Correlation of Sir, Halide/Halogen, and Copper Mirror Tests

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ABSTRACT
With the advent of RoHS and WEEE and the concern of some companies to eliminate halogen-containing compounds from their products, it is vital to have an understanding of halogen compounds and how to detect them. Halogens are a series of nonmetal elements from Group 17 in the periodic table. These elements are fluorine, chlorine, bromine, iodine, and astatine. A halide ion is a halogen atom bearing a negative charge. Halides can be part of the flux activator system that aid in oxide removal in either a solder paste or flux for wave soldering.

Halide content can be determined by qualitative or quantitative tests. The silver chromate method is a quick and inexpensive qualitative test method used to determine halides in a flux. This test is performed by placing the flux on silver chromate test paper. The halides in the flux react with the silver chromate and produce a characteristic color change on the test paper. A quantitative measure of halides is done by ion chromatography. This quantitative test is quite expensive and time consuming.

Test methods have also been developed to determine the activity of the fluxes in solder paste and wave solder. Most commonly used are the copper mirror and SIR (surface insulation resistance) tests. Copper mirror testing determines the activity of the flux by the effect the flux has on bright copper mirror films which have been vacuum deposited on clear glass. Based on J-STD 004B, the flux can be classified based on its activity levels as determined by this test.

SIR is an electrical test that measures a change over time in the electrical current between electrodes on the surface of a PCB. It is performed at high temperature and humidity levels, typically 85°C and 85% RH. Ionic residue, left on the PCB after reflow, from flux activators may cause low (i.e. poor) SIR readings.

This paper will discuss the theories behind these test techniques, their differences, and how the presence of halides in the flux activators will affect the SIR and copper mirror results

Key words: Halogen, halide, SIR, copper mirror, flux, silver chromate, ion chromatography

Halides/Halogens

It is important to clarify the distinction between halogens and halides. A halogen is any one of the elements from Group 17 IUPAC Style (formerly: VII, VIIA) of the periodic table, comprising fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). A halide is a binary compound, of which one part is a halogen atom and the other part is an element or radical that is less electronegative than the halogen that produces a fluoride, chloride, bromide, iodide, or astatide compound. The halide bond is ionic. A halide ion is a halogen atom bearing a negative charge.

These differences are important, because a material or residue can be halide-free, but still have halogen compounds. This is possible if the halogen bond is covalent. For example, suppose that a flux residue on an assembled electronics component is tested for halide content using the silver chromate test. This test is conducted so that the resulting electronics product can be declared "halogen-free." The silver chromate test is popular because it is fast and inexpensive. The test reveals that there are no halides in the residue. However, the test cannot determine if there are covalently bonded halogen atoms in the residue. This determination can only be accomplished by using the more expensive and laborious oxygen bomb and ion chromatography techniques.

Unfortunately, some misinformed people will use the silver chromate test and declare a product to be halogen-free when it is not.

Silver Chromate Testing

The silver chromate test is a quick, inexpensive, qualitative test to determine if halides are present in a flux. A representative flux sample is placed on a piece of test paper for 1 to 2 minutes. The test paper is evaluated for a color change. A yellowish color on the test paper designates the presence of chlorides or bromines. Figure 1shows an example of the paper before the flux is added. Figure 2 shows the color change after exposure to a halide. Amines, cyanides and isocyanates also cause test failures. Silver chromate paper does not specify a quantitative amount of halogens present.

Figure 1: Example of a silver chromate paper untreated

Figure 2: Example of a silver chromate color change

Oxygen Bomb and Ion Chromatography

Alone, ion chromatography only determines ionic halide content quantitatively, covalently bonded halogens are not detected. Because the covalent bonds must be broken in order to be analyzed with ion chromatography, oxygen bomb combustion should be used prior to ion chromatography, providing a more accurate halide content. By association, the quantitative halogen content can be determined.

Oxygen bomb combustion burns off organic materials at a very high temperature and breaks the covalent bonds of all halogens. The remaining ash, containing ionic halides and inorganic materials, is dissolved in an aqueous solution and run through the ion chromatograph.

Ion chromatography is a form of liquid chromatography where the retention is controlled by ionic interactions between ions of the solute and the stationary phase. The ions separate based on ionic interactions within the columns. Several standards are also run. The retention times from the chromatograms are reported. These retention times will be used to calculate the amount of halides in the sample of flux.

Copper Mirror Testing

The copper mirror test is designed to determine the activity of the flux by the amount of copper removed from the vacuum-deposited copper mirror films on glass. The copper metal is approximately 50nm thick and the finished mirror permits 10+/-5% transmission of normal incident light of a nominal wave length of 500nm, before the copper mirror test.

