FLAME RETARDED COMPOUNDS

By VAMP TECH
Foundamental Aspects of the Flame Retardancy

1. Combustion
2. Testing FR Compounds
3. FR Additives
4. FR Mechanisms
5. Advantages and Disadvantages
Combustion

- Step I - Heating
- Step II - Softening/Melting
- Step III - Degradation
- Step IV - Decomposition
- Step V - Oxidation

Fig. 3.2 Fire triangle (according to Emmons [4])
Fire Development

Fig. 3.1 Phases in the course of a fire (after Becker [3])
Combustion Influencing Factors

- Stability of the chemical bond (III-IV)
- Specific Heat (I)
- Thermal Conductivity (I)
- CHAR formation (IV)
- Not flammable gases (IV)
- Flash ignition temperature (V)
- Self ignition temperature (V)
- Oxygen concentration (V)
FIRE PREVENTION, INHIBITION, EXTINCTION

TARGET  retardando the flame spread

HOW  interrupting one or more steps of the combustion process

MEANS

• Polymers that do no burn at high striking conditions because their molecules are very stable to degradation and decomposition (PPS, PPO, PTFE, PSU, PEEK).

• Polymers which are modified, during their synthesis process, with flame retardant co-monomers (PC+TBBA, PBT+TBBA)

• Polymers alloys (ABS+PSU, PS+PPO, ABS+PC, PA66+PPS)

• Add flame-retardant additives into the polymers during the compounding process. (most commonly used in thermoplastics)
**THE FLAME RETARDING PROCESS BY ADDITIVATION**

**How?**

- Additives generating **heavy gases** during decomposition \(\rightarrow\) barrier between the polymer and the surrounding oxygen (e.g.: ammonium carbonate, ammonium phosphate, halogen derivatives, nitrogen-rich additives, organic phosphorus additives)

- **CHAR** forming additives (e.g. red phosphorus, intumescent systems) or additives involving **endothermic reactions** (e.g.: ATH, MDH) \(\rightarrow\) heat development reduction

- Additives that help maintaining the **physical integrity** of the finished part (e.g.: filler - glass fibre- PTFE fiber)
METHODS FOR EVALUATING FLAME RETARDANCY

- **UL94** – Horizontal, vertical and 5VA or 5VB burning test

- **GWT** in two versions: **GWIT** and **GWFI**

- **Needle** test

- Limiting Oxygen Index (**LOI**) test

- Comparative Tracking Index (**CTI**), an integration of the above-mentioned test methods
9 500 w (125 mm) Vertical Burning Test; 5VA or 5VB

(ASTM D 5048 or ISO 10351)

9.1 Test criteria

9.1.1 Material shall be classified 5VA or 5VB on the basis of test results obtained on small bar and plaque specimens when tested as described in (9.2.1 – 9.6.5).

*Exception: For materials that are submitted for a 5VB rating only (i.e., the manufacturer does not seek the 5VA rating), plaque specimens do not need to be tested.*

9.1.1 revised May 22, 2001

9.1.2 Materials classified 5VA or 5VB shall also comply with the requirements described in 8.1.1–8.6.1 for materials classified V-0, V-1 and V-2.

9.1.2 revised July 29, 1997

9.1.3 Table 9.1 specifies the material classifications.
FLAMMABILITY TESTING

UL 94 flammability in general

The most widely accepted flammability performance standards for plastic materials are UL94 ratings. These are intended to identify a material’s ability to extinguish a flame, once ignited. Several ratings can be applied based on the rate of burning, time to extinguish, ability to resist dripping, and whether or not drips are burning. Each material tested may receive several ratings based on colour and/or thickness. When specifying a material for an application, the UL rating should be applicable for the thinnest wall section in the plastic part. The UL rating should always be reported with the thickness: just reporting the UL rating without mentioning thickness is insufficient.
UL94HB
Where flammability is a safety requirement, HB materials are normally not permitted. In general, HB classified materials are not recommended for electrical applications except for mechanical and/or decorative purposes. Sometimes misunderstood: non-FR materials (or materials that are not meant to be FR materials) do not automatically meet HB requirements. UL94HB is - although the least severe - a flammability classification, and has to be checked by testing.
UL94V0, V1 and V2

The vertical tests take the same specimens as are used for the HB test. Burning times, glowing times, when dripping occurs, and whether or not the cotton beneath ignites, are all noted. Flaming drips - widely recognised as a main source for the spread of fire or flames - distinguish V1 from V2.
UL94-5V

UL94-5V is the most severe of all UL classifications. It involves two steps:

**Step 1**
A standard flammability bar is mounted vertically and subjected to each of five applications of a 127 mm flame, five seconds duration. To pass, no bar specimen may burn with flaming or glowing combustion for more than 60 seconds after the fifth flame application. Also, no burning drips are allowed that ignite cotton placed beneath the samples. The total procedure is repeated with five bars.
Step 2
A plaque - with the same thickness as the bars - is tested in a horizontal position with the same flame. The total procedure is repeated with three plaques. Two classifications result from this horizontal test: 5VB and 5VA.

