

# Technical Paper

## Low Halogen Polymers for Electronics Applications

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## **Introduction**

Environmental stewardship has become the *modus operandi* for the electronics industry. Once considered a polluting industry, the electronics businesses have transformed into environmental practice leaders through regulated and non-regulated activities. Legislations such as RoHS, ELV and WEEE<sup>1</sup> have required the elimination of certain hazardous materials. Meanwhile, producers and OEMs continue the search for economical means to lead the way toward environmentally friendly practices. Organizations, like Greenpeace, grade electronics for environmental design.<sup>2</sup>

Certain chemical elements are hazardous, or are thought to be hazardous to humans and/or the environment. It is important to note that the definition of hazardous has been expanding. It no longer includes primary use and/or initial manufacturing but includes disposal practices and long term potential for release of toxic substances. With that in consideration, current interest is focused on halogen containing materials and how to remove them from electronics. . Halogens are the group 7 elements on the periodic table and include Fluorine (F), Chlorine (Cl), Bromine (Br), Iodine (I) and Astatine (At). Of primary interest are Brand Cl which are most commonly found in flame retardants and PVC. These are widely used throughout the electronics industry. It is interesting to note that while F usage in applications such as lubricants and cabling is widespread, it has attracted little attention from an environmental risk aspect. This is likely due to a variable of reasons including the unique electrical properties of the fluoropolymers as well as the more limited volume associated with such applications.

The use of Polyvinyl Chloride (PVC) at Tyco Electronics, as well as the rest of the electronics industry, is of serious concern. However, there is a substantial difference in end application use of PVC versus standard Br flame retardant engineering polymers. This includes a difference in not only basic material characteristic, but also processing methods and flammability requirements. Therefore, the PVC topic will not be addressed in this paper.

Brominated flame retardants (BFR) are quite common. Bromine is a highly efficient and cost effective flame retardant and has proven to be unparalleled in performance. Combining BFR with a metal oxide synergist, such as antimony oxide or zinc borate, provides excellent flammability resistance. Not all brominated flame retardants are of the same chemical structure nor indicate the same risk. While the environmental impact and personal exposure impact of BFRs is widely known, the results are hotly debated. Further, the same tests and analyses have not been made on non-halogenated FR. Risk assessments and environmental studies on these additives should be part of the overall environmental risk assessment.

Polymers burn because they are made from fuel. The carbon-hydrogen bonds break down at high temperature to produce flammable gases. Preventing flames can be achieved using one of these methods<sup>3</sup>:

1. Absorbing the heat from combustion
2. Forming a non-flammable char which excludes oxygen

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<sup>1</sup> EU directives 2002/95/EC, 2000/53/EC and 2002/96/EC respectively.

<sup>2</sup> <http://www.greenpeace.org/raw/content/international/press/reports/guide-greener-electronics-8-edition.pdf>

<sup>3</sup> Landrock, Arthur H., *Handbook of Plastics Flammability and Combustion Toxicology*, Noyes Publications, Park Ridge, NJ, 1983.

3. Decomposing the polymer to enhance drip formation, which removes the polymer from the flame front
4. Chemically evolving gases which quench the flame
5. Reacting to form chemicals that burn less easily

Both brominated and chlorinated flame retardants, combined with synergist oxides, take advantage of many of these approaches. Bromine is a great char former and its efficiency is superior to F and Cl as a flame retardant.<sup>4</sup> The development of brominated flame retardants has saved countless lives by extinguishing flames before they destroy equipment, homes and businesses. In some industries, the use of BFRs has been limited due to the potential evolution of toxic gases during combustion. For example, the aerospace industry uses polymers in a populated confined space where toxic combustion by-products can be as much of an issue as flame spread. A materials scientist must consider the application criteria for flame spread and formation of toxic gases and smoke.

While BFRs are quite efficient, there is public concern regarding their safety.<sup>5</sup> In this paper we will examine the risks of fire in electronics, the methods used to mitigate polymer flammability and some options for migrating to polymer compounds which do not contain the halogens bromine or chlorine.

### **UL Flammability Tests**

The Underwriters Laboratory has created several flame rating standards for polymers. These standard test methods provide a uniform test method to assess flammability of polymeric materials. The most common tests are the UL94HB test and UL94V tests. UL 94, The Standard for Flammability of Plastic Materials for Parts in Devices and Appliances, is harmonized with IEC 60707, 60695-11-10 and 60695-11-20 as well as ISO 9772 and 9773.