A representative test sample of liquid flux, paste flux, or solder paste is deposited on the copper mirror next to a control sample of standard rosin flux class A, type II, grade WW of federal specification LLL-R-626 diluted in 2-propanol. The copper mirror, with the samples deposited, is placed into a temperature- and humidity-controlled chamber for 24 hours before the sample is evaluated. The chamber is set at 50% +/-5% and a temperature of 23°C +/-3°C. Evaluation is per J-STD-004.

From the copper mirror test results, the corrosive properties of the flux are determined based on the amount of the copper film removed. There are three levels of flux activity classification: low (L), moderate (M), and high (H). Low classified flux shows no removal of the copper film. The control sample will fall into the low category. Figure 3 shows a copper mirror with a low activity.

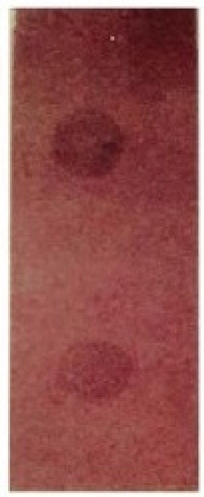

Figure 3: Copper mirror low activity level (IPC-004B-3-1)

With breakthrough in the copper film of at least than 50%, and removal of copper around the perimeter, Figure 3 shows an example of moderate activity level (classification M).

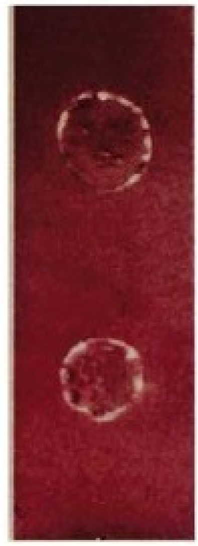

Figure 4: Copper mirror moderate activity level (IPC-004B-3-1)

When the copper film is completely removed, or shows>50% breakthrough, the flux is classified as H. Figure 5 shows an example of the high activity level

Figure 5: Copper mirror high flux activity level (IPC-004B-3-1)

Along with the flux corrosive properties, the J.-STD-004 flux identification system also takes into consideration the halide content. The classification designates whether the flux composition is: rosin-based (RO), resins-based (RE), organic acid-based (OR), or inorganic-based (IN). The classification is further broken down into the percent of halides (by weight). A 0 or 1 indicates the absence or presence of halides, respectively. Oxygen bomb followed by ion chromatography is the quantitative measure of halides. The complete flux identification systems will designate the flux composition, activity levels and halide content: ROL0, ROL1, ROM1, ROM0, ROH0, ROH1, etc. For example, ROL1 would indicate a rosin-based flux with a low flux activity and the presence of halides.

Surface Insulation Resistance

Surface insulation resistance, SIR, is an electrical test that characterizes fluxes by determining the degradation of electrical insulation resistance of board specimens after exposure to heat and humidity. It measures a change in the current over time between electrodes on the surface of a PCB. SIR testing determines the long-term electrical reliability of flux residues, specifically conductive and corrosive properties. The testing is performed at high temperature and humidity levels, typically 40°C and 90% RH, per J-STD-004. The paste or flux is printed and reflowed on a test board as seen in Figure 6.

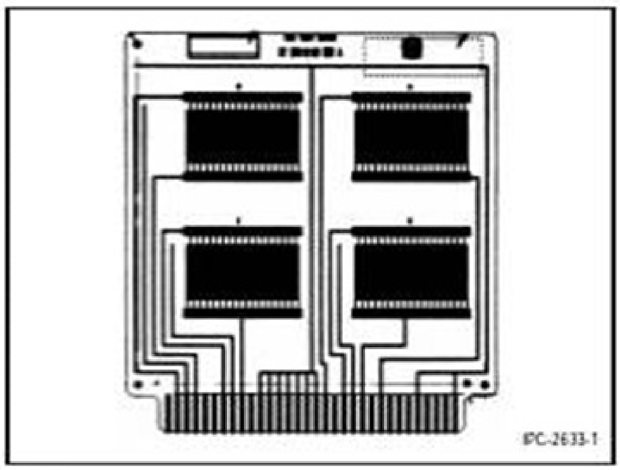

Figure 6: Test Pattern from IPC-B-24

The SIR board remains in a controlled temperature and humidity chamber where a voltage (5 volts) is applied to the board electrical contacts. The measurements are taken every 20 minutes for 168 hours. For a “pass”, the resistance data should be greater than 1E8 ohms for all measurements. The board is also visually evaluated for corrosiveness by looking for the formation of dendrites. An example of dendrites can be seen in Figure 7. Dendrites will form as the flux residue corrodes the metal, forming a positively charged ion. The metal ions migrate towards the negatively charged trace, ultimately resulting in lower SIR readings.