- 5VB allows holes (burn-through)
- 5VA does not allow holes

UL94-5VA is the most stringent of all UL tests, specified for fire enclosures on larger office machines. For those applications with expected wall thickness of less than 1.5 mm, glass filled material grades should be used.
SUMMARY OF THE UL94 RATING

HB
slow burning on a horizontal specimen
burning rate < 76 mm/min for thickness < 3 mm
burning rate < 38 mm/min for thickness > 3 mm

5V
burning stops within 60 seconds after five applications of a flame - larger than used in V-testing - each of five seconds, to a testbar

5VB
plaque specimens may have a burn-through (have a hole)

5VA
plaque specimens may not have a burn-through (no hole) - highest UL rating
# SUMMARY OF THE UL94V RATING

<table>
<thead>
<tr>
<th>Criteria</th>
<th>UL 94V 0</th>
<th>UL 94V 1</th>
<th>UL 94V 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Afterflame time for each individual specimen $t_1$ (first flame application) and $t_2$ (second application)</td>
<td>$\leq 10$ s</td>
<td>$\leq 30$ s</td>
<td>$\leq 30$ s</td>
</tr>
<tr>
<td>Total afterflame time for each set of 5 specimens ($t_1+t_2$)</td>
<td>$\leq 50$ s</td>
<td>$\leq 250$ s</td>
<td>$\leq 250$ s</td>
</tr>
<tr>
<td>Afterflame + afterglow time for each individual specimen after the second flame application ($t_2+t_3$)</td>
<td>$\leq 30$ s</td>
<td>$\leq 60$ s</td>
<td>$\leq 60$ s</td>
</tr>
<tr>
<td>Afterflame and/or afterglow of any specimen up to the clamp</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td>Cotton indicator ignited by flaming particles or drops</td>
<td>NO</td>
<td>NO</td>
<td>YES</td>
</tr>
</tbody>
</table>
GLOW WIRE TEST

Specifications:
DIN IEC 60695-2-11
DIN VDE 0471-2-1
NBN C 06-301
NF C 20-455
AS 2420, App.B

Specimens: Finished part

Procedure in brief:
The specimen is pressed for 30 s against the heated glow-wire with a force 1N.
The glow-wire is held horizontally, with the specimen in the most unfavourable position with respect to the construction of the article
• Glow-wire temperatures: 550 to 850 °C (100 K steps) 960 °C
• Dripping height: 200 mm
• Substrate: tissue paper on pinewood
• Depth of penetration limited to 7 mm
Assessment:

Flames, glowing particles or flaming particles must not act as an ignition source in the vicinity of the specimen (paper not ignited, wood not scorched)

Afterglow time $\leq 30\ s$
Afterburn time $\leq 30\ s$

GWT IEC 60695-2-11

According to this standard, tests should be carried out on the finished part and, in particular, on its most critical point in terms of thickness and position.
NEW STANDARDS

CEI – IEC 60695 will become ISO – CEI 13943

INNOVATION

The materials will be qualified not only as finished parts but also as specimens with the dimensions of 60 mm x 60 mm or more and thickness values between 0.75 mm and 3 mm (usually thickness values of 1 mm, 2 mm and 3 mm are used) as shown in the next slides.
It’s the temperature 25 °C higher than the max. temperature at which there is no flame development (ignition). Between 900°C and 960°C the increment is 30°C.

Example of GWIT definition: 775/2

A material that does not ignite @ 750°C on a 2 mm-thick specimen
GLOW WIRE TEST

CEI – IEC 60695 – 2 – 12

GWFI - Glow Wire Flammability Index

The exact temperature at which the flame extinguishes in less than 30 seconds.

Example of GWFI definition: 750/2

Max. temperature at which the flame extinguishes in less than 30 seconds on a 2-mm thick specimen.
# GLOW WIRE TEST

