that individuals can query companies about the substances in their products. Companies must respond in 45 days. Greenpeace, the World Wildlife Fund and other NGOs are encouraging consumers to make such queries by publishing form letters on their websites for consumers to send in.

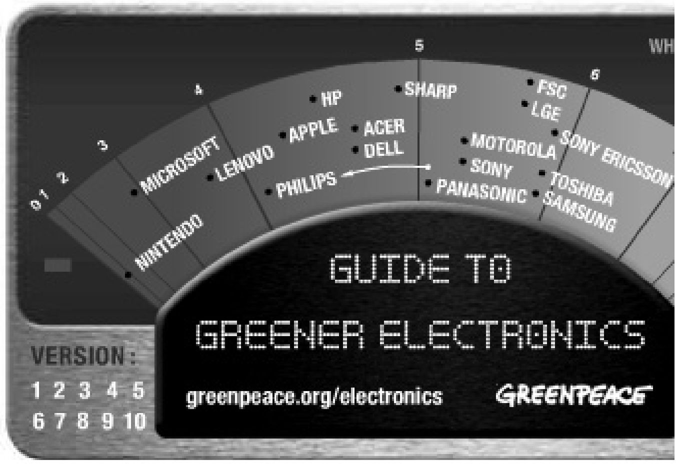

Figure 1. Greenpeace's "Guide to Greener Electronics."

We believe that the combination of RoHS, REACH and the NGOs will continue to create interest by electronics companies to be halogen-free, in a sense just to avoid any hassles. This is evidenced by outside packaging on a Sony Home Theater receiver in which their halogen-free proclamation is listed as part of their "eco info" as shown in Figure 2.

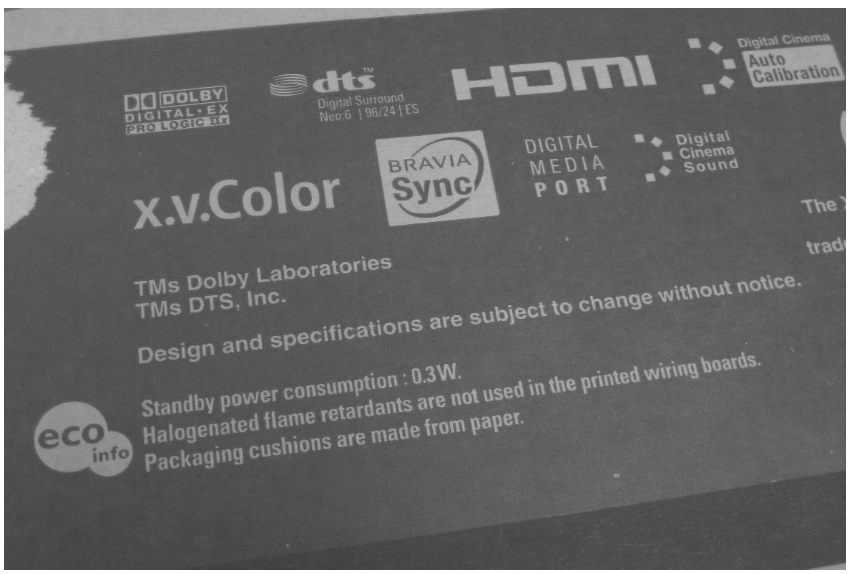

Figure 2. Sony Home Theater Receiver Box

CHALLENGE #1: DEFINING HALOGEN-FREE

In its simplest definition, halogen-free means does not contain any of the elements in Group 7 (17) of the periodic table. Those elements are chlorine(Cl), bromine(Br), fluorine(F), iodine(I), and astatine(At). Relative to the electronics industry, the primary halogens used are Cl and Br. F is occasionally used in fluxes for soldering, but is currently not receiving much attention. Therefore, the electronics definition of halogen-free is typically defined as Cl- and Br-free.

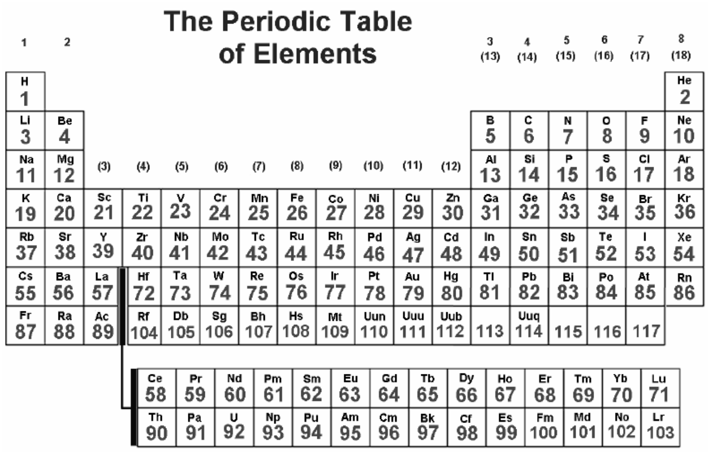

Figure 3. Periodic Table of Elements

At the time of this article, there are four standards in the electronics industry that address halogen content. Those standards are:

- JPCA-ES-01-2003
    - Free Download: http://www.jpca.net/jp/e/standard_pdf/jpca-es01-2003.pdf
    - Designed around PCB's
    - Halogen-free definitions
        - <900 ppm Cl and
        - <900 ppm Br
- IEC 61249-2-21 (2003)
    - Designed around PCB's
    - Halogen-free definitions
        - <900 ppm Cl and
        - <900 ppm Br and
        - <1500 ppm total Cl & Br
- IPC 4101B
    - Designed around PCB's
    - Halogen-free definitions
        - <900 ppm Cl and
        - <900 ppm Br and
        - <1500 ppm total Cl & Br
- IPC J-STD-004
    - Designed around soldering fluxes
    - Defines halide content (not halogen content)
    - Halide free defined as <500 ppm total halide (Cl+Br+F+I)

The differences in the standards are the source of much of the confusion on what halogen-free actually means. The IPC is developing the J-STD-709 which is designed to better provide guidance on low halogen electronics. As of December 2008, the J-STD-709 specification is still not complete. There is interest in changing the 900 ppm limits up to 1000 ppm to mesh with the RoHS legislation. It will also likely only focus of Br and Cl from flame retardants and PVC. However, once Br or Cl is identified, it is very difficult to say with any certainty where that halogen is coming from. Therefore, electronics companies will likely restrict halogens from all sources making their life easier.