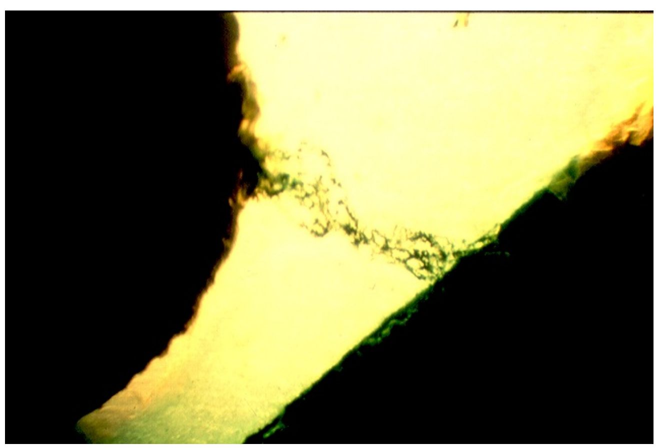

Figure 7: Example of a dendrite

Copper Mirror Results vs. SIR Results

Both copper mirror testing and SIR testing provide information about the corrosive properties of flux residues. Cleaning of flux residues prior to SIR testing is based on flux type, low will be in the no-clean state, moderate can be cleaned or in the no-clean state, and high must always be cleaned.

Figure 8 shows a flux classification of low, no breakthrough on the copper mirror, and no dendritic growth and a resistance of $1x10^8$ ohms for SIR (the flux residues were not cleaned prior to testing).

Figure 8: Example of low activity SIR

With moderate flux activity, less than 50% of the copper mirror area will be removed. Minor corrosion is present and acceptable. As in the low activity, SIR results show no evidence of dendritic growth and all resistance measurements are above 1E8 ohms, shown in figure 9. The flux residues were cleaned prior to testing.

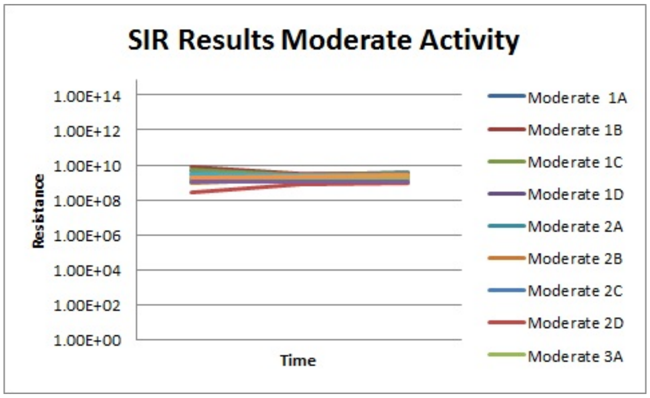

Figure 9: Example of moderate activity SIR

High flux activity is designated when more than 50% of the test area of the copper mirror is removed. Again, SIR results showed no evidence of dendritic growth and all the resistance measurements are above1E8 ohms, shown in figure 10. The flux residues were not cleaned prior to testing.

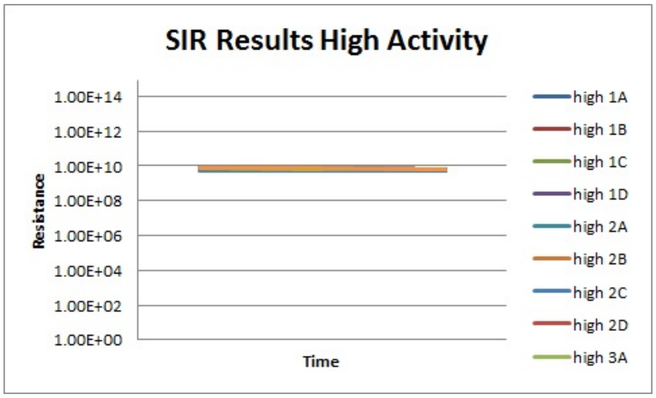

Figure 10: Example of high activity SIR

Due to the nature of high activity residues, the residues need to be cleaned before the being subjected to SIR testing.

Conclusion

SIR testing determines the long-term reliability of a PWB with flux residues in a humid environment, whereas copper mirror testing is a short-term measurement of flux activity. Both tests used together show how the flux activity affects SIR. Copper mirror testing seems to be more sensitive to higher activity based on the amount of copper removed from the mirror. The SIR corrosiveness can be seen in the dendritic growth; however, if no dendrites form, there is no change in the resistance values. The higher activity fluxes typically have a higher SIR resistance value as they are cleaned before testing.

Acknowledgement
Portions of this paper were presented at SMTAI 2011, Fort Worth, TX.

