Halides and Halogens. What do I need to know?

Abstract

With halogen-containing substances in the public eye due to scrutiny by the European Union and a variety of non-governmental organizations (NGOs) as possible additions to the list of substances banned from electronics, we at EFD have received numerous inquiries from customers asking how this subject will affect them and their processes. Having just overcome the hurdle of RoHS (Restriction of Hazardous Substances), they want to know what halogens and halides are, and what changes they should be prepared for if required to stop using them.

Halide-free materials are not new. Some segments of the electronics industry have been sensitive to halides and their significance for decades. This paper will give the reader a working knowledge of halogens and halides. Armed with this education, the reader will be able to make informed decisions when required to use halogen-free materials, either because regulations dictate it or social pressure makes acceptance preferable to resistance.

Key Words: halide, halogen, bromine, chlorine, flame retardant, RoHS

What are halogens and halides?

At their most basic level, halogens are the electronegative elements in column 17 of the periodic table, including fluorine (F), chlorine, (Cl), bromine (Br), iodine (I) and astatine (At). In electronics applications, iodine and astatine are rarely if ever used. A halide is a chemical compound that contains a halogen. A host of halides are essential to human life, including a wide variety of salts and acids. Chlorine is used to keep drinking water safe. Halides are present abundantly throughout nature in minerals, animals and plants.

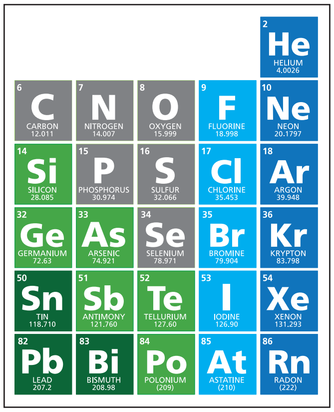

Figure 1: Columns 14 through 18 of the periodic table of elements

Where are halogens found in an electronics assembly?

Chlorine, as found in circuit boards, is primarily in the form of residual materials left over from production of non-brominated epoxy resins used to assemble circuit boards. It is difficult to remove all the chlorinated compounds produced in epoxy resin and minor quantities of sodium chloride and other chlorides can be found. Concentrations are typically below 100ppm.

Bromine in electronics is most commonly bound to brominated flame retardants (BFRs). Brominated flame retardants have been in common and effective usage for the last few decades to combat fire risk and property damage. Brominated flame retardant use is not limited to electronics. It is also in common usage in furniture, construction materials and textiles.

Other sources of halogens in circuit boards include fiberglass sizing, epoxy curing agents and accelerators, resin wetting and de-foaming agents, flux residues, and contamination from handling. In the broader category of "electronics," many plastics, papers, coatings, sealants, lubricants, and adhesives are added to the list of sources.

Why are halogens of concern?

There are both known and suspected risks associated with halogens in electronics. Hundreds of studies have been performed to determine the immediate and long-term effects of various halogenated compounds in both laboratory and outdoor environments. Both the groups supporting a ban on halogens and the groups opposing a ban reference specific studies as proof that their point of view is correct.

Figure 2: Burning E-waste to reclaim precious metals

The most widely publicized risk is associated with byproducts of uncontrolled disposal by incineration, which produces dioxins and furans. Modern incineration technology, in comparison to uncontrolled burning, has virtually eliminated concerns over dioxin and furan production from waste disposal in modern facilities. Given the global waste disposal economy, proponents of halogen elimination point to the fact that it is impossible to predict where or how an electronic product will be disposed of.

Dioxins

Dioxins are naturally occurring materials. Everybody has some dioxins in them. They enter the body primarily through food.

Common usage of the term “dioxin” refers to halogenated dibenzo compounds including polychlorinated dibenzo-dioxins (PCDDs), polychlorinated dibenzo-furans (PCDFs) polybrominated dibenzo-dioxins (PBDDs) and polybrominated dibenzo-furans (PBDFs). There are 210 known dioxin and furan family compounds. Of those 210, 7 dioxins and 10 furans are tracked by the US Environmental Protection Agency for computation of total dioxin contribution to the environment.

Sources of dioxin include a wide variety of combustion and chemical processing methods, along with natural sources such as forest fires. In 2008, the EPA estimated dioxin and furan production from human associated sources in the United States was roughly equivalent to the estimated dioxin and furan production from documented wild fires in the United States over the same period.

Both dibenzo-dioxins and dibenzo-furans have 8 bond sites that chlorine and bromine can attach. The number and position of attached chlorine or bromine atoms determines whether the dioxin has any toxic properties. Dioxins that enter the body are poorly metabolized and accumulate in fatty tissue and the liver. The most toxic dioxin is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). There is no known safe exposure level to TCDD. Several dibenzo-dioxins are established carcinogens and dibenzo-furan testing classifies furans as predictably carcinogenic.

