

Halogens in Lead Free Solder Paste

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Abstract

The use of Halogens in lead free solder paste has become a topic of considerable discussion among solder paste producers, electronic equipment OEM's and Non-Governmental Organizations. Industry standards for halogen content have been or are being established by industry groups. The reason for the use of halogen containing materials is discussed, as well as the viability of zero halogen solder paste.

Introduction

Over the past 2 years, the use of halogen containing products in electronics assemblies has become a highly visible and controversial topic. European Directory 2002/95/EC that went into effect on July 1, 2006 includes a Restriction of Hazardous Substances, also known as RoHS.

Types of Halogen Bearing Materials

The RoHS list of restricted materials includes 2 formerly common types of Halogen Flame Retardants, Polybrominated Biphenyls and Polychlorinated Biphenyls. There is little or no controversy in excluding materials on the RoHS list from soldering materials like solder paste and wave soldering flux. RoHS declarations

include a certification that these halogen bearing flame retardants are not intentionally added to soldering materials.

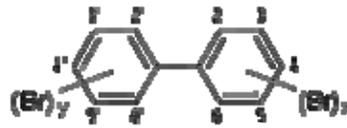


Figure 1. Polybrominated Biphenyl

This is where the story becomes complex, and controversial. But let's take a step back and discuss the utility of halogens and halides in soldering materials. Solder paste is composed of 2 major components, solder powder and a thick flux. Flux has many functions. Flux must enable efficient, repeatable stencil printing. It also requires some degree of tackiness to hold components in place prior to the solder reflow process. It also needs to prevent the oxidation of solder powder and Cu surfaces and/or reduce metal oxides in the powder and along the surfaces being soldered together. Finally, flux residue in no-clean paste needs to have high electrical resistivity and hydrophobicity to prevent electrical circuit failures.

Ionic Halides versus Covalent

Halogens

Ionic halides are well known as effective activators in soldering fluxes. However, ionic materials in solder paste are hygroscopic and corrosive, resulting in reduced shelf-life in typical solder paste formulations. During the solder paste printing process, hygroscopic pastes can have unstable rheology in the presence of humidity.

Moisture absorption often reduces the viscosity of solder paste, making the paste unsuitable for stencil printing. Post reflow residue can become electrically conductive and possibly continue to corrode metal surfaces, especially in the presence of moisture.

One alternative to the use of ionic halides is the addition of covalently bonded halogenated compounds. This is where the controversy begins. RoHS requires certification that no polybrominated or polychlorinated biphenyls are intentionally added to the flux formula. There are no current regulations against other covalently bonded halogen compounds. However, Non-Governmental Organizations like Greenpeace have made a mission of protecting the environment by disclosing which brands of mobile devices and computers contain halogenated flame retardants and PVC (polyvinylchloride). In addition to being very commonly used in printed circuit board laminates, and as additives to plastic housing and components, these halogenated compounds are also found in many common solder paste formulations.

Halogens in Laminate

Halogenated compounds have become ubiquitous as flame retardants in printed

circuit board laminate. According to the IPC (Institute for Printed Circuits), 80% of the worlds laminated circuit boards use Tetrabromobisphenol (a), or TBBPA. The use of TBBPA is under attack in Germany and Sweden. The German Umwelt Bundes AMT and the Swedish Kemikalieinspektionen have pending regulations to ban TBBPA.

Halogens are also useful in solder paste formulations. They can allow solder paste flux survive longer, hotter thermal excursions associated with lead free reflow soldering. They also serve as a stable source for ionic halide when exposed to high temperatures.

Industry Standards for Halogen

Content

Several industry groups have settled on a standard for Halogen use. IPC has a pending standard (IPC J-STD-709) for a low halogen product that (as of 6/18/09) allows up to 1000 ppm each of bromine and chlorine if the source is a flame retardant, PVC, or PVC congener. No limit is placed on halogens from other sources. The International Electrochemical Commission has adapted a standard which allows up to 900 ppm each of Br and Cl, but no more than 1500 ppm combined (IEC 61249-2-21). The Japan Printed Circuit Association uses 900 ppm Bromine and 900 ppm Chlorine as the standard.

Non-ionic halogens are relatively inert until a pre-determined temperature is reached. At elevated temperatures or in the presence of strong bases they can give off Cl^- or Br^- as ionic species, behaving as halide activators during the reflow process in surface mount assembly.

NGO's Involvement

Consumer brand protection may be the biggest driver for reducing or eliminating halogens in solder paste. In July, Greenpeace published its 12th version of its guide to greener electronics. Companies who made a commitment to reduce or eliminate PVC and halogens from their products were rewarded with increased green ratings. Some companies who had previously discussed halogen free plans at industry conferences, but who had not yet executed these plans, were downgraded in their rating.

It is hard to determine how much impact the Greenpeace rating has on consumer decision making. Companies like Apple, Samsung and Nokia continue to win share in the mobile device marketplace. It may be a coincidence that their Greenpeace rating has also increased. The most likely scenario is that superior design, performance, cost, and the foresight to avoid controversial material sets in combination are the key to market share growth.

Eliminating Halogen Content

Similarly, elimination of all halogen bearing materials from solder paste seems to be the best route today. More modern formulation sets are available that eliminate the need to use halogens in solder paste. Many companies are using industry norms as a standard for halogen content. One has to ask why 900 or 1,000 ppm halogen is acceptable when 0 intentionally added halogen free formulations have been on the market since 2003.

Another issue is measurement of the halogen content. Method EN-14582-B has become one of the industry standards

for measuring halogen content in solder paste. In this method, paste is completely oxidized, converting any covalent halogen into its ionic form. Ion chromatography then measures the amount of halide in the post oxidation sample. The issue with this method is that there is no resolution between halide content before the oxidation/combustion and after. To be completely accurate, one would consider running an ion chromatograph of a pre-oxidized sample, but this is currently not the standard procedure. Most 3rd party labs who conduct the halogen bomb/IC test report a minimum detection level of 50 ppm, or about 6% of the current industry standard of 900 ppm. However, it has been reported that the gage R&R of this test method may not be very high. It has been reported that sample size and sample preparation (paste, paste flux or reflowed solder paste) can affect the test results.¹ Zero intentionally added halogen eliminates these issues.

Halogens, namely Brominated and Chlorinated flame retardants can increase the activation of solder paste, without compromising shelf life or stencil life. Their use is common, and the industry has set a standard of between 900 to 1000 ppm. However, more modern solder paste formulations exist that eliminate the use of halogen based materials in solder paste. The use of zero halogen materials has been widely accepted by major OEM's who want to be on the right side of Greenpeace's guide to greener electronics manufacturers.

¹ Poon, Long, Wang: EMI Asia July 1, 2008