Appendix: J-STD-004A vs -004B
In December 2008 IPC J-STD-004A was superseded by J-STD-004B[i]. J-STD-004B is likely more appropriate for modern high density electronics. Nash and Bastow discussed SIR and the differences between these two standards at APEX 2010[ii]. A summary chart of the differences is below. See their paper for details

		SIR	
	Parameters	J-STD-004A	J-STD-004B
Temp. & Humidity Stress	Temp/Humidity	85C, 85%RH, 168 hours	40C, 90%RH, 168 hours
	Stress Bias	45 - 50 Volts DC	5V (8 mil spacing) or 25V/mm
	Pre-Bias Stabilization Period	3 hours at T&H	1 hour at T&H
	Measurement Bias	-100 Volts DC	5V (8 mil spacing) or 25V/mm
	Time of Readings	24, 96, 168 hours	At least once every 20 minutes
Criteria	Control	>1E9 Ohms, 96 hours to end	>1E9 Ohms, 96 hours to end
	SIR data	>1E8 Ohms @ 96, 168 hours	>1E8 Ohms @ All Measurments
	Dendrites/Corrosion	None > 25% of spacing	None > 20% of spacing

References

[i] http://www.ipc.org/TOC/IPC-J-STD-004B.pdf, "IPC J-STD-004 standard, Requirements for soldering fluxes, 2008."

[ii] Nash, C, Bastow, E, "Understanding SIR," APEX 2010, Las Vegas, NV.

Correlation of SIR, Halide/Halogen, and Copper Mirror Tests

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With Thanks to Nicole Palma

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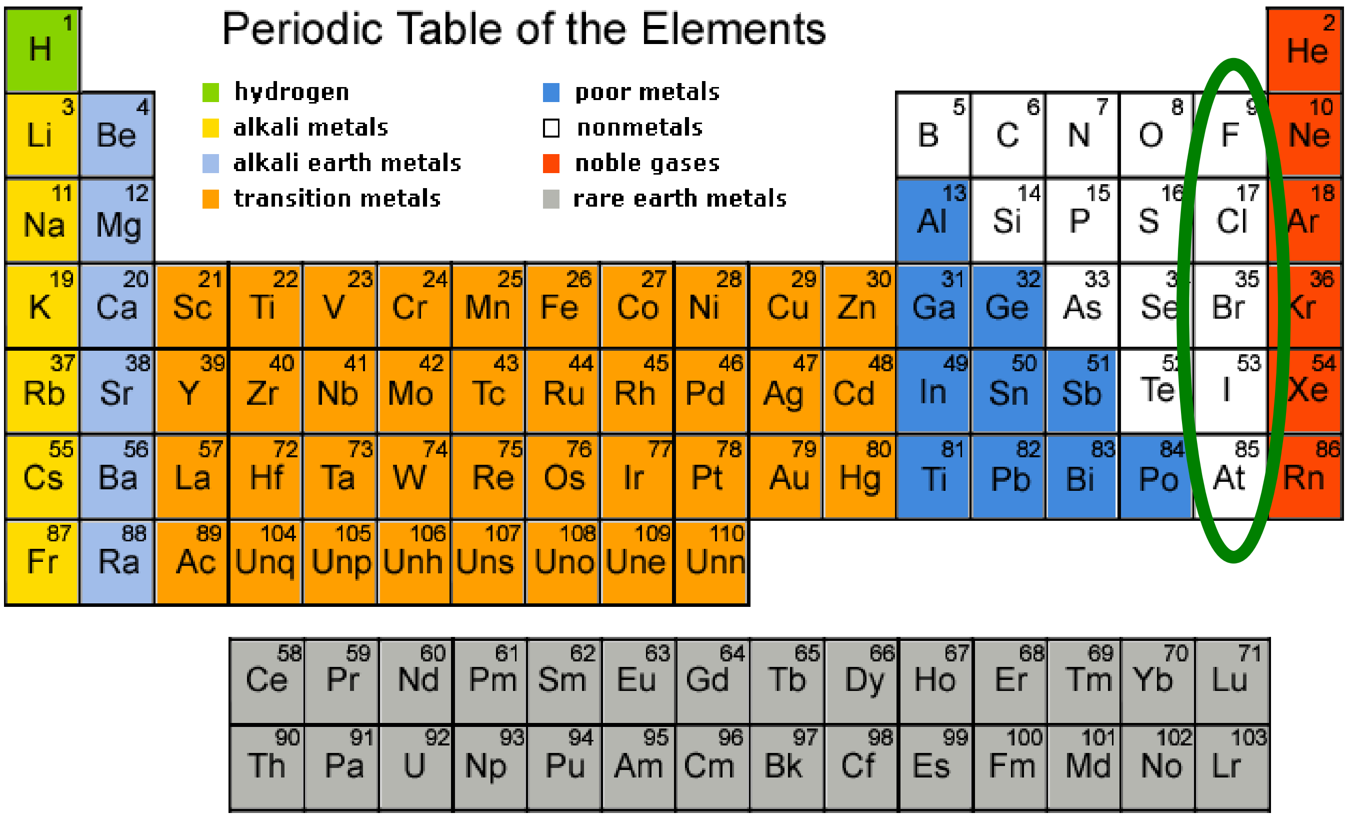
IPC APEX 2012

