Halogen Free Electronics

Dan Donahoe
Michelle Poliskie

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Awareness of the Issues

• Perspectives:
  – Human survival depends on technology [1]
  – Material technology is new:
    • First thermosetting plastic, Bakelite, was patented in 1909 [3]
    • Nylon, a thermoplastic, was patented in 1938 [4]
  – A political will favoring environmental stewardship has developed worldwide
    • How does one define environmentally friendly, “halogen free”?

• Limits of knowledge:
  – Greenpeace argues the “Precautionary Principle” [2]:
    • Taking action to eliminate suspect chemicals before all evidence is collected,
      because scientific evidence may never be conclusive
    • This principle is key to Epidemiology, accredited to John Snow and the removal of
      a water pump handle during a cholera outbreak in 1854 [5].
Environmental Issues

- Key events creating the environmental political arena:
  - Minamata disease 1956 resulted in the fatal mercury poisoning of ~2000 people in Japan
  - Rachel Carson’s 1962 book Silent Spring raised concerns about pesticides
  - Greenpeace (1972) grew out of protests against nuclear weapon testing
  - Love Canal incident (1978)
  - Global warming [6, 7]

Environmental Laws and Regulations

- United States Legislation:
  - Clean Air Act of 1963
  - Environmental Protection Agency (EPA) created in 1970
  - Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980
    - Created the “Superfund”
    - Law was passed in response to Love Canal
  - Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA)
    - Source of the familiar Material Safety Data Sheet (MSDS)

- European Union Legislation:
  - Restriction on the Use of Certain of Hazardous Substances in Electrical and Electronic Equipment (RoHS) 2002/95/EC
  - Waste Electrical and Electronic Equipment (WEEE) 2002/96/EC
  - Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) EC/2006/1907

- Safety regulations based on standards
  - UL 1950 for IT and business equipment [46]
Environmental Standards - Electronics

- Existing Standards:
  - Materials for Printed Boards and Other Interconnecting Structures IEC 61249-2-216
  - Halogen Free Copper Clad Laminate for Test Method JPCA-ES-01-20037
  - Specifications for Base Materials for Rigid and Multilayer Printed Boards IPC-4101B
  - Requirements for Solder Fluxes IPC-STD-004A9

- Pending Standards:
    - Issues include levels (900 or 1000 ppm threshold for Br and Cl) and definition (article as in JIG Material Declaration, component as in IPC T-50 or homogeneous as in RoHS) [8, 9, 10]

Damage due to Fires

- In 2003, residential fires in the United States alone caused 2,740 deaths and 13,230 injuries [18]
- An example of fire losses due to lack of fire retardants
  - A fire in The Station nightclub in West Warwick, Rhode Island on 20 Feb. 2003 claimed 100 lives and injured hundreds more
Greenpeace Audit of PCs

- Greenpeace published an inspection of 5 laptops in 2006 [17]
  - Brands: Acer, Apple, Dell, HP, Sony
  - Substances tested: Pb, Hg, hexavalent chromium (Cr⁶⁺), brominated flame retardants (BFRs), polybrominated flame retardants (PBDEs), tetrabromobisphenol A (TBBPA), polyvinyl chloride (PVC)
- Lead was reported in solder of one brand of laptop
- PVC was found on wires in several models
- Bromine was found in 25% of all components and materials
- High concentrations (greater than RoHS limits of 0.1%) of PBDEs (TBBPA, decaBDE, monaBDE) were detected

Verification of Compliance

- How do regulators verify compliance with halogen-free electronics requirements?
  - Taking a parallel with RoHS, little government enforcement has occurred
- IPC Certificate of Compliance [16]
General Presence of Bromine and Chlorine in Electronics

<table>
<thead>
<tr>
<th>Part Type</th>
<th>Potential Halogen Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical Plastic Parts (thermoplastics)</td>
<td>BFRs/CFRs used in certain flame retardants ABS, HIPS, PC, PS, Polyimide (PI) and PBT resins</td>
</tr>
<tr>
<td>Cables</td>
<td>BFRs used in cable/wire insulation material</td>
</tr>
<tr>
<td>Printed Circuit Boards</td>
<td>BFRs added or reacted into FR-4 and other epoxy resins. Certain solder masks, cover coat, and conformal coatings also contain halogens. Chlorinated organic materials are used in the commercial manufacture of epoxy resins and sodium chloride is a byproduct from this process.</td>
</tr>
<tr>
<td>Electronic Components</td>
<td>BFRs added or reacted into FR-4 and other epoxy resins, mold compounds, plastic packages, thermal interface materials, die attach, underfills. Certain solder masks, cover coats and conformal coatings also contain halogens.</td>
</tr>
<tr>
<td>Connectors</td>
<td>BFRs used in certain flame-rated PBT and PA resins</td>
</tr>
<tr>
<td>Films, Adhesives, Tapes</td>
<td>PVC used in certain magnetic tapes (is this right?)</td>
</tr>
<tr>
<td>Vibration dampering parts</td>
<td>PVC used in shock absorbing or vibration dampering resins</td>
</tr>
<tr>
<td>Soldering pastes/fluxes</td>
<td>Br and Cl used in certain fluxes to improve soldering. While process chemicals such as flux are not within the scope of this standard, any solder flux residue that is part of the electronic product is within the scope of this standard.</td>
</tr>
</tbody>
</table>