#### **UL94HB<sup>6</sup>**

The UL94HB, or horizontal burn, test method uses a 0.83 to 3 mm thick polymer bar which is at least 100mm long. A flame is applied to the end of the bar for 30 seconds. To achieve an HB rating, the materials must cease to combust before reaching the 100mm mark with an average burn rate of 75mm per minute or less. The material can be rated as HB to a thickness down to 0.83mm. Figure 1 below shows an example UL “Yellow Card” which provides the certification values for a particular compound (A DSM 4/6 nylon).<sup>7</sup> In this case, the material has a flammability rating of HB for all thicknesses tested. An HB rating or better is readily achievable for many plastics. UL recognizes 35,398 grades of polymers with an HB rating or better and 15,789 grades with a rating of HB.<sup>8</sup> This test is similar, although slightly more

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<sup>4</sup> Kuryla and Pap, *Flame Retardancy of Polymeric Materials*, Volume 4, Marcel Dekker, New York, NY, 1978.


<sup>5</sup> Thomas A. McDonald, *Polybrominated Diphenylether Levels among United States Residents: Daily Intake and Risk of Harm to the Developing Brain and Reproductive Organs*, Integrated Environmental Assessment and Management, Volume 1, Number 4, pp. 343–354.

<sup>6</sup> UL 94, Test for Flammability of Plastic Materials for Parts in Devices and Appliances, Underwriters Laboratories, 29JAN01, ISBN 0-7629-0082-2.

<sup>7</sup> UL Yellow Cards can be downloaded from the Underwriters Laboratory (UL) website at <http://iq.ul.com>. This yellow card downloaded on 25JUN08.

<sup>8</sup> Search results from the Underwriters Laboratory (UL) website at <http://iq.ul.com> using a search on flammability rating of HB or better.

stringent, to the FMVSS 302 which governs the use of materials in the automobile passenger compartment. The primary criterion is a slow flame spread that would allow the user to detect and either stop or remove them self from the situation.



**Underwriters  
Laboratories**

**Component Plastics Recognition**

E47960

Component - Plastics

**DSM ENGINEERING PLASTICS B V**

POSTBUS 604, GELEEN 6160 AP NL

**TS200F6**  
Polyamide 4/6 (PA4/6), glass reinforced, "Stanyl", furnished as pellets

Color	Min Thk (mm)	Flame Class	HWI	HAI	RTI Elec	RTI Imp	RTI Str
<b>ALL</b>	<b>0.83</b>	<b>HB</b>	<b>3</b>	<b>0</b>	-	-	-
	<b>1.5</b>	<b>HB</b>	<b>3</b>	<b>0</b>	-	-	-
	<b>3.0</b>	<b>HB</b>	<b>0</b>	<b>0</b>	-	-	-

Comparative Tracking Index (CTI): **1**

High-Voltage Arc Tracking Rate (HVRT): **1**

Dielectric Strength (kV/mm): **31**

Dimensional Stability (%): **0**


High Volt, Low Current Arc Resis (D495): **5**

Volume Resistivity (10<sup>9</sup>ohm-cm): **12**

UL94 small-scale test data does not pertain to building materials, furnishings and related contents. UL94 small-scale test data is intended solely for determining the flammability of plastic materials used in the components and parts of end-product devices and appliances, where the acceptability of the combination is determined by ULI.

Report Date: 2003-01-02  
Last Revised: 2007-08-30

Underwriters Laboratories Inc®



**Figure 1. UL “Yellow Card” showing the UL qualification values for a 4/6 polyamide. This material has a flammability rating of HB for all thicknesses reported.**

### UL94V<sup>9</sup>

UL94V is a more stringent flammability test than the UL94HB test. The UL94V test method uses bars of different thickness to determine the flammability rating of the bar at thickness. A 15mm long, 13 mm wide polymer bar with the desired test thickness is oriented vertically above a Bunsen burner with a layer of surgical cotton placed 300 mm below the test sample. First, the bottom of the test sample is ignited by applying a flame with the Bunsen burner for a 10 second dwell time after which the flame is removed. The combustion time duration is recorded. For either the V0 or V1 rating, any flaming droplets must not ignite the surgical cotton. The flame is applied at a set rate and angle for a maximum of 2 applications per bar. The flammability score depends upon the performance metrics listed in the table below. The test can be repeated at varying thicknesses to determine the minimum thickness for which a V-0 rating can be obtained. This vertical burn test has three performance categories. V-0 is the most severe requirement, while V2 is the least severe. Flaming drips is one of the key differences between the V-0 and V2 rating. V1 falls between these two performance ratings and allows a longer combustion time compared to V-0. The differences between V1 and V-0 are fairly small and it is rare that engineering polymers of interest to the connector industry are engineered to a performance ranking of V1. The most significant difference between the V ranking and HB ranking is that V rated materials must self extinguish.

<sup>9</sup> UL 94, Test for Flammability of Plastic Materials for Parts in Devices and Appliances, Underwriters Laboratories, 29JAN01, ISBN 0-7629-0082-2.

Table 1. Table of UL94 Flame Ratings.

	94V-0	94V1	94V2
Total combustion time in seconds for 10 flame applications	50	250	250
Maximum time for any individual flame occurrence	10	30	30
Glowing combustion time in seconds	30	60	60
Cotton indicator ignited by flaming particles or drops	Not allowed	Not allowed	Allowed but cannot ignite cotton more than briefly.