Overview

- Halogens and Halides
- Copper Mirror
- SIR
- Copper Mirror and SIR Correlation
- Conclusions

Halides/Halogens



Courtesy of http://www.elementsdatabase.com

Green Evolution: Current Need vs. Long-Term Effect

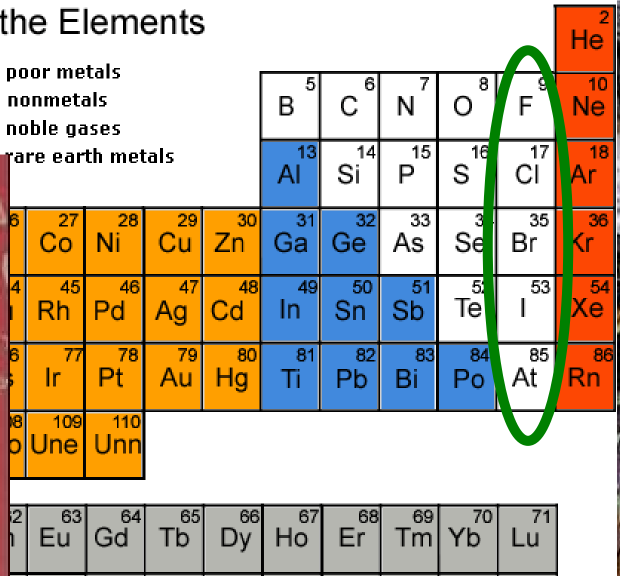
- In 1948, Paul Hermann Müller was awarded the Nobel Prize for developing DDT that virtually eradicated malaria and yellow fever from most developed countries
- In 1962, Rachel Carson's *Silent Spring* began a widespread ban on DDT use