* Table taken verbatim from draft standard.

Why are Halogens Bad?

Q: People eat table salt (Na⁺ Cl⁻), why are halogens bad?

A: Reactive starting reagents and decomposition products from halogenated polymers and flame retardants are caustic (using PVC as an example)

CH₂=CHCl (vinyl chloride) \[\rightarrow\] (CH(CI)-CH₂)\n
\[\text{polymerize}\]

OSHA TWA = 5 molar ppm with an A1 Carcinogen Rating [26]

\[\text{HCl} + \text{CO}_2 + (2,3,7,8 – \text{tetrachlorodibenzo-p-dioxin})\]

OSHA TWA: 200 ppm [28]
The plastics industry typically adds more to the US GDP than petroleum or electronics.

Petrochemical By-Products are Starting Materials for Thermoplastics

<table>
<thead>
<tr>
<th>Hydrocarbon Type</th>
<th>Chemistry [31]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffins</td>
<td>( C_nH_{2n+2} )</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>Cyclohexanes: ( C_nH_{2n} )</td>
</tr>
<tr>
<td>Aromatics</td>
<td>Cyclohexenes</td>
</tr>
</tbody>
</table>

- Oil-refining by-products result in the production of commodity plastics such as polyethylene (represented above), polyvinyl chloride and polystyrene.
**Why are Flame Retardants Necessary?**

<table>
<thead>
<tr>
<th>Polymer Type</th>
<th>Chemical Structure</th>
<th>Flammability (ASTM D635) (ipm) [33]</th>
<th>Millions of Metric Tons of Production in 1993 [32]</th>
<th>Important for electronics production?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>(-\text{CH}_2\text{-CH}_2)_n</td>
<td>1.0</td>
<td>24.7</td>
<td></td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>(-\text{CH(Cl)}\text{-CH}_2)_n</td>
<td>Self-extinguishing</td>
<td>14.8</td>
<td>√</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>(-\text{CH(CH}_3\text{-CH}_2)_n</td>
<td>0.7-1.0</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>Polystyrene</td>
<td>(-\text{CH(C}_6\text{H}_5\text{-CH}_2)_n</td>
<td>1.0-1.5</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>Phenolic and Cresylic Polymers (e.g. Bakelite)</td>
<td>Structure Omitted: Crosslinked Aromatic Rings</td>
<td>Self-extinguishing</td>
<td>2.6</td>
<td>√</td>
</tr>
</tbody>
</table>

- Some of the highest production polymers exhibit the highest flammability

**Components of Polymer Formulations [34, 35]**

- **Processing Reagents**
  - Plasticizers (~64 wt%)
  - Blowing Agents
  - Antistatic Agents
  - Heat Stabilizers

- **Environmental Stabilizers**
  - Flame Retardants (~15 wt%)
  - UV stabilizers
  - Antioxidants

- **Pigments/Colorants**
- **Fillers**
- **Reagents**
  - Cross-linking agents
  - Unreacted starting materials

Additives comprise a large percentage of the total weight of polymer formulations, but relative concentrations vary based on the base resin.
Flame Retardants

Additive
Def: compounded into the formulation

Reactive
Def: covalently bonded to the polymer structure

Classification is an issue for China and California RoHS, IEC 61249-2-21, JPCA-ES-01-1999, California Proposition 65 compliance

Inorganic (e.g., talc, antimony trioxide)
1. Typically synergists
2. Reduce the need for large quantities of flame retardants
3. Primarily work by forming a protective layer or emitting a gas that eliminates the presence of O₂

Organic (e.g., phosphorous, halogenated)
Typically inhibit reactions through reaction with gaseous by-products

Classification of Flame Retardants [36]

1. Cost
2. Changes in Physical Properties
   • High conc. (≥ 40 wt%) of halogenated FR required, resulting in changes in color, mechanical properties, etc.
3. Efficacy of the chemical reactions

   Iodine
   \[ r = 1.33 \text{ Å} \]
   electron affinity = \(-296.2 \text{ kJ/mol}\)