Passing the UL 94V test with a V-0 rating requires efficient flame retardant performance, either from an inherently flame retardant material or from an additive package. Getting a V-0 rating at a small thickness is even more challenging. Some materials have excellent flammability characteristics until the thickness is reduced below a critical level. Thinner samples are more likely to drip and have greater surface area to encourage combustion after the removal of the flame. Figure 2 is an example of a UL "yellow card" for a specific 4/6 nylon from DSM. It has a V-0 rating at all thicknesses tested, down to 0.67 mm.<sup>10</sup> Figure 3 shows another UL "yellow card" for a polyamide 6,6, which is rated as V-0 for thick test bars, but the performance ranking drops to HB at the thinnest samples tested.<sup>11</sup>

<sup>10</sup> UL Yellow Cards can be downloaded from the Underwriters Laboratory (UL) website at <http://iq.ul.com>. This yellow card downloaded on 25JUN08.

<sup>11</sup> Ibid.

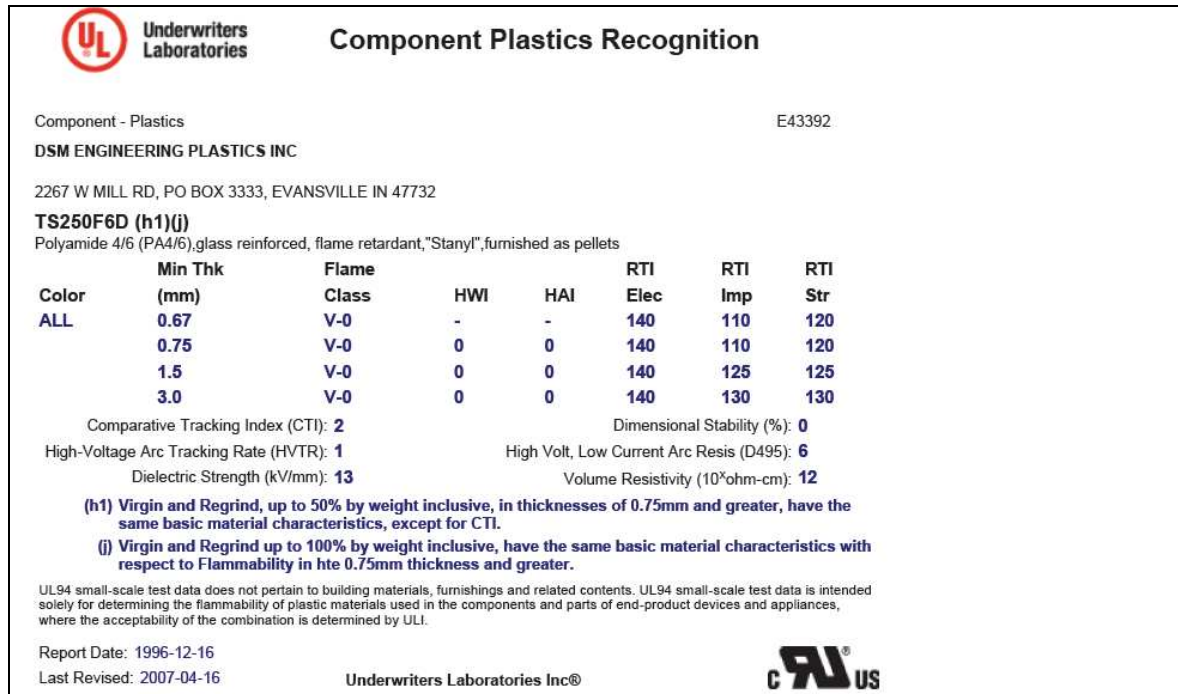


Figure 2. UL “Yellow Card” showing the UL qualification values for a different 4/6 polyamide. This material has a flammability rating of V-0 for all thicknesses reported.