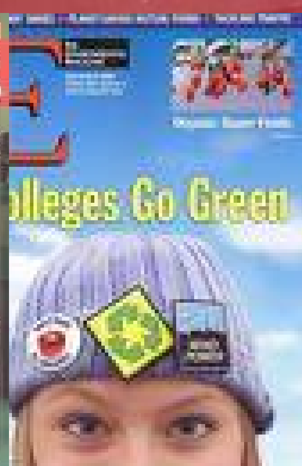
From Nobel Prize

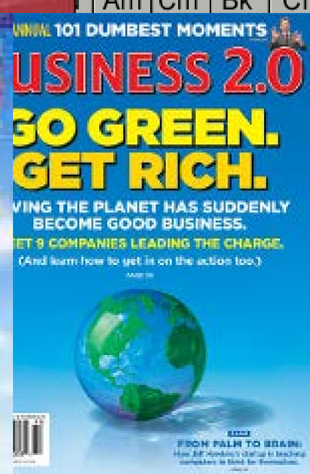
to

EPA Ban

Halogens and Green Movement



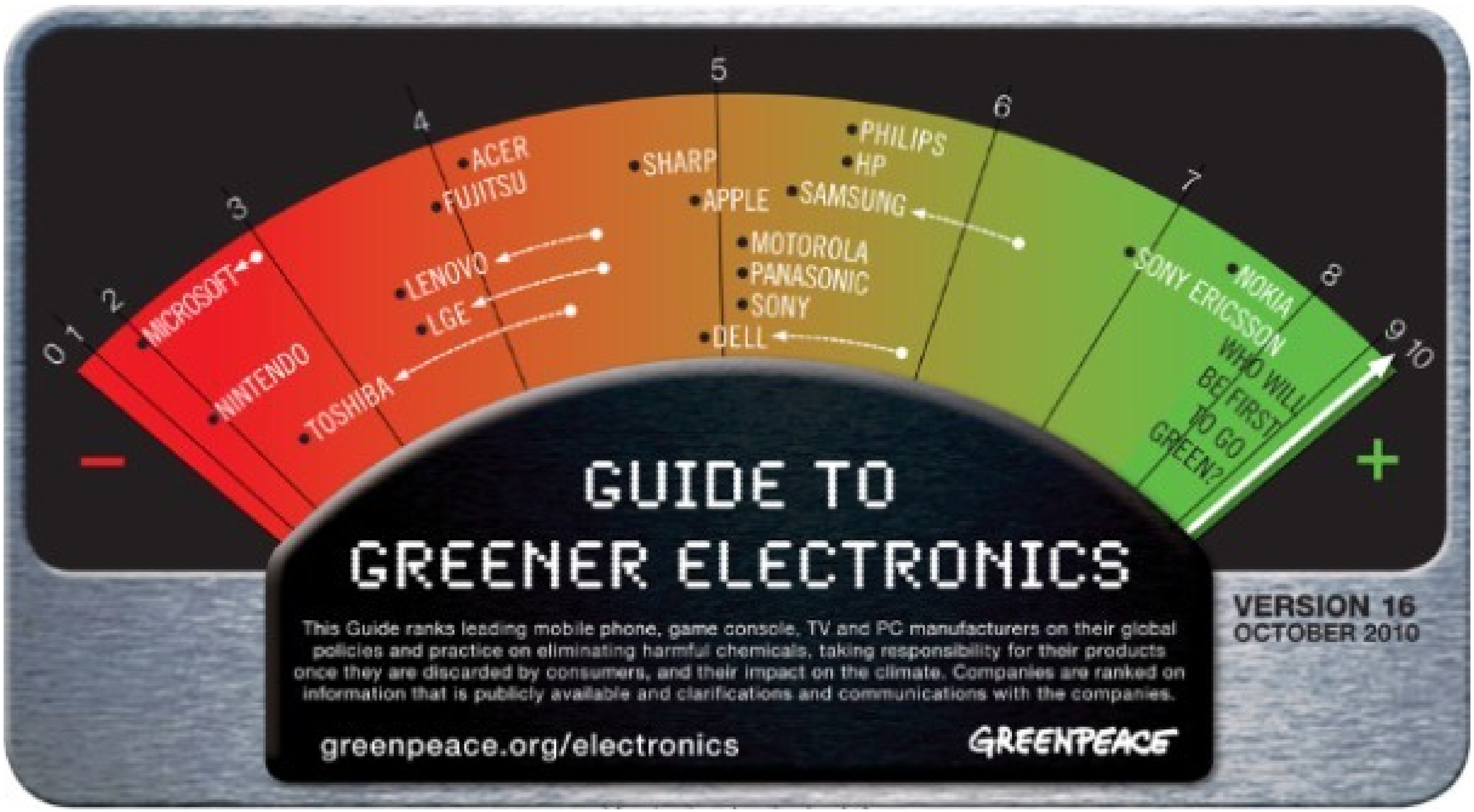




ED A farmer in rural Taizhou, China, readies sweet potatoes for market beside circu
rds burned so metals could be extracted. The region has long been a major dump si
-waste, but a crackdown by authorities has reduced illegal trade.

Courtesy of http://www.elementsdatabase.com

Greenpeace Greener Guide



Burning Halogens can produce toxic gases

Burning Insulation
From Wires

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Halogens in Electronics

- PCB Laminate Materials
  - HF alternatives are more expensive to manufacture and may be more sensitive in high reliability applications
- Components
  - HF components are being developed, but can be challenging in complex IC's
- PVC (primarily in cables)
  - HF alternatives are often more brittle and more costly
- **Soldering Materials**
  - **HF materials could suffer in soldering performance (HIP, graping, long profiles)**

Halogen-Free vs. Halide-Free

HALOGEN FREE

- It does not contain Cl, Br, F, I, or At
- 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

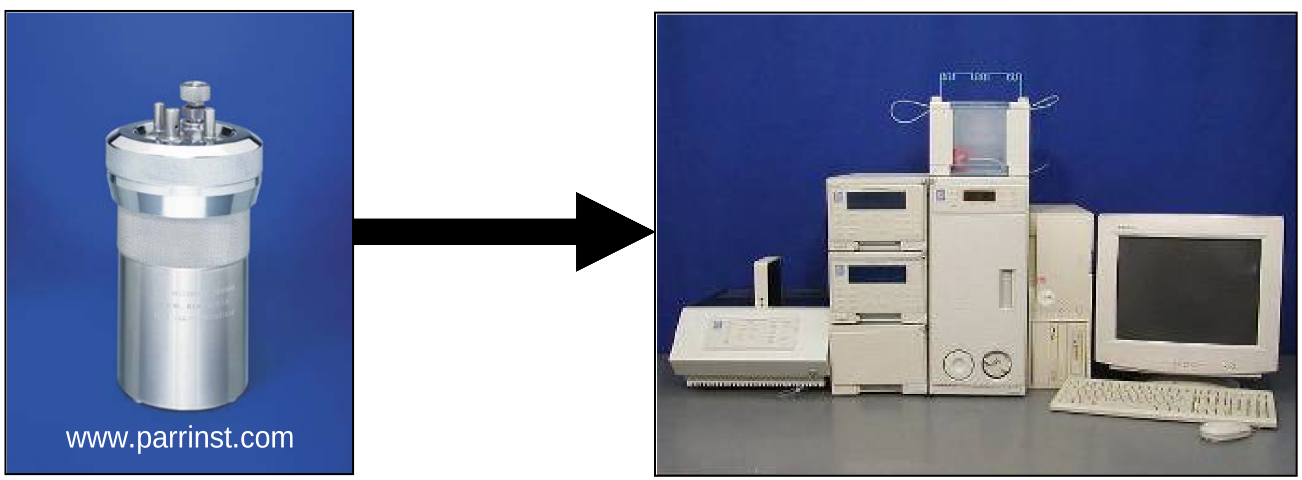
- Should be "halide ion-free" as it is defined in electronics as not containing "ionic halides".
- Concern is reliability
  - Corrosion
  - Dendritic growth
- Activators in flux
- Issues:
  - Is halide-free actually more reliable than halide-contained?
  - How do you test fluxes for halide content?