CHALLENGE #2: HALOGEN-FREE PCB's

Brominated flame retardants have been commonly used in the fabrication of printed circuit boards. There are now some halogen-free alternatives that are readily available on the market today. There is still a great deal of concern as to how these materials will affect the assembly process and since halogen-free still represents less than 10% of the laminate market[1], the industry still lacks production experience to define process and reliability windows.

The prices of the halogen-free PCB's are higher than that of their halogenated counterparts. A great deal of this cost difference is just economies of scale. However, there is also a key challenge that PCB fabricators face. The halogen-free materials tend to be more rigid. The drilling process of PCB fabrication suffers from this physical property. It is estimated that the drill life could be compromised by as much as 25%[2].

This is by no means insignificant and will likely mean the halogenated PCB's will always cost more to manufacture. That cost will probably be reflected in selling prices to the PCB assembler.

The good news is that many of the halogen-free board properties that are of concern to the assembler are as good or better than comparable halogenated boards. By comparing data sheets from a number of suppliers, it is easy to see that the halogen-free boards generally have lower CTE. They have longer T-260 and T-288 times and a higher Td temperature. These all mean that the board will be better suited for multiple reflow processes and will be able to withstand higher reflow temperatures.

From a reliability perspective, there is a significant amount of differing information relative to CAF resistance. A CAF (conductive anode filament) is an electrochemical failure in which a filament grows between inner layers of the PCB. This usually happens when some type of inner layer delamination occurs allowing space for the filament to grow. This delamination is a result of the CTE mismatch between the epoxy resin and glass fibers. Work done by Nan Ya[2] suggests that the halogen-free boards exhibit a greater resistance to CAF formation. In another study performed by CALCE[3], shows that halogen-free boards are more prone to CAF formation. This conflicting data should be very concerning for anyone producing high reliability assemblies. As more independent work becomes available, it will become more clear as to whether CAF formation is a significant concern or not.

CHALLENGE #3: HALOGEN-FREE vs. HALIDE-FREE FLUXES

By definition, a halide is any compound containing a halogen. Table salt (NaCl), for example, is a halide. By this definition, halide-free would mean a product does not contain any halogenated compounds. However, that is not exactly how the term is used for soldering fluxes. A flux that is classified as halide-free by the IPC/J-STD-004 is actually only free of ionic halides.
Classifying fluxes based on their halide content is not a new concept. IPC, as well as other standard bodies such as IEC and JIS, has classified electronic soldering fluxes for decades to determine their potential corrosiveness if left uncleaned on an electronics assembly. The classification method categorizes fluxes as L, M, or H based on their level of corrosiveness. In addition, the fluxes are rated for halide content as 0 or 1.
The difference between these terms is critical because those seeking halogen-free electronics should not assume that a halide-free flux complies with their halogen-free requirements.

The test method that the IPC recommends for halide content of fluxes is ion chromatography. The challenge with ion chromatography when used alone is that it only identifies the ionic variant. Covalently bonded halides have bonds that are more difficult to break and are not detected. In addition, there are chemicals that have similar retention times to Cl- and Br- which can result in non-halides being misidentified as halides.

Ion chromatography preceded by oxygen bomb combustion (EN 14582) is a more accurate way of testing for the presence of halogens as all forms are detected, both ionic and covalent species. This test method involves subjecting a sample of material to an oxygen bomb combustion in which the all of the organic material is burnt off at very high temperatures. Halogenated compounds are converted into fluoride, bromide or chloride ions. The remaining ash consists of the halogens and other inorganic materials and is dissolved into an absorption solution. That solution is then run through ion chromatography in which a true reading of the halide content can be determined. All halogen bonds, including any covalently bonded halides are broken through the oxygen bomb process and are detected by ion chromatography.

The simplified test method used in IPC J-STD-004 for halide content creates confusion for those attempting to assemble halogen-free electronics. It is not sufficient to simply accept terms such as "halide-free by ion chromatography" or "L0 per J-STD-004." To be halogen-free, one must require testing on the paste or flux to follow the EN14582 test method. It is expected that the J-STD-004 will eventually be updated to include this more accurate test method. However, the updating process can take a year or more.

CHALLENGE #4: ASSEMBLY PROCESS IMPLICATIONS

Without a doubt, the removal of halogens from solder pastes and fluxes will have the greatest potential impact to the board assembly process. Halogens are used in these products to aid in the soldering performance by providing powerful oxide removal capabilities to enhance wetting. Combine that with the fact that the industry is in the middle of a Pb-Free transition in which they are required to use alloys that don't wet as well as their Pb contain predecessors.

In a solder paste, halogen removal has the potential to negatively impact wetting and coalescence. This will be most evident in applications that require long profiles or those which require very small deposits of solder paste. Because of this, two relatively new defects can become more prevalent. The first is what is called "the graping phenomenon." Graping is essentially an incomplete coalescence of the solder paste leaving a rough uneven surface as seen in Figure 4.

Graping occurs when oxide forms on the outside of the printed paste deposit and the activators are not able to remove it. The smaller the deposit, the more surface area exposed to oxidation relative to total flux. Therefore, small deposits such as 0201's put a very high demand on the flux activator. Halogen-free materials will likely be more prone to graping.

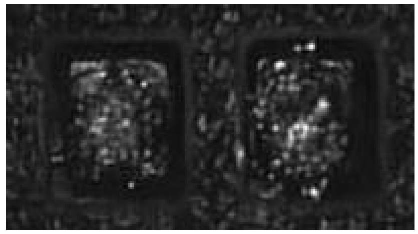

Figure 4. Incomplete Coalescence (aka graping)

The second defect likely to become more common during the halogen-free transition is the head-in-pillow defect. Head-in-pillow happens during the reflow process when using a BGA component or PWB that is prone to warping. As the BGA or PWB warps, it creates separation between the ball and the solder paste deposit. At the reflow stage, both the solder paste and the ball go molten, but are not in contact with each other. An oxide layer will build up on the molten solder making it less likely to coalesce together when they come back into contact with one another during cool down. The resultant open solder joint will look like the illustration shown in Figure 5.

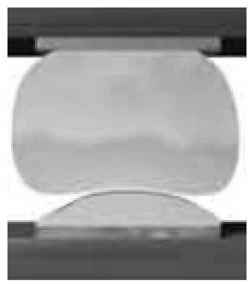

Figure 5. Head-in-Pillow Solder Joint

As a result of graping and head-in-pillow solder joints, solder paste manufacturers will have a challenge formulating halogen-free solder pastes that perform as well as the current halogen contained materials. Improving the reflow performance isn't that simple though. As the activator is modified it can adversely affect the print performance, stencil life, and shelf life. Therefore, when evaluating the halogen-free materials, it is essential to carefully examine the reflow performance, but don't skimp on the print portion of the evaluation.