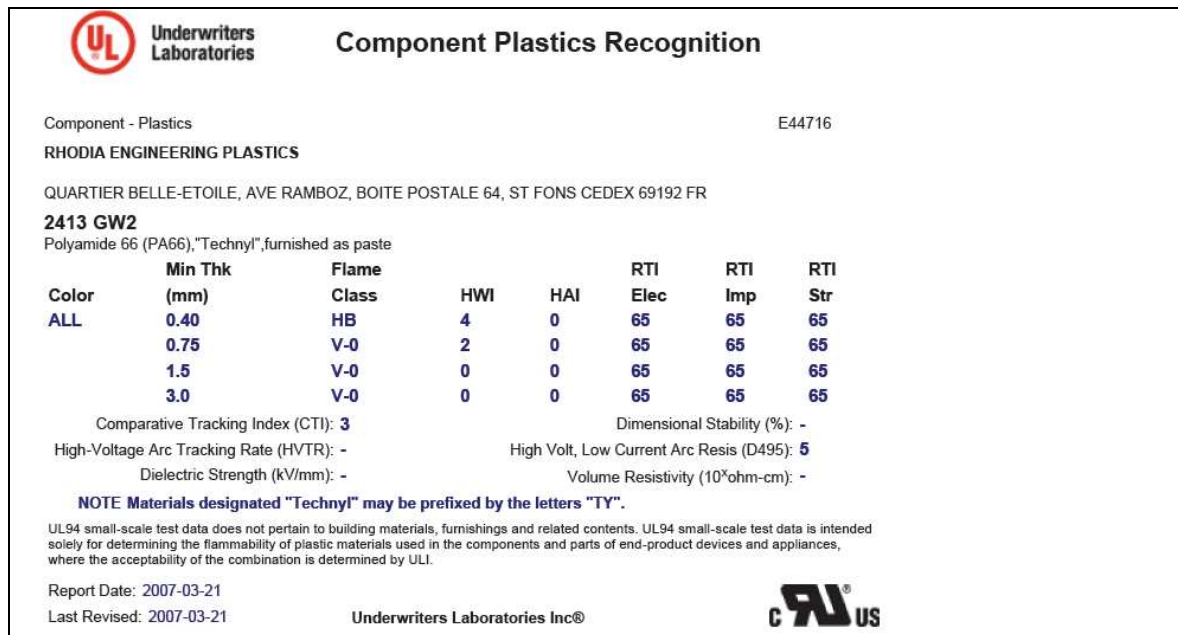


Figure 3. UL “Yellow Card” showing the UL qualification values for a polyamide 6,6. This material has a flammability rating of V-0 for thicker samples, but the flammability rating drops to HB at the smallest thickness of 0.4mm.

## UL94 5V<sup>12</sup>

The UL94 5VA or 5VB test classifications are similar in test method to UL94 V-0, but the acceptability requirements are more severe. Materials classified as 5VA or 5VB must also pass UL94 V-0, V-1 and V-2. The test method is similar to UL94 except for the flame application. The flame is applied at an angle of 20 degrees for 5 seconds, then removed for 5 seconds. The cycle is repeated until the flame has been applied 5 times. After the fifth flame application, the after flame time, afterglow time and indications of flaming drips are recorded. Table 2 indicated the flammability classification ratings for the 5V test.

Table 2. Material classification ratings for UL94 5V tests

Criteria	UL94 5VA	UL94 5VB
After flame time and afterglow time after 5 <sup>th</sup> flame application	<= 60 seconds	<= 60 seconds
Cotton ignited by flaming particles or drops	No	No
Burn through of any plaque specimen	No	Yes

### A Special Case: Polyamides (Nylons)

Some polyamide materials employ a drip technique to achieve an improved flammability score. When the flame heats the polymer, the viscosity of the polymer drops quickly allowing it to melt and flow or drip away prior to reaching a temperature sufficient to initiate or sustain burning. This effect is even more pronounced in thin gage samples where the compound heats very quickly. Some unfilled Polycarbonate (PC) resins can also obtain this rating. This allows for flame retardancy coupled with clarity which can be unique.

### Using these ratings:

The test methods described above are used to ensure that each compound tested is evaluated in an unbiased manner. Most polymers used in the connector industry are ranked as V-0, V2 or HB. Flammability tests are not normally made using connector products.<sup>13</sup> Rather, the industry manufactures products using UL recognized polymers. For example, a connector product may be marketed as constructed from a UL94 V-0 plastic, which means that the housing was molded using a product which passes the UL94 V-0 requirements. Additionally, some materials at very thin thicknesses, distort or are unable to be tested under the traditional UL 94 vertical test. In that case, an alternate method UL 94 VTM method can be used. This is a rather uncommon rating but as molded wall thicknesses become thinner, the VTM test has become more prevalent.

Since we know that the thickness of the test bar affects the flammability rating, the dimensions of the connector housing impact the effective flammability of the final product. Ideally, the often used product terminology “constructed from a UL94 V-0 plastic” would

<sup>12</sup> UL 94, Test for Flammability of Plastic Materials for Parts in Devices and Appliances, Underwriters Laboratories, 29JAN01, ISBN 0-7629-0082-2

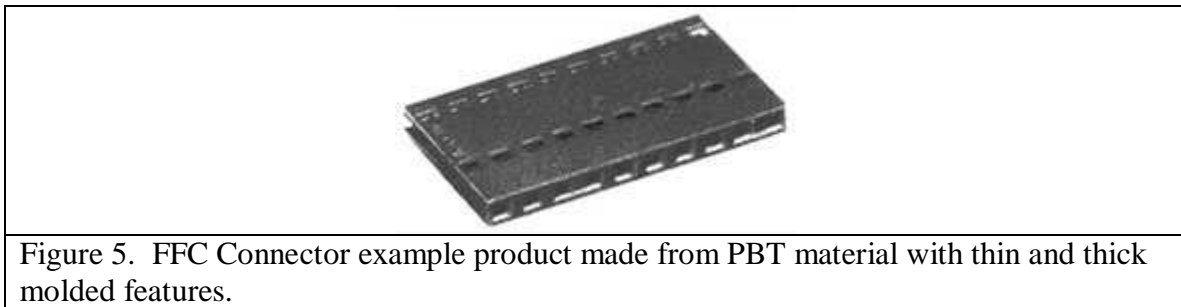
<sup>13</sup> This holds true for the communications, consumer electronics, computer and automotive markets. Some products in the industrial and test markets (e.g., home appliances) require glow wire style flammability tests on the final product geometry.