Silver Chromate Testing

- Quick, inexpensive, qualitative
- Visual inspection for a color change

Oxygen Bomb and Ion Chromatography

- Quantitative halogen content
- Must be used together



Testing for Halogen Content

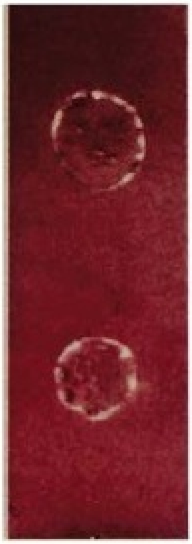
- **Silver Chromate Paper Test (qualitative)**
  - Changes color in the presence of Cl^- or Br^-
  - Does not detect covalently bonded halides
- **Titration (quantitative)**
  - Solution titrated to endpoint and Cl- equivalent is calculated
  - Only detects ionic halides and many chemicals can cause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

Copper Mirror Testing

- Activity level of un-reflowed flux determined
- Low

Copper Mirror Testing

- Activity level of un-reflowed flux determined
- Moderate

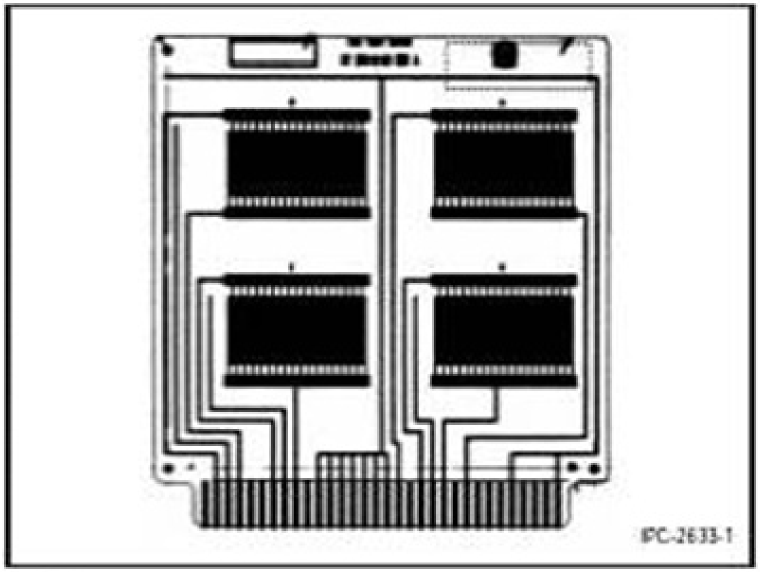


Copper Mirror Testing

- Activity level of un-reflowed flux determined
- High

Surface Insulation Resistance (SIR)

- Measurement of change in current, over time in high temperature and humidity
- Long-term electrical reliability of flux residues
- Reflowed flux residue



SIR 004A vs. 004B

Thanks to Eric Bastow and Chris Nash

J-STD-004A vs. -004B

		SIR	
Parameters		J-STD-004A	J-STD-004B
Temp. & Humidity Stress	Temp/Humidity	85C, 85%RH, 168 hours	40C, 90%RH, 168 hours
	Stress Bias	45 - 50 Volts DC	5V (8 mil spacing) or 25V/mm
	Pre-Bias Stabilization Period	3 hours at T&H	1 hour at T&H
	Measurement Bias	-100 Volts DC	5V (8 mil spacing) or 25V/mm
	Time of Readings	24, 96, 168 hours	At least once every 20 minutes
Criteria	Control	>1E9 Ohms, 96 hours to end	>1E9 Ohms, 96 hours to end
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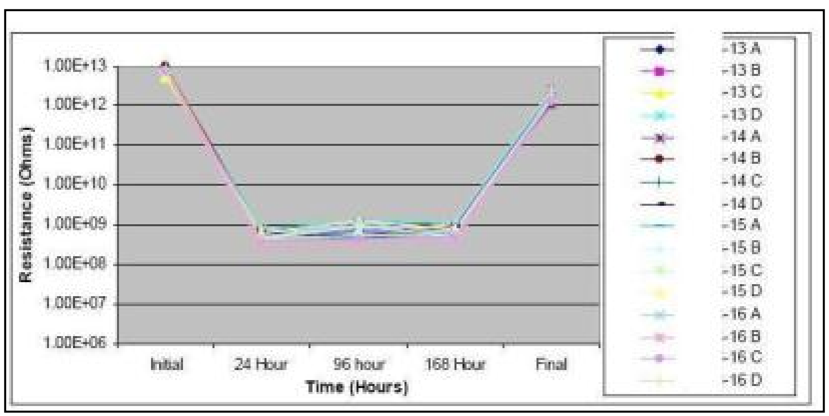
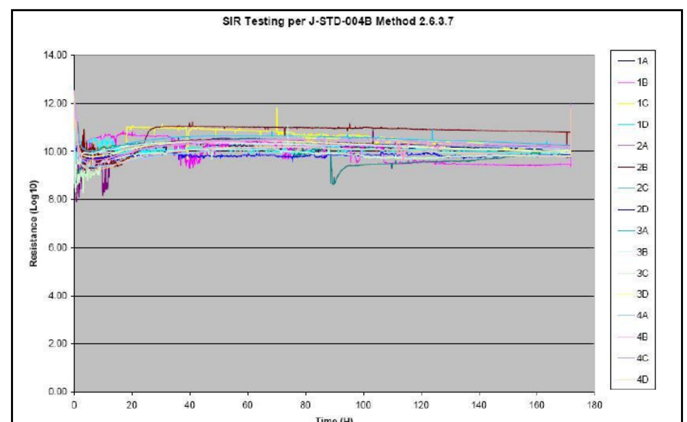
	Dendrites/Corrosion	None > 25% of spacing	None > 20% of spacing