SUMMARY

As the industry is moving toward promoting environmentally friendly, or "green," electronics, there continues to be a rapid minimization and/or elimination of halogenated compound use. This can have an adverse effect on material costs, product reliability, and process yields. Understanding the halogen-free material properties is key to successfully assembling more environmentally friendly electronics.

References

1. Aghazadeh M.; "Halogen Free…A Global Perspective;" IPC Halogen Free Symposium; Scottsdale, AZ; January 2008
2. Lee FY; "Halogen-Free Materials Manufacturing and Supply Chain Challenges;" IPC Halogen Free Symposium; Scottsdale, AZ; January 2008
3. Sood B; "Comparison of Halogen Free and Halogenated Printed Circuit Board Laminate Materials Subjected to Pb-free Soldering Conditions;" IPC It's Not Easy Being Green; Boston, MA, July 2008

A Halogen-free Process

Testing & Implementing

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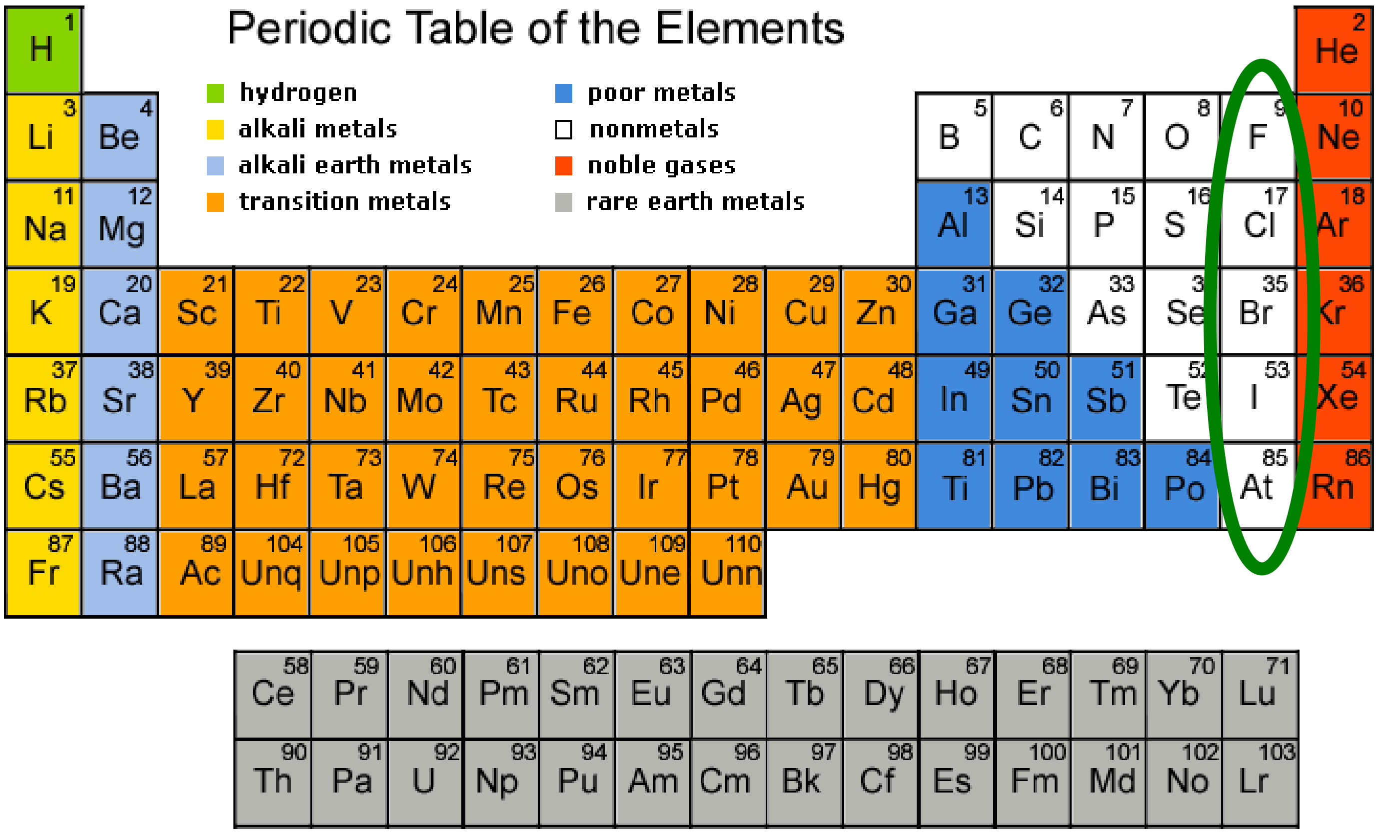
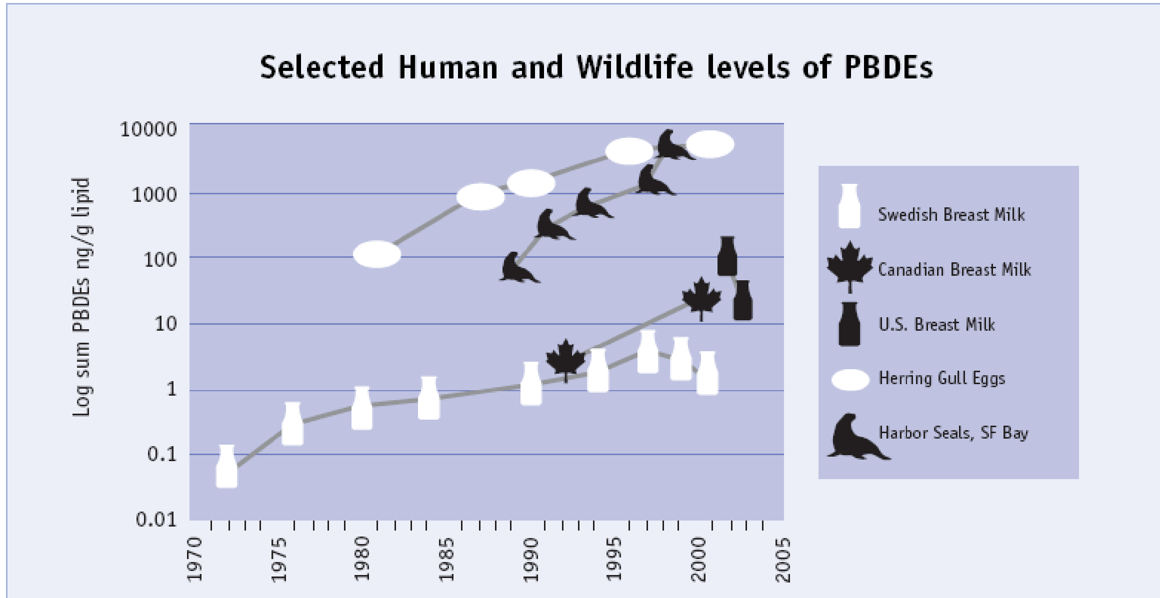
Halogens and Green Movement