specify that the plastic was rated to V-0 at a thickness smaller than the thinnest section of the connector. In praxis this is not the case. UL94V cannot test products below a thickness of 0.38mm<sup>14</sup>. This minimum test thickness is greater for some materials if the material is susceptible to warping during the test. The reality is that some connector designs have features that are smaller than the minimum test thickness value. To further complicate a connector rating, in many cases, the bulk of a connector can be relatively thick, with only small fractions of the total including very thin sections. Thus, the selection criterion for an appropriate minimum thickness value for the UL94 test can be non-uniform applied across the industry.

The UL94 test has performance rankings intended to differentiate between compounds which can resist burning and those that cannot. The applicability of these standards to electronic applications is less clear since the test is idealized to a laboratory test sample which cannot be directly related to the final product geometry.

#### An Electrical Connector Example

As an example of flame rating performances as specified, we can consider an example FFC connector, Tyco Electronics part number 1-487378-0 as shown in Figure 5. This product is injection molded using a PBT material, which uses a brominated flame retardant in order to provide adequate UL94 performance. An example PBT UL Yellow card is shown in Figure 6. Since the material has been certified by UL at different thicknesses, we can see that the flammability rating of the material degrades as the thickness is reduced. At a thickness of 0.75mm, the material is qualified as UL 94V-0. At a thickness of 0.41mm, the rating drops to UL 94V-2. When we consider these flammability rankings relative to the connector from our example, the wall thicknesses must be used. Wall thicknesses in this product vary from 1.5mm in the thicker sections down to 0.3mm in the thinnest walls. This product, like many in the industry<sup>15</sup>, is specified as being molded from a UL 94V-0 material.



<sup>14</sup> During the test, the residual stress in the molded bar can lead to curling and warping which alters the test geometry unacceptably. Tests bars warp more readily at thinner gages.

<sup>15</sup> Molex offers a similar style part, 70430, which is also made of flame retardant polyester and is also marketed as being made with a UL 94V-0 rated material.