SIR Change Impacts Materials

- Coupon preparation becomes more critical with -004B
- In general, solder pastes that pass -004A will also pass -004B
- Most wave fluxes have issues (see below)

	Anticipated SIR Performance	
	004A (85C)	004B (40C)
Low Rosin/Rosin Free	Better	Worse
Rosin Containing	Worse	Better

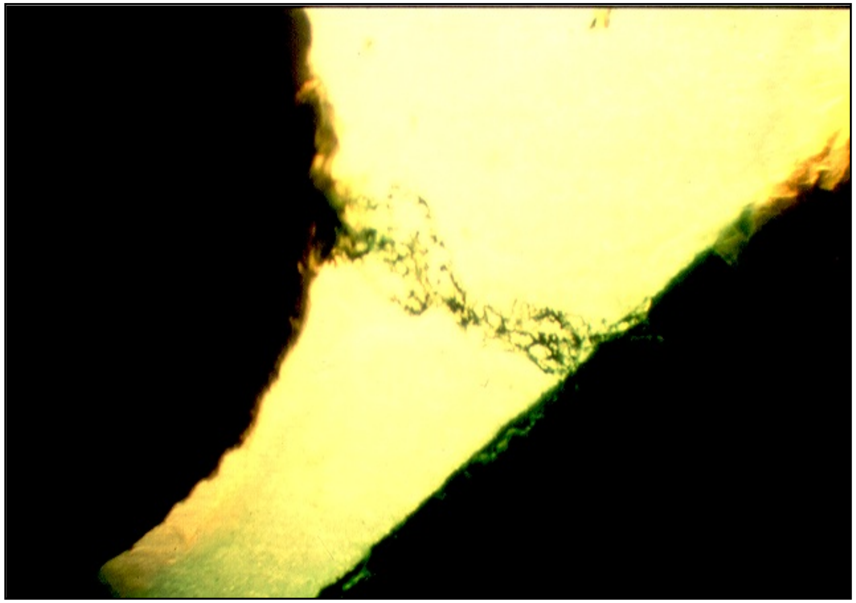
Coupon Preparation Matters

- **Method A (1)–** IPC manual brush and rinse method followed by 2 hour 50°C bake
- **Method B (4)–** Cleaning with commercially available aqueous solution in inline cleaning equipment
- **Method C (5)–** No cleaning – as received from PCB manufacturer
- **Method D (2)–** Brush scrubbed with alcohol, brush scrubbed with DI water, brush scrubbed with alcohol, no bake
- **Method E (3)–** Alternative IPC cleaning method (ionic contamination method)

Cleaning Method	24 HR AVG	96 HR AVG	168 HR AVG
A	1.99E+10	1.59E+10	1.06E+10
B	8.92E+09	7.44E+09	4.85E+09
C	6.53E+09	5.93E+09	3.93E+09
D	1.70E+10	1.22E+10	9.39E+09
E	1.63E+10	1.24E+10	9.37E+09

Surface Insulation Resistance (SIR)

- Visually evaluation for dendrites
- Form as flux residue corrodes metal



Testing Parameters

- Copper mirror testing of low, moderate, and high submitted in SIR chambers for testing
- SIR boards for low in the uncleaned state, moderate and high flux residues removed for testing (per IPC J.STD)
- All samples did not contain halogens

SIR on Low Activity No Halogens

SIR on Moderate Activity No Halogens