   Bromine
   \[ r = 1.14 \text{ Å} \]
   electron affinity = \(-324.5 \text{ kJ/mol}\)

   Chlorine
   \[ r = 0.99 \text{ Å} \]
   electron affinity = \(-348.7 \text{ kJ/mol}\)

   Fluorine
   \[ r = 0.64 \text{ Å} \]
   electron affinity = \(-327.8 \text{ kJ/mol}\)

Decreasing Flame Retardant Efficacy [37]

4. Compatibility with Polymer Matrix

5. Disassociation temperature for desired operation conditions
   - Choose a compound which will release HBr before ignition (must look at the combustion temperature of the polymer matrix)
   - Therefore, decabromodiphenyloxide is typically compounded into polyethylene

Attributes of Flame Retardants [38]
The Combustion Process Described as a Reaction

\[ \text{Fuel} + \text{O}_2 \rightarrow \text{gaseous products} + \text{char} \]

(e.g., polymer)

To stop the depolymerization (free radical) reaction:
- Remove reactants and thermal energy
- free radicals from the polymer chain
- fuel
- oxygen

Mechanisms for Flame Retardants

1. Flame retardants (e.g., Hexamine Cobalt (III) Chloride) react to form inert gas (e.g., CO\textsubscript{2}, N\textsubscript{2}) reducing the concentration of oxygen [39]

\[
6\text{Co(NH}_3\text{)}_6\text{Cl}_3 \rightarrow 6\text{CoCl}_2 + N_2 (g) + 6\text{NH}_4\text{Cl} + 28\text{NH}_3 (g)
\]

Fuel + O\textsubscript{2} \xrightarrow{\Delta} CO\textsubscript{2} + CO + H\textsubscript{2}O

2. Inhibit gaseous phase free radical chemistry that occurs during combustion [39]

\[
\begin{align*}
\text{HBr} + \text{OH}^* &\rightarrow \text{H}_2\text{O} + \text{Br}^* \\
\text{HBr} + 0.5\text{O}_2 &\rightarrow \text{OH}^* + \text{Br}^* \\
\text{HBr} + \text{CH}_4^* &\rightarrow \text{CH}_4 + \text{Br}^* \\
\text{H}^* + \text{Br}^* + \text{H}_2 &\rightarrow \text{HBr} + \text{H}_2
\end{align*}
\]

3. Inhibit ignition by acting as a thermal sink to lower the temperature of the polymer (e.g., metal hydroxides, aluminum trihydroxide (ATH)) [39]

\[
2\text{Al(OH}_3\text{)} \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \quad \Delta H = 1050 \text{kJ/kg}
\]
Identification of the polymer resin

Confirmation of the presence of halogens

Quantification of halides

Technique Standards

Energy Dispersive Spectroscopy (EDS) None known

Fourier Transform Infrared Spectroscopy (FTIR) None known

X-ray Fluorescence (XRF) None known

Inductively coupled plasma mass spectroscopy (ICP-MS) J-STD-004A

• Compliance testing standards will be dictated by the concentration limits set by legislation
The Future of Flame Retardants

1. Inorganic Compounds [41]
   • Future target for regulation

2. Switch to other types of polymers
   • Thermoplastic Elastomers (TPE) to replace PVC [42]
   • Still require flame retardants

3. Nanocomposites

4. Reactive Organic Compounds
   • Polymerize upon application of heat
   • Form biologically benign by-products

Example: Technologies from JJI Industries [41]

Antimony Chemistry: Greenpeace’s New Initiative

Stibnite ores

<table>
<thead>
<tr>
<th>Lead and arsenic impurities</th>
<th>Mining, purification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony metal + Oxygen</td>
<td></td>
</tr>
<tr>
<td>Sb₂O₃</td>
<td></td>
</tr>
</tbody>
</table>

- No known regulations for antimony
- Arsenic is typically found as an impurity to flame retardants in concentrations of [43,44]:
  - 430 mg/kg in mattress materials
  - 0.014 mg/kg-day has caused skin lesions when it occurs in drinking water
Conclusions – in the Form of Questions

• Are there substitute non-halogen materials?
  – Yes, manufacturers are working to supply substitute materials [21, 24]
• This substitution of materials is similar to implementation issues raised with RoHS [23]
  – Were there surprise problems with RoHS? Yes [25]
• Will the environmental community continue to impose new requirements?
• Does “non-halogen” guarantee health and safety?
  – What new problems may be introduced by introducing alternate materials?

References

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16. IPC 1752 Materials Declaration
25. ASHRAE TC 9.9, Particulate and Gaseous Contamination in Datacom Environments (in press).
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