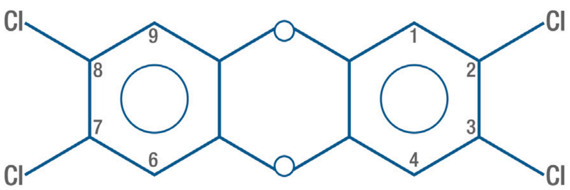

Figure 2: 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD)

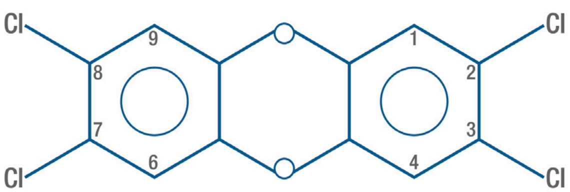

Figure 4: 2,3,7,8 tetrachlorodibenzo-p-furan (TCDF)

Brominated Flame Retardants (BFRs)

Brominated flame retardants come in many compositions. The only property some have in common is a single bromine atom. Surveys of water samples, animals and humans have found the presence of BFRs. Some BFRs are persistent in the environment. Some BFRs do bio-accumulate, but are also rapidly eliminated so that a substantial, extended duration source of exposure is required for adverse effects to be realized. Grouping all BFRs together is no more appropriate than grouping all 210 dioxins and furans. A collection of studies over 10 years was assessed by the European Union in 2007. The conclusion was that the continued use of DecaBDE and TBBPA, which represent over 95% of BFR use in electronics, do not pose human or environmental risks.

Figure 3: E-Waste

Despite the European studies, there remains a constituency lobbying against those BFRs that are persistent; there is concern over the long-term impacts on humans and animals. Testing of particular BFRs in pure form in laboratory environments has produced measureable effects given prolonged exposure of sufficiently high dosage. Testing of other BFRs suggest that some are benign. Assessment of the effects on humans and creatures in the wild is less well understood. Individual BFRs, such as polybrominated biphenyls (PBBs) that have established toxic properties are either no longer manufactured or in the process of discontinuation.

How will halogen-free materials be different?

The “Green” social movement has created an environment in which it can be to the financial advantage of a company to be halogen-free as a demonstration of corporate responsibility. It is left to the technologists to figure out how to supply safe, high-quality products that meet corporate environmental goals. Research into halogen-free materials for circuit board manufacture started in the 1990’s in Europe as companies began to address halogen concerns. Depending on what materials you are using, there may be no difference in your process because you may already be “halide free.”

The governing document defining “halide free” in Europe is IEC 61249-2 Specification for Non-Halogenated Epoxide/Woven E-glass Laminates for Defined Flammability. This specification defines both the term non-halogenated and flammability performance requirements. The definition of non-halogenated in this document is 1500ppm with a maximum chlorine content of 900ppm and maximum bromine content of 900ppm.

IPC-J-STD-004a defines halide-free fluxes as a flux containing <500ppm chlorine (bromine and fluorine converted to chlorine equivalent by molecular weight.)

The primary replacements for BFRs are phosphorous-based materials. These materials are typically more hydrophilic, so moisture sensitivity ratings are lower. In most cases, significantly more halogen-free material is required by mass to achieve the same level of flammability resistance. Side effects include shorter shelf life, greater

PCB stiffness and lower coefficient of thermal expansion (CTE). Of potential benefit, some halogen-free laminate systems have greater thermal stability than traditional FR-4. Phosphorous-based chemistries are currently more costly and the majority are supplied out of Europe and Asia. The process window for successful board manufacture is smaller than with FR-4, requiring close cooperation between material vendors and board fabricators.

Halide-free fluxes are typically less active than their halogenated predecessors. A consequence is that many do not wet as well and have a smaller profile process window. Component lead solderability has a greater effect on joint quality. In addition to changes in the reflow process, migration to halide-free reflow may necessitate other material changes to accommodate the limitations of halide- free flux chemistry.

Conclusion

The decision to produce a halogen-free electronics product is not based on existing regulation. Those halogenated compounds that have established risks have been removed from the market. The key drivers for the major multinational players with halogen-free implementation plans are a combination of public perception of environmental sensitivity and a choice on the side of caution to avoid the cost of a last- minute shift in the face of possible future legislation.

Currently available halogen-free materials are not identical in performance to their halogenated counterparts and require more attention to detail to accommodate the smaller process windows associated with them. Their long-term performance is less well understood.

Development of halogen-free materials continues to advance. As the desirable properties of halogen-free materials increase relative to their undesirable properties, their acceptance will increase. Whole new avenues of research into inherently flame- resistant materials promise profound changes in how flammability risk is balanced against environmental concerns. Until those potentials are realized, it is left to technologists to make the best of what they are given to work with.

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