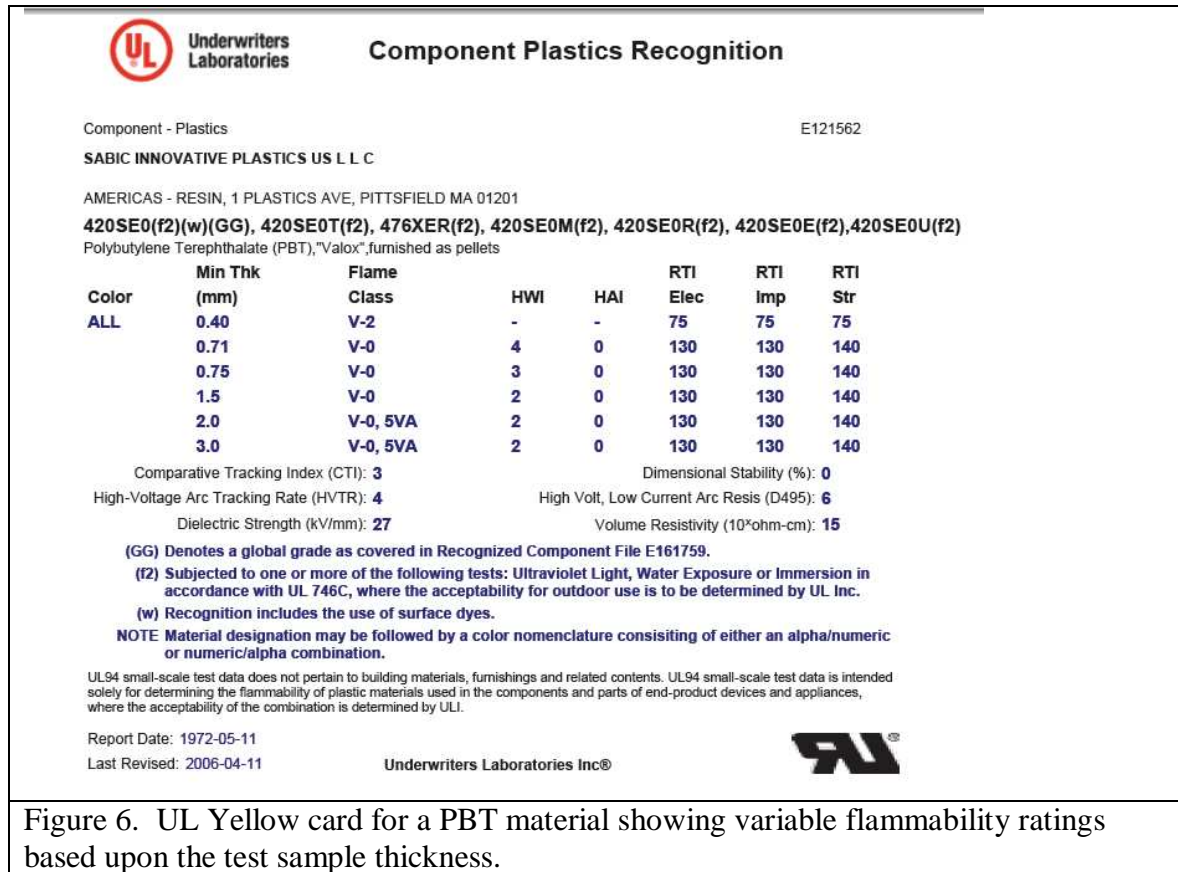


Figure 6. UL Yellow card for a PBT material showing variable flammability ratings based upon the test sample thickness.

### Source of Ignition and Flame

Flame retardants are added to polymers to help prevent the spread of fire. When engineering an electronics device for fire retardancy, a key engineering parameter is the source of flame. Without an ignition source, flammability is not an issue. Ignition sources have two fundamental categories: internal and external. An external source is an unrelated flame such as would be found when a device comes into contact with a candle. The flame from the candle can ignite the exterior of an electronics device if it comes into contact. The other source of ignition is internal to the device and relates to power sources. The International Electrotechnical Committee (IEC) has proposed a standard, IEC 62368, to define these sources and the required flammability requirements.<sup>16</sup>

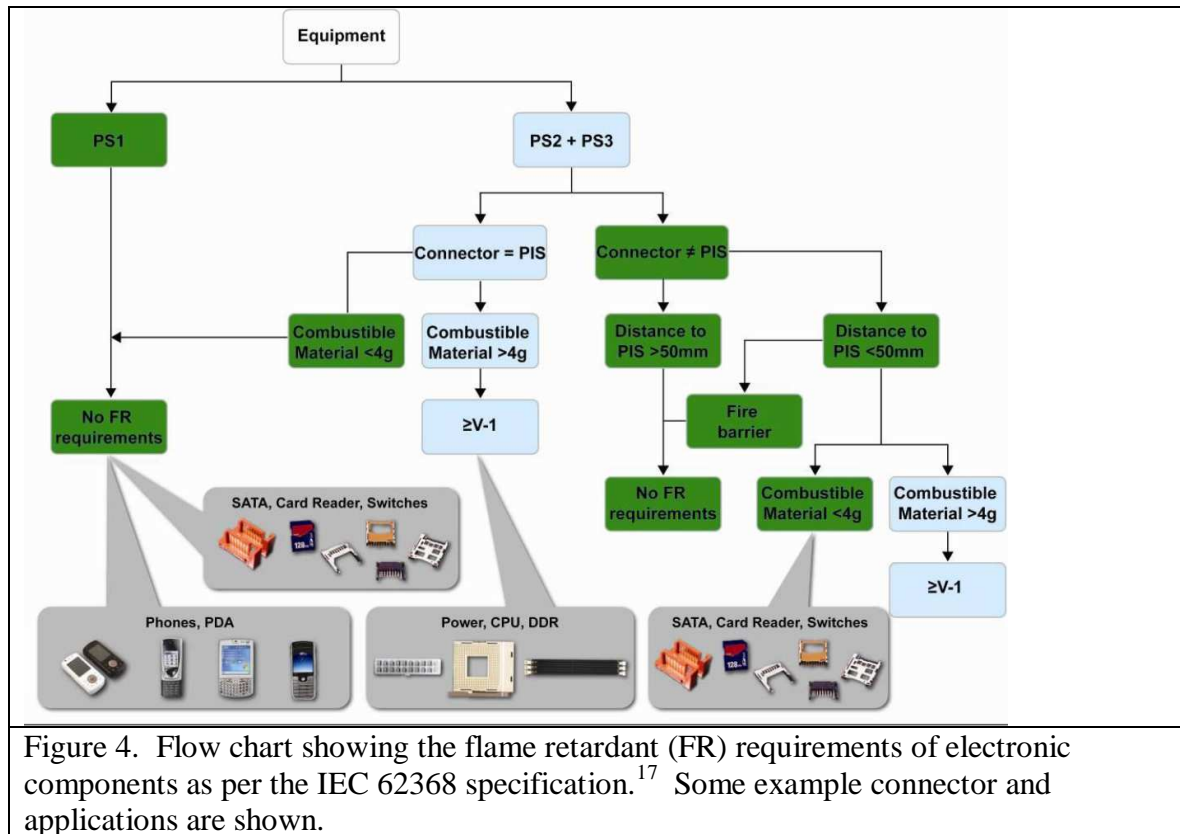
An internal ignition source is defined as a powered connection at a given power level. The IEC has defined three internal power source levels: PS1, PS2 and PS3. Table 2 below describes the possible internal ignition sources in electronics. These definitions are critical since they define the flame retardancy requirements of the connectors.