Courtesy of http://www.elementsdatabase.com

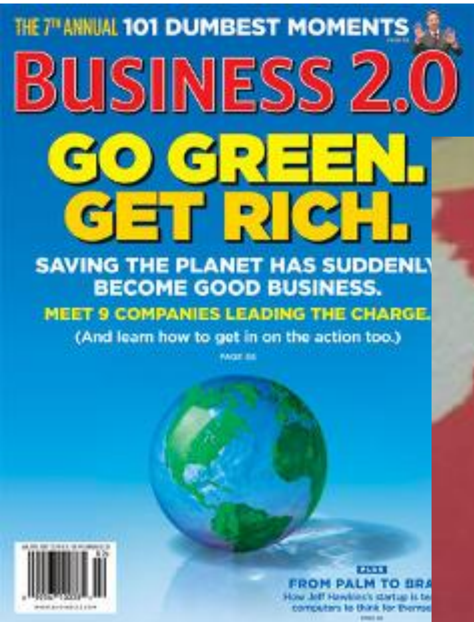
Halogen Free is an Emotional Issue

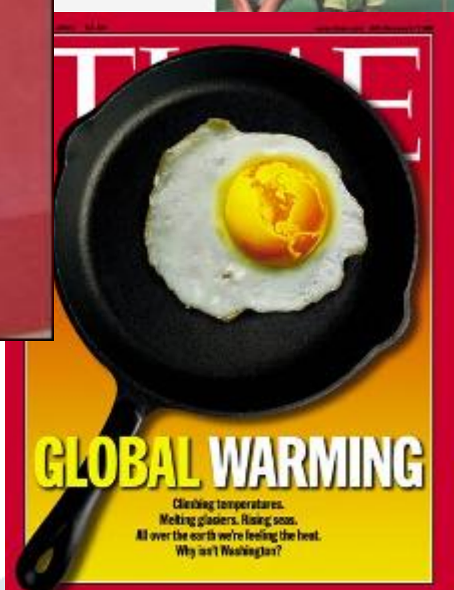
DUMPED A farmer in rural Taizhou, China, readies sweet potatoes for market beside circuit boards burned so metals could be extracted. The region has long been a major dump site for e-waste, but a crackdown by authorities has reduced illegal trade.



Source: from Clean Production Action, Hites 2004 (18); Lunder, 2003 (20).

Marketing Targets the Consumers Emotions





Key HF Implementation Challenges

- Defining Halogen-Free
- Halogen-Free PCB’s and Cables
- Halogen-Free vs. Halide-Free Fluxes
- Assembly Process Implications and New Challenges

Defining Halogen-Free: Legislation

- RoHS
  - Restricts three specific halogenated compounds
- RoHS 2
  - Likely will restrict several additional halogenated compounds
- REACH
  - Doesn’t restrict, but requires specific actions if many halogenated compounds are used (SVHC)
- California Legislation
  - Developing laws similar to EU REACH

Defining Halogen-Free: Industry Standards

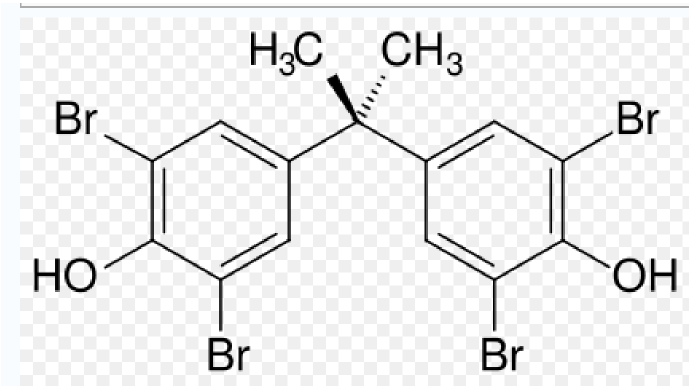
- J-STD-709 (DOA)
  - Not Yet Released
  - ~1000ppm maximum Cl
  - ~1000ppm maximum Br
  - Boards / Components
- J-STD-004b
  - Fluxes and/for solder pastes
  - <0.05% (500ppm) total halides (L0)
  - Looking at <0.09% (900ppm) total Halogens
  - Halogen Test Pending / Not mandatory
  - BS EN14582 – O2 Bomb / IC
- JPCA-ES-01-2003
  - Br <0.09wt% (900ppm)
  - Cl <0.09wt% (900ppm)
  - Base Materials
- IEC 61249-2-21
  - 900ppm maximum Cl
  - 900ppm maximum Br
  - 1500 ppm Cl+Br
- IPC-4101B
  - HDI
  - 900ppm maximum Cl
  - 900ppm maximum Br
  - 1500ppm Cl+Br

Defining Halogen-Free: HF Test Method

- Oxygen Bomb + Ion Chromatography
  - Item is burned at high temperature volatilizing organics and leaving behind only halide and inorganics in the ash
  - Ion chromatography is run on the ash providing a "true" identification of halogen content.