<table>
<thead>
<tr>
<th>GWIT °C</th>
<th>Tolerance °K</th>
<th>GWFI °C</th>
<th>Tolerance °K</th>
</tr>
</thead>
<tbody>
<tr>
<td>IEC 60695-2-13</td>
<td></td>
<td>IEC 60695-2-12</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>± 10</td>
<td>550</td>
<td>± 10</td>
</tr>
<tr>
<td>550</td>
<td>± 10</td>
<td>600</td>
<td>± 10</td>
</tr>
<tr>
<td>600</td>
<td>± 10</td>
<td>650</td>
<td>± 10</td>
</tr>
<tr>
<td>650</td>
<td>± 10</td>
<td>700</td>
<td>± 10</td>
</tr>
<tr>
<td>700</td>
<td>± 10</td>
<td>750</td>
<td>± 10</td>
</tr>
<tr>
<td>750</td>
<td>± 10</td>
<td>800</td>
<td>± 15</td>
</tr>
<tr>
<td>800</td>
<td>± 15</td>
<td>850</td>
<td>± 15</td>
</tr>
<tr>
<td>850</td>
<td>± 15</td>
<td>900</td>
<td>± 15</td>
</tr>
<tr>
<td>900</td>
<td>± 15</td>
<td>960</td>
<td>± 15</td>
</tr>
<tr>
<td>960</td>
<td>± 15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table of Glow Wire test temperatures
NEEDLE TEST

IEC 60695 – 2 – 2

Flame application time:
5 – 10 – 20 – 30 – 60 – 120 s

Assessment:

Afterburn time ≤ 30 s

Flames, glowing particles, flaming particles must not act as an ignition source in the vicinity of the specimen (paper not ignited, wood not scratched)
NEEDLE TEST

b) position d'essai (exemple)
test position (example)

Dimensions en millimètres

Fig. 1. — Brûleur-aiguille.
Needle burner.
LIMITING OXIGEN INDEX (LOI)

The O$_2$ percentage at which the sample burns for more than 3 min or the flame spreads for more than 5 cm within 3 min.
COMPARATIVE TRACKING INDEX

HYPODERMIC NEEDLE
AGO IPODERMICO

DROPS OF TEST SOLUTION
GOCCE DI SOLUZIONE ELETTROLITICA

60°

ELECTRODE

SPECIMEN
PROVINO

4mm
COMPARATIVE TRACKING INDEX

It is expressed as that voltage which causes tracking after 50 drops of 0.1% of ammonium chloride solution have fallen on the material. The results of testing the nominal 3 mm thickness are considered representative of the material’s performance in any thickness.

<table>
<thead>
<tr>
<th>CTI Range (in volts)</th>
<th>Assigned PLC</th>
</tr>
</thead>
<tbody>
<tr>
<td>600 and greater</td>
<td>0</td>
</tr>
<tr>
<td>400 through 599</td>
<td>1</td>
</tr>
<tr>
<td>250 through 399</td>
<td>2</td>
</tr>
<tr>
<td>175 through 249</td>
<td>3</td>
</tr>
<tr>
<td>100 through 174</td>
<td>4</td>
</tr>
<tr>
<td>Less than 100</td>
<td>5</td>
</tr>
</tbody>
</table>
FLAME RETARDANT FAMILIES

Chemical nature of the additives

• Monomeric halogenated additives (Br-Cl)

• Polymeric halogenated additives (Br)

  Note: For better performing the a.m. Halogenated additives need synergistic additives (usually metal-oxides or metal-salts)

• Red phosphorus
Alternative to the previous ones are the following halogen and red phosphor free additives.

- additives with a high nitrogen content
- additives with a high content of organic phosphorus
- intumescent additives (mixtures of nitrogen, organic phosphorus and hydroxides)
- hydrated salts and oxides (alluminium, magnesium, zinc and boron)

Developed to fulfill the new regulatory issues and market requests
### MAIN COMBINATIONS BETWEEN POLYMERS AND FLAME-RETARDANT ADDITIVES

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Halogenated Additives</th>
<th>Monomeric and Polymeric Halogenated Additives</th>
<th>Halogen-Free Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ABS</td>
<td>• monomeric + synergists</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAN</td>
<td>• polymeric + synergist</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC / ABS blends</td>
<td></td>
<td>Monomeric and polymeric halogenated additives</td>
<td></td>
</tr>
<tr>
<td>Polypropylene homopolymer and co-polymer</td>
<td>Halogenated additives:</td>
<td>• monomeric + synergists</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• polymeric + synergist</td>
<td>Halogen-free additives:</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• intumescent products</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• hydrated salts and oxides</td>
</tr>
</tbody>
</table>
MAIN COMBINATIONS BETWEEN POLYMERS AND FLAME-RETARDANT ADDITIVES

Polyamide 6

Halogenated additives:
• monomeric + synergists
• Polimeric + synergist

Halogen-free additives:
• hydrated salts and oxides
• organic phosphorus
• nitrogen-rich additives

Polyamide 66

Halogenated additives:
• monomeric + synergists
• Polimeric + synergist

Halogen-free additives:
• hydrated salts and oxides
• organic phosphorus
• nitrogen-rich additives
• Red phosphorus
## MAIN COMBINATIONS BETWEEN POLYMERS AND FLAME-RETARDANT ADDITIVES