<sup>16</sup> International Electrotechnical Committee, Standard IEC62368, will take effect in January 2009.

Table 2. Possible Ignition Sources as defined by IEC 62368.

Power Levels	Performance ranking	Possible ignition source (PIS)
PS1	$\leq 15$ watts after 3 seconds $\leq 500$ watts for $\leq 3$ seconds	No
PS2 + PS3	$> PS1$ $\leq 100$ watts after 5 seconds	Arcing risk if voltage $> 50V$ $>15VA$

Figure 4 shows a diagram of flammability requirements as defined by the IEC standard. For PS1 applications, there are *no* flame retardant requirements. This is a substantial development. The fundamental premise is that an appreciable fire cannot start using power of 15 watts or less. Many of these applications are currently made using V-0 rated materials and the new specification suggests that these products could be made with HB rated materials, with *no* impact to the risk of internal fire.



Higher level power sources can have variable flame retardant (FR) requirements depending on the application. If the connector is a possible ignition source and the combustible material, *i.e.*, the polymer compound, is less than 4g, then no FR is required. If the component is larger than 4g then it must be rated at least to UL94 V-1.

<sup>17</sup> Sidiki, Tamim, *et al*, "Green Design in Electronics", Computex 2008, Taipei, Taiwan, 4JUN08.

If the connector is not a possible ignition source, the flammability must still be evaluated. In this case, the concern is the proximity to an external ignition source. If it is farther than 50 mm, then the connector does not require any FR. If it is closer than 50 mm and there is a fire barrier (*e.g.*, a metal shell around the connector) then no FR is required. If it is closer than 50mm and there is no fire barrier, then products with less than 4g of combustible material do not require FR, while those larger than 4g require at least a V-1 rating.

### **Options for Migrating to Low Halogen Polymer Compounds**

Reducing the halogen levels in polymers used in typical connectors is technically feasible. The challenge is to complete this task in the most cost effective manner. There are three strategies to achieve this objective: 1) use inherently flame retardant materials which are naturally low in halogens, 2) use materials which can be made flame retardant using non-halogenated flame retardant packages and 3) use materials which have no flame retardant additives for applications which may no longer require a V-0 rating.

#### **Inherently Low Halogen Materials**

Some polymer systems are inherently flame retardant and thus can easily meet the "no halogen" requirement. The most common examples are Liquid Crystal Polymer (LCP), Polyphenylene Sulfide (PPS), Polyetherimide (PEI) and Polyether Sulfone (PES). LCP is a commonly used material but suffers from a limited supply chain and relatively high cost. They also tend to be relatively weak under compressive loads and can suffer from some elongation limitations. The global supply of LCP is currently sufficient to meet our needs, but is expected to be short if users migrate more to LCP to solve lead free solderability concerns and to avoid halogens. PPS is also a candidate material. While this material can contain residual chlorine, it is likely to be exempted from many customer requirements for low halogen products. PPS is also relatively expensive, and may require post processing in order to provide an acceptable part. PES and PEI are also inherently flame retardant. They have lower temperature performance than LCP and PPS, have issues molding into thin walls and are also somewhat expensive.

#### **Non-Halogenated Flame Retardants**

Bromine is an efficient flame retardant – this makes it particularly popular. In the halogen free design space, the flame retardant options are generally oxides and phosphorous bearing materials. These flame retardants are less efficient and thus require higher loading levels in order to achieve V-0 flammability performance. This can be detrimental to the mechanical, electrical and processing performance of these grades. However, some grades have shown success and are commercially available.

Polyamide materials have shown the greatest affinity for non-halogenated FR packages. High temperature nylons (HTN) are available which have properties only slightly inferior to their brominated counterparts. While these compounds are generally more expensive than brominated versions, they are gaining market appeal. The same trend holds true for lower temperature polyamide 6,6. Interestingly, lower temperature polyamides (6,6 and 6), unfilled grades have traditionally utilized the non-halogenated flame retardant melamine cyanurate. These same grades are migrating the BFR additive packages to improve flammability performance for home appliance applications.

An extremely common engineering thermoplastic for the connector industry is polybutylene terephthalate (PBT). A few non-halogenated versions of this polymer have been introduced, but the flammability performance is generally poor and there is a substantial price increase. Many times, the offsets are not pure PBT but have incorporated PET into the formulation which can be more difficult to process and mold. A similar polyester, PCT, also shows difficulty in achieving a non-halogenated flammability rating without sacrificing properties. Since both of these resins are low cost materials, converting products using these resins to non-halogenated version could be quite expensive.