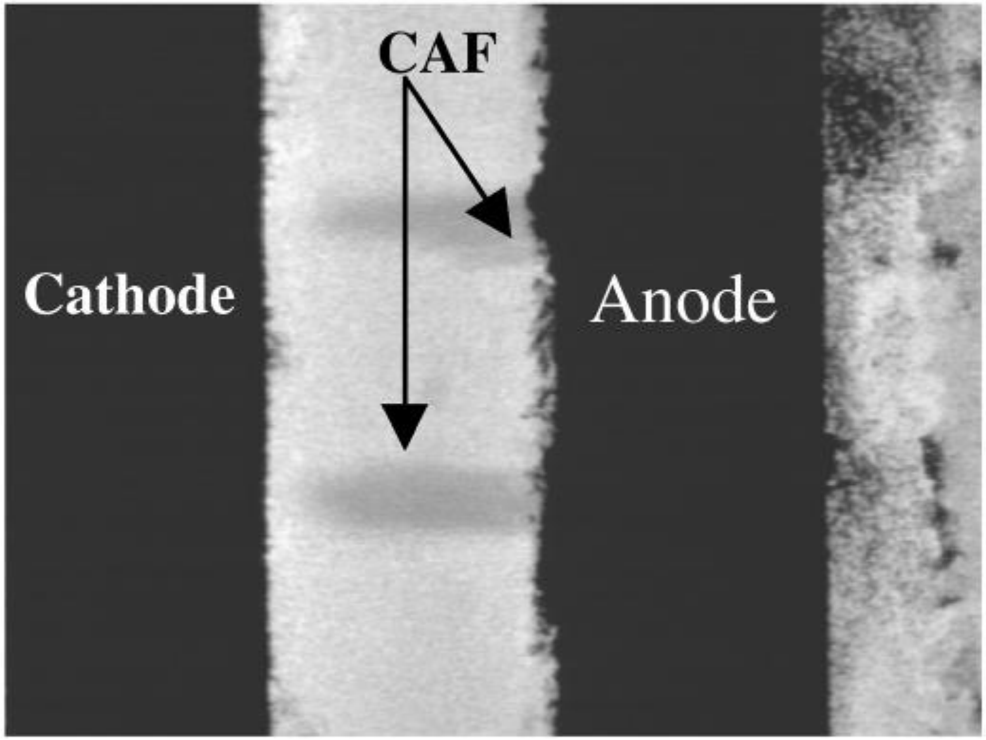
Halogen-Free PCB's and Cables: Where are the Halogens?

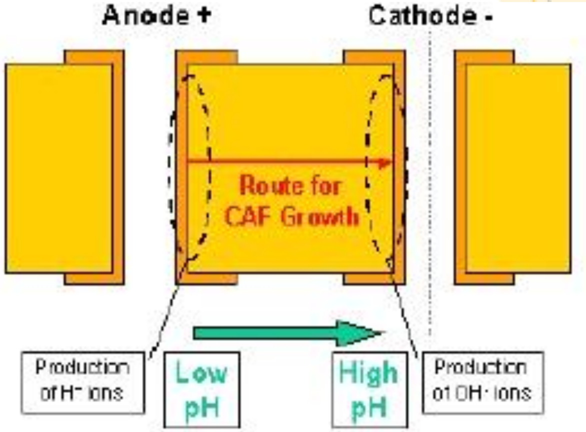
- PWBs have typically relied on brominated flame retardants, the most common one used is **Tetrabromobisphenol A** (TBBPA)



- Hence, the concern for potential listing it as a chemical for RoHS 2 or other legislation inclusion

Halogen-Free PCB's and Cables: CAF Growth Potential





Conductive anodic filament formation (CAF) is a failure mode for printed wiring boards (PWBs) in which a conductive filament forms along the epoxy resin/fiberglass interface growing from anode to cathode.

Ref: L.J. Turbini, W.R. Bent, W.J. Ready, "IMPACT OF HIGHER MELTING LEAD-FREE SOLDERS ON THE RELIABILITY OF PRINTED WIRING ASSEMBLIES", SMTA International, Chicago, IL, September 20-24, 2000.

Halogen-Free PCB’s and Cables: Not Just the Flame Retardant!

- CFR’s and BFR’s are typically the primary focus.
- PVC cable jackets – Difficult!
- Mechanical parts such as fans

Halogen-Free vs. Halide-Free: Overview

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?

Halogen-Free vs. Halide-Free: Identification based on bonds

- 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 Ionic Halides

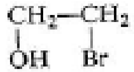
Name	*Structure*	*Melting point (°C)*
Dimethylamine hydrochloride	$(CH_3)_2NH{\cdot}HCl$	170
Diethylamine hydrochloride	$(C_2H_5)_2NH{\cdot}HCl$	227
Diethylamine hydrobromide	$(C_2H_5)_2NH{\cdot}HBr$	218
Aniline hydrochloride	$C_6H_5NH_2{\cdot}HCl$	196
Pyridine hydrobromide	$C_5H_5N{\cdot}HBr$	200d
Pyridine hydrochloride	$C_5H_5N{\cdot}HCl$	145
Ethanolamine hydrochloride	$H_2NCH_2CH_2OH{\cdot}HCl$	84
Diethanolamine hydrochloride	$(HOCH_2CH_2)_2NH{\cdot}HCl$	liquid
Triethanolamine hydrochloride	$(HOCH_2CH_2)_3N{\cdot}HCl$	177

Some Covalently Bonded Halides

Benzyl chloride

$H_2C{=}CH{-}CH_2Br$

Allyl bromide
3-Bromo-1-propene



Ethylene bromohydrin
2-Bromoethanol

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

Halogen-Free vs. Halide-Free: Is Halogen-Free More Reliable?

- Organic acids can cause corrosion and dendritic growth
  - Entrapment of residual activator is crucial following reflow
- Higher mass percentage of halide free activator necessary
  - Less room for other flux constituents (i.e. rheology)