<table>
<thead>
<tr>
<th>Polymer Combination</th>
<th>Halogenated Additives</th>
<th>Halogen-free Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybutylene terephtalate (PBT) and polyethylene terephtalate (PET)</td>
<td>• Polimeric + synergist</td>
<td>• Organic phosphorus&lt;br&gt;• Nitrogen-rich additives</td>
</tr>
<tr>
<td>Modified polyphenylene oxide (PPEm)</td>
<td></td>
<td>Halogen-free additives:&lt;br&gt;• Organic phosphorus</td>
</tr>
<tr>
<td>Polysulphone (PSU) and polyphenylene sulphide (PPS)</td>
<td>Intrinsically flame-retarded</td>
<td></td>
</tr>
<tr>
<td>Aromatic polyamide (PAA)</td>
<td>Halogenated additives:&lt;br&gt;• Polimeric + synergist</td>
<td></td>
</tr>
</tbody>
</table>
ADVANTAGES AND DISADVANTAGES OF THE FLAME-RETARDANT GROUPS

<table>
<thead>
<tr>
<th>Flame-retardant group</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomeric halogen additives</td>
<td>• Lower price</td>
<td>• Low thermal stability</td>
</tr>
<tr>
<td></td>
<td>• Total colorability</td>
<td>• Low UV resistance</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Easy corrosion of metallic parts</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Low CTI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• High density and toxicity of smokes</td>
</tr>
</tbody>
</table>
ADVANTAGES AND DISADVANTAGES OF THE FLAME-RETARDANT GROUPS

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<th>Flame-retardant group</th>
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<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymeric halogenated additives</td>
<td>• Total colorability</td>
<td>• High price</td>
</tr>
<tr>
<td></td>
<td>• Medium-to-high CTI</td>
<td>• High density and toxicity of smokes</td>
</tr>
<tr>
<td></td>
<td>• Medium-to-high mechanical properties</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• High thermal stability</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Optimum surface</td>
<td></td>
</tr>
</tbody>
</table>
ADVANTAGES AND disadvantages OF THE FLAME-RETARDANT GROUPS

<table>
<thead>
<tr>
<th>Flame-retardant group</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| Red phosphorus        | •High mechanical properties  
                           •High CTI  
                           •Low optical density of smokes | •Effective only on PA66  
                           •Bad colorability: only brown, black and dark colours  
                           •possible formation of phosphates in humid warm environments  
                           •Medium-to-high smoke toxicity |
ADVANTAGES AND DISADVANTAGES OF THE FLAME-RETARDANT GROUPS

<table>
<thead>
<tr>
<th>Flame-retardant group</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen-rich additives</td>
<td>• Total colorability</td>
<td>• Low UL94 on reinforced and filled compounds</td>
</tr>
<tr>
<td></td>
<td>• Good mechanical properties</td>
<td>• Limited stability in the injection moulding machine</td>
</tr>
<tr>
<td></td>
<td>• High CTI</td>
<td>• Medium-to-high toxicity of smokes</td>
</tr>
<tr>
<td></td>
<td>• Optimum GWIT and GWFI</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Low optical density of smokes</td>
<td></td>
</tr>
</tbody>
</table>
## ADVANTAGES AND DISADVANTAGES OF THE FLAME-RETARDANT GROUPS

<table>
<thead>
<tr>
<th>Flame-retardant group</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| **Organic phosphorus additives** | • Total colorability  
• High mechanical properties  
• Optimum CTI  
• Optimum GWIT and GWFI  
• High flow  
• Low optical density of smokes | • High price  
• Medium-to-high UL94  
• Medium thermal properties |
ADVANTAGES AND DISADVANTAGES OF THE FLAME-RETARDANT GROUPS

<table>
<thead>
<tr>
<th>Flame-retardant group</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intumescent additives</td>
<td>• Total colorability</td>
<td>• Medium-to-high UL94</td>
</tr>
<tr>
<td></td>
<td>• Low optical density and toxicity of smokes</td>
<td>• Medium-to-high mechanical properties</td>
</tr>
<tr>
<td></td>
<td>• Optimum CTI</td>
<td>• Limited stability in the injection moulding machine</td>
</tr>
<tr>
<td></td>
<td>• Medium GWIT and GWFI</td>
<td></td>
</tr>
</tbody>
</table>

ADVANTAGES:
- Total colorability
- Low optical density and toxicity of smokes
- Optimum CTI
- Medium GWIT and GWFI

DISADVANTAGES:
- Medium-to-high UL94
- Medium-to-high mechanical properties
- Limited stability in the injection moulding machine
ADVANTAGES AND DISADVANTAGES OF THE FLAME-RETARDANT GROUPS

<table>
<thead>
<tr>
<th>Flame-retardant group</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| **Hydrated salts and oxides** | •Total colorability  
•Low optical density and toxicity of smokes  
•Optimum CTI  
•Optimum GWIT and GWFI | •High concentration (high specific weight)  
•Low mechanical properties |