### HB Rated Compounds

The third approach is to use materials which have an HB flame rating. This approach cannot be applied to every product since some products will require a V-0 or V-1 flammability rating. In this approach, the halogenated flame retardant is removed from the polymer compound. This preserves, or possibly improves, the mechanical, electrical and processing performance of the compound while eliminating the halogen. The polymer can typically obtain an HB rating which is sufficient for many applications. Further, since the base resin can be retained, the conversion cost can be relatively low since the mold tooling can likely be used to make the non-halogenated product since the polymer shrink rates can be engineered to remain the same as the brominated version.

To consider the impact this might have on material selection, we can analyze the spectrum of available polymer materials. A query of the UL yellow card file allows a profile of existing qualified materials. Figure 5 shows a chart of registered polymer compounds with various flammability ratings. In this analysis, we use the ranking process where V-0 is better than V-2 which is better than HB from a flammability perspective. UL recognizes 35,398 different polymer compounds with flammability ratings (HB or better). 15,789 of those are rated at HB and 18,465 are rated at V-0. But if we take a closer look at the V-0 rated materials, we see that only 10.7% of them are rated at V-0 down to 0.4mm. Using HB rated materials may avail new compounds or sources of supply not previously available.

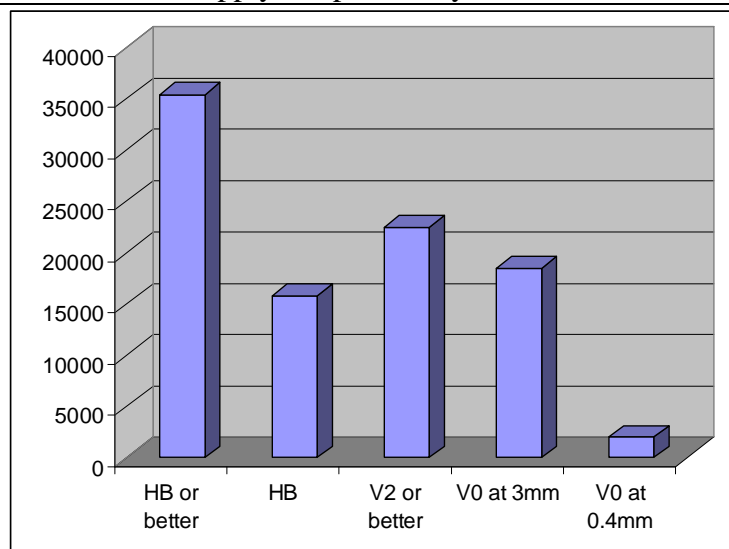


Figure 5. UL recognized grades falling into various categories. Achieving a V-0 rating at a small thickness is the most restrictive category.

Using HB rated materials may have some restrictions within the context of normal Tyco Electronics operating methods. Some of products are customer specific and we know the product application. In this case, we can apply the rules of the IEC standard to determine the flammability requirements of the application. In other cases, we don't know the exact product use, but we know the final application. For example, small consumer electronics items, such as mobile phones, are employing HB rated materials in all of their applications.

Some OEMS are considering the relaxation of flammability requirements to allow the use of V-2 rated polymers. This offers little advantage for low halogen purposes and for costing since many engineering thermoplastics will still require some level of flame retardant in order to achieve V-2 rating. It may be feasible to achieve a better performing halogen free flame retardant polymer at a V-2 rating is the volume loading of flame retardant can be reduced. This improves cost and mechanical performance when compared to a V-0 material, but the degree of change may be quite small.

The problematic application of these approaches for Tyco Electronics is standard catalog items. In this case, the OEM product application is not known (the product may even be sold through distribution, further removing us from the product application). Catalog items are often rated at maximum current rating and are not directly related to the power levels actually used, a key metric in the IEC classification. The same product could be used for a low power application that is used for a high power application – these would require different flammability requirements. Thus, an issue for using this approach is to determine the structural/organizational hurdles involved with addressing an unknown customer application. There are potential advantages from use of an HB resin in regards to weight savings as well as less corrosive environment.

### **Conclusions**

1. The requirements for flammability, based on the UL test methods and the new IEC specification, and the customer need for low halogen materials have been summarized.
2. Some low halogen polymer compounds are commercially available, but each of them incurs some cost and/or performance penalty. Some future innovations in polymer chemistry may improve the performance and cost over time.
3. The proposed IEC standard allows the use of HB flammability rated materials in certain product applications. This may be a cost effective and rapid route to halogen free product development. Figure 4 shows the decision tree used to determine flammability rating requirements.
4. While the environmental impact and personal exposure impact of BFRs is widely known, the results are debated. Further, the same environmental impact tests and analyses have not been made on non-halogenated FR.