Dendrites on SIR coupon after processing with halide free flux

Some Halide Free Activators

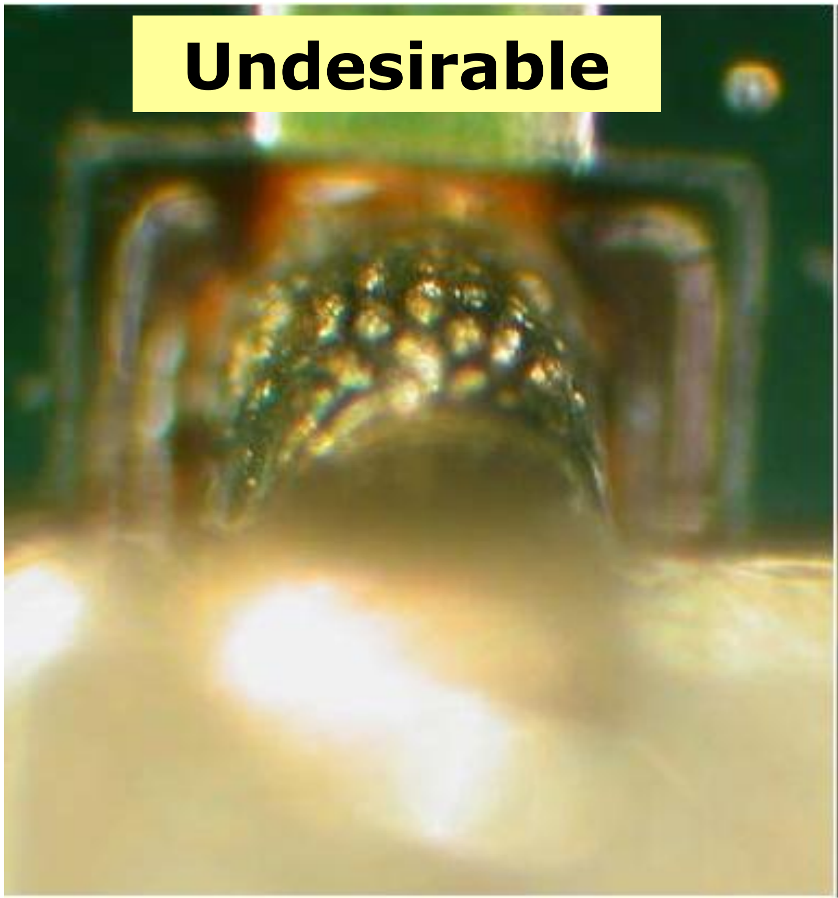
Name	*Structure*	*Melting point (°C)*	*pK1*	*pK2*	*Solubility in 100 parts water*
Citric acid	$HOOCCH_2C(OH)(COOH)CH_2COOH$	152	3.128	4.761	59
Fumaric acid	$HOOCCH{=}CHCOOH$	299d	3.1	4.6	0.6
Tartaric acid	$HOOCCH(OH)CH(OH)COOH$	210	3.22	4.81	139
Glutamic acid	$HOOCCH_2CH_2CH(NH)_2COOH$	200s	2.162(+1)	4.272(0)	0.8
Malic acid	$HOOCCH_2CH(OH)COOH$	131			55.8
Phthalic acid	C_6H_4-1,2-$(COOH)_2$	210d	2.95	5.408	0.6
Levulinic acid	$CH_3COCH_2CH_2COOH$	30			∞
Stearic acid	$CH_3(CH_2)_{16}COOH$	67			Slightly
Benzoic acid	C_6H_5COOH	122	4.204		0.29

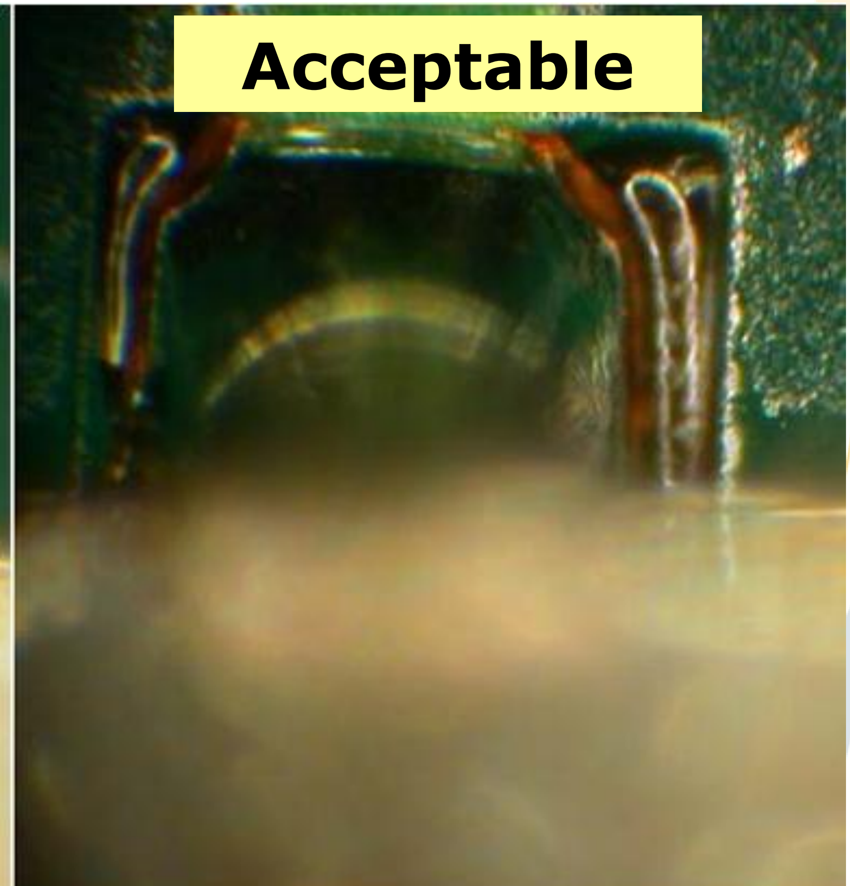
Ref: Lee, NC; *Reflow Soldering Processes and Troubleshooting: SMT, BGA, and Flip Chip Technologies*; 2004

Halogen-Free vs. Halide-Free: Testing For Halogen Content

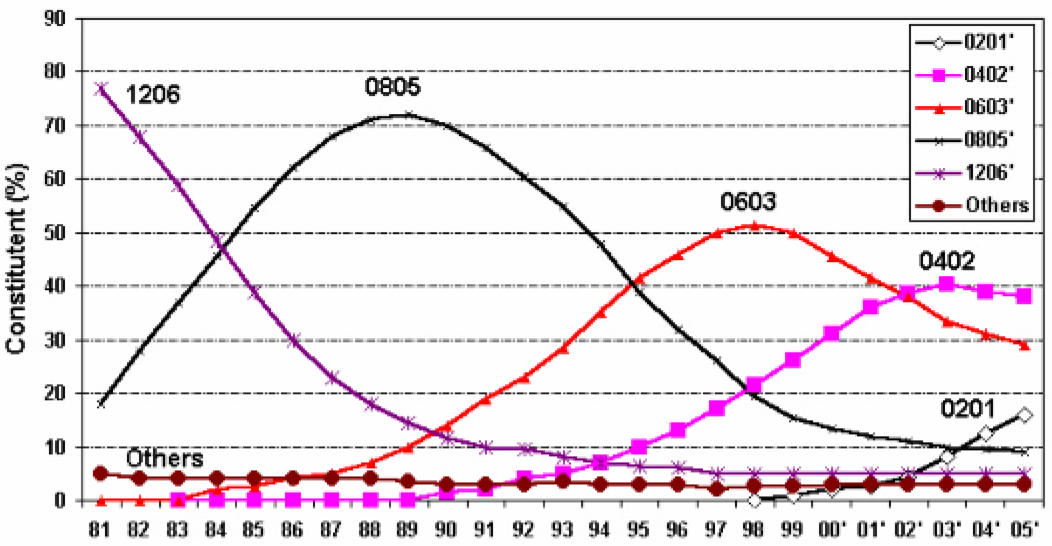
- Silver Chromate Paper Test (qualitative)
  - Changes color in the presence of Cl^- or Br^-
  - Does not detect Covalently bonded halides
- Titration (quantitative)
  - Solution titrated to endpoint and Cl- equivalent is calculated
  - Only detects ionic halides and many chemicals can cause false positive 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 inorganic compounds in the ash
  - Ion chromatography is run on the ash providing a "true" identification of halide content.

HF Assembly Implications: Graping

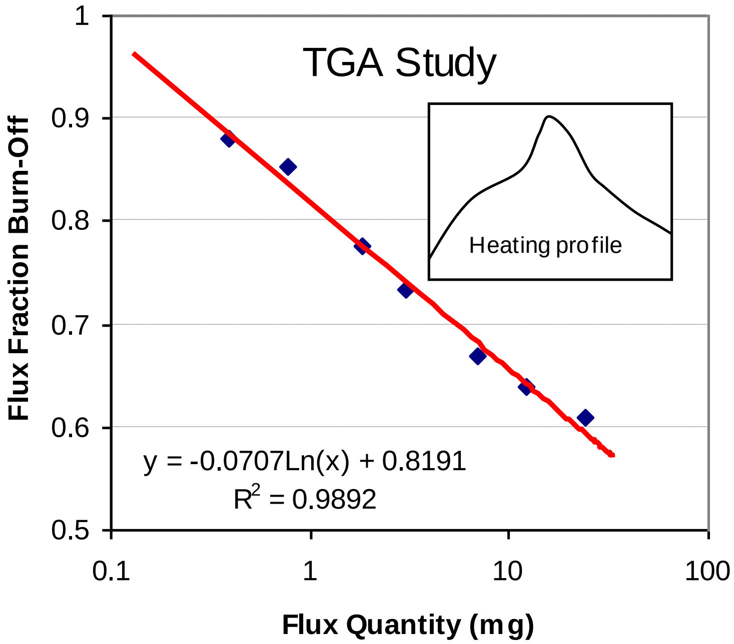




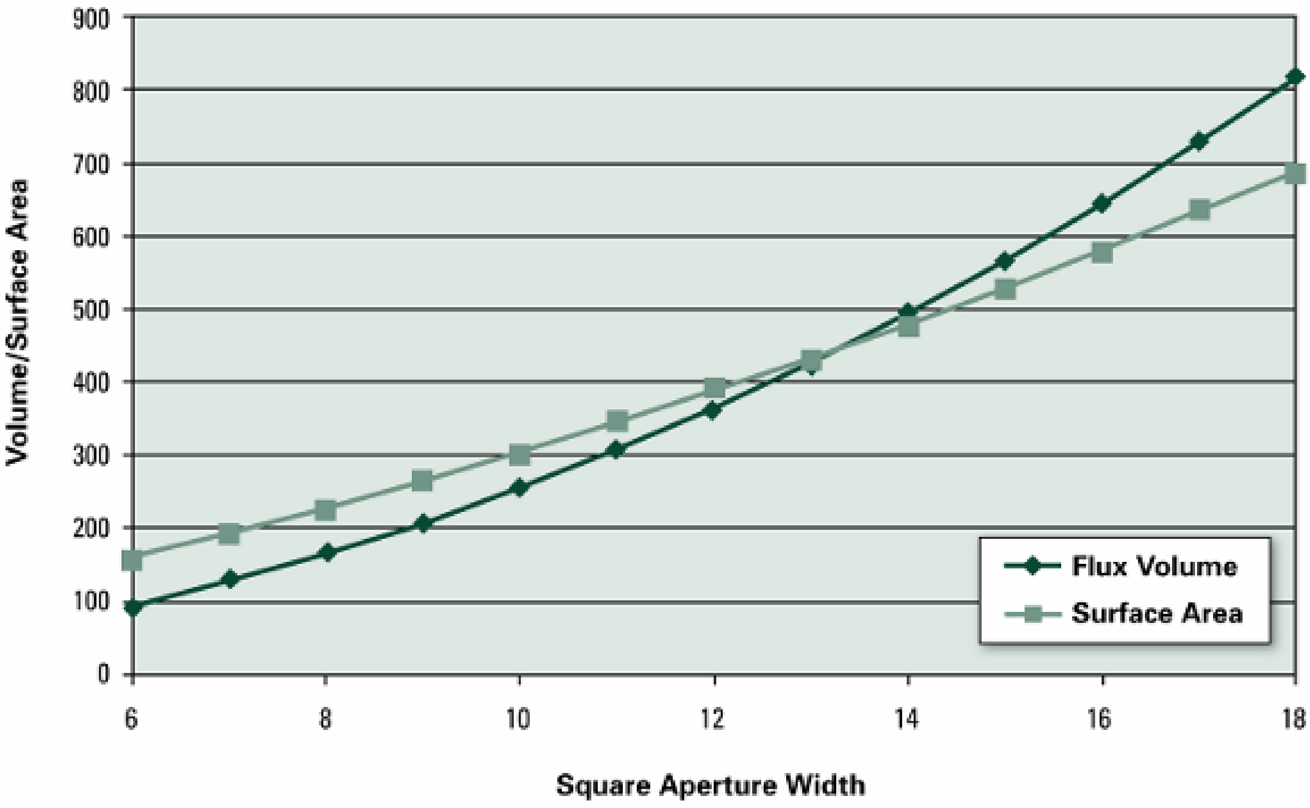
HF Assembly Implications: Graping a result of Miniaturization



Flux Fraction Burn-Off and Flux Volume
(reflow profile with a peak temperature of 230°C)



HF Assembly Implications: Graping and Fluxing Capacity



$V_{square} = S^2 \times h \times 50\%$

$SA_{square} = 4(s \times h) + s^2$

Oxidation during the reflow process occurs only on the surface of the paste deposit.

HF Assembly Implications: Head-in-Pillow Definition

- What is head-in-pillow?
  - A defect in which both the solder paste and the BGA ball reflow but they do not coalesce together.
- How does it happen?
  - Component warps during preheat and soak of profile
  - Paste and ball separate prior to melting
  - Paste and ball coalesce separately
  - Oxide layer forms on surface of molten solder
  - Component warps back during cool down but it is already solidified or oxide layer is too thick for paste and ball to coalesce together.

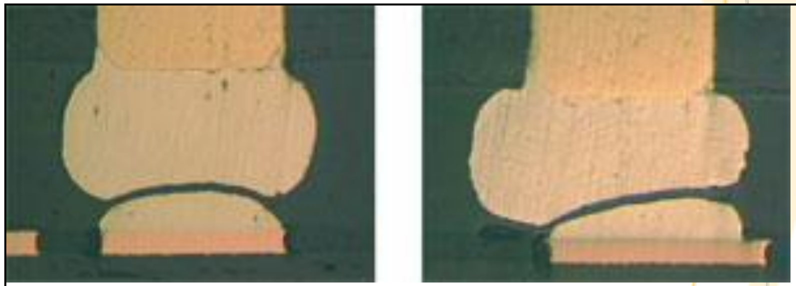
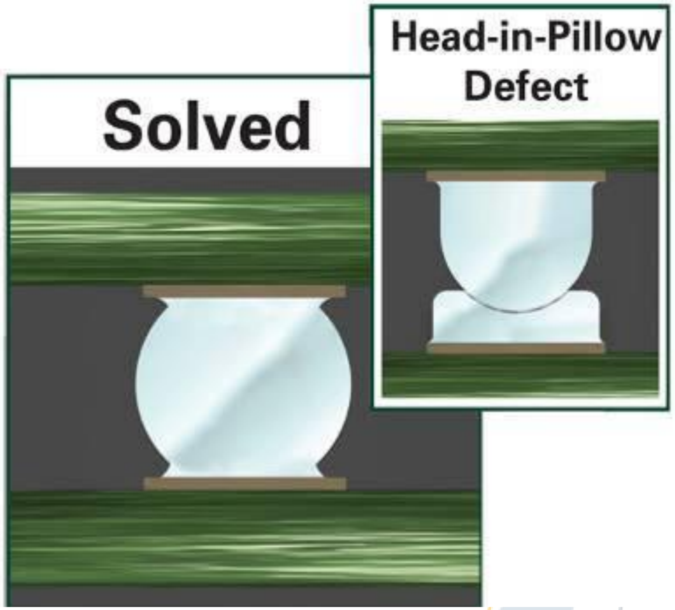


Image Source: http://www.electronicsincanada.com/index.php/BGA-Socket-Processing.html

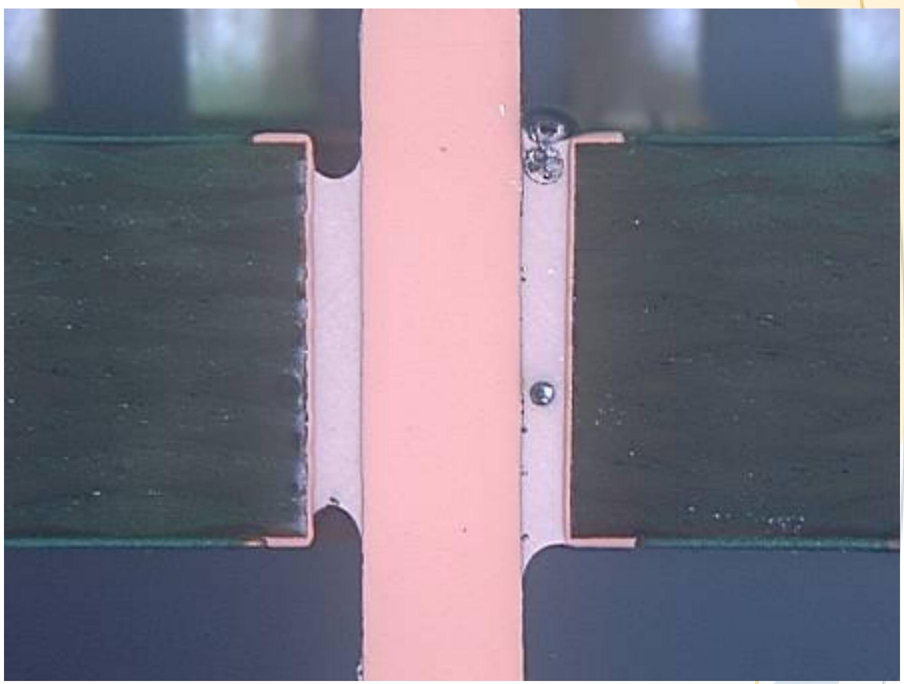
HF Assembly Implications: HIP Reduction in an HF Era

- Component and PCB Considerations:
  - Implications of HF materials on warp
- Solder Paste Options:
  - Excellent activity (halogen contained) or new oxidation barriers (HF) critical
- Other Considerations (not HF Related):
  - Reflow profiles
  - Solder paste slump and printing
  - Paste alloy and ball alloy mismatch
  - Flux dipping and solder paste



HF Assembly Implications: Wave Soldering

- Hole Fill on Thick Boards
  - Already a challenge with Pb-Free; eliminating halogens makes this more challenging
  - Higher solids content materials possible
- Testing Halogen Content of the Residue
  - Low solids fluxes do not have much residue
  - 0.5 to 1.0 g of residue needed to run oxygen bomb test



Halogen-Free Summary

- Push toward Halogen-Free is environmental first and legislative second
- HF options are available for boards and components.
  - HF typically higher cost
  - HF often equivalent or better in performance
- HF Soldering Materials present big challenges for the assembly process
- Know what the halogen content is of the material you are using.
- Ask for Halogen content by Oxygen bomb method.

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Mario Scalzo is a Senior Technical Support Engineer for Indium Corporation and is located at their global headquarters, in Clinton, NY.

Mario supports all of Indium's current product lines, with emphasis on advanced surface mount (SMT) problem solving. He has worked closely with the Asian & North American regional teams on several customer projects, including a long-term assignment with Indium's Asia-Pacific Operations in Singapore.

Mario joined Indium in 2000 as a Quality Flux Technician, and spent 2 years as a Quality Engineer. This troubleshooting experience has given him a depth-of-knowledge beyond the normal product training and taught him how to anticipate customer concerns.

Mario is active in several industry organizations, including the Surface Mount Technology Association (SMTA) and the American Chemical Society (ACS). He has presented at several conferences nationally and internationally.

Mario has a bachelor's in chemistry from Saint Anselm College, with a certificate from the American Chemical Society for Professional Education and minors in Physics and Fine Art. He is an SMTA-certified SMT Process Engineer, an IPC A-600/610 Certified Inspection Specialist and has earned his Six Sigma Black Belt from Dartmouth College's Thayer School